Geometrical effects on energy transfer in disordered open quantum systems

M. Mohseni,1,2 A. Shabani,3 S. Lloyd,4 Y. Omar,2,5 and H. Rabitz3

1Center for Excitonics, Research Laboratory of Electronics, Massachusetts Institute of Technology, Cambridge, MA 02139
2Physics of Information Group, Instituto de Telecomunicações, P-1049-001 Lisbon, Portugal
3Department of Chemistry, Princeton University, Princeton, New Jersey 08544
4Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139
5CEMAPRE, ISEG, Universidade Técnica de Lisboa, P-1200-781 Lisbon, Portugal

We explore various design principles for efficient excitation energy transport in complex quantum systems. We investigate energy transfer efficiency in randomly disordered geometries consisting of up to 20 chromophores to explore spatial and spectral properties of small natural/artificial Light-Harvesting Complexes (LHC). We find significant statistical correlations among highly efficient random structures with respect to ground state properties, excitonic energy gaps, multichromophoric spatial connectivity, and path strengths. These correlations can even exist beyond the optimal regime of environment-assisted quantum transport. For random configurations embedded in spatial dimensions of 30 Å and 50 Å, we observe that the transport efficiency saturates to its maximum value if the systems contain 7 and 14 chromophores respectively. Remarkably, these optimum values coincide with the number of chlorophylls in (Fenna-Matthews-Olson) FMO protein complex and LHC II monomers, respectively, suggesting a potential natural optimization with respect to chromophoric density.

PACS numbers:

Inspired by recent observations of Environment-Assisted Quantum Transport (ENAQT) in biological light-harvesting systems [1][10], one problem of fundamental and practical relevance is to engineer excitonic energy migration in disordered materials and nano-structures by exploiting the interplay of quantum effects and environmental interactions. Specifically, one might develop radically novel design principles by manipulating delocalized exciton dynamics through engineering coherent couplings of free Hamiltonian and/or the environmental interactions to generate optimal efficiency. If one can fully understand the fundamental microscopic processes involved [11][12], it will be in principle possible to use structure for steering the ultrafast migration of excitons via quantum interference effects. Thus the excitons could be guided around defects and through interfaces in disordered systems with potentially important application in photodetection, bio-sensing, and photovoltaic light-harvesting [13].

In this work, we investigate underlying geometrical and dynamical physical principles for efficient energy transport in generic random multichromophoric structures typically far from symmetrized configurations considered in Refs [14][15]. Our work is motivated based on the recent studies on disorder biological light-harvesting systems [11], such as Fenna-Matthews-Olson (FMO) of green sulfur bacteria [1][8], reaction center (RC) of purple bacteria [16], and light-harvesting complex II of higher plants [17]. In particular, we investigate generic disordered configurations of up to 20 chromophores. We examine the energy transfer efficiency of the uniform distributions of the random light-harvesting complexes, as well as important subsets of these samples, encapsulated in a sphere of fixed diameter. For spatial sizes of 30 Å and 50 Å, corresponding to FMO and LHCII dimensions, we find transport efficiency increases as a function of the number of chromophores and saturates at optimal values of 7 and 14 sites respectively. Remarkably, these are indeed the number of chlorophylls for FMO and LHCII monomers implying a potential optimization with respect to chromophoric density.

Moreover, we compute the energy transfer efficiency (ETE) of the uniform distributions of the random complexes consisting of 7 chromophores encapsulated in spherical dimension of various diameters interacting with a phononic bath. This allows us to compare our results with the performance of a well-characterized natural LHC such as the FMO complex. A similar study has been performed in Ref. [18], which have concludes that the FMO geometry with such high efficiency is extremely rare. In contrast to conclusions drawn in the Ref. [18], here we find that FMO performance is not rare if one uses a more accurate dynamical model, an appropriate measure of efficiency, and limits the search space to those configurations with similar compactness level as the FMO itself. We use ETE as yield function for performance of these random systems and use a time-convolution master equation (TC2) [19] to estimated energy transport efficiency beyond perturbative and Markovian regimes [9][10]. We extensively explore the effect of spatial compactness on the transport efficiency and robustness due to its potential significance as recently reported in [10]. These simulations show that for larger size complexes the optimal configurations are not robust with respect to angular orientation of dipole moments in contrast to highly dense systems such as FMO.

To explore potential geometrical patterns, we examine possible spatial and energetic correlations among 103 random multichromophoric samples embedded in a fixed diameter sphere ranging from 30 Å to 100 Å. We find that significant statistical correlations can exist among very high- and low-efficient samples even in suboptimal regime of chromophoric density, beyond the robust ENAQT regime [10]. Specifically, we find certain structural similarities among various Frenkel exciton Hamiltonians of the high/low efficient random configurations with respect to ground state properties, excitonic en-
ergy gap structures, and spatial connections. Moreover, we intro-
duce a new measure of spatial path strength that can quan-
tify an underlying structural mechanism for the performance of
light-harvesting systems in a given dimension.

This paper is organized as follows: In section II, we de-
scribe our physical model and review the non-local master
equation that was derived and analyzed in Ref. [9] to effi-
ciently calculate ETE in multichromophoric systems. In sec-
tion III, we examine the variation of ETE with the number
of chromophores in fixed dimensions. In the section IV, we
explore the role of chromophoric density in energy transfer
as a dominating parameter [10]. In the subsequent sections
we explore the roles of other physical parameters in transport
including, ground state energy properties, average excitation
energy, structure and strength of chromophoric connectivity.

I. THEORETICAL MODEL OF RANDOM
MULTICHROMOPHORIC SYSTEMS

Based on the generalized Bloch-Redfield master equations
introduced by Cao [20], we have recently derived the well-
known time nonlocal master equation TC2 without making
the usual weak system-bath coupling assumption [9]. By pro-
viding an error analysis, we could show that TC2 can be em-
ployed for highly efficient while reliable estimation of en-
ergy transfer efficiency in light-harvesting complexes for both
weak and intermediate system-bath coupling strengths and
memory time scales. Here, we summarize the main steps of
our approach. More technical details can be found in Ref. [9].

The dynamics of a photosynthetic system interacting with
surrounding scaffold protein and solvent can be understood
by starting from a general time evolution formulation of open
quantum systems. The total system-bath Hamiltonian can be
expressed as

\[ H_{\text{total}} = H_S + H_{ph} + H_{S-ph} \] (1)

where

\[ H_S = \sum_{j,k} \epsilon_j |j\rangle \langle j| + J_{jk} |j\rangle \langle k|, \]

\[ H_{ph} = \sum_j \hbar \omega_j (p_{j,\xi}^2 + q_{j,\xi}^2)/2, \]

\[ H_{S-ph} = \sum_j S_j B_j. \]

The phonon bath is modeled as a set of harmonic oscillators.
Here \( |j\rangle \) denotes an excitation state in a chromophore spatially
located at site \( j \). The diagonal site energies are denoted by \( \epsilon_j \)
that include reorganization energy shifts \( \lambda_j = \sum_\xi \hbar \omega_\xi d_{j,\xi}^2/2 \)
due to interactions with a phonon bath; \( d_{j,\xi} \) is the dimen-
sionless displacement of the \( j, \xi \)th phonon mode from its
equilibrium configuration. The strengths of dipole-dipole in-
teractions between chromophores in different sites are rep-
resented by \( J_{jk} \). The operators \( S_i = |j\rangle \langle j| \) and \( B_j =\)
\[- \sum_\xi \hbar \omega_\xi d_{j,\xi} q_{j,\xi} \] are system and bath operators. Here,
we assume that each site is linearly interacting with a separate
phonon bath. The overall dynamics of the system is given by
Liouvillian equation:

\[ \frac{\partial \rho_S(t)}{\partial t} = -i \hbar \langle [H_{\text{total}}, \rho_{SB}(t)] \rangle_{ph} = \langle \mathcal{L}_{\text{total}}(\rho_{SB}(t)) \rangle_{ph} \] (2)

where \( \rho_{SB} \) denotes the system-bath state, and \( \langle ... \rangle_{ph} \) indicates
an average over phonon bath degrees of freedom. The Liou-
villian superoperator \( \mathcal{L}_{\text{total}} \) is the sum of superoperators \( \mathcal{L}_S, \)
\( \mathcal{L}_{ph} \) and \( \mathcal{L}_{S-ph} \) associated to \( H_S, H_{ph} \) and \( H_{S-ph} \) respec-
tively. The time evolved density operator of the multichro-
morphic systems in the interaction picture can be expressed by
the propagator:

\[ \hat{\rho}(t) = \langle T_+ \exp \left[ \int_0^t \mathcal{L}_{\text{total}}(s) ds \right] \rangle_{ph} \rho(0) \] (3)

where \( \hat{O} \) denotes the interaction picture representation for an
operator \( O \). If we expand the above time-ordered exponential
function, we arrive at the Dyson expansion for time evolu-
tion of the density operator. This expansion involves mul-
time bath correlation functions \( \langle \hat{B}(t_{i1})...\hat{B}(t_{in}) \rangle_{ph} \), for any
\( B = B_j \). According to generalized Wick’s theorem, for a
system interacting with a bosonic (photonic and/or phononic)
bath these higher order bath correlation functions can be ex-
actly described by various combinations of only two-time cor-
relation functions of the form \( \prod_{l,k} \langle \mathcal{I}_+ \hat{B}(t_{i_k}) \hat{B}(t_{i_l}) \rangle \), where
\( \mathcal{I}_+ \) is the index ordering operator. Assuming such Gaussian
property for bath fluctuations, the most general approach to
solve the master equation (2) is to utilize a path integral for-
malism, leading to HEOM [21]. However, such general ap-
proach is impractical for our purpose as the computational re-
sources required for simulating the energy transfer dynamics
of photosynthetic complexes grow significantly with increas-
ing size of the system, and with decreasing bath cutoff fre-
quency and ambient temperature.

We derived a numerically efficient method for simulation of
complex excitonic systems by incorporating some physical
approximations in addition to Gaussian property to map
quantum dynamics into a single solvable time-nonlocal equa-
tion, see Ref. [9]. The main approximation is involved with a
special truncation of higher-order bath correlation functions.
Specifically, we assumed that generalized Wick’s expansion

\[ \langle \hat{B}(t_{i_1})...\hat{B}(t_{i_n}) \rangle_{ph} = \sum_{\text{pairs } l,k} \prod_{l,k} \langle \mathcal{I}_+ \hat{B}(t_{i_k}) \hat{B}(t_{i_l}) \rangle \] (4)

can be approximated as

\[ \langle \hat{B}(t_{i_1})...\hat{B}(t_{i_n}) \rangle \approx \langle \mathcal{I}_+ \hat{B}(t_{i_1}) \hat{B}(t_{i_2}) \rangle \langle \mathcal{I}_+ \hat{B}(t_{i_k})...\hat{B}(t_{i_{2n}}) \rangle \] (5)

for \( t_3 > t_2 > ... > t_{2n} \). In other words, we disregard some
fast decaying terms in the generalized Wick’s expansion, but
keep the slow decaying leading terms such that a two-point
correlation can be factored out. This approximation can be
understood phenomenologically by noting that two-point cor-
relation functions \( C_j(t-t_1) = \langle \hat{B}_j(t) \hat{B}_j(t_1) \rangle \) typically decay
deviation over a characteristic time, e.g., for a Lorentzian spectral
function and at high ambient temperature \( T \), the correlation functions decay
exponentially as $\lambda(2/\beta - i\gamma)e^{-\gamma(t-t_i)}$ where $\gamma^{-1}$ is the relaxation time of phonons and $\beta = (k_B T)^{-1} < \gamma^{-1}$. The approximation is valid in the limit of time scales $t$ longer than $\gamma^{-1}$. As we see below, in calculating ETE we are considering an integration over time therefore this approximation can provide good results even if $\gamma$ is not large or in another word we are in a relatively non-Markovian regime.

Using this approximation we arrive at the time non-local master equation, TC2, as:

$$\frac{\partial}{\partial t} \rho(t) = \mathcal{L}_S \rho(t) + \mathcal{L}_{e-h} \rho(t)$$

$$- \sum_j |S_j\rangle \frac{1}{\hbar^2} \int_0^t C_j(t-t') e^{i\gamma(t-t')} S_j \rho(t') dt' - \text{h.c.}$$

where $\mathcal{L}_{e-h} = - \sum_j \gamma_j^{\text{loss}} \{ |j\rangle \langle j| \} - r_{\text{trap}} \{ |\text{trap}\rangle \langle \text{trap}| \}$, h.c. stands for Hermitian conjugate, and $\{,\}$ is the anti-commutator ($[,,]$ is the commutator). The vector $|\text{trap}\rangle$ denotes the state of the site (bacteriochlorophyll (BChl)) connected to the reaction center. The term $\mathcal{L}_{e-h}$ captures two different competing electron-hole pair recombination processes that determine the energy transfer efficiency of light harvesting complexes. The first process, loss, is due to dissipation to the environment at each site that happens within the time-scale of 1 ns. This adverse environmental effect guarantees that the energy transfer efficiency has a value less than one. The second recombination process, trap, is due to successful trapping at one or more reaction center(s).

A biologically relevant function for exploring the performance of light-harvesting complexes is the ETE as defined in Refs. [22][23][24], that is the total probability of exciton being successfully trapped:

$$\eta = 2r_{\text{trap}} \int_0^\infty \langle \text{trap}|\rho(t)|\text{trap}\rangle dt$$

We provide a formal derivation of the energy transfer efficiency in Ref. [9]. ETE measures the likelihood of successful trapping, weighted by trapping rate: it quantifies the excitation availability whenever the reaction center is ready to operate within a period much shorter than the exciton life-time [22]. Note that this definition is very different than the first passage time [18][24], which quantifies the time-scale of first arrival of the exciton to the trapping sites. The latter definition is not necessarily correlated with the efficiency of quantum transport. In other words, for certain quantum processes the first passage time can be very short, compared to all other time-scales, but the transport mechanism could be still inefficient. In such cases, the excitations are typically delocalized over the regions that have very small overlaps with the reaction center and thus dissipate into the environment.

The primary motivation for the truncation of correlation functions introduced above is to lead us to a special time non-local master equation that is solvable in the frequency domain. To estimate the regimes of the applicability of this method, one would ideally need to account quantitatively for the errors introduced by the generalized Wick’s expansion truncation. We presented an approximate estimation of such inaccuracy in Ref. [9] for computing energy transfer efficiency by defining an upper bound for the error as

$$\Delta \eta = 2r_{\text{trap}} \int_0^\infty \langle \text{trap}|\rho(t) - \rho_{TC2}(t)|\text{trap}\rangle dt$$

where $\rho(t)$ is the exact density matrix of the system and $\rho_{TC2}(t)$ is the solution to the TC2 master equation. Note that an exact account of errors in various regimes of interest is equivalent to calculation of the general evolution of the density operator of the system that we intend to avoid. In Ref. [9], using a combination of phenomenological and analytical approaches, we found an approximate error bound for weak and intermediate system-bath couplings and bath memory time-scales, thus quantifying the reliability of our approach in such regimes. We also tested the accuracy of our method for by examining its predication in simulating quantum dynamics of FMO complex at room temperature compare to HEOM as a general benchmark [25]. We showed that oscillatory time evolution of the population of BChls in the FMO using our approach are relatively close to those predicted by HEOM [9].

Here, we would like to apply TC2 master equation to explore the interplay of structurally-induced quantum coherence and environmental interactions for a large number of small-size random light-harvesting complexes with different chromophoric density. We choose the magnitudes of dipole moment similar to the FMO, but with arbitrary random orientations, site energy, and locations bounded in any given diameter of the spherical space. Our results hold for other materials with different dipole moment magnitudes by an appropriate renormalization of distances in spherical coordinate. We set the nearest neighbor distances by a lower bound of $5 \AA$.
FIG. 2: The effect of chromophoric compactness on ETE for different system-bath coupling strength. We simulate ETE for $10^4$ different configurations of 7 chromophores embedded in a sphere of fixed diameter $d$ ranging from 30 Å to 100 Å. The initial and target chromophores are located on the north and south poles of the spheres. The ETE histogram is depicted for reorganization energies of $\lambda = 0 \text{cm}^{-1}$ (blue), $\lambda = 35 \text{cm}^{-1}$ (green) and $\lambda = 350 \text{cm}^{-1}$ (red). At $\lambda = 35 \text{cm}^{-1}$ and $d = 60$ a uniform distribution in all classes of ETE is observed. Below $d = 60$ the samples are mostly high efficient and above $d = 60$ they become mostly low efficient. For $\lambda = 0$ and $350$, this transition happens around $d = 40$ indicating that optimality and robustness of ETE can both be enhanced by the appropriate level of environmental fluctuations. The FMO complex belong to an ultra-high performing population represented by green bars in $d = 30$ implying the highest degree of efficiency and fault-tolerance in such chromophoric density and noise level due to intrinsic limitation of the dipole-dipole approximation [26]. As we would like to explore the generic behavior of multichromophoric systems, here we do not account for spatial constraints due to particular size of each chromophore or a specific scaffold protein. We assume that the initial excitation and trapping sites are located at the surface of the sphere encapsulating a given configuration. That enables us to avoid a large amount of trivial optimal solutions in the configuration spaces; i.e. those in which the original donor and final acceptor sites are nearest neighbors. Thus the excitation has to travel through the entire length of the multichromophoric complex and generally experience multi-path quantum interference in the regime of interest with intermediate system-bath coupling strength.

A. Optimal number of chromophores

Here, we explore the dependency of ETE on the number of chromophores for small light-harvesting complexes. In Fig. 1, we plot ETE for random complexes consist of 2 to 20 chromophores embedded in spheres of diameter $d = 30$ Å, and $d = 50$ Å with environmental parameters given in [27]. The average ETE for 1000 random configurations is computed for fixed diameters and number of chromophores. The standard deviation in these samples is depicted in the Fig. 1 inset. We observe that ETE increases monotonically by increasing the number of chromophores for different compactness levels. It is remarkable that for $d = 30$, which is the same as the diameter of the FMO complex, the number seven represents the minimal set of chromophores necessary to obtain high efficiency of 98%. Although, slightly higher ETE can be obtained by additional sites, that would be practically inefficient considering the amount of work required to form such extremely
dense multichromophoric system for a marginal improvement in ETE. Here, the minimalist nature of natural selection might be at work: complexity is added until high efficiency and robustness is attained, and no further. A similar behavior can be seen for \( d = 50 \) which coincides with the spatial size of LHCII. In such a distance, the ETE also saturates by increasing the number of sites and reaches to its optimal value for 14 chromophores. Any extra chromophore may improve the average efficiency by less than 1%. Ironically 14 is the number of chromophores of the LHCII monomers in higher plants.

We expect that such saturation of ETE with respect to the number of multichromophores to occur for other range of compactness levels. It is of great importance if similar comparisons with larger natural photosynthetic complexes can be demonstrated. That would imply a potential natural optimization with respect to the number of chromophoric arrangements in various spatial dimension. Similar studies for larger artificial light-harvesting complexes could be of significant value for estimating the minimal number of chromophores needed to achieve a desired efficiency considering the physical and chemical spatial constraints in a realistic environmental condition. Such studies are beyond the scope of the current manuscript and will be undertaken in subsequent works. Next, we explore the role of chromophoric density by considering a fixed number of molecules in various spatial dimension.

II. FUNDAMENTAL ROLE OF CHROMOPHORIC DENSITY

We investigate the efficiency of random light-harvesting complexes, sampled from uniform distributions, embedded in a sphere of given diameter, \( d \), ranging from 30\( \AA \) to 100\( \AA \). For each compactness level defined by a fixed diameter, we categorize the population of \( 10^4 \) random arrangements in various classes based on their respective ETE and reorganization energies. Figure 3 shows the histograms of such populations for various multichromophoric diameters for three different values of reorganization energy chosen from the three different regions of system-bath couplings strength including, intermediate regime, e.g., \( \lambda = 35cm^{-1} \) (green bars), fully coherent regime with virtually no environment \( 0cm^{-1} \) (blue bars), and strong environmental interactions, e.g. \( 350cm^{-1} \) (red bars).

Let’s first examine the results associated to those complexes living in the similar environment as FMO (green bars in Fig. 2). Observe that an overwhelming amount of random configurations have efficiencies comparable to the FMO complex for compactness level of about \( d = 30 \) \( \AA \). Thus, in contrast to conclusions drawn in the Ref. [18], the FMO performance is not rare if one limit the parameter space to those configurations that have a similar compactness as the FMO protein complex. Also, here we are using ETE as a measure of performance which capture long-time behavior on the same order as trapping time-scale. In addition, we use a TC2 dynamical equations that can go beyond Haken-Strobel model and captures relaxations as well as pure dephasing process.

Our results in Fig. 2 introduce an additional degree of the robustness of the FMO. It implies excellent tolerance with respect to the BChls locations, provided that its boundaries and environment are not changing radically. This robustness is different than relative insensitivity of FMO transport efficiency to dipole orientations and site energies that were reported by us in Ref. [10]. Notably, as we increase the size of random complexes from 30 \( \AA \) to 100 \( \AA \), for fixed \( \lambda = 35cm^{-1} \) (green bars), the histograms are drastically changing from being sharply picked at high ETE to have sharp spectrum at low ETE, with average ETE dropping monotonically from 94\% in \( d = 30 \) \( \AA \) to 3\% in \( d = 100 \) \( \AA \). In the intermediate sizes, \( d = 50 \) \( \AA \) to \( d = 70 \) \( \AA \), we observe that these samples are more or less evenly distributed in all efficiency levels with mean value of about 50 \% efficiency for \( d = 60 \) \( \AA \). This implies a smooth transition in ETE standard deviation, as a function of an effective parameter \( \mu^2/d^3 \), with optimal values within the range of \( d = 60 \) \( \AA \).

One might expect that simple geometrical patterns can fully describe the variations of ETE in a given spatial dimension. For example, it is intuitively expected that straight line arrangements of the chromophores from initial excitation to

![FIG. 3: Three samples of chromophoric arrangements from the 10^4 random configuration in Fig. 2 for d = 60\( \AA \) and \( \lambda = 35cm^{-1} \). These samples have distinct energy transfer efficiencies including very low efficiency of less than 1\% in (a), intermediate efficiency of about 50\% in (b), and high efficiency of around 93\% in (c). It can be observed that simple geometrical considerations of spatial coordinates of chromophoric dipole moments cannot fully account for the significant discrepancies in their efficiencies.](image-url)
FIG. 4: The average (a) and the standard deviation (b) of ETE in the samples given in Fig. 2. The average ETE drops monotonically by increasing the diameter of the sphere from \( d = 30 \) Å to \( d = 100 \) Å. The standard deviation shows maximum around \( d = 60 \) Å (40) for \( \lambda = 35cm^{-1} \) (0 or 350). In such compactness regimes, the diverse populations of random configurations from very low to very high efficiency implies lack of robustness due to significant involvement of other physical parameters in guiding the exciton migration ETE, beyond the dominating factor of chromophoric density.

FIG. 5: The overlap between the Hamiltonian ground state and the trapping site for the ratio of the average top 100 efficient random samples over bottom 100 configurations. Although high efficiency geometries have larger overlap, especially at dimension \( d = 60 \) Å, the overlap of ground at trapping site cannot fully account for the large discrepancies among top 100 efficient and 100 low efficient configurations.

trapping site should lead to more efficient configurations in a fixed dimension. However, by inspection of the actual locations of the chromophores for three random samples associated to diameter of \( d = 60 \) Å we note that these apparently similar samples have significantly different energy transfer efficiencies, see Fig. 3. Thus, other structural and dynamical correlations should play important roles in discriminating among various samples with respect to ETE. We consider a variety of possible scenarios in the following sections. One potential important factor is the effect of environmental interactions on the shape of the ETE histograms and its transition from mostly efficient to mostly inefficient regimes.

To study the impact of ENAQT on the above phenomenon, we simulate ETE for random chromophoric configurations in two extreme environmental cases in Fig. 2. Blue bars represent the ETE for the ideal case of isolated systems and red bars show ETE for the systems that are strongly interacting with their surroundings (e.g., one order of magnitude stronger reorganization energies). The general features of the ETE histogram persist but transitions occur in smaller dimensions for both of these cases around \( d = 35 \) Å to \( d = 45 \) Å. Thus the existence of ETE statistical transition is independent of ENAQT. This phenomenon is essentially a direct manifestation of quantum dynamics driven by the internal Hamiltonian, but its effect is modulated by reorganization energy. The ENAQT phenomenon can be seen here by noting that those configurations operating at \( \lambda = 35cm^{-1} \), represented by green bars, always have higher ETE at all compactness levels.

Overall, by careful inspection of these results two main questions arise: How does the ETE behave as a function of the chromophoric density? What are the possible classical and/or quantum correlations, in the spatial and energetic structure of these random multichromophoric geometries, discriminating ultra high or low efficiencies in any fixed diameter? We addressed the former question in details in the Ref. [10] by examining the variation of the average transport efficiency for random configurations of up to 20 chromophores in two different compactness level. We observed that the chromophoric density of the FMO complex and LHCII to be around the optimal values for spatial dimensions of \( d = 30 \) Å and \( d = 50 \) Å respectively. Here, we investigate the latter question.

In the following sections, we explore underlying structural and physical principle(s) for very high- or low-efficient 7-chromophoric configurations in any of the histograms in Fig. 2 beyond the dominating factor of compactness. In the first step of our analysis of Fig. 2 we compute the average ETE over all random samples in various spatial dimensions to emphasize that very weak or strong environments are suboptimal in all ranges, see Fig. 4 (a). In Fig. 4 (b) the standard deviation of the average ETE is plotted for the same compactness levels highlighting the diversity of configurations with a maximum pick at the range \( d = 40 \) to \( d = 60 \) Å for different reorganization energy values.

III. GROUND STATE ENERGY OVERLAPS

Based on the definition of ETE one generally expects that the overlap of lowest exciton state (ground state) with trapping site to be a good indicator of any potential correlations among
FIG. 6: The histogram of excitonic energy levels for 100 efficient samples and 100 lowest samples chosen from all $10^4$ configurations embedded in spheres with different fixed diameters ranging from $d = 30 \text{Å}$ to $d = 100 \text{Å}$ in Fig. 2. It can be observed that for the entire range of spatial dimensions low efficiency samples have energy gaps significantly larger than the phonons average energy $63 \text{ cm}^{-1}$, and thus cannot use the bath as a energy sink to enhance exciton funneling in a fixed excitation limit. On the contrary, for top 100 highly efficient samples, we see that their average energy gap is sharply picked around $100 \text{ cm}^{-1}$ or less for dimensions larger than $d = 40 \text{Å}$. We note that for $d = 30 \text{Å}$ there is significant insensitivity with respect to these energy mismatches.

highly efficient samples. This overlap is indeed very high for the FMO complex, about 0.94. In order to test this hypothesis we have diagonalized the free Hamiltonian of the top 100 high efficiency and bottom 100 low efficiency random samples, and calculated the average overlap between ground excitonic state with trapping. Fig. 5 shows the ratio of such average overlaps for highest 100 samples to lowest 100 samples. We note that some global correlations exist as the ground state overlap is bigger by a factor up to 4.5 for the high efficient samples in most compactness levels with maximum enhancement around $d = 60 \text{Å}$. However, this correlation is incomplete, since it cannot account for huge discrepancies in ETE within each distribution. In particular, this measure cannot accurately discriminate ultra high (low) efficient samples (top/low 10 configurations) from the rest of geometries. Moreover, it cannot directly account for the role of environment.

IV. EXCITONIC-PHONONIC ENERGY CONVERGENCE

One measure that can potentially capture the role of environment in discriminating among various configurations is the compatibility of exciton energy gaps with phonon energies. In the weak system-bath couplings the multiphonon transitions are not common and most of environment induced dynamics is driven by single phonon transitions. In such regimes, those configurations that have exciton energy gaps comparable with the energies of phonons can easily use the bath as an energy sink. This can lead to enhancement of funneling toward trapping sites by passing extra energy to phonons in a fixed excitation manifold. Using bosonic distribution function, a rough estimation of the average energy of a phonon can be simply evaluated by ignoring the protein chemical energy, as follows:

$$\int_0^\infty d\omega J(\omega) \omega / (\exp(\beta \omega) - 1)$$

$$\int_0^\infty d\omega J(\omega) / (\exp(\beta \omega) - 1)$$ (9)
where \( J(\omega) \) is the Lorentzian spectral density. Using the above relation the average energy of a single phonon is about 64 cm\(^{-1}\), assuming bath with cutoff frequency of 50 cm\(^{-1}\) at room temperature. We also compute the average energy gaps, \( g \), for the bottom 100 and top 100 efficiency samples. The distribution of such samples based on their average exciton gaps in various compactness levels is shown in Fig. 6. We observe that bottom 100 samples (grey bars) have average energy gaps between 200 to 400 cm\(^{-1}\) with large standard deviation of about 200 cm\(^{-1}\), see Fig. 6. Thus, there is typically an energy mismatch between typical exciton gaps and phonon energies. On the contrary, the top 100 efficient samples have energy gaps of about 100 cm\(^{-1}\) with smaller standard deviation of about 50 cm\(^{-1}\). Consequently, there is a considerable chance of system-bath energy exchange facilitating exciton transfer. A more accurate description of the exciton band gap correlations should include multi-phonon transitions for strong system-bath couplings that can be captured in Förster theory [28] or modified Redfield theory [29]. However, our data suggest that one- or two-phonon transitions that are relevant in the intermediate regimes can be captured by our dynamical equations Eq. [6].

V. SPATIAL CONNECTIVITY

In the classical regime of incoherent hopping, a simple design principle for the multichromophoric systems, coupled via dipole-dipole interactions, to achieve high ETE would be to align chromophores on a straight line connecting the initial and target sites. In Fig. 3, we observe that relatively similar patterns might lead to configurations with very different ETE. By enlarging the spherical size encapsulating the samples, the average inter-chromophoric couplings become weaker, therefore the quantum coherence would be attenuated. Thus, we expect that the measure of proximity to the axis connecting the initial and target chromophores, \( z \), takes lower (higher) values for high (low) efficiency samples. To this end, we examine this measure defined as the average distance of the 5 intermediating chromophores from the Z axis. This numerical study, plotted in Fig. 8 confirms such intuition to some extent. The average distance of total number of random configurations from the Z axis is plotted, as well as such distances for top 100 (high-efficient) and bottom 100 (low-efficient) samples. It can be seen that the average distances for these different classes become more distinct by increasing the dimension of the sphere. For diameter 100 Å, the top 100 samples on average are closer to Z axis compare to the total populations with a ratio of 0.6. On the other hand, this feature is less important for more compact geometries and for low-efficient configurations suggesting that simple geometrical consideration per se cannot fully determine the performance of an excitonic energy transfer system.

VI. PATH STRENGTHS

One important structural feature of light harvesting complexes is the spatial connectivity of their constituent chromophores. Here we demonstrate that such geometrical parameters in the site base could provide an underlying physical explanation for the vast diversity of high or low energy transfer efficiency of random configurations embedded in a fixed volume, Fig. 2. We first define the concept of spatial path and its path strength between initial and trapping sites.

Generally, for any \( m \)-chromophoric system, there are \( \sum_{k=0}^{m-2} \frac{(m-2)!}{(m-k-2)!} \) spatial paths each including different cou-
plunging combinations of $0 \leq k \leq m - 2$ chromophores connecting initial and target sites. Label the initial site as 1 and the target site as 7. A path defined by interconnecting chromophores $\{c_1, \ldots, c_k|1 < c_j < 7\}$, has path strength, $h_{c_1 \ldots c_k}$, defined as the inverse of the total time scale of going through the path from the chromophore 1 to 7. This time scale $h_{c_1 \ldots c_k}^{-1}$ is given by the sum of the inverse of coupling strengths between neighboring sites given by the off-diagonal elements of the Hamiltonian $H$

$$h_{c_1 \ldots c_k}^{-1} = |H_{1, c_1}|^{-1} + \sum_{j=1}^{k-1} |H_{c_j, c_{j+1}}|^{-1} + |H_{c_k, 7}|^{-1} \quad (10)$$

and the trivial path of sites 1 and 7 direct connection has strength $H_{1,7}$. For a light harvesting complex consisting of 7 chromophores, there are 326 spatial paths each including a different coupling combination of one to five chromophores. In order to study any potential relationship between the path strength (as defined above) and ETE, we compute the path strength for all the paths for the most and least efficient configurations, from 10000 random 7-chromophoric samples in a given sphere with diameter 30 Å to 100 Å. The results are demonstrated in Fig. 9 where in each fixed $d$ the right (left) histogram demonstrates the number of paths for a given range of path strength, in energy units of $cm^{-1}$, for the most (least) efficient sample. A considerable energy gap of about $1500 cm^{-1}$ in the left panel is observed that is one order of magnitude bigger than those in the right panel for all volumes. There are a few strong paths that dominate the energy transport in the low efficient samples. In contrast, a large number of paths are contributing to quantum transport for high performing samples in the right panel. These alternative paths could help avoiding quantum localization due to static or dynamical disorders leading to a substantial enhancement of energy transport efficiency.

We note that there are significant path strength gaps of about $1500 cm^{-1}$ in the left panel (ultra low ETE samples) which are one order of magnitude bigger than those in the right panel (ultra high ETE samples with gaps of less than $150 cm^{-1}$) at all compactness levels. Incidentally, for low efficiency random configurations there are a few paths that completely dominate the energy transport whereas the high efficient samples contain a large number of, more or less, uniformly distributing spatial paths that contribute to quantum transport. One reasonable explanation is that light harvesting complexes with a few effective paths for exciton transport are more susceptible to large energy mismatches due to static or dynamical disorders leading to quantum localization. By contrast, those complexes with a large number of active spatial path become more robust to disorders or defects by providing alternative routes of transport. Moreover, the multipath systems can better exploit the environmental fluctuations to overcome energy mismatches which otherwise lead to exciton localizations. A similar robustness to defects due to redundant paths has been recently observed experimentally for energy transfer in certain artificial light-harvesting complexes [30, 31] and numerically simulated using an incoherent Förster model. These artificial systems are synthesized from self assembly of tobacco mosaic virus scaffold protein in disc and rod geometries which in the latter up to thousands of chromophores can be positioned spirally. Overall, the concept of path strength provides a rather straighforward explanation for the diversity of configurations in the ETE histograms presented in the Fig. 2.

To investigate this phenomenon beyond the highest or lowest efficient configurations, we have performed statistical studies on different ensembles of the samples, see Fig. 9.
FIG. 10: (a) The number of pathways with path strength larger than $1000 \text{cm}^{-1}$ statistically averaged over $m$ highest ETE samples. The horizontal axis shows the number of high ETE samples included in the statistical computation. It can be observed that top 500 high efficient configurations have no dominant pathways. If we enlarge the number of configurations beyond top 500, i.e., including samples with intermediate ETE, a few paths with strong strength will appear. (b) The number of spatial pathways with strength larger than $1000 \text{cm}^{-1}$ statistically averaged over $m$ lowest ETE samples. The horizontal axis shows the number of low ETE samples contributed to the statistical average. In sharp contrast to histogram (a), the energy transfer in the low efficient configurations is dominated by a few channels with very strong path strength. This property is attenuated when we increase the number of statistical samples to include more efficient ETE configurations. These results demonstrate that the path strength, defined by Eq. 10, is a suitable measure for quantifying the geometrical mechanism for the performance of light-harvesting systems in a given spatial dimension.

(a) and (b). We observe that for the low efficient configurations the excitonic energy is carried through a few dominant pathways whose strength is one or two order of magnitude larger than the rest of pathways. Thus, for $m$ top or bottom samples we count the number of the paths with strength larger than $1000 \text{cm}^{-1}$ as a measure for having a few dominant paths. In Figs. 10 (a) and (b) we compute the average of this measure for $m$ high and low ETE samples ($m = 10 - 90, 100 - 900, 1000 - 5000$) and for $d = 30, 60, 90 \text{Å}$. Remarkably, it can be observed that all of top 500 high efficient samples do not have any number of dominant paths, see Fig. 10 (a). However, as we compute the average over a larger number of high efficient samples some stronger paths will emerge. As expected, the inverse behavior is observed for low efficient samples presented in Fig. 10 (b), where the low ETE configurations have some dominant pathways that disappear as we enlarge number of low ETE samples. These results demonstrate that the path strength, defined by Eq. 10, capture the spatial correlations among top/low ETE structures and thus can provide an underlying geometrical description for the efficiency of light-harvesting complexes.

VII. CONCLUSION

We studied distributions of random arrangements of chromophores in volumes of various diameters as a function of chromophoric density, reorganization energy, and their interplay. We demonstrated that the chromophoric density play a major role in determining the performance of few-chromophoric systems embedded in various spherical volumes. We found that for random mutlichromophoric systems with fixed sizes 30 Å and 50 Å, 7 and 14 chromophores are indeed the minimum numbers to achieve a high ETE, similar to those values for FMO and LHCII respectively. After our original observations of these optimal chromophoric numbers in biological LHC [10], a similar result has been recently reported [32].

We observed significant statistical correlations in the low- and high-end efficient random structures with respect to average exciton energy gaps and multichromophoric spatial connectivity at the intermediate system-bath couplings. Moreover, we have investigated possible statistical correlations between quantum entanglement and performance of random chromophoric configurations. Specifically, we simulated the dynamics of excitons for many high/low ETE samples and calculated the entanglement measure based on Ref. [33]. Our simulations showed no particular patterns from which one can conclude that the presence of quantum entanglement is a significant indicator of efficient energy transport.

Overall, we observed two distinct parameter regimes for efficient energy transport: Ideally one can design molecular configurations to reside in the so-called Quantum Goldilocks regime [10, 34] where there is an energy-scale convergence for coherent and incoherent processes leading to optimality and robustness. However, if such regime is practically inaccessible, here we found alternative scenarios for potential optimal material design beyond Goldilocks regime where certain configurations could still have high energy efficiencies, but they become very sensitive to defects or environmental fluctuations. These model studies could be useful for design of structured molecular aggregates such as self-assembled dyes on tubular J-aggregates [35, 36] and virus-based templates aggregates [37, 38], with potential applications to photovoltaic devices, photosensing, and biological sensing.
Acknowledgments

We thank A. Ishizaki, M. Sarovar, K. B. Whaley, for useful discussions. We acknowledge funding from DARPA under the QuBE program, NSF, ENI, ISI, NEC, Lockheed Martin, Intel, and from project IT-PQuantum, as well as from Fundação para a Ciência e a Tecnologia (Portugal), namely through programme POCTI/POCI/PTDC, and projects SFRH/BPD/71897/2010 and PTDC/EEA-TEL/103402/2008 QuantPrivTel, partially funded by EU-FEDER.

[1] G.S. Engel, T. R. Calhoun, E. L. Read, T. K. Ahn, T. Mancal, Y. C. Cheng, R. E. Blankenship and G. R. Fleming, Nature 446, 782 (2007).
[2] M. Mohseni, P. Rebentrost, S. Lloyd, and A. Aspuru-Guzik, J. Chem. Phys. 129, 174106 (2008).
[3] P. Rebentrost, M. Mohseni, A. Aspuru-Guzik, J. Phys. Chem. B 113, 9942 (2009).
[4] P. Rebentrost, M. Mohseni, I. Kassal, S. Lloyd, and A. Aspuru-Guzik, New J. of Phys., 11, 033003 (2009).
[5] M.B. Plenio and S.F. Huelga, New J. Phys. 10, 113019 (2008).
[6] J. Cao, R. Silbey, J. Phys. Chem. A 113, 13826 (2009).
[7] F. Caruso, A. W. Chin, A. Datta, S. F. Huelga, M. B. Plenio Phys. Rev. A 81, 062346 (2010).
[8] G. Panitchayangkoon, D. Hayes, K. A. Fransted, J. R. Caram, E. Harel, J. Wen, R. E. Blankenship, G. S. Engel, Proc. Nat. Acad. Sci 107, 12766 (2010).
[9] A. Shabani, M. Mohseni, H. Rabitz, S. Lloyd, Phys. Rev. E, 86 011915 (2012).
[10] M. Mohseni, A. Shabani, H. Rabitz, S. Lloyd, arXiv: 1103.3823.
[11] R.E. Blankenship, Molecular Mechanism of Photosynthesis (Blackwell Science, London, 2002).
[12] V. May and O. Kuhn, Charge and Energy Transfer Dynamics in Molecular Systems (Wiley-VCH, Weinheim, 2004).
[13] "Quantum Effects in Bilogy" Edited by M. Mohseni, Y. Omar, G. Engel, and M. Plenio, in preparation (Cambremridge University Press, Cambridge, UK, 2013).
[14] S. Lloyd and M. Mohseni, New Journal of Physics, 12, 075020 (2010).
[15] D. Abasto, M. Mohseni, S. Lloyd, P. Zanardi, Phil. Trans. R. Soc. A. 375, 37013 (2012).
[16] H. Lee, Y.-C. Cheng, and G.R. Fleming, Science 316, 1462 (2007).
[17] T. R. Calhoun, N. S. Ginsberg, G. S. Schlau-Cohen, Y.-C. Cheng, M. Ballottari, R. Bassi, and G. R. Fleming, J. Phys. Chem. B 113, 16291 (2009).
[18] T. Scholak, F. D. Melo, T. Wellens, F. Mintert, A. Buchleitner, arXiv:0912.3560 (2009).
[19] H. -P. Breuer and F. Petruccione, The Theory of Open Quantum Systems (Oxford University Press, New York, 2002).
[20] J. Cao, J. Chem. Phys. 107, 8 (1997).
[21] A. Ishizaki and G. R. Fleming, J. Chem. Phys. 130, 234110 (2009).
[22] T. Ritz, S. Park, and K. Schulten, J. Phys. Chem. B 105, 8259 (2001).
[23] A. Olaya-Castro. C. Fan Lee, F. Fassioli Olsen, and N. F. Johnson, Phys. Rev. B 78, 085115 (2008).
[24] S. Hoyer, M. Sarovar and K. B. Whaley., New J. Phys. 12, 065041 (2010).
[25] A. Ishizaki, G.R. Fleming, Proc. Nat. Acad. Sci USA 106, 17255 (2009).
[26] G. D. Scholes, Annu. Rev. Phys. Chem. 54 , 57-87 (2003).
[27] In this work, whenever it is not specified otherwise, the environmental parameters for the FMO complex are chosen according to the estimated values of reorganization energy 35 cm$^{-1}$, bath cutoff frequency 50 cm$^{-1}$, temperature 298 $^\circ$K, trapping rate of 1 ps, excition life-time of 1 ns.
[28] T. Förster, in Modern Quantum Chemistry, Istanbul Lectures, edited by O. Sinanoglu (Academic, New York, 1965), Vol. 3, pp. 93–137.
[29] M. Yang and G. R. Fleming, Chem Phys 275, 355 (2002).
[30] Ying-Zhong Ma, Rebekah A. Miller, Graham R. Fleming, and Matthew B. Francis, J. Phys. Chem. B, 112, 22 (2008).
[31] R. A. Miller, N. Stephanopoulos, J. M. McFarland, A. S. Rosko, P. L. Geissler, and M. B. Francis, JACS (2010).
[32] S. Jesenko, M. Znidaric, available at arXiv:1204.4721.
[33] M. Sarovar, A. Ishizaki, G. R. Fleming, and K. B. Whaley, Nature Physics 6, 462 (2010).
[34] S. Lloyd, M. Mohseni, A. Shabani, H. Rabitz, available at arXiv: 1111.4982.
[35] D. M. Eisele, et. al., Nature Nanotechnology 4, 658 (2009).
[36] D. M. Eisele et al. Nature Chemistry, 4, 655 (2012).
[37] Y. S. Nam, et. al., J. AM. CHEM. SOC., 132, 1462 (2010).
[38] X. Dang, et. al., Nature Nanotechnology, 6, 377 (2011).