Natural Light Harvesting Systems: Unraveling the quantum puzzles

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In natural light harvesting systems, the sequential quantum events of photon absorption by specialized biological antenna complexes, charge separation, exciton formation and energy transfer to localized reaction centers culminates in the conversion of solar to chemical energy. A notable feature in these processes is the exceptionally high efficiencies (> 95%) at which excitation is transferred from the illuminated protein complex site to the reaction centers. Such high exciton propagation within a system of interwoven biomolecular network structures, is yet to be replicated in artificial light harvesting complexes. A clue to unraveling the quantum puzzles of nature may lie in the observation of long lived coherences lasting several picoseconds in the electronic spectra of photosynthetic complexes, even in noisy environmental baths. However the exact nature of the association between the high energy propagation rates and strength of quantum coherences remains largely unsolved. A number of experimental and theoretical studies have been devoted to unlocking the links between quantum processes and information protocols, in the hope of finding answers to nature’s puzzling mode of energy propagation. This review presents developments in quantum theories, and links information-theoretic aspects with photosynthetic light-harvesting processes in biomolecular systems. There is examination of various attempts to pinpoint the processes that underpin coherence features arising from the light harvesting activities of biomolecular systems, with particular emphasis on the effects that factors such non-Markovianity, zeno mechanisms, teleportation, quantum predictability and the role of multipartite states have on the quantum dynamics of biomolecular systems. A discussion of how quantum thermodynamical principles and agent-based modeling and simulation approaches can improve our understanding of natural photosynthetic systems is included.

I. INTRODUCTION

Photosynthesis is an important quantum process which contributes significantly to the world’s yearly biomass yield. During this process, light absorption followed by charge separation and efficient energy transfer to a reaction center (RC) are performed by specialized pigment-protein (LH) complexes [1–7]. The conversion of solar energy to chemical energy takes place at the reaction center, with the chemical reactions providing the driving force for the adenosine triphosphate complex, ATP. This co-enzyme forms the basis of critical cellular processes needed for survival of the supported species. The theory of excitonic energy transfer in light harvesting systems (LHS) has been a topic of interest over several decades [1–5, 8–20]. The light harvesting complexes from different species vary in their structural arrangements, but possess the common attribute of viable excitation propagation even in adverse, noisy environments.

The absorption of a photon results in the formation of an excited quasi-particle known as the exciton (correlated electron-hole pair), on one or more optically active molecular sites occupied by molecular complexes, known as chromophores. One well studied pigment-protein complex is the Fenna–Matthews–Olson (FMO) complex of the green sulfur bacteria [21–27, 34, 35] shown in Fig. 1 for two species of the bacteria. The FMO acts as the prototypical system for quantum studies during photosynthetic activities, mainly due to numerical tractability of its known crystallographic structure, as well as the wide range of experimental results available for this system. The FMO complex trimer is made up of three symmetry equivalent monomer subunits, with each subunit constituting eight bacteriochlorophyll (BChl)a molecules (Fig. 2) supported by a cage of protein molecules. The chromophore sites numbered 3 and 4 are located near the reaction center, and thus are closely linked to the sink region where energy is released, while chromophore sites 1 and 2 are strongly coupled to each other dissipating energy via site 3. The sites 1, 6, and 8 are located at the baseplate which connects to the chlorosomes that receive electronic excitation. The eighth chromophore plays a critical role in the topological connectivity of large molecular structures, and in this regard is critical to the existence of multipartite states. The Fenna-Matthews-Olson (FMO) protein complex is sandwiched between the large peripheral chlorosome antenna complex and the reaction center (RC), so that excitation originating at the antenna site propagates through the FMO to the reaction center. In the case of the purple photosynthetic bacteria, there exist two different types of light harvesting molecular system units with ring-like structures, known as LH1 and LH2 (Fig. 3). The core LH1 complex is directly linked to the RC by surrounding it, while the peripheral LH2 complexes transfers energy to the LH1 complex. Hence the photosynthetic apparatus of both the green sulphur and purple
bacteria constitute molecular complexes with two main distinct roles based on whether the molecular complex is directly or indirectly linked with the reaction center.

The FMO complex exhibits strong quantum beating that lasts (> 600 fs), which currently is not fully accounted for by any theoretical predictions. The long-lasting coherent dynamics are indicated as cross-peak oscillations in two-dimensional echo-spectra results [23, 25–27]. The noted exceptionally high efficiencies ( > 95%) at which excitation propagates between the light harvesting complexes before reaching the reaction center (RC) pigment-protein complex [2, 4, 5] is yet to be realized in artificial light harvesting complexes. Two-dimensional photon-echo based experiments [26] in which the time delays of fast pulses are manipulated to provide a map of excitation and emission frequencies at select duration of time delay, is a reliable technique for examining energy transfer processes. Recent progress in photon based instrumentation involving detection and counting techniques, has facilitated the reconstruction of a system’s state via the promising quantum-state tomography approach, which allow quantum states and their associated density matrices to be estimated with a high degree of accuracy [28–33].

II. CHALLENGES IN THEORETICAL MODELING AND THE COHERENT PROPAGATION MODEL

A major difficulty in the theoretical modeling of the energy transfer process arises due to the almost equivalent match in energy scales (10 – 100 cm$^{-1}$) of two competing processes: exciton delocalization and decoherence due to lattice vibrations in light-harvesting systems. The Markovian approximation, in which an infinitely short correlation reservoir time is assumed, becomes unreliable in the time regime where there is delicate interplay between the two

FIG. 1: (Left) Crystal structure of the Fenna-Matthews-Olson protein complex from the sulphur bacteria species, *Chlorobaculum Tepidum* obtained using the pdb code:3EnI from http://www.rcsb.org/pdb/download [21, 22]. (Right) Crystal structure of the Fenna-Matthews-Olson protein complex from the sulphur bacteria species, *Prosthecochloris Aestuarii* obtained using the pdb code:3EOJ.

FIG. 2: (left) FMO complex monomer subunit constituting eight bacteriochlorophyll (BChl)a molecules and (right) Simplified trimer configuration, in which the eighth BChl-a is positioned close to the first chromophore molecule of a neighbouring monomer. This results in strong inter-monomer interactions for excitations present at sites 8 and 1.
main competing processes. The complexity of modeling large complex molecules against a background of noisy processes also presents numerical challenges in verifying the links between the coherence times and the excitation energy transfer times. As a consequence, simpler forms of the spectral density of the bath oscillators are assumed to provide tractability, at the expense of accuracy of computed results. In a recent work [35], a signal processing technique was employed to construct reservoir systems models with increased accuracy and decreased computational cost. The electronic degrees of freedom of molecular complexes involved in photon excitation (at the solar illumination site) and those involved in the excitation transfer between chromophores are noted to be intrinsically mixed with other degrees of freedom (reservoir, impurities) present in the system. The validity of the usual procedure of eradicating environmental variables to construct a pure reduced density matrix is still debatable, with regard to non-Markovian effects (discussed in Section V). Consequently, many findings related to photosynthetic systems involve model systems which are subject to assumptions, that introduce artifacts which influence the final outcome of the results.

In current theoretical studies of photosynthetic systems, the once popular classically derived exciton hopping model [1, 8, 9] has been replaced by modern approaches based on the quantum coherence properties of the exciton [11, 13, 14, 36–39]. In the coherent propagation scheme, the exciton is modeled as delocalized excitation that spans the real crystal space [11, 13] as an extended entangled system [15, 16]. The exciton is considered to be in a state of existence at several lattice sites, traversing multiple paths simultaneously, and undergoing a process of continuous interferences. In essence, it is these interferences that give rise to the uniquely quantum behavior in many solids. In a molecular crystal, the degree of exciton delocalization is influenced by the environmental bath of phonons and other dissipative factors (impurities and trapping centers). In optimal situations, the superposed states may be considered to direct the exciton to find the most efficient route to the site where energy conversion takes place. The system “checks” many states simultaneously, and selects the “winner” sites, this idea was proposed in an earlier work which examined the Grover-like search by excitonic states [46]. In the original implementation of the Grover search [49, 50], the location of an item in an unsorted database containing N elements is attempted. While this process requires $O(N)$ steps during classical computation, Grover [49] showed that only $O(\sqrt{N})$ steps is required in the presence of quantum interference effects. We point out that in Ref. [46], the subtle links between the role of the excitonic superposed states and experimental observations of quantum coherences in noisy environments has not been rigorously shown.

The important role of spin dynamics [51, 52] of molecular systems during the photosynthetic process needs mention. Spintronic systems involve spin-up and spin-down charge carriers, and the information encoded in spins may be used to exploit quantum coherence aspects of the global system. When exposed to sunlight, the absorption of a photon may result in both the intra-molecular and inter-molecular transfer of electrons and exciton, which give rise to radical-molecules with unpaired electrons or a different orientation of spin structures. Importantly, these subtle changes in spin structure of the biomolecules enable different routes of energy propagation due to changes in the chemical environment, and spin-specific responses to the lattice vibrations [53]. To date, the role of molecular spintronics in light harvesting properties has not been fully examined. From a quantum physics viewpoint, photosynthetic system appear to present a viable platform in which to explore the quantum coherence properties arising from spin dynamics of an extended biological network system.
III. APPROACHES USED TO EXAMINE QUANTUM PHOTOSYNTHESE

In many studies of quantum systems, the analysis of excitation transfer involves a reduced description in which the electronic system (including the couplings between subsystems) of interest are treated separately from the lattice vibrational modes at the site of the molecular pigments. In earlier works, the Redfield procedure employing the Born-Markov and secular approximations \[57, 59\] and the non-Markovian approach based on the integro-differential equation using perturbation theory \[60\], have been used to examine the quantum dynamical evolution of exciton states. A generalized Bloch-Redfield (GBR) equation technique \[61\] showed that temperature and spatial—temporal correlations in noise cannot be optimized simultaneously to yield the best energy propagation efficiencies. The collective system of exciton-vibronic modes was proposed as a likely reason for experimental observations of coherent oscillations \[62\], however this model was not supported by experimental work involving doped samples of the FMO complex \[53\].

Based on the quantum Markovian master equation of the Lindblad form, the time evolution of the reduced open exciton state \[64, 65\] has been employed in several studies \[66, 67\] with emphasis on system-bath correlations \[73, 74\]. Noise generated by thermal effects in non-equilibrium systems may be favorable to the existence of quantum coherence. It was noted \[66, 67\] that optimal transport occurred at intermediate noise level, with very strong or weak noise levels resulting in lower performances, sharing some commonness in similar requirements for the stochastic resonance phenomenon to occur. These attributes also appear to be consistent with the level of noise perturbations required in the Grover-like search by excitonic states \[46\]. In earlier works on the influence of thermal noise \[66, 67\], the disturbances were incorporated in a local dephasing Lindblad master equation form within the site basis.

We note the failings of the Lindblad form \[58, 60\] for a range of temperatures and other dissipation factors. To understand the weakness of the Lindblad form, we consider a continuous semigroup of linearly bounded operators, \( T_t \), at time \( t \), which contracts in the Hilbert space by virtue of the trace and positivity preserving conditions Quantum states in general, can be associated with dynamical semigroups which constitute the group of bounded operators satisfying: (i) \( T_0 = I \), where \( I \) is the identity, (ii) \( T_{t+v} = T_t + T_v \), \( t, v \geq 0 \), (iii) \( || T_t \rho || \leq || \rho || \) for \( t \geq 0 \) for \( \forall \) state \( \rho \) in \( \mathcal{H} \), where \( || A || = Tr(|A^\dagger A|) \) and (iv) the existence of a continuous map \( t \rightarrow T \) for \( \forall t > 0 \). The set of non-unitary contractive semigroup \( T_t \) in decaying states is invariably linked to time irreversibility, with unitary \( (T^1 = T^{-1}) \) and the completely non-unitary contractions may be analyzed using the Langer-Sz-Nagy-Foias theorem (LSNF) \[70\]. The LSNF theorem states that \( T \) can be decomposed into a unitary component \( T^u \) and a non-unitary component \( T^n \), accordingly for every semigroup \( T_t \), the Hilbert space \( \mathcal{H} \) can be split into two subspaces: \( \mathcal{H} = \mathcal{H}^u \oplus \mathcal{H}^n \), where \( T^u \) (\( T^n \)) is associated with \( \mathcal{H}^u \) (\( \mathcal{H}^n \)).

The similar focus of the LSNF theorem and Lindblad theory can be revealed by utilizing the Hille-Yoshida generator for a dynamical semigroup \[71, 72\]. This generator yields a master equation (of the Lindblad form) that governs the evolution of \( \rho \) \[64, 65\]:

\[
\frac{d}{dt} \rho(t) = -i[H, \rho(t)] + \sum_{k,l=1}^{d} \mathcal{L}_{kl} (\rho(t))
\]

\[
= -i[H, \rho(t)] + \frac{1}{2} \sum_{k,l=1}^{d} \alpha_{kl} \left( 2 \chi_k \rho(t) \chi_l^\dagger - \chi_k^\dagger \chi_l \rho(t) \right),
\]

\[
= -i[H, \rho(t)] + \sum_{k=1}^{d} \gamma_k \left( \mathcal{L}_k \rho(t) \mathcal{L}_k^\dagger - \frac{1}{2} \{ \mathcal{L}_k^\dagger \mathcal{L}_k, \rho(t) \} \right)
\]

where the Lindblad operators, \( \mathcal{L}_{kl} \) generate the map from the initial to the final density operators of \( \rho \) and \( \mathcal{H} \) arises

The search is ongoing for a comprehensive theory that can fully account for the observed long-lasting coherent dynamics in natural systems with light harvesting potential. There may exist specific subspaces of information theoretic entities, which give rise to oscillations that persist for the observed duration of time seen in experimental results. Lately, we examined links between the observed coherence and the environment-assisted transfer mechanisms based on the Zeno-effect \[55\]. The quantum Zeno effect is the retarded time evolution of a quantum state subject to frequent measurements, with the reverse effect that leads to enhancement in time evolution, known as anti-Zeno effect. The results in Ref.\[55\] indicate that sites of a dissipative nature act indirectly as detectors, to induce anti-Zeno-like effects, thereby facilitating information feedback into the specific partitions in the biomolecular system. In earlier work \[56\], it was shown that repeated measurements in disordered systems can induce a quantum anti-Zeno effect with ability to enhance quantum transport under certain conditions. These works \[55, 56\] highlight the importance of the Zeno mechanisms in photosynthetic processes, and the Zeno mechanism-measurement theory point to the critical role of quantum mechanical principles during photosynthesis.
from a combination of the isolated system Hamiltonian, $\mathcal{H}_s$, and a system-environment interaction operator. $\{\chi_k\}^{d}_{k=0}$ form the basis in the linear operator space, with $\chi_0 = I$, where $I$ denotes the identity. The terms $\{a_{kl}\}$ in Eq. (2) constitute the positive definite $d$-dimensional Hermitian Gorini-Kossakowski-Sudarshan matrix $\mathcal{A}$ [65], with spectrum $\{\gamma_k\}$. The first term in Eq. (2) (or (3)) represents reversibility in system dynamics, and the symmetrized Lindblad operators, $\mathcal{L}_\gamma$, incorporate environmental effects within the Born-Markov approximation and therefore act as the source of non-unitary dynamics.

The Lindblad form in Eq. (3) ensures the positivity of density operators at any time, however it is applicable only to weak to moderately weak system-reservoir couplings, when Markov approximation holds, and breaks down in instances when the complete positivity of density operators is violated. This could occur in the initial stage of evolution dynamics due to back flow of information from the reservoir bath at very short time durations which are comparable to the bath memory times [75]. In these instances, there appears to be a feedback action from the reservoir variables. Time appears not to have a preferred direction in this regime and quantum processes therefore proceed (in the initial period) with some degree of symmetry with respect to time reversal. One notes that the finite time-scale of the vibrational environment becomes relevant during this quantum dynamical regime.

It may therefore be appropriate to use a non-Lindblad set of relations to describe the system dynamics during the initial period of quantum evolution. To this end, the non-perturbative hierarchical equations of motion (HEOM) technique [38, 76, 77] which incorporates finite time scale of the dynamics in the vibrational environment, comes across as a viable tool in the study of ultrafast quantum processes. The HEOM technique is based on a hierarchy of equations, in which the reduced density operator of the system couples to a system of auxiliary operators. These operators enable flexible tuning of complex environments centered on the correlation time of the bath, its spectral density and spatial noise correlations. The HEOM model interpolates between the Bloch-Redfield and the Förster regimes, and includes higher vibrational energies present in the environmental bath, incorporating a second-order cumulant expansion that is exact for a harmonic bath.

A study employing the HEOM technique [77] showed that the spectral density, which determines the decoherence and relaxation rate, played a critical role in the duration of coherent oscillations. The results in Ref. [78] highlighted the links between strong coupling interactions required for fast thermalization processes and experimental observations of long-lasting coherent oscillations. In another work employing the HEOM technique [78], the interplay between electronic and vibronic degrees of freedom of the trimer model of the FMO complex was used to highlight a likely underestimation of the life-time of electronic coherences captured by two-dimensional spectra results. More recently the HEOM technique [79] was used to investigate changes to transitions between sites and the protein environment, with results showing robustness of excitation propagation when defects are introduced into the molecular environment. The latter results is of particular interest to the possibility that biological systems may adapt accordingly to achieve favorable characteristics to realize optimum outcome in its functionality.

The quasi-adiabatic path integral (QAPI) technique [50, 51] is another useful tool that provides reliable results at short reservoir correlation times, however it requires intense computational efforts at the low temperature regime. This approach is thus unsuitable for structured reservoir systems that incorporate both narrow and broad spectral bands. In a recent work Kim et. al. [82], employed an all-atom description of the photosynthetic complex within a semi-classical framework to examine the Fenna-Matthews-Olson complex, and noted subtle differences in the role of vibrational modes at the ensemble and single-complex levels. Coherence was seen to be weaker at the ensemble level, and stronger at the single-complex level, while thermal fluctuations in the chromophore couplings was seen to induce some redundancy in the coherent energy-transfer pathway [82]. These results are interesting considering that a semi-classical framework was employed to show that the coupling strength and fluctuations within biomolecular systems play important roles in the coherent electronic transfer processes in photosynthetic systems. We next describe the non-Hermitian quantum mechanical approach from which other salient features, such as topological defects, can be revealed during energy propagation in organic systems.

IV. THE NON-HERMITIAN QUANTUM MECHANICAL APPROACH

It is well known that Non-Hermitian systems [83, 90] play important roles in the dynamics of open quantum systems. In particular, the appearance of non-Hermitian terms (both real and imaginary) have profound implications for various physical and biochemical systems that can be modeled as open quantum systems. The striking difference between non-Hermitian physics and Hermitian physics lies in the occurrence of degeneracies such as exceptional points which are topological defects that occur when two eigenvalues of an operator coalesce. This may occur as a result of changes in selected system parameters. Two mutually orthogonal states then merge into one self-orthogonal state, resulting in a singularity in the spectrum [90] with many intriguing effects. The critical parameter values at which the singularity appear are considered as exceptional points. These points are known to be located in the vicinity of a level repulsion [90] and unlike degenerate points, only a single eigenfunction exists at the exceptional point. There appears to
be a decrease in information content due to the appearance of the singularity in the spectrum, however the exact
details of information transfer to neighboring subsystem is currently not known. The exceptional point remains to
be observed experimentally, however there has been predictions that its existence during photosynthesis may assist
in distinguishing classical and quantum modes of transport [84].

Quantum systems with non-Hermitian components evolve differently from those of a purely Hermitian Hamiltonian,
with the lifetimes of states associated with the non-Hermitian Hamiltonian remaining finite. The differences between
non-Hermitian and pure Hermitian nature of Hamiltonians can be examined using the quantum brachistochrone concept,
linked to the minimum time taken to transverse the path between two locations of a particle under a set
of constraints. It is known that the passage time of evolution of an initial state into the final state can be made
arbitrarily small for a time-evolution operator that is non-Hermitian but PT-symmetric [89]. This result has been
generalized to non-PT-symmetric dissipative systems [87], with indications [87, 89] that propagation in non-Hermitian
quantum mechanics proceed faster than those of Hermitian systems. The latter feature has relevance to problems
examining the efficient propagation times noted in light harvesting systems.

The presence of non-Hermitian attributes also gives rise to quasi-bound resonance states in the continuum reservoir
partition [85]. While the real and imaginary components of the non-Hermitian eigenfunctions evolve independently
during avoided level crossing, dynamical phase transitions arise due to the distinct nature of the two components
[85], along with a bifurcation of the time scales associated with the lifetimes of the resonance states. Short-lived and
long-lived quantum states present during non-Hermitian dynamics influence the dynamics of the non-ideal exciton
result from the Pauli exclusion interactions between electrons and holes [91] in material systems. It is known
that Pauli exclusion processes operate independently of the widely known coulomb processes in fermion systems, and
contribute to hermiticity of excitonic Hamiltonians [47]. In a recent study [47], the non-ideal bosonic features of
excitons was examined using a non-Hermitian open quantum system approach. The work in Ref. [47] showed that
long-lived quantum coherence in photosynthetic complexes may be assisted by small bosonic deviation measures, and
the involvement of high number of excitons during energy exchanges could help realize a highly correlated molecular
environment conducive to energy transport.

The rich dynamics inherent in non-Hermitian quantum dynamics remains to be fully exploited, especially in studies
involving the non-equilibrium quantum dynamics of dissipative molecular systems. In a recent work, Yi et. al. [40]
introduced complex terms for the inter-site couplings for the Fenna-Matthews-Olson (FMO) complex, and obtained
higher maximal energy transfer efficiencies compared to efficiencies linked to real inter-site couplings. An earlier
work [84] which examined the non-Hermitian two-level dimer system showed that coherence features persisted under
certain environment conditions. Of specific significance is the demonstration that exceptional points may appear at
critical temperatures for the dimer model [84]. The results in Ref. [84] also showed that some coherence features
were retained during evolutions when the couplings of different subsystems to the environment becomes equal to each
other. The subsystems of the dimer are seen to be unmeasured by the environmental sources when there is equivalent
couplings to the dissipation channels. To this end, the indistinguishability of the sources of decoherence may result
in the preservation of some coherence during dynamics of the photosynthetic dimer system.

A. Quantum measurements and quantum photosynthesis

The subject of quantum measurements is a critical area of investigation in the foundations of quantum mechanics,
as it well known that the interface between theoretical models and realistic outcomes (such as optical spectra) lies in
direct measurements. Quantum systems undergoing measurements have counterintuitive properties, with the state of
the system altered as a result of measurement. The boundary between classical and quantum physics is blurred by
quantum measurements. In general, the results obtained in experiments are very much dependent on the instrument
setup, and the quantity that is being determined and quantified via measurements. It is possible that other quantum
signatures may be present (aside from coherence oscillations) and has not, to date been detected or observed due to
the coarse resolutions of the monitoring instruments.

Quantum measurements involve the use of large-scale macroscopic devices to elucidate quantum features of a small-
scale microscopic systems (e.g. photons). This procedure is based on the assumption that superpositions present
in a system of dimensions that scales several orders of magnitude smaller than that of the monitoring system, is
transferred to the macroscopic measuring device. It certainly appears rather challenging to justify this assumption.
Hobson [92] proposed that in the case of an apparatus performing ideal measurement that is able to distinguish
between the distinct entities of a superposed system, the composite system-apparatus state becomes entangled by
virtue of the Nonlocality attribute. Thus the unitary evolution of the global composite state is left intact, and there
occurs coherent transfer of the original superposition present in the observed system to the global superposed state.
These results are verifiable using nonlocal two-photon interferometry experiments [92], and can be used to improve
tomography techniques of fragile quantum systems [29, 31].
The deep links between quantum measurement and the peculiar features of biosystems that yield enhanced energy transfer efficiencies is a promising area for future studies, in view of advancements in tomography based reconstructions of the density matrix of entangled systems [30]. Through tomography measurement techniques [33], it may be possible to map out the global density matrix of multipartite states in large biomolecular systems. The inclusion of quantum measurement principles is expected to assist in the examination of correlation measures, particularly in the vicinity of the exceptional point, and in the understanding of the quantum dynamics of light harvesting systems.

V. ROLE OF NON-MARKOVIANITY IN QUANTUM PHOTOSYNTHESIS

Non-Markovianity is a property that is intricately linked to the violation of the trace preserving, completely positive (CP) mapping attributes of quantum dynamical semigroups [68, 69]. The mathematical maps in Markovian environments, possess divisibility and provide tractability when characterizing the evolution dynamics of memoryless quantum systems. As mentioned in Section III, this numerical tractability was the key reason for its use in earlier works [57]. Non-Markovian dynamics dominates in the presence of strong system-environment coupling regime or when un-factorized initial conditions exist between the system and environment. Pechukas [94] showed that non-Markovianity may be present as an artifact of the product of the initial conditions, \( \rho_s(0) \otimes \rho_r(0) \), where \( \rho_s (\rho_r) \) denote the density operator specific to the system, s (reservoir, r). There seems to be a non-observance of a statistical interpretation for the reduced dynamics of the quantum system as a result of non-Markovian dynamics. While it is known that non-Markovianity arises as a result of the interconnectedness of past and future events and quantum interferences, the origins of this peculiar attribute in quantum systems still remains unresolved.

Current measures of non-Markovianity are generally based on the deviations of existing quantum structure from the continuous, completely positive semi-group attributes of Markovian evolution characterized by the dynamical map \( \rho(0) \rightarrow \rho(t) = \Phi(t, 0)\rho(0) \). Due to varying characteristics of different distance measures (e.g. trace distance, Bures distance, Hilbert-Schmidt distance [28]), there is no unique quantifiable measure of non-Markovianity in quantum systems. The distinguishability quantified by the decrease in the trace-distance, \( D[\rho_1, \rho_2] \) between two system states, \( \rho_1, \rho_2 \) is well known measure, that does not increase under all completely positive, trace preserving maps [95]. Accordingly, \( \sigma = dD[\rho_1, \rho_2, t]/dt \) assumes respective negative or positive values, when information flows outwards or into a system, that is coupled to its environment. The increase of trace distance during any time interval is therefore taken as a signature of non-Markovianity [95]. An alternative measure is based on divisibility [68, 69], which incorporates the characteristics of quantum correlations of the ancilla component of an entangled system evolving under a trace preserving completely positive quantum channel. There has been discussions related to the equivalence of these two measures of non-Markovianity, with agreements that the underlying generic features of the quantum system remains a critical factor for the two measures to be reconciled. There are other measures, some of which that are easily computable, introduced in recent years, however we omit discussion of these for the sake of brevity. Nevertheless, the myriad of ways that non-Markovianity can be examined only serves to highlight the challenges in adopting a rigorous study of the contributions of non-Markovian dynamics to coherent oscillations in photosynthetic systems.

We consider briefly earlier studies on the role of non-Markovianity in enhancing the photosynthetic activities of biomolecular systems. Several works have shown that the environment noise (both Markovian and non-Markovian) can enhance the propagation of energy in light harvesting systems [11, 53, 68, 67], with the fine interplay between quantum coherence and environmental noise determining the optimal functionality of photosynthetic systems. Non-Markovian processes are generally prominent in the reorganization energy regime [61] where the energy transfer efficiency is the highest. This may be due to preservation of coherences along critical pathways, as non-Markovian effects have been noted to increase the lifetime of entanglement [67]. The exciton entanglement dynamics of the Fenna-Matthews-Olson (FMO) pigment-protein complex in an earlier work [12] also showed increased oscillations of entanglement in the non-Markovian regime. Violations of forward time translations may interfere with the optimal balance of quantum and incoherent dynamics required for efficient energy transfer, however this possibility needs further verification via rigorous numerical computations using realistic parameters of photosynthetic systems.

In a recent work [68], we examined the non-Markovian dynamics in a multipartite system of two initially correlated atomic qubits, each located in a single-mode leaky cavity that is coupled to a bosonic reservoir. The atom-cavity-reservoir system is analogous to the photosynthetic model that constitutes the donor and acceptor protein pigment complexes, coupled to the third party represented by the phonon dissipative sink (see Fig. 4). This work showed the dominance of non-Markovian features in several two-qubit partitions, and in particular, highlighted that non-Markovianity in the cavity-cavity subsystem was optimized in the vicinity of the exceptional point. It was noted that the fidelity of the cavity-cavity partition experiences a minimum at this unique topological point [68]. This result demonstrates that segments of biomolecular chains may act as quantum channels, and local minima in the fidelity measures could arise due to merging of the two eigenvalues at the topological defect. In another related study on
FIG. 4: Simplified model of the donor and acceptor protein pigment complexes with discrete energy levels, in which the acceptor is linked to a dissipative sink reservoir with continuous frequency spectrum. Energy from the acceptor flows into the reservoir with time.

photosynthetic systems [55], the time domains involved during effective Zeno or anti-Zeno dynamics have been noted to be of the same order of magnitude as the non-Markovian time scale of the reservoir correlation dynamics. An earlier study [55] highlighted the subtle links in decay rates due to the Zeno mechanism and information flow between specific partitions of entangled systems. These findings have implications for a joint Zeno effect-non-Markovian action in the critical tripartite states of the donor-acceptor-sink model of photosynthetic biosystems.

VI. COHERENCE AND ENTANGLEMENT

Despite the wide range of techniques employed in modeling studies and experimental observations of oscillatory structures, processes of classical origins and those with an intrinsically quantum mechanical coherence origins have not been fully demarcated in light harvesting systems. The detection of the transition point at which a classical world departs to give way to one dominated by quantum effects remains unresolved, even though there are distinct differences between classical and quantum systems. There exist no transformation in which a quantum world can be mapped onto a larger region of deterministic outcomes, however it can be conjectured that elements which are uniquely quantum vanish beyond a critical system size. Experimental results point to the possibility that photosynthetic systems possess a greater content of quantum correlations, and for this reason, the role of coherence and entanglement entities play a critical role in their dynamics in noisy conditions.

The appearance of quantum entanglement allows the maximal knowledge of a composite system, but does not come with the freedom to assign a specific state to subsystem without discarding its links to other subsystems. This includes one of several puzzling properties of quantum states, with quantum entanglement noted as a valuable resource for the implementation of quantum computation and quantum communication protocols [28, 99, 100]. These protocols include quantum teleportation [101-103], dense coding [104], quantum cryptography [105, 106] and remote state preparation [107]. Entanglement as an entity is capable of continual destruction and regeneration in a composite system-environment setup [108], even if no prior correlation existed between the subsystems. In some systems, entanglement may vanish at a certain finite time prior to the decay of the coherences [109-112, 114]. These issues are a topic of interest, as entanglement as a resource is meaningless if it vanishes rapidly.

Separable or non-entangled states may possess other kinds of non classical correlations such as the quantum discord [113-117], based on the difference between quantum and classical information content in entangled systems (see Fig. 5). The quantum discord is more robust than entanglement, and is not susceptible to sudden death occurrences. The discord entity can also be created by local operations on the measured system via non-unital channels [118]. Interestingly, in the case of two-qubit states undergoing non-dissipative decoherences, it is possible that the discord remains resilient under certain conditions during non-Markovian evolutions [119]. The occurrence of a constant quantum discord has been demonstrated in an earlier work on the quantum processing attributes of J-aggregate systems [120]. There are other interesting properties of this measure, such as, two positive discord states can be mixed to obtain a zero-discord classical state, and zero-discord classical states in orthogonal directions can be merged.
FIG. 5: Relationship between conditional quantum entropies $H(A|B)$ and $H(B|A)$, mutual information $I(A:B)$, the locally accessible classical correlation $J(A:B)$ and the inaccessible information quantified by the quantum discord $D(A:B)$. $J(A:B)$ is the maximized content obtained by measuring $B$.

The quantum discord is not restricted by the monogamy rule which is a requirement for the concurrence measure during entanglement sharing.

The intriguing features of quantum discord described in the earlier paragraphs, have potential applications within the non-Markovian environment of light harvesting systems. The discord measure as well as other non classical correlations may be used to examine the occurrences of quantum phase transitions and quantum communication protocols in biomolecular systems. It has been noted that for all known quantum information protocols dependent on quantifiable two-qubit discord, there exist noisy evolutions in the state space for which coherence is preserved and where communication protocols are unaffected by noise. The theoretical framework under which these result were obtained, may be easily extended to examine the presence of strong coherences, in the noisy environments of photosynthetic systems.

There have been few genuine attempts to link entanglement and the quantum discord measure to processes which sustain bio-cellular activities at physiological temperatures. There are obvious difficulties to these efforts, as the relationship between coherence and entanglement remains subtle, with no known demonstrable explicit link. Decoherence in open quantum systems may take an infinite amount of time to vanish unlike entanglement. This may be due to factors such as the degree of robustness of the initial state of the quantum system under study, and presence of non-Markovian dynamical entities. It is highly likely that robustly entangled states as initial states are more resistant to decoherence processes than uncorrelated states at the start. Thus the number of molecular sites excited by photons, as well as the intensity of illumination at the antenna sites, are key factors involved in further understanding the coherence phenomena in biosystems.

VII. MULTIPARTITE STATES IN LIGHT HARVESTING SYSTEMS

Entanglement or non-classical correlations that spans over several lattice sites, may be represented by multipartite states. For instance, a qubit state $\Psi$ associated with $N > 2$ subsystems appear in the multipartite state form as

$$|\Psi\rangle = \sum_{n=1}^{N} c_n \left( |0\rangle^{\otimes (n-1)} \otimes |1\rangle \otimes |0\rangle^{\otimes (N-n)} \right)$$

with coefficients $c_n$, and $|0\rangle, |1\rangle$ are orthonormal basis vectors of a two-dimensional state space. The symmetric Dicke state with just one excitation appear as

$$|W_N\rangle = \frac{1}{\sqrt{N}} \left( |100...0\rangle + |010...0\rangle + ... + |001...0\rangle \right),$$

where $N$ is the number of subsystems.
while the GHZ states are obtained as

$$|GHZ_N\rangle = \alpha |0\rangle \otimes |0\rangle \otimes \cdots |0\rangle + \beta |1\rangle \otimes |1\rangle \otimes \cdots |1\rangle$$

where $|\alpha|^2 + |\beta|^2 = 1$. Multiparticle states possess a rich source of local and nonlocal correlations due to the multitude of partitions available within a group of entangled qubits, and have relevance in the realistic situation of an entire photosynthetic membrane constituting many FMO complexes and thousands of bacteriochlorophylls. Such a structural platform facilitates the formation of a large cluster of massively entangled excitonic qubits. Multiparticle states are generally fragile compared to bipartite states, and in this regard, appear unlikely to play a dominant role in the presence of decoherence effects in organic systems. However there have been predictions that such states can exist even at physiologically high temperatures \([12, 124]\) in solids, and play an important role in the quantum properties of molecular systems.

Multiparticle states are also of interest in photosynthetic systems, from the point of the “principle of quantum information causality”, founded on the mathematical formulations of quantum information causality \([125]\). This principle states that the maximum amount of quantum information that can be transferred from one state to another, is bounded by the quantum system’s dimension, and is not reliant on any physical resources previously shared by the communicating states. The dimension of a quantum system here, refers to the number of different possible pathways available to a measured system. This means that light harvesting systems with large dimensions hold higher quantum communication capacities, and multiparticle states are favorable participants of quantum information processing during photosynthesis.

Unlike bipartite states, the examination of the robustness of quantum states is a challenging task in multiparticle states, as the entanglement and non-classical correlations are not to easy categorize. There also exist no simple route to the specification of entanglement or quantum discord in multi-state quantum systems. There are variations in the robustness of different types of multiparticle states (Dicke, GHZ, W or cluster states) under decoherence processes as noted in earlier studies \([126, 127]\). For instance, the W state is known to be highly robust in its genuine multiparticle entanglement with respect to loss of a single excitation \([128]\). However it is uncertain whether the W state is more robust against decoherence than the GHZ states, mainly due to the incompatibility of comparison of the dynamics of the two types of states during a decoherence process. The W states belong, in the case of the three qubit symmetric pure states, to the group characterized by two distinct Majorana spinors \([129]\). On the other hand, the GHZ states belong to the group characterized by three distinct Majorana spinors. In the case of GHZ states which undergo decoherence \([113]\), the entanglement decays faster when there is increase in the number of initially entangled particles. Differences between the GHZ and W states also exist in terms of their polygamous nature, for instance, the generalized W states can be mono or polygamous while the generalized GHZ states exhibit only monogamy features with respect to the quantum deficit measure \([129]\).

We have examined the exciton entanglement dynamics of the Fenna-Matthews-Olson (FMO) pigment-protein complex from the green sulfur bacteria of the species, Prosthecochloris \((P.)\) aestuarii \([130]\) using typical values of the reservoir characteristics at cryogenic and physiological temperatures \([12]\). The light-harvesting system was considered as a global system constituting several smaller subsystems interconnected via quantum correlations, where the important contribution of specific tasks such as teleportation \([101, 102]\) and quantum state splitting \([131, 132]\) within a noisy environment was demonstrated. In Ref. \([12]\), the exploration of how quantum communication protocols such as quantum teleportation \([101, 102]\), and quantum secret sharing \([132]\), are utilized by multiparticle states to assist energy transfer in photosynthetic processes was detailed. It was shown that in largely extended light harvesting systems with intricate network connectivity, multiparticle states appear robust with respect to decoherence processes \([12]\). In particular, quantum information processing involving teleportation followed by the decodification tasks in W states of the FMO complex may account for experimental results which show persistence of coherent oscillations at physiological temperatures.

Recently, a protocol called quantum energy teleportation (QET) \([133]\) was proposed to show the viability of energy teleportation, thus a quasi-particle is able to effectively transfer energy to another point in space via local operations and classical communication. The elegance of this proposal \([133]\) lies in the fact that it is information instead of tangible energy that is transferred to the distant site, consequently there is no violation in energy conservation nor generation of heat during the propagation of quantum information. This principle may be extended to examine teleportation processes in photosynthetic systems, where information transfer between specific sites results in extraction of energy from the surrounding phonon bath environment. The interplay between information and energy in correlated biomolecular systems has implications for possible role of quantum thermodynamical principles, which we examine next.
VIII. QUANTUM THERMODYNAMICS, ENERGY AND INFORMATION

Thermodynamic principles are traditionally used to track with accuracy, processes that involve exchanges of energy and work in classical systems. The translation of similar schemes to quantum systems has been an intense area of investigation in the last few years [134–141], despite the well known links between information theory and thermodynamics, based on the parallels between Shannon’s uncertainty function and the entropy function. This is due to the challenges involved in categorizing work in terms of entanglement, mutual information, quantum discord and other probabilistic measures of correlations (both classical and quantum). As a consequence of the varying characteristics of different correlation measures, there appears to be no single quantifiable measure, or a unique definition of work or energy dissipation in quantum systems. The identifiable measures of work in quantum systems have a statistical distribution linked to various evolution routes taken by the quantum systems. In this regard the work or energy transformations that occur in quantum systems are distinctly different from analogous measures present in classical systems. Interestingly, the work measure in quantum systems has a rich structure attached to it by the inherent link between a probabilistic interpretation of work or energy, and quantum statistical mechanics in the non-equilibrium regime. These reasons form the key motivation to include the role of quantum thermodynamics in light harvesting systems which operate in the “far-from-equilibrium” regime.

Initial studies of links between thermodynamics and quantum correlations commenced with demonstration of the association between energy and information theory, in the context of computation energy cost [142]. Landauer’s erasure principle showed that any irreversible process expands work due to the entropy transfer from the degrees of freedom, coded as information entities outwards into the environment [142]. Decades earlier, Szilard had used the Maxwell’s demon model to show that $k_B T \ln 2$ of work can be extracted from a thermodynamic cycle, and highlighted that a positive entropy production in measurement compensates for the work gain [143]. This ensures that the second law of thermodynamics is left intact. This idea has recently been used to compute the binding energies of composite boson systems [144], and may be extended to examine non-ideal photosynthetic excitons from a quantum informative-theoretic perspective.

The extension of thermodynamic principles to non-equilibrium conditions is a very challenging task. The mathematics of non-equilibrium statistical dynamics appear tractable only in the near-equilibrium regime with approximately linear structures. To this end, the entropy production fluctuating theorem [145], differs from several mathematical formalisms in its applicability to states that are operating in the far from equilibrium regime. This theorem stems from the Jarzynsky relation [146] that is applicable to states undergoing dynamical evolutions in unstable regimes, The Jarzynski relation [146] yields a neat and tractable relationship between the distribution of work performed on a classical system by an external force and the free energy difference between the initial and final states. The significance of the Jarzynski relation lies in the fact that quantities at equilibrium, such as energies, are linked to non-equilibrium paths associated with measurements. Though the relation has been obtained for classical systems, it holds equally well for quantum systems, as demonstrated recently [147].

The principles of the Szilard engine has been extended via the fluctuation theorem [145] to the formulation of thermodynamic work based on a time forward and backward shifting technique [135]. The average dissipated work $\langle W \rangle_{\text{diss}}$ required to translate a system from one canonical equilibrium state to another one without change in temperature $T$ is obtained as [135, 148]

$$\langle W \rangle_{\text{diss}} = \langle W \rangle - \Delta F = kT \langle \ln \frac{\rho}{\bar{\rho}} \rangle. \quad (7)$$

$\langle W \rangle_{\text{diss}}$ is therefore the additional work, other than the difference in free energy $\Delta F$, that is required for the transition process. $\rho = \rho(\Gamma; t)$ is the probability density associated with observing the system in the micro-state $\Gamma = (q, p)$, at time $t$ for position (momentum) $q, p$. $\langle \cdots \rangle$ denotes the averaging of $\rho$, and $\bar{\rho} = \bar{\rho}(\bar{\Gamma}; t)$ is the time-reversed distribution observed at phase point $\bar{\Gamma} = (q, -p)$ for the same duration as the forward process.

The dissipated work (7) is also obtainable in terms the relative entropy, $D(\rho||\bar{\rho})$ between $\rho$ and $\bar{\rho}$ [136]

$$\langle W \rangle_{\text{diss}} = kT D(\rho||\bar{\rho}), \quad (8)$$

where $D(\rho||\bar{\rho})$ is the relative entropy between $\rho$ and $\bar{\rho}$. From Eq(8) the gain in total entropy (system plus heat bath) in the forward process, $\Delta S$, is given by [136]

$$\Delta S = k \langle \ln \frac{\rho}{\bar{\rho}} \rangle = kD(\rho||\bar{\rho}). \quad (9)$$

The classical result in Eq. 9 can be seen in quantum settings via extension of $D(\rho||\bar{\rho})$ to its quantum counterpart based on the relative entropy [147, 149]
Unlike the classical entropy measure, the quantum entropy obeys the sub-additivity property, which results in subsystems acquiring a greater entropy than the whole system. Eq. (9) reveals the deep links between dissipation and the non-Markovianity measure. As pointed out in Section V, the latter is linked to non-divisible maps in systems which undergo non-contractive quantum evolution and can be represented by the relative entropy, \( D(\rho\parallel \tilde{\rho}) \). We note that \( D \) is essentially a distance measure. This means that the quantity of dissipated work, \( \langle W \rangle_{\text{diss}} \) decreases with time, during a positive Markovian process. Conversely, the rate of increase in the dissipated work at \( t' > t \) is sufficient but not a necessary signature of non-Markovianity. Other works \cite{135, 136} have shown that the work extracted from a system is determined by the mutual information present in the system-environment configuration, and quantum correlations can be quantified based on thermodynamic principles \cite{137}. In a study on multipartite systems \cite{138}, the connection between entanglement generation and work power was shown, with optimal work extraction achievable without generation of any form of entanglement. However it is possible that entanglement can be created with extraction of a large power output \cite{139}. It would be worthwhile to pursue these ideas within the correlated environment of molecular systems in future investigations involving quantum thermodynamics aspects of photosynthesis.

A. Predictive Power

Recently, a vivid and rather profound view of the system-environment dynamics was given in terms of the system’s ability to predict its future interactions with one or more sections of its surroundings in classical systems \cite{140}. In the case of living systems, the ability of the biological system to “foretell” future events is fundamental to increasing the survival of the supported species, as it increases the success rate of various tasks needed for cellular functioning. The change in system state as part of its response to a changing environment may be interpreted as a form of implicit computation that is performed by the system. This gives rise to un-factorized states of existence of the system-environment system due to temporal correlations at all times (past and future). In systems that possess predictive power \cite{150}, it was shown that the information theoretic measure of the inefficiency of the predictive process (the non-predictive information) can be equated to thermodynamic inefficiency. This inefficiency is based on the work dissipated during the duration that the system evolves from one point to another. The ideas proposed by Still et. al. \cite{150} highlight that the effective use of information and efficient thermodynamic operation are intertwined operations, and best studied as dual measures during the evolution of a system.

The connections between predictive power of information entities and thermodynamic processes has been extended to quantum systems in a very recent work \cite{140}. It was shown that the change in system entropy, conditional on the presence of relevant environmental variables, is a measure of the computation’s thermodynamic inefficiency based on the entropy change \cite{140}

\[
\beta W_{\text{lost}}[\rho_{S,X} \rightarrow \rho'_{S,X}] = \ln 2[H(S|X') - H(S|X)] = \ln 2[I(S : X) - I(S : X')],
\]

where \( \beta = 1/k_B T \) denotes the inverse temperature, and meanings of the entropy terms \( H(S|X'), H(S|X), I(S : X) \) appear in Fig. 5. \( S \) and \( X \) denote respectively, the finite quantum system, and \( X \) is a subset of the surrounding environment that is correlated to \( S \). \( X \) evolves via

\[
\rho_X \rightarrow \rho'_X = \mathcal{E}(\rho_X)
\]

where \( \mathcal{E} \) denotes a quantum channel.

Grimsmo \cite{140} employed a simple quantum model to illustrate that the entropy change is a measure of ineffective use of information \cite{140}, consistent with the idea demonstrated earlier for classical systems \cite{150}. Environmental coherence of the central system was shown to improve predictability to an amount quantified by a negative (quantum) constituent of the dissipated work \cite{140}. The thermodynamic inefficiency of the most energetically efficient classical approximation of a quantum system provides an operational interpretation to quantum discord. Thus for the case of two correlated systems, \( A \) and \( B \), the non-predictive quantum information held by \( B \) equals its lost work potential if the system \( A \) changes state, and in the case where \( A \) assumes a classical state, the lost work is given by the quantum discord present in \( B \) before the change. Therefore the quantum discord can be seen to quantify the reduction in work potential under an optimal classical approximation of some part of the system surroundings \cite{140}. We note that in an earlier work \cite{141}, the operational definitions of the quantum and classical correlations in a bipartite quantum state was given in terms the amount of work needed to erase various types of correlations. In particular, the work required to erase the quantum correlation is one that will culminates in the appearance of a separable state, the mutual information was specified in terms of the minimal work needed to reduce a bipartite system to a product state, eliminating all traces of correlations \cite{141}. 

Systems with high predictive powers have implications for the semigroup law and contractions in the Hilbert space of Hilbert-Schmidt operators, with likely violations of forward time translations. Non-Markovianity and quantum predictability may have similar origins, and investigations of possible common grounds will contribute to further understanding of the thermodynamic operations of biomolecular systems during photosynthesis. We emphasize that the concept of a system’s predictive power with respect to a changing environment, remains to be tested within a non-Hermitian framework. In this regard, there are ample opportunities to seek out new findings within the myriad of models where non-Hermitianity can manifest itself, other than in the case of biomolecular systems.

B. Far from equilibrium regime in light harvesting systems

Based on the discussions in the earlier sections, it is clear that thermodynamic principles from an information theoretic review, has practical relevance in the highly correlated environment of light harvesting systems. As the photosynthetic process involves a sudden creation of an initial excitation, the biomolecular system is transferred to a “far from equilibrium” operating regime. The interconnected biomolecules and the surrounding environment undergo rather chaotic fluctuations determined by external parameters (temperature, solar illumination). The non-equilibrium dynamics involves a complex interplay of system-environment dynamics and non-Markovian predictive-type back-action of the environment on the system. Depending on the spectral profile of the environmental bath, there is rapid shift to an equilibrium state (short bath memory) or a non-equilibrium state of system-environment (long bath memory).

We note that both the Crooks [143] and Jarzynski equality relations [144] are valid for open quantum systems [147], and independent of the system-environment coupling strength and structures present within the thermal environment. The quantum versions of the fluctuation relations therefore, are suitable to be applied to the quantum environment of biomolecules at higher temperatures, quantum systems that undergo “far-from-equilibrium” fluctuations, may incorporate useful information based on predictive powers, that is distinct from a background noise. The system’s predictive ability [150] may enable some robustness against decoherence, similar to the comparatively long duration of strong coherent oscillations observed in spectroscopy experiments. It is expected that parameters linked to any form of structure within the environments other than white noise, may be critical to the embedded system’s predictability, with influence on the complicated interplay between different entities of quantum correlations. The embedded system itself may use its predictive abilities to tune or even select favorable characteristics of the environment giving rise to fluctuations that result in optimized transport properties. Quantum systems may “select” the range of parameters where there is matching in time scales operating within the system and those of the system-environment time scales, as is the case in photosynthetic systems. These issues imply some patterns of evolution based on a continuous process of realizing optimality of critical activities within a biological network of biomolecules embedded in chaotic environments, and relevant to the correlated, “far from equilibrium” dynamics of photosynthetic systems.

The thermodynamic efficiency appear as a viable measure of the ability of molecular systems to dissipate minimal solar energy, while transporting the reserve energy from the receiving end to the destination site where energy conversion takes place. This operational efficiency highlights the need to comprehend the fundamental quantum thermodynamics processes at work, and the factors that govern the energy conversion at the reaction center [151]. Light harvesting systems viewed as quantum thermodynamic optimal machines, also provide a reliable framework from which salient observations can be made, and applied to other structures which are independent specific biochemical features such as neural network structures. Schneider [152] has highlighted the use of Shannon’s theorem for communication channels to describe “machine capacity” of molecular systems. The availability of a complex coding of a molecular machine’s operation improves its efficiency (by reducing the frequency of malfunctioning). While dissipation processes and thermal noise restricts the “machine capacity”, there is opportunity to increase the chances of survival by careful control of the accuracy of information exchanges between the distinct components constituting the organism. These ideas are expected to provide further insight into one of nature’s best nano-machines, and reveal vital clues to fabrication of artificial quantum molecular systems.

C. Agent-based modeling and simulation approach of photosynthetic biomolecular systems

The scenario that that biomolecules “think” and “act” like intelligent biological networks [152–155] may appear far fetched, however the presence of these attributes may be investigated via an agent-based modeling and simulation approach [156–158]. Tasks that require some self-learning may be formulated as the optimization of expected outcomes (such as the high conversion efficiencies) within the framework of quantum correlations that operate in some specific subspaces, that can be considered as domains of agents. In more a simplified model involving the green sulfur bacteria, each FMO monomer may be viewed as an independent unit endowed with quantum correlations that mimic
the role of interacting agents. These agents may obey a set of basic rules as well as self-learning rules that adapt to a changing environment, and therefore possess quantum memory which may coded as classical or non-classical correlations. Overall, the agent seeks to achieve a set of goals, and in the case of photosynthetic biological structures, this would be to maximize energy transfer with the optimum efficiency that is achievable at the prevailing environmental conditions. While the agent is considered to act independently, the further extensions of these ideas to an emergent behavior attributed to a collection of multi-agents may be examined in simulation studies of light harvesting systems. Furthermore there is motivation to pursue the links between agent-based rules and the quantum predictive power proposed in Ref. [140], to examine the optimality of biomolecular structural layouts for energy transport and other information processing properties.

IX. CONCLUSIONS

In the preceding sections, we have discussed various topics of importance to studies of quantum correlation dynamics in natural light harvesting systems. The last ten years has seen a surge of interest in this topic, with agreements and conflicting results between different research groups. This should not be surprising as there are differing interpretations, and approaches of undertaking quantum mechanical studies, including attempts to extract quantum structures in highly complex systems of molecular structures. There have been numerous studies with various perspectives and terminologies that has been proposed in the literature, and we remind readers that only some references have been represented in this review. And the challenges of dealing with some seemingly basic foundations of quantum physics, must be held in view, when quantum information-theoretic interpretations are made of experimental results of light harvesting systems.

Two critical measures based on the efficiency of energy propagation, and robustness in quantum coherence appear vital to photosynthetic processes. While the energy transfer efficiency is linked to the overall network connectivity and structural configuration of biomolecules, the strength of quantum coherence appears to be dependent on the system’s response to a changing environment. There is a fine interplay between two seemingly counteracting effects, one based on maintenance of structure while the second is dependent on a changing environment. This review has examined some possible ways to unify these core functions of the light harvesting process, via use of the elements of quantum informative protocols and quantum thermodynamical principles. The examination of the links between the predictive power, non-Markovianity and thermodynamic quantities presents a rigorous and unified approach that could provide deep insights to understanding nature’s mode of energy propagation. Future investigations using these ideas will help seek further understanding of the links between quantum rules and nature’s design of biological network structures, that constitute living forms which harvest solar energy with remarkable efficiencies.

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