DECOHERENCE RHAPSODY IN THE PHOTOSYNTHESIS PROCESS

CLAUDIA NEGULESCU

Abstract. It is said that classical theories are sometimes inappropriate to describe very efficient biological processes in nature, which seem to be better understood via quantum mechanical models. We are however still very far from understanding how quantum features can survive in open quantum systems. In this paper the author shall present a simple mathematical model for the illustration of the excitation energy transfer in photosynthesis complexes, and shall study numerically the environmental induced decoherence effect and its influence on the emergence of classicality in nature. The model is based on the Schrödinger equation, describing the propagation of an absorbed excitation through a spin-chain towards a reaction center, and this in permanent interaction with a vibrational environment.

Keywords: Quantum mechanics, system-environment entanglement, decoherence, reduced density matrix, Schrödinger equation, numerical simulation, photosynthesis, spin-boson model, excitation energy transfer, spin-chain, harmonic-oscillator chain.

1. Background and motivation

Biological processes present facilities and performances which are very impressive and cannot be adequately explained with the only use of traditional (classical) approaches. A certain amount of quantum coherent properties is thought to be used by Nature in order to enhance the efficiency of the underlying processes. For example, the property of non-locality (correlations between distant atoms/molecules) can be the main reason for the impressive speed with which our brain treats information, or for the quasi perfect efficiency of the excitation energy transfer in photosynthesis complexes. The question which arises immediately is: *How can quantum features survive in an open quantum system subject to a permanent environmental disorder or noise*?

The goal of the present paper is to give firstly a simple overview of the thematic of open quantum systems (embedded in an external environment) and also the related *decoherence phenomenon*, and secondly to model mathematically some efficient energy transfer phenomena occurring in nature. A better understanding of how Nature transfers so efficiently excitations through a given network is an essential step in several domains, as information processing, neural science, light-harvesting techniques, *etc.*

Date: November 19, 2020.

Quantum decoherence is a typical quantum-mechanical effect and is considered nowadays to be the key concept in the description of the transition from the quantum to the classical world [4, 5, 7, 16, 21, 23]. Let us explain now this effect a little bit more.

Some of the main distinctive characteristics of quantum mechanics (with no analogue in classical mechanics) are:

- discreteness (some dynamical variables, as for ex. the energy, were found to take only discrete values, contrary to the predictions of classical mechanics);
- wave-particle dualism (quantum particles display inseparable wave-like and particle-like properties, for ex. on one hand diffraction and interference, on the other hand mass, velocity and energy are associated to the particle);
- tunneling (phenomenon in which a particle penetrates a potential energy barrier higher than the total energy of the particle);
- coherence.

Coherence is probably one of the most striking illustrations with far-reaching repercussions. It is related to concepts like entanglement, superposition, measurement problem, decoherence, openness of quantum systems, pure/mixed states, *etc.* In this paper we shall deal with this type of illustration of quantum mechanics, in particular with its "disappearance" (called decoherence), phenomenon which is still badly understood today, however of paramount importance for the understanding of several events in nature.

The axioms of quantum mechanics allow superposition states, meaning normalized sums of admissible wave functions are once more admissible wave functions. It is then possible to construct non-localized states that lack a classical interpretation, for instance, by summing two states localized far apart from each other. The observable mark of such a quantum mechanical superposition state is the presence of interference fringes in the probability distribution associated to the superposition state [8]. We stress that this phenomenon does not have a classical explanation: classically, a probability distribution corresponding to the free evolution of a single particle follows the free Liouville equation, so, by linearity, two colliding probability densities sum up without creating an interference pattern.

Nonetheless, at human scale no quantum superposition states are revealed and in general quantum effects are difficult to observe, so the question arises, on why and how does the interference pattern disappear. Such a phenomenon is called *decoherence* and its explanation lies in the fact that macroscopic objects undergo a continuous interaction with an external environment (such as air molecules, fields), which causes the loss of the phase relations between the different states in the superposition. Thus, the state of the system becomes a statistical mixture in which the quantum effects are "suppressed". In this sense, the system looses its quantum nature and its state admits a classical interpretation.

We remark that the transition from the quantum to the classical regime due to decoherence is different from the semi-classical limit, where the classical behaviour is recovered exploiting the smallness of Planck's constant (see [2, 21] for more details).

Understanding the emergence of decoherence is important not only for the better comprehension of quantum mechanics (quantum measurement problem, emergence of classical mechanics from the quantum one, relation with the arrow of time), but also for applications. For example, in quantum computation (QC), electron spin resonance (ESR), and nuclear magnetic resonance (NMR) it is of central importance to preserve the quantum behaviour, so decoherence is not desired and efforts are made in order to avoid or control it [26, 28]. Biological processes, as for example the photosynthesis system or some brain mechanisms like sensory perception, consciousness, memory, as well as the magnetic orientation of migrant birds, seem to use quantum mechanics (in particular coherence) in order to enhance the efficiency of the underlying processes or simply to enable these ones. Given the complexity of biological systems and the enormous sensitivity of quantum states to external perturbations, a natural question arises then: "How can this be? Why does decoherence not destroy immediately the nice quantum properties ?" It is believed that even if quantum coherence and entanglement in living systems are limited to very short time intervals, it is sufficient to generate a clear benefit in the above mentioned processes [10, 14, 17, 19]. Thus a better understanding of how biological systems achieve to preserve quantum coherence in ambient conditions is an essential step towards a lot of practical applications.

In this paper we are interested in modelling the transfer of energy (photons), harvested via the photosynthesis antennae and propagated towards the reaction centre, where the photosynthesis reaction takes place. In particular, we are interested in the dynamics of a single excitation through a chain of two-level systems (standing for the chlorophyll molecules) and coupled to a bath of vibrational environments. Special attention shall be payed to the influence of the environment on the perfect excitation energy transfer through the chain (decoherence). Such models can be useful also for the modelling of the firing in a neural network, as well as for information processing. Indeed, one of the main considerations for the design of a quantum computer is an infrastructure which can rapidly and robustly transport qubits between different sites where qubit-operations can be performed. This infrastructure can be thought to be a sort of quantum-channel, for example composed of two-level systems like spin-particles, and permitting the propagation of the quantum information (excitation transfer).

The present paper was thought to introduce the unfamiliar reader to this field and to provide the main ideas underlying the excitation energy transfer in the photosynthesis process. A further objective is to lay the foundations for preparing a second paper, whose aim shall be to study in more details the here presented mathematical model, in order to better understand the performances of the excitation energy transfer in photosynthesis, despite the openness of the quantum system. The literature is full of papers in this domain, of all kind, however a simple introduction was missing, as well as a detailed discussion about the relation to classical models. This first paper aims also to thwart this shortcoming.

The outline of this paper is the following. Section 2 is thought to be an introduction to the main quantum mechanical concepts, in order to acquaint the unfamiliar reader with the somehow hardly accessible subject of this paper. Section 3 presents in a very concise manner some simple decoherence models, introduced in literature. Section 4 is the main part of this work, concerning the mathematical modelling of the excitation energy transfer in an environmental embedded spin-chain. The related numerical investigations are presented in Section 5 . At the end the author exposes in Section 6 a classical counterpart of the here presented quantum mechanical model, for a more classical description of the energy transfer.

2. Quantum states, superpositions, pure/mixed states

Let us start with a small prelude of some quantum mechanical notion. We do not intend here to give a detailed introduction to quantum mechanics or to introduce exhaustively the mathematical tools needed for its description. Very nice textbooks exist for this and we refer the interested reader to the references [3, 8, 12]. Nevertheless we need to give some short definitions, useful for a better comprehension of the coming study. This shall be done in a very short manner. The reader acquainted with this theory may skip this part.

States/Observables/Dynamics. A (vector) state (or wave-function) ψ is a complete quantum mechanical description of a physical system and belongs to a complex Hilbert-space $\mathcal{H}$. It contains the maximal information one can have about the system. The linear Schrödinger equation governs the dynamics of the wave-function, *i.e.*

$$\mathbf{i}\hbar\, \partial_t \psi = H\psi\,, \tag{1}$$

where H is the Hamiltonian (self-adjoint operator on $\mathcal{H}$), corresponding to the energy of the system. An observable is a property of a quantum system (like position, momentum, energy *etc*), that can be measured in experiments. It is represented by a self-adjoint operator $\mathcal{O} : \psi \in \mathcal{H} \to \mathcal{O}\psi \in \mathcal{H}$. The possible outcomes of a measurement of an observable $\mathcal{O}$ are the points of the spectrum of $\mathcal{O}$ (the eigenvalues in the case of a discrete spectrum). The measurement process causes an abrupt change in the state of the system. For example in the discrete spectrum case, the state ψ transforms after the measurement into the eigenvector corresponding to the measured eigenvalue. In general, the outcome of a measure cannot be predicted with certainty. For discrete spectra the probability of obtaining the eigenvalue λ_i when the system is in the state ψ is given by $|\langle\psi_i, \psi\rangle|^2$, where ψ_i is the eigenvector corresponding to the eigenvalue λ_i. The average or expectation value in a series of measurements of an observable $\mathcal{O}$ when the system is in the state ψ is given by $\langle\psi, \mathcal{O}\psi\rangle$.

Superposition-principle. The Schrödinger equation (1) being a linear (deterministic) equation, any linear combination of solutions $\psi = \sum_i \alpha_i \psi_i$, with $\alpha_i \in \mathbb{C}$, is a new solution of (1). Such a superposition state ψ describes a completely new physical state of the system, and not merely a statistical description of the component states. All the components ψ_i are simultaneously present in the state of the system. The superposition-principle forms a spine of quantum mechanics, however remark that the superposition states are extremely fragile and can be "destroyed" (or better delocalized) simply by a weak interaction with the environment.

Quantum entanglement. Suppose we have a quantum system $\mathcal{S}$ which is composed of two subsystems $\mathcal{S}_1, \mathcal{S}_2$. A state vector ψ of the whole system $\mathcal{S}$ is called entangled with respect to the subsystems $\mathcal{S}_1, \mathcal{S}_2$ if it cannot be factorized, meaning that it cannot be written as a tensor product of two state-vectors ψ_1, ψ_2 belonging to the two subsystems, *e.g.* $\psi \neq \psi_1 \otimes \psi_2$. To give an example, let us denote the state vectors of $\mathcal{S}_1$ by θ and those of $\mathcal{S}_2$ by ϕ. Then $\psi := \frac{1}{\sqrt{2}}(\theta_1 \otimes \phi_1 \pm \theta_2 \otimes \phi_2)$ are entangled (not separable) states, whereas $\psi := \frac{1}{\sqrt{2}}(\theta_1 \pm \theta_2) \otimes \phi$ are not-entangled states. Entanglement suggests that Nature is essentially non-local and it is the entanglement process which is thought to be the main quantum mechanical feature permitting to get effectively quantum computation.

Pure/mixed states. The distinction between pure and mixed states is delicate to explain. A pure state is described by a wave-function ψ, whereas a mixed state cannot be identified with a well-defined wave-function and requires the introduction of a new concept, namely the density matrix formalism. In a mixed state we say that the system may be with probability $p_i \geq 0$ (with $\sum_i p_i = 1$) in a state described by a wave-function ψ_i. In other words, a mixed state (statistical mixture) expresses insufficient information about the state of the system, in the sense that the system is in one of the different states ψ_i (not in all of them simultaneously), however the observer does not know in which one. In this mixed state, the expectation value of any operator $\mathcal{O}$ is given by $\sum_i p_i \langle \psi_i, \mathcal{O}\psi_i \rangle$.

Density matrix/Reduced density matrix. The density matrix is a very useful tool permitting to study composite (entangled) systems. Let us assume we have a central quantum system of interest ($\mathcal{A}$) which is in permanent interaction with its environment ($\mathcal{E}$), the observer is however only interested in the dynamics of the central system $\mathcal{A}$. The problem is now, that due to the entanglement between the two subsystems $\mathcal{A}$ and $\mathcal{E}$, one cannot describe separately system $\mathcal{A}$ by means of pure wave-vectors θ. It is only the whole system $\mathcal{A} + \mathcal{E}$ which can be described via a pure state ψ, which includes all the information about the whole (entangled) system $\mathcal{S}$. The (reduced) density matrix comes now into play.

Given a pure state of $\mathcal{S}$ under the form of a superposition of several basis states corresponding to the whole entangled system, namely $\psi := \sum_i \alpha_i \psi_i$, the corresponding density matrix is defined as $\rho := |\psi\rangle \langle\psi| = \sum_{i,j} \alpha_i \overline{\alpha_j} |\psi_i\rangle \langle\psi_j|$, using the bra-ket notation. It gives the same information about the state as the wave-function ψ, and the two representations are completely equivalent in the isolated situation. The off-diagonal terms $i \neq j$ embody the quantum coherence between the different basis states of the system $\Rightarrow$ occurrence of an interference pattern. It turns out that the expectation value of the measurements of an observable $\mathcal{O}$ (of the system in state ψ) is given by $\langle \psi, \mathcal{O}\psi \rangle = Tr(\rho\, \mathcal{O})$.

The real power of the density operator arises when we wish to know the properties of one sub-system ($\mathcal{A}$) independently of its connections to the rest of the system (the environment $\mathcal{E}$). In this case we remove the rest of the system by tracing out the environmental degrees of freedom, creating a new object, called reduced density matrix $\rho_{\mathcal{A}} = Tr_{\mathcal{E}}\, \rho$. This new operator provides an elegant way for investigating one sub-system only. All the influences of the environment on the central system are now automatically enclosed into this new object. Passing from an isolated quantum system to an open one, is passing from pure states (density matrix) to mixed states (reduced density matrix). The reduced density matrix of a mixed state corresponding to the "statistical ensemble" $\{p_i, \langle\psi_i|\}_i$ is given by $\rho_{\mathcal{A}} = \sum_i p_i\, |\psi_i\rangle\langle\psi_i|$. In this mixed state case, the average of the measurements of an observable $\mathcal{O}$ is given by $\sum_i p_i\, \langle\psi_i, \mathcal{O}\psi_i\rangle = Tr(\rho_{\mathcal{A}}\,\mathcal{O})$.

Two-level systems. Two-level systems contain two basis states, the system space being thus a two-dimensional complex Hilbert-space. Some standard examples are the spin one-half particle at rest, the ammoniac molecule, when only the ground and the first excited energy levels are considered, a photon and its polarization, *etc.* Two-state systems are the simplest quantum systems that can exist, they are idealizations of real physical systems, when other degrees of freedom are ignored.

The mathematical description of two-level systems is for each situation the same. Let $\{0,1\}$, $\{\uparrow,\downarrow\}$ or $\{\begin{pmatrix} 1 \\ 0 \end{pmatrix}, \begin{pmatrix} 0 \\ 1 \end{pmatrix}\}$ denote the basis set of the two-dimensional complex Hilbert-space. A "qubit" (a vector-state of the system) is a superposition of these two basis states, meaning

$$\psi = a\,|\uparrow\rangle + b\,|\downarrow\rangle \quad \text{or} \quad \psi = a\begin{pmatrix} 1 \\ 0 \end{pmatrix} + b\begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} a \\ b \end{pmatrix}, \quad a, b \in \mathbb{C}\,.$$

To describe the time evolution of a qubit, we need to introduce general unitary transformations (rotations) of the state. Using the vector-representation, the rotation of the spin-state can be represented with the help of the 2×2 complex Pauli matrices

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -\mathbf{i} \\ \mathbf{i} & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

The effects of these hermitian, traceless matrices are the following: σ_x swaps the two components of the spin (spin-flip), σ_z inverts the sign of the second component (phase-shift) and finally σ_y is doing both (phase-shift and spin-flip).

If the spin-1/2 particle is moving, additional degrees of freedom have to be taken into account, and one represents the wave-function of the spin-1/2 particle as a "spinor", namely

$$\psi(t,x) = \psi_\uparrow(t,x) \otimes \begin{pmatrix} 1 \\ 0 \end{pmatrix} + \psi_\downarrow(t,x) \otimes \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} \psi_\uparrow(t,x) \\ \psi_\downarrow(t,x) \end{pmatrix},$$

living in $\mathcal{H} = L^2(\mathbb{R};\mathbb{C}) \otimes \mathbb{C}^2$ or $\mathcal{H} = L^2(\mathbb{R};\mathbb{C}^2)$. The Hamiltonian operators completely specify then the dynamics of such wave-functions.

Hamiltonians. Let us give here some simple examples of Hamiltonians describing some typical quantum mechanical situations.

Single electron dynamics in a potential field. An electron moving in a given (or self-consistently computed) electric potential V is described by a wave-function $\psi(t, \mathbf{x})$ solution of the Schrödinger equation (1) with Hamiltonian given by

$$H_{elec} := -\frac{\hbar^2}{2m}\Delta + V\,.$$

Free dynamics of a spin-1/2 particle. The free dynamics of a particle with spin is described by the spinor wave-function $(\psi_\uparrow(t,\mathbf{x}),\psi_\downarrow(t,\mathbf{x}))$ and the corresponding Hamiltonian

$$H_0 := -\frac{\hbar^2}{2m}\Delta\otimes Id_{\mathbb{C}^2} + Id_{L^2}\otimes\alpha\sigma_z = \begin{pmatrix} -\frac{\hbar^2}{2m}\Delta+\alpha & 0 \\ 0 & -\frac{\hbar^2}{2m}\Delta-\alpha \end{pmatrix}. \tag{2}$$

Let us observe here that the two terms on the diagonal of H_0 correspond to the Hamiltonians acting on the two uncoupled configurations, namely spin-up and spin-down. These two configurations are separated in energy by the energy-amount of 2α. The two spin basis states can also be seen as two energy-levels of a system, with different energies, and no interaction or coupling between these bands is existing in this case.

Single particle entering into interaction with a spin-1/2 particle at rest. Consider now the situation of a composed system, consisting of one particle moving on $\mathbb{R}$ and described by a wave-function $\psi(t,x)$, encountering a spin-1/2 particle localized in y_0, with whom it enters into interaction. The whole "particle-spin" system is described by the spinor wave-function $(\psi_\uparrow(t,x),\psi_\downarrow(t,x))$. The Hamiltonian $H = H_0 + H_{int}$ is composed of two parts, the free Hamiltonian H_0 given in (2), describing the free independent evolution of the particle and the spin, and the particle-spin interaction Hamiltonian which can be for ex. of the form

$$H_{int} := \beta\,\delta_{y_0}\otimes\sigma_y\,.$$

This interaction Hamiltonian depicts a phase+spin flip action of strength β, arising at the moment and location when the particle encounters the spin-particle. It forces a coupling (and energy-exchange) between the two spin-up and spin-down configurations (energy-bands).

Hamiltonian of a quantum harmonic oscillator. In quantum mechanics, the harmonic oscillator has the status of a single particle, subject to a quadratic potential energy, which produces a restoring force against displacement from the equilibrium. The associated Hamiltonian is of the form

$$H_{osc} := -\frac{\hbar^2}{2m}\partial_{xx} + \frac{m\omega_c^2}{2}x^2\,,$$

where ω_c is the frequency of oscillation. This Hamiltonian can provide a model for many kinds of oscillating resp. vibrating systems including electromagnetic fields (photons) resp. vibrational fields (phonons).

The form of the energy spectrum suggests a different and complementary interpretation of the harmonic oscillator, in terms of annihilation and creation operators, defined as

$$\mathbf{a} := \frac{1}{\sqrt{2m\,\omega_c\,\hbar}}\left(m\,\omega_c\,x + \mathbf{i}p\right), \qquad \mathbf{a}^\dagger := \frac{1}{\sqrt{2m\,\omega_c\,\hbar}}\left(m\,\omega_c\,x - \mathbf{i}p\right). \tag{3}$$

Using these so-called "ladder"-operators, the Hamiltonian of the quantum harmonic oscillator can be rewritten as

$$H_{osc} = \hbar\,\omega_c(\mathbf{a}^\dagger\,\mathbf{a} + \frac{1}{2}\,Id)\,.$$

This operator yields the energy levels of the harmonic oscillator, the corresponding eigenstates forming a ladder of even and odd wave-functions with energy difference of $\hbar\,\omega_c$. The annihilation and creation operators correspond to the destruction and the formation of a quantum of energy. In particular they descend and climb the energy levels step by step, namely one has

$$\mathbf{a}\,\psi_n = \sqrt{n}\,\psi_{n-1}\,, \quad \mathbf{a}^\dagger\,\psi_n = \sqrt{n+1}\,\psi_{n+1}\,,$$

which is why they are called ladder-operators. The two interpretations of the quantum harmonic oscillator illustrate once again the "duality" of quantum mechanics.

3. Decoherence phenomenon

After having introduced some fundamental notion, let us try now to explain in more details what one understands under decoherence of a quantum mechanical system.
The Schrödinger equation describes the (unitary) dynamics of an isolated system. However systems in nature are never completely isolated. To give only one example, at the precise moment of measurement, the system enters into interaction with the measurement apparatus (the environment) such that it is no more isolated and the Schrödinger equation is hence no more adequate for the exclusive description of the system. Indeed, the interaction with the measurement apparatus singles out those states which can be effectively measured, and excludes most other states, such as non-classical superpositions, so classicality emerges. It was thus recognized that the openness of quantum systems is essential for explaining how quantum systems "loose" their quantum properties and become effectively classical. The key concept is the entanglement, namely two entangled subsystems (central system + environment) are described by a quantum state that cannot be splitted into two separate quantum states for each individual system. Entangled states encapsulate quantum correlations between the two subsystems and quantum coherence is delocalized into the whole entangled system-environment state. So, when one observes (or measures) only the (central) system, usually this one behaves classically, due to the "decoherence" process, which is nothing else than the loss of quantum coherence, which leaks out into the environment. Briefly, decoherence describes the emergence of classical mechanics from quantum mechanics by information leakage. In fact, there is no destruction of the quantum properties, for ex. the superpositions, but an extension to include also the environment, a sort of delocalization of the quantum information. The tracing over the environment has exactly the effect of inducing the transition $\rho_{pure} \rightarrow \rho_{mixed}$.

The decoherence is not a spontaneous process, but is evolving continuously in time. In the following we are going to present some simple decoherence models proposed by the author in previous works.

3.1. **Some simple decoherence models.** There are several physical systems in nature which are submitted to decoherence effects. It is hence a rather huge (and even impossible) task to model all of these complex systems in order to study the therein occurring decoherence. However, very often, it is enough to concentrate on simpler models and begin by considering the interaction of a general central system $\mathcal{S}$ with an environment $\mathcal{E}$. The central system can be represented either by a particle (continuous coordinates in the phase space) moving in a given potential (for ex. harmonic potential), or by a spin-1/2 particle at rest (discrete coordinates, two-level system). Likewise, concerning the environment, one can either use a collection of harmonic oscillators (oscillator-environment, vibrational models) or a collection of spin-particles (spin-environment models) for its description. The interaction mechanism between central system and environment as well as the choice of the different parameters, are fundamental to describe a well-specified physical situation. Let us now introduce some simple decoherence models.

3.1.1. *Heavy-light particle model [1,2].* In this first example, the author considers a central system consisting of a heavy particle, appearing initially under the form of a superposition of two states localized in $\pm X_0$ and moving towards each other (see Fig. 1). This particle is imagined to be exposed during its evolution to an environment, consisting of one (or several) light particle (the environment), coming from infinity and interacting with the heavy particle before disappearing again at infinity. The effect of this scattering process is that the light particles carry away some information about the heavy central particle (as for ex. of its position) and the composite system (heavy-light particles) becomes entangled. The ensuing "delocalization" of the phase relations of the two heavy-particle bumps into the whole composite system induces inevitably some loss of quantum characteristics of the central system. This quantum characteristics are visible when the two bumps (heavy particle density matrix) encounter and an interference pattern (representing the existing coherences between the two bumps) emerges, which is damped by decoherence.
According to the principles of quantum mechanics, the time evolution of the wave function $\psi_\varepsilon(t, X, x)$ representing the heavy-light quantum system, is given by the Schrödinger equation

$$\left\{ \begin{array}{l} \mathbf{i}\partial_t \psi_\varepsilon \;=\; -\dfrac{1}{2M}\Delta_X \psi_\varepsilon - \dfrac{1}{2\varepsilon M}\Delta_x \psi_\varepsilon + \dfrac{\alpha}{\varepsilon} V(x - X)\, \psi_\varepsilon, \\ \psi_\varepsilon(0, X, x) = \psi_\varepsilon^0(X, x)\,, \end{array} \right. \tag{4}$$

where we used units in which $\hbar = 1$, M is the mass and X the spatial coordinate of the heavy particle, while εM is the mass and x the spatial coordinate of the light one. So ε is the ratio between the mass of the light particle and the mass of the heavy one, and the regime $\varepsilon \ll 1$, which we call the *small mass ratio* regime, permits the study of the decoherence without deformation.

3.1.2. *Particle-spin model [6].* In contrast to the previous toy-model, the environment is this time modelled via a collection of stationary spin-1/2 particles (two-level systems), which enter into interaction with the central particle when this one is passing over them (see Fig. 2). The central system is again given initially under the form of a superposition

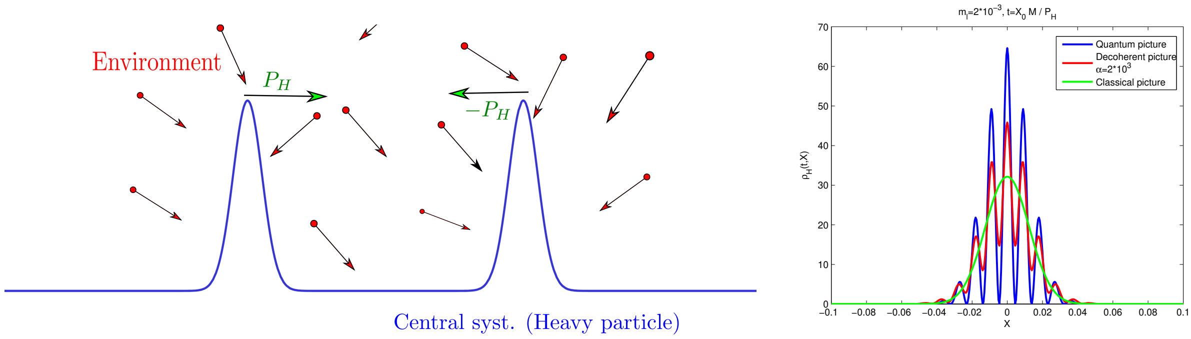

FIGURE 1. Left: The whole system, composed of a heavy-particle in a superposition state (central system) and the environment (several light particles). Right: Interference pattern at overlap time, damped by decoherence.

of two states localized in $\pm X_0$, moving towards each other. This model is a little bit more realistic than the previous one, as it permits to handle simultaneous particle-environment interactions, and not only successive two-body heavy-light interactions. Tracing over the environment, and observing the central heavy particle, would lead to similar decoherence results as in the previous section. However, tracing over the central system, and observing the changements caused on the environment owing to the scattering process with the heavy particle, is a different point of view of the decoherence study and can be related to the Wilson cloud chamber experiment (see Fig. 2). In this experiment, a very energetic α-particle (central system), emitted in a radially symmetric way by a radioactive source, ionizes atoms of a super-saturated vapor (environment). The ionized atoms condensate and form a sequence of droplets. The tracks one observes in real experiments look explicitly like classical particle trajectories, and have no more quantum characteristics. This is a typical example of quantum-to-classical transition and was studied numerically in [6]. The mathematical model employed to describe this situation was again the Schrödinger equation, however with Delta-Dirac point interactions for the modelling of the particle-environment correlations.

3.2. **Some simple models for coherence resistance.** It seems that Nature is able to control the decoherence effect of the environment on the central quantum system, in particular to slow down decoherence processes. Understanding how one can improve the persistence of coherence of a central quantum system can be of primary importance for quantum computation. Some ideas of how Nature may control the decoherence, are:

- *Near-far, nested environments [27].* Nested (combined) environments may be exploited to control or improve the coherence of the central system. Assuming a tripartite system (central system + near environment + far environment) without direct coupling between the central system and the far environment, but with a strong coupling between the near and the far environment, this configuration seems indeed to protect the central system against decoherence. In other words, the coherence loss of the near environment stabilizes somehow the coherence of the

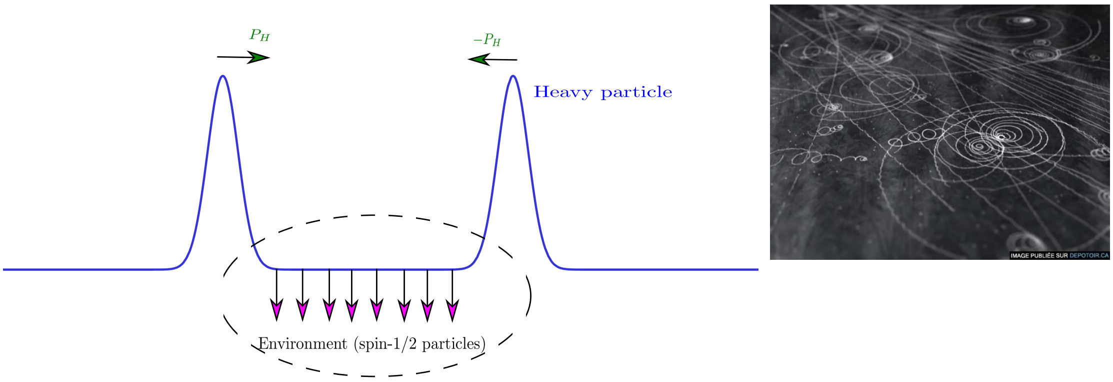

Figure 2. Left: Whole system, composed of a central system (continuous particle) and an environment (collection of several non-interacting spin-1/2 particles). Right: The Wilson cloud chamber and the observed classical trajectories [physicsopenlab.org].

central quantum system.

- *White noise [15].* Another strategy to suppress or simply slow down the decoherence process is to employ external uncontrollable white noise fields. Indeed, this strategy is based on the fact, that it is possible to control disorder (the decoherence) via much more disorder (white noise, which is the extreme of disorder compared to colored noise).

Other coherence-control strategies are based on the Zeno effect, the dynamical decoupling methods, *etc.*

4. Energy transfer in photosynthesis processes

Technologies which make use of solar photovoltaics, capturing light (photons) with semiconductors and transforming this energy into electric currents, exist, recall for ex. the solar panels. There are however some problems with such devices, namely the produced energy is not so easy to transport and to store, the solar panels are not so efficient (around 20%), not so reliable (produce maximum amount of energy around midday on sunny days), the involved materials are environmentally unfriendly and dangerous, and the technology is very expensive. What we need is an efficient, clean and trusty manner to produce and store the energy coming from the sun, for a use whenever and wherever needed, much the same as the natural process of photosynthesis.

Photosynthesis is the process by which plants transform light energy into chemical energy. In particular they capture the sun's energy (a broad spectrum of it) via their leafs (chlorophyll molecules), transfer the absorbed photons (excitation transfer through a network of pigments) towards a reaction centre, where these are used to enable the photosynthesis reaction to take place, namely

$$6\,CO_2 + 6\,H_2O \to^{photons} 6\,O_2 + C_6H_{12}O_6\,.$$

The sun's energy is thus transformed into a chemical energy, stored in the carbohydrate molecule, necessary for the growth of the plant (see Fig 3). During this process carbon dioxide is consumed and oxygen released, such that photosynthesis contributes to clean and maintain the oxygen content of our Earth's atmosphere. It is thus an extremely important process, one of those making life possible on Earth.

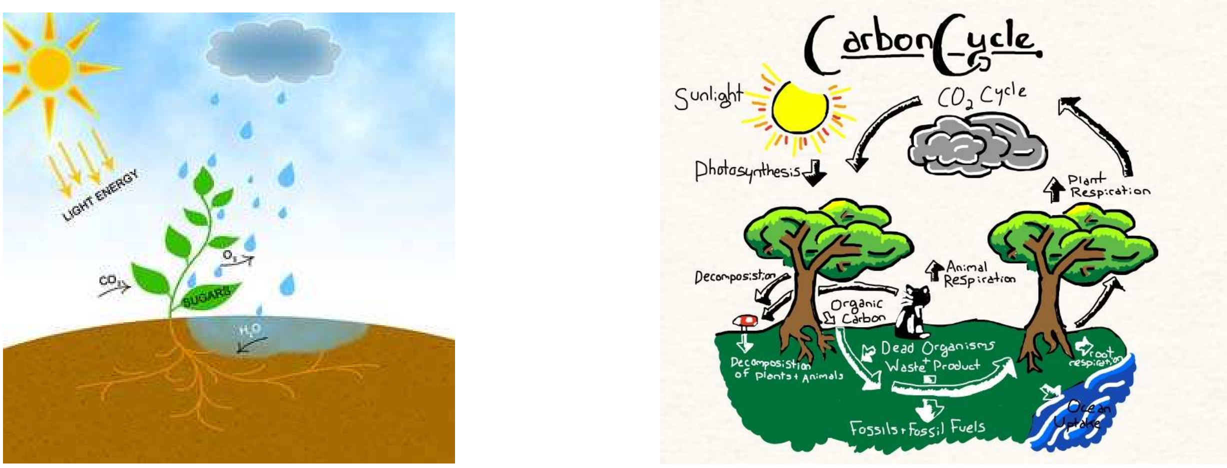

FIGURE 3. The photosynthesis process in plants on the left [https://study.com] and the carbon cycle on the right [https://quizizz.com].

Biological systems are very complex, in particular the photosynthesis process involves many distinctive stages. In this paper we are only interested in the modelling and the understanding of the efficient excitation energy transfer, from the absorption of the photons to their delivery to the reaction center. This energy transfer in plants is remarkably fast and efficient, in the sense that the probability of an absorbed photon, to contribute to the charge-separation in the reaction center, is nearly 100%. A better comprehension of this perfect efficiency would be a very important step in the domain of *information processing*. Several questions arise naturally, when thinking about this efficient energy transfer:

- What is the mechanism behind the performance of the excitation energy transfer in photosynthesis systems?
- Is it an incoherent hopping of the photons from one atom to the next one (classical mechanism), or rather a coherent transfer (quantum mechanical mechanism) or eventually an intermediate regime (environment assisted quantum transfer)?
- If the mechanism involves quantum mechanical means, how can this be, keeping in mind that photosynthesis takes place in a warm, wet and noisy environment, such that decoherence should immediately occur?

The consideration of such questions led to the persuasion that the "environmental assisted transport" could be the most efficient one, which means that the interplay between coherent and incoherent excitation energy transfer can enhance the transport processes in photosynthesis devices [9, 18, 24, 25].

The aim of this paper is not to answer to all these questions, but rather to introduce a mathematical toy-model, describing the excitation energy transfer in a chain of atoms (two-level systems), embedded in a vibrational environment (bath of harmonic oscillators), and to test numerically which set of parameters brings the most efficient energy transfer. This shall permit to gain some understanding of the phenomenon and prepare the foundations for a more detailed/far-reaching forthcoming work.

4.1. **The Spin-Boson model.** The enormous complexity of biological systems necessitates for their investigation firstly the design of simplified toy-models. A simple mechanism to study the energy transfer in photosynthesis systems can be imagined as follows (see Fig. 4 and 5).

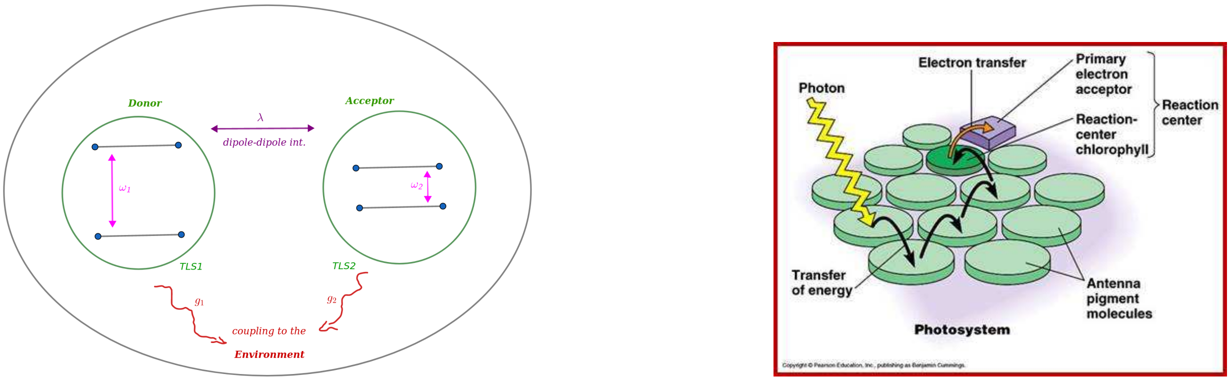

FIGURE 4. Left: Simplified model, composed of a central system, the dimer (a pair of tow-level systems TLS) and the environment (cavity, harmonic oscillator, heat bath). Right: Process of energy transfer through a pigment network [www.hammiverse.com].

A linear chain (network) of N interacting two-level systems (denoted in the sequel simply by TLS) is embedded in a vibrational environment (one phonon, described by a harmonic oscillator). The whole system, composed of the spin-chain and the environment is represented in a simplified manner in Figure 5. The Hilbert-space corresponding to this whole system is given by $\mathcal{H} := L^2(\mathbb{R};\mathbb{C}^2) \otimes L^2(\mathbb{R};\mathbb{C}^2) \otimes \cdots \otimes L^2(\mathbb{R};\mathbb{C}^2)$. A general state of $\mathcal{H}$ is represented through a linear combination of factorized states, namely $\Psi(t,\cdot) := \sum_\sigma c_\sigma\, \psi^1_\sigma(t,\cdot) \otimes \cdots \otimes \psi^N_\sigma(t,\cdot)$, where $c_\sigma \in \mathbb{C}$, $\psi^l_\sigma(t,\cdot) \in L^2(\mathbb{R};\mathbb{C}^2)$ and the upper indices $l = 1, \cdots, N$ symbolize the association to the l-th atom.

The dynamics of the wavefunction Ψ is governed by the Schrödinger equation

$$\mathbf{i}\hbar\, \partial_t \Psi(t,\cdot) = H\, \Psi(t,\cdot)\,, \tag{5}$$

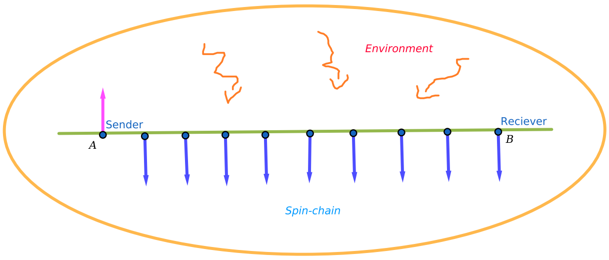

FIGURE 5. Sketch of the considered spin-chain, embedded in an exteriour environment. The first TLS is initially excited, and shall be then transferred towards the receiver.

with H the Hamiltonian of the whole system, consisting of three parts corresponding to the dynamics of the central spin-chain ($\mathcal{S}$), the vibrational environment ($\mathcal{E}$) as well as the interaction between these two subsystems ($\mathcal{I}$), *i.e.*

$$H = H_{\mathcal{S}} + H_{\mathcal{E}} + H_{\mathcal{I}}\,.$$

To specify each of these three Hamiltonians, it is useful to index an operator acting only on the l-th two-level system by l, as for example

$$\sigma_l^z := \Pi_{i=1}^{l-1} Id \otimes \sigma_z \otimes \Pi_{i=l+1}^{N} Id\,, \quad \forall l = 1, \cdots, N\,,$$

and to define for $l < j$ the operator

$$\sigma_l^+\,\sigma_j^- := \Pi_{i=1}^{l-1} Id \otimes \sigma^+ \otimes \Pi_{i=l+1}^{j-1} Id \otimes \sigma^- \otimes \Pi_{i=j+1}^{N} Id\,,$$

where $\sigma^\pm := \frac{\sigma_x \pm \mathbf{i}\,\sigma_y}{2}$ are the raising $(+)$ resp. lowering $(-)$ operators of the corresponding two-level atoms and Id is the identity operator on $L^2(\mathbb{R};\mathbb{C}^2)$. The action of this last operator is the raising of the spin at position l and the lowering of the spin at position j.

With this notation, let us start with the specification of $H_{\mathcal{S}}$, which represents the free Hamiltonian of the spin-chain, meaning of the N interacting two-level systems, given by

$$H_{\mathcal{S}} := \frac{\hbar}{2}\sum_{l=1}^{N} \omega_l \sigma_l^z + \sum_{l=1}^{N-1} \lambda_l \left(\sigma_l^+\,\sigma_{l+1}^- + \sigma_l^-\,\sigma_{l+1}^+\right)\,,$$

with λ_l the strength of the interaction (of dipole-dipole type) between the l^{th} and the $(l+1)^{th}$ neighbouring TLSs and $\hbar\omega_l$ the transition energy between ground and excited state of the l-th TLS. The term $\sigma_l^+\,\sigma_{l+1}^- + \sigma_l^-\,\sigma_{l+1}^+$ can be interpreted as a process, during which an excitation of the l-th atom is generated at the expense of the de-excitation of the neighbouring $(l+1)$-th atom and vice-versa, and all this with “probability” $\lambda_l > 0$. The interaction between the different two-level systems yields an entanglement between the different atoms of the spin-chain and an ensuing delocalization of the excitation among them (so-called Frenkel exciton). This interaction enables the physical mechanism of "excitation energy transfer".

The vibrational environment is represented in our model as a unique harmonic oscillator bath, described by the Hamiltonian

$$H_{\mathcal{E}} := \hbar\,\omega_c \left(\mathbf{a}^\dagger\, \mathbf{a} + \frac{1}{2}\, Id \right) ,$$

where ω_c is the quantum harmonic oscillator's frequency and $\mathbf{a}$ resp. $\mathbf{a}^\dagger$ are the so-called phonon annihilation resp. creation operators defined in (3). A more realistic environment has to include several harmonic oscillators (phonons), would however require more degrees of freedom (leading to a multi-dimensional problem) and hence huge computational costs. We shall thus restrict our study for the moment to an environment consisting of only one vibrational phonon.

The interaction between the spin-chain and the environmental bath depends now on the decoherence problem one wants to analyze. Let us treat here a pure dephasing decoherence effect, without dissipation (no energy losses of the central system towards the environment and vice versa), which shall destroy the phase relations between the excited states of the different TLSs, yielding a more localized excitation and thus leading to a more classical picture. In this case, the interaction Hamiltonian is given by the spin-boson model

$$H_{\mathcal{I}} := \frac{\hbar}{2}\, \left(\mathbf{a}^\dagger + \mathbf{a}\right) \sum_{l=1}^{N} g_l\, \sigma_l^z\, .$$

Let us observe here that the two operators σ_l^z resp. $\left(\mathbf{a}^\dagger + \mathbf{a}\right)$ act on different sub-systems (degrees of freedom), in particular σ_l^z acts on the spin (discrete degree of freedom) of the l-th atom, whereas $\left(\mathbf{a}^\dagger + \mathbf{a}\right)$ acts on the phonon representing the environment (continuous degree of freedom). The z-components of the spins couple linearly to the oscillator with g_l being the corresponding coupling strengths, fact which indicates that the system-environment coupling is considered as weak. Furthermore, due to $[H_{\mathcal{I}}, \sigma_z] = 0$, the excitation is conserved. In real life situations, both dissipation and dephasing decoherence are present. However, the time-scale of decoherence is typically many orders of magnitude shorter than the time-scale of the thermal relaxation, thus this model can be regarded as a good representation of such rapid decoherence processes, during which the amount of dissipation is negligible, but entropy is produced.

Remark 4.1. *Depending on the strength of the dipole-dipole interaction as compared to the strength of the chain-environment interaction, two kinds of situations can arise. When the coupling with the environment is the dominant interaction, then the classical Föster theory [11] can be applied for the description of the excitation energy transfer, due to decoherence reasons. In this case the energy transfer manifests itself somehow like an incoherent "hopping" of the excitation from one atom to the next one. On the other hand,* *if the TLSs interaction is the dominant one, then models based on quantum theory have to be used [10, 14, 20, 22]. In this case the excitation is delocalized over several atoms and a coherent energy transfer occurs. It is this last case we shall investigate here.*

Not all 2^N spin-configurations are participating to the exciton energy transfer, but only N of them, in particular those with only one excited state in the spin-chain, and this due to the fact that the number of excitations is conserved in our model and that we supposed that initially only one excitation is generated. For this reason, we shall regroup here only the participating configurations in a spinor wave-function

$$\Psi \in (L^2(\mathbb{R};\mathbb{C}))^N\,, \qquad \Psi(t,\cdot) := (\psi_l(t,\cdot))_{l=1}^N\,, \qquad \psi_l(t,\cdot) = \psi_{--\cdots-+-\cdots-}\,,$$

where the + sign represents the excited state and the wave-function ψ_l corresponds to the configuration with the excitation localized at the l-th atom.
The Hamiltonian restricted to this single-excitation subspace is given by the $N \times N$ matrix

$$H := \begin{pmatrix} \mathcal{H}_{osc} + \epsilon_1 + \gamma_1(x) & \lambda_1\, Id & & 0 \\ \lambda_1\, Id & \mathcal{H}_{osc} + \epsilon_2 + \gamma_2(x) & \lambda_2\, Id & 0 \\ \vdots & & \ddots & \vdots \\ 0 & 0 & \lambda_{N-1}\, Id & \mathcal{H}_{osc} + \epsilon_N + \gamma_N(x) \end{pmatrix}, \qquad (6)$$

with the harmonic oscillator operator $\mathcal{H}_{osc}$, energy levels and coupling constants given by

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

where $s_j^{(l)} := \pm 1$ is the sign of the j-th atom in the l-th configuration, namely $+1$ for the excited state and -1 for the ground state.

Let us first remark that the off-diagonal terms correspond to the inter-molecular dipole-dipole interactions, permitting the coupling between the different energy-bands of the system. Secondly, let us observe that the action of the environment on the spin-chain can be simply interpreted as a dynamical modulation of the TLS transition energies. In particular, this modulation shifts constantly the transition energies of the molecules, permitting or avoiding in this manner the excitation transfer. One can also consider much simpler models, where the quantum environment is simply replaced by time-dependent fluctuations of the inter-molecular transition energies, fluctuations which can be controlled from outside in order to boost the excitation energy transfer. This is the basis of the Haken-Stobl-Reineker model [13].

To summarize, the molecular inter-coupling between the TLSs and the chain-environment coupling are the two fundamental interaction mechanisms determining the nature of the excitation energy transfer in photosynthesis complexes. The dynamics of the system is now completely determined by the eigenvalues and eigenvectors of the real and symmetric Hamiltonian matrix (6), or in other words by the unitary time-evolution operator

$\mathcal{U}(t) := e^{-\frac{\mathbf{i}}{\hbar} t H}$.

The aim of the next section shall be to solve numerically the linear Schrödinger equation (5) with the above introduced Hamiltonian (6) in order to study some important quantities, which shall permit to evaluate the excitation energy transfer from one part of the spin chain to the other.

One quantity of interest for the study of the transfer performances is the **site occupation probability** $\mathcal{P}_l(t)$. The probability of the l-th two-level system to be in the excited state at instant t, is given by

$$\mathcal{P}_l(t) := ||\psi_l(t,\cdot)||^2_{L^2}\,, \quad \forall l = 1, \cdots, N\,, \tag{7}$$

quantity which shall permit to study the localization of the excitation.

Let us now try to quantify the quantumness of the central spin-system. Quantum systems in contact with an environment "loose" their quantum properties and an initially pure state becomes mixed and hence more classical. This loss of purity of the central spin-system is a consequence of the entanglement with the environment and it is this entanglement which can be quantified by the **von Neumann entropy**, defined as

$$\mathcal{S}(t) := -Tr\left[\rho_{\mathcal{S}}(t)\, \ln(\rho_{\mathcal{S}}(t))\right]\,, \tag{8}$$

where $\rho_{\mathcal{S}}(t)$ is the reduced density matrix corresponding to the spin-chain. This reduced density matrix is obtained by tracing out the environment from the full density matrix ρ, namely

$$\rho(t,x,x') := \Psi(t,x)\,\overline{\Psi(t,x')}^t\,, \qquad \rho_{\mathcal{S}}(t) := \int_{\mathbb{R}} \rho(t,x,x)\,dx\,.$$

For a pure state the entropy is zero (symbolizing that the maximal information is available on the system), while it is strictly positive for a mixed state (indicating a complete or partial ignorance about the preparation of the state). This von Neumann entropy matches with our intuition about entropy in the classical sense, and can be seen as a generalization to quantum mechanics. It is somehow a measure of the correlations present between two subsystems, in our case the environment on one hand and the spin-chain on the other hand.

5. NUMERICAL SIMULATION OF THE EXCITATION ENERGY TRANSFER

Let us investigate now numerically the excitation energy transfer process in a photosynthesis complex via the model introduced above. Hence, the aim is to solve numerically the full quantum mechanical dynamics

$$\mathbf{i}\hbar\,\partial_t \Psi(t,\cdot) = H\Psi(t,\cdot)\,, \qquad t \in [0, T_\star]\,, \tag{9}$$

with initial condition $\Psi_{ini} := \Psi(0,\cdot) = (\psi^{ini}_{+-\cdots-}, 0, \cdots, 0)^t$, describing the fact that the first atom is initially in an excited state (has already absorbed one photon), whereas the remaining atoms are in their ground state. Let

$$\psi^{ini}_{+-\cdots-}(x) := K\, e^{-\frac{(x-q_0)^2}{4\,\sigma^2}}\, e^{\mathbf{i}\frac{p_0\,x}{\hbar}}\,, \qquad x \in [-L/2, L/2]\,, \quad p_0, q_0 \in \mathbb{R},\ \ \sigma > 0\,,$$

whith $K > 0$ a normalization constant such that $||\psi^{ini}_{+-\cdots-}||^2_{L^2} = 1$, initial condition which gives the probability distribution in the x-variable of the first spin. Initially, no system-environment correlations are assumed. The evolution of the complete system (9) will however lead immediately to correlations (entanglement) between the two subsystems. Periodic boundary conditions are chosen in the x-variable, however they are of no importance as the boundary is never reached during the simulation time, the vibration of the molecules remaining close to zero.

The numerical scheme used for the discretization of (9) is the Crank-Nicolson scheme, briefly summarized here. Discretizing the time and space variables as

$$0 =: t_0 \leq \cdots \leq t_k \leq \cdots t_{N_t} := T_\star \,, \quad t_k := k\,\Delta t\,, \quad \Delta t := T_\star/N_t\,,$$

$$-L/2 =: x_1 \leq \cdots \leq x_j \leq \cdots x_{N_x+1} := L/2\,, \quad x_j := -L/2 + (j-1)\Delta x\,, \quad \Delta x := L/N_x\,,$$

we are searching for each time-step t_k for an approximation $\Psi^k_j \in \mathbb{C}^N$ of the wave-function $\Psi(t^k, x_j)$, where $k = 1, \cdots, N_t$ and $j = 1, \cdots, N_x$, by solving

$$\mathbf{i}\,\hbar\,\frac{\Psi^{k+1} - \Psi^k}{\Delta t} = H\,\frac{\Psi^{k+1} + \Psi^k}{2}\,, \qquad \forall k = 0\,, \cdots, N_t - 1\,, \tag{10}$$

or equivalently

$$\left(Id + \frac{\mathbf{i}\Delta t}{2\hbar}\,H\right)\,\Psi^{k+1} = \left(Id - \frac{\mathbf{i}\Delta t}{2\hbar}\,H\right)\,\Psi^k\,, \qquad \forall k = 0\,, \cdots, N_t - 1\,.$$

We shall start this procedure from the initial condition $\Psi^0_j := \Psi_{ini}(x_j)$ and shall use the boundary conditions $\Psi^k_{N_x+1} = \Psi^k_1$. Remark that, for simplicity reasons, we explicited only the semi-discrete version of the Crank-Nicolson scheme. One has still to discretize the Hamiltonian H in the x-variable, by using the standard discretization of the Laplacian

$$-\frac{\hbar^2}{2m}\partial_{xx}\Psi(t_k, x_j) \sim -\frac{\hbar^2}{2m}\left(\frac{\Psi^k_{j+1} - 2\Psi^k_j + \Psi^k_{j-1}}{(\Delta x)^2}\right)\,, \quad \forall k, j\,.$$

The parameters chosen for our simulations are summarized in Table 1.

L	1	$N_x,\ dx$	$200,\ 5*10^{-3}$
$T_\star$	0.1	$N_t,\ dt$	$2000,\ 5*10^{-5}$
ε	10^{-1}	$\hbar,\ m$	$\varepsilon\,, 1$
N	$3, \cdots, 20$	λ_0	20
ω_c	50	ω_k	$\omega_\star - k\,,\ \omega_\star = 10 + \frac{50}{2-N}$
g_k	$g_\star - k\,,\ g_\star = 10 + \frac{100}{2-N}$	σ	$\varepsilon/4$
q_0	-0.03	p_0	$4/(3\,\varepsilon)$

TABLE 1. Parameters used in the numerical simulations.

Having described in detail the numerical scheme, let us pass now to the numerical tests. For each parameter regime a different dynamical behaviour emerges, in particular coherent dynamics, de-localization, decoherence, and so on, shall become visible.

5.1. **Un-perturbed, coherent excitation energy transfer.** The aim is now to study the performances of our spin-channel to transport the absorbed excitation (some kind of information) from one end of the chain to the other end, and this for various lengths N of the spin-chain, discussing firstly the purely quantum mechanical framework (isolated system) and then introducing an environment to investigate its influence on the transport. Thus let us start first by considering the quantum coherent dynamics associated to $H_{\mathcal{S}}$ only, in order to illustrate how such a "quantum" transfer looks like.

The first test concerns a short chain of $N = 3$ spin-particles, with uniform coupling-strengths $\lambda_k = \lambda_0 = 20$ and no interaction with the environment ($g_l \equiv 0$). On the left of Figure 6 we plotted the time-evolution of the occupation rate of the three possible configurations, namely $||\psi_j(t,\cdot)||^2_{L^2}$, for $j = 1, 2, 3$. What one observes is that initially the excitation is localized on the first atom ($||\psi_1(t = 0,\cdot)||^2_{L^2} = 1$), travels then in time through the spin-chain, to attain after a time of $t^\star = 0.011$, the final spin-state ($||\psi_3(t^\star,\cdot)||^2_{L^2} = 1$) and the process reverses. This excitation transfer occurs fully coherently, as one can observe immediately that the initial excitation is "dispersed" over several spins before being refocused on the final spin, fact which is typically considered as a quantum mechanical feature (quantum revival). Two important remarks have to be done now. On one hand, the coherent excitation transfer is accompanied by a periodic motion between the first and the last atom of the spin-chain, with a frequency of $\frac{1}{2\,t^\star}$. A sink is thus needed after the last atom, in order to absorb the arriving excitation. On the other hand, the excitation energy transfer seems to be perfect ($||\psi_3(t^\star,\cdot)||^2_{L^2} = 1$) in the mentioned time-interval of $t^\star$. In a spin chain with uniform coupling-strengths λ_0 between neighbouring atoms, this perfect

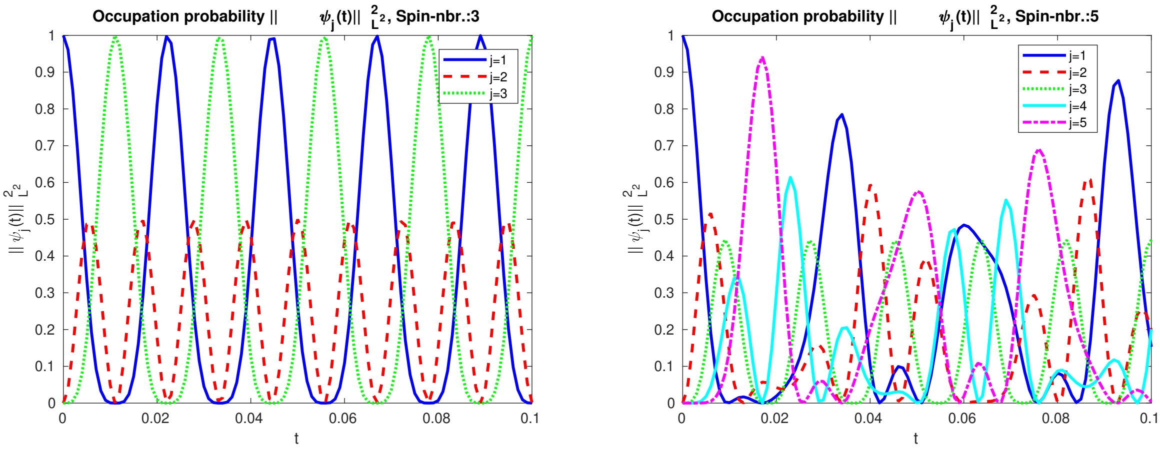

FIGURE 6. Occupation rate of the different spin-configurations, for $N = 3$ (left) and $N = 5$ (right). Uniform coupling-strengths and no interaction with the environment.

transfer can only be achieved for $N = 2$ or $N = 3$. Indeed, one can observe that for $N = 5$ (Right of Fig. 6) and for $N = 14$, 20 (Fig. 7) the excitation spreads out over several atoms and does not reach any more with probability one the final state, in other words it does no more refocus on the last TLS. It seems moreover that the probability of the excitation to reach the final state is reducing with the length of the spin-chain N and the time to reach this maximum probability grows (linearly) with N, as shown in Fig. 8. In particular one finds in the homogeneous coupling-strength case that $t^\star(N) \sim \frac{\hbar}{2\,\lambda_0}\,N + cst$.

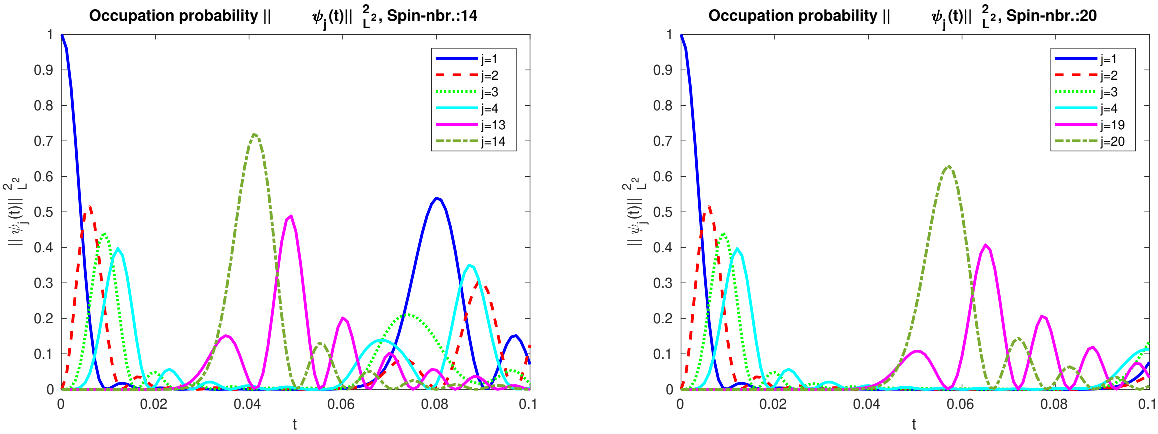

FIGURE 7. Occupation rate of the different spin-configurations, for $N = 14$ (left) and $N = 20$ (right). Uniform coupling-strengths and no interaction with the environment.

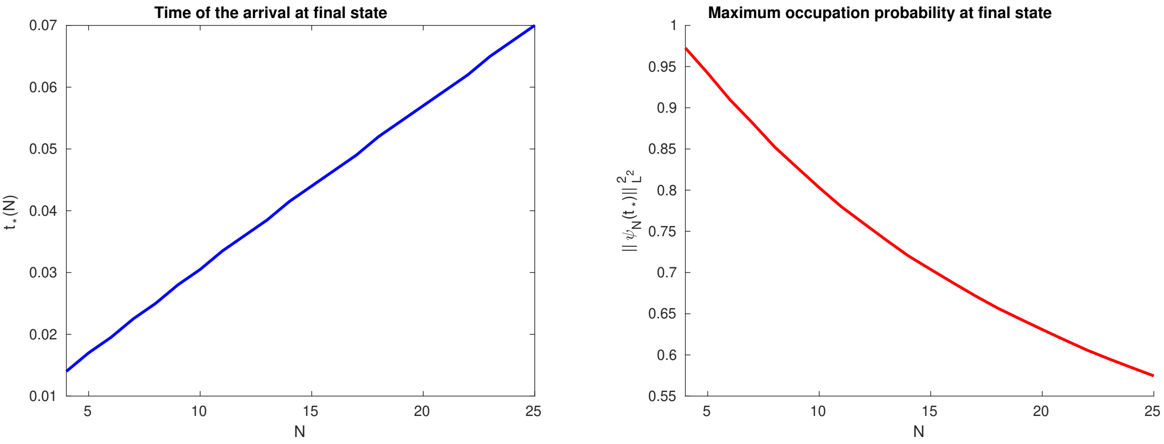

FIGURE 8. Left: Time $t^\star$ for an excitation to reach the final state, as a function of N. Right: Maximum occupation probability of the final state at time $t^\star$.

The main reason for this imperfect (coherent) excitation transfer is the dispersion of the initial excitation over the whole spin-chain. The transfer can be however improved by manipulating the coupling strengths, either all over the spin-chain or only at the extreme points (boundary control). The manipulation which leads to a perfect excitation transfer can be found by carrying out a spectral analysis of the Hamiltonian, in particular by determining the eigenvalues and eigenvectors of the system, in order to understand which configuration is the best one for a perfect excitation transfer [29]. The parameters to be chosen to get such a perfect transfer, are obtained by asking that

$$e^{-\frac{i}{\hbar}\,t^\star H}\,\Psi_{ini} = \Psi_{out}\,, \quad \Psi_{out}(x) = (0, 0, \cdots, \psi^{out}_{-\cdots-+}(x))^t\,, \quad ||\psi^{out}_{-\cdots-+}||^2_{L^2} = 1\,,$$

meaning that the initial condition evolves during the time $t^\star$ into the final state Ψ_{out} which describes the fact that only the last spin is excited.

Let us first start with the adjustment of all spin-coupling strengths. In Figure 9 we plotted the density probabilities for $N = 14$ and $N = 20$ in the case of a well-defined choice of these coupling strengths, namely $\lambda_l := \lambda_0 \sqrt{l\,(N-l)}$, $\lambda_0 = 20$ and $l = 1, \cdots, N-1$ [29]. A perfect excitation transfer can be indeed observed. The excitation travels along the spin-chain, and due to the special structure of the coupling-strengths, refocuses at the other end, with occupation probability one. The process then reverses, the time-scale for an excitation to reach the final end of the chain is given by $t^\star = \frac{\pi\,\hbar}{2\,\lambda_0}$. These coupling strengths are however not so physical, as the maximum strength is given by $\lambda_{max} := \lambda_0\,N/2$, which is increasing with N. To be closer to reality it would be better to fix the maximum strength to λ_{max} and to choose $\lambda_0 := 2\,\lambda_{max}/N$. The corresponding plots are shown in Fig. 10. In this case, the time for the excitation to reach the other end of the chain grows linearly with N as $t^\star(N) = \frac{\pi\,\hbar}{4\,\lambda_{max}}\,N$. Remark here that for information processing it is very important to know accurately the transfer time, in order to read out the information at the right moment.

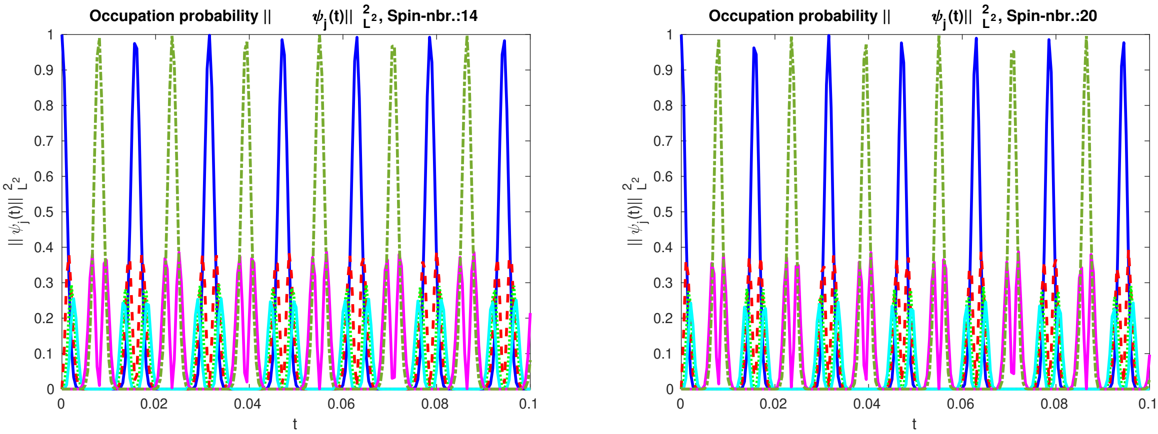

FIGURE 9. Occupation rate of diff. spin-configurations, for $N = 14$ (left, $j = 1, 2, 3, 4, 13, 14$) and $N = 20$ (right, $j = 1, 2, 3, 4, 19, 20$). Modulated coupling strengths, no interaction with environment, $t^\star(N) = \frac{\pi\,\hbar}{2\,\lambda_0} = \frac{\pi\,\hbar}{4\,\lambda_{max}}\,N\,,\ \ \lambda_{max} = \lambda_0\,N/2$.

As a final test, we choose now homogeneous coupling strengths except for the extreme sites, namely $\lambda_l := \lambda_0$ for all $l = 2, \cdots, N-2$, and $\lambda_1 = \lambda_{N-1} = N^{-1/6}\,\lambda_0$. This is

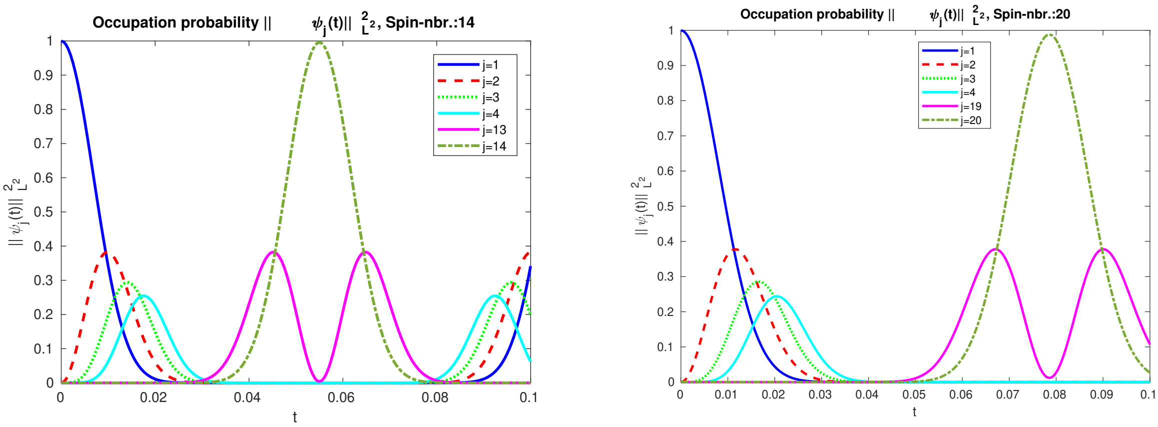

FIGURE 10. Occupation rate of diff. spin-configurations, for $N = 14$ (left) and $N = 20$ (right). Modulated coupling-strengths, no interaction with the environment, $t^\star(N) = \frac{\pi\,\hbar}{4\,\lambda_{max}}\,N$ and $\lambda_{max} = \lambda_0$.

the so-called *optimal coupling regime* and one observes (see Fig. 11) that an "almost" perfect transport is achieved, in a transfer time of $t^\star(N) = \frac{2\,\hbar}{\lambda_0\,\pi}\,N$. These plots have to be compared with the corresponding plots with uniform couplings, namely Fig. 7.

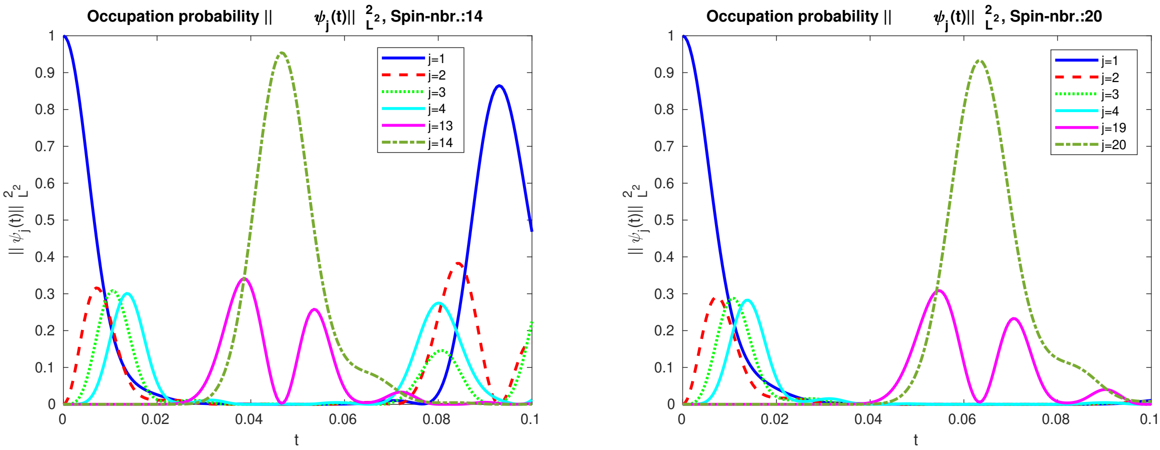

FIGURE 11. Occupation rate of diff. spin-configurations, for $N = 14$ (left) and $N = 20$ (right). Homogeneous coupling-strengths, except for the extreme TLSs., $t^\star(N) = \frac{2\,\hbar}{\lambda_0\,\pi}\,N$ and $\lambda_{1,N-1} = N^{-1/6}\,\lambda_0$.

The phenomenon we just observed by adjusting the coupling coefficients is called *quantum revival*. The initial wave-function spreads out over the entire spin-system, however after some time the spreading inverses and the wave-function is reconstituted at the last spin, reconstructing approximately the initial wave-function. The key argument for this spreading and refocusing is the dispersion relation, which defines how each mode of the wave-packet evolves with respect to the others modes, and shows also after which time the phases of these different modes realign. This phenomenon is common for all dispersive systems, with discrete energy-levels, satisfying a special condition for the spacings of the successive energy-levels, such that the phases of the different modes realign at the last spin.

Let us summarize what we have learned from this Section, where only the unperturbed, isolated spin-chain was considered:

- the here presented model permits a fully coherent propagation of an energy excitation through a spin-chain;
- it does however not always allow for a perfect state transfer, because of wave-packet dispersion;
- perfect or almost perfect transfer properties have been achieved for a specific class of Hamiltonians, with well-engineered coupling strengths among the TLSs. These coupling strengths can be found by performing a spectral study of the Hamiltonian.

One could remark now that Nature, through its millenary evolution, has selected the best possible configurations and rejected the bad ones, or simply that it evolves permanently, adapting the coupling-strengths to the incoming light (photons). However, one important aspect has still to be taken into account, namely the vulnerability of this perfect transfer to uncontrolled, random external perturbations (environment) and the ensuing decoherence.

5.2. **Effect of the environment on the excitation transfer.** The perfect excitation energy transfer we observed in the last section in the case of an isolated spin-chain, is an important step in the field of quantum information processing, for example in the aim to exchange information between distant nodes in a computer. But any real system is inevitably exposed to its surrounding environment, such that achieving a perfect transfer from one end to the other one, in a non-isolated spin-network, is a more delicate task. Nature, despite its diversity seems to be able to achieve 100% perfect excitation energy transfer in real photosynthesis complexes, under each circumstance. Let us thus explore in this section which is the effect of a vibrational (dephasing) environment on our excitation energy transfer in the spin-chain. In particular we are interested in the vulnerability of the almost/perfect energy transfer configurations, when introducing random perturbations coming from the environment.

In the first test case, the author was interested in exploring the effect of a random dephasing environment on the modulated spin-configuration, which leads in the isolated case to perfect transfer. Figure 12 shows on the left the un-perturbed occupation probability of several spin-configurations, for $N = 14$, when the coupling-strengths are modulated via the formula $\lambda_l := \lambda_0 \sqrt{l\,(N-l)}$, $\lambda_0 = 20$. On the right of Figure 12, the same test-case was plotted, however in the situation where the environment is perturbing the spin-chain. A random perturbation was introduced via the chain-environment coupling coefficients $\tilde{g}_l = \gamma_l\, g_l$, where γ_l is randomly chosen in $[0,1]$ and g_l is given in Table 1. The central spin-chain seems to be somehow slightly perturbed by the interaction with the environment. To compare, the author tested then the robustness of the second test-case, namely the optimal coupling regime given by $\lambda_l := \lambda_0$ for all $l = 2, \cdots, N-2$, and $\lambda_1 = \lambda_{N-1} = N^{-1/6}\,\lambda_0$. This configuration seems to be more sensitive to the same type of environmental perturbation, as observed in Figure 13. Perturbation theory permits to gain more detailed insight in the stability properties of this mathematical eigenvalue problem.

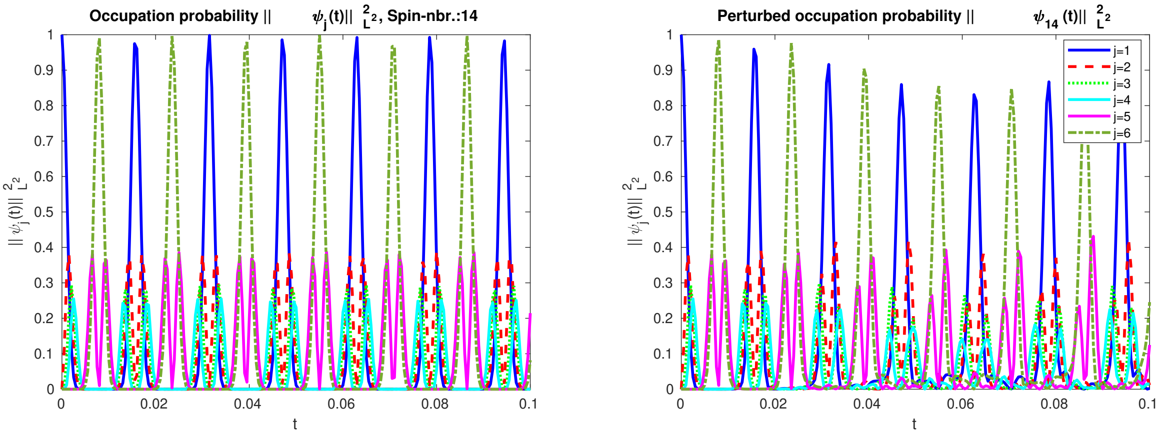

FIGURE 12. Left: Occupation rate of diff. spin-configurations, for $N = 14$ in the modulated spin-configuration. Right: The corresponding perturbed situation.

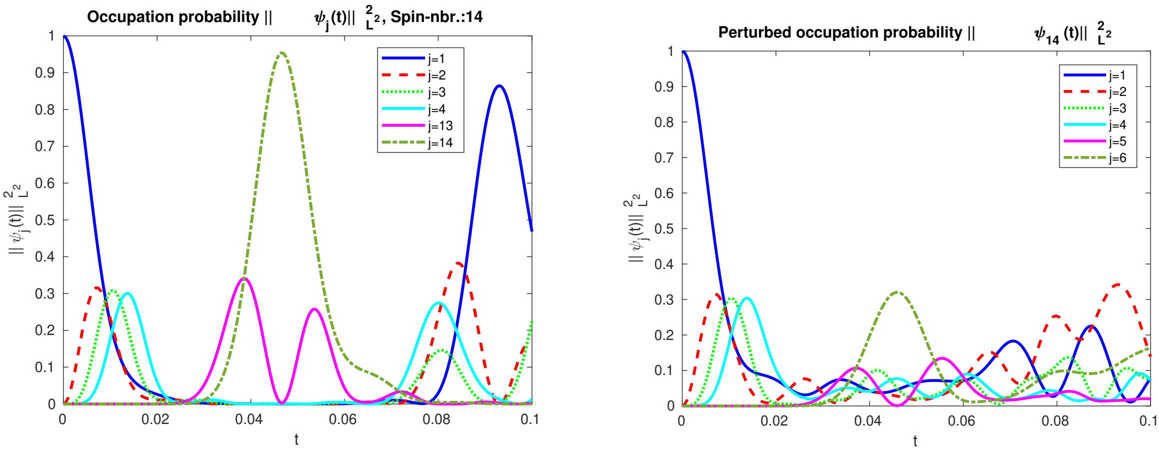

FIGURE 13. Occupation rate of diff. spin-configurations, for $N = 14$ in the optimal coupling spin-configuration. Right: The corresponding perturbed situation.

In order to investigate in more details the influence of the environment on the excitation transfer, let us take a look at the entanglement entropy in these two cases. The entanglement entropy is a manner to measure the entanglement of a spin-chain with its environment, and hence to investigate somehow the quantumness of our central spin-system. Figure 14 illustrates the time-behaviour of the entropy $\mathcal{S}(t)$, defined in formula (8), and this for two chain-lengths $N = 14$ and $N = 20$ and the two different test-cases investigated above. What can be observed is firstly that entropy increases in time, which is natural, as the entanglement of the system with the environment becomes more and more important with the advance in time. Secondly, the entanglement of the central system with the environment seems to be more important in the second test case, namely the optimal coupling regime, fact which was also observed above.

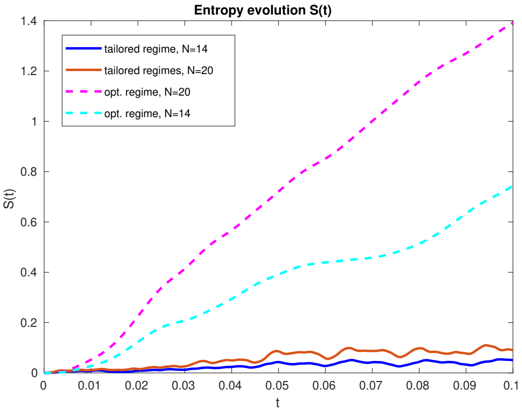

FIGURE 14. Time evolution of the entanglement entropy between the environment and the spin-chain, for $N = 14$ and $N = 20$ and two different regimes: the tailored coupling-strength regime and the optimal coupling regime.

Entanglement with the environment is associated in general with entropy production and thus is not expected to lead to improvements in the efficiency of the process. However, let us come now to a situation where the environmental noise can help to enhance the excitation transfer. A typical example is a situation, where the excitation was trapped at some moment in a coherent stationary state, for example in an eigenstate of the corresponding Hamiltonian. In this case, without perturbation from outside, the solution of the Schrödinger equation is stationary and the excitation will remain in that state for all the times, without being able to reach the reaction center. This is illustrated in the left plot of Fig. 15, where the initial condition corresponds exactly to one of the eigenvectors of the unperturbed Hamiltonian $H = H_{\mathcal{S}} + H_{\mathcal{E}}$, in the uniform coupling regime. In this situation, the introduction of an interaction with the environment leads to disorder and noise, permitting to get out of the stationary state, and the transport of the excitation becomes again possible, as seen in the right plot of Fig. 15.

As a conclusion of this section, the author observed that:

- the influence of the environment on a well-tailored spin-configuration can be rather drastic in some situations and destroy the perfect excitation energy transfer $\Rightarrow$ coherence escaped into the environment;

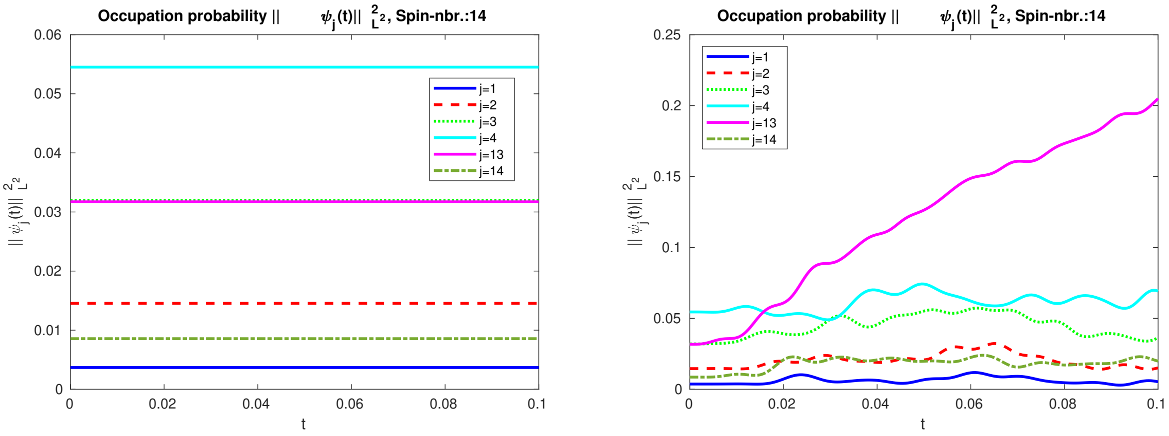

FIGURE 15. Occupation rate of different spin-configurations, for $N = 14$, in the uniform coupling regime, with an initial condition corresponding to one eigenvector of $H = H_{\mathcal{S}} + H_{\mathcal{E}}$. Left: Un-perturbed case. Right: Perturbed case.

- however in some specific situations, the environment can help and enhance the excitation transfer, simply by destroying, via vibrations, the coherent trapping.

So, coupling of a system to its surrounding environment is not necessarily a disadvantage, can however cause damage. The interplay of an unavoidable noise and the internal quantum coherence seems to play an important role in the optimal operation of biological systems.

6. A CLASSICAL ENERGY-TRANSFER MODEL

The motion of many wave-like phenomena in nature are often well-described with the help of classical harmonic oscillators. So, what is not so clear with the mathematical modelling of the previous chapters, is to which extent one must evoke quantum features to explain the excitation energy transfer in photosynthesis processes. To clarify this fact, let us consider a classical counterpart of the quantum mechanical model introduced above, in the aim to investigate the ability of a classical model to reproduce certain aspects of the excitation transfer, as for example coherence, aspects often viewed as typical quantum mechanical features.

One can consider a $1D$ chain of N particles, with masses $\{m_i\}_{i=1}^N$, coupled to each other via $N+1$ springs of spring-constants $\{\kappa_j\}_{j=1}^{N+1}$, as illustrated in Fig. 16. The first mass m_1 is excited via an external force term $f_{ex}(t) := \alpha \sin(\omega t)$, and we suppose that each mass is subject to a friction force, with friction coefficients $\{\eta_i\}_{i=1}^N$ (for the moment a standard picture of N coupled damped oscillators).

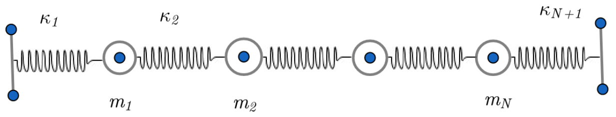

FIGURE 16. A $1D$ chain of N coupled masses, the first mass being excited from the exterior.

Denoting by $\{x_i(t)\}_{i=1}^N$ the displacements of the masses with respect to their equilibrium positions, the time-evolution of these quantities is given by the following coupled system of ODEs, coming from Newton's laws, namely

$$\begin{cases} m_1\, x_1^{''}(t) &=& -\kappa_1\, x_1(t) - \kappa_2\,(x_1(t)-x_2(t)) - \eta_1\, x_1'(t) + f_{ex}(t) \\ m_i\, x_i^{''}(t) &=& -\kappa_i\,(x_i(t)-x_{i-1}(t)) - \kappa_{i+1}\,(x_i(t)-x_{i+1}(t)) - \eta_i\, x_i'(t)\,, \quad \forall i=2,\cdots,N-1 \\ m_N\, x_N^{''}(t) &=& -\kappa_N\,(x_N(t)-x_{N-1}(t)) - \kappa_{N+1}\, x_N(t) - \eta_N\, x_N'(t)\,. \end{cases} \tag{11}$$

We recognize in this system the force excerced on particle i through the spring-coupling with the $(i-1)^{th}$ particle, namely $F_{c,(i-1)\to i} := -\kappa_i\,(x_i(t)-x_{i-1}(t))$, as well as the dissipative force acting on particle i, namely $F_{r,i} = -\eta_i\, x_i'(t)$. This system can be rewritten in matrix form as

$$X^{''}(t) = -K\, X(t) - R\, X'(t) + S(t)\,, \tag{12}$$

with the position vector $X(t) := (x_1(t),\cdots,x_N(t))^t$, the source vector $S(t) := (f_{ex}(t)/m_1, 0, \cdots, 0)^t$ and the matrices $R := diag(\frac{\eta_1}{m_1}, \frac{\eta_2}{m_2}, \cdots, \frac{\eta_N}{m_N})$ as well as

$$K := \begin{pmatrix} (\kappa_1+\kappa_2)/m_1 & -\kappa_2/m_1 & 0 & \cdots \\ -\kappa_2/m_2 & (\kappa_2+\kappa_3)/m_2 & -\kappa_3/m_2 & \cdots \\ \vdots & & \ddots & \ddots \\ \cdots & 0 & -\kappa_N/m_N & (\kappa_N+\kappa_{N+1})/m_N \end{pmatrix}.$$

Let us remark here that Newton's system (12) can be seen as a (slightly differing) classical counterpart of the Schrödinger equation (9). The matrix K is rather similar to the Hamiltonian (6) if one does not consider the environmental influence (no x-variable). This similarity is however rather superficial, the real link between both systems will be detailed later (see (13)). The total mechanical (kinetic + potential) energy of the system, meaning the N-coupled masses, is given by the formula

$$\mathcal{E}_{tot}(t) := \frac{1}{2}\sum_{i=1}^{N} m_i\,[v_i(t)]^2 + \frac{1}{2}\sum_{i=1}^{N+1} \kappa_i\,[x_i(t)-x_{i-1}(t)]^2\,,$$

and the rate of change of this energy in time (the power) is

$$\begin{aligned} \frac{d\mathcal{E}_{tot}(t)}{dt} &= \sum_{i=1}^{N} F_i(t)\, v_i(t) + \sum_{i=1}^{N+1} \kappa_i\,(x_i(t)-x_{i-1}(t))\,(v_i(t)-v_{i-1}(t)) \\ &= -\sum_{i=1}^{N} \eta_i\, |v_i(t)|^2 + f_{ex}(t)\, v_1(t)\,, \end{aligned}$$

where we used the notation $v_i(t) := x_i'(t)$ for the velocity of each mass, and $F_i(t) = m_i v_i'(t)$ for the force exerced on this mass by the surrounding masses. Remark also that we introduced ghost points $x_0 \equiv 0$ and $x_{N+1} \equiv 0$ to simplify the formulae. Let us observe here that the rate of change of the mechanical energy of the whole system is governed by the friction energy loss and the exteriour energy supply. The power administrated to the system by the exterior force is $p_{in}(t) = f_{ex}(t)\, v_1(t)$.

In order to analyze how the energy and the power is transferred from one mass to the other, we shall associate to a mass the following local energy

$$\left\{ \begin{array}{lcl} e_1(t) & := & \frac{1}{2} m_1 \,[v_1(t)]^2 + \frac{1}{2}\kappa_1\,[x_1(t) - x_0(t)]^2 + \frac{1}{4}\kappa_2\,[x_2(t) - x_1(t)]^2 \\ e_i(t) & := & \frac{1}{2} m_i \,[v_i(t)]^2 + \frac{1}{4}\kappa_i\,[x_i(t) - x_{i-1}(t)]^2 + \frac{1}{4}\kappa_{i+1}\,[x_{i+1}(t) - x_i(t)]^2 \,, \quad \forall i = 2, \cdots, N-1 \\ e_N(t) & := & \frac{1}{2} m_N \,[v_N(t)]^2 + \frac{1}{4}\kappa_N\,[x_N(t) - x_{N-1}(t)]^2 + \frac{1}{2}\kappa_{N+1}\,[x_{N+1}(t) - x_N(t)]^2 \,, \end{array} \right.$$

as well as the following local power $p_i(t) = e_i'(t)$

$$\begin{array}{lcl} p_1(t) & := & F_1(t)\, v_1(t) + \kappa_1\,(x_1(t) - x_0(t))\,(v_1(t) - v_0(t)) + \frac{1}{2}\kappa_2\,(x_2(t) - x_1(t))\,(v_2(t) - v_1(t)) \\ & = & -\frac{1}{2}\kappa_2\,(x_1(t) - x_2(t))\,(v_1(t) + v_2(t)) - \eta_1 |v_1(t)|^2 + f_{ex}(t)\, v_1(t) \\ p_i(t) & := & F_i(t)\, v_i(t) + \frac{\kappa_i}{2}\,(x_i(t) - x_{i-1}(t))\,(v_i(t) - v_{i-1}(t)) + \frac{\kappa_{i+1}}{2}\,(x_{i+1}(t) - x_i(t))\,(v_{i+1}(t) - v_i(t))\,, \\ & = & -\frac{\kappa_i}{2}\,(x_i(t) - x_{i-1}(t))\,(v_i(t) + v_{i-1}(t)) - \frac{\kappa_{i+1}}{2}\,(x_i(t) - x_{i+1}(t))\,(v_i(t) + v_{i+1}(t)) - \eta_i |v_i(t)|^2 \\ p_N(t) & := & F_N(t)\, v_N(t) + \frac{1}{2}\kappa_N\,(x_N(t) - x_{N-1}(t))\,(v_N(t) - v_{N-1}(t)) + \kappa_{N+1}\, x_N(t)\, v_N(t) \\ & = & -\frac{1}{2}\kappa_N\,(x_N(t) - x_{N-1}(t))\,(v_N(t) + v_{N-1}(t)) - \eta_N |v_N(t)|^2 \,. \end{array}$$

Energy escapes from a given oscillator via two channels, namely via the friction term which dissipates the energy towards the exteriour (the bath), as well as via the coupling with the two neighbours. Of interest are also the mean energy and the mean power transfer, for driving frequencies ω near one of the eigen-frequencies of the system, where the mean is taken over a period of the excitation force, namely

$$(\overline{e_i})_k := \frac{1}{T}\int_{kT}^{(k+1)T} e_i(t)\, dt\,, \quad (\overline{p_i})_k := \frac{1}{T}\int_{kT}^{(k+1)T} p_i(t)\, dt\,, \quad T = \frac{2\pi}{\omega}\,, \quad k \geq 0\,.$$

To illustrate the energy transfer we plotted in Figure 17 the dynamics of the harmonic oscillator chain, in particular we depicted the evolution of the amplitude of the first and 7^{th} atom in the chain, as well as their local energies, for an excitation frequency near resp. far from an eigenvalue of the coupled system. In this test case, the total number of masses is $N = 14$, the first masses are supposed frictionless, *i.e.* $\eta_i = 0$ for $i = 1, \cdots, 7$, and the second part of the chain is assumed to absorbe the incoming energy via friction, *i.e.* $\eta_i = 0.2$ for $i = 8, \cdots, 14$. The corresponding eigenfrequencies $\nu_\star = \omega_\star / 2\pi$ belong to the set $\{0.3171; 0.6541; 0.9785; 1.2908; \ldots; 3.1657\}$. What can be observed is firstly that under the action of the external force $f_{ext}(t)$ and after some brief transition regime, the system asymptotically attains a stationary state where the masses execute synchronized mouvements with the same frequency as the external force. The driving force deposits energy into the system during some time-intervals, and takes out energy during other intervals, except in the resonance regime, where the external force always supplies the system with energy. The damping force always takes out energy from the system. For steady-state solutions, driving and damping terms balance out. Thus, for excitation frequencies near an eigenfrequency of the system, more energy is put into the system, and the excitation is very well transferred from one mass to the other due to energy-momentum matching, whereas more difficulties are encountered if the excitation frequency is far from an eigenfrequency, as can be observed on the two plots of Figure 17. On Figure 18 are shown the corresponding mean energy and power transfers.

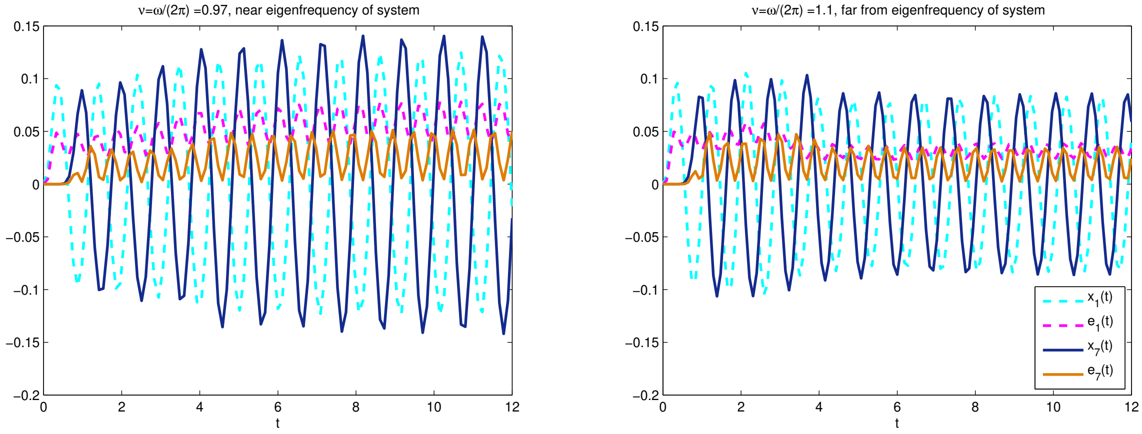

FIGURE 17. Time-evolution of the position $x_i(t)$, energy $e_i(t)$ and power $p_i(t)$ for two excitation frequencies, near (left plot) and far from (right plot) an eigenfrequency of the system. Here $N = 14$, $m_i = 0.1$, $\kappa_i = 10$ and $f_{ex}(t) := \sin(\omega t)$, $\omega = 2\pi\,\nu$.

One can now use this simple model to deepen the understanding of the excitation energy transfer in photosynthesis complexes, by comparing this classical, intuitive model with the quantum one. Several differences have immediately to be mentioned.

- Initial excitation versus permanent external excitation:
  In the quantum model, the excitation was initially introduced in the model, by stimulating the first two-level system, which has absorbed one photon (initial condition). The systems evolves then according to the free dynamics. In the classical model, there is a permanent excitation from outside, via the external force term $f_{ex}(t)$, which drives the system dynamics. The question which arises immediately is which of these two descriptions is better adapted to model the light absorption in the photosynthesis process?
- Interaction with the environment:
  In the quantum model, the interaction with the environment is of dephasing type, no energy is lost during this interaction, the dephasing is introducing only decoherence, via the entanglement of the spin-chain with the surroundings. Contrary to this, in

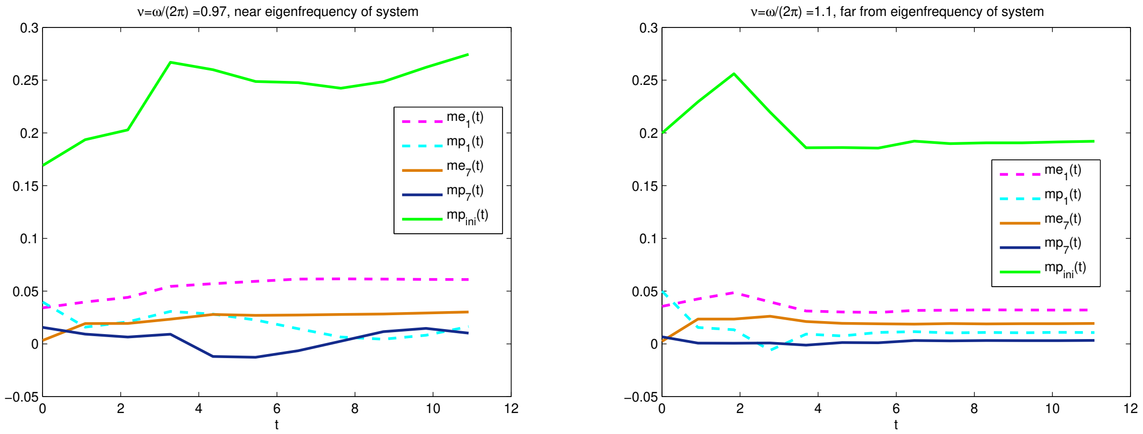

FIGURE 18. Time-evolution of the mean energy $\overline{e_i}(t)$ and mean power $\overline{p_i}(t)$ over a period $T = 1/\nu$, for two excitation frequencies, near and far from an eigenfrequency of the system. Here $N = 14$, $m_i = 0.1$, $\kappa_i = 10$ and $f_{ex}(t) := \sin(\omega t)$, $\omega = 2\pi\,\nu$.

the classical model, a friction term is added, which dissipates the energy. As we are interested only in a dephasing-interaction with the environment, the question which arises naturally is how one can model a dephasing in the classical framework?

Forgetting about these two disparities, let us compare now the classical and quantum isolated systems, in order to understand if there is some distinction, in particular we are interested whether classical coherence is equal in this model to quantum coherence. The two models we want to compare are the Schrödinger equation on one hand and the coupled Newton system on the other hand, namely

$$\mathbf{i}\,\hbar\partial_t\Psi(t) = H\,\Psi(t)\,, \qquad X''(t) = -K\,X(t)\,.$$

Supposing that the matrix K is symmetric and positive definite (which is true for example when all the masses of the oscillator are equal), then one can find a unique symmetric and positive definite matrix A, such that $A^2 = K$. Thus, let us now introduce the new complex variable

$$Z(t) := X(t) + \mathbf{i}\,W(t)\,, \quad \text{with} \quad A\,W(t) = X'(t)\,.$$

With this transformation, one obtains immediately the two systems to be compared

$$\mathbf{i}\,\hbar\partial_t\Psi(t) = H\,\Psi(t)\,, \qquad \mathbf{i}\,\hbar Z'(t) = \hbar\,A\,Z(t)\,. \tag{13}$$

If the coefficients (energies, masses, coupling constants) in the quantum and classical problems are chosen such that both matrices H and $\hbar\,A$ have the same eigenvalues, then after a scaling of both vectors Ψ and Z one obtains the same problems. Hence we can conclude that in the isolated framework, our quantum spin-chain problem is completely equivalent to a classical harmonic oscillator problem, so quantum and classical coherences represent the same phenomena in this simple model. This equivalence seems to come essentially from the correspondance between the classical and the quantum eigenfrequencies.

In a more general framework, is there finally a difference between quantum and classical behaviours? We have seen, that if only one excitation is present in the spin-chain, then only N single-excitation configurations contribute to the excitation dynamics, and this situation is exactly mapped, in the isolated case, on a chain of N classical harmonic oscillators, as proven above. In the case of multiple excitations, the number of configurations contributing to the dynamics increases up to 2^N, such that this time the equivalent classical counterpart model needs 2^N classical harmonic oscillators. It could be hence, that the advantage of quantum mechanics in such energy excitation transfer situations, comes not from the coherent dynamics of the excitation (which seems to be in both quantum and classical framework equivalent), but rather from the "escaladation" of classical harmonic oscillators needed for the same process (energy transfer).

Furthermore, if it has been observed that quantum features permit to enhance the excitation energy transfer in photosynthesis complexes, let us give here some other hints where to search for the reasons of such a primacy of quantum models:

- a more detailed investigation of the interaction with the environment has to be done, as this could be the main point which brings a difference in our simple problem. Indeed, the quantum entanglement between the central system and the environment could have no analogue in classical mechanics. For this, the question of how to model the dephasing effect in the classical model is of great importance;
- more realistic environments could be modelled, for example several phonons describing different interacting or non-interacting baths;
- a more realistic central system could be modelled, for example 2D chains permitting multiple paths.

All these directions, in particular the investigation of the environmental induced dephasing, its influence on the excitation energy transfer and its (possible?) description via a classical noise process, are aim of the next work. The idea is to get a better understanding of what are the real quantum properties which permit to enhance the excitation energy transfer, aspects which seem to be more enigmatical than initially thought, as we have seen in this section. It can be that dephasing exhibits non-classical attributes, depending on the nature of the system-environment interactions, attributes which lead to the EET-enhancement.

7. Conclusions and prospects

The aim of this paper was to introduce a simple mathematical model for the description of the excitation energy transfer in photosynthesis complexes. The reasons were:

- to provide an introduction in the math. modelling of the photosynthesis process;
- to illustrate with some simple examples how an excitation can be transferred using the dynamics of a spin-chain Hamiltonian;
- to prepare the mathematical formalism and techniques required for a deeper mathematical study of the excitation energy transfer, study postponed to a second forthcoming paper;

- to make the analogy with a simple classical harmonic-oscillator chain model.

Despite the numerous experimental and theoretical studies, we still have a lot of uncertainties about how plants can transfer the absorbed photon with such a big efficiency, and which is the mechanism behind. One of the open questions is the role of a vibrational environment on the quantum-mechanical coherent propagation of the excitation. It seems that Nature has performed, through its millenary evolution, a full optimization of the excitation energy transfer via a tricky interplay between the coherent quantum dynamics and the unavoidable presence of noise, induced by the environment. Organisms change over time as a result of changes in the environment. These changes allow an organism to better adapt to its environment, to survive and have more offspring. The studies performed above provide a good example of how one could reinforce/boost the excitation energy transfer in artificial systems, are however no evidence of how Nature proceeds. Indeed, the here presented model seems to be too simple to clearly separate quantum and classical features in the excitation energy transfer. More realistic models have to be investigated.

The model presented above in the framework of the excitation energy transfer in photosynthesis complexes can be also used to describe several other energy transfer phenomena in biological systems, as for example the firing in a neuronal network and the ensuing decoherence due to interaction with the surrounding environment. The property of non-locality (correlations between distant molecules) observed in the excitation energy transfer of photosynthesis systems may be the fundamental property permitting to explain the exceptional speed with which our brain treats informations, such that the same questions arise as for the here presented application.

Acknowledgments. The author would like to acknowledge support from the CNRS-IEA project N^o 295470 *NASOQUAD* (Numerical and Analytical Study Of QUAntum Decoherence, 2020-2022).

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Université de Toulouse & CNRS, UPS, Institut de Mathématiques de Toulouse UMR 5219, F-31062 Toulouse, France.

E-mail address: `claudia.negulescu@math.univ-toulouse.fr`