Degree Project C in Chemistry

Theoretical Chemistry

Decoherence-assisted transport in pigment protein complexes

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To the dawn,
...And may one know what you want this boat for, was what the king did in fact ask when he had finally managed to install himself with a reasonable degree of comfort on the cleaning woman’s chair, To go in search of the unknown island, replied the man, What unknown island, asked the king, suppressing his laughter, as if he had before him one of those utter madmen obsessed with sea voyages, whom it would be as well not to cross, at least not straightaway, The unknown island, the man said again, Nonsense, there are no more unknown islands, Who told you, sir, that there are no more unknown islands, They’re all on the maps, Only the known islands are on the maps, And what is this unknown island you want to go in search of, If I could tell you that, it wouldn’t be unknown, Have you heard someone talking about it, asked the king, more serious now, No, no one, In that case, why do you insist that it exists, Simply because there can’t possibly not be an unknown island, And you came here to ask me for a boat, Yes, I came here to ask you for a boat, And who are you that I should give you a boat, And who are you to refuse me one, I am the king of this kingdom, and all the boats in the kingdom belong to me, You belong to them far more than they belong to you, What do you mean, asked the king, troubled, I mean that without them you’re nothing, whereas, without you, they can still set sail...

José Saramago

The tale of the unknown island.
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Abstract

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by Adrià Sonet

Two chlorophylls of the FMO complex, the light-harvesting complex of the green sulfur bacteria, are modeled as two coupled qubits, each surrounded by one spin-bath simulating the environment. The dynamics of the system at a non-zero temperature provide exact analytical expressions for the transition probability and the coherence. It is shown that the decoherence-inducing interaction with the environment enhances the electronic energy transfer. Also the correlations in terms of entanglement and nonlocality are quantitatively studied, sensitively differing when introducing a decay term to resemble both chlorophylls being in their ground states. It is proved that nonlocality is a stronger form of correlation than entanglement.

Keywords: Entanglement, concurrence, nonlocality, electronic energy transfer, FMO complex, light-harvesting complex.
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1 Introduction

Recently, scientists of the apparently divergent branches that are biology and physics, both connected to chemistry from distinct approaches, have shown interest in one same fact: there is evidence of biological systems using mechanisms that can only be explained from a quantum point of view. Furthermore, this is found in such a non-trivial engine as the remarkably efficient electronic energy transfer between excited chlorophylls at a physiological temperature, which is a basic feature for photosynthetic organisms. This discovery [1] has raised the interest of the scientific community for this research field because the deep understanding of this phenomenon can provide us with knowledge about how to take advantage of quantum properties. For instance, this could be applied in the development of an artificial light harvesting device to produce more efficient solar cells, but also in more general cases and it can even shed some light to face the difficulties experienced in the construction of the desired quantum computer.

Quantum information theory is a discipline emerged just a few decades ago, being its main attribute to regard the systems under study in terms of information transfer, a concept arisen from the very foundations of quantum mechanics. Concerning the investigation of the highly efficient electronic energy transfer in biological systems, it provides a methodology to deal with the case under study through the assumption that the most efficient information transport between two systems is achieved when they are correlated. In this sense, two types of quantum correlations will be contemplated: entanglement and nonlocality, the later being a stronger form of correlation. Usually, these quantum properties are not detected in a system surrounded by an environment due to the decoherence effect induced by their interaction, which is supposed to remove the previous correlations, i.e. irrevocably lose the shared information. However, it has been proved experimentally [1] as well as with numerical calculations [2, 3] that the quantum nature is sustained longer than expected. The environment enhancing these quantum properties is the fact that gives rise to the title of this report: "Decoherence-assisted transport in pigment protein complexes".

The scope of this project is to investigate the electronic energy transfer and evaluate the correlations between two chlorophylls of the FMO complex involved in the first steps of the photosynthesis of the green sulfur bacteria. The two chromophores will be modeled as two qubits representing the ground and excited state of each chromophore and the environment will be regarded as two nuclear spin-baths surrounding each qubit, as similarly done in [4] and expanded in [5]. By solving the time dependent Schrödinger equation we aim to find the analytical expressions for the transition probability together with the quantification of entanglement and nonlocality. These concepts will be mapped for different temperatures as a function of the coupling with the environment and the time.

The outline of the report is as follows: next section introduces the theory needed to face the problem and accomplish the objective of the project. In section 3 the model to simulate the system is developed. The results are presented and discussed in section 4. The report ends with the conclusions.
2 Background

The framework of this project can be considered to have of two distinct approaches, mainly differing in their viewpoints:

- The biological perspective, supplying the system under study and the topic to investigate.
- The physical perspective, providing the tools and the methods to carry out the research.

In this section, we give the background of these two approaches.

2.1 Biological approach

2.1.1 Light-harvesting complexes

The light-harvesting complexes, abbreviated as LHC, are complexes that consist of several subunits of proteins enclosing distinct photosynthetic pigments such as chlorophylls. Altogether they constitute a larger supercomplex of a photosystem, a basic unit in the photosynthesis.

Plants, algae and some bacteria are photosynthetic organisms that transform the light energy to chemical energy gathered in the new bonds formed during synthesis of carbohydrates in the process known as photosynthesis, requiring water and carbon dioxide and also obtaining oxygen gas as a product. In this process the LHC has the function of harvesting photons in the region called antenna and shuttling the collected energy to the reaction centre of the photosystem. This mechanism has two main stages:

1. Capture of a photon through the pigment, which leads to the promotion of one electron from the ground state to a higher energy level when the energy of the absorbed photon matches that of an electronic transition. This results in the pigment being in an excited electronic state.

The most common type of pigment are the chlorophylls. These molecules consist of a chlorin ring with a magnesium ion at the centre:

![Figure 2.1: Structure of the bacteriochlorophyll a, the molecule we will focus on later in this report. Instead of a chlorin ring (20 π electrons), it has a bacteriochlorin cycle, which presents one double bond less, resulting in 18 π electrons in its ring. Image obtained from the Protein Data Bank [6].](image-url)
The fate of the electronic excitation of the pigment can be any of these:

(a) Returning to the ground state.

(b) Reorganizing to another electronic state in the same molecule.

(c) Having a close molecule, the excitation energy may be transferred, through electromagnetic interactions, from one molecule to the other.

2. The process described in (c) is the one that occurs in LHC due to the specific and optimized positions of the pigments. This Electronic Energy Transfer (EET) is also known as Förster resonance energy transfer because it was this German scientist in [7] who described the mechanism of the energy transfer from a donor chromophore to an acceptor chromophore through non-radiative dipole–dipole coupling.

Through EET between different chlorophylls, the excited state is shuttled to the reaction centre. Once there, a charge separation is achieved, which in turn is used to initiate a complex series of chemical reactions that end up capturing the energy in the form of chemical bonds.

2.1.2 The FMO complex

The FMO complex is the LHC of green sulfur bacteria that transfers energy from the chlorosome (the antenna) to the reaction centre [8]. These FMO proteins have been found to be embedded in the cytoplasmatic membrane. The EET takes place through the exciton interaction of several bacteriochlorophyll $a$ molecules (shown in Figure 2.1).

A group of organisms that generally live in low-light environments are green sulfur bacteria. Unlike the cyanobacteria, they neither produce oxygen nor use water as the electron donor, instead they typically take advantage of hydrogen sulfide. The ability to capture light energy and rapidly deliver it to the reaction centre is essential to these bacteria, as some see only a few photons of light per chlorophyll per day. To achieve this efficiency, the bacteria containing chlorosome structures acting like antennas, each containing up to 250,000 chlorophyll molecules, mostly bacteriochlorophyll with small amounts of carotenoids and quinones surrounded by a galactolipid monolayer with ten different proteins attached to it. For this reason, contrary to other LHC, the FMO complex is not responsible for the first step described in the previous page, of capturing the photons. Its only function is to transfer the electronic energy by transferring the excited state of the bacteriochlorophylls towards the reaction centre.

The structure of the FMO complex consists of three subunits:

![Figure 2.2: The C3 symmetry axis of the trimer, identified with a red triangle, is perpendicular to the membrane plane. Image extracted from the Protein Data Bank [6] using the Jmol software.](image-url)
Each subunit of the trimer is able to carry out its function independently of the others, thus it is reasonable to restrict the system studied to just one of them. Each single subunit contains seven bacteriochlorophyll \( a \) molecules wrapped in a protein (365/366 aminoacids) that consists of 15 strands of \( \beta \)-sheet, six short lengths of \( \alpha \)-helix, and a few regions of irregular conformation:

![Image of FMO subunit structure](image)

(a) One subunit with its seven inner bacteriochlorophylls. (b) Relative positions of the bacteriochlorophylls.

Figure 2.3: Structure of one FMO subunit. Image obtained with PyMOL visualizing the pdb file of the FMO complex found in the Protein Data Bank [6].

### 2.1.3 Efficient electronic energy transfer

It is known that the EET described in the previous page happens on a time scale of picoseconds and appears to be extremely efficient, specifically close to 100%, as shown in [9]. This unexpected feature is thought to be provided by quantum properties such as entanglement, perhaps being enhanced by the assistance of the environment. The FMO complex appears to be a suitable system for studying this fact because its pigments have the unique function of transporting the electronic energy. This framework provides us with the study subject of this project.
2.2 Physical approach

Quantum theory is a mathematical model of the physical world. We will rely on it with the purpose of simulating EET between two chlorophylls surrounded by a suitable environment. The following concepts of quantum mechanics are needed to be clarified in order to formulate an appropriate model to study the effect of the environment in the energy transfer.

2.2.1 Bra-ket notation and foundations of quantum mechanics

The notation system used in this report is the standardized and widespread in quantum mechanics bra-ket notation, also known as Dirac notation due to the fact that it was introduced by Paul Dirac in [10]. It is proved to be a simple and convenient way to refer to quantum states. A state is a complete description of a physical system; in quantum mechanics, it is expressed as a ray in a Hilbert space \( \mathcal{H} \). An example of a quantum state representation is:

\[ |\psi\rangle. \]

A ray is an equivalent class of vectors that differ by multiplication of a non-zero complex scalar, commonly called the global phase factor. From this definition, one can ensure that \( |\psi\rangle \), having unit norm, and \( e^{i\theta}|\psi\rangle \) describe the same physical state, where \( |e^{i\theta}| = 1 \). Nevertheless, one should bear in mind that although the global phase factor does not affect the physical predictions, the relative phases of the coefficients of an expansion in a multilevel system do play a significant role.

Part of the appeal of this notation is its usefulness in the formal manipulations that we shall perform. Composed of angle brackets and vertical bars, one can refer to the inner product of the two quantum states \( |\psi\rangle \) and \( |\varphi\rangle \) in terms of \( \langle \text{bra} | \text{ket} \rangle \) notation as:

\[ \langle |\psi\rangle, |\varphi\rangle \rangle \equiv \langle \psi | \varphi \rangle, \]

calling the left vector \( \langle \psi \rangle \) the bra and the right one \( |\varphi\rangle \) the ket. In quantum mechanics, this expression is typically interpreted as the probability amplitude for the state \( |\varphi\rangle \) to collapse into the state \( |\psi\rangle \) in a measurement. It should be pointed out that the bra \( \langle \psi \rangle \) is said to be the dual vector of the ket \( |\psi\rangle \), so taking \( \lambda \) as a complex number and \( \lambda^* \) being its complex conjugate, the correspondence between a bra and a ket is antilinear:

\[ \lambda_1|\psi_1\rangle + \lambda_2|\psi_2\rangle \implies \lambda_1^*\langle \psi_1 | + \lambda_2^*|\psi_2\rangle. \]

According to this definition, the inner product above can be written as a matrix multiplication of a row vector with a column vector, obtaining a complex number as a result:

\[ \langle \psi | \varphi \rangle = (\psi_1^* \psi_2^* \ldots \psi_n^*) \begin{pmatrix} \varphi_1 \\ \varphi_2 \\ \vdots \\ \varphi_n \end{pmatrix}. \]
These rules lead to the following properties of the scalar product:

\[ \langle \psi | \varphi \rangle = \langle \varphi | \psi \rangle^*, \]

\[ \langle \varphi | \lambda_1 \psi_1 + \lambda_2 \psi_2 \rangle = \lambda_1 \langle \varphi | \psi_1 \rangle + \lambda_2 \langle \varphi | \psi_2 \rangle, \]

\[ \langle \lambda_1 \varphi_1 + \lambda_2 \varphi_2 | \psi \rangle = \lambda_1^* \langle \varphi_1 | \psi \rangle + \lambda_2^* \langle \varphi_2 | \psi \rangle. \]

The bra-ket notation can also be used to define the outer product of the two vectors:

\[
|\varphi\rangle\langle\psi| = \begin{pmatrix}
\varphi_1 \\
\varphi_2 \\
\vdots \\
\varphi_n \\
\end{pmatrix}
\begin{pmatrix}
\psi_1^* & \psi_2^* & \cdots & \psi_n^* \\
\end{pmatrix},
\]

where “\(\doteq\)” means that the bra and ket are in matrix representation with respect to some basis. It should be emphasized that the order of symbols is of critical importance: in this illustration, the result of the outer product is, as expected, a \(n \times n\) matrix. The expression above is a suitable way to define a linear operator on a \(n\)-dimensional Hilbert space \(\mathcal{H}\).

A linear operator is, by definition, a linear transformation that associates with every entity on which it acts, another entity. In terms of our study case, the linear operators can act on kets giving other kets, or on bras giving other bras. A representative example of this second situation would be to specify the linear operator \(A\) as a square matrix and the bra \(\langle \psi |\) as a row vector, then \(\langle \psi | A\) is another row vector that can be calculated by normal matrix multiplication.

It shall be mentioned another specific application of the outer product: the construction of projection operators. For instance, given a ket \(|\psi\rangle\) of norm 1, the orthogonal projection onto the subspace spanned by \(|\psi\rangle\) is:

\[ |\psi\rangle\langle\psi|. \]

One should also make reference to the fact that every operator has a corresponding adjoint. The adjoint of the linear operator \(A\) is defined by:

\[ \langle \psi | A^\dagger | \varphi \rangle = \langle \varphi | A | \psi \rangle^*, \]

being \(A^\dagger\) the Hermitian conjugate (or adjoint) of the \(A\) matrix, that is to say the conjugate transpose of \(A\): \(A^\dagger = (A^T)^*\). \(A\) is self-adjoint (or Hermitian) if \(A = A^\dagger\).

An observable is a property of a physical system that, in principle, can be measured. In quantum mechanics, an observable is a self-adjoint operator, which in a Hilbert space \(\mathcal{H}\) has a spectral representation: its eigenstates form a complete orthonormal basis in \(\mathcal{H}\). The self-adjoint operator \(A\) can be expressed as:

\[ A = \sum_n a_n P_n. \]

Here, each \(a_n\) is an eigenvalue of \(A\) and \(P_n\) is the corresponding orthogonal projection onto the space of eigenvectors with eigenvalue \(a_n\). \(A\) being a self-adjoint operator, it follows that \(a_n\) is real-valued.
In quantum mechanics, the numerical outcome of a measurement of the observable $A$ is an eigenvalue of $A$. Just after the measurement, the quantum state is the eigenstate of $A$ associated with the measured eigenvalue. If the quantum state just prior to the measurement is $|\psi\rangle$, then the outcome $a_n$ is obtained with probability:

$$P(a_n) = ||P_n|\psi\rangle||^2 = \langle \varphi | P_n | \psi \rangle.$$  

From these last two expressions one can deduce the expectation value of the observable represented by the operator $A$ for the physical system in the state $|\psi\rangle$ is:

$$\langle A \rangle = \langle \psi | A | \psi \rangle.$$  

The tensor product is a way of putting vector spaces together to form larger vector spaces. It can also be used analogously for matrices, resulting in bigger matrices. As an illustrative example, the tensor product of the two states $|\varphi\rangle$ and $|\psi\rangle$ can be described using the bra-ket notation as:

$$|\varphi\rangle \otimes |\psi\rangle = |\varphi\rangle |\psi\rangle = |\varphi \psi\rangle = \begin{pmatrix} \varphi_1 \times \psi_1 \\ \varphi_1 \times \psi_2 \\ \vdots \\ \varphi_n \times \psi_n \end{pmatrix} \otimes \begin{pmatrix} \psi_1 \\ \psi_2 \\ \vdots \\ \psi_n \end{pmatrix} = \begin{pmatrix} \varphi_1 \times \psi_1 \\ \varphi_1 \times \psi_2 \\ \vdots \\ \varphi_n \times \psi_n \end{pmatrix} \otimes \begin{pmatrix} \psi_1 \\ \psi_2 \\ \vdots \\ \psi_n \end{pmatrix}.$$  

This construction is crucial to understand the quantum mechanics of multiparticle systems due to the postulate asserting that the state space of a composite physical system is the tensor product of the state spaces of the physical subsystems. This means that if a system $A$ is prepared in the state $|\psi\rangle_A$ and a system $B$ is prepared in the state $|\varphi\rangle_B$, then their joint composite system’s state is the tensor product $|\psi\rangle_A \otimes |\varphi\rangle_B$. One should also bear in mind that an operator acting trivially on the system $B$ can be denoted by $M_A \otimes I_B$, where $I_B$ is the identity on $\mathcal{H}_B$.

The dynamics of a quantum state are generated by the self-adjoint Hermitian operator called the Hamiltonian of the system. The time evolution of the state vector $|\psi(t)\rangle$ is governed by the Schrödinger equation:

$$i\hbar \frac{d}{dt} |\psi(t)\rangle = H |\psi(t)\rangle,$$  

where $H$ is the Hamiltonian operator that represents the observable associated with the total energy of the system and $\hbar$ is related to the Planck’s constant $\hbar$ by the expression $\hbar = \frac{h}{2\pi}$; in practice, it is common to absorb the factor into $H$, effectively setting $\hbar = 1$. 

7
Owing to the fact that the evolution of a closed quantum system is described by a unitary transformation, the state $|\psi\rangle$ of the system at time $t_1$ is related to the state $|\psi'\rangle$ of the system at time $t_2$ by a unitary operator $U$ which depends on the times $t_1$ and $t_2$:

$$|\psi'(t_2)\rangle = U(t_1, t_2) |\psi(t_1)\rangle.$$  \hfill (2.2)

The connection between the Hamiltonian picture of dynamics and the unitary operator picture appears to be provided by writing down the solution of Schrödinger’s equation. Considering $H$ as time-independent, the expression may be written as:

$$U = e^{-iHt},$$

where we have put $t_1 = 0$ and $t_2 = t$.

### 2.2.2 The qubit

The indivisible unit of classical information is the bit, which takes one of the two possible values $\{0, 1\}$. The corresponding unit in quantum information is called the “quantum bit” or qubit and it represents a state in the simplest quantum system one can think of: a two-dimensional state space, which is the smallest non-trivial Hilbert space. Supposing $|0\rangle$ and $|1\rangle$ constitute an orthonormal basis for the mentioned state space, then an arbitrary state vector in that state space is:

$$|\psi\rangle = a|0\rangle + b|1\rangle,$$ \hfill (2.3)

where $a$ and $b$ are complex numbers that represent the probability amplitudes and satisfy $|a|^2 + |b|^2 = 1$. This is an equivalent condition to $|\psi\rangle$ being a unit vector and so $\langle\psi|\psi\rangle = 1$, which is often known as the normalization condition for state vectors.

It is of great importance to understand the implications of considering a qubit as a state in a two-dimensional Hilbert space that can take any value of the form described in equation (2.3). Here arises the divergence with the classical bit: rather than being either $|0\rangle$ or $|1\rangle$, a qubit is a superposition of both states.

Referring again to the expression (2.3), we can perform a measurement that projects the qubit onto the basis $\{0, 1\}$, obtaining the outcome $|0\rangle$ with probability $|a|^2$, and the outcome $|1\rangle$ with probability $|b|^2$. Furthermore, the measurement irrevocably disturbs the state (with the only exception of the cases in which $a = 0$ or $b = 0$). If the value of the qubit is initially unknown, there is no way to determine $a$ and $b$ with that single measurement, or any other measurement one can think of. However, after doing the measurement, the quantum bit has been prepared in a known state, either $|0\rangle$ or $|1\rangle$, that differs (in general) from its previous state.

It should also be considered the fact that not only the coefficients $a$ and $b$ provide information about the probabilities of the outcomes of a measurement in the $\{0, 1\}$ basis, but also about the physical significance of the relative phase.
An illustrative example of a qubit that has been widely studied among chemists and physicists is the spin state of an object with spin-$\frac{1}{2}$, for instance an electron. Here, $|0\rangle$ and $|1\rangle$ are the spin up $|↑\rangle$ and spin down $|↓\rangle$ states along a particular axis such as the $z$-axis. Being $\vec{S} = \frac{\hbar}{2} \vec{\sigma}$ the total spin operator, the two real numbers that describe the orientation of the spin in the three-dimensional space are the polar angle $θ$ and the azimuthal angle $ϕ$: $|θ,ϕ\rangle = \cos \frac{θ}{2} |↑\rangle + \sin \frac{θ}{2} e^{-iϕ} |↓\rangle$. Therefore, $⟨\vec{σ}\rangle$ represents the spin direction since $⟨θ,ϕ|\vec{σ}|θ,ϕ\rangle = (\sin θ \cos ϕ, \sin θ \sin ϕ, \cos θ)$. Another significant example of a two-state system is provided by a photon, which can have two independent polarizations.

### 2.2.3 The density operator

The axioms described in this previous section are intended to characterize the quantum behaviour of one complete system. However, most of the time we are not able to understand the physics of the whole system. Instead, we are rather content to focus our attention on just a little corner, an individual subsystem of a composite quantum system.

Under these circumstances in which the state of the whole system is not perfectly determined, the axioms mentioned above appear to be violated: the states are not any more rays, the measurements are no longer orthogonal projections and the evolution is not unitary. Even so, we should at least be able to incorporate into the formalism the incomplete information we possess about the system so that our predictions make maximal use of this partial information.

In that sense, we shall introduce a very useful mathematical tool that provides an alternative convenient formulation for describing quantum systems whose state is not completely known: the density operator. This new language enables us to refer to a quantum system that is in one of a number of states $|ψ_i\rangle$ with respective probabilities $p_i$. Being $\{p_i, |ψ_i\rangle\}$ an ensemble of pure states, the density operator is:

$$\rho \equiv \sum_i p_i |ψ_i\rangle⟨ψ_i|.$$  \hspace{1cm} (2.4)

It should be emphasized that a statistical mixture of states with the classical probabilities $p_i$ of the state vectors $|ψ_i\rangle$ must not be confused with a system whose state $|ψ\rangle$ is a linear combination of states, as in the qubit expression (2.3). It must be stressed that for a linear combination of $|ψ_i\rangle$ there exists, in general, interference effects between these states due to the cross terms obtained when the modulus of the probability amplitudes is squared. These cross terms play an important role in quantum mechanics.

Therefore, it is impossible, in general, to describe a statistical mixture by an "average state vector” which would be a superposition of states $|ψ_i\rangle$ due to the fact that a weighted sum of probabilities can never obtain interference terms between the various states $|ψ_i\rangle$ of a statistical mixture. Actually, it is an "average operator” and not an "average vector” which permits a simple description of the statistical mixture of states: the density operator. Thus, it turns out that all the postulates of quantum mechanics shall be reformulated in terms of the density operator language.
At this point we should define the mathematical concept of *trace*, since it is going to be used in the following paragraphs. In linear algebra, the trace of an $n \times n$ square matrix $A$ is defined to be the sum of the elements on the main diagonal of $A$:

$$\text{Tr}(A) = a_{11} + a_{22} + \ldots + a_{nn} = \sum_{i=1}^{n} a_{ii}.$$ 

An example of application of the trace is to calculate the expectation value of an observable $M$ in the state $\rho = \sum p_i |\psi_i\rangle \langle \psi_i|$, which can be expressed as

$$\langle M \rangle = \sum p_i \langle \psi_i | M | \psi_i \rangle = \text{Tr}(M \rho).$$

In terms of the density matrix formulation, we shall distinguish these two particular cases:

(a) A pure state is a quantum system whose state $|\psi\rangle$ is known exactly, which means that it can be described just as well by a density operator as by a state vector. Hence, the density operator is simply $\rho = |\psi\rangle \langle \psi|$. From its definition, it can be deduced that $\rho = \rho^\dagger$, which implies that it is self-adjoint and corresponds to an Hermitian operator. The fact that $\rho$ is a projector leads to the following properties, only satisfied for the pure case: $\rho^2 = \rho$ and $\text{Tr}(\rho^2) = 1$. In other words, when the state of the subsystem is a ray, we say that the state is pure.

(b) A mixed state is said to describe an ensemble of mutually orthogonal pure quantum states, which are defined to be the eigenstates of the density operator of the system, each occurring with a specified probability. The density matrix for the system is thus:

$$\rho = \sum_{i} p_i \rho_i = \sum_{i} p_i \sum_{j} p_{ij} |\psi_{ij}\rangle \langle \psi_{ij}|.$$  \hspace{1cm} (2.5)

In this scenario, $\rho$ is said to be a mixture of the states $\rho_i$ with probabilities $p_i$. In a statistical mixture of states, $\rho$ is no longer a projector. Therefore, in general $\rho^2 \neq \rho$ and consequently $\text{Tr}(\rho^2) \leq 1$.

It is remarkable to notice that even if the joint system is in a pure state (*i.e.* it is known exactly), each subsystem can be found to be in a mixed state, that is, a state about which we apparently do not have complete knowledge. This strange property, that the joint state of a system can be maximally known yet a subsystem be in a mixed state, is another hallmark of entanglement.

The deepest application of the density operator is as a descriptive tool for subsystems of a composite quantum system. Such a description is provided by the *reduced density operator*, which is so useful as to be virtually indispensable in the analysis of composite quantum systems. By considering two physical systems $A$ and $B$ whose state is described by a density operator $\rho_{AB}$, the characterization of the state of system $A$ is given by the reduced density operator:

$$\rho_A \equiv \text{Tr}_B(\rho_{AB}),$$ \hspace{1cm} (2.6)

where $\text{Tr}_B$ is a map of operators known as the *partial trace* over the system $B$. The partial trace is defined by:

$$\text{Tr}_B\left(|a_1\rangle \langle a_2| \otimes |b_1\rangle \langle b_2|\right) \equiv |a_1\rangle \langle a_2| \text{Tr}\left(|b_1\rangle \langle b_2|\right)$$

being $|a_1\rangle$ and $|a_2\rangle$ any two vectors in the state space of $A$, and $|b_1\rangle$ and $|b_2\rangle$ any two vectors in the
state space of $B$. The trace operation on the right hand side is the usual trace operation for system $B$, so $\text{Tr}(\langle b_1 | b_2 \rangle) = \langle b_2 | b_1 \rangle$. By this, we are able to calculate the expectation value of an operator $M$ acting on a system composed of $A$ and $B$, but affecting only $A$ (i.e. acting trivially on $B$):

$$\langle M \rangle = \langle \psi_{AB} | M \otimes I | \psi_{AB} \rangle = \text{Tr}(M \rho_A) = \text{Tr} \left( M \text{ Tr}_B(\rho_{AB}) \right).$$

### 2.2.4 Correlations

The correlation between two subsystems of a composite quantum system is described to be the influence that each one produces to the other, which has the consequence of the subsystems sharing mutual information. This notion is widely used to measure the total correlations between the two subsystems of a bipartite quantum system and can be related to the entropy of the reduced density operator. The quantum description of entropy was defined by von Neumann [11] and has a classical analogue introduced by Shannon [12].

To clarify the concept of correlation one can think of the following example: considering two subsystems $A$ and $B$, each having the marginal probabilities $p(a)$ and $p(b)$ to collapse to their respective states $a$ and $b$ after a measurement, the mathematical definition of correlation is related to the joint probability to measure $p(a, b)$:

- if $p(a, b) = p(a) p(b)$ then there is no correlation between $A$ and $B$.
- if $p(a, b) \neq p(a) p(b)$ then it exists a correlation.

We shall emphasize that the correlations between different parts of a physical system can be decomposed into various contributions: classical correlations need to be distinguished from the quantum correlations, which include entanglement and nonlocality.

### 2.2.5 Entanglement

Quantum entanglement is a physical phenomenon that occurs when a particle influences another in such a way that the quantum state of each particle cannot be described independently, that is to say the state of the whole system cannot be expressed as a convex sum of the product of individual states.

As an illustrative example, one can consider a system composed of two qubits named $\alpha$ and $\beta$, which appear to be unentangled if it is possible to write the state of the whole system as:

$$|\psi_{\alpha\beta} \rangle = |\psi_{\alpha} \rangle \otimes |\psi_{\beta} \rangle,$$

otherwise, in the case that it is impossible to describe them likewise, we shall consider them to be entangled.

The purest form of entanglement between two subsystems is commonly denoted by the abbreviation MES, acronym of Maximally Entangled State. An example of a MES system composed of two qubits $\alpha$ and $\beta$ can be:

$$|\psi_{\alpha\beta} \rangle = \frac{1}{\sqrt{2}} \left( |00 \rangle + |11 \rangle \right).$$
In this particular case, the measurement of an observable appears to give a completely random result: probability $\frac{1}{2}$ to collapse to any of the two possible states $|00\rangle$ and $|11\rangle$. Therefore, if the two qubits are distantly separated and we perform a local measurement to any of them, we acquire no information about the preparation of the state, this information is hidden.

The critical difference between classical correlations and entanglement is that the latter cannot be created locally: the only way to entangle $\alpha$ and $\beta$ is for the two subsystems to directly interact with each other. The novelty is that, even when $\alpha$ and $\beta$ are distantly separated, we cannot accurately regard $\alpha$ and $\beta$ as two separate qubits, and therefore use classical information to characterize how they are correlated: when a measurement of $\alpha$ is performed and a particular outcome is known to have been obtained, then the density matrix of $\beta$ does change. They are more than only correlated, they are a single inseparable entity, thus, entangled.

By definition, any entangled pure state of two qubits appears to violate some Bell inequality (see p.14) for a certain set of correlation measurements. It is not difficult to generalize the argument to an arbitrary bipartite pure state. For these states, then, ”entangled” is equivalent to ”Bell-inequality violating”. However, for bipartite mixed states later on we will see that the situation is more subtle.

Now coming back to the definition of unentanglement (2.7) and focusing our attention on pure states, we can clearly appreciate that depending on the basis we use to express the state of the system it can be not-so-easy to distinguish whether it is possible to write it as a product of states or not. In that sense, one can prove this fact by computing the reduced density matrix of one state: getting the eigenvalues 1 and 0 implies it is a pure product state, so the subsystems are unentangled.

There exists a more general procedure to prove the entanglement of the two qubits composing a pure state system. It applies to the fact that the quantum state of this type of systems can always be described by the expression:

$$|\psi_{\alpha\beta}\rangle = a |00\rangle + b |01\rangle + c |10\rangle + d |11\rangle,$$

(2.8)

the coefficients being complex numbers. In this general case, the definition of $|\psi_{\alpha\beta}\rangle$ as a pure product state that represents unentangled subsystems is exactly equivalent to the following condition:

$$ad - bc = 0. \quad (2.9)$$

This not only represents a strong condition for the unentanglement to happen, but also gives an idea of how sensitive are unentangled subsystems to small changes and so to become entangled. From that we can ensure that it is impossible to find a product state by chance.

---

1 To prove the validity of equation (2.9) one can think of an arbitrary product state:

$$|\psi\rangle = (\alpha|0\rangle + \beta|1\rangle) (\gamma|0\rangle + \delta|1\rangle) = \sum_{\alpha,\beta,\gamma,\delta} (\alpha\gamma b|00\rangle + \alpha\delta b|01\rangle + \beta\gamma c|10\rangle + \beta\delta c|11\rangle).$$

Then, $ad - bc = \alpha\gamma\beta\delta - \alpha\delta\beta\gamma = 0$, which verifies that $|\psi\rangle = |\varphi\rangle|\varphi'\rangle \rightarrow ad - bc = 0$. To check if it is also true that $|\psi\rangle = |\varphi\rangle|\varphi'\rangle \rightarrow ad - bc = 0$, one can define $a = \frac{\alpha b}{bc}$ and develop the expression:

$$|\psi\rangle = \sum_{\alpha,\beta,\gamma,\delta} \left( \alpha\gamma b|00\rangle + \alpha\delta b|01\rangle + \beta\gamma c|10\rangle + \beta\delta c|11\rangle \right) = (b|00\rangle + d|11\rangle) + (a|00\rangle + \beta\delta|11\rangle - b|00\rangle + d|11\rangle) = (b|00\rangle + d|11\rangle) + (a|00\rangle + \beta\delta|11\rangle) = (b|00\rangle + d|11\rangle).$$

Hence, the validity of the condition given in equation (2.9) is proved.
The amount of entanglement between two subsystems can be quantified. One can detect that two qubits are almost unentangled, or locate others that hold a maximally entangled state (MES). This statement implies that there are degrees of entanglement. The quantification of this feature for pure states can for instance be given by the following measures:

(a) Geometric entanglement: defined in [13] and revised a few years later in [14], this concept relies on the shortest geometrical distance between the considered state and the set of product states:

\[ \Delta(\psi_{\alpha \beta}) = \min_{P_{\alpha \beta}} \left( 1 - \left| \langle P_{\alpha \beta} | \psi_{\alpha \beta} \rangle \right| \right). \quad (2.10) \]

According to this definition, the unentangled subsystems present a geometric entanglement value of \( \Delta = 0 \), in contrast to the maximally entangled states with \( \Delta(\text{MES}) = (1 - \frac{1}{\sqrt{2}}) \) for qubits.

(b) Concurrence: defined in [15], it relies on the expression (2.9) in order to define the concept of concurrence \( C \) as a measuring scale of how much entangled are two qubits:

\[ 0 \leq C(\psi_{\alpha \beta}) = 2 \left| \begin{vmatrix} a & -b \end{vmatrix} \right| \leq 1, \quad (2.11) \]

with the maximally entangled states having the value \( C(\text{MES}) = 1 \).

2.2.6 Concurrence

As previously noted, the two systems \( A \) and \( B \) are not entangled if and only if one can write the \( \rho_{AB} \) as a separable state, that is to say there exists at least one decomposition of the form:

\[ \rho_{AB} = \sum_i p_i |\psi_i^A\rangle \langle \psi_i^A| \otimes |\psi_i^B\rangle \langle \psi_i^B|, \quad (2.12) \]

otherwise, if it happens to be impossible to write them like that, one can ensure that \( A \) and \( B \) are entangled.

At this point arises the main obstacle for evaluating the entanglement in the case of mixed states: the decomposition freedom, i.e. the decomposition is not uniquely given by \( \rho \). As already announced in 1935 by Schrödinger [16], being \( \rho \) a non-pure state, there are infinite forms it can be decomposed into. This appears to be a delicate complication to cope with for mixed states.

Fortunately, in [15] Wootters proposed a general method to quantify the entanglement between two qubits in an arbitrary mixed state. He refers to this new concept as concurrence.

The procedure to calculate concurrence can be summarized in the steps detailed in the following page.
Concurrence, methodology for quantifying entanglement:
1. write the operator \( \hat{\rho} \) in the product basis \( \{|00\rangle, |10\rangle, |01\rangle, |11\rangle\} \mapsto \text{matrix } \rho \)
2. matrix \( \rho \mapsto \text{complex conjugate matrix } \rho^* \)
3. define \( \tilde{\rho} = \sigma_y \otimes \sigma_y \rho^* \sigma_y \otimes \sigma_y \) (see p.15)
4. find the eigenvalues of \( \tilde{\rho} \mapsto \lambda_1 \geq \lambda_2 \geq \lambda_3 \geq \lambda_4 \)
5. calculate \( \sqrt{\lambda_1} - \sqrt{\lambda_2} - \sqrt{\lambda_3} - \sqrt{\lambda_4} \):
   - if the result is > 0 \( \mapsto \hat{\rho} \) is entangled
   - if not \( \mapsto \hat{\rho} \) is separable, thus not entangled

Hence, the definition of concurrence as a natural measure of entanglement is:

\[
C(\rho) \equiv \max \{ 0, \sqrt{\lambda_1} - \sqrt{\lambda_2} - \sqrt{\lambda_3} - \sqrt{\lambda_4} \}.
\] (2.13)

giving 0 only for separable states, \textit{i.e.} unentangled, and it reduces to equation (2.11) for product states. This expression minimizes the average entanglement of the pure states of the decomposition of \( \rho \) over all its possible decompositions. In other words, concurrence determines the minimal marginal von Neumann entropy.

2.2.7 Nonlocality

The concept of nonlocality arises from Einstein’s discomfort with the fundamental concept implicit in quantum mechanics which is quantum entanglement. He, along with Podolsky and Rosen, expressed their disagreement in [17], proposing the famous well-known EPR paradox. They believed that a \textit{complete} description of a physical reality should meet a strong criterion, which was named \textit{locality}, so that an action performed to a system must not modify the description of another system at distance. In other words, they were looking for a theory consistent with a deterministic world, \textit{i.e.} a reality that is objective and independent of an observer. And this is not the case of QM, as for two systems being entangled, a measurement in one modifies the state of the other.

EPR, unsatisfied by this indeterminacy, attempted to prove that the QM description was not able to cope with both realism and locality, defining realism as the property of an observable to be independent of an observer, and locality referred to the physical impossibility that a system could influence another system at distance. They seemed to envision a more complete description of the world, the so-called local hidden-variable theories, in which a measurement is actually fundamentally deterministic, but appeared to be probabilistic because some degrees of freedom are not precisely known.

It was not until 1964 when John Bell came up with an idea to test EPR’s locality: the Bell inequality [18]. Is is a criterion for two correlated systems to show independent probability distributions, that is to say, systems that fulfil both the conditions of realism and locality. Some entangled pair of quantum systems appear to violate this criterion, thus they present correlations in conflict with fulfilment of both realism and locality. Such correlations are called nonlocal.
For a direct application of the nonlocality criterion it is convenient to express the general study
case of the two-qubit density matrix $\rho$ in terms of the standard Bloch representation:

$$\rho = \frac{1}{4} \left( I \otimes I + \vec{r} \cdot \vec{\sigma} \otimes I + I \otimes \vec{s} \cdot \vec{\sigma} + \sum_{n,m=1}^{3} T_{n,m} \sigma_n \otimes \sigma_m \right)$$  \hspace{1cm} (2.14)

where $\vec{r}$ and $\vec{s}$ are unit vectors in $\mathbb{R}^3$, $I$ is the two-by-two identity matrix and $T_{n,m} = \text{Tr} \left[ \rho (\sigma_n \otimes \sigma_m) \right]$. Here the first and second terms are associated with the two qubits in the sense $\text{Tr} \rho = \frac{1}{2} \left( I + \vec{r} \cdot \vec{\sigma} \right)$ and vice versa, and the last term includes information about their correlation. Also one should bear in mind that $\vec{\sigma}$ is a vector consisting of Pauli matrices,

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$  \hspace{1cm} (2.15)

The two-qubit Bell inequality derived by Clauser, Horne, Shimony and Holt (CHSH) [19] is formulated as:

$$|\langle B_{\text{CHSH}} \rangle| = |\text{Tr} \left( \rho B_{\text{CHSH}} \right) | \leq 2,$$  \hspace{1cm} (2.16)

where the Bell-CHSH operator $\hat{B}_{\text{CHSH}}$ is given by:

$$\hat{B}_{\text{CHSH}} = \vec{a} \cdot \vec{\sigma} \otimes (\vec{b} + \vec{b}^{\prime}) \cdot \vec{\sigma} + \vec{a}^{\prime} \cdot \vec{\sigma} \otimes (\vec{b} - \vec{b}^{\prime}) \cdot \vec{\sigma},$$  \hspace{1cm} (2.17)

where $\vec{a}, \vec{a}^{\prime}$ and $\vec{b}, \vec{b}^{\prime}$ are two pairs of measurement directions pertaining to the two subsystems.

The Bell inequality (2.16) describes the case when the correlations are local. Its violation clearly evidences the existence of nonlocal correlations. However, the value that $\langle \hat{B}_{\text{CHSH}} \rangle$ can take depends on the basis choice, which means that this form of Bell inequality requires to test for several choices of measurement directions. For this reason, the Horodecki family developed a criterion to maximize the expectation value of the Bell-CHSH operator for mixed states of two qubits [20]. This represents a directly applicable method for quantifying the nonlocality for a mixed two-qubit state. The procedure, analogous to the quantification of entanglement in terms of concurrence, can be described by following these specific steps:

**Methodology for quantifying nonlocality:**

1. \textbf{calculate the correlation matrix $T$}:
   $$T = \begin{pmatrix} T_{xx} & T_{xy} & T_{xz} \\ T_{yx} & T_{yy} & T_{yz} \\ T_{zx} & T_{zy} & T_{zz} \end{pmatrix},$$
   where $T_{n,m} = \text{Tr} \left[ \rho_{AB} \sigma_n^A \otimes \sigma_m^B \right]$

2. \textbf{calculate the correlation matrix squared}:
   $$|T|^2 = T^T T$$

3. \textbf{find the eigenvalues of} $|T|^2 \mapsto \lambda_1 \geq \lambda_2 \geq \lambda_3$

4. \textbf{define} $M(\rho) = \lambda_1 + \lambda_2 \leq 2$
According to the Horodecki theorem [20], the maximum expectation value \( \langle \hat{B}_{CHSH} \rangle \) for a given state \( \rho \) is \( 2 \sqrt{M(\rho)} \), where the calculation of \( M(\rho) \) is described in the box above. Hence, the condition for violating the Bell-CHSH inequality is \( M(\rho) > 1 \). To measure the degree of nonlocality, in this report it will be used another function of \( M(\rho) \), the same as proposed in [21], due to the fact that for two-qubit pure states coincides to concurrence. This measure is

\[
B(\rho) \equiv \sqrt{\max\{0, M(\rho) - 1\}},
\]

(2.18)

where for \( B(\rho) = 0 \), the state \( \rho \) satisfies the Bell-CHSH inequality and for \( B(\rho) = 1 \), the inequality is maximally violated. As \( B(\rho) > 0 \) increases with \( M(\rho) \), the method can be used to quantify the nonlocality, referring to it as a measure of the violation of the Bell-CHSH inequality and thus as a measure of the degree of nonlocality.

### 2.2.8 Entanglement versus Nonlocality

Werner in 1989 [22] pointed out that the two forms of quantum correlations represented by entanglement and nonlocality are, in general, different types of correlations. The relation between these two concepts can be analysed taking a look at the schematic Figure 2.4: it is shown that entanglement is a weaker form of correlation than nonlocality. For pure states, the concept of nonlocality coincides with that of entanglement.

![Figure 2.4: Both non-entanglement and locality are convex sets.](image)

### 2.2.9 Decoherence

The nonlocal correlations between two subsystems are extremely fragile and tend to decay very rapidly in practice. The reason is that our whole quantum system is inevitably in contact with a much larger system, its environment. It is virtually impossible to perfectly isolate a quantum system from its environment: interactions between a quantum system and its environment establish nonlocal correlations between the two. Eventually, the correlations that were initially encoded between the subsystems turn out to be swapped into correlations between the subsystems and their environment. At that stage, one can no longer access the correlated information by observing only the systems: the information is irrevocably lost. Even if the coupling between device and environment is quite weak, this happens to a macroscopic device remarkably quickly.

Historically, the decoherence concept has been used to refer just to a phase damping process. In [23] it was recognized that phase damping has a unique role in the transition from quantum to classical physics: for certain environmental couplings, it occurs on a time scale which is much faster than any amplitude damping process and can therefore be much more important in determining the loss of quantum coherence.
The major point of it all has been the emergence of classicality due to environmental interactions: the entanglement destroys the coherence of a superposition of states of $A$, so that some of the phases in the superposition become inaccessible if one looks at $A$ alone. This situation might be described by saying that the state of system $A$ collapses: it is in one of a set of alternative states, each being assigned a probability. When a microscopic quantum system interacts with a macroscopic apparatus, decoherence drives the "collapse" of the wave function for all practical purposes.

In a more technical terms, decoherence can be described by a superoperator. One can think of the environment as a device that frequently "scatters" off the system, then due to the fact that the state of the environment is not monitored, the off-diagonal terms in the density matrix of the system decay rapidly in a preferred basis, typically a spatially localized basis selected by the nature of the coupling of the system to the environment. The key idea is that, for macroscopic systems, one cannot hope to keep track of all microscopic degrees of freedom. Thus, the time scale for decoherence is set by the scattering rate, which can be much larger than the damping rate for the system.

The concept of decoherence provides a reasonable answer for the situation proposed by Schrödinger: although it is possible to describe the state of a cat as a superposition of the cat’s health states $|\text{cat}\rangle = \frac{1}{\sqrt{2}} (|\text{dead}\rangle + |\text{alive}\rangle )$, it can never be experienced like that because it is an extremely unstable situation, thus the cat is always either alive or dead. The explanation is that the cat is never isolated from its environment: if someone was to prepare the state $|\text{cat}\rangle$, the quantum information encoded in the superposition of $|\text{dead}\rangle$ and $|\text{alive}\rangle$ would immediately be transferred to correlations between the cat and the environment, and thus becoming completely inaccessible. In effect, the environment continually "does measurements" on the cat, projecting it onto either the state $|\text{dead}\rangle$ or $|\text{alive}\rangle$. This process is an example of decoherence.

In this sense, it would be reasonable to think that for our study case of the energy transfer between the chlorophylls of the FMO complex, the possible quantum entanglement that could exist between two chromophores being regarded as two qubits is erased in an extremely short period of time due to the decoherent effect caused by the interaction with the environment [24]. However, several recent studies have provided evidence in the opposite direction: ultrafast spectroscopic techniques have claimed to reveal long-lasting quantum coherence in biological systems, including the photosynthetic LHC of a species of green sulfur bacteria [1, 25], a species of purple bacteria [26], and two species of marine cryptophyte algae [27]. Pigment-protein light-harvesting antennas in the photosynthetic complex transfer excitonic energy rapidly and efficiently [28] through a series of electronic excitations to the reaction center [29]. The efficiency of the energy transfer through the network of chromophores and the evidence of quantum coherence has led to discussions about the assistant role of the environment in the quantum transfer process and the degree to which it may contribute to the transport efficiency. This rather odd but stimulating fact is the challenging purpose of study for this project: to investigate whether the decohering effect of the environment can contribute to increase the efficiency rate of the energy transfer.
3 Model system

3.1 No environmental interaction

The model proposed to study the remarkably high efficiency of the EET between the inner chlorophylls of the FMO complex consists of referring to two of the seven chlorophylls as two coupled qubits, i.e. a coupled pair of two-level systems, with the lowest level representing the ground state and the highest depicting an excited state, see Figure 3.1. This represents our simple picture of the model, appearing to be similar to the one presented in [4] and expanded in [5].

By using the notation $|\psi\rangle \otimes |\varphi\rangle = |\psi\varphi\rangle$ introduced previously, the first approach presents only two possible states, $|10\rangle$ and $|01\rangle$, out of the four that one can think about. The two remaining states, $|00\rangle$ and $|11\rangle$, have not yet been considered for the following reasons. On the one hand, due to the fact that the green sulphur bacteria receive just a few light quanta it is reasonable to make the approximation of considering only one excitation at a time, that is to say not taking into account two simultaneous excitations, therefore the state $|11\rangle$ is excluded in this model. On the other hand, the state $|00\rangle$ is not yet contemplated in order to start the analysis of a model as simple as possible, and the only states needed to simulate the EET are the single-excitation states. However, this third state will be taken under consideration later on in this report, contributing as a decay of the transition probability.

The Hamiltonian of our system is taken to be:

$$H_{XY} = \frac{1}{2} J \left( \sigma^x_{\kappa} \otimes \sigma^y_{\eta} + \sigma^y_{\kappa} \otimes \sigma^y_{\eta} \right) - \frac{\epsilon_{\kappa}}{2} \sigma^z_{\kappa} \otimes \hat{I}_{\eta} - \frac{\epsilon_{\eta}}{2} \hat{I}_{\kappa} \otimes \sigma^z_{\eta} \overset{\text{3.1}}{=} \begin{pmatrix} -\left( \frac{\epsilon_{\kappa}}{2} + \frac{\epsilon_{\eta}}{2} \right) & 0 & 0 & 0 \\ 0 & \epsilon_{\kappa} & J & 0 \\ 0 & J & \epsilon_{\eta} & 0 \\ 0 & 0 & 0 & \frac{\epsilon_{\kappa}}{2} + \frac{\epsilon_{\eta}}{2} \end{pmatrix},$$

where the first term describes an XY-type of qubit-qubit interaction [30] and the two last terms refer to the excitation energy of each qubit. Developing this equation one can define the Hamiltonian of our particular model represented in the Figure 3.1 as:
\[ H = \epsilon_\kappa |10\rangle\langle 10| + \epsilon_\eta |01\rangle\langle 01| + J (|10\rangle\langle 01| + |01\rangle\langle 10|). \]  

(3.2)

The full two-qubit density matrix will take the form of a 4 × 4 matrix. The time dependent wavefunction of this system is given by the expression:

\[ |\psi(t)\rangle = c_{10}(t)|10\rangle + c_{01}(t)|01\rangle. \]  

(3.3)

An initial state is chosen that describes the first chlorophyll in its excited state and the second in the ground state. The system thus is described by \( |\psi(0)\rangle = |10\rangle \), i.e.:

\[
\begin{aligned}
&c_{10}(0) = 1, \\
&c_{01}(0) = 0.
\end{aligned}
\]  

(3.4)

The coefficients \( c_{10}(t) \) and \( c_{01}(t) \) contain information of the transition probability \( |10\rangle \rightarrow |01\rangle \) and can provide us with knowledge about the quantum phenomenon of coherence. To analytically calculate \( c_{10}(t) \) and \( c_{01}(t) \) one needs to solve the time dependent Schrödinger equation:

\[ i \frac{d}{dt} |\psi(t)\rangle = H |\psi(t)\rangle, \]  

(3.5)

where \( H \) is a time independent operator given by the equation (3.2). By combining the expressions (3.4) and (3.5) one obtains:

\[
\begin{aligned}
i \frac{dc_{10}}{dt} &= c_{10} H_{10,10} + c_{01} H_{10,01}, \\
i \frac{dc_{01}}{dt} &= c_{10} H_{01,10} + c_{01} H_{01,01}.
\end{aligned}
\]  

(3.6)

The solution gives the time-dependent coefficients of the equation (3.3):

\[
\begin{aligned}
c_{10}(t) &= \cos \left( t \sqrt{J^2 + \Delta^2} \right) + i \frac{\Delta}{\sqrt{J^2 + \Delta^2}} \sin \left( t \sqrt{J^2 + \Delta^2} \right), \\
c_{01}(t) &= i \frac{J}{\sqrt{J^2 + \Delta^2}} \cos \left( t \sqrt{J^2 + \Delta^2} \right),
\end{aligned}
\]  

(3.6)

defining \( \Delta = \frac{\epsilon_{10} - \epsilon_{01}}{2} \). As a test, one can verify that it is true \( |c_{10}(t)|^2 + |c_{01}(t)|^2 = 1 \). Due to the Hamiltonian and the initial conditions, the density matrix will take the simplified form:

\[
\rho(t) = |\psi(t)\rangle \langle \psi(t)| \doteq \begin{pmatrix}
0 & 0 & 0 & 0 \\
0 & |c_{10}|^2 & c_{10} \ast c_{01} & 0 \\
0 & c_{10} \ast c_{01} & |c_{01}|^2 & 0 \\
0 & 0 & 0 & 0
\end{pmatrix},
\]  

(3.7)

which provides us with information about the transition probabilities in the diagonal terms, and about the coherence in the off-diagonal terms.

The transition probability from \( |10\rangle \) to \( |01\rangle \) is:

\[ P = |c_{01}(t)|^2 = \frac{J^2}{J^2 + \Delta^2} \sin^2(t \sqrt{J^2 + \Delta^2}). \]  

(3.8)
The maximal probability will occur when the condition \( \sin^2(t \sqrt{J^2 + \Delta^2}) = 1 \) is satisfied, which yields:

\[ P_{\text{max}} = \frac{J^2}{J^2 + \Delta^2}. \]  

(3.9)

This expression has been obtained in [4]. This means that only in the case when \( \epsilon_{10} = \epsilon_{01} \) the excitation is transferred with certainty \( P_{\text{max}} = 1 \). One goal of this project is to show that in a generic case \( \epsilon_1 \neq \epsilon_2 \) for a system in contact with two spin environments, decoherence can enhance the EET.

The coherence of the system, found in the off-diagonal terms of the density matrix, is given by:

\[
C_{10,01} = c_{10} c_{01}^* = C_{01,10}^*,
\]

\[
C_{10,01} = \frac{J \Delta}{J^2 + \Delta^2} \sin^2 \left( t \sqrt{J^2 + \Delta^2} \right) \pm \frac{i J}{\sqrt{J^2 + \Delta^2}} \sin \left( t \sqrt{J^2 + \Delta^2} \right) \cos \left( t \sqrt{J^2 + \Delta^2} \right).
\]  

(3.10)

This expression of the coherence is composed of two clearly distinguishable parts, one real and the other imaginary:

\[
R(C_{10,01}) = \frac{J \Delta}{J^2 + \Delta^2} \sin^2 \left( t \sqrt{J^2 + \Delta^2} \right),
\]  

(3.11)

\[
I(C_{10,01}) = \frac{J}{\sqrt{J^2 + \Delta^2}} \sin \left( t \sqrt{J^2 + \Delta^2} \right) \cos \left( t \sqrt{J^2 + \Delta^2} \right).
\]  

(3.12)

Alternatively, one may characterize the coherence by using the polar form \( C_{10,01} = |C_{10,01}| e^{i \arg(C_{10,01})} \):

\[
|C_{10,01}| = \sqrt{\left( R(C_{10,01}) \right)^2 + \left( I(C_{10,01}) \right)^2},
\]  

(3.13)

\[
\arg(C_{10,01}) = \arctan \left( \frac{I(C_{10,01})}{R(C_{10,01})} \right).
\]  

(3.14)
3.2 Including the environmental interaction

The next step of the simulation is to incorporate the interaction between our two-qubit system and its environment. We model the environment as two nuclear spin baths, taking into account the coupling between each one to one chlorophyll at a time. The reason of modelling each qubit having a different environment is to improve the simulation and make it more similar to the real case: in the FMO complex each chlorophyll is localized in a different part of the protein, surrounded by different aminoacids, which means that each chlorophyll faces a distinct environment. Being $\gamma_\kappa$ and $\gamma_\eta$ the coupling constants, the scheme of the system is similar to the one proposed in [4] and looks like:

$$
E_k |0\rangle \rightarrow |1\rangle \quad \text{qubit}\; \kappa
$$

$$
E_\eta |0\rangle \rightarrow |1\rangle \quad \text{qubit}\; \eta
$$

Figure 3.2: Two qubit model including the interaction with the environment.

The Hamiltonian of the whole system reads:

$$
H = H_{q_\kappa-q_\eta} + H_{B_\kappa} + H_{B_\eta} + H_{q_\kappa-B_\kappa} + H_{q_\eta-B_\eta},
$$

(3.15)

being $q_i$ the two qubits representing the two chromophores, $B_i$ the two spin-baths modelling the environment and $q_i - B_i$ the interaction between each qubit with its spin-bath. The component $H_{q_i-B_i}$ is identical to the Hamiltonian in equation (3.2), considering just the dimer formed by the two qubits. The Hamiltonian corresponding to the spin-bath interacting with qubit $i$ is:

$$
H_{B_i} = \alpha_i \sum_{k=1}^{N_i} S^z_{i,k} = \alpha_i S^z_{i,(\text{total})},
$$

(3.16)

$\alpha_i$ being a constant that provides the strength of the local energy of the spin-bath and $N_i$ the number of spins in the bath. The qubit-bath at site $i$ interaction is represented by:

$$
H_{q_i-B_i} = \sum_{k=1}^{N_i} \gamma_{i,k} |i\rangle\langle i| S^z_{i,k} = \gamma_{i,(\text{total})} |i\rangle\langle i| S^z_{i,(\text{total})},
$$

(3.17)

By combining equations (3.2), (3.16) and (3.17), the total Hamiltonian in equation (3.15) takes the form:

$$
H = J \left( |0\rangle\langle 0| + |1\rangle\langle 1| \right) + \sum_{i=1}^{2} \left( \varepsilon_i |i\rangle\langle i| + \alpha_i S^z_i + \gamma_i |i\rangle\langle i| S^z_i \right).
$$

(3.18)
To describe the spin-bath state space one should define the vector $|j, m\rangle$ as the known eigenvectors of the angular momentum operator:

$$S_z |j, m\rangle = m |j, m\rangle,$$

where $j = 0, ..., \frac{N}{2}$ and $m = -j, ..., 0, ..., j$.

### 3.2.1 At zero temperature

At zero temperature, the spin-bath is initially described by the pure state:

$$|\psi_B(0)\rangle = \bigg| \frac{N_\kappa}{2}, -\frac{N_\kappa}{2} \bigg\rangle \otimes \bigg| \frac{N_\eta}{2}, -\frac{N_\eta}{2} \bigg\rangle,$$

i.e. all the spins in the lowest energy state.

The Hamiltonian can be expressed in the basis set, which is the single excitation subspace:

$$H = \begin{pmatrix}
\varepsilon_\kappa - \alpha_\kappa \frac{N_\kappa}{2} - \frac{\gamma_\kappa N_\kappa}{2} & J \\
J & \varepsilon_\eta - \alpha_\eta \frac{N_\eta}{2} - \frac{\gamma_\eta N_\eta}{2}
\end{pmatrix} = \begin{pmatrix}
\frac{\varepsilon_\kappa + \varepsilon_\eta}{2} - \frac{\gamma_\kappa N_\kappa + \gamma_\eta N_\eta}{4} & J \\
J & \frac{\varepsilon_\kappa + \varepsilon_\eta}{2} - \frac{\gamma_\kappa N_\kappa + \gamma_\eta N_\eta}{4}
\end{pmatrix} + \begin{pmatrix}
\Delta_{N_\kappa N_\eta} & J \\
J & -\Delta_{N_\kappa N_\eta}
\end{pmatrix},$$

where the first term has no physical influence, being the second term the one that contains significant information. Here, the new $\Delta_{N_\kappa N_\eta}$ is defined by:

$$\Delta_{N_\kappa N_\eta} = \frac{\varepsilon_\kappa - \varepsilon_\eta}{2} + \frac{\gamma_\eta N_\eta - \gamma_\kappa N_\kappa}{4}.$$

It is remarkable to notice that in the last matrix of equation (3.22) there is no contribution of the $\alpha_i$, which are the constants that provide the strength of the local energy of each the spin-bath. The not inclusion of this term denotes that the spin-baths by themselves are going to influence neither the transition probability nor the coherence, though they do contribute due to their interaction with each qubit.

The expression for the time-dependent coefficients of equation (3.3) is the same obtained in the case without environmental interaction (3.6), but with the $\Delta_{N_\kappa N_\eta}$ that includes the coupling constants:

$$\begin{cases}
c_{10}(t) = \cos \left(t \sqrt{J^2 + \Delta_{N_\kappa N_\eta}^2} \right) + i \frac{\Delta_{N_\kappa N_\eta}}{\sqrt{J^2 + \Delta_{N_\kappa N_\eta}^2}} \sin \left(t \sqrt{J^2 + \Delta_{N_\kappa N_\eta}^2} \right)
\end{cases}$$

$$\begin{cases}
c_{01}(t) = i \frac{J}{\sqrt{J^2 + \Delta_{N_\kappa N_\eta}^2}} \cos \left(t \sqrt{J^2 + \Delta_{N_\kappa N_\eta}^2} \right)
\end{cases} \quad (3.24)$$
The transition probability from $|1\rangle$ to $|2\rangle$ for this case has the same expression as (3.30), which is the same obtained in [4] but taking the different $\Delta_{N_e,N_\eta}$:

$$P = |c_{01}(t)|^2 = \frac{J^2}{J^2 + \Delta_{N_e,N_\eta}^2} \sin^2 \left( t \sqrt{J^2 + \Delta_{N_e,N_\eta}^2} \right).$$ (3.25)

It is obvious now that, for specially chosen parameters of the baths ($\gamma_i$ or $N_i$), it is possible to compensate for the energy difference between two levels of the dimer, such that $\Delta_{N_e,N_\eta} = 0$ and $P = 1$, namely, by setting:

$$\frac{\varepsilon_\eta - \varepsilon_\kappa}{2} = \frac{\gamma_\eta N_\eta - \gamma_\kappa N_\kappa}{4}.$$ (3.26)

This represents a very simple mechanism of increasing the transition probability in the system.

The expression for the coherence is the same as (3.10), but using the different $\Delta_{N_e,N_\eta}$. Analogously to the previous case, coherence can described taking several forms, all being presented in the equations (3.11), (3.12), (3.13), (4.2.1).

### 3.2.2 At non-zero temperature

The temperature can be taken into account in our system model introducing it through the environment, that is to say, using the spin-baths. Their couplings with each qubit will enable the spreading of the temperature across the whole system. To achieve this, the temperature has to be included in the initial state of each bath according to the canonical distribution:

$$\rho_B(0) = \prod_{i=1}^{2} \frac{1}{Z_i} e^{-\beta\alpha_i S^z_i},$$ (3.27)

where $Z_i$ is the partition of each spin-bath:

$$Z_i = \sum_{j_i=0}^{N_i/2} \sum_{m_i=-j_i}^{j_i} \nu(N_i,j_i) \langle j_i,m_i|e^{-\beta\alpha_i S^z_i}|j_i,m_i\rangle = \sum_{j_i=0}^{N_i/2} \nu(N_i,j_i) \frac{\sinh \beta\alpha_i(j_i + \frac{1}{2})}{\sinh \left( \frac{\beta\alpha_i}{2} \right)},$$ (3.28)

here $\beta$ representing the inverse temperature and $\nu(N_i,j_i)$ the multiplicity of the $j_i$, which is the irreductible representation obtained by adding $N_i$ spin $\frac{1}{2}$. Explicitly:

$$\nu(N_i,j_i) = \frac{(2j_i + 1)N_i!}{(\frac{N_i}{2} + 1 + j_i)! (\frac{N_i}{2} - j_i)!}.$$ (3.29)

Applying to the expressions above one can prove that the transition probability for the non-zero temperature case is given by:

$$P(T \neq 0) = \text{Tr}_B[\langle 01|U(t)|10 \rangle \rho_B(0) \langle 10|U(t)^\dagger|01 \rangle],$$
\[
P(T \neq 0) = \frac{1}{Z_{\kappa}Z_{\eta}} \sum_{j_n=0}^{N_{\kappa}/2} \sum_{j_n=0}^{N_{\eta}/2} \sum_{j_q} \sum_{m_{\kappa}} \sum_{m_{\eta}} \frac{J^2}{J^2 + \Delta_{m_{\kappa}m_{\eta}}^2} \sin^2 \left( t \sqrt{J^2 + \Delta_{m_{\kappa}m_{\eta}}^2} \right) \times
\]
\[
\times \nu(N_{\kappa}, j_n) \nu(N_{\eta}, j_q) e^{-\beta \alpha_{m_{\kappa}} - \beta \alpha_{m_{\eta}}},
\]

where \( P_{m_{\kappa}m_{\eta}}(T=0) \) represents the expression of the transition probability for the zero temperature, though in this case the \( \Delta_{m_{\kappa}m_{\eta}} \) is defined to be:

\[
\Delta_{m_{\kappa}m_{\eta}} = \frac{\epsilon_{\kappa} - \epsilon_{\eta}}{2} + \frac{\gamma_{m_{\kappa}} - \gamma_{m_{\eta}}}{2}.
\]

The coherence expressions for the non-zero temperature will have an analogous relation with the ones for the zero temperature as the corresponding found for the transition probability: it is a matter of substituting each type of coherence equation for the zero temperature (3.10), (3.11), (3.12), (3.13), (4.2.1) inside the general expression, bearing in mind the different definition of \( \Delta_{m_{\kappa}m_{\eta}} \):

\[
C_{10,01}(T \neq 0) = \frac{1}{Z_{\kappa}Z_{\eta}} \sum_{j_n=0}^{N_{\kappa}/2} \sum_{j_n=0}^{N_{\eta}/2} \sum_{j_q} \sum_{m_{\kappa}} \sum_{m_{\eta}} C_{10,01,m_{\kappa}m_{\eta}}(T=0) \nu(N_{\kappa}, j_n) \nu(N_{\eta}, j_q) e^{-\beta \alpha_{m_{\kappa}} - \beta \alpha_{m_{\eta}}}.
\]

3.3 Concurrence

The procedure for quantifying the entanglement of our system model regards to the concept of concurrence. The methodology for its calculation follows these steps:

1. operator \( \hat{\rho} \rightarrow \rho \) matrix

\[
\rho = \begin{pmatrix}
0 & 0 & 0 & 0 \\
0 & 1 - P & C_{10,01} & 0 \\
0 & C_{10,01}^* & P & 0 \\
0 & 0 & 0 & 0
\end{pmatrix},
\]

2. matrix \( \rho \rightarrow \) complex conjugate matrix \( \rho^* \)

\[
\rho^* = \begin{pmatrix}
0 & 0 & 0 & 0 \\
0 & 1 - P & C_{10,01}^* & 0 \\
0 & C_{10,01} & P & 0 \\
0 & 0 & 0 & 0
\end{pmatrix},
\]

3. define \( \tilde{\rho} = \sigma_y \otimes \sigma_y \rho^* \sigma_y \otimes \sigma_y \)

\[
\tilde{\rho} = \begin{pmatrix}
0 & 0 & 0 & 0 \\
0 & P & C_{10,01} & 0 \\
0 & C_{10,01}^* & 1 - P & 0 \\
0 & 0 & 0 & 0
\end{pmatrix},
\]
4. find the eigenvalues of \( \tilde{\rho} \mapsto \lambda_1 \geq \lambda_2 \geq \cdots \geq \lambda_n \)

\[
\tilde{\rho} = \begin{pmatrix}
0 & 0 & 0 & 0 \\
0 & P(1-P) + |C_{10,01}|^2 & P(C_{10,01} + C_{10,01}^*) & 0 \\
0 & (1-P)(C_{10,01} + C_{10,01}^*) & P(1-P) + |C_{10,01}|^2 & 0 \\
0 & 0 & 0 & 0
\end{pmatrix},
\]

The eigenvalues of this matrix are:

- \( \lambda_1 = P(1-P) + |C_{10,01}|^2 + 2|C_{10,01}|\sqrt{P(1-P)} = (\sqrt{P(1-P)} + |C_{10,01}|)^2 \)
- \( \lambda_2 = P(1-P) + |C_{10,01}|^2 - 2|C_{10,01}|\sqrt{P(1-P)} = (\sqrt{P(1-P)} - |C_{10,01}|)^2 \)
- \( \lambda_3 = \lambda_4 = 0 \)

5. calculate \( \sqrt{\lambda_1} - \sqrt{\lambda_2} - \sqrt{\lambda_3} - \sqrt{\lambda_4} \):

\[
C(\rho) = 2|C_{10,01}| \tag{3.33}
\]

### 3.4 Nonlocality

The quantification of nonlocality for our model system described by the density matrix indicated in the previous page can be calculated using the methodology described in the background:

1. calculation of the correlation matrix \( T \):

\[
T = \begin{pmatrix}
2|C_{10,01}| & 0 & 0 \\
0 & 2|C_{10,01}| & 0 \\
0 & 0 & -1
\end{pmatrix},
\]

where \( T_{n,m} = \text{Tr} [ \rho_{AB} \sigma_A^n \sigma_B^m ] \)

2. correlation matrix squared \( |T|^2 = T^T T \)

\[
|T|^2 = \begin{pmatrix}
4|C_{10,01}|^2 & 0 & 0 \\
0 & 4|C_{10,01}|^2 & 0 \\
0 & 0 & 1
\end{pmatrix},
\]

3. find the eigenvalues of \( |T|^2 \)

\[ 1 \geq 4|C_{10,01}|^2 \geq 4|C_{10,01}|^2 \]

4. \( M(\rho) = 1 + 4|C_{10,01}|^2 \leq 2 \)

5. \( B(\rho) \equiv \sqrt{\max \{0, M(\rho) - 1\}} \)

\[
B(\rho) = 2|C_{10,01}| = C(\rho) \tag{3.34}
\]

Our particular system described by the mentioned density matrix presents the feature that the expression for the nonlocality is the same as for the concurrence. Thus, the degree of nonlocality and entanglement happens to be identical for this class of two-qubit states.
3.5 Decay

Until now, the states considered have been $|10\rangle$ and $|01\rangle$, both representing one chlorophyll in the excited state and the other in the ground state. The next goal is to consider the state $|00\rangle$, i.e. both chlorophylls in their respective ground states, which may be thought to represent a decay due to the emission of a photon.

The inclusion of the $|00\rangle$ state in the dynamics can be done from first principles: in this case one should reconsider the model from the very beginning, which means modifying the Hamiltonian by adding a term that induces decay. However, in this report we have considered that incorporating this state from a higher level will provide us with results good enough to simulate a realistic model. The idea is to modify the density matrix including an amplitude decay. To accomplish this one can define the exponential decay as

$$d = 1 - e^{-kt}, \quad (3.35)$$

being $k$ an exponential factor. The following $4 \times 4$ matrices, known as Kraus operators, induce the decay from $|1\rangle$ to $|0\rangle$ of each qubit $\kappa$ and $\eta$:

$$E^{(\kappa)}_1 = \sqrt{d} |0\rangle\langle 1| \otimes (|0\rangle\langle 0| + |1\rangle\langle 1|) =$$

$$= \begin{pmatrix}
0 & 0 & \sqrt{d} & 0 \\
0 & 0 & 0 & \sqrt{d} \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0
\end{pmatrix}, \quad (3.36)$$

$$E^{(\eta)}_1 = (|0\rangle\langle 0| + |1\rangle\langle 1|) \otimes \sqrt{d} |0\rangle\langle 1| =$$

$$= \begin{pmatrix}
0 & \sqrt{d} & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & \sqrt{d} \\
0 & 0 & 0 & 0
\end{pmatrix}. \quad (3.37)$$

The mapping of the new density matrix must be trace and positivity preserving. To achieve this, one can introduce these other Kraus operators:

$$E^{(\kappa)}_0 = (|0\rangle\langle 0| + \sqrt{1-d} |1\rangle\langle 1|) \otimes (|0\rangle\langle 0| + |1\rangle\langle 1|) =$$

$$= \begin{pmatrix}
1 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 \\
0 & 0 & \sqrt{1-d} & 0 \\
0 & 0 & 0 & \sqrt{1-d}
\end{pmatrix}, \quad (3.38)$$

$$E^{(\eta)}_0 = (|0\rangle\langle 0| + |1\rangle\langle 1|) \otimes (|0\rangle\langle 0| + \sqrt{1-d} |1\rangle\langle 1|) =$$

$$= \begin{pmatrix}
1 & 0 & 0 & 0 \\
0 & \sqrt{1-d} & 0 & 0 \\
0 & 0 & 1 & 0 \\
0 & 0 & 0 & \sqrt{1-d}
\end{pmatrix}. \quad (3.39)$$

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The new density matrix describing the two-qubit system will have the form:

\[ \rho(t) = \frac{1}{2} (E^{(\kappa)}_0 \rho E^{(\kappa)}_0 + E^{(\kappa)}_1 \rho E^{(\kappa)}_1 + E^{(\eta)}_0 \rho E^{(\eta)}_0 + E^{(\eta)}_1 \rho E^{(\eta)}_1) \]

\[ \cong \begin{pmatrix} \frac{1}{2} d & 0 & 0 & 0 \\ 0 & \frac{1}{2} (2 - d) (1 - P) & \sqrt{1 - d} C_{10,01} & 0 \\ 0 & \sqrt{1 - d} C_{10,01} & P - \frac{d}{2} P & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}. \] (3.40)

The comparison between this density matrix and the other used in the previous sections makes one to realize that this has a non-zero term in the top-right position. The new transition probability from \(|10\rangle\) to \(|01\rangle\) takes the form:

\[ P = P_0 - \frac{d}{2} P_0, \] (3.41)

being \(P_0\) the transition probability defined in equation (3.30). Directly from the density matrix one can also define the concurrence of the new system as:

\[ C = \max \{ 0, 2 \sqrt{1 - d} |C_{10,01}| \}. \] (3.42)

To deduce the expression for nonlocality, the three eigenvalues of the squared correlation matrix need to be evaluated: \(\lambda_a = (d - 1)^2\) and \(\lambda_b = \lambda_c = 4 (1 - d) |C_{10,01}|^2\). Only after comparing these expressions and ordering them so that \(\lambda_1 \geq \lambda_2 \geq \lambda_3\), one can define the two possible formulas for nonlocality \(B = \sqrt{\max \{ 0, \lambda_1 + \lambda_2 - 1 \}}\) can take:

- if \(\lambda_a \geq \lambda_b\) then \(B = \sqrt{\max \{ 0, (1 - d)^2 + 4 (1 - d) |C_{10,01}|^2 - 1 \}}\).
- if \(\lambda_a < \lambda_b\) then \(B = \sqrt{\max \{ 0, 8 (1 - d) |C_{10,01}|^2 - 1 \}}\).
## 3.6 Summary of concepts

<table>
<thead>
<tr>
<th>Concept</th>
<th>Abbrev.</th>
<th>Expression for $X(0)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transition probability</td>
<td>$P = P_0 - \frac{d}{2} P_0$</td>
<td>$\frac{1}{Z_\kappa Z_\eta} \sum_{j_\kappa=0}^{N_\kappa/2} \sum_{j_\eta=0}^{N_\eta/2} \sum_{j_\kappa=-j_\kappa}^{N_\kappa/2} \sum_{j_\eta=-j_\eta}^{N_\eta/2} \frac{J^2}{\sqrt{J^2 + \Delta_{m_\kappa m_\eta}^2}} \times \sin^2 \left( t \sqrt{J^2 + \Delta_{m_\kappa m_\eta}^2} \right) \nu(N_\kappa, j_\kappa) \nu(N_\eta, j_\eta) \times e^{-\beta \alpha_\kappa m_\kappa - \beta \alpha_\eta m_\eta}$</td>
</tr>
<tr>
<td>Coherence (real)</td>
<td>$R(C_{10,01}) = \sqrt{1 - d} R(C_{10,010})$</td>
<td>$\frac{1}{Z_\kappa Z_\eta} \sum_{j_\kappa=0}^{N_\kappa/2} \sum_{j_\eta=0}^{N_\eta/2} \sum_{j_\kappa=-j_\kappa}^{N_\kappa/2} \sum_{j_\eta=-j_\eta}^{N_\eta/2} \frac{J \Delta_{m_\kappa m_\eta}}{\sqrt{J^2 + \Delta_{m_\kappa m_\eta}^2}} \times \sin \left( t \sqrt{J^2 + \Delta_{m_\kappa m_\eta}^2} \right) \nu(N_\kappa, j_\kappa) \nu(N_\eta, j_\eta) \times e^{-\beta \alpha_\kappa m_\kappa - \beta \alpha_\eta m_\eta}$</td>
</tr>
<tr>
<td>Coherence (imaginary)</td>
<td>$I(C_{10,01}) = \sqrt{1 - d} I(C_{10,010})$</td>
<td>$\frac{1}{Z_\kappa Z_\eta} \sum_{j_\kappa=0}^{N_\kappa/2} \sum_{j_\eta=0}^{N_\eta/2} \sum_{j_\kappa=-j_\kappa}^{N_\kappa/2} \sum_{j_\eta=-j_\eta}^{N_\eta/2} \frac{J}{\sqrt{J^2 + \Delta_{m_\kappa m_\eta}^2}} \times \sin \left( t \sqrt{J^2 + \Delta_{m_\kappa m_\eta}^2} \right) \cos \left( t \sqrt{J^2 + \Delta_{m_\kappa m_\eta}^2} \right) \nu(N_\kappa, j_\kappa) \nu(N_\eta, j_\eta) e^{-\beta \alpha_\kappa m_\kappa - \beta \alpha_\eta m_\eta}$</td>
</tr>
<tr>
<td>Coherence (phase)</td>
<td>$\arg(C_{10,01}) = \arctan \left( \frac{I(C_{10,01})}{R(C_{10,01})} \right)$</td>
<td>$\max \left{ 0, 2 \sqrt{1 - d} \sqrt{R(C_{10,01})^2 + I(C_{10,01})^2} \right}$</td>
</tr>
<tr>
<td>Concurrence</td>
<td>$C$</td>
<td>$\max \left{ 0, 2 \sqrt{1 - d} \sqrt{R(C_{10,01})^2 + I(C_{10,01})^2} \right}$</td>
</tr>
<tr>
<td>Nonlocality</td>
<td>$B$</td>
<td>$\left{ \sqrt{\max \left{ 0, (1 - d)^2 + 4 (1 - d) \left( R(C_{10,01})^2 + I(C_{10,01})^2 \right) - 1 \right}}, \sqrt{\max \left{ 0, 8 (1 - d) \left</td>
</tr>
</tbody>
</table>

being $\Delta_{m_\kappa m_\eta} = \frac{\epsilon_\kappa - \epsilon_\eta}{2} + \frac{\gamma_{m_\kappa} - \gamma_{m_\eta}}{2}$ and $d = 1 - e^{-kt}$. 

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4 Results and discussion

The analytical expressions found in the modeling section are analysed in this chapter: the transition probability, the coherence, the quantification of entanglement, which is concurrence and appears to be the same as nonlocality if $d = 0$, as well as the data obtained with the inclusion of a decay term corresponding to the contribution of the ground state.

Each plot consists of representing the data obtained evaluating the mentioned expressions for the coupling constant qubit-spin-bath $\gamma$ taking the range from 0 to 15 $\text{ps}^{-1}$ and for a period of time up to 2 ps, as it is known from experimental observation [1, 25] and theoretical predictions [31] that the increased EET rate occurs on time scales of a few hundred femtoseconds. The temperatures considered are 77 and 298 K. The parameters used for the variables are the same as the ones given in [4]: $\frac{\epsilon_\eta - \epsilon_s}{2} = J = 10 \text{ ps}^{-1}$, $\alpha_\kappa = \alpha_\eta = 250 \text{ ps}^{-1}$ and $N_\kappa = 10$ but $N_\eta = 20$. These last values have been chosen not to be equal in order to obtain plots containing more significant information.

4.1 Transition probability

Figure 4.1: Transition probability as a function of time $(t)$ and the coupling to the spin-baths $(\gamma)$.

The first outstanding feature of Figure 4.1 is the wavelike character presented by the transition probability at both temperatures. These beatings are a typical phenomenon in systems with quantum behaviour and occur, as expected, on time scales in the order of a few hundred femtoseconds.

A remarkable issue of these outcomes is the fact that the maximum of the transition probability is achieved for a non-vanishing interaction with the environment, and this is true for both temperatures. One can even go a little bit further and affirm that for a higher temperature, the maximum probability is found in a higher value of the coupling constant $\gamma$. In our concrete cases, $\max \{\gamma_{77}\} = 4.12 \text{ ps}^{-1}$ and $\max \{\gamma_{298}\} = 4.66 \text{ ps}^{-1}$.

Another difference that emerges when comparing the plots of the two temperatures is that, in the 298 K case, the range of values taken by the transition probability is narrower than for the 77 K: it neither reaches the 100% nor the 0%. Apparently, it rapidly tends to an average value somewhere in the middle. This also seems to happen for the lowest temperature, though much more slowly.

To test this statement one can compute the transition probability for a longer period of time using the maximum $\gamma$ of each temperature, i.e. the values specified above.
This longer-time figure shows that the assertion above is only a half truth: up to two ps for both temperatures the transition probability gets to be narrower, specially in the case of 298 K, but when considering longer periods of time one can clearly see that such extrapolation cannot be done: the so-called quantum revivals appear to play a significant role. These are typical quantum phenomena due to the wavelike character. One can also assume that the higher the temperature, the more frequent the revivals.

In addition, it shall be pointed out the fact that the average value of the transition probability for both temperatures is found to be, as mentioned, between 0 and 1, though this last plot sheds some more light to the question: it is always below 0.5, as one can note comparing the red and green lines to the grey background line. Furthermore, the higher the temperature, the lower the average transition probability. This behaviour could be explained by the fact that for a higher temperature there are more states available in the spin-baths, with the consequence of the information diffusing into them and thus being partially lost.

### 4.2 Coherence

![Figure 4.3: Coherence (real part) as a function of time (t) and the coupling to the spin-baths ($\gamma$).](image)

The plots of the real contribution of the off-diagonal terms of the system’s density matrix present the tendency of increasing the coherence when the taking higher $\gamma$ values. In the case of 298 K, most
of the depicted values are very close to zero.

Figure 4.4: Coherence (imaginary part) as a function of time (t) and the coupling to the spin-baths ($\gamma$).

The behaviour of the imaginary part of coherence shows an interesting feature: it appears to be related to the transition probability depicted in Figure 4.1 in the sense that the maximum values of the latter coincide to be at the same time and $\gamma$ as the lines which the imaginary coherence takes the value of zero.

Due to the fact that in both cases, real and imaginary coherence, the values that present extra connotations and may provide us with stimulating study cases are the ones that get to be zero, it has been thought to be useful to plot them in one graph. Because of numerical approximations and intrinsic accuracy of the code, the values printed are not only the zeros but a short range close to zero; this explains the apparently too wide lines of some regions.

Figure 4.5: Coherence, zero values of the real (red) and imaginary (green) contributions.
4.2.1 Phase

Special emphasis must be put when analysing the data obtained from the phase plots. It has been considered convenient to attach the graphs at 0, 77 and 298 K in order to have a more complete picture of the effect of the temperature.

Figure 4.6: Coherence (phase) as a function of time (t) and the coupling to the spin-baths (γ).
The interpretation of these plots is closely related to the previous figures of the zero values of the real and imaginary coherences. The explanation to this fact is implicit in the definition of the phase:

$$\text{arg}(C_{10,01}) = \arctan \left( \frac{I(C_{10,01})}{R(C_{10,01})} \right).$$

One can distinguish two particular aspects that deserve to be studied deeply:

(a) Singularities. They are points surrounded by two half circles, being each a continuous gradient. For instance, in the zero temperature plot, the point with $t = 0.15 \text{ ps}$ and $\gamma = 4 \text{ ps}^{-1}$ is a singularity. They arise in the cases when $R(C_{10,01}) = I(C_{10,01}) = 0$ is satisfied. One can prove this comparing the phase plots with the zero-coherence plots: the singularities only appear when a red line crosses a green line. For this reason in the 77 K plot there are no singularities above $\gamma = 4.12 \text{ ps}^{-1}$.

(b) Line jumps. One can recognize them because of the sudden color change from black to yellow, i.e. from $-\pi/2$ to $\pi/2$. This full $\pi$ gap can be explained by looking at the shape of the arctangent function: the jump occurs because of the fact that, assuming we are moving to the left, when one reaches the far left ($-\pi/2$, black) a discontinuity is encountered. To solve this, the Fortran90 code has been programmed to continue from the far right zone ($\pi/2$, yellow), producing the discontinuous jump.

4.3 Concurrence and nonlocality

(a) $T=77 \text{ K}$

(b) $T=298 \text{ K}$

Figure 4.8: Concurrence and nonlocality as a function of time ($t$) and the coupling to the spin-baths ($\gamma$); for this density matrix they appear to look exactly the same.
The data shown in these plots include the of the real and the imaginary coherences, as specified in the expression:

\[ B = C = 2 \sqrt{R(C_{10,01})^2 + I(C_{10,01})^2}. \] (4.1)

One should notice that for both temperatures (though it can be more clearly observed in the 77 K) the "holes" surrounded by very high concurrence/nonlocality are in the same position as the highest transition probability. For instance, the point with \( t = 0.15 \) ps and \( \gamma = 4.12 \) ps\(^{-1} \) used to correspond to a maximum, now is a minimum.

### 4.4 Decay

As already mentioned in the development of the model, the state representing the two chlorophylls in their ground state is populated in the presence of an exponential decay. The decay rate \( k \) has been chosen to take the values 0.1 and 1, with this last one simulating a more rapid decay.

#### 4.4.1 Transition probability

![Transition probability with decay as a function of time (t) and the coupling to the spin-baths (γ).](image)

Figure 4.9: Transition probability with decay as a function of time (t) and the coupling to the spin-baths (γ).
The behaviour is as expected: the transition probability decreases faster at both temperatures, but it more rapidly with the highest exponential factor. However, it is not-so-clear if after longer times it will continue decaying until a zero value or not. For this reason, we have also computed the transition probability for a longer period of time using the $\gamma$ giving the first maximal $P$ of each temperature.

![Graphs showing transition probability decay](image)

Figure 4.10: Transition probability with decay for the $\gamma$ giving the first maximal $P$ of each temperature.

The two plots of Figure 4.10 show that the two chosen exponential factors produce a different decay only during the first picoseconds, but after 40 ps their deviations are hardly appreciable.

Another conclusion is that even including the state of the system with the two chlorophylls in their ground state, the transition probability does not decay to zero. Instead, it ends up trapped with an average value a little bit below 0.25, lower for the higher temperature. This is a direct consequence of the treatment of the decay, which entails that even for an infinite time, the decay will only absorb half of the total transition probability. Thus, it makes sense that without decay the average is approximately 0.4, but now near to 0.2.

### 4.4.2 Concurrence

In the last two sections of these report results, corresponding to the concepts of concurrence and nonlocality with decay, it is convenient to redefine the legend and its colors with the purpose of including information that otherwise would have been kept hidden behind the formal definitions of these notions.
Regarding to the mathematical expressions of concurrence and nonlocality, one should remember that in both cases the final value is the maximum between zero and another term. In the previous case without decay, this second term is always greater or equal than zero, so the first condition never applies. What is more, because of the particular form taken by the density matrix of our system, the concurrence and nonlocality appear to have the same mentioned second term, so the data and the plots obtained were exactly the same for both concepts.

The inclusion of the state $|00\rangle$ adds a decay term and modifies the density matrix of the system. Therefore, concurrence and nonlocality will differ substantially, affecting the data produced and the plots obtained. Furthermore, this change in the density matrix may provoke that either the concurrence, the nonlocality, none of them, or both, would need to apply to the first condition and be zero in order to still take values from 0 to 1. We have considered convenient to include this significant information in the plots: the white color is designed to the case when the quantity vanishes.

In none of the case the second term of concurrence is below zero, i.e. the first condition never applies. The behaviour of concurrence is the expected, it decreases due to the exponential decay. The higher the value given to the exponential factor, the faster the decay.

Figure 4.11: Concurrence with decay as a function of time ($t$) and the coupling to the spin-baths ($\gamma$).
4.4.3 Nonlocality

The nonlocality presented by our system with the inclusion of the exponential decay, \textit{i.e.} allowing the state \(|00\rangle\) to happen so that both chlorophylls can be on their ground states, appears to be the most astonishing and unexpected result of this project. The nonlocality dramatically decreases fast and with no possible stopper: so it does for the small exponential factor, but when it takes the bigger value, nonlocality is extraordinarily erased almost instantly, leaving a plot mostly filled with white. The huge difference when compared to concurrence is only due to mentioned second term, that can ve negative only for nonlocality.

Analogously to the property described in [32] relating entanglement with respect to coherence and naming the singular behaviour as "entanglement sudden death", the particular feature observed in our system and its density matrix is proposed to be relied as "nonlocality sudden death" with respect to entanglement. It provides an irrefutable evidence of nonlocality being a stronger form of correlation than entanglement.
5 Conclusions

The influence of the environment on two of the chlorophylls of the FMO complex has been studied. The two chlorophylls have been modeled as a pair of two-level systems (qubits), the two levels representing the ground and excited state of each chlorophyll. The environment has been modeled as two separated spin-baths each interacting on one chlorophyll. The single-excitation dynamics of the system at non-zero temperature has enabled us to determine analytical expressions for the transition probability and the correlations of entanglement and nonlocality between the qubits, and therefore, we could investigate the effect of their coupling with the environment. The model has been extended by introducing a decay term to simulate the population of both chlorophylls in their ground state.

After analyzing the results, one can assert that the maximum transition probability between two chlorophylls is reached for a non-vanishing interaction with the environment. For higher temperatures it is achieved when the coupling constant $\gamma$ takes higher values, though in this case the probability decreases faster and has narrower beats than for lower temperatures. For longer times, the phenomenon of quantum revivals is observed. Hence, one can affirm that the decoherent effect of the environment assists the electronic energy transfer. Furthermore, the coherence provides us with evidence of phase singularities being found at physiological temperature, a fact that might be tested experimentally and would represent a clear sign of the wave-like nature of the EET.

The quantification of entanglement and nonlocality appears to be exactly the same for the first model considered, which only takes into account the single-excitation state. This fact is due to the particular form of the density matrix: the non-zero terms are only found in the central square. However, when the possibility of both chlorophylls to decay into their ground state is included in the description of the dynamics, the density matrix gains a non-zero term in the upper-left side, being the central square also modified. This subtle but sensitive change has the consequence of concurrence and nonlocality taking distinct expressions and therefore the respective plots become qualitatively different: while the concurrence experiences the expected progressive decrease, nonlocality suffers a drastic decay which leads to its early extinction, a process which we label "nonlocality sudden death". This evidences the nonlocality being a stronger form of correlation than entanglement.

Further research that can be done to extend this project would be to expand the model taking into account the seven chlorophylls of the FMO complex in order to obtain a simulation closer to reality. Additionally, introducing the doubly excited state may enable this model to simulate the EET of photosynthetic organisms exposed to larger amount of light, for instance plants. Another refinement of the model that can be carried out is to incorporate the decay term at the Hamiltonian level.
References


