Quantum nonlocality in the excitation energy transfer in the Fenna-Matthews-Olson complex

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Pigment protein complexes involved in photosynthesis are remarkably efficient in transferring excitation energy from light harvesting antenna molecules to a reaction centre, where it is converted to and stored as chemical energy. Recent experimental and theoretical studies suggest that quantum coherence and correlations may play a role in this excitation energy transfer (EET). We examine whether bipartite quantum nonlocality, a property that verifies a strong correlation between two quantum systems, exists between different pairs of chromophores in the Fenna-Matthews-Olson (FMO) complex and how this is related to the amount of bipartite entanglement. In particular, it is tested in what way these correlation properties are affected by different initial conditions. When modeling the EET in the FMO complex with the hierarchically coupled equations of motions, it is found that bipartite nonlocality indeed exists for some pairs of chromophores. It seems like the choice of initial condition strongly affects whether nonlocality is found or not. It is also seen that nonlocality and entanglement are two different properties in this system. In particular, nonlocality only exists on a very short timescale and then drops to zero in a very abrupt manner; a feature we choose to call nonlocality sudden death. Quantum entanglement between chromophore pairs, on the other hand, is oscillating and exponentially decaying and follow thereby a pattern more similar to the chromophore population dynamics.

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I. INTRODUCTION

In recent years, there has been an increasing interest in studying biological systems in terms of the existence of nontrivial quantum effects to improve biological functions. Especially the excitation energy transfer (EET) in photosynthetic complexes has been heavily studied since quantum coherence between excited states in the Fenna-Matthews-Olson (FMO) complex was experimentally verified by two dimensional electronic spectroscopy (2DES). Not only was the existence of coherent pathways in the FMO complex revealed, quantum coherence was also shown to last much longer than expected for such large and noisy systems, and a hypothesis is that this may play a role in the known very efficient EET in photosynthetic complexes. Since then, several attempts to explain why photosynthetic complexes could benefit from coherent EET have been made. One such is that the quantum coherence could help to direct the energy flow towards the reaction centre in a unidirectional manner. This would prevent the energy dissipation that follows from a semi-classical state-to-state transfer, i.e., when only one state is occupied at the time.

The experimental evidence for coherent EET in the FMO complex motivates the development of new methods to model the excited state dynamics of chromophores in a surrounding protein scaffold. It has become clear that Markovian models can not capture the behaviour of the system-environment interactions in these systems and hence non-Markovian models have to be considered. Based on the hierarchial expansion technique developed in Refs., Ishizaki and Fleming refined the theoretical framework to be a suitable tool for investigating the excited state dynamics in a photosynthetic complex. This form of hierarchically coupled equations of motions (HEOM) has served as the benchmarking method for these systems since it is able to describe quantum coherent motion and incoherent electron hopping in a unified manner. Using this method, Sarovar et al. examined quantum entanglement in the FMO complex and found that bipartite entanglement of chromophores exists on a time scale relevant for the mechanism of EET. Since entanglement can be used as a resource in quantum information processing tasks, it was speculated if the findings could play a role in explaining the near unity efficiency for these complexes to convert solar light into chemical energy.

Quantum nonlocality, as introduced by Bell, is another correlation property of composite quantum systems. While quantum entanglement, already mentioned by Schrödinger...
as the key property that distinguishes quantum mechanics from the classical world, is a meaningful property only for quantum systems, nonlocality is given by a criterion that is formed without specifying whether the systems are quantum mechanical or not. In the quantum-mechanical context, although entanglement and nonlocality are the same for pure states, this is not in general true for mixed states, i.e., they are inequivalent properties for such composite quantum systems.\textsuperscript{13,14} In particular, nonlocality is a stronger correlation property than entanglement in the sense that nonlocality implies entanglement but not vice versa.\textsuperscript{15}

The aim of this study is to examine whether bipartite nonlocality can exist in the EET in the FMO complex in its natural habitat, which would imply a striking nonclassical feature of this process. By studying the existence of quantum nonlocality in such a complex, it is possible to add knowledge about if and how quantum effects play a role in photosynthesis; knowledge that could be of interest for artificial photosynthesis and solar cells as well as for quantum computation. In a recent study\textsuperscript{16}, a considerable enhancement in the efficiency due to quantum coherence was found in a model system for a photosynthesis mimicking solar cell. If such discoveries can be connected to the existence of quantum nonlocality, it would be desirable to explore the underlying physics of such phenomena further.

The outline of this article is as follows. Section II describes the FMO complex and the methods used to model the EET in this system while Section III presents the procedure of calculating the bipartite nonlocality for different pairs of chromophores. This is followed by an account of the numerical details in Section IV. The results and a discussion of the most important findings are found in Section V. The article ends with conclusions in Section VI.

II. MODELING THE EET IN THE FMO COMPLEX

The EET in the FMO complex in its natural habitat has been modeled by employing the HEOM method.\textsuperscript{5,11} A description of the FMO complex as well as the quantities and conditions used to model the EET, can be found in Section II A. Section II B gives a brief review of the HEOM based model of the FMO complex, modified by including an explicit mechanism for the trapping at the reaction center.
A. The FMO complex

The FMO complex is a photosynthetic complex found in green sulfur bacteria, *Chlorobaculum tepidum*. It consists of three identical monomers, each one containing seven chlorophylls embedded in a protein scaffold as can be seen in Fig. 1. The structure of this complex as well as its site energies and inter-site couplings have been experimentally investigated by different spectroscopic methods and the system has been used as a model for larger light harvesting complexes for more than 35 years.

Unlike other light harvesting systems, the FMO complex does not include any antenna molecules. In other words, it is not responsible for capturing the light energy but only transferring it to the reaction centre. The antenna molecules are located in such a way that they can transfer excitation energy to the three monomer units. Since each FMO monomer functions independently from the other, it is justified to restrict the system studied to one monomer.

Calculations suggest that the most favourable orientation of the chromophores are that chlorophylls 3 and 4 are linked directly to the reaction centre. This result has been confirmed experimentally when examining the FMO complex with masspectrometry. Since the structure of the FMO is known, this implies that chlorophylls 1 and 6 connect to the base plate (that is the part of the antenna molecule complex that connects it to the FMO). The simplest way to model the EET in the FMO complex would hence be to assume a localized excitation on either chlorophyll 1 or 6 as the initial conditions for the EET. This
can be written as
\[ \hat{\rho}_{\text{localized}} = |x\rangle \langle x|, \]  
where \( \hat{\rho}_{\text{localized}} \) is the density operator describing the initial state of the EET in the FMO complex and \( x \) is the state of either chlorophyll 1 or 6. However, since the distance between the antenna molecules and the base plate as well as the distance between the base plate and the FMO are so large, a more realistic model could be to assume that an exciton is transferred from the base plate to the FMO by Förster resonance energy transfer (FRET)\(^{20}\). This would populate the FMO excitonic eigenstates in proportion to their occurrence at chlorophyll 1 or 6. The initial states can hence be written as
\[ \hat{\rho}_{\text{FRET}} = \sum_{k=1}^{7} |\langle x | e_i \rangle|^2 |e_i \rangle \langle e_i|, \]  
where \( |e_i \rangle \) denotes an exciton state.

The individual chromophores in the FMO complex can be modeled as two level systems (TLSs) for which only the \( S_0 \rightarrow S_1 \) transition is taken into account. Furthermore, since Green sulfur bacteria receive very little sunlight in their natural habitat\(^{11}\), it is reasonable to assume that the FMO complex only contains one such excitation at the time. This reduces the electronic Hamiltonian of the FMO complex (one monomer) to have the form
\[ \hat{H}_e = \sum_{k=1}^{7} E_k |k\rangle \langle k| + \sum_{k \neq l} J_{kl} |k\rangle \langle l|, \]  
where \( E_k \) is the electronic excitation energy of chromophore \( k \) when being in its excited state (such that \( |k\rangle = |S_{00}^1 \ldots S_{07}^k \ldots S_{00}^7 \rangle \) where the superscript denotes the site) and \( J_{kl} \) is the dipole coupling term between chromophore \( k \) and \( l \). The coupling term is a parameter describing the electrostatic interaction between the charge distribution of the two chromophores and depends strongly on the dipole moment orientations of the molecules. It can be calculated from the chromophores position in the protein complex structure\(^{4}\).

**B. The HEOM method for the FMO complex**

HEOM\(^{511}\) is a numerically exact method in which the environmental influence on a quantum system is treated in a statistical manner. For the FMO complex, the system of interest is the seven chromophores in one of the monomers with the Hamiltonian given
in Eq. (3). The protein scaffold is modeled as a set of harmonic oscillator modes, i.e., a phonon bath, which represents nuclear motion, both intramolecular and those of the environment. The transfer of excitation energy from one chromophore to another occurs via non-equilibrium nuclear configuration (phonon states) in accordance with a vertical Franck-Condon transition. The phonons, locally coupled to each chromophore \( k \), relax to their equilibrium states under energy loss. This so-called reorganization energy, denoted \( \lambda_k \), can be measured via the Stokes shift magnitude.\(^5\)\(^{21}\)

The memory of the local environment of chromophore \( k \) is characterized by a relaxation function \( \Gamma_k(t) \), modeled as an overdamped Brownian oscillator which takes the form

\[
\Gamma_k(t) = 2\lambda_ke^{-\gamma_k t}.
\]

The parameter \( \gamma_k \) represents the timescale of the fluctuations and energy dissipation for the \( k \)th chromophore and is related to the non-Markovian behaviour of the dynamics. The relaxation function, and hence \( \gamma_k \), can be investigated by 2DES\(^5\)\(^{21}\).

The time dependent density operator \( \hat{\rho}(t) \) describing the EET in the FMO complex is obtained by solving a set of hierarchically coupled equations of motion,

\[
\frac{\partial}{\partial t} \hat{\zeta}(n, t) = -\left( i\mathcal{L}_e + \sum_{k=1}^{7} n_k \gamma_k \right) \hat{\zeta}(n, t) + \sum_{k=1}^{7} \left[ \Phi_k \hat{\zeta}(n_k^+, t) + n_k \Theta_k \hat{\zeta}(n_k^-, t) \right],
\]

where the operator \( \hat{\zeta}(0, t) \) is identical to \( \hat{\rho}(t) \) while the higher order operators \( \hat{\zeta}(n \neq 0, t) \) are auxiliary operators. Here, \( n \) is a set of nonnegative integers, \( n = (n_1, n_2, .., n_7) \). The notation \( n_k^+(n_k^-) \) stands for adding (substracting) 1 to the corresponding \( n_k \) in \( n \). The Liouvillian superoperator \( \mathcal{L}_e \) is composed of the electronic Hamiltonian of the FMO complex and the site reorganization energies, and takes the form

\[
\mathcal{L}_e \hat{g} = [\hat{H}_e + \sum_{k=1}^{7} \lambda_k |k\rangle \langle k|, \hat{g}]
\]

with \([\cdot, \cdot]\) the commutator and \( \hat{g} \) any linear operator acting on the Hilbert space of the FMO complex. The superoperators \( \Phi_k \) and \( \Theta_k \) are so called phonon-induced relaxation operators and correspond to the influence of the environmental fluctuations. They have the forms

\[
\Phi_k \hat{g} = i[V_k, \hat{g}]
\]

7
and

\[ \Theta_k \hat{g} = i \frac{2\lambda_k}{\beta \hbar^2} [\hat{V}_k, \hat{g}] + \frac{\lambda_k}{\hbar} \gamma_k \{ \hat{V}_k, \hat{g} \} \]  

(8)

with

\[ \hat{V}_k = |k\rangle \langle k| \]  

(9)

and \{·,·\} the anti-commutator. Here, \( \beta = (k_B T)^{-1} \) with \( k_B \) being the Boltzmann constant and \( T \) the temperature of the phonon bath.

The HEOM can be truncated by setting

\[ \frac{\partial}{\partial t} \hat{\zeta}(n, t) = -i \mathcal{L}_e \hat{\zeta}(n, t), \]  

(10)

for all \( n \) satisfying \( n_1 + n_2 + \ldots + n_7 = N \), \( N \) being the truncation level. This condition will terminate the generation of the auxiliary operators.

Following Ref.\textsuperscript{22}, a Liouvillian that models the trapping of excitation of chromophores 3 and 4 is added to the right-hand side of Eq. (5). It has the form

\[ \mathcal{L}_{\text{trap}} \hat{\zeta}(n, t) = -r_{\text{trap}} \{|3\rangle \langle 3|, \hat{\zeta}(n, t)\} - r_{\text{trap}} \{|4\rangle \langle 4|, \hat{\zeta}(n, t)\}, \]  

(11)

where \( r_{\text{trap}} \) is the trapping rate, assumed to be the same for chromophores 3 and 4. When comparing with Eq. (5) it can be seen that adding this Liouvillian makes the population of chromophore 3 and 4 decay faster than for the other chromophores.

The density operator describing the EET in the FMO complex takes the form

\[ \hat{\rho}(t) = \sum_{k=1}^{7} \rho_{kk}(t) |k\rangle \langle k| \]

(12)

\[ + \sum_{k=1}^{7} \sum_{l>k}^{7} (\rho_{kl}(t) |k\rangle \langle l| + \rho_{lk}^*(t) |l\rangle \langle k|), \]

where \( |k\rangle \) is the site basis state corresponding to chromophore \( k \) being in the excited state, \( S^1_k \), and the remaining chromophores in their ground states, \( S^0_{\neq k} \). Here, \( \rho_{kk} \) is the population of site \( k \) and \( \rho_{kl} \) describes the coherence between sites \( k \) and \( l \).
III. MEASURING BIPARTITE QUANTUM NONLOCALITY BETWEEN CHROMOPHORES IN THE FMO COMPLEX

Quantum nonlocality is a property of composite quantum systems whose states show correlations that cannot be explained by a theory incorporating local realism\textsuperscript{24}. The existence of nonlocality was discovered when Bell derived\textsuperscript{12} an upper bound (Bell’s inequality) for correlations between two systems to be local, and then showed that the correlations within certain composite quantum systems may exceed this limit.

Since Bell’s original formulation of his inequality, there has been other Bell-like inequalities. One such that is suitable for investigating bipartite nonlocality for TLSs like the chromophore states in the FMO complex is the CHSH inequality\textsuperscript{23}. It states that any set of variables $a, a', b$ and $b'$ that can take values $\pm 1$ must satisfy

$$ |\langle ab \rangle + \langle ab' \rangle + \langle a'b \rangle - \langle a'b' \rangle| \leq 2 \quad (13) $$

if the principle of local realism\textsuperscript{23} applies to measurements of the pairs $a, a'$ and $b, b'$ at distant locations.

To test the validity of the CHSH inequality for measurements on two distant TLSs, described as a composite quantum system with density operator $\hat{\rho}$, the operator

$$ \hat{B}_{\text{CHSH}} = a \cdot \hat{\sigma} \otimes (b + b') \cdot \hat{\sigma} $$

$$ + a' \cdot \hat{\sigma} \otimes (b - b') \cdot \hat{\sigma}, \quad (14) $$
can be used. Here, $a, a', b$ and $b'$ are unit vectors in $R^3$ and $\sigma$ is a vector consisting of Pauli operators. The correlation in $\hat{\rho}$ is said to be nonlocal if $|\langle \hat{B}_{\text{CHSH}} \rangle| = |\text{Tr} (\hat{\rho} \hat{B}_{\text{CHSH}})| > 2$ for at least one choice of $a, a', b$ and $b'$.

A necessary and sufficient condition for the correlation between any two TLSs to be nonlocal has been developed by Horodecki et al.\textsuperscript{25}. This criterion is based on a quantity $M(\hat{\rho})$ that maximizes the expectation value of the Bell operator in Eq.(14) such that

$$ \max_{a, a', b, b'} |\langle \hat{B}_{\text{CHSH}} \rangle| = 2\sqrt{M(\hat{\rho})}. \quad (15) $$

$M(\hat{\rho})$ is found as

$$ M(\hat{\rho}) = \mu_p + \mu_q, \quad (16) $$
where $\mu_p$ and $\mu_q$ are the two greatest eigenvalues of the matrix $|T(\hat{\rho})|^2 = T(\hat{\rho})^T T(\hat{\rho})$ with $T(\hat{\rho})$ given as
\[
T(\hat{\rho}) = \begin{pmatrix}
t_{xx} & t_{yx} & t_{zx} \\
t_{xy} & t_{yy} & t_{zy} \\
t_{xz} & t_{yz} & t_{zz}
\end{pmatrix}.
\] (17)

The elements of $T(\hat{\rho})$ are given as $t_{ij} = Tr(\hat{\rho} \hat{\sigma}_i \otimes \hat{\sigma}_j)$ for all combinations of Pauli operators $\hat{\sigma}_i$. The correlation is nonlocal whenever $1 < M(\hat{\rho}) \leq 2$, where the maximum value is given by the Cirel’son bound\(^\text{26}\).

As a measure of the amount of nonlocality we use the quantity\(^\text{13}\)
\[
B(\hat{\rho}) = \sqrt{\max\{ (M(\hat{\rho}) - 1), 0 \}}.
\] (18)

This measure is directly comparable with concurrence $C(\hat{\rho})$\(^\text{27}\) - the measure that was used to analyze the amount of bipartite entanglement in the FMO complex by Sarovar et al\(^\text{1}\).

The time evolution of the composite system of chromophores $n$ and $m$ in the FMO complex can be found by calculating the reduced density operator from the density operator given in Eq. (12). This is done by tracing $\hat{\rho}(t)$ over the other five chromophore degrees of freedom. The resulting density operator will be of the form
\[
\hat{\rho}_{nm} = \left[ \operatorname{Tr}(\hat{\rho}) - (\rho_{mm} + \rho_{nn}) \right] |S_0^n S_0^m\rangle \langle S_0^n S_0^m| \\
+ \rho_{nm} |S_0^n S_1^m\rangle \langle S_0^n S_1^m| + \rho_{nm} |S_1^n S_0^m\rangle \langle S_1^n S_0^m| \\
+ \rho_{nm} |S_1^n S_1^m\rangle \langle S_0^n S_1^m| + \rho_{nn} |S_1^n S_0^m\rangle \langle S_1^n S_0^m|,
\] (19)

where $S_0^n$ and $S_1^n$ denotes the ground state and excited state for chromophore $n$.

The eigenvalues of $|T(\hat{\rho}_{nm})|^2$ are given by
\[
\mu_1 = \mu_2 = 4 |\rho_{nm}|^2
\] (20)

and
\[
\mu_3 = [\operatorname{Tr}(\hat{\rho}) - 2(\rho_{mm} + \rho_{nn})]^2.
\] (21)

Finally, since $\mu_1 = \mu_2$ are degenerate eigenvalues, $M(\hat{\rho}_{nm})$ is given as
\[
M(\hat{\rho}_{nm}) = \max\{ 8 |\rho_{nm}|^2, 4 |\rho_{nm}|^2 \\
+ [\operatorname{Tr}(\hat{\rho}) - 2(\rho_{mm} + \rho_{nn})]^2 \}.
\] (22)
IV. NUMERICAL DETAILS

The parameters of our numerical model were chosen in accordance with previous works on the EET in the FMO complex. As the electronic FMO Hamiltonian for *Chlorobaculum tepidum* in the site basis, we used

\[
H_e = \begin{pmatrix}
200 & -87.7 & 5.5 & -5.9 & 6.7 & -13.7 & -9.9 \\
-87.7 & 320 & 30.8 & 8.2 & 0.7 & 11.8 & 4.3 \\
5.5 & 30.8 & 0 & -53.5 & -2.2 & -9.6 & 6.0 \\
-5.9 & 8.2 & -53.5 & 110 & -70.7 & -17.0 & -63.3 \\
6.7 & 0.7 & -2.2 & -70.7 & 270 & 81.1 & -1.3 \\
-13.7 & 11.8 & -9.6 & -17.0 & 81.1 & 420 & 39.7 \\
-9.9 & 4.3 & 6.0 & -63.3 & -1.3 & 39.7 & 230 \\
\end{pmatrix},
\]

where all numbers are in units of cm\(^{-1}\) with a total offset of 12 210 cm\(^{-1}\). The reorganization energy \(\lambda_k\) and the relaxation time-scale \(\gamma_k\) were assumed to have the same values, 35 cm\(^{-1}\) and 50 fs\(^{-1}\)\(^{22}\), respectively, for all seven chromophores\(^{21}\). The time scale for the trapping by the reaction center was set to 1 ps\(^{4,29}\) and the bath temperature to 300 K (same as in Ref\(^{20}\)).

The HEOM (Eq. (5)) were numerically integrated in the range 0 to 1000 fs using the Runge-Kutta-Dormand-Prince method\(^{30}\). To measure the convergence of the HEOM solution, we use the trace distance defined as\(^{31}\)

\[
D(\hat{\rho}, \hat{\rho}') = \frac{1}{2} \text{Tr} |\hat{\rho} - \hat{\rho}'|
\]

for any pair of density matrices \(\hat{\rho}\) and \(\hat{\rho}'\) of the system. By comparing the density matrices obtained at different truncation levels of the HEOM, we find that sufficient accuracy for most purposes should be achieved with \(N \approx 6\), see Fig. 2.

V. RESULTS AND DISCUSSION

Our simulations shows that bipartite quantum nonlocality only exists when the localized initial conditions according to Eq. (1) are used. For these initial conditions nonlocality is found for two composite chromophore systems; chromophore 1 and 2 when chromophore 1 is initially excited, and chromophore 5 and 6 when chromophore 6 is initially excited. These
Figure 2. (Color online) Convergence of the density operator with respect to the truncation level of the HEOM. The change in the density operator on going from level \( N \) to level \( M = N + 1 \) is characterized by the logarithm of the corresponding trace distance \( D(N, M) \). The initial excitation is either on chromophore 1 (upper panel) or chromophore 6 (lower panel). Notice how at the higher truncation levels the change in the trace distance is comparable to the numerical noise.

results are presented in Figs. 3 and 4 together with the time dependence of the bipartite entanglement for the same pairs of chromophores.

When the initial conditions corresponding to FRET from the antenna molecules to the FMO is used (Eq. (2)) no nonlocality is found even though entanglement still exists. In particular, a considerable amount of quantum entanglement exists for chromophore 1 and 2 when the exciton states are projected on chromophore 1 (corresponding to \( x = 1 \) in Eq. (2)) as well as for chromophore 5 and 6 when the exciton states are projected on chromophore 6 (corresponding to \( x = 6 \) in Eq. (2)). These results can be seen in Figs. 5 and 6.

As can be seen in Figs. 3, 4, 5 and 6, bipartite nonlocality and entanglement are clearly two different properties for the EET in the FMO complex when the HEOM method is used to model the dynamics. For the FRET initial conditions, nonlocality is not found for any pairs of chromophores, while entanglement survives to some extent. Furthermore, for the localized initial conditions, entanglement dynamics is similar to the chromophores population dynamics shown in Fig. 7, i.e., oscillating and exponentially decaying, while the nonlocality does not show any oscillating features at all. Instead it drops to zero on a very short time.
Figure 3. (Color online) Nonlocality (blue) and concurrence (red) for the chromophore pair 1 and 2 as a function of time when chromophore 1 is initially excited.

Figure 4. (Color online) Nonlocality (blue) and concurrence (red) for the chromophore pair 5 and 6 as a function of time when chromophore 6 is initially excited.

scale. Thus, nonlocality can undergo a form of "sudden death" in the FMO system with these initial conditions, in the sense that nonlocality may have a finite life-time despite the fact that entanglement undergoes an exponential decay. This "nonlocality sudden death" (NSD) is a phenomenon analogous to the "entanglement sudden death", i.e., the occurrence
Figure 5. (Color online) Nonlocality (blue) and concurrence (red) for the chromophore pair 1 and 2 as a function of time when exciton states projected on chromophore 1 is used as the initial condition.

of finite-time entanglement in coherent systems, which has been predicted and observed in quantum optical systems.

NSD is a striking manifestation of that nonlocality and entanglement are different properties of mixed quantum states. For the EET in the FMO complex, this difference can be understood when considering that the measure of bipartite entanglement, concurrence, in this system is given as $C(\hat{\rho}_{nm}) = 2|\rho_{nm}|$, i.e., two times the coherence between the two states. Thus, the model itself implies the existence of entanglement. Nonlocality on the other hand, may also depend on the population of the other chromophores in the system via the nondegenerate eigenvalue $\mu_3$ of $|T(\hat{\rho})|^2$.

The chromophore pair 1 and 2 forms the strongest coupling of all chromophore pairs ($J_{12}=-87.7$ cm$^{-1}$) and there is also another noticeable feature for this pair; chromophore 2 has a higher site energy than chromophore 1. This means that the EET from the initially excited chromophore 1 (excitation donor) to chromophore 2 (excitation acceptor) is energetically unfavoured if the system should be seen as a composition of two separable subsystems. Maybe the great extent of nonlocality (and hence entanglement) will play a role in the EET between these two chromophores. A similar conclusion was made in when analyzing the EET in the FMO complex in terms of entanglement.
Figure 6. (Color online) Nonlocality (blue) and concurrence (red) for the chromophore pair 5 and 6 as a function of time when exciton states projected on chromophore 6 is used as the initial condition.

Figure 7. (Color online) Population of chromophore states as a function of time when chromophore 1 (upper panel) or chromophore 6 (lower panel) is initially excited.

The pair 5 and 6 is the next strongest coupled one ($J_{56} = 81.1 \text{ cm}^{-1}$) and so it seems, like for the pair 1 and 2, there is an agreement between the coupling strength and the amount of nonlocality. This is according to what could be expected since entanglement is a necessary condition for nonlocality to exist and the creation of entanglement, in turn,
is depending on the coupling strength (since the coherence between two states depends on the coupling strength). As noted before though, nonlocality also depends on the population of the other chromophores in the system. For example, chromophore 4 and 7 are strongly coupled as well (-63.3 cm$^{-1}$) but still do not show nonlocal correlations. Our calculations suggest that another necessary condition for nonlocality to exist between chromophore 1 and 2 respectively 5 and 6, is that chromophore 1 respectively 6 has to be target for the initial excitation in the complex. The same is not true for entanglement.

VI. CONCLUSIONS

This work has contributed to the investigation of the FMO complex in considering bipartite quantum nonlocality between different chromophores rather than bipartite quantum entanglement as in previous studies. The computations show that for localized initial conditions, nonlocality does exist for some pairs of chromophores in the system. It is only observed for those chromophore pairs where one of them receives the initial excitation of the system though. A strong coupling is a necessary but not sufficient condition for creating nonlocal correlation between chromophore pairs.

The fact that no nonlocality is observed when more realistic initial conditions (FRET from the antenna molecules to the FMO) are used could indicate that nonlocality is of no importance when considering EET in the FMO in nature. Since entanglement, and hence quantum coherence, is also suppressed in this case it seems like a localized initial excitation would be preferred in an artificial photosynthetic complex$^{16}$. Finally, it seems that nonlocality is more sensitive than entanglement for open system effects and it would hence be even more challenging to find a quantum system in nature with long-lived nonlocal correlations.

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