

# Natural light harvesting systems: unraveling the quantum puzzles

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**Abstract** 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. The high speed of excitation 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 observations of long lived coherences lasting several picoseconds in the electronic spectra of photosynthetic complexes, which occurs 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 the answers to nature's puzzling mode of energy propagation. This review presents recent 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

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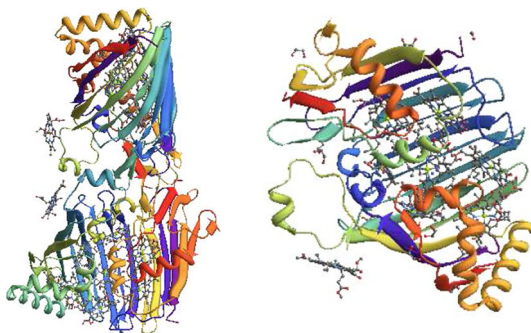
principles and agent-based modeling and simulation approaches can improve our understanding of natural photosynthetic systems is included.

**Keywords** Exciton dynamics · Quantum coherence · Non-hermitian · Non-Markovianity · Composite bosons · Hilbert space · Light harvesting complexes

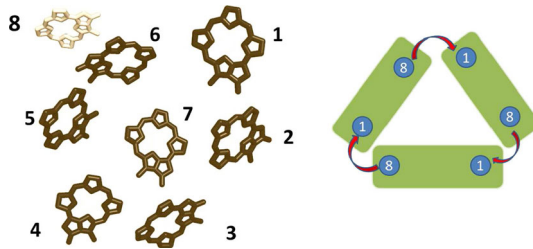
## 1 Introduction

Photosynthesis is an important quantum process which contributes significantly to the world's yearly biomass yield. During photosynthesis, 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 for 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 enabling excitation propagation even in adverse, noisy environments.

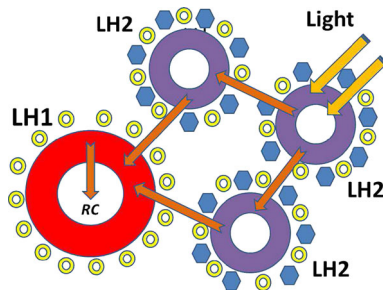
The absorption of a photon results in the formation of an excited quasi-particle known as the exciton (correlated electron-hole pair), on one or more optically active molecular sites occupied by molecular complexes, known as chromophores. One well studied pigment-protein complex is the Fenna–Matthews–Olson (FMO) complex of the green sulfur bacteria [21–29] 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, and availability of a wide range of experimental results for this system. The FMO complex trimer is made up of three symmetry equivalent monomer subunits, with each subunit



**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



**Fig. 3** Schematics of the photosynthetic apparatus of purple bacteria, in which the yellow carotenoids and different BChls protein complexes (blue, purple and red) absorb solar energy. The excitation is transferred via excitonic propagation (indicated by orange arrows) from the LH2 antenna complexes to the LH1 complex, and then to the reaction center (RC) where energy conversion to chemical form occurs. This figure is based on the photosynthetic apparatus scheme which appears in Ref. [19]

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 excitations. 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), and 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 play an important role by transferring energy to the LH1 complex. Hence the photosynthetic apparatus of both the green sulphur and purple bacteria are formed from molecular complexes with two distinct roles based on whether the molecular complex is directly or indirectly linked to the reaction center.

The FMO complex exhibits strong quantum beating lasting ( $> 600$  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 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 to a high degree of accuracy [30–35].

## 2 Exciton dynamics of the FMO complex

In this section, we examine the exciton dynamics of the Fenna–Matthews–Olson (FMO) complex using the site energies of the BChl molecules based on experimental findings of its crystal structure [36]. The coupling energies between BChl molecules derived using the dipole-dipole approximation are obtained from Ref. [37]. Photon absorption by a BChl molecule causes a newly created exciton to spread rapidly to the adjacent units while interacting with a bath of phonons. The propagating exciton may be distinguished from an excitation localized at a specific BChl site. Excitonic states can be represented as qubit states by associating a qubit with the presence (or absence) of an exciton at a specific energy level determined by the exciton Hamiltonian. Each energy level is then modeled as a two-level system, using  $|0\rangle_{e_i}$  ( $|1\rangle_{e_i}$ ) which denotes the absence (presence) of an excitation at the specified energy level  $j$ . One or more BChl sites may contribute predominantly to a specific qubit state, as will be shown shortly. We employ the effective exciton Hamiltonian defined in the basis of the  $Q_y$  one-exciton states, where the  $Q_y$  bandwidth is associated with the lowest excited state of the BChl molecule. Using known site and coupling energies between BChl molecules [36, 37], the Hermitian Hamiltonian,  $\hat{H}_{ex}$  of the FMO complex with eight BChl sites is given in units of  $\text{cm}^{-1}$  as

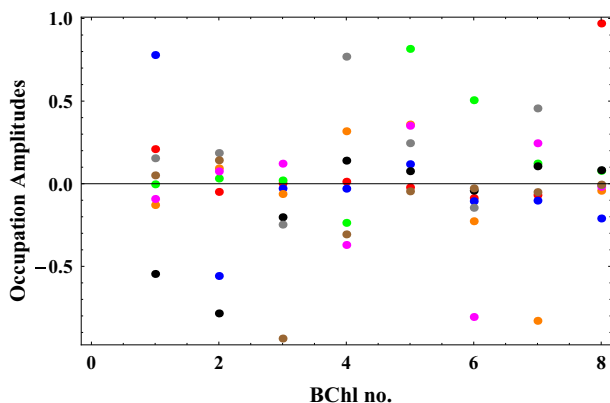
$$\hat{H}_{ex} = \begin{pmatrix} 310.0 & -97.9 & 5.5 & -5.8 & 6.7 & -12.1 & -10.3 & 37.5 \\ -97.9 & 230.0 & 30.1 & 7.3 & 2.0 & 11.5 & 4.8 & 7.9 \\ 5.5 & 30.1 & 0.0 & -58.8 & -1.5 & -9.6 & 4.7 & 1.5 \\ -5.8 & 7.3 & -58.8 & 180. & -64.9 & -17.4 & -64.4 & -1.7 \\ 6.7 & 2.0 & -1.5 & -64.9 & 405. & 89.0 & -6.4 & 4.5 \\ -12.1 & 11.5 & -9.6 & -17.4 & 89. & 320. & 31.7 & -9.7 \\ -10.3 & 4.8 & 4.7 & -64.4 & -6.4 & 31.7 & 270 & -11.4 \\ 37.5 & 7.9 & 1.5 & -1.7 & 4.5 & -9.7 & -11.4 & 505.0 \end{pmatrix}. \quad (1)$$

**Table 1** Delocalized exciton qubit states provided as linear combinations of probability occupation amplitudes associated with the eight BChl sites

	$E_x(\text{cm}^{-1})$	BChl 1	BChl 2	BChl 3	BChl 4	BChl 5	BChl 6	BChl 7	BChl 8
$ 1\rangle_{e_8}$	514.3	0.209	-0.049	0.002	0.012	-0.022	-0.087	-0.069	0.969
$ 1\rangle_{e_7}$	478.4	-0.004	0.032	0.020	-0.237	0.816	0.505	0.122	0.078
$ 1\rangle_{e_6}$	374.1	0.779	-0.558	-0.029	-0.030	0.118	-0.106	-0.102	-0.210
$ 1\rangle_{e_5}$	303.7	-0.129	0.093	-0.062	0.318	0.358	-0.227	-0.830	-0.042
$ 1\rangle_{e_4}$	262.4	-0.092	0.075	0.121	-0.371	0.351	-0.806	0.245	-0.019
$ 1\rangle_{e_3}$	167.3	-0.546	-0.784	-0.203	0.140	0.076	-0.042	0.106	0.082
$ 1\rangle_{e_2}$	143.9	0.154	0.186	-0.247	0.769	0.245	-0.146	0.456	-0.008
$ 1\rangle_{e_1}$	-24.2	0.051	0.142	-0.937	-0.307	-0.046	-0.028	-0.051	-0.005

The excitonic qubit states are labeled according to decreasing energies ( $\text{cm}^{-1}$ ) for the FMO complex

The eigen-energies and eigenstates of excitations described by  $\hat{H}_{ex}$  (1) can be evaluated to reveal the eight excitonic qubits (labelled in order of increasing energy) as shown in Table 1. Each exciton state appears to be present at two or more BChl sites. For instance, the lowest energy exciton qubit state  $|1\rangle_{e_1}$  with energy  $-24.2 \text{ cm}^{-1}$  is localized at BChls 3 and 4, while the qubit state  $|1\rangle_{e_2}$  with energy  $143.9 \text{ cm}^{-1}$  is localized predominantly at BChls 4 and 7. The qubit state  $|1\rangle_{e_8}$  with the maximum energy  $514.3 \text{ cm}^{-1}$  has maximal localization at BChls 8. In Fig. 4, the probability amplitudes of exciton occupation at the different BChl site is shown, highlighting that each exciton qubit state has simultaneous occupation at several BChl sites, an intrinsically quantum attribute. Figure 4 shows that at some BChl sites, there appears to be clustering of qubits (1, 3, 8) with one qubit appearing with a comparatively large probability amplitude. Interestingly, BChl 8 shows non-trivial amplitudes for some qubits, highlighting its important role during photosynthesis. Earlier works have



**Fig. 4** The probability amplitudes of exciton occupation at the eight BChls of the FMO complex, evaluated using the Hermitian Hamiltonian,  $\hat{H}_{ex}$  in Eq. 1. The eight exciton qubits are coded using *different colored dots*

generally focussed on a model of FMO complex with seven BChl sites, generally ignoring the eight BChl site. Due to the superposed state involving all the eight BChls of the FMO complex, each exciton can be expressed as a linear combination of the excited state wave functions of the individual BChl. We discuss further the implications of the unique state of existence of quantum superposed states under the “coherent propagation scheme” discussed in Sect. 3.

The system of the two-level excitonic qubit in contact with a bath of phonons is described by the Hamiltonian

$$H = \omega_0 \sigma_+ \sigma_- \sum_{\mathbf{q}} \hbar \omega_{\mathbf{q}} b_{\mathbf{q}}^{\dagger} b_{\mathbf{q}} + \sum_{\mathbf{q}} \lambda_{\mathbf{q}} \left( \sigma_- b_{\mathbf{q}}^{\dagger} + \sigma_+ b_{\mathbf{q}} \right), \quad (2)$$

where  $\sigma_+ = |1\rangle\langle 0|$  and  $\sigma_- = |0\rangle\langle 1|$ , are the respective Pauli raising and lowering operators of the exciton with transition frequency,  $\omega_0$ . In order to introduce some degree of tractability, each qubit is considered as coupled to its own reservoir of phonons, which appear as the second term on the right hand side of Eq. (2). The terms,  $b_{\mathbf{q}}^{\dagger}$  and  $b_{\mathbf{q}}$  are the respective phonon creation and annihilation operators with wave vector  $\mathbf{q}$ . The last term of Eq. (2) denotes the qubit-oscillator interaction Hamiltonian which we assume to be linear combination of the phonon operators.  $\lambda_{\mathbf{q}}$  is the coupling between the qubit and the environment and is characterized by the spectral density function, such as,  $J(\omega) = \sum_{\mathbf{q}} \lambda_{\mathbf{q}}^2 \delta(\omega - \omega_{\mathbf{q}})$ .

Analytical expressions for the dynamical evolutions of the excitonic qubit can be obtained by considering Lorentzian forms for the spectral density arising from the interaction between the BChl exciton and the phonon bath

$$J(\omega) = \frac{1}{2\pi} \gamma_0 \left( \frac{\Delta\omega}{2} \right)^2 \frac{1}{(\omega_0 - \delta - \omega)^2 + \left( \frac{\Delta\omega}{2} \right)^2} \quad (3)$$

whose central peak is detuned from the exciton transition frequency  $\omega_0$  by an amount  $\delta$ . The full width at half-maximum  $\Delta\omega$  is linked to the reservoir correlation time  $\tau_B$  via  $\Delta\omega = \frac{2}{\tau_B}$ . The parameter  $\gamma_0$  is associated with the relaxation time scale  $\tau_R$  of the exciton via the relation  $\tau_R = \gamma_0^{-1}$ . The reservoir correlation and exciton relaxation parameters, which are dependent on the temperature, may be employed as semi-empirical variables to reduce the computational times required to examine the dynamics of excitons.

The excitonic qubit decays to oscillator states in the reservoir undergoing a transition from the excited state  $|1\rangle_e$  to the ground state  $|0\rangle_e$ . The initial state of the qubit with its corresponding reservoir in the vacuum state appear as

$$|\phi_i\rangle = |1\rangle_e \otimes \prod_{k=1}^{N'} |0_k\rangle_r = |1\rangle_e \otimes |0\rangle_r, \quad (4)$$

where  $|0\rangle_r$  implies that all  $N'$  wavevector modes of the reservoir are unoccupied in the initial state. The subscripts  $e$  and  $r$  refer to the excitonic qubit and the corresponding

reservoir respectively.  $|\phi_i\rangle$  undergoes subsequent decay of the following form

$$|\phi_i\rangle \longrightarrow u(t) |1\rangle_e |0\rangle_r + v(t) |0\rangle_e |1\rangle_r, \quad (5)$$

We consider that  $|1\rangle_r$  denotes a collective state of the reservoir

$$|1\rangle_r = \frac{1}{v(t)} \sum_n \lambda_{\{n\}}(t) |\{n\}\rangle, \quad (6)$$

where  $\{n\}$  denotes an occupation scheme in which  $n_i$  oscillators with wavevector  $k = i$  are present in the reservoir. We define the state  $|\{n\}\rangle$  as  $|\{n\}\rangle = |n_0, n_1, n_2 \dots n_i \dots n_{N'}\rangle$ . In the collective reservoir state, the phonon oscillators can be present at all allowed modes, including simultaneous excitation of several phonon states.

The time-convolutionless (TCL) projection operator technique [38] is employed to obtain the coefficient  $u(t)$  [see Eq. (5)],

$$\dot{u}(t) = - \int_0^t \int d\omega J(\omega) \exp[i(\omega_0 - \omega)(t - t_1)] u(t_1) dt_1, \quad (7)$$

The Laplace transformation of Eq. (7) with initial condition  $u(0) = 1$  and the form of spectral density in Eq. (3) yields the solution [38]

$$u(t) = e^{-(\Delta\omega/2 - i\delta)t/2} \left[ \cosh\left(\frac{\xi t}{2}\right) + \frac{\Delta\omega/2 - i\delta}{\xi} \sinh\left(\frac{\xi t}{2}\right) \right], \quad (8)$$

where  $\xi = \sqrt{(\Delta\omega/2 - i\delta)^2 - \gamma_0 \Delta\omega}$ . The exciton population difference,  $\Delta P$ , a signature of coherence, has been evaluated [12] using  $|u(t)|^2$  (Eq. (8)). The results in Ref. [12] show that at small  $\Delta\omega/2 \sim 20 \text{ cm}^{-1}$  or large reservoir correlation times and large  $\gamma_0$  (or small exciton relaxation times), there is increased time period (up to 1 ps) over which the population difference,  $\Delta P$  remains resilient. This appears to be in agreement experimental results of the FMO complex of *P. aestuarii* [39]. We have presented a model of exciton dynamics based on a convenient (and semi-empirical) Lorentzian form of the spectral density (Eq. 3) and employed the collective state of the reservoir (Eq. 6). While we have focussed on the quantum dynamics of the FMO complex, the prototypical features of this system related to energy propagation provides a reference point from which the quantum properties of other energy harvesting molecular systems may be examined. In the next section, we discuss the challenges involved in the modeling excitation propagation in organic molecular systems, with emphasis on the unique features presented by the coherent propagation model, which also appears in the results of Table 1.

### 3 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 ( $10 - 100 \text{ cm}^{-1}$ ) 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 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. In general simpler forms of the spectral density of the bath oscillators are assumed (see Eq. 3) to provide tractability, at the expense of accuracy of computed results. In a recent work [29], 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 associated with the excitation transfer between chromophores are noted to be intricately mixed with environmental 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 Sect. 6). Consequently, many findings related to photosynthetic systems involve model systems which are subject to assumptions, introducing 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, 40–43]. In the coherent propagation scheme which we briefly examined in Sect. 2, the exciton is modeled as delocalized excitation which spans the real crystal space [44–48] as an extended entangled system [49–51]. The exciton is considered to be in a state of existence at several lattice or BChl sites (Fig. 3), traversing multiple paths simultaneously, and undergoing a process of continuous interferences. This model is based on Feynman's "sum over histories" rule which incorporates all possible paths between two points, including phase interferences. In essence, it is these interferences which give rise to the uniquely quantum behavior present 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 [49]. In the original implementation of the Grover search [52, 53], 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 [52] showed that only  $O(\sqrt{N})$  steps are required in the presence of quantum interference effects. In Ref. [49] however, the subtle link between the appearance 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 [54–56] 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 induce intra-molecular and inter-molecular transfer of electrons, holes, and excitons, giving rise to radical-molecules with unpaired electrons or a different orientation of spin structures. Importantly, these subtle alterations in spin structure of the biomolecules enable different routes of energy propagation via changes in the chemical environment, and spin-specific responses to the lattice vibrations [57]. To date, the role of molecular spintronics in light harvesting properties has not been fully examined. From a quantum information theoretic perspective, 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.

The search is ongoing for a comprehensive theory which 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 the strong coherences noted in experimental works, despite the presence of a background of oscillators. Lately, we examined links between the observed coherence and the environment-assisted transfer mechanisms based on the Zeno-effect [58]. The quantum Zeno effect is the retarded time evolution of a quantum state subject to frequent measurements, with the reverse effect resulting in enhancement of quantum dynamical evolution, known as anti-Zeno effect. The results in Ref. [58] 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 of the biomolecular system. In an earlier work [59], repeated measurements in disordered systems was seen to induce a quantum anti-Zeno effect with ability to enhance quantum transport under certain conditions. These works [58,59] 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.

#### 4 Approaches to examining the quantum dynamics of photosynthesis

Several studies of excitation transfer in quantum systems [38,60,61] have employed 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. The Redfield procedure employing the Born-Markov and secular approximations [38,60,61] and the non-Markovian approach based on the integro-differential equation using perturbation theory [62], have been used to examine the quantum dynamical evolution of exciton states. A generalized Bloch-Redfield (GBR) equation technique [63] revealed that temperature and spatial–temporal correlations in noise, partly arising from the vibrational motion of proteins, 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 [64], however this model was not supported by experimental work involving doped samples of the FMO complex [65].

Based on the quantum Markovian master equation of the Lindblad form, the time evolution of the reduced open exciton state [66,67] has been employed in some works [68,69] with inclusion of system-bath correlations [70,71]. Noise which may arise due to static disorder, dynamical stochastic fluctuations, or due to vibrational motion of proteins which are dependent on thermal effects in non-equilibrium systems, are attributes favorable to the existence of quantum coherence. Optimal transport may occur at intermediate noise levels [68,69], with very strong or weak noise levels resulting in lower performances. Similar requirements are also needed for the stochastic resonance phenomenon to occur. These conditions also appear to be consistent with the level of noise perturbations required in the Grover-like search by excitonic states [49]. In earlier works on the influence of thermal noise [68,69], the disturbances were incorporated in a local dephasing Lindblad master equation form within the site basis.

We note the failings of the Lindblad form [72,73] for a range of temperatures and other dissipation factors in quantum systems. To understand the weakness of the Lindblad form, we consider a continuous semigroup of linearly bounded operators,  $\mathcal{T}_t$ , 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 form the group of bounded operators satisfying: (i)  $\mathcal{T}_0 = \mathcal{I}$ , where  $\mathcal{I}$  is the identity, (ii)  $\mathcal{T}_{u+v} = \mathcal{T}_u + \mathcal{T}_v, \forall u, v \geq 0$ , (iii)  $\|\mathcal{T}_t \rho\| \leq \|\phi\|$  for  $t \geq 0$  for  $\forall$  state  $\rho$  in  $\mathcal{H}$ , where  $\|A\| = Tr[\sqrt{A^\dagger A}]$  and (iv) the existence of a continuous map  $t \rightarrow \mathcal{T}$  for  $\forall t > 0$ . The set of non-unitary contractive semigroup  $\mathcal{T}_t$  in decaying states is invariably linked to time irreversibility, with unitary ( $\mathcal{T}^\dagger = \mathcal{T}^{-1}$ ) and the completely non-unitary contractions may be analyzed using the Langer–Sz–Nagy–Foiias theorem (LSNF) [74]. The LSNF theorem states that  $\mathcal{T}$  can be decomposed into a unitary component  $\mathcal{T}^u$  and a non-unitary component  $\mathcal{T}^n$ , accordingly for every semigroup  $\mathcal{T}_t$ , the Hilbert space  $\mathcal{H}$  can be split into two subspaces:  $\mathcal{H} = \mathcal{H}^u \oplus \mathcal{H}^n$ , where  $\mathcal{T}^u$  ( $\mathcal{T}^n$ ) 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 [75,76]. This generator yields a master equation (of the Lindblad form) which governs the evolution of  $\rho$  [66,67]:

$$\frac{d}{dt} \rho(t) = -i[\mathcal{H}, \rho(t)] + \sum_{k,l=1}^d \mathcal{L}_{kl}(\rho(t)) \tag{9}$$

$$= -i[\mathcal{H}, \rho(t)] + \frac{1}{2} \sum_{k,l=1}^d a_{kl} \left( 2\chi_k \rho(t) \chi_l^\dagger - \{\chi_k^\dagger \chi_l, \rho(t)\} \right), \tag{10}$$

$$= -i[\mathcal{H}, \rho(t)] + \sum_{k=1}^d \gamma_k \left( \mathcal{L}_k \rho(t) \mathcal{L}_k^\dagger - \frac{1}{2} \{ \mathcal{L}_k^\dagger \mathcal{L}_k, \rho(t) \} \right) \tag{11}$$

where the Lindblad operators,  $\mathcal{L}_{kl}$  generate the map from the initial to the final density operators of  $\rho$  and  $\mathcal{H}$  arises from a combination of the isolated system Hamiltonian,  $\mathcal{H}_s$  and a system-environment interaction operator.  $\{\chi_k\}_{k=0}^d$  form the basis in the linear operator space, with  $\chi_0 = \mathcal{I}$ , where  $\mathcal{I}$  denotes the identity. The terms  $(a_{kl})$  in Eq. (10) constitute the positive definite  $d$ -dimensional Hermitian Gorini–Kossakowski–Sudarshan matrix  $\mathcal{A}$  [67], with spectrum  $\{\gamma_k\}$ . The first term in Eq. (10) [or (11)] represents reversibility in system dynamics, and the symmetrized Lindblad operators,  $\mathcal{L}_k$  incorporate environmental effects within the Born-Markov approximation and therefore act as the source of non-unitary dynamics.

The Lindblad form in Eq. (11) 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 [77]. 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. As a consequence, 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 [42, 78, 79] 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, includes higher vibrational energies present in the environmental bath, and incorporates a second-order cumulant expansion that is exact for a harmonic bath.

A study employing the HEOM technique [79] 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. [79] highlights 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 [80], 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 [81] was used to investigate changes to transitions between sites and the protein environment, with results showing robusticity of excitation propagation when defects are introduced into the molecular environment. These findings are of particular relevance to the possibility that a biological system may adapt accordingly to achieve favorable characteristics to realize optimum out-

come in its functionality. We further examine the ability of biological systems to adapt according to environmental changes using thermodynamic principles in Sect. 9.

The quasi-adiabatic path integral (QAPI) technique [82, 83] 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. [84], 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 level of redundancy in the coherent energy-transfer pathway [84]. These results are interesting, as 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.

## 5 The non-Hermitian quantum mechanical approach

It is well known that Non-Hermitian systems [85–93] 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 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 [92, 93] 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 [92, 93] 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 how information is transferred to neighboring subsystems 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 [86].

Quantum systems with non-Hermitian components evolve differently from those of a purely Hermitian Hamiltonian, with finite lifetimes of states associated with attributes of the non-Hermitian Hamiltonian. The differences between non-Hermitian and pure Hermitian nature of Hamiltonians can be examined using the quantum brachistochrone concept, which is linked to the minimum time taken to transverse the path between two locations of a particle under a set of constraints. The passage time of evolu-

tion of an initial state into the final state can be made arbitrarily small for a time-evolution operator which is non-Hermitian but  $PT$ -symmetric [91]. This result has been generalized to non- $PT$ -symmetric dissipative systems [89], with indications [89,91] 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 [87]. 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 [87], 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 which result from the Pauli exclusion principle acting on electrons and holes [94] in material systems. Pauli exclusion based processes which operate independently of the well known Coulomb processes in fermion systems, contribute to hermiticity of excitonic Hamiltonians [50]. In a recent study [50], the non-ideal bosonic features of excitons was examined using a non-Hermitian open quantum system approach. Long-lived quantum coherence in photosynthetic complexes may be assisted by small bosonic deviation measures [50], with involvement of a large number of excitons during energy exchanges. These conditions could help realize a highly correlated molecular environment conducive to efficient 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. Yi et al. [95] recently introduced complex terms for the inter-site couplings for the Fenna–Matthews–Olson (FMO) complex, and obtained higher maximal energy transfer efficiencies compared to those linked to real inter-site couplings. An earlier work [86] which utilized the non-Hermitian two-level dimer model showed the persistence of coherence features under specific environment conditions. Of relevance to photosynthesis is the demonstration that exceptional points may appear at critical temperatures for the dimer model [86]. It appears that some coherence features are retained during evolutions when the couplings of different subsystems to the environment becomes equal to each other [86]. 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 coherence during dynamics of the photosynthetic dimer system.

### 5.1 Quantum measurements during 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 classi-

cal 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 [96] 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 [96], and can be used to improve tomographic measurements of fragile quantum systems [31–33] such as natural light harvesting molecular networks.

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 [32]. Through tomography measurement techniques [97], 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.

## 6 Non-Markovianity and 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 semi-groups [72, 73]. The mathematical maps in Markovian environments, possess divisibility and provide tractability when characterizing the evolution dynamics of memoryless quantum systems. As mentioned in Sect. 4, this numerical tractability was the key reason for its use to improve the models employed in earlier works [60] which examined the dynamics of a quantum system in contact with external reservoir. 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 [98] demonstrated 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.

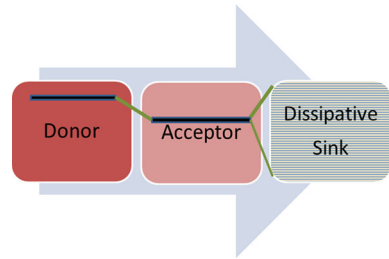
Current measures of non-Markovianity are generally based on the deviations of existing quantum structure from the continuous, completely positive semi-group attributes of Markovian evolution characterized by the dynamical map  $\rho(0) \mapsto \rho(t) = \Phi(t, 0)\rho(0)$ . Due to varying characteristics of different distance measures (e.g. trace distance, Bures distance, Hilbert-Schmidt distance [30]), there is no unique quantifiable measure of non-Markovianity in quantum systems. The distinguishability attribute 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 [99]. 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 [99]. An alternative measure is based on divisibility [100, 101], 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 several discussions related to the equivalence of these two measures of non-Markovianity, with the overall agreement 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, which we omit discussing in greater details here. Nevertheless, the myriad of ways that non-Markovianity can be defined and 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 well known 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, 58, 68, 69], 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 [63] where the energy transfer efficiency is optimized. This may be due to preservation of coherences along critical pathways, as non-Markovian effects have been noted to increase the lifetime of entanglement effects [68, 69]. The exciton entanglement dynamics of the Fenna–Matthews–Olson (FMO) pigment-protein complex in an earlier work [12] also showed increased oscillations of entanglement attributes 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.

Recently we examined the non-Markovian dynamics in a multipartite system of two initially correlated atomic qubits [102], with each qubit placed in a single-mode leaky



**Fig. 5** 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



cavity coupled to a bosonic reservoir. The atom-cavity-reservoir system is analogous to the photosynthetic model constituting the donor and acceptor protein pigment complexes, with the latter coupled to a third entity represented by the phonon dissipative sink (see Fig. 5). This work [102] showed the dominance of non-Markovian features in several two-qubit partitions, with maximal non-Markovianity present in the cavity-cavity subsystem 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 [102]. On the basis of these results, segments of biomolecular chains appear to act as quantum channels, with the local minima in the fidelity measures possibly arising from the merger of the two eigenvalues at the topological defect. Further investigations are needed to confirm the roles of molecular chains as part of an intricate quantum network model system endowed with some degree of quantum information processing abilities, and to examine the unique roles of exceptional points in these systems.

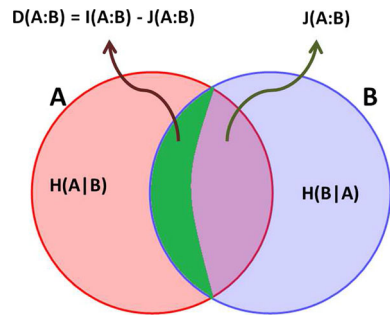
In another related study on photosynthetic systems [58], the time domains involved during effective Zeno or anti-Zeno dynamics appeared to be of the same order of magnitude as the non-Markovian time scale of the reservoir correlation dynamics. An earlier study [58] highlighted the subtle links in decay 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.

## 7 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.



**Fig. 6** 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  $B$  [118–120]



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 [30, 103, 104]. These protocols include quantum teleportation [105–107], dense coding [108], quantum cryptography [109, 110] and remote state preparation [111]. Entanglement as an entity is capable of continual destruction and regeneration in a composite system–environment setup [112], 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 [113–117]. 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 [118–120], based on the difference between quantum and classical information content in entangled systems (see Fig. 6). 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 [121]. 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 [122]. The occurrence of a constant quantum discord has been demonstrated in an earlier work on the quantum processing attributes of J-aggregate systems [123]. 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 to form a non-zero discord state [124]. The quantum discord is not restricted by the monogamy rule [112] 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 communica-

tion protocols are unaffected by noise [125]. The theoretical framework under which these results were obtained [125], 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 [126]. There are obvious difficulties to these efforts, as the relationship between coherence and entanglement remains subtle, with no known demonstrable explicit link between the two entities. 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.

## 8 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 is present in the multipartite state as

$$|\Psi\rangle = \sum_{n=1}^N c_n \left( |0\rangle^{\otimes(n-1)} \otimes |1\rangle \otimes |0\rangle^{\otimes(N-n)} \right) \quad (12)$$

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 appears as

$$|W_N\rangle = \frac{1}{\sqrt{N}} (|100\dots 0\rangle + |01\dots 0\rangle + \dots + |0\dots 01\rangle), \quad (13)$$

while the GHZ states are obtained as

$$\begin{aligned} |GHZ_N\rangle &= \alpha \underbrace{|0\rangle \otimes |0\rangle \otimes \dots \otimes |0\rangle}_N + \beta \underbrace{|1\rangle \otimes |1\rangle \otimes \dots \otimes |1\rangle}_N \\ &= \alpha |0\rangle^{\otimes N} + \beta |1\rangle^{\otimes N} \end{aligned} \quad (14)$$

where  $|\alpha|^2 + |\beta|^2 = 1$ . Multipartite 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. Multipartite 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 [12,127] in solids, and play an important role in the quantum properties of molecular systems.

Multipartite 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 [128]. 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 almost certainly, multipartite states are favored participants of quantum information processing during photosynthesis.

Unlike bipartite states, the examination of the robustness of quantum states is a challenging task in multipartite states, as the entanglement and non-classical correlations are not to easy categorize for such states. There 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 multipartite states (Dicke, GHZ, W or cluster states) under decoherence processes as noted in earlier studies [129,130]. For instance, the W state is known to be highly robust as a multipartite entangled state, with respect to loss of a single excitation [131]. 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 [132]. 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 [133], 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 [132].

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* [39] 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 [105,106] and quantum state splitting [134,135] within a noisy environment was demonstrated. Quantum communication protocols such as quantum teleportation [105,106], and quantum secret sharing [135], are utilized by multipartite states to assist energy transfer during photosynthetic processes [12]. In largely extended light harvesting systems with intricate network connectivity, multipartite 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 known as quantum energy teleportation (QET) [136] was proposed to show the viability of energy teleportation between two remote sites. Through this scheme, 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 [136] lies in the fact that it is information instead of tangible energy that is being transferred from one point to another. As a consequence 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 the possible role of quantum thermodynamical principles, which we examine in the next section.

## 9 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 [137–144], 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 stand distinct from analogous measures which appear 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 for considering quantum thermodynamic factors in light harvesting systems, which can be viewed as operating 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 [145, 146]. 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 [145, 146]. 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 gained during the cycle [147]. 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 [148], 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 [149] differs from several mathematical formalisms in its applicability to states that are operating in the far from equilibrium regime. This theorem stems from the Jarzynski relation [150] which is employed in the examination of states that undergo dynamical evolutions in the unstable regimes. The Jarzynski relation [150] 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 between equilibrium states, 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 [151].

The principles of the Szilard engine has been extended via the fluctuation theorem [149] to the formulation of thermodynamic work based on a time forward and backward shifting technique [138]. 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 [138, 152]

$$\langle W \rangle_{\text{diss}} = \langle W \rangle - \Delta F = kT \left\langle \ln \frac{\rho}{\tilde{\rho}} \right\rangle. \quad (15)$$

$\langle W \rangle_{\text{diss}}$  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)  $q(p)$ .  $\langle \cdot \rangle$  denotes the averaging of  $\rho$ , and  $\tilde{\rho} = \tilde{\rho}(\tilde{\Gamma}; t)$  is the time-reversed distribution observed at phase point  $\tilde{\Gamma} = (q, -p)$  for the same duration as the forward process.

The dissipated work (15) is also obtainable in terms the relative entropy,  $D(\rho \parallel \tilde{\rho})$  between  $\rho$  and  $\tilde{\rho}$  [139]

$$\langle W \rangle_{\text{diss}} = kT D(\rho \parallel \tilde{\rho}), \quad (16)$$

where  $D(\rho \parallel \tilde{\rho})$  is the relative entropy between  $\rho$  and  $\tilde{\rho}$ . From Eq. 16, the gain in total entropy (system plus heat bath) in the forward process,  $\Delta S$ , is given by [139]

$$\Delta S = k \left\langle \ln \frac{\rho}{\tilde{\rho}} \right\rangle = k D(\rho \parallel \tilde{\rho}). \quad (17)$$

The classical result in Eq. 17 can be seen in quantum settings via extension of  $D(\rho \parallel \tilde{\rho})$  to its quantum counterpart based on the relative entropy [151, 153].

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. Equation (16) reveals the deep links between dissipation and the non-Markovianity measure. As pointed out in Sect. 6, the latter is linked to non-divisible maps in systems which undergo non-contractive quantum evolution and can be represented by the relative entropy,  $D(\rho\|\tilde{\rho})$ . 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 [140, 141] 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 [142]. In a study on multipartite systems [137], 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 [137]. It would be worthwhile to pursue these ideas within the correlated environment of molecular systems in future investigations involving quantum thermodynamics aspects of photosynthesis.

### 9.1 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 [154]. In the case of living systems, the ability of the biological system to “foretell” future events becomes fundamental to increasing the survival of the supported species, as it also enhances 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 [154], 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. [154] 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 [143]. 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 [143]

$$\beta W_{\text{lost}}[\rho_{SX} \rightarrow \rho'_{SX}] = \ln 2[H(S|X') - H(S|X)] \quad (18)$$

$$= \ln 2[I(S : X) - I(S : X')], \quad (19)$$

where  $\beta = 1/k_B T$  denotes the inverse temperature, while the meanings of the entropy terms ( $H(S|X')$ ,  $H(S|X)$ ,  $I(S : X)$ ) are made explicit in Fig. 6.  $S$  denotes the finite quantum system, while  $X$  is a subset of the surrounding environment that is correlated with  $S$ .  $X$  evolves via

$$\rho_X \rightarrow \rho'_X = \mathcal{E}(\rho_X) \quad (20)$$

where  $\mathcal{E}$  denotes a quantum channel.

Grimsmo [143] employed a simple quantum model to illustrate that the entropy change is a measure of ineffective use of information [143], consistent with the idea demonstrated earlier for classical systems [154]. Environmental coherence of the central system was shown to improve predictability to an amount quantified by a negative (quantum) constituent of the dissipated work [143]. 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  $B$  prior to the changes in  $A$ . 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 [143].

In an earlier work [144], 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 culminate 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, whereby all traces of correlations are eliminated [144]. These ideas may be extended to examine work that is dissipated in select regions of biomolecular systems due to dynamical stochastic fluctuations occurring in other regions of the photosynthetic membrane holding the bacteriochlorophylls. With a similar focus, changes in work or energy in select segments of biomolecules due to environmental fluctuations arising from the vibrational motion of protein molecules in spatially separate regions may also be assessed. Future investigations may consider the detailed examination of optimized conditions involving temperatures, solar illumination levels or structural arrangements of the molecular sub-units, that yield minimal dissipation of energy placed at the initial site of excitation.

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 common origins, and the 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, aside from biomolecular systems.



## 9.2 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 perspective, 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 the Crooks [149] and Jarzynski equality relations [150] are valid for open quantum systems [151], and are independent of the system-environment coupling strength and discrete structures present in the thermal environment. The quantum versions of the fluctuation relations therefore appear suitable to be employed in investigating the quantum environment of biomolecules at higher temperatures. The latter systems which undergo “far-from-equilibrium” fluctuations, may incorporate useful information based on predictive powers, that is distinct from the background noise. The system’s predictive ability [154] may have enabled some robustness against decoherence, reflected by 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” a range of parameters when there is match in time scales of the system and its environment. Such control action gives rise to a pattern of evolution based on a continuous process of realizing optimality in critical activities within a biological network of biomolecules embedded in chaotic environments. This may occur during the “far from equilibrium” dynamical evolution 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. The operational efficiency highlights the need to comprehend the fundamental quantum thermodynamics processes at work, and closely examine the factors that govern the energy conversion at the reaction center [155]. 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 [156] has highlighted the use of Shannon’s theorem for communication channels to describe “machine capacity” of molecular systems. The availability of a complex code 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.

### 9.3 Agent-based modeling and simulation approach of photosynthetic biomolecular systems

A scenario where biomolecules “think” and “act” like intelligent biological networks [156–159] may appear far fetched, however the presence of these attributes may be investigated using an agent-based modeling and simulation approach [160–162]. 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, otherwise considered as domains of agents. In the more 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 incorporate 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, 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. [143], to examine the optimality of biomolecular structural layouts for energy transport and other information processing [163, 164] properties.

## 10 Conclusions

In the preceding sections, we have discussed various topics of importance to studies of quantum correlated 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 and extracting quantum structures from 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, by employing 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 comprehension of the links between quantum rules and nature's design of biological network structures, which constitute living forms which are able to harvest solar energy with remarkable efficiencies.

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