Centrosymmetry enhances quantum transport in disordered molecular networks

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Abstract
For more than 50 years we have known that photosynthetic systems harvest solar energy with almost unit quantum efficiency. However, recent experimental evidence of quantum coherence during the excitonic energy transport in photosynthetic organisms challenges our understanding of this fundamental biological function. Currently, and despite numerous efforts, the causal connection between coherence and efficiency is still a matter of debate. We show, through extensive simulations of quantum coherent transport on networks, that three dimensional structures characterized by centro-symmetric Hamiltonians are statistically more efficient than random arrangements. Moreover, a strong correlation of centro-symmetry with quantum efficiency is also observed under the coherent transport dynamics induced by experimentally estimated electronic Hamiltonians of the Fenna–Mathew–Olson complex of sulfur bacteria and of the cryptophyte PC645 complex of marine algae. The application of a genetic algorithm results in a set of optimized Hamiltonians only when seeded from the experimentally estimated Hamiltonian. These results suggest that what appears to be geometrically disordered complexes may well exhibit an inherent hidden symmetry which enhances the energy transport between chromophores. We are confident that our results will motivate research to explore the properties of nearly centro-symmetric Hamiltonians in realistic environments, and to unveil
the role of symmetries for quantum effects in biology. The unravelling of such symmetries may open novel perspectives and suggest new design principles in the development of artificial devices.

Keywords: quantum transport, transport dynamics, quantum statistical methods, random networks

1. Introduction

The apparatus used by photosynthetic organisms to harvest the Sun’s energy is both complex and highly efficient. Although it appears differently in different species, some features always persist: photons are absorbed by pigments, usually chlorophyll or carotenoid molecules, and transmitted to a reaction center (RC), where the primary chemical reactions of photosynthesis occur [1]. Photosynthetic structures contain far more chlorophyll molecules than RCs, and the former constitute molecular networks which pass the energy of an absorbed photon to the RC, where it is trapped [1–3].

In recent years, ultrafast optics and nonlinear spectroscopy experiments provided new insight into excitonic energy transport in photosynthetic organisms [4–7]. These experiments report the existence of long coherence times, suggesting that quantum coherence may play a fundamental role in the highly efficient transport of excitations, and trigger renewed theoretical interest. At least two crucial questions are currently at the center of the debate: first, how can quantum coherence persist in very noisy systems as are photosynthetic units, working at physiological temperatures? And, second, which design principles of genuine quantum character mediate efficient transport and are compatible with the known structural properties of light harvesting units? It is this latter question which we will address hereafter. We will see that constructive multi-path quantum interference induced by a specific symmetry property can give rise to efficient—i.e. rapid and essentially complete—excitation transfer from the donor to the acceptor site, on transient time scales which are short as compared to characteristic time scales of environmental (dynamical) noise.

A well established strategy to simulate the quantum excitation transport in such molecular complexes is the dynamical propagation of the electronic excitation in the presence of the many degrees of freedom of the environment [8–13]. This line of thought may suggest that proper tuning of the interaction between system and environment is responsible for the long coherence times and efficient transport. However, simulations based on numerically exact path integral methods in the presence of realistic environmental vibronic fluctuations yield coherence times (τc ∼ 250 fs) [13] shorter than the experimentally reported ones (τc ∼ 660 fs) [5] at T = 77 K. More recent numerical approaches [14, 15] appear to reproduce the experimental findings. Yet, since the experimental results were obtained by measurements on ensembles of individually slightly different molecules, the coherence time for a single molecule would actually be expected to be significantly longer (see, e.g., [16, 17] for a discussion on this subject), so that, in the light of these diverse observations, the case appears to be open for further debate. One reason being that the complexity of the quantum
dynamics grows exponentially with the number of strongly coupled degrees of freedom [13], rendering approximations unavoidable, even in full-fledged computational approaches.

Since, in addition, also the available experimental data characterizing the complexes have large uncertainties, virtually all computational methods use effective descriptions. This is a very sensible and valuable strategy when one seeks to model the average trend of the dynamics by incorporating a minimal set of experimentally accessible fitting parameters. One must not forget, however, that the non-trivial, system-specific information on complex quantum systems is inscribed into the fluctuations of characteristic observables, rather than in their average behavior [18–22]. By definition, it cannot be inferred by the inspection of expectation values. Notwithstanding its undeniable merits, the computational approach therefore has its limitations when it comes to unveil the necessary and sufficient structural elements which guarantee some optimality properties, e.g. with regard to transport efficiencies.

On the other hand, simplified models [23–28] that mimic the excitonic dynamics by those of two coupled two level systems interacting with the environment may help to identify some minimal ingredients that must be included into a general theory. However, because of their simplicity, they disregard many of the structural features of the light harvesting complexes—possibly those that are most relevant for the transport efficiency in realistic systems.

Therefore, given the multifaceted state of affairs, we here attempt to incorporate most of the documented properties of the electronic Hamiltonians that underlie excitonic transport in biological tissue, and yet to outline a model as simple as possible [29, 30]. In an abstract setting, that perceives light harvesting units as 3D random networks, we will see that they are very likely to perform efficiently—on sufficiently short time scales such that the environmental noise cannot establish its detrimental effect on quantum coherent transport phenomena—whenever their Hamiltonians exhibit centro-symmetry. We then test the applicability of this abstract design-principle for FMO8 and PC645 light harvesting complexes, and show that the centro-symmetry of these increases if their Hamiltonians are optimized towards efficient coherent transport. Note that our present approach is not meant to substitute for, or compete with, a faithful and accurate ab initio modelling of real biological objects, with their various degrees of freedom coupled with variable strength. We rather seek to import an alternative, statistical perspective, and to unveil possible design principles which do not immediately emerge, or even may be masked by competing effects, in ab initio calculations.

2. Random networks

Inspired by the structure of the Fenna–Mathew–Olson (FMO) network—seven (FMO7) [31, 32] or eight (FMO8) [33] chromophores that are connected through dipolar interactions—we study the simplest possible random model which can grasp its essential ingredients: a small random network with \( N \) identical sites, which completely neglects the individual chromophores’ couplings to their local environments, and where coherent transport of a single excitation is generated by the Hamiltonian

\[ H = \sum_{\langle i,j \rangle} J_{ij} \sigma_i \sigma_j \]

Indeed, we will therefore come up here with a deliberately simple and somewhat abstract model, which restricts the Hamiltonian description of the system to a single excitation of the electronic degrees of freedom on a graph-like configuration space. The influence of the—possibly strongly coupled—vibrational degrees of freedom will be accounted for phenomenologically, by statistical sampling over the graph conformation.
\[ H = \sum_{i,j=1}^{N} V_{ij} \sigma_+^{(i)} \sigma_-^{(i)} . \]  

Here, \( \sigma_+^{(i)} \) and \( \sigma_-^{(i)} \) mediate excitations and de-excitations of sites \( j \) and \( i \), from the local electronic ground state to the local excited state, and vice versa. The excitation transfer \( \sigma_+^{(i)} \sigma_-^{(i)} \) from site \( i \) to site \( j \) has a strength \( V_{ij} = \alpha / r_{ij}^3 \), consistent with an isotropic dipolar interaction, with \( r_{ij} = |\vec{r}_i - \vec{r}_j| \) and the \( \vec{r}_j \) the position vectors of individual sites. Input and output sites define the poles of a sphere of diameter \( d \). The positions of the remaining molecular sites are randomly chosen within this sphere. This induces a random distribution of the remaining \( V_{ij} \). Networks for which one of the distances \( r_{ij} \) is smaller than \( d/20 \) are discarded in the analysis, in order to avoid singular coupling strengths \([30] \).

The excitation is initially injected at the input site \( |\text{in}\rangle = |1\rangle \), from where it is to be transferred to the output site \( |\text{out}\rangle = |N\rangle \). The coupling constant \( V_{1N} = \alpha / d^3 \) between these two sites sets the natural time-scale of the coherent dynamics induced by \( H \). The intuition is that the additional sites, if properly placed, can mediate a multitude of transition amplitudes from input to output, which interfere constructively upon transmission, and thus dramatically accelerate and enhance the excitation transfer. Wave packet-like coherent refocussing thus allows for an essentially deterministic delivery of the excitation at the output site, on time scales faster than that of environment-induced decoherence (see also figure 2 below). Hereafter, a network will therefore be considered efficient if the initial excitation is transferred to the output site in a time significantly shorter than the Rabi coupling time \( T = \pi / 2 |V_{1N}| \) between \( |\text{in}\rangle \) and \( |\text{out}\rangle \), with high probability. For a quantitative assessment, we define the figure of merit \([29, 34]\)

\[ \mathcal{P} = \max_{t \in [0, T]} \left| \langle N | e^{-iHt} | 1 \rangle \right|^2 . \quad T = 0.1 \times \frac{\pi}{2 |V_{1N}|} . \]  

Indeed, we showed earlier that \( \mathcal{P} \) fluctuates strongly with different realizations of the random molecular network, and reaches large values close to unity with finite probability \([29, 35]\). However, while it is therefore natural to ask for necessary and/or sufficient conditions on the networks’ structure such as to guarantee large values of \( \mathcal{P} \), no design principles were so far identified. This is the purpose of our present contribution. A similar question has recently been tackled by means of a complex network analysis showing that pairs of closely separated sites render transport properties more robust against perturbations \([36]\).

Note that the efficiency quantifier \( \mathcal{P} \) as defined in equation (2) is distinct from other measures of transfer efficiency, which e.g. take the long-time integral of the acceptor population, or consider the population of a sink connected to the latter. However, as shown in \([30, 34, 48]\), these different measures are strongly correlated with each other. We will come back to this issue in section 5, where we will argue that the conclusions of this paper are not specific to our definition of efficiency.

While the isotropic model here employed can be extended to account for different dipolar orientations, we verified that this does not qualitatively change the results presented below (see also \([30]\)). The same is true for the precise choice of the cutoff distance \( d/20 \), provided it is chosen much smaller than \( d \), to provide enough freedom to randomly place the sites within the sphere.
3. Efficiency versus centro symmetry

While near-optimal random networks—in the sense of giving rise to large values of $\mathcal{P} \approx 1$—do not exhibit apparent symmetries in their 3D geometry, it was observed that the individual sites’ populations $P_i(t) = \left| \left< i | e^{-iHt} | 1 \right> \right|^2$, $i = 1,...,N$, approximately fulfill $P_i(t) \approx P_{N-i+1}(t_\text{max} - t)$ (see figure 2 in [35]), where $t_\text{max}$ is the time where the maximum is reached in equation (2). In other words, the populations indeed do display a near-symmetric structure on the time axis, under exchange of input and output site, as well as of properly defined pairs of intermediate sites. This must be inherited from an exchange symmetry of pairs of two-site coupling matrix elements of the underlying Hamiltonian, and evokes an analogy with $N \times N$ centro-symmetric matrices, which are defined by $H_{ij} = H_{N-j+1,N-i+1}$, i.e., $AH = HA$, where $A$ is the exchange matrix, $A_{ij} = \delta_{i,N-j+1}$, that exchanges site 1 with site $N$, 2 with $N-1$, etc. This type of Hamiltonians is known to be tunable towards optimal excitation transfer, under specific topological constraints [37–39].

We therefore quantify the transfer efficiency (2) of a given 3D network’s Hamiltonian, and correlate this with the Hamiltonian’s centro-symmetry, measured by

$$e = \frac{1}{N} \min S \left\| H - A^{-1}HA \right\|,$$

where $\| ... \|$ denotes the Hilbert–Schmidt norm, i.e., $\| X \| = \sqrt{\text{Tr} X^\dagger X}$ [40]. The quantity $e$ measures the root mean square deviation of a network Hamiltonian from its image under $A$, minimized over all possible permutations $S$ of the intermediate sites $2, ..., N - 1$. Figure 1
shows the correlation plot on a triple logarithmic scale, for \( N = 7 \) and \( 10^8 \) independent random realizations of the network.

A very strong and, given the variance of \( \mathcal{P} \) and \( \epsilon \) over several orders of magnitude, unambiguous correlation between centro-symmetry (small values of \( \epsilon \)) and transfer efficiencies is evident. So is the rather low probability to generate a high efficiency molecular conformation by random sampling. The tail of the distribution at \((\log \epsilon, \log \mathcal{P}) \approx (2, -8)\)—which appears even more pronounced in the linear color scale of figure 2 (top left)—is formed by configurations where one of the sites is placed very close to the input or the output site [30]. Therefore, the value of the minimum distance \( d/20 \) (see above) determines the length of this tail, but otherwise leaves the correlation plot essentially unchanged. In figure 1, we chose units such that \( V_{L,N} = 0.07 \), corresponding to a dipolar coupling strength \( \alpha = 0.07d^3 \). Note, however,
that the transfer efficiency $\mathcal{P}$ is independent of $\alpha$ according to equation (2), whereas $e$ is proportional to $\alpha$. Therefore, choosing a different value of $\alpha$ only leads to a constant shift on the $\log(e)$-axis, without affecting the correlations between $\mathcal{P}$ and $e$ observed in figure 1.

This strong statistical correlation between $e$ and $\mathcal{P}$ implies that an iterative search for highly efficient networks in conformation space will with very high probability move towards higher degrees of centro-symmetry, and hence acts as an evolutionary funnel. This is confirmed by a genetic algorithm [41] that optimizes the structure of the networks to achieve maximum efficiency: starting from random networks, located with high probability close to the global maximum of the distribution in figure 1, i.e., approximately at $\log(e) \approx -0.5$, $\log(\mathcal{P}) \approx -3$, the algorithm generates configurations with almost unit efficiency and very high centro-symmetry (i.e., very small $e$). An exemplary output configuration is indicated by the white circle in figure 1: while the deviation from the centro-symmetry is reduced by approximately two orders of magnitude, the network’s efficiency increases by about three orders of magnitude.

4. Quantum-enhanced efficiency versus dynamical noise

That the observed correlation between $\mathcal{P}$ and $e$ is in itself of quantum origin is suggested by our initially formulated intuition on the role of the intermediate sites which mediate the excitation transfer from $\ket{\text{in}}$ to $\ket{\text{out}}$: large transfer efficiencies as quantified by (2) are a consequence of constructive quantum interference of the transition amplitudes along distinct sequences of the intermediate sites. This is underpinned by inspection of the analogously generated correlation plots in figure 2, though now in the additional presence of environment-induced dephasing (dynamical noise) locally at each individual molecular site. The excitation transfer dynamics is then no longer described by the unitary evolution alone, but rather by a Lindblad equation

$$\dot{\rho}(t) = -\mathcal{L}_\rho(\rho(t)) + \mathcal{L}_{\text{dep}}(\rho(t)), \quad \text{with the Lindblad term}$$

$$\mathcal{L}_{\text{dep}}(\rho) = -4\gamma \sum_{i \neq j=1}^{N} |i\rangle \langle j| \rho |j\rangle \langle i|,$$  

and $|i\rangle$ and $|j\rangle$ the $N$-site electronic state where the excitation is located at the $i^{th}$, respectively $j^{th}$ site. Two time scales now compete [34, 48]: the characteristic time scale of the coherent dynamics as generated by $H$, and the characteristic dephasing time $\gamma^{-1}$. As the dephasing rate $\gamma$ is tuned from zero over one and ten to hundred incoherent events per Rabi coupling time $T$, the distribution in the correlation plot in figure 2 essentially rotates from a strongly increasing efficiency with increasing centro-symmetry to an essentially centro-symmetry-independent distribution, at the largest dephasing rates. Note that the correlation prevails even for relatively large dephasing rates of $\gamma = 10 T^{-1}$, what corresponds to one incoherent event within the time interval $\mathcal{T} = T/10$ that we chose to define $\mathcal{P}$ in (2). (This interval roughly corresponds to the time scale associated with the average coupling between different sites.) For even larger dephasing rate ($\gamma = 100 T^{-1}$)—where quantum coherences are almost completely destroyed within the time scale $\mathcal{T}$, and therefore the regime of classical transport is reached [34, 48]—the correlation between efficiency and centro-symmetry is lost, see figure 2 (right bottom). Hence, centro-symmetry enhances quantum but no classical transport, and, in the presence of dynamical noise, can do so only on transient time scales comparable to the dephasing time.
5. Light harvesting Hamiltonians

We now validate the relevance of our above findings for the actual design of light harvesting complexes. As in chapters 2 and 3, we will restrict ourselves to the regime of purely coherent transport dynamics (see also the discussion at the end of this chapter). Clearly, the strong correlation between transfer efficiency and centro-symmetry of the network, evident from figures 1 and 2, was deduced from unrestricted, uniform statistical sampling over a random Hamiltonian of the form (1), while actual biological functional units are sufficiently well characterized (by spectroscopic means) to locate them in a comparably small sub-volume of conformation space. Therefore, we now focus on the trade-off between centro-symmetry and transfer efficiency, using published data of the FMO8 protein [45] and the PC645 [46] light harvesting complexes (of sulfur bacteria and marine algae, respectively) as our point of departure. Both these complexes are represented by a network of eight dipole-coupled two-level systems, and thus comply with our abstract model from above, in terms of their characteristic size. However, the data are garnished with error bars, and the exact numbers depend on the authors (see, e.g., [45] and [47]—we will rely on [45] hereafter). We will show below that Hamiltonians with coupling matrix elements very close to the ones reported in the literature [45, 46] can indeed support efficient coherent transport, and that they are statistically significantly more centro-symmetric than the experimentally proposed ones, or than their unbiased benchmarks.

In order to define a statistically unbiased benchmark against which we can gauge the centro-symmetry properties of the FMO8 and PC645 Hamiltonians, we use an ensemble of random Hamiltonian matrices of type (1), constructed as follows: their off-diagonal elements are identically and independently distributed random variables, which are all chosen from the same Gaussian distribution. The mean value and the standard deviation of this distribution are given by the mean and the standard deviation of the off-diagonal elements of the published effective Hamiltonians of the FMO8 and PC645 complex, respectively, see tables 1 and 2 (right entries). Furthermore, our model completely neglects all couplings of its constituents to any environmental degree of freedom, in particular environment-induced shifts of the on-site energies. This implies the neglect of diagonal disorder which is generic for real pigment protein complexes, and thus represents a stark abstraction from what currently available structure data are telling us. Note, however, that these are inferred from equilibrium absorption spectra, while we advocate a non-equilibrium perspective on the transport process here under debate, with at least some of the environmental degrees of freedom strongly coupled and therefore actively involved in the transient quantum dynamics. Rather than incorporating them explicitly into our model, we here (partially) account for them by statistical sampling. (We come back to this issue at the end of this section.)

The distribution of the centro-symmetry \( \epsilon \) thus obtained is represented by the green histograms, for FMO8 and PC645, respectively, in figure 3 (for an ensemble of \( 10^2 \) random Hamiltonians), and defines our unbiased benchmark distribution. For FMO8, the input site is the site recently added to the structure of the protein, and the output site is usually named ‘site 3’ in the biological literature [45, 47]. For PC645, we identify the DBVc and PCBd82 molecules with the input and output sites, respectively [46].

The vertical lines in figure 3 indicate the centro-symmetries of the FMO8 and PC645 Hamiltonians, respectively, as extracted from the published data [45, 46], see tables 1 and 2.
In both cases, the complexes’ centro-symmetries are located in the bulk of the unbiased distributions. The associated time evolution of the single site populations are presented in figure 4, which clearly shows very unsatisfactory coherent transfer efficiencies, for both molecular networks.

We now assess how close FMO8 and PC645 structures are to more centro-symmetric conformations, with higher transfer efficiencies. For this purpose, we generate a new ensemble of network Hamiltonians, by repeated execution of a simple genetic algorithm. The algorithm works as follows: (i) take the actual FMO8 or PC645 Hamiltonian, see table 1 or 2 (right matrix entries), as original Hamiltonian $H^*$. (ii) Starting from $H^*$, generate $M = 100$ new Hamiltonians by randomly perturbing all matrix elements $H_{ij}$ of $H^*$, according to a Gaussian distribution with standard deviation $\sigma$, initially set to $\sigma_0 = H_{ij}/10$. (iii) From these new Hamiltonians (and $H^*$), choose the one with the largest efficiency $\mathcal{P}$ (as quantified by equation (2)). This Hamiltonian defines the new $H^*$. (iv) Repeat steps (ii) and (iii) until the maximum number $N = 10^4$ of

Table 1. Off-diagonal elements (in cm$^{-1}$) of the average Hamiltonian after optimizing the FMO8 structure with a genetic algorithm (left), and of the original, spectroscopically inferred FMO8 Hamiltonian (right) [45]. The rows in the Hamiltonian (from top to bottom) correspond to the sites labeled by 8, 1, 2, 4, 5, 6, 7 and 3 in [45]. (Note that there is a sign difference with the respect to the Hamiltonian published in [47]: $-97.9$ instead of $94.8$, as discussed in [45].) Mean value and standard deviation of the original off-diagonal matrix elements: $\bar{V} = -4.4$ and $\Delta V = 34.5$.

Table 2. Off-diagonal elements (in cm$^{-1}$) of the average Hamiltonian after optimizing the PC645 structure with a genetic algorithm (left), and of the original, spectroscopically inferred PC645 Hamiltonian (right) [46]. The rows in the Hamiltonian (from top to bottom) correspond to the sites labeled by DBVc, DBVd, MBVa, MBVb, PCBc158, PCBd158, PCBs82, and PCBd82 as in [46]. Mean value and standard deviation of the original off-diagonal matrix elements: $\bar{V} = 21.3$ and $\Delta V = 67.0$.

(right entries). In both cases, the complexes’ centro-symmetries are located in the bulk of the unbiased distributions. The associated time evolution of the single site populations are presented in figure 4, which clearly shows very unsatisfactory coherent transfer efficiencies, for both molecular networks.

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Figure 3. Green: centro-symmetry distributions for Gaussian random ensembles with mean and standard deviation extracted from the original FMO8 (left) and PC645 (right) structure data [45, 46] (off-diagonal elements), listed in tables 1 and 2. Vertical lines indicate the actual centro-symmetries inferred from these data sets. Blue: centro-symmetry distributions for efficient systems obtained by evolutionary optimization of the FMO8 and PC645 Hamiltonians.

Figure 4. Single-site populations under coherent time evolution induced by FMO8 (left) and PC645 (right) light harvesting Hamiltonians, with inter-site coupling matrix elements extracted from published structure data [46, 47], see tables 1 and 2, and on-site energies replaced by their mean. Initially, the excitation is located at site 1. Clearly, the transfer efficiency towards site 8 is mediocre, for FMO8 as well as for PC645. Site labels 1 and 8 here correspond to sites 8 and 3 as labeled in the FMO8 literature [45, 47], and to DBVc and PCBd81 for PC645 [46], respectively.
iterations is reached. At the \( n \)th iteration, perturb the matrix element \( H_{ij} \) by a Gaussian distribution with standard deviation \( \sigma = \sigma_0 n \).

Repeating this algorithm \( 10^2 \) times (with the same initialization \( H^0 \)) yields an ensemble of optimized Hamiltonians resulting in the blue histograms in figure 3, which are clearly shifted towards higher centro-symmetries (i.e., smaller values of \( \epsilon \)). We verified that all the thus optimized Hamiltonians mediate essentially perfect excitation transfer \( \mathcal{P} > 0.9 \). Moreover, even the average Hamiltonian obtained from an equally weighted sum of the optimized ensemble does so! This is clearly demonstrated by figure 5, where the time dependence of the individual site populations is monitored, as generated by this average Hamiltonian. Since different, individually optimized Hamiltonians generally do not commute, this is a highly non-trivial result which underpins that evolutionary optimization seeded by the FMO8 and PC645 structures converges into essentially optimal transfer efficiencies, in a statistically robust sense. In particular, this observation suggests that centro-symmetric, optimized Hamiltonians all exhibit a common property that is robust under averaging and associated with their high coherent transfer efficiency. Finally, inspection of the thus obtained average optimal Hamiltonian’s matrix elements shows that most of them can be obtained by weak perturbation of those inferred spectroscopically, see tables 1 and 2.

In contrast to the above results, the very same genetic algorithm, when seeded by the elements of our random benchmark ensembles, produces significantly lower transport efficiencies, see figure 6(a) for the random FMO ensemble. Both the initial and the optimized distributions of efficiencies are strongly peaked at values of \( \mathcal{P} \) smaller than 0.05. This is due to the fact that, in the original FMO Hamiltonian, the direct coupling element between the input and the output site assumes a relatively small value \( V_{1,8} = 1.5 \text{ cm}^{-1} \), see table 1 (right). This

**Figure 5.** Single-site populations under coherent time evolution induced by genetically optimized FMO8 (left) and PC645 (right) light harvesting Hamiltonians, see tables 1 and 2 (left matrix entries), with inter-site coupling matrix elements given by an equally weighted average over \( 10^2 \) optimized Hamiltonians generated by the genetic algorithm. Site labeling as in figure 4. Essentially optimal transfer efficiencies are achieved in both cases.
leads to a large value of the reference time $T$, over which the maximum is taken in equation (2). To obtain a fair comparison, we therefore repeated the optimization for a different ensemble of random initial Hamiltonians, where we set this coupling element equal to the one of the original FMO, whereas all other elements are randomly chosen in the same way as before. As evident from figure 6(b), the pre-optimization efficiency of this ensemble is comparable to the one of the original FMO Hamiltonian. In this case, the genetic algorithm works much better than for the completely random ensemble displayed in figure 6(a)—though not as good as for the original FMO (where, as stated above, all optimized Hamiltonians reach $\rho > 0.9$). In contrast to the case of the optimization seeded by the original FMO, however, the average Hamiltonian now exhibits a significantly lower efficiency ($\rho \approx 0.3$). Furthermore, we have checked that, for both random ensembles shown in figure 6, the distribution of centrosymmetry, indicated by the green histograms in figure 3, is essentially unaffected after application of the genetic algorithm. This markedly distinct behavior of the genetic optimization for FMO8 and PC645 on the one hand, and for random benchmark Hamiltonians on the other, again points at the existence of an inherent hidden symmetry associated with, both, high transfer efficiency and increased centrosymmetry which is, to some extent, already present in the initial FMO8 and PC645 data. This property must be encoded in those correlations (or higher statistical moments) of the actual FMO8 and PC645 structures which are eliminated when replaced by the above Gaussian ensembles. It is not surprising that this symmetry is not immediately apparent: the determination of the elements of the effective Hamiltonian is a complex process that requires the calculation of dipolar interactions and the fitting of experimental data. Small variations of the parameters produce comparable but different data [45, 47], and this hides any symmetry in the system.

It is important to recall that our above results are valid for different measures of the transport efficiency. Our measure (2) is given by the maximum occupation of the output site.
within time $T = T/10$. Alternatively, the efficiency can also be quantified by integrating the output occupation $P_x(t) = \left( 1 \exp \left( -iHt \right) \right)^2$ over a certain time window—or, closely related to that (see [30], chapter 5/6)—in terms of the average transfer time to a sink irreversibly coupled to the output site. As an example, let us consider the asymptotic output probability $P_{as} = \lim_{T \to \infty} \int_0^T dt P_N(t)/T$. Applying the same genetic algorithm as described above—but optimizing with respect to $P_{as}$—we have checked that the above conclusions remain valid: the optimized FMO Hamiltonians (all of which reach $P_{as}$ close to the maximum value 1/2) are significantly more centrosymmetric than the original FMO Hamiltonian. Furthermore, the average optimized Hamiltonian remains efficient ($P_{as} = 0.49$) and similarly close to the original one as before (see table 1). Finally, starting the optimization from a randomly chosen Hamiltonian, the optimization is less efficient and does not increase centrosymmetry. This similar behavior for different transport measures is not surprising if we look, e.g., at figure 5 (left): due to coherent oscillations between the input and output site, a large maximum output occupation is also associated with a large integrated output probability, and vice versa [30, 48].

Finally, let us comment on the role of the diagonal disorder which we have neglected so far: as evident from table 3 (right), the experimentally determined values for the FMO Hamiltonian [45] exhibit a strong asymmetry between the diagonal entries $E_{in} = \langle \text{in} | H | \text{in} \rangle$ corresponding to the input site (the largest one of all diagonal entries) and $E_{out}$ (the lowest one). Since perfect, coherent excitation transfer, i.e. $P = 1$, requires $E_{in} = E_{out}$ (due to the fact that the expectation value of $H$ is conserved under coherent evolution, and therefore $\langle \text{in} | H | \text{in} \rangle = \langle \text{out} | H | \text{out} \rangle$ if $P = 1$), this strong asymmetry leads to correspondingly inefficient coherent transfer. Indeed, equation (2) yields a very low value, i.e. $P = 8.6 \times 10^{-4}$, for the original Hamiltonian displayed in table 3 (right). When seeded by this Hamiltonian, the same genetic algorithm as described above yields an ensemble of optimized Hamiltonians, see figure 7. We see that, upon optimization, deviation from centrosymmetry drops from 90 to 40–80, whereas the efficiency increases to values between 0.1 and 0.8 (average efficiency: 0.38). Moreover, the data again shows a clear correlation between centrosymmetry and efficiency: e.g., for $\epsilon > 60$, most Hamiltonians exhibit efficiencies close to 0.2, whereas the average efficiency increases to approximately 0.4 for more centrosymmetric Hamiltonians with $\epsilon < 60$. In accord with the above discussion, however, the increase in efficiency is now mainly due to a decrease in diagonal asymmetry rather than to suitable tuning of the off-diagonal matrix elements—as evident from the average optimized Hamiltonian, see table 3 (left), where the input energy is reduced from 505 to 160.

Since diagonal disorder is a consequence of the coupling of the electronic to vibrational or other environmental degrees of freedom, locally at each individual molecular site, its dominance over the off-diagonal disorder expresses the non-perturbative coupling of electronic and (at least some) environmental degrees of freedom. Furthermore, present estimates for environmental time scales (between 50 and 100 fs [56]) are considerably shorter than the coherent transfer time ($t = 0.09 T \approx 500$ fs) for our optimized FMO Hamiltonian observed in figure 5 (left). This ultimately suggests a picture where the dominant environmental degrees of freedom need to be considered as system constituents which ‘dress’ the electronic degree of freedom, and are to be included in the coherent dynamics on the typical excitation transfer time scales here considered. To validate our centro-symmetry scenario in such an extended model
with vibronic [50] rather than electronic excitations) will require a much improved understanding of the relevant energy and time scales associated with these strongly coupled degrees of freedom, possibly extractable from molecular dynamics simulations [55], though beyond the scope of our present contribution.

6. Conclusions

We have seen that in 3D random networks, (nearly) centro-symmetric Hamiltonians mediate coherence-induced, highly efficient quantum transport. Furthermore, a careful analysis of the reported coupling matrix elements of the biologically relevant light harvesting complexes FMO8 and PC645, together with the (unavoidable) associated error margins, suggests that centro-symmetry may also be a (quantum) design principle used by Nature (although, as explained at the end of the previous section, the influence of realistic environmental couplings still has to be clarified): when neglecting on-site energy shifts induced by the coupling to background degrees of freedom, the available structure data are in a statistical sense close to centro-symmetric conformations. Moreover, our results suggest the presence of further hidden symmetries in the FMO8 and PC645 structures—the precise characterization of which remains

Table 3. Diagonal and off-diagonal elements (in cm$^{-1}$) of the average Hamiltonian after optimizing the FMO8 structure with a genetic algorithm (left), and of the original, spectroscopically inferred FMO8 Hamiltonian (right) [45]. Mean value and standard deviation of the original diagonal matrix elements: $\overline{H} = 278$ and $\Delta H = 141$.

\[
\begin{bmatrix}
160/505 & 56.9/37.5 & 8.4/7.5 & 1.7/1.7 & 4.6/4.5 & -11.2/-9.7 & -12.4/-11.4 & 1.5/1.5 \\
... & 147/310 & -82.2/-97.9 & -6.0/-5.8 & 6.5/6.7 & -11.3/-12.1 & -11.3/-10.3 & 5.7/5.5 \\
... & ... & 206/230 & 6.8/7.3 & 2.0/2.0 & 11.3/11.5 & 4.6/4.8 & 50.8/30.1 \\
... & ... & ... & 45.7/180 & -70.1/-64.9 & -17.7/-17.4 & -68.5/-64.4 & -92.6/-58.8 \\
... & ... & ... & ... & 296/405 & 94.0/89.0 & -6.4/-6.4 & -1.5/-1.5 \\
... & ... & ... & ... & ... & 205/320 & 32.1/31.7 & -9.8/-9.6 \\
... & ... & ... & ... & ... & ... & 169/270 & 4.7/4.7 \\
... & ... & ... & ... & ... & ... & ... & 0/0
\end{bmatrix}
\]
an interesting subject for future studies. These inherent hidden symmetries emerge locally in the conformation space of 3D random networks and are, in this respect, reminiscent of local symmetries in complex and/or chaotic quantum systems [18, 51, 52]. While such local symmetries are typically not given by explicitly defined integrals of motion and therefore are hard to detect, they may nonetheless dramatically impact the system’s dynamical properties [51, 53]. Beyond the realm of biology, we trust that our findings may inspire new design principles for devices for efficient energy transduction [54], which define another paradigmatic testing ground for truly complex quantum transport. Furthermore, we are confident that the here unveiled conspiracy of symmetry and quantum coherence in an apparently disordered system may help to achieve a deeper understanding of non-trivial structural properties also in other biological systems [49].

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