Quantum Entanglement in Fenna–Matthews–Olson Photosynthetic Light–Harvesting complexes: A Short Review of Analysis Methods

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Abstract. The Fenna-Matthews-Olson light-harvesting complexes have become a center of attention due to their high excitation energy transfer efficiency, which may surpass 98%. Experimental results reveal the presence of quantum entanglement in the protein structure, which seems to be associated to such a remarkably high efficiency. Notably, Redfield and Lindblad master equations have been already used to model the chromophore excitation in the protein complex as well as its interactions with the environment. The entanglement arising during the process has been quantified through several measures. This work provides a short review of methods used to model the above described system. It is also discussed the introduction of two nonconventional measures addressed to quantify the emergent entanglement.

1. Introduction

Light harvesting is a fundamental step in the process of photosynthesis. There, light-harvesting complexes (LHCs) rapidly transfer quantum excitation by directing it towards a reaction center (via dipole-dipole interactions of the constituents –chlorophylls–), where charge separation fuels the electron transport chain, oxidizing water, reducing NADP\(^+\) and catalyzing the synthesis of ATP [1]. The FMO complex is a homotrimer (Figure 1A) in which the monomers (Figure 1B) are bind to either seven or eight bacteriochlorophyll \(a\) molecules (BChl \(a\)) [3], Figures 1C and 1D, respectively. The related high light-harvesting efficiency is typically of 98% [4], which makes the modeling and study of such system a subject of interest in quantum theory and energetics. The transfer energy observed in the FMO–LHCs indicates that populations and coherences are strongly coupled and exhibit long–live oscillations even at room-temperature [4].

The study of the coupled quantum dissipative dynamics associated to the coherences and populations of the FMO–LHCs resulted in a variety of approaches addressed to get acceptable solutions. Despite non-Markovian and exact methods are required for the complete understanding of the coherence properties, Markovian approaches like those associated to the Redfield and Lindblad master equations provide good approximations [5]. Nevertheless, the Redfield equation may not describe completely the oscillatory profile of the populations and the long-live character of the coherences, which out of equilibrium could give rise to non-physical density matrices [4]. In contrast, the Lindblad equation guarantees physically acceptable density matrices due to its close relationship with the stochastic Schrödinger equation (a quantum mechanical analog of Langevin equations) [4].
The present work is addressed to revisit the methods used to model quantum effects in the Fenna-Matthews-Olson (FMO) complex, which is a pigment-protein LHC in green sulfur bacterium known by the persistence of its electronic excitation coherence within a thermal environment, and can be studied as an open quantum system characterized by either static or dynamic disorder [2]. We compare different non-Markovian approaches which are popular to model the quantum dynamics of the BChl molecules. In particular, to simplify and quantify some useful measures of quantum entanglement, we pay attention to the case of a single dimer \( (N = 2) \) in further discussion when it applies, otherwise \( N = 7, 8 \), which illustrates the interaction of two chromophores [4].

In Section 2 we revisit the application of the above mentioned quantum master equations to model light-harvesting complexes. Section 3 discussed some of the measures preferred to quantify the entanglement evolution in LHCs. It is also used the Rényi entropy as a global entropy measure [8] for comparison. Section 4 uses the method reported in [4] to define the parameters of the Lindblad equation, via the Redfield equation, which are completed by the thermal equilibrium restrictions. The analysis of entanglement measures is discussed in the same section. Some conclusions and directions for future research are given in Section 5.

2. Master equations in the modeling quantum dynamics of FMO LHC’s

The quantum dynamics model is represented barely by the Hamiltonian

\[
H = H_s + H_e + H_{s−e},
\]

where \( s \) and \( e \) refer to the system and environment respectively. Thus, \( H_s \) describes mainly the dipole-dipole interactions among BChls and \( H_{s−e} \) the interaction between them and the protein environment (the complementary FMO structure).

It has been reported by spectroscopy studies that among pigment molecules (BChls chromophores) contained in FMO LHC’s, only a single BChl will be excited at a given time [3]. Those single-occupation states (the site-occupation basis) are represented as \(|k\rangle = |000...0\rangle\) in terms of the two-level chromophore states. This representation is also present in the Frenkel exciton model [9]. The \( H_s \) Hamiltonian term then reads

\[
H_s = \sum_{i=1}^{N} \epsilon_i |i\rangle \langle i| + \sum_{1\leq i,j \leq N} J_{ij} (|i\rangle \langle j| + |j\rangle \langle i|).
\]

(1)

Thus including terms for the energy of each excited chromophore \( \epsilon_i \) and their couplings \( J_{ij} \). \( H_{s−e} \) interaction between the system and the bath (environment) is commonly simplified and
represented as an excitonic linear response in terms of bath-modes couplings $Q_i$ with the site-occupation modes [3]:

$$H_{s-e} = \sum_{i=1}^{N} |i\rangle \langle i| \otimes Q_i.$$  

(2)

The environment is then normally assumed as a continuum thermal bath with Markovian properties. Quantum Master Equations (QME’s) differ from conventional quantum equations by considering the time evolution for the density matrix $\rho_s$ of the main system under analysis (a quantum open system) together with that of the external medium $\rho_e$. Thus, open systems master equations normally split $\rho_s$ from the bath evolution $\rho_e$ by tracing out the entire state $\rho_{s-e}$: $\rho_s = \text{Tr}_e \rho_{s-e}$.

In any case, diagonal elements of $\rho_s$ (populations) are expected to become stabilized in the equilibrium as function of the temperature, while, the off-diagonal elements (coherences) should naturally go to zero, showing that the system approaches from a maximum level of entanglement towards a thermal equilibrium resulting in a mixed-separable state of statistical species. The Redfield and Lindblad master equations are, in a first glance, good approximations helping to understand the dynamics of the system. In the following, we simplify $\rho_s$ as $\rho$ and we assume $N$ as its dimension (the number of BCHls involved in the analysis).

2.1. Redfield’s master equation

Redfield’s master equation [10] uses the density matrix formalism and it goes further than previous transition probability theories by considering the rate of change of the off-diagonal elements of the density matrix, no longer assuming that these elements are zero. This approach is very useful for representing open systems, assuming that the environment and the system being studied are two interacting subsystems, $A$ and $B$, as a part of a larger system $A + B$. Redfield’s equation describes the interaction between both subsystems, a relatively simple one (the excitation energy transfer inside a protein) and a more complex one (a thermal bath or the surroundings of a photosynthetic protein) [10]. The equation currently is written as

$$\dot{\rho} = -\frac{i}{\hbar} [H, \rho] - \frac{1}{\hbar^2} \sum_{m} [S_m, \Lambda_m \rho - \rho \Lambda_m^\dagger] \rightarrow \dot{\bar{\rho}} = -\frac{i}{\hbar} \text{Diag}(\epsilon_i - \epsilon_j) \bar{\rho} - \kappa^{(R)} \bar{\rho},$$  

(3)

where $S_m, \Lambda_m$ are operators physically describing the coupling with the environment. For FMO BCHls, they can be obtained from the spectroscopy [14]. In addition, for the sake of computer efficiency, these differential equations normally are translated into the superoperator-supervector version (SO-SV) by using the rule

$$(A \rho B)_{ij} = \sum_{k,l} A_{ik} \rho_{kl} B_{lj} = \sum_{k,l} (A \otimes B^T)_{ij,kl} \rho_{kl},$$  

(4)

which transforms a matrix product in the product of a super-operator $A \otimes B^T$ with a super-vector $\rho$ using double indices as components. Then, in order to skip $\rho$ trapped between some operators at the end in (3) by expressing each component of $\dot{\rho}$ as the product of a superoperator with a supervector. Thus, $\bar{\rho} = (\rho_{11}, \rho_{12}, ... , \rho_{1N}, \rho_{21}, ... , \rho_{2N}, ... , \rho_{NN})$ is the density matrix expressed as a supervector, while $\kappa = (\kappa_{ij,kl})$ is a superoperator doubling in size to $S_m, \Lambda_m$, an $N^2 \times N^2$ matrix. Thus, for (3), the equation on the right side is the SO-SV version of Lindblad equation, with

$$\kappa^{(R)}_{ij,kl} = \frac{1}{\hbar^2} \sum_m \left( \sum_s (S_{ms} \Lambda_{mk} \delta_{lj} + \delta_{ik} S_{mj} \Lambda_{ms}^* - (\Lambda_{mk} S_{mj} + S_{mj} \Lambda_{ms}^*)) \right).$$  

(5)

As the latter is expressed in the basis of $H_s$, the first term adopts its diagonal form.
2.2. Lindblad’s master equation

Lindblad’s master equation [11] is useful when interactions are derived from the explicit form in terms of the generators of a dynamical semigroup. Lindblad’s equation shows certain advantages over Redfield one by introducing two restrictions: a) to assume the semigroup is norm continuous, and b) it is completely positive. It could be expressed as

$$\dot{\rho} = -\frac{i}{\hbar}[H, \rho] - \frac{1}{\hbar^2} \sum_{\alpha} \left( V_{\alpha} \rho V_{\alpha}^\dagger - \frac{1}{2} \{ \rho, V_{\alpha}^\dagger V_{\alpha} \} \right) \rightarrow \dot{\vec{\rho}} = -\frac{i}{\hbar} \text{Diag}(\epsilon_i - \epsilon_j) \vec{\rho} - \kappa^{(L)} \vec{\rho},$$  \hspace{1cm} (6)

where $V_{\alpha}$ is an orthonormal basis of $N^2$ matrices. It is as well derived as the partial trace on the states of the bath and the Markovian assumption for the evolution [11]. Nonetheless, interactions are represented in terms of a canonical basis for the operators, then the relation of $V_{\alpha}$ with the physical arrangement is not always direct (despite, for FMO BChls, some authors have proposed interaction terms directly based on the Lindblad operators $V_{\alpha}$ [12]). As before, after application of (4), we get the SO-SV version on the right side written in the basis of $H_s$, with

$$\kappa_{ij,kl}^{(S)} = \frac{1}{\hbar^2} \sum_{\alpha} \left( V_{\alpha i k} V_{\alpha j l}^* - \frac{1}{2} \sum_s \left( \delta_{ik} V_{\alpha s j}^* V_{\alpha s i} + \delta_{jl} V_{\alpha s k}^* V_{\alpha s i} \right) \right).$$  \hspace{1cm} (7)

2.3. Master equations under the secular approximation

Solution of equations (3) and (6) in their SO-SV version are well known for the linear differential equations systems. Despite, their analytical approach can be difficult because the complex conformation of matrices $\kappa^{(R)}$ and $\kappa^{(L)}$. In an approximated solution, secular approximation is a handmade correction often justified via a weak-coupling (Born-Markov) approximation [13], where the system coherences and populations are uncoupled ensuring there are only population-population and coherence-coherence interactions. The secular condition is then stated as

$$\kappa_{ij,kl}^{(S)} = \left( \delta_{ij} \delta_{kl} + \delta_{ik} \delta_{jl} (1 - \delta_{ij} \delta_{kl}) \right) \kappa_{ij,kl},$$  \hspace{1cm} (8)

where $\kappa$ is the Redfield or Lindblad superoperator on which approximation is applied. This approach guarantee physically acceptable time evolution results. Clearly, in the SO-SV version it reads

$$\vec{\dot{\rho}} = -\frac{i}{\hbar} \text{Diag}(\epsilon_i - \epsilon_j) \vec{\rho} - \kappa^{(S)} \vec{\rho}.$$  \hspace{1cm} (9)

2.4. Conditions in the thermal equilibrium

Master equations involve parameters and models which not always assure the thermal equilibrium with the environment at $t \rightarrow \infty$. Such conditions attain to the equilibrium of populations

$$\lim_{t \rightarrow \infty} \rho_{ii} = \rho_{i\text{eq}} = \frac{e^{-\beta \epsilon_i}}{\sum_{j=1}^{N} e^{-\beta \epsilon_j}},$$  \hspace{1cm} (10)

with $\beta = (kT)^{-1}$ ($T$ is the equilibrium temperature and $k$ is the Boltzmann constant). It implies there exists a supervector $\vec{\rho}_{ij} = \delta_{ij} e^{-\beta \epsilon_i}$, which is an eigenvector of $\kappa$

$$\sum_{k=1}^{N} \kappa_{ij,kl} e^{-\beta \epsilon_k} = 0$$  \hspace{1cm} (11)

The above formalism is general for non-Markovian QME applicable to the analysis of FMO BChls. Despite complete analysis involving the seven BChls have been performed [3], we adopt a
dimer approach in order to analyse the entanglement behavior between a couple of BChls. In [4], the Lindblad equation for a dimer (the located interaction between two BChls) was reproduced getting some free parameters from the Redfield equation including physical terms reported in literature [14] together with mandatory conditions in the equilibrium. This approach is adopted in the Section 4 to reach our entanglement analysis.

3. Alternative entanglement measures and the Rényi Entropy

As it is well known, given a system $S$ with two subsystems $A$ and $B$, which are entangled complements of each other being picked from the full system ($S = A + B$). If $B$ is traced from $\rho$ as $\rho_A = \text{Tr}_B \rho$, then when $\rho$ is a pure state, the entanglement is normally measured by the von Neumann entropy

$$S_A = -\text{Tr}(\rho_A \ln \rho_A),$$

which depicts the mutual entanglement between those parts. In [3], the concurrence is directly assumed as the typical concurrence for two system (obtained by tracing the other $N - 2$ BChls):

$$C_{\text{Sarovar}} = 4|\rho_{12}|^2$$

(here, we consider the monotone obtained squaring the quantity considered there), which is obtained for a two-part system [15].

Nevertheless, by following the previous definition on our LHC with $N$ chromophores: $\rho = \sum_{i,j=1}^{N} \rho_{ij} |i\rangle \langle j|$ in the site-occupation basis, then isolating the system $A$ containing the single chromophore $k$ ($B = S \setminus A$), it is possible to show

$$\rho_A = \text{Tr}_B \rho = (1 - \rho_{kk})|0_k\rangle \langle 0_k| + \rho_k|1_k\rangle \langle 1_k| \rightarrow C_{\text{VN}} = 4\rho_{kk}(1 - \rho_{kk}),$$

which is associated to the von Neumann entropy between two subsystems. $C_{\text{VN}} = C_{\text{Sarovar}}$ only if the state is pure, which is normally not the case. Alternatively, an imperfect measure of global entanglement is the Rényi entropy of order $\alpha$, which has further importance since it can construct the whole entanglement spectrum of $\rho_S$

$$S_\alpha^2(\rho) = \frac{1}{1 - \alpha} \ln \text{Tr} \rho^{\alpha}_S, \quad \alpha > 0.$$  

At the limit $\alpha \rightarrow 1$ one has $S_1^2(\rho) = S_{\text{VN}}(\rho)$. Thus, we will use the alternative quantity $S_2^2(\rho)$ ($\alpha = 2$) to explore alternatively the entropy in simple models for the chromophores entanglement in LHC’s. In the entanglement analysis in this work, we will compare these entanglement measures ($C_{\text{Sarovar}}, C_{\text{VN}}$ and $S_2^2(\rho)$) under the light-harvesting process for a couple of BChls in the approach given by [4]. Such measurement should have a common point of comparison during the quantum excitation transference among the LHC BChls.

4. Quantum entanglement evolution in a dimer through several measures

In the current work we analyze the behavior of entanglement of chromophores illustrated through a simple dimer model following the approach of [4] to compare Redfield and Lindblad approaches together combined with the entanglement measures previously presented and referred to the related works of FMO LHC’s [3, 5, 16].
Figure 2. Entanglement evolution of a dimer during its relaxation measured through $C_{Sarovar}$, $C_{VN}$ and $S_2^R(\rho)$. On the left, using Redfield approach and on the right using Lindblad’s one. Rényi entropy, $S_2^R(\rho)$, is reported in color in agreement with the color bar besides.
The superoperators $\kappa^{(R)}$ have been reproduced from [4] ranging temperatures from 77$^\circ$K to 347$^\circ$K for two different values of coupling strengths between the system and the bath: $\lambda_a = 35$cm$^{-1}$ and $\lambda_b = 65$cm$^{-1}$. They are two cases widely discussed in the literature due to their experimental centrality (Figure 2). By following the procedure stated in [4], $\kappa^{(L)}$ is obtained for the same set of parameters than $\kappa^{(R)}$ by imposing the thermal equilibrium conditions (10) together with the adjusted $\kappa^{(R)}$ and some assumptions about the fulfilling of maximal correlations among $\sum_\alpha V_{\alpha ij}$. Despite $\kappa^{(S)}$ can be then obtained from such two approaches by imposing (8), we do not analyse this simpler approach.

The $H_s$ considered in [4] corresponds to a couple of BHCls:

$$H_s = \begin{pmatrix} 0 & -71.3 \\ -71.3 & 46.4 \end{pmatrix},$$

which is given in cm$^{-1}$, as it is common in spectroscopy (multiplying by the factor $200\pi c$, with $c$ the velocity of the light, it could be transformed in s$^{-1}$, the natural units for $\hbar^{-1} H_s$ and $\dot{\rho}$). By diagonalizing, we get $\epsilon_1 = -58.1$cm$^{-1}$, $\epsilon_2 = 98.2$cm$^{-1}$. QME in the form of SO-SV let to calculate the evolution of $\dot{\rho} = (\rho_{11}, \rho_{12}, \rho_{21}, \rho_{22})$. In our analysis, the system is initialized in the higher energy level for the dimer as in [3]: $\rho = (0, 0, 0, 1)$, instead as in [4] (note, $\epsilon_1 < \epsilon_2$), thus representing a relaxation of the system (operating during a relaxation time around of 0.5 ps).

The numerical results presented in this article to obtain $\kappa^{(L)}$ from the thermal equilibrium conditions and the comparison with $\kappa^{(R)}$ uses the values for the Redfield relaxation superoperators corresponding to the Hamiltonian and the entanglement measures given by [4]. The results are synthetically presented in Figure 2 reporting the concurrences $C_{Sarovar}$ and $C_{VN}$ in a phase diagram in the first 0.5ps of evolution. Additionally, the Rényi entropy $S^{2}_R(\rho)$ is represented as the curve color through the evolution (besides, color bar reports its values). Each plot shows the Redfield approach on the left and Lindblad one on the right (secular approach is not further discussed since its limited results provide no information of interest) for several temperatures of operation 77, 131, 185, 239, 293, 347$^\circ$K and the two coupling strengths reported before.

The phase plots in Figure 2 shows the entanglement evolution in the relaxation process through comparable entanglement measures. Some main aspects can be pointed out there. While $C_{Sarovar}$ and $C_{VN}$ are physically limited to [0, 1], the first aspect, also reported in [4], is about the divergence from the physical restrictions of $\rho$ in the Redfield’s approach (plots d-l, where $C_{Sarovar}$ diverges). Meanwhile, Lindblad’s approach maintains the correct values for both concurrences together with the oscillations for large T-values noted by [4] in such model, thus reproducing the oscillatory behavior for the excitation transference. Another aspect to be observed around of entanglement measures is the sudden entanglement peak reported by [3], which is advisable in all convergent models for $C_{Sarovar}$ as well as for $C_{VN}$. Note when $C_{Sarovar}$ converges to zero because coherences become extinct as the system approaches to the equilibrium, $C_{VN}$ converges to a finite value depending from the populations in the thermal equilibrium, then on the temperature and the energy spectrum. While, $S^{2}_R(\rho)$ exhibits certain delay to reach maximum values. In any case, plots provide characteristic information about the behavior of dimer, particularly that related with their inner correlations.

5. Conclusions and future work

The modeling of FMO LHC’s interactions represents in general a problem of interest in the understanding of EET dynamics under a practical scope. The use of Redfield and Lindblad quantum master equations, despite their particular limitations can provide information about which is happening in the complex in terms of quantum biological effects. Rényi entropy and concurrences reproduces a sudden increase of entanglement in the system during short intervals of time lasting only few picoseconds under its relaxation.
Although superficially mentioned in many other references [3–5], the accurate description of the quantum dynamics for a system of an increasing number of chromophores is still an open problem because the precise values and models involved remain unknown. The correct modeling of this behavior might prove to be useful for the design and characterization of modified versions of this protein with a larger light-absorbance spectrum, particularly those based on non-Markovian approaches (as the Hierarchical Equations of Motion, HEOM). Further experimental results have been reported evaluating the ability of these protein structures to perform EET under varied conditions, both systemic and environmental [14,16]. It has inspired future studies to include the possibility of structural mutations in the protein with biogenesis methodologies [1,16] which should be first modeled by more effective approaches.

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