

# FMO complexes' efficiency explained in terms of Quantum networks

Francesco De Stefano

## Contents

<b>Introduction</b>	<b>2</b>
<b>1 The setup: open quantum systems</b>	<b>3</b>
<b>2 Quantum networks: a general model</b>	<b>5</b>
2.1 The uniform case . . . . .	6
2.1.1 No dissipation, no dephasing . . . . .	8
2.1.2 Reintroducing dephasing and dissipation . . . . .	9
<b>3 The FMO complex</b>	<b>12</b>
<b>Conclusions</b>	<b>16</b>
<b>Appendix</b>	<b>17</b>
<b>References</b>	<b>18</b>

# Introduction

There is no doubt that quantum mechanics is present, at least from a fundamental point of view, in biology but how it can effectively be relevant in biological processes is still in debate. Indeed, the environments in which quantum mechanics usually works are completely different from the hot and fuzzy ones in which life operates. However, recent results suggest that, against all odds, quantum mechanics is not only the natural theory underlying any natural process but it can also explain some effects that a classical context cannot do. Thus, the decoherence usually found in macroscopic objects, such as the ones considered in biology (proteins, receptors, genes, etc.), which reduces all quantum effects to classical ones, is, in a way that is not totally clarified yet, interrupted.

The first attempt of introducing physics and, specially, quantum mechanics to the complex realm of biology was perhaps made by one of the founders of the first, Erwin Schrödinger, who in 1944 published a book entitled *What is life?*, in which he tried to explain the possible mechanisms underlying the living cells, with particular relevance to the mechanism of inheritance, suggesting the possibility of genes to be the responsible and that mutations are caused by nothing else than a quantum hop (it is important to remark that all milestone discoveries about DNA, its structure and its fundamental role in the transmission of genetic heritage, were made just under ten years later).

Despite its promises, these enlightening ideas were, if not completely abandoned, set aside, considered too "philosophical" and in any case far from the relevant experiments and observations of that time. This was the scientific common thought until about fifteen years ago, when something began to show up: the explanation, by the use of quantum mechanics, of the excitation transfer in the Fenna–Matthews–Olson (FMO) complex, a pigment-protein complex appearing in green sulfur bacteria, which revealed to be very efficient. Indeed, the ability of some bacteria and of the plants to have a very efficient photosynthesis (as the ratio of transformed energy and received energy) was known but a pure classical random walk could not explain such an optimization. Beyond this, many other biological processes have found an explanation in the quantum world, despite all the expectations: the enzymatic activity, the cellular respiration, the olfaction, the magnetoreception of the robin red-breast, ability which helps this species of bird to orient itself and the mutation process, proposed by Schrödinger himself. All these and others that may be not cited undergo to a new blended scientific branch, the quantum biology. The prominence of this new area of study is still debated by the most sceptical and many other steps it has to do before becoming a solid scientific theory but, if its prediction will be shown to be true, it could be very revolutionary, not only from a pure theoretical point of view but also in the application to technology.

The aim of this project is to discuss, as far as possible, the first of these processes: modelling the FMO complex as a network composed by 7 nodes, with undirected links and the reaction centre, where the excitation is finally transferred for the photosynthesis, as an 8th node, to which the other are linked in an irreversible directed way, and the use of quantum mechanics, in particular, the use of a master equation to describe the evolution of the network, allows us to have at least an idea on how bacteria and plants could carry out the photosynthesis. Moreover and surprisingly, such an efficiency would not have been achieved if noise was not considered, contrary to all expectations since noise is universally accepted as one of the most destroyers of the efficiency.

In the first section, the quantum mechanical setup is illustrated; in the second section, the general model of a network with  $N$  nodes and one sink is given and a simple application to a fully connected and uniform network is shown since it is possible to extrapolate analytical results which will help us to understand the differences between a pure classical approach and using quantum mechanics and will also guide us in the practical description of the protein; in the third section, the FMO complex is analysed in the same spirit of the uniform network, trying to make contact to the experimental outcomes.

# 1 The setup: open quantum systems

The natural setup in which one can model the FMO complex and, in general, a biological object is an open system: it would be not fair to consider such a system as closed, with no interaction with the surrounding environment.

We usually lead, at least in pedagogical courses on quantum mechanics or in fundamental research, with closed quantum systems. The entire framework of quantum mechanics can be summarized by its postulates, whose aim is to give a definition to the following 4 entities:

- State: a state  $|\psi\rangle$  is a vector of an Hilbert space  $\mathcal{H}$ ,  $|\psi\rangle \in \mathcal{H}$ .
- Measurement: all possible quantum measurements are described by an observable which takes the form of an hermitian operator  $O$ ; by spectral theorem, one can write  $O = \sum_i \lambda_i |\lambda_i\rangle\langle\lambda_i|$ , where  $\lambda_i$  are the eigenvalues and  $|\lambda_i\rangle$  the corresponding eigenvectors. The probability of obtaining  $\lambda_i$  as the result of measurement, before the measurement itself, of the observable  $O$  in a state  $|\psi\rangle$  is  $P = |\langle\psi|\lambda_i\rangle|^2$  whereas after the measurement a state  $|\lambda_i\rangle$  is measured if  $\lambda_i$  is the outcome.
- Evolution: the evolution of a quantum system is given by an unitary transformation  $|\psi(t)\rangle = U|\psi(0)\rangle$ , with  $UU^\dagger = U^\dagger U = I$ ; in practice, the state  $|\psi(t)\rangle$  satisfies the Schrödinger equation  $\frac{\partial}{\partial t}|\psi(t)\rangle = -i\hbar H|\psi(t)\rangle$ .
- Composite systems: when a quantum system is composed by  $N$  subsystems, the total Hilbert space is represented by the tensor product of the individual Hilbert spaces,  $H_T = H_1 \otimes H_2 \otimes \dots \otimes H_N$ .

When dealing with many of these systems, it is, however, useful to define the density operator  $\rho$ :

$$\rho = \sum_i \rho_i |\psi_i\rangle\langle\psi_i| \quad (1)$$

Fixing an arbitrary basis  $\{|i\rangle\}_1^N$  of the Hilbert space, then

$$\rho = \sum_{i,j} \rho_{i,j} |i\rangle\langle j| \quad (2)$$

and the density operator acquires a matrix form

$$\rho = \begin{pmatrix} \rho_{00} & \rho_{01} & \cdots & \rho_{0N} \\ \rho_{10} & \rho_{11} & \cdots & \rho_{1N} \\ \vdots & \vdots & \ddots & \vdots \\ \rho_{N0} & \rho_{N1} & \cdots & \rho_{NN} \end{pmatrix} \quad (3)$$

The evolution equation for this operator is obtained directly applying the Schrödinger equation; the result is the von-Neumann equation ( $\hbar = 1$  unity)

$$\dot{\rho} = -i[H, \rho] \quad (4)$$

This equation carries the evolution of the density matrix which is very useful because it can describe the population of the various states, that, in our practical case, will be the sites of the network. A simple example of a two-level system is composed by two states, said  $|0\rangle$  and  $|1\rangle$  the ground and the excited state, respectively; considering an Hamiltonian (where the zero energy is set to zero)

$$H = E|1\rangle\langle 1| + \Omega(|0\rangle\langle 1| + |1\rangle\langle 0|) \quad (5)$$

what one finds applying the (4) is the following system of differential equations

$$\begin{aligned} \dot{\rho}_{00} &= -i\Omega(\rho_{10} - \rho_{01}) \\ \dot{\rho}_{01} &= -i\Omega(\rho_{11} - \rho_{00}) + iE\rho_{01} \\ \dot{\rho}_{10} &= -i\Omega(\rho_{00} - \rho_{11}) - iE\rho_{10} \\ \dot{\rho}_{11} &= -i\Omega(\rho_{01} - \rho_{10}) \end{aligned} \quad (6)$$

Provided that the initial state is the excited state  $|1\rangle$ , one can solve this system of coupled equations; the numerical solution of this is found using Mathematica and is shown in "Simple two-level system.nb" (where, for the sake of simplicity, we have fixed  $E = \Omega = 1$ ): as final result, there is a plot of the two states populations, in blue the population of  $|1\rangle$  and in orange the population of  $|0\rangle$ . These are also

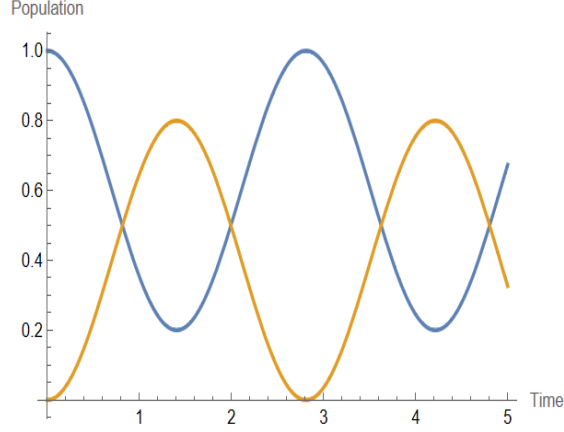


Figure 1: Plot of the population as a function of time (in blue the population of the excited state and in orange the population of the ground state)

called Rabi oscillations.

Now, is time to face the problem of the interaction of a quantum system with the environment; this study revealed to be very useful, among other things, in the development of quantum computing but now the need of considering open quantum system is even more clear: biological object cannot be identified as ideal closed quantum systems and there is a source of noise which surely could cause dissipation. The trick that is common in this area of study is to consider the whole system, the environment and the system (like, for instance, the seen two-level system), as, by means of one of the postulates, the tensor product of the two corresponding Hilbert spaces

$$\mathcal{H}_T = \mathcal{H}_S \otimes \mathcal{H}_E \quad (7)$$

and then, define the so-called reduced density matrix by tracing out the environment, in a process which is similar to calculate the marginal probability, so in practice

$$\rho_S = Tr_E [\rho_T] \quad (8)$$

The von-Neumann equation (4) still works but only applied to  $\rho_T$ , the evolution equation of the system of interest S only will be a little bit modified by this operation. There are several ways to obtain this new equation; the "simplest" is consider a Markovian evolution, that is an evolved state is the result of only the previous state. The result is the so-called Lindblad master equation and the derivation can be found in many references like [1,2]

$$\dot{\rho} = -i[H, \rho] + \sum_i \left( -\{L_i^\dagger L_i, \rho\} + 2L_i \rho L_i^\dagger \right) \quad (9)$$

where the curly brackets represent, as usual, an anticommutator and the  $L_i$  are called Lindblad operators and are usually combinations of jump operators. Thus, solving this equation, one can obtain the more realistic population of a state of a system when it is interacting with the surrounding environment and so, can be used for our purposes.

## 2 Quantum networks: a general model

In order to describe the FMO complex, it is useful to describe and analyze, in full generality, a network of  $N+1$  nodes, of which  $N$  are referred as the sites and the  $N+1$ -th is referred as the sink. In practice, the sites can be linked whatever they want and this connection is mediated by the interaction that they have to each other and finally, there is one site, say, without loss of generality, the node  $N$  that is irreversibly linked to the sink (a single directed link whereas, between sites, the arrows are generally undirected, as in the following figure). Moreover, as the FMO complex, we consider a fully connected

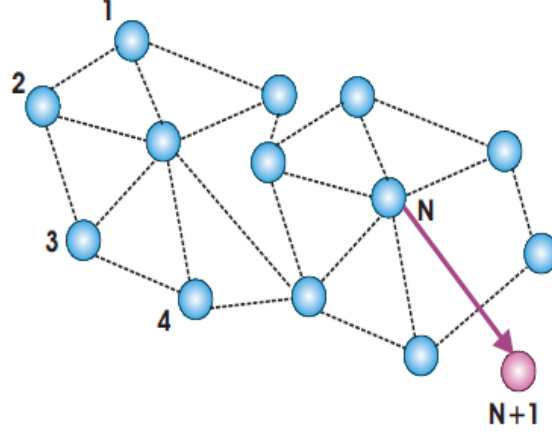


Figure 2: The network: the blue nodes are the sites and the links are bilateral while the purple node is the sink which is irreversibly connected to site  $N$

network. Our final goal is finding, assuming that the site 1 has received the photon by a light source (the Sun) and so carries all the excitation, how this excitation walks between the various sites and arrives to the sink where presumably there is a reaction centre and mainly, how much this process is efficient, in terms of speed but specially in terms of how much excitation is lost in the process and how much, instead, arrives in the final destination. This evolution can be calculated by means of the master equation (9), so what is left is understanding what is the Hamiltonian of our system and then, analyzing the possible noise effects caused by the environment and so, give an explicit form to the Lindblad operators.

The Hamiltonian of our system is similar to our former two-level system but now it could be useful to write it in terms of jump operators, since we have  $N$  sites. We naturally assume that each site has its own energy and that the interaction between the various sites, which is a hopping rate that describes how the excitation is transferred among the sites, connects each site with another

$$H = \sum_{j=1}^N \hbar\omega_j \sigma_j^+ \sigma_j^- + \sum_{j \neq l} \hbar v_{j,l} (\sigma_j^- \sigma_l^+ + \sigma_j^+ \sigma_l^-) \quad (10)$$

where  $\hbar\omega_j$  are the site energies,  $\hbar v_{j,l}$  the hopping rates and  $\sigma_j^+, \sigma_j^-$  the jump operators. At this point, the environmental effects come in the game; these can be divided in two categories:

1. Dissipative effects: as usual even in classical mechanics, there should be a loss of the energy for the excitation in walking through the sites; this term can also be seen as the responsible of decays: indeed, closed quantum systems do not decay because what is lost is right there the interaction with the environment. The extra piece that has to be added to the von-Neumann equation, is

$$\sum_j \Gamma_j (-\{\sigma_j^+ \sigma_j^-, \rho\} + 2\sigma_j^- \rho \sigma_j^+) \quad (11)$$

where the Lindblad operators are simply jump operators referred to the single site.

2. Dephasing effects: this is a pure quantum effect that destroys the phase coherence of any superposition state in the system randomizing the local excitation of a site; this is introduced to test

”how much quantum mechanical” the process is, in the sense that one expects an huge dephasing in classical contexts. However, the fact that this does not happen in FMO complexes and indeed, they have the ability to somewhat control it, suggest that this is a fundamental effect in understanding the efficiency of excitation transfer. The piece coming in the master equation is

$$\sum_j \gamma_j (-\{\sigma_j^+ \sigma_j^-, \rho\} + 2\sigma_j^+ \sigma_j^- \rho \sigma_j^+ \sigma_j^-) \quad (12)$$

and so the Lindblad operator is such that only locally there is dephasing, namely we do not consider spatial correlations.

Finally, one has to consider the decay to the sink; this can easily be carried considering the following equation

$$\rho_{sink}(t) \equiv \rho_{N+1N+1}(t) = 2\Gamma_{N+1} \int_0^t dt' \rho_{NN}(t') \quad (13)$$

so, in the end, all the excitation minus that lost in dissipation, is expected in the sink, no matter how long it takes.

Then, one has to solve the system of couple differential equations given by the master equation, provided the Hamiltonian and the Lindblad operators, and the sink equation (13), assuming, as initial condition, that all the excitation is initially at the site 1. Before solving it numerically, it could useful to analyze a case in which this system is analytically solved.

## 2.1 The uniform case

We have already said that the FMO complex is a fully connected network; in general we expect that not only the various sites have different local energies but we can argue that hopping rates are larger for closer sites, weaker for distant ones. However, to let the system of equations easier to solve analytically, we consider, at a first sight, the uniform case, namely we assume that every local energies are equal,  $\omega_j = \omega \quad \forall j$ , and also that every hopping rates are equal,  $\hbar v_{j,l} = J \quad \forall j \neq l$ . Moreover, we assume also the same dissipation rate and the same dephasing rate,  $\Gamma_i = \Gamma$  and  $\gamma_i = \gamma$ . In such conditions, it is simple to show that the master equation reduces to the following

$$\dot{\rho}_{ij} = -[2\Gamma + \Gamma_{N+1}(\delta_{iN} + \delta_{jN}) + 2\gamma - 2\gamma\delta_{ij}] \rho_{ij} + iJ \left( \sum_{l \neq j} \rho_{il} - \sum_{l \neq i} \rho_{lj} \right) \quad (14)$$

To this we have to add the equation for the population of the sink

$$\dot{\rho}_{sink}(t) = 2\Gamma_{N+1} \rho_{NN}(t) \quad (15)$$

and one could also quantify the population of the environment by considering

$$\dot{\rho}_{00}(t) = 2 \sum_{j=1}^N \Gamma_j \rho_{jj}(t) \quad (16)$$

Provided that the entire population is initially in the site 1, one could solve this system of equations numerically; however, if we want to extrapolate some analytical results, it is convenient to consider the so-called collective variables

$$\begin{aligned} R_i &= \sum_{j=1}^N \rho_{ij} \\ \Lambda &= \sum_{i=1}^N R_i = \sum_{i,j=1}^N \rho_{ij} \end{aligned} \quad (17)$$

Doing these substitutions, it is shown in the Appendix that our problem is reduced to solve the following system

$$\begin{aligned}
\dot{\Lambda} &= -2(\Gamma + \gamma)\Lambda - 2\Gamma_{N+1}X + 2\gamma(1 - \rho_{00} - \rho_{sink}) \\
\dot{X} &= -(2\Gamma + 2\gamma + \Gamma_{N+1})X + (2\gamma - \Gamma_{N+1})\rho_{NN} - JNY \\
\dot{Y} &= -(2\Gamma + 2\gamma + \Gamma_{N+1})Y + JNX - J\Lambda \\
\dot{\rho}_{NN} &= -2(\Gamma + \Gamma_{N+1})\rho_{NN} - 2JY \\
\dot{\rho}_{00} &= 2\gamma(1 - \rho_{00} - \rho_{sink}) \\
\dot{\rho}_{sink} &= 2\Gamma_{N+1}\rho_{NN}
\end{aligned} \tag{18}$$

where  $X = Re(R_N)$  and  $Y = Im(R_N)$ . The initial conditions are so

$$\begin{aligned}
\Lambda(0) &= 1 \\
X(0) &= 0 \\
Y(0) &= 0 \\
\rho_{NN}(0) &= 0 \\
\rho_{00}(0) &= 0 \\
\rho_{sink}(0) &= 0
\end{aligned} \tag{19}$$

In the mathematica notebook "Master equation in uniform case.nb" we have solved this system numerically which is surely simpler to write  $(N+1) \times (N+1)$  coupled equations (that's why one introduces collective variables). We can use this to compare to our attempt to obtain an analytical solution. The trick is considering Laplace transformation

$$\tilde{f}(s) = \int_0^\infty dt f(t) e^{-st} \tag{20}$$

because its derivative is

$$\tilde{\dot{f}}(s) = s\tilde{f}(s) - f(0) \tag{21}$$

Thus, doing so, the system (18) of differential equations is reduced to a system of algebraic equations as following

$$\begin{aligned}
(s + 2\Gamma + 2\gamma)\tilde{\Lambda} + 2\Gamma_{N+1}\tilde{X} + 2\gamma\tilde{\rho}_{00} + 2\gamma\tilde{\rho}_{sink} - 2\frac{\gamma}{s} - 1 &= 0 \\
(s + 2\Gamma + 2\gamma + \Gamma_{N+1})\tilde{X} + (\Gamma_{N+1} - 2\gamma)\tilde{\rho}_{NN} + JN\tilde{Y} &= 0 \\
(s + 2\Gamma + 2\gamma + \Gamma_{N+1})\tilde{Y} + J\tilde{\Lambda} - JN\tilde{X} &= 0 \\
(s + 2\Gamma + 2\Gamma_{N+1})\tilde{\rho}_{NN} + 2J\tilde{Y} &= 0 \\
(s + 2\Gamma)\tilde{\rho}_{00} + 2\Gamma\tilde{\rho}_{sink} - 2\frac{\Gamma}{s} &= 0 \\
s\tilde{\rho}_{sink} - 2\Gamma_{N+1}\tilde{\rho}_{NN} &= 0
\end{aligned} \tag{22}$$

The last equation can be easily solved so in the end one has a system of five equations in five unknown variables. The most accurate method to solve such a system is the Cramer method which is the best suitable for many variables and equations. Thus what one has, for each unknown variable, is the characteristic polynomial at the denominator which is a polynomial of the fifth order in the parameter  $s$ ; however, in the end, we obtain the Laplace transforms of our variables, so one has to anti-transform

$$f(t) = \int_0^\infty ds \tilde{f}(s) e^{st} \tag{23}$$

thus, for each solution, we have to perform a definite integral. This integral can be easily made by making use of the Residues but it reveals useful only if at the denominator we have well defined poles. In general, however, having a fifth order polynomial in  $s$ , because of the Abel-Ruffini theorem, there is no resolution formula for fifth order (or higher) polynomials, thus there is no warranty that we can find five roots and so five poles. In practice, even if we have bypassed the problem of finding solution

of a system of coupled differential equations with a simpler algebraic system of equations, in the end there is an integration to perform and there is no certainty that it will be feasible. At this point, gave up the possibility to obtain an analytical solution for our variables (specially  $\rho_{sink}$ ) at any time, it comes to help the final value theorem, which, at least, tell us the solution at very late times. Indeed, it states that

$$\lim_{t \rightarrow \infty} f(t) = \lim_{s \rightarrow 0} s \tilde{f}(s) \quad (24)$$

And so we can analyze, for instance, the population of the sink at late times, which is exactly one of the aspects in which we are interested.

Anyway, before consider this most general case, let us consider a sub-case in which we have an analytical solution (that is, the anti-transform is calculable) for all time.

### 2.1.1 No dissipation, no dephasing

In this sub-case, the only Lindblad operator, that is, the only connection to the environment is the decay to the sink, namely  $\Gamma = \gamma = 0$ . In such conditions, the algebraic system (22) is reduced to the following

$$\begin{aligned} s\tilde{\Lambda} + 2\Gamma_{N+1}\tilde{X} - 1 &= 0 \\ (s + \Gamma_{N+1})\tilde{X} + \Gamma_{N+1}\tilde{\rho}_{NN} + JN\tilde{Y} &= 0 \\ (s + \Gamma_{N+1})\tilde{Y} + J\tilde{\Lambda} - JN\tilde{X} &= 0 \\ (s + 2\Gamma_{N+1})\tilde{\rho}_{NN} + 2J\tilde{Y} &= 0 \\ s\tilde{\rho}_{00} &= 0 \\ s\tilde{\rho}_{sink} - 2\Gamma_{N+1}\tilde{\rho}_{NN} &= 0 \end{aligned} \quad (25)$$

Again, the last equation is simply solved by substitution and the penultimate equation is in agreement with the fact that, without dissipation, the environment will be never populated. Thus, here we are left with a system of only four equations and four unknowns, then when we calculate the anti-transform we always have poles because the characteristic polynomial will be of the fourth order, for which there exists a resolution formula. Being interested in  $\rho_{sink}$  and so in  $\rho_{NN}$  by the last equation, what one could find is

$$\tilde{\rho}_{NN}(s) = \frac{2J^2(s + \Gamma_{N+1})}{(s - s_1^+)(s - s_1^-)(s - s_2^+)(s - s_2^-)} \quad (26)$$

where  $s_1^+, s_1^-, s_2^+, s_2^-$  are the roots of

$$\Delta(s) = s(s + \Gamma_{N+1}) + J^2(Ns + 2\Gamma_{N+1})(Ns - 2\Gamma_{N+1} + 2N\Gamma_{N+1}) = 0$$

Then, one has to perform the anti-transform

$$\rho_{NN}(t) = \int_0^\infty ds \tilde{\rho}_{NN}(s) e^{st} \quad (27)$$

and finally use the (13). Instead of going through these details, we may be interested in the population of the sink at very late times; using the final value theorem, we obtain that

$$\lim_{t \rightarrow \infty} \rho_{NN}(t) = \lim_{s \rightarrow 0} s \tilde{\rho}_{NN}(s) \quad (28)$$

Performing this, one easily finds that

$$\rho_{sink}(\infty) = \frac{1}{N-1} \quad (29)$$

which becomes vanishing for large N. We can compare with "Master equation in uniform case.nb" setting vanishing dissipation and dephasing.

This is a very surprisingly result because, at least classically, one expects that random walking through the nodes, now matter how long it takes, but in the end all the population is expected in the sink, since there is no environmental dissipation and the sink attracts the excitation to itself.



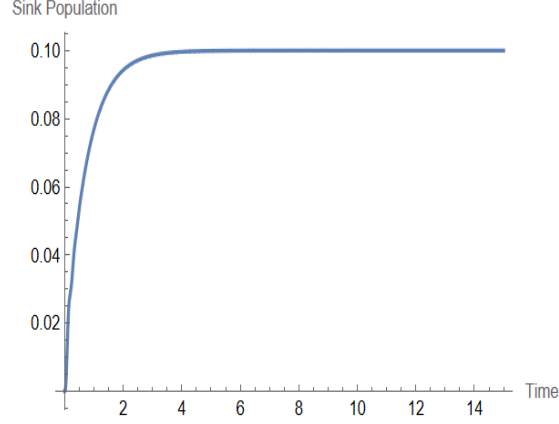


Figure 3: A network with  $N=11$  nodes (plus one node representing the sink) and no dissipation, no dephasing, in the uniform case; the other parameters are chosen randomly. We note that the population of the sink exhibits, in agreement, a plateau at late times at  $\frac{1}{11-1} = \frac{1}{10}$ .

The explanation to this strange phenomenon should belong to the quantum world; indeed, it could be possible that there is some sort of destructive interference between the sites which does not allow to the excitation to fully reach the  $N$ -th node, from which it transfers to the sink. A more realistic situation is that in which we allow the various sites to have different local energies, that is  $\omega_i \neq \omega \quad \forall i$ ; in this case, the master equation is a little modified, as we will see later, but repeating the same steps done before and considering again the case of no dissipation and no dephasing, one can show that [3]

$$\rho_{sink}(\infty) = \frac{1}{N - D - 1} \quad (30)$$

where  $D$  is the number of sites with different energies. We note that if all sites have different local energies, that is  $D = N - 2$ , then the population of the sink approaches unity. This is another contradictory fact because one would expect that disorder always inhibits transfer. However, and this is one of the main aspects of the present project, the quantum mechanics allows things like noise to enhance the transfer of the excitation.

### 2.1.2 Reintroducing dephasing and dissipation

Let us come back to the system of equations (22); we are interested in the sink population, whose, at least, the Laplacian transform is known and it can be shown to be

$$\tilde{\rho}_{sink}(s) = 4J^2\Gamma_{N+1} \frac{(s + \Gamma_a)(s + \Gamma_b)}{s\Delta(s)} \quad (31)$$

where

$$\begin{aligned} \Delta(s) = & (s + 2\Gamma)(s + \Gamma_a)(s + \Gamma_b)^2(s + \Gamma_c) + \\ & + 4J^2\Gamma_{N+1}(4\gamma(s + \gamma + 2\Gamma) - J^2\Gamma_{N+1}(s - 2\gamma + 2\Gamma)) + \\ & + 4J^2N(s + 2\Gamma)(\gamma(s + 2\Gamma_a) - \Gamma_{N+1}\gamma + \Gamma_{N+1}^2) + \\ & + J^2N^2(s + 2\Gamma)(s + \Gamma_a)(s + \Gamma_c) \end{aligned} \quad (32)$$

and

$$\begin{aligned} \Gamma_a &= 2\gamma + 2\Gamma \\ \Gamma_b &= 2\gamma + 2\Gamma + \Gamma_{N+1} \\ \Gamma_c &= 2\Gamma + 2\Gamma_{N+1} \end{aligned}$$

Not being  $\rho_{sink}$  available for all times, we make use of the final value theorem which tells us that

$$\rho_{sink}(\infty) = 4J^2\Gamma_{N+1} \frac{\Gamma_a\Gamma_b}{\Delta(0)} \quad (33)$$

These calculations have been performed using the software Maple and the results are shown in "Analytical sink solution at late times.mw". One can re-obtain the solution of lack of dissipation and dephasing from the previous formula. What we are interested for is what happens with dephasing; the dissipation, of course, will lower the value of the excitation that can reach the sink but let us assume that there is no dissipation and so there is pure dephasing. In the Maple script, is shown that

$$\rho_{sink}(\infty)|_{\Gamma=0} = \lim_{\Gamma \rightarrow 0} 4J^2\Gamma_{N+1} \frac{\Gamma_a\Gamma_b}{\Delta(0)} = 1 \quad (34)$$

so the population of the sink will carry all the excitation. This means that the pure dephasing acts as well as all sites energies are different and the destructive interference encountered in the case of no dephasing is here dammed by the effect of dephasing that allows to the various sites to change (uniformly) their phase. We can compare with the Mathematica solution; three different cases are shown:  $\frac{\gamma}{\Gamma_{N+1}} \ll 1$ ,  $\frac{\gamma}{\Gamma_{N+1}} \sim 1$  and  $\frac{\gamma}{\Gamma_{N+1}} \gg 1$ .

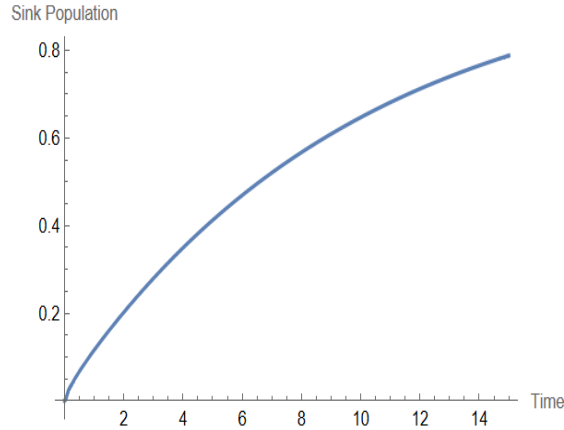


Figure 4: A network with  $N=11$  nodes (plus one node representing the sink) and no dissipation in the uniform case with  $\frac{\gamma}{\Gamma_{N+1}} \ll 1$ : it takes a bit of time to reach the plateau.

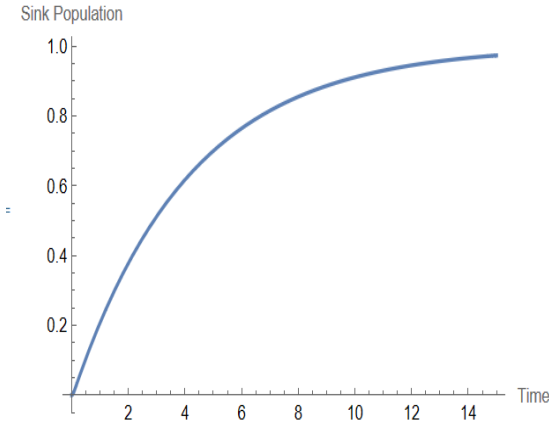


Figure 5: A network with  $N=11$  nodes (plus one node representing the sink) and no dissipation in the uniform case with  $\frac{\gamma}{\Gamma_{N+1}} \sim 1$ : it reaches the plateau in a reasonable amount of time.

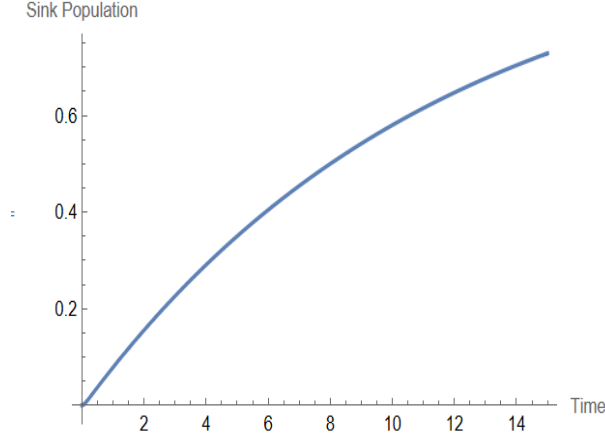


Figure 6: A network with  $N=11$  nodes (plus one node representing the sink) and no dissipation in the uniform case with  $\frac{\gamma}{\Gamma_{N+1}} \gg 1$ : it takes again a bit of time to reach the plateau.

What we see is that in all three cases, as expected, the unity population is reached but the time that they employ is different: in other words they reach the unity population at different speeds. The relative slow velocity of the first case is expected because it has to make contact with the case of no dephasing at all whereas the third case is more difficult to understand; it could be the result of the quantum Zeno effect, which occurs when numerous subsequent measurements are performed but maybe, and even simpler, they could be the result of the classical line broadening effect: indeed, an huge dephasing should be the signal of decoherence.

Finally, we can analyze the case of pure dissipation; one naturally expects that

$$\rho_{sink}(\infty)|_{\Gamma \neq 0, \gamma=0} < \rho_{sink}(\infty)|_{\Gamma=0, \gamma=0} = \frac{1}{N-1} \quad (35)$$

Indeed, using the Mathematica notebook, we confirm this expectation.

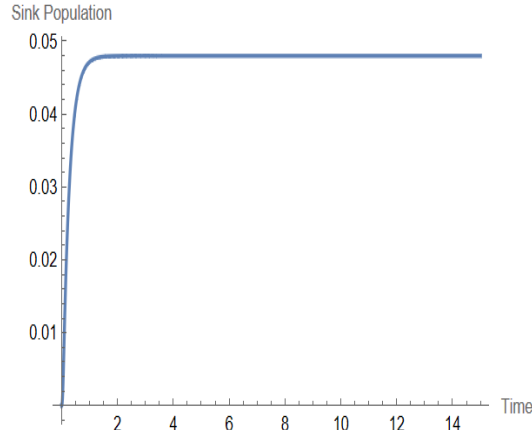


Figure 7: A network with  $N=11$  nodes (plus one node representing the sink) and no dephasing in the uniform case with  $\Gamma = 2$ : the plateau is located below  $\frac{1}{10}$ .

### 3 The FMO complex

Now, the whole discussion we have made for generic networks has to be applied to our practical example: the Fenna-Matthew-Olson complex. First of all, we have to understand how this pigment-protein can be modelled as a network; to this aim, what come to help are the observations and experimental results under the x-ray spectroscopy. What is found [4] is that the FMO complex has three identical units,

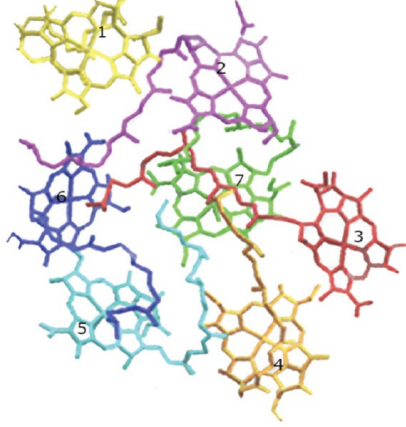


Figure 8: The FMO complex model

each of one are composed by seven chlorophylla molecules; thus, we can think at the FMO complex as a network of 7 nodes plus one, which is the reaction centre, for a total of 8 nodes [5]. Another experimental observation suggests that it is the site 3 to be linked to the reaction centre, which will have the role of the sink. Even the site energies and the coupling constants are measured [3] and they can be summarized in the following Hamiltonian [4]

$$H = \begin{pmatrix} 215 & -104.1 & 5.1 & -4.3 & 4.7 & -15.1 & -7.8 \\ -104.1 & 220.0 & 32.6 & 7.1 & 5.4 & 8.3 & 0.8 \\ 5.1 & 32.6 & 0.0 & -46.8 & 1.0 & -8.1 & 5.1 \\ -4.3 & 7.1 & -46.8 & 125.0 & -70.7 & -14.7 & -61.5 \\ 4.7 & 5.4 & 1.0 & -70.7 & 450.0 & 89.7 & -2.5 \\ -15.1 & 8.3 & -8.1 & -14.7 & 89.7 & 330.0 & 32.7 \\ -7.8 & 0.8 & 5.1 & -61.5 & -2.5 & 32.7 & 280.0 \end{pmatrix} \quad (36)$$

where all numbers are given in units of  $cm^{-1}$  and the zero energy is shifted for all sites by 12230. We have so different local site energies, as we see from the diagonal, and a little reminiscence of the fact that closer sites interact more than distant ones, as we can see moving away from the diagonal. Then, we are no longer in the uniform case; however, we assume that every sites have a similar dissipation rate, since the measured lifetime of an exciton is of the order of 1 ns and then, we assume  $2\Gamma_i = 2\Gamma = \frac{1}{188}cm^{-1} \quad \forall i$ . Finally, we choose (arbitrarily)  $\Gamma_{3,8} = \frac{62.8}{1.88}cm^{-1}$ . Thus, the system of equations we have to solve is most generally

$$\begin{aligned} \dot{\rho}_{ij} &= -i[H, \rho_{ij}] - [2\Gamma + \Gamma_{3,8}(\delta_{i3} + \delta_{j3}) + 2\gamma_i + 2\gamma_j - 2\gamma_i\delta_{ij}] \rho_{ij} \\ \dot{\rho}_{sink}(t) &= 2\Gamma_{3,8}\rho_{33}(t) \end{aligned} \quad (37)$$

In order to solve this system, we have used the Mathematica notebook "FMO complex.nb", where we used again a numerical differential solver algorithm; after inserting the parameters in unity of  $ps^{-1}$ , the 8x8 coupled differential equations are formalized in one simple equation, with the help of some auxiliary matrices which aim to represent exactly the system above (37). Indeed, it is as well as we have added a zero row and a zero column to our Hamiltonian in order to set  $\rho_{88}$  as our sink and other adjustments are made in order to match the formal expression (37) and the equation written in the Mathematica notebook. Finally, we have chosen some values for the  $\gamma_i$  (which, from an advanced study, revealed to be the optimal ones) and, again, we have set the initial conditions such that, initially,

the whole excitation is carried by the first site.  
Three different cases are shown in the notebook:

1. The noiseless case: assuming that there is no dissipation and no dephasing but only von Neumann plus decay to the sink, we observe that, after a rapid increase, the population of the sink slows down and reaches a plateau (in the notebook we have calculated also the sink population after 10 ps, resulting about 61.08 %) and this is the result of the destructive interference that we have faced in the generic N nodes network case. This can also be explained noting the large difference between the site 3, which is linked to the sink and sites 1 and 2, from the energetic point of view: this causes the fact that the transfer to the site 3 is not efficient.
2. Only dissipation case: given the relative small value of the dissipation rate, there is not much difference with the previous case but only a little slowing down, as expected, of the sink population (after 10 ps it results about 60.88 %).
3. General case with dephasing: with dephasing, we assist to the desirable effect of enhance of the excitation transfer; playing with the parameters  $\gamma_i$  one can observe the same behaviour analyzed in the previous section, that is for small and large values one has not too much enhancing but one can optimize this and finding some values, like those in the notebook, that enhance the excitation transfer to about 91.74 % after 10 ps.

These three cases are clearly shown in the figures.

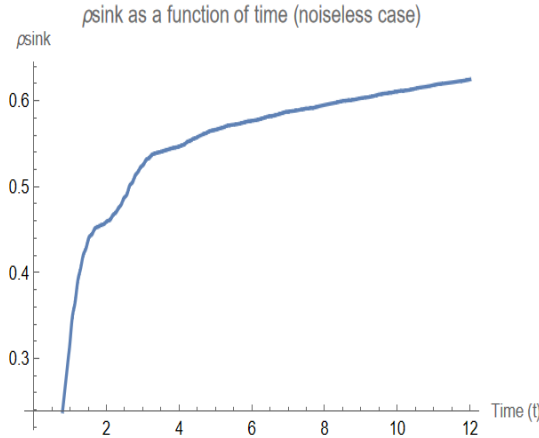


Figure 9: The sink population in the noiseless case: the coherent dynamics and the destructive interference hinder the excitation transfer to site 3 and then, to the sink.

Thus, the experimental fact that FMO complexes have a very highly efficient excitation transfer can be explained in terms of the ability that such structures have to control the dephasing. Then and surprisingly, not only the noise assist this transfer (which, at least classically, may seem counterintuitive) but, moreover, the dephasing noise is in some way controlled in order to enhance, as much as possible, the excitation transfer, "selecting values" of optimal dephasing which are neither "too small" or "too large". This ability translates in an highly efficient photosynthesis: since the most of the received energy reaches the reaction centre (sink), there is very good ratio of the energy transformed (in oxygen and sugars, sources of livelihood for these bacteria and plants) and the received energy. However, still much has to be done in order to understand this mechanism, even because the efficiency of these complexes is shown to be even larger than what is calculated in the present project; indeed, of course our approach has several limits and here we want to subline only two of them. The first is the form we gave to the Lindblad operator associated to the dephasing which was, in some sense, too ideal; in fact, the small size of the complex compared to the correlation length of the bath and the fact that the time scales of the interactions are of the same order of the bath correlation time suggest that there is a spatial correlation in the noise. In practice, this translates in the need of substituting the Lindblad operator given for the dephasing (12) with the following little more involved

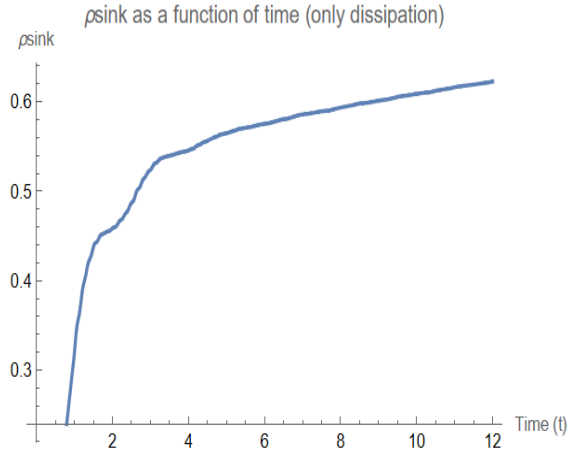


Figure 10: The sink population with dissipation: there is not much difference with the previous case, due to the value of  $\Gamma$ ; if one enlarges this value, the plateau would be suppressed.

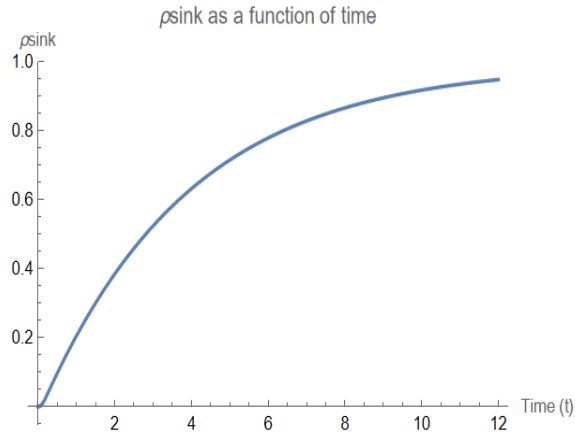


Figure 11: The sink population in the general case: the dephasing allows an enhance of the excitation transfer.

one

$$\sum_{jl} \gamma_{jl} (-\sigma_j^+ \sigma_j^- \sigma_l^+ \sigma_l^- \rho - \rho \sigma_l^+ \sigma_l^- \rho \sigma_j^+ \sigma_j^- + \sigma_j^+ \sigma_j^- \rho \sigma_l^+ \sigma_l^- + \sigma_l^+ \sigma_l^- \rho \sigma_j^+ \sigma_j^-) \quad (38)$$

One can show that, with this new operator, we assist to a further enhance of the excitation transfer, once found the optimal dephasing rate values.

The second relevant problem with our approach is surely the very beginning hypothesis of Markovian evolution: indeed, in practice, there could be some non-Markovian effects and, in order to take into account them, one has to consider the details of the environment.

Despite of these limits, however, we hope that, at least, the main idea of how the FMO complexes can enhance the excitation transfer is outlined: they, without all previous expectations, make use of quantum mechanics and, more precisely, of the mechanism of the optimization of dephasing to reach the most efficient energy transfer.

## Conclusions

We are still far away from a complete understanding of how life works and how it is possible that macro-molecules as proteins, like the FMO complex, which moreover act in hot and noisy environments, make advantage of quantum mechanics and indeed, they even enhance their efficiency by controlling the noise. What is more surprising is that such a mechanism of optimization of the dephasing has been naturally developed by green sulfur bacteria as well as plants by natural selection, probably as the outcome of many and subsequent mutations. By using a very simple network model and describing the dynamics with a Markovian master equation, we have seen how the noise is a fundamental element to enhance the excitation transfer; even though this approach has its own limits (non Markovian effects, form of Lindblad operators), it allows us to perceive a sense of what maybe it happens in the pigment-proteins which lead to the photosynthesis. Going forward, we hope that in future we have a better understanding of this mechanism and specially how FMO complexes effectively select the best dephasing rates (there are already a plethora of new outcomes, as outlined in [6,7,8]); moreover, beyond this fundamental prospect, studying the quantum mechanically properties of the photosynthesis could be very useful in technology, where an enhance of the efficiency in solar panels is a welcome thing, since, at the time of writing, the most efficient ones do not overcome the 50 %.

Thus, quantum biology, this area of study born with Schrödinger and which has obtained some prominence only in the last decade, could be a revolution if some steps forward will be made, supported by experimental observations [9], not only for understanding of the underling mechanism of the nature but also for eventual applications to technology. Indeed, there is much that we can still learn from Nature about the Nature itself and ourselves.



## Appendix

It is came the time to show how we obtain the (18) with the help of the collective variables (17). The equations of motion are

$$\begin{aligned}\dot{\rho}_{ij} &= -[2\Gamma + \Gamma_{N+1} (\delta_{iN} + \delta_{jN}) + 2\gamma - 2\gamma\delta_{ij}] \rho_{ij} + iJ \left( \sum_{l \neq j} \rho_{il} - \sum_{l \neq i} \rho_{lj} \right) \\ \dot{\rho}_{00}(t) &= 2 \sum_{j=1}^N \Gamma_j \rho_{jj}(t)\end{aligned}\tag{39}$$

Substituting the collective variables, we can reexpress these as

$$\begin{aligned}\dot{\rho}_{ii} &= -2\Gamma \rho_{ii} + iJ (R_i - \bar{R}_i), \quad i \neq N \\ \dot{\rho}_{ij} &= -2(\Gamma + \gamma) \rho_{ij} + iJ (R_i - \bar{R}_j), \quad i \neq N, j \neq N \\ \dot{\rho}_{iN} &= -(2\Gamma + 2\gamma + \Gamma_{N+1}) \rho_{iN} + iJ (R_i - \bar{R}_N) \\ \dot{\rho}_{NN} &= -2(\Gamma_{N+1} + \Gamma) \rho_{NN} + iJ (R_N - \bar{R}_N) \\ \dot{\rho}_{00} &= 2\Gamma \text{Tr} \rho\end{aligned}\tag{40}$$

where  $\bar{R}_i$  is the complex conjugate of  $R_i$ . Moreover, we have

$$\begin{aligned}\dot{R}_i &= -iJ\Lambda + iJNR_i - 2(\Gamma + \gamma) R_i - \Gamma_{N+1}\rho_{iN} + 2\gamma\rho_{ii} \\ \dot{R}_N &= -iJ\Lambda + iJNR_N - (2\Gamma + 2\gamma + \Gamma_{N+1}) R_N + (2\Gamma - \Gamma_{N+1}) \rho_{NN} \\ \dot{\Lambda} &= -2(\Gamma + \gamma) \Lambda - \Gamma_{N+1} (R_N + \bar{R}_N) + 2\gamma \text{Tr} \rho\end{aligned}\tag{41}$$

Since there is just a single excitation

$$1 = \text{Tr} \rho + \rho_{00} + \rho_{\text{sink}}\tag{42}$$

Finally, considering that the  $R_i$  variables are complex and  $\Lambda$  is real, we can write

$$R_N = X + iY\tag{43}$$

Then, in the end, we obtain the closed system of coupled differential equations (18)

$$\begin{aligned}\dot{\Lambda} &= -2(\Gamma + \gamma) \Lambda - 2\Gamma_{N+1}X + 2\gamma(1 - \rho_{00} - \rho_{\text{sink}}) \\ \dot{X} &= -(2\Gamma + 2\gamma + \Gamma_{N+1}) X + (2\gamma - \Gamma_{N+1}) \rho_{NN} - JNY \\ \dot{Y} &= -(2\Gamma + 2\gamma + \Gamma_{N+1}) Y + JNX - J\Lambda \\ \dot{\rho}_{NN} &= -2(\Gamma + \Gamma_{N+1}) \rho_{NN} - 2JY \\ \dot{\rho}_{00} &= 2\gamma(1 - \rho_{00} - \rho_{\text{sink}}) \\ \dot{\rho}_{\text{sink}} &= 2\Gamma_{N+1}\rho_{NN}\end{aligned}\tag{44}$$

## References

- [1] D. Manzano (2020), *A short introduction to the Lindblad Master Equation*, arXiv:1906.04478v3 [quant-ph].
- [2] M. A. Nielsen, I. L. Chuang (2010), *Quantum Computation and Quantum Information*, Cambridge University Press, 10th Anniversary Ed.
- [3] F. Caruso, A. W. Chin, A. Datta, S. F. Huelga, M. B. Plenio (2009), *Highly efficient energy excitation transfer in light-harvesting complexes: The fundamental role of noise-assisted transport*, arXiv:0901.4454v2 [quant-ph].
- [4] J. Adolphs and T. Renger, *How Proteins Trigger Excitation Energy Transfer in the FMO Complex of Green Sulfur Bacteria*, Biophysical Journal, Volume 91, October 2006, pages 2778–2797.
- [5] M. B. Plenio, S. F. Huelga (2008), *Dephasing assisted transport: Quantum networks and biomolecules*, arXiv:0807.4902v1 [quant-ph].
- [6] S. Lloyd, M. Mohseni, A. Shabani, H. Rabitz (2011), *The quantum Goldilocks effect: on the convergence of timescales in quantum transport*, arXiv:1111.4982v1 [quant-ph].
- [7] E. J. O'Reilly, A. Olaya-Castro (2014), *Non-classicality of the molecular vibrations assisting exciton energy transfer at room temperature*, DOI: 10.1038/ncomms4012.
- [8] M. O. Scully, K. R. Chapin, K. E. Dorfmana, M. B. Kimb, and A. Svidzinskya (2011), *Quantum heat engine power can be increased by noise-induced coherence*, [www.pnas.org/cgi/doi/10.1073/pnas.1110234108](http://www.pnas.org/cgi/doi/10.1073/pnas.1110234108).
- [9] M. Ferretti, A. Pandit, E. Romero, D. Zigmantas (2014), *The nature of coherences in the B820 bacteriochlorophyll dimer revealed by two-dimensional electronic spectroscopy*, DOI: 10.1039/c3cp54634a.