The dependence of exciton transport efficiency on spatial patterns of correlation within the spectral bath

Kenley M Pelzer\(^1\), Andrew F Fidler\(^1\), Graham B Griffin\(^1\), Stephen K Gray\(^2\) and Gregory S Engel\(^1,3\)

\(^1\) James Franck Institute, Institute for Biophysical Dynamics and Department of Chemistry, The University of Chicago, 929 East 57th Street, Chicago, IL 60637, USA
\(^2\) Center for Nanoscale Materials, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439, USA
E-mail: gsengel@uchicago.edu

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Abstract. Spatial correlations in spectral bath motions have been proposed to explain long-lived coherence in exciton transport. Systems of interest, ranging from photosynthetic complexes to organic photovoltaics, contain inhomogeneous environments. We consider the possibility that the degree of spatial correlation varies throughout an exciton transport system. We model exciton transport in the Fenna–Matthews–Olson complex (FMO), a photosynthetic light-harvesting complex. Although it remains unclear whether significant spatial correlations exist in FMO, its very high exciton transport efficiency makes it an interesting case for studies of exciton transport. We also simulate a highly symmetric ten-site model system. We use an extension of the environment-assisted quantum transport model to simulate transport, allowing the spatial correlation function to vary throughout the system. We demonstrate both via analysis and via simulation that exciton transport efficiency is most sensitive to changes in correlation between the site coupled to the trap and its neighboring sites. This asymmetry in sensitivity is highly robust and appears irrespective of changes in parameters such as transition dipole orientations and initial conditions. Our results suggest that in the design of exciton transport...
systems, efforts to increase efficiency by controlling spatial correlation should be focused on the region near the site of exciton trapping.

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1. Introduction

Recent spectroscopic data on photosynthetic complexes has revealed evidence of long-lived electronic coherence in excited systems [1–6]. Complexes from green and purple bacteria, cryptophytes and green plants have all shown evidence of persistent quantum coherence. Recently, similar effects have been observed in artificial small molecules engineered to support long-lived electronic coherences [7], as well as in intrachain energy transfer in conjugated polymer chains [8]. A variety of theoretical models have been developed to explore the role of long-lived coherence in exciton transport. Many of these models speculate that coherent dynamics contribute to the high exciton transport efficiency of some photosynthetic systems [9–18], which approaches 100% [19–22]. Although the idea that long-lived coherence promotes transport has generated intense interest in the relationship between coherence and efficiency, the mechanism behind the persistence of quantum coherence is not entirely understood.

One design principle proposed to support long-lived electronic coherences is nanometer-scale spatial correlation of environmental fluctuations leading to correlation between the excitation energies of the various chromophores [3, 23, 24]. This spatial correlation in spectral motions effectively decreases dephasing and increases the lifetime of electronic coherences. The existence of such spatial correlations is highly controversial: molecular dynamics simulations of the Fenna–Matthews–Olson complex (FMO), a seven-site exciton transport system which exhibits long-lived coherence, suggest that spatial correlation is minimal and the independent bath approximation is valid [25, 26]. A lack of spatial correlation has also been suggested by simulations of the exciton transport complex light-harvesting system II [27]. Models of photosynthetic energy transfer which incorporate spatial correlation in excitation energies have
produced mixed results, with some finding little impact on exciton transport \cite{28, 29} and others suggesting that transport is sensitive to such correlations \cite{12, 15, 30–34}. These conflicting results suggest that the role of spatial correlation in exciton transport in photosynthesis deserves further examination. Regardless of whether these spatial correlations are present and influential in FMO or other biological systems, they may be of interest in the development of synthetic exciton transport systems: either by accident or by design, such systems may have significant spatial correlations. We seek to understand whether spatially correlated environmental fluctuations could promote efficiency in such systems.

Various theoretical models of exciton transport have incorporated spatial correlation in environmental noise \cite{12, 15, 28–37}. However, previous work has made the simplifying assumption that the function relating spatial correlation to distance between sites is the same throughout the entire system. We see no reason why this assumption should be universally valid. Inhomogeneities in the environment, or even inhomogeneities in the system that affect the system–bath interaction, could lead to very different degrees of spatial correlation throughout the system. Given the complex and powerful relationship between environmental noise and transport efficiency, oversimplification of the spatial correlation in noise could obscure important features of the relationship between correlation and efficiency. In this study, we discard the assumption that the function determining spatial correlation must be constant throughout the system. We find that the relationship between correlation and transport efficiency shows surprising variations based on the spatial distribution of correlations in noise.

In this study, we simulate two systems using the environment-assisted quantum transport (EnAQT) model developed simultaneously by Rebentrost et al \cite{16} and Plenio and Huelga \cite{17}. First, we examine FMO, an interesting case due to its known long-lived coherences and its high exciton transport efficiency. The limitation of working with FMO is that it has a highly asymmetric geometry, making it difficult to ascertain whether an asymmetry in sensitivity to correlation is simply a result of the asymmetric geometry of the system. For this reason, we also study a highly symmetric ten-site model system. Because the relationship between correlation and efficiency is highly sensitive to inter-site couplings (which are determined both by geometry and by the orientations of the transition dipoles), we test three distinct transition dipole orientations in our calculations of the model system to confirm that our results are robust to such differences in couplings. In our FMO calculations, we test two different starting states to confirm that the results are robust to changes in initial conditions. We also simulate FMO under various levels of environmental noise to assess whether our results are consistent under different environmental conditions.

After defining the EnAQT model, we begin by demonstrating analytically that efficiency should be most sensitive to changes in correlation in the region containing the site coupled to the trap and its adjacent sites. We then simulate each of the cases described above, allowing spatial correlation to vary across different regions of the system. Our simulation results are consistent with our analysis: we find that the exciton transport efficiency is most sensitive to changes in correlation in the region near the trap. As expected from the known non-monotonic relationship between dephasing and efficiency \cite{16, 17}, correlation (which directly determines the dephasing rate) can either increase or decrease efficiency; however, regardless of whether correlation positively or negatively affects efficiency, the greatest sensitivity to correlation occurs when the spatial correlation is applied to the region near the trap. Our results suggest that in the design of exciton transport systems, efforts to increase efficiency by controlling spatial correlation are best focused in the region near the site of trapping.
2. A modified environment-assisted quantum transport model for exciton transport

2.1. Description of simulated systems

2.1.1. Fenna–Matthews–Olson complex. We first simulate exciton transport in the FMO complex from *Chlorobacter tepidum*, a green sulfur bacteria. This complex is shown in figure 1(a). FMO transfers energy from the chlorosome antenna to the reaction center where the primary charge separation event occurs. In nature, FMO exists in trimers. The monomers within this trimer are weakly coupled to one another; therefore, for the sake of simplicity, we model only a single monomer pictured in figure 1(a). Some theoretical work [26, 38, 26] has incorporated the eighth chromophore in FMO that was discovered in 2009 [39] and may receive some of the initial excitation in photosynthesis [40]; we choose to omit this chromophore because the majority of the spectroscopic data on FMO has provided information on only the seven chromophores shown in figure 1 [41–48]. Because we perform some simulations using an initial condition corresponding to a spectroscopic experiment, working with the thoroughly studied seven chromophores is appropriate.

The source of excitation (which transfers the initial excitonic energy to the system) and the trap (which transfers the energy irreversibly to a reaction center) are noted in the figure. In FMO, sites 1 and 6 are closest to the chlorosome antenna that absorbs photons during photosynthesis and serves as the source of excitation energy; thus, the initial exciton density is concentrated primarily on sites 1 and 6 in vivo. Based on its proximity to the reaction center, site 3 is believed to be the site coupled to the trap, transferring the excitation to the reaction center where charge separation occurs. In photosynthesis, the exciton travels from sites 1 and 6 through the system and arrives at site 3, from which it is trapped as it moves to the reaction center. A few distances, describing the distance between the centers of two sites, are noted in the figure to describe the dimensions of the system.

2.1.2. Elongated square bipyramidal model system. This system is a highly symmetric elongated square bipyramid, belonging to the $D_{4h}$ point group. In this model system, we have defined site 1 to be coupled to the source of initial excitation. Site 10 is the site coupled to the trap that transfers its exciton density irreversibly out of the system. This model system is pictured in figure 1(b). This geometry was chosen for several reasons. Firstly, the simple shape and symmetry allows us to define what region should be considered ‘near the trap’ and what region should be considered ‘near the source’. Such definitions of regions are not as straightforward with FMO. Secondly, with ten sites the system was large enough to divide into sections of higher and lower correlation while still small enough to make the simulations computationally tractable. Most importantly, the high symmetry of the system allows a pure examination of sensitivity to variations in spatial correlation patterns. Any analysis of FMO is clouded by its asymmetric geometry, site energies and couplings: a finding that efficiency is more sensitive to correlation near the trap than to correlation near the source may simply be a result of the rich structure within the Hamiltonian. In the model system, the region that we define as ‘near the source’ is geometrically and energetically identical to the region that we define as ‘near the trap’, eliminating this confusion in the interpretation of results.

Our study explores the one-exciton manifold, where only one excitation is present in the system at a given time. The one-exciton manifold has been used in most models of photosynthetic energy transport because many light-harvesting complexes such as FMO
Figure 1. Structures of the two systems studied. Site numberings are given that will be used to refer to the structures in the text. Panel (a) shows the structure of the FMO complex, with the chromophores (the sites of excitation) shown in green and the protein backbone shown in gray. Panel (b) shows the ten-site model system.

function in very low-light environments. For synthetic systems such as solar cells the one-exciton assumption may be quite inaccurate, and exploring ways to simulate a many-exciton manifold is an important topic for future research. However, such development of more complex models is beyond the scope of this study.
2.2. Model of exciton transport

The EnAQT model was originally proposed as a model for exciton transport in FMO [16, 17]. The ability of this method to treat the complexities of coherent and incoherent dynamics within a simple and computationally tractable framework, and the fact that the model can be very easily adjusted to treat a generic system, make it an excellent model for our study. To allow manipulation of spatial correlation in noise, we make the rate of dephasing, $\gamma$, a site-dependent parameter that varies throughout the system. Otherwise, the model is identical to that presented in the work of Rebentrost et al [16], and is described as follows. In the following equations, we use site 10 as the site coupled to the trap, as in the case of the model system; when these equations are used for FMO, site 3 is used instead.

The equation of motion for the density matrix is

$$\dot{\rho}(t) = -L\rho = -[L_{\text{sys}} + L_{\text{recomb}} + L_{\text{trap}} + L_{\text{dissip}}]\rho.$$  (1)

The action of the system Liouville operator is

$$L_{\text{sys}}\rho = (i/\hbar) \left( H_{\text{sys}}\rho - \rho H_{\text{sys}}^{*} \right).$$  (2)

The system Hamiltonian, $H_{\text{sys}}$, in the site basis is

$$H_{\text{sys}} = \sum_{m=1}^{10} E_{m} |m\rangle\langle m| + \sum_{n<m}^{10} V_{mn} (|m\rangle\langle n| + |n\rangle\langle m|),$$  (3)

where $E_{m}$ gives the site energy of site $m$ and $V_{mn}$ gives the couplings between sites $m$ and $n$. For our calculations of FMO, the site energies and couplings are drawn from an experimentally derived Hamiltonian [49, 50]. FMO has an uneven energy landscape with the site coupled to the trap having the lowest site energy. For our calculations of the model system we set $E_{m}$ to zero for all sites; this again simplifies the interpretation of our results by avoiding asymmetries in the system that would be caused by an uneven energy landscape. We assume that the size of the sites in the model system is small relative to the distance between them, allowing us to use a dipole–dipole model for calculating the couplings in the model system. The coupling between two sites is defined as

$$V_{AB} = \frac{1}{4\pi\epsilon_{0}} \left[ \frac{R^{5} \mu_{A} \cdot \mu_{B} - 3(\mu_{A} \cdot R)(\mu_{B} \cdot R)}{R^{5}} \right]$$

where $\mu$ represents the transition dipole of each site. $R$ is the vector connecting any two sites and $R$ is the norm of this vector. The dipoles are assumed to have a magnitude of 5 Debye. The magnitudes of the inter-site couplings range from 0.0006 to 20.98 cm$^{-1}$, depending on the distance between the sites and the orientation of their transition dipoles.

The recombination and trapping operators, which are anti-Hermitian and non-unitary, act on the density matrix as

$$L_{\text{recomb}}\rho = (i/\hbar) \left( H_{\text{recomb}}\rho - \rho H_{\text{recomb}}^{*} \right),$$  (4)

$$L_{\text{trap}}\rho = (i/\hbar) \left( H_{\text{trap}}\rho - \rho H_{\text{trap}}^{*} \right)$$  (5)

with

$$H_{\text{recomb}} = -i\hbar \Lambda \sum_{m=1}^{10} |m\rangle\langle m|,$$  (6)

$$H_{\text{trap}} = -i\hbar \kappa |10\rangle\langle 10|.$$  (7)

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$H_{\text{recomb}}$ represents exciton recombination, where $\Lambda$ is the rate of exciton recombination and the rate of recombination is equal on all sites. $H_{\text{trap}}$ represents exciton trapping (in which the excitation is permanently removed from the system) at site 10 (the site coupled to the trap). The recombination rate, $\Lambda$, is set to 10 excitons per nanosecond for FMO ($\hbar \Lambda = 0.33 \text{ cm}^{-1}$) and 1 exciton per nanosecond in the model system ($\hbar \Lambda = 0.033 \text{ cm}^{-1}$). One exciton per nanosecond is the recombination rate originally used in the EnAQT model; however, we increased it here to provide a clearer picture of the competition between trapping and recombination that exists in all exciton transport systems. The trapping rate, $\kappa$, is set to 1 exciton per picosecond in FMO ($\hbar \kappa = 33 \text{ cm}^{-1}$) and 0.1 excitons per picosecond for the model system ($\hbar \kappa = 3.3 \text{ cm}^{-1}$). (A lower trapping rate was chosen for the model system to keep a safe distance from the quantum Zeno regime, where the trapping rate becomes so high that it induces localization and decreases efficiency. This localization occurs when the high trapping rate serves as an observation or measurement that localizes the exciton via the quantum Zeno effect [51, 52]. This regime begins at different trapping rates for different systems: for FMO the quantum Zeno regime begins around a trapping rate of $\sim 17$ excitons per picosecond, while for the model system the quantum Zeno regime begins between $\sim 4$ and 5 excitons per picosecond depending on the orientation of the transition dipoles.)

$L_{\text{dissip}}$ represents the pure-dephasing Lindblad operator, which acts on the density matrix as follows:

$$L_{\text{dissip}}(\rho(t)) = \gamma \left( \sum_m A_m \rho(t) A_m^\dagger - \frac{1}{2} A_m A_m^\dagger \rho(t) - \frac{1}{2} \rho(t) A_m A_m^\dagger \right)$$

with $\gamma$ being the temperature-dependent dephasing rate and $A_m = |m\rangle \langle m|$. This treatment of dephasing is Markovian, with no temporal correlation in the spectral bath. In Liouville space, this Lindblad operator can be represented as [12]

$$[L_{\text{dissip}}(\rho)]_{mn, mn} = \gamma (1 - \delta_{mn}) \rho_{mn}$$

showing that it leads to dephasing of the off-diagonal elements of the density matrix at rate $\gamma$.

Because the dephasing rate is fundamentally an effect caused by environmental noise, $\gamma$ is a function of spatial correlations in environmental noise. Higher correlations effectively reduce the noise between two correlated sites, thus lowering the dephasing rate and increasing coherence lifetimes. We therefore allow $\gamma$ to vary across the system as a function of the correlation matrix, which is defined as follows.

For each calculation, the system is given a particular matrix representing spatial correlations

$$C_{mn} = \exp(-r_{mn}/r_c),$$

where $r_{mn}$ is the distance between sites $m$ and $n$ and $r_c$ is the radius of correlation. A larger radius of correlation physically corresponds to a slower decay of correlation with distance, or a stronger correlation between two sites given a constant distance. All correlation matrices used for our calculations are checked to confirm that they are positive semidefinite, which prevents non-physical spatial correlation patterns. For example, a system in which sites 1 and 3 are perfectly correlated with site 2 but sites 1 and 3 have zero correlation with each other is unrealistic and would not lead to a positive semidefinite correlation matrix.

To test the effect of increasing correlation in a limited region, we perform simulations in which spatial correlation is non-zero only in a limited region: either the region containing the
site coupled to the trap and its neighboring sites, or the region containing the site coupled to
the source and its neighboring sites. For brevity of notation, we will refer to these as ‘the region
near the trap’ and ‘the region near the source’. In the region where there is no spatial correlation,
the correlation matrix is simply $C_{mn} = \delta_{mn}$.

In the case of FMO, we define the region near the trap as sites 3, 4 and 7 (sites 4 and 7 have the smallest
distances from site 3). We define the region near the source in FMO as sites 1, 2 and 6 (chosen because sites 1 and 6 are the sites of photosynthetic initial excitation, and site 2 has the smallest average distance to sites 1 and 6). In the case of the ten-site model
system, the region near the trap is defined as sites 6–10. The region near the source in the
model system is defined as sites 1–5. The correlation matrices for these cases are given in the
supplementary data (available from stacks.iop.org/NJP/15/095019/mmedia). For each case we
also perform a simulation with zero correlation throughout the system; that is, $C_{mn} = \delta_{mn}$ for all
$m$ and $n$.

We calculate the dephasing rate for two sites $m$ and $n$ as
\[
\gamma_{mn} = \Gamma (1 - C_{mn}) ,
\]
where $\Gamma$ is the temperature-dependent dephasing rate between two uncorrelated sites. This
relationship between dephasing and correlation has been previously derived by Haken and
Strobl \cite{53} as well as Mukamel \cite{54}. Details of the derivation are shown in the appendix.

Our observable of interest is efficiency, calculated as
\[
\eta = 2\kappa \int_0^\infty \rho_{\text{trap,trap}} (t) \, dt ,
\]
where $\kappa$ is the rate of trapping; ‘trap’ refers to site 3 for FMO and site 10 for the model system, the
sites where the exciton is transferred irreversibly to a reaction center. Simulations were run with
an 0.2 fs time step using a fourth-order Runge–Kutta numerical method \cite{55} for propagating $\rho$. Simulations were continued until the total density remaining in the system (exciton density that
has not recombined or been trapped) was less than $10^{-4}$.

In figure 2, for the FMO system with independent baths (uncorrelated noise, or $C_{mn} = \delta_{mn}$),
we plot the efficiency $\eta$. We see that this quantity has a non-monotonic trajectory as dephasing
increases. This illustrates the non-monotonic relationship between dephasing and efficiency
presented in previous EnAQT literature \cite{16,17} and labeled later as the ‘Goldilocks effect’ \cite{56},
in which a ‘just right’ level of dephasing optimizes efficiency. This non-monotonic relationship
between dephasing and efficiency will shape the results of our simulations.

3. Analysis of the relationship between correlation and efficiency

We can analyze efficiency by calculating the equation of motion for the population of the site
coupled to the trap. As shown in equation (12), efficiency is simply the integration over time of
the diagonal element of the density matrix corresponding to this site. The equation of motion
for this population can be derived from the equation of motion of the full density matrix. The
equation of motion for the site coupled to the trap in FMO, site 3 is
\[
\dot{\rho}_{3,3}^{\text{FMO}} = \frac{2}{\hbar} \left[ \rho_{3,3} (t) \, \text{Im} (H_{3,3}) \right] + \frac{2}{\hbar} \sum_{k=1,k \neq 3}^7 H_{3,k} \, \text{Im} \left( \rho_{k,3} (t) \right) .
\]
The Lindblad operator for dissipation or dephasing does not appear in this equation because \( \gamma_{ij} = 0 \) for \( i = j \). To derive the relationship between efficiency and the coherences, we take the integral of equation (13) over time:

\[
\int_0^\infty \dot{\rho}_{3,3}^{\text{FMO}} \, dt = \int_0^\infty \frac{2}{\hbar} \left[ \rho_{3,3} (t) \, \text{Im} (H_{3,3}) \right] dt + \int_0^\infty \frac{2}{\hbar} \left[ \sum_{k=1,k\neq 3}^7 H_{3,k} \left( \text{Im} (\rho_{k,3} (t)) \right) \right] dt. \tag{14}
\]

\( \text{Im} (H_{3,3}) = \hbar \kappa + \hbar \Lambda \), where \( \Lambda \) (the recombination rate) is two orders of magnitude smaller than \( \kappa \) (the trapping rate) for both FMO and the model system. Therefore to a first approximation \( \text{Im} (H_{3,3}) \approx \hbar \kappa \). Substituting \( \text{Im} (H_{3,3}) \approx \hbar \kappa \) and \( \hbar = 1 \) we find

\[
\int_0^\infty \dot{\rho}_{3,3}^{\text{FMO}} \, dt \approx 2\kappa \int_0^\infty \rho_{3,3} (t) \, dt + 2 \int_0^\infty \left[ \sum_{k=1,k\neq 3}^7 H_{3,k} \left( \text{Im} (\rho_{k,3} (t)) \right) \right] dt. \tag{15}
\]

The first term on the right-hand side of equation (15) is equal to \( \eta \) as shown in equation (12), and the left-hand side of equation (15) can be solved as

\[
\int_0^\infty \dot{\rho}_{3,3}^{\text{FMO}} \, dt = \rho_{3,3} (\infty) - \rho_{3,3} (0). \tag{16}
\]

At \( t = 0 \) and \( \infty \) the population on site 3 is zero, therefore

\[
\int_0^\infty \dot{\rho}_{3,3}^{\text{FMO}} \, dt = 0. \tag{17}
\]
Setting the left-hand side of equation (13) to zero, we find

$$\eta \approx -2 \int_0^\infty \left[ \sum_{k=1, k \neq 3}^7 H_{3,k} \left( \text{Im} (\rho_{k,3} (t)) \right) \right] \, dt. \quad (18)$$

An equivalent equation describes efficiency for the site coupled to the trap in the model system. For simplicity of notation, in the following text $\rho_{k,10}$ for the model system and $\rho_{k,3}$ for FMO will both be referred to as $\rho_{k,\text{trap}}$ to reflect that fact that sites 3 and 10 both irreversibly transfer excitonic density to the trap.

We see from equation (18) that efficiency is determined by the imaginary part of the coherences involving the site coupled to the trap ($\text{Im} (\rho_{k,3})$), weighted by their couplings with the site coupled to the trap ($H_{3,k}$). The inter-site couplings are a function of distance, with sites closer to the trap having larger couplings $H_{3,k}$. This observation leads to the simple conclusion that coherences between the site coupled to the trap and sites near the trap have a greater impact on efficiency than coherences between the site coupled to the trap and more distant sites. Coherences are directly impacted by the spatial correlation between the two sites: with larger correlation, the dephasing rate (that pushes coherences toward zero via the Lindblad operator) is smaller. The relationship between correlation and dephasing is equivalent regardless of whether the sites are near the trap or near the source, however, the coherences with sites near the trap are weighted more heavily by the $H_{3,k}$ elements in the equation of motion for $\rho_{3,3}$. Thus, our analysis leads to the prediction that altering spatial correlation (and thus coherences) in the region including the site coupled to the trap and its neighboring sites will have a strong effect on efficiency.

Altering spatial correlation in the region closest to the source will not directly act on efficiency via equation (18). When greater spatial correlation is applied in the region near the source, the dephasing terms that act on the coherences $\rho_{k,\text{trap}}$ are not altered. Rather, the coherences $\rho_{i,j}; i, j \leq 5$ (in the case of the model system) and $\rho_{i,j}; i, j = 1, 2, 6$ (in the case of FMO) are altered by the greater correlation. By the same reasoning applied in the previous paragraph, these coherences are most powerful in influencing the populations of sites near the source due to the close proximity and thus larger couplings. Spatial correlation near the source must have some effect on the population of the site coupled to the trap; although the coherences that are affected by the correlation do not act directly via equation (18), they eventually exert an indirect influence because all of the equations of motion of the density matrix elements are coupled. However, we propose that the very direct influence on efficiency of correlation between the site coupled to the trap and its neighboring sites will generally make efficiency much more sensitive to changes in correlation in the region near the trap. We expect that efficiency will be relatively insensitive to changes in correlation in the region near the source.

4. Relationships between spatial correlation and efficiency in simulations

Although our analysis suggests that sensitivity to correlation is greatest near the trap, the EnAQT model creates a complex transport process in which the equations of motions of all density matrix elements are coupled and exciton transport is (as we will show below) extremely sensitive to the energetic landscape. To confirm that in spite of this complexity, the effects described in equation (18) dominate the sensitivity to correlation, we verify our analytic prediction with simulations of exciton transport in a variety of systems.
In this section, we show that for both the FMO system and the model system, simulations support the prediction that efficiency is most sensitive to changes in spatial correlation in the region near the trap. We show that this finding is robust to changes in initial conditions, environmental noise and orientation of transition dipoles.

4.1. Fenna–Matthews–Olson complex

Our simulations use the EnAQT model defined in section 2. As previously described, we correlate the spectral bath motions in a limited region either near the trap or near the source, with zero correlation in the rest of the system ($C_{mn} = \delta_{mn}$). We compute the efficiency for the case with limited non-zero correlation as well as the case with zero correlation throughout the entire system. The difference between these two efficiencies shows the effect of correlating the bath fluctuations a limited region.

As discussed above, dephasing is a direct function of spatial correlation, and a complex non-monotonic relationship exists between dephasing and efficiency. Therefore, we test a range of values for $r_c$, the radius of correlation for the region with non-zero spatial correlation. To confirm that our results are not an artifact of initial conditions, two initial conditions are tested for FMO. Firstly, we test an initial condition in which the initial excitation is evenly spread between sites 1 and 6 (the sites closest to the photon-absorbing chlorosome that is the source of energy in photosynthesis). We will refer to this as the ‘photosynthetic case’. Secondly, we test a spectroscopic initial condition, which corresponds to the state of an excited ensemble after the first two laser pulses of a two-dimensional electronic spectroscopy experiment. In this case, the initial density is not limited to the region near the source but rather is spread throughout the system. We will refer to this as the ‘spectroscopic case’. To confirm that our results are robust with respect to changes in environmental noise, the calculations were performed for three values of $\Gamma_1$, where $\Gamma_1$ is the rate of dephasing between two uncorrelated sites and a larger $\Gamma_1$ corresponds to an increase in environmental noise. $\Gamma_1$ values of 3.18, 318 and 31 800 cm$^{-1}$ were tested.$^4$ (For comparison, $k_B T = 210$ cm$^{-1}$ at room temperature.) We see in the ‘Goldilocks curve’ of figure 2 that $\Gamma = 318$ cm$^{-1}$ corresponds to a system fairly close to the optimal dephasing rate, whereas $\Gamma = 3.18/31 800$ cm$^{-1}$ correspond to very cold/hot systems that are far from the optimal dephasing rate.

For the photosynthetic case, plots showing the change in efficiency with respect to $r_c$ are shown in figure 3. Note that we show absolute changes in efficiency, not percentage changes: for example, an increase in efficiency from 0.5 to 0.6 is expressed as 0.1, where an efficiency of 1 reflects perfect quantum efficiency. Raw efficiencies are shown in figure S1 in the supplementary data (available from stacks.iop.org/NJP/15/095019/mmedia). We see that although the effect of spatially correlating bath fluctuations depends on $r_c$ and on the level of environmental noise, for all values of $r_c$ the effect of correlating fluctuations near the trap tends to be stronger. Figure 4 shows the equivalent calculations for the spectroscopic initial condition. Raw efficiencies are shown in figure S2 of the supplementary data. The results for the spectroscopic case are qualitatively nearly identical, showing that the results in figure 3 are not an artifact of the very asymmetric photosynthetic initial condition in which density is concentrated near the source.

We see that spatial correlation reduces efficiency in low-noise environments, increases efficiency in high-noise environments and has a non-monotonic effect in the intermediate

$^4$ Formally, when the dephasing rate, $\Gamma$, is quoted in wavenumbers, the value should be represented as $\hbar \Gamma$, but for simplicity we use here the convention from the literature and omit $\hbar$. 

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Figure 3. Effect of spatially correlating the bath fluctuations in a limited region of the FMO complex for the case of a photosynthetic initial condition. Varying levels of dephasing are shown, with $\Gamma = 3.18\,\text{cm}^{-1}$ in (a), $\Gamma = 318\,\text{cm}^{-1}$ in (b) and $\Gamma = 31800\,\text{cm}^{-1}$ in (c). The red line with diamond markers reflects the change in efficiency when fluctuations are correlated in the region near the trap.
regime. This complex relationship is not surprising given the non-monotonic relationship between dephasing and efficiency demonstrated in previous EnAQT literature [16, 17] and reflected in figure 2. The EnAQT model proposes that at low noise levels, increasing noise (thus increasing dephasing) helps efficiency by preventing the Anderson localization that can occur in a coherent superposition of states. At higher noise levels, increasing noise or dephasing hurts efficiency via the quantum Zeno effect or ‘watchdog’ effect, in which dephasing serves as an observation of a quantum system that collapses the wavefunction to a localized state and inhibits transport. When we spatially correlate the bath fluctuations, we change the model by lowering dephasing in the correlated region. Thus, in a low-noise environment correlation hurts and in a high-noise environment correlation helps. Figure 3(b), in which $\Gamma = 318\, \text{cm}^{-1}$, represents a situation when the system is fairly close to the peak of the curve shown in figure 2. In this case, a small increase in correlation (decreasing noise) pushes the system to the peak of the curve and increases efficiency, but as $r_c$ becomes larger and we see a greater decrease in dephasing, the system travels down the left side of the peak and efficiency decreases. However, the important point is that regardless of whether the effect of correlation is positive or negative, the effect tends to be greater when bath motions are correlated near the trap, consistent with our analysis in section 3.

In cases such as figures 3(b) and 4(b), in which the effect of correlation changes from positive to negative as $r_c$ increases, comparing the effect of correlation near the source with the effect of correlation near the trap becomes complicated by the curves crossing zero at slightly different places. These differences in crossing points are a consequence of the fact that changing the correlation pattern changes the non-monotonic ‘Goldilocks’ curve relating noise to efficiency. We illustrate this difference in the Goldilocks curves for FMO, using the spectroscopic initial condition, in figure 5. Three curves are shown: increased correlation near the trap in red diamond markers, increased correlation near the source in blue square markers and $C_{mn} = \delta_{mn}$ in green round markers. Noise in the system was varied and the Goldilocks curve reflecting the relationship between dephasing and efficiency is shown. What is noteworthy is that correlating bath fluctuations near the trap significantly changes where the curve peaks: the effect of dephasing changes from positive to negative at a different point. Thus, in examining the effect of correlation on efficiency, there may be $r_c$ values for which correlation has a positive effect on efficiency for one correlation pattern but correlation has a negative effect on efficiency for another correlation pattern, as we see around $5 < r_c < 10\, \text{nm}$ in figures 3(b) and 4(b). Very near these crossing points, the situation becomes more complex and we may find exceptions to the rule that the effect of correlation near the trap is always larger; in fact there will be an $r_c$ at which the curves intersect and the effect of correlation on efficiency is equal for the two correlation patterns. However, these exceptions, by definition of occurring near the crossing point, would be cases where the effects are quite small.
Figure 4. Effect of spatially correlating the bath fluctuations in a limited region of the FMO complex for the case of a spectroscopic initial condition. Varying levels of dephasing are shown, with $\Gamma = 3.18\text{ cm}^{-1}$ in (a), $\Gamma = 318\text{ cm}^{-1}$ in (b) and $\Gamma = 31800\text{ cm}^{-1}$ in (c). The red line with diamond markers reflects the change in efficiency when fluctuations are correlated in the region near the trap.
Figure 4. (Continued) relative to the case in which $C_{mn} = \delta_{mn}$. The blue line with square markers shows the change in efficiency when fluctuations are correlated in the region near the source. We again see that although the effect of correlating spectral bath motions can be positive or negative, the efficiency is much more sensitive to changes in correlation near the trap.

![Graph](image)

Figure 5. Relationship between dephasing and efficiency for FMO, using a spectroscopic initial condition and varying correlation patterns. The red line with diamond markers illustrates the case of increased correlation near the trap, the blue line with square markers illustrates increased correlation near the source and the green line with round markers illustrates the case where $C_{mn} = \delta_{mn}$. We see that changing the correlation pattern can shift the peak of the ‘Goldilocks curve’ that reflects the non-monotonic relationship between dephasing and efficiency.

4.2. Square bipyramidal model system

The simulations of the model system are also consistent with the prediction that efficiency is most sensitive to bath correlations near the site coupled to the trap. In figure 6 we show the effect of spatially correlating bath fluctuations on the ten-site model system pictured in figure 1(b). Raw efficiencies are shown in the supplementary data in figure S3 (available from stacks.iop.org/NJP/15/095019/mmedia). To confirm that our results were robust to the orientation of the transition dipoles (which have a major effect on the couplings) we tested three possible orientations of the transition dipoles. The transition dipole orientations are shown by the arrows in the images on the upper left of each graph. Figure 6(a) illustrates a case in which the transition dipoles point outwards from the center of the system, figure 6(b) illustrates a case in which the dipoles all point upward in the direction of the source and figure 6(c) illustrates a more complex pattern in which all dipoles lie parallel to the planes created by sites 2–5 and 6–9. All systems are tested at the same level of environmental noise, with $\Gamma = 1590 \text{ cm}^{-1}$.

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Figure 6. Effect of spatially correlating the bath fluctuations in a limited region of the ten-site model system. $r_c$ is shown on a logarithmic scale due to its large range. Panel (a) illustrates a case in which the transition dipoles of the sites are oriented outwards from the center of the system. Panel (b) illustrates a case in which all dipoles point upwards in the direction of the source. Panel (c) illustrates a more complex arrangement of dipoles in which all dipoles are parallel to the planes created by sites 2–5 and 6–9. The red line with diamond markers reflects
efficiency, the pattern of greater sensitivity to correlation near the trap is consistent regardless of dipole orientation. As in FMO, the effect of spatial correlation can be positive or negative, but correlation has the most significant effect in the region near the trap. Both FMO and the model system continue to exhibit changes in efficiency at very high $r_c$ values, but while the efficiencies in FMO flatten out around $r_c$ values of 50–100 nm (an order of magnitude larger than the size of the complex), the model system continues to show small changes in efficiency at much higher $r_c$ values. The model system’s sensitivity to the radius of correlation at high $r_c$ is due in part to the slightly larger distances between sites in the model system, making the ratio $r_{mn}/r_c$ somewhat larger. More importantly, this difference in sensitivity reflects the strong influence of couplings in shaping the relationship between correlation and efficiency. Comparing FMO to the model system, the relationship between correlation and efficiency is both qualitatively and quantitatively different. These differences make it especially striking that both systems consistently exhibit greater sensitivity to correlation near the trap. With the model system, we again see support of our analytic prediction that correlation between the site coupled to the trap and its neighboring sites is more powerful than correlation near the source in determining efficiency.

5. Discussion and conclusions

Both analytically and via simulation, we have demonstrated that efficiency of quantum transport is most sensitive to changes in spatial correlation in the region near the trap. Even large degrees of spatial correlation can have surprisingly little effect on efficiency when they occur in regions of the system more distant from the trap. Our simulations show that this trend is highly robust to changes in the system and its environment. By simulating both FMO and a symmetric model system, we established that the observed trend was not simply an artifact of FMO’s geometrical and energetic asymmetry. We demonstrate that the same trend is observed in FMO using two distinct initial conditions, and that the same trend is observed at three very different levels of environmental noise. Because quantum transport is highly sensitive to couplings and because couplings are a function of transition dipole orientations, we test three sets of dipole orientations for our model system, and again find consistent results. Due to the non-monotonic relationship between dephasing and efficiency, the effect of spatial correlation can be positive or negative, and the direction of this effect is influenced by many factors, including environmental noise, the radius of correlation, and the system couplings. However, irrespective of the direction of the effect of spatial correlation, we see that efficiency is most sensitive to spatial correlation in the region near the trap.

Our model involves certain simplifications that could be improved upon in future work. By treating spatial correlation via the Lindblad operator, we treat only spatial correlations in site energies. Couplings between the sites are assumed to be constant, but in reality, the spectral bath
causes fluctuations in couplings as well as site energies. Although the effect on couplings can be minimal if the relative orientation of the sites is fairly rigid, biological systems such as FMO are likely to have significant noise in their couplings, and atomistic modeling of FMO by Olbrich et al [25] indicates that coupling/coupling correlations as well as site energy/coupling correlations may be present. Huo and Coker [57] as well as Chen and Silbey [58] have presented work in which spatial correlations involving couplings were incorporated into the model, and both studies found effects on the energy transfer process. In future work, it may be useful to extend this study of spatial patterns in correlation to consider correlations in coupling fluctuations.

In this work we chose to work with a Markovian model for the sake of simplicity, with the belief that our findings will shed some light on the more complex non-Markovian case that includes temporal correlation in the spectral bath. Generally speaking, non-Markovian effects have been shown to affect the time scale of coherence as well as the population transfer time scales [59–62]. These non-Markovian effects are magnified with large reorganization energies, small couplings and longer time scales of correlation within the bath [60]. For most condensed phase systems at room temperature the time scale of correlation in the bath is below 100 fs and the coupling, reorganization energy and energy mismatch are all on the same order of magnitude. Thus, we expect that our results will be qualitatively accurate in spite of the Markovian approximation. Past work comparing Markovian and non-Markovian models for light-harvesting complexes [61, 62] concluded that energy transfer efficiency differs between the Markovian and non-Markovian cases; however, in the study of spatial correlation, previous research indicates that qualitative trends are similar between Markovian and non-Markovian models. Huo and Coker [57] apply a non-Markovian model to the study of spatial correlation in inter-site energies as well as in couplings, and conclude that the findings of a Markovian model of correlated fluctuations presented by Chen and Silbey [58] are ‘general and robust’. In considering non-Markovian effects, it is also important to consider the fact that the sensitivity to correlation near the trap demonstrated in this paper is highly robust regardless of whether dephasing increases or decreases efficiency for a particular case. This suggests that even if the Markovian approximation influences the relationship between dephasing and efficiency, the key findings of this paper are likely to be qualitatively accurate.

Although we expect that our results would not qualitatively differ between the Markovian and non-Markovian cases, one important advantage of non-Markovian models is that it is possible to define a finite temperature. Although some temperature effects are present in the EnAQT model via the temperature-dependence of \( \gamma \) (which depends on both temperature and strength of coupling to the bath), it is impossible to rigorously define temperature in Markovian models due to the infinite temperature nature of a bath with no temporal correlation. A defined temperature may be useful when comparing results to experiments done at a particular temperature, as in the case of the non-Markovian modeling presented by Chen and Silbey [9] in which they simulate FMO at 77 and 300 K, the temperatures that were used in spectroscopic work on FMO [5, 6]. A clearly defined temperature may also be important in materials design when exploring the function of materials at differing temperatures. Therefore, for certain applications, an extension of this model to include non-Markovian effects and permit a defined temperature may be useful.

Our results indicate that treating the spatial correlation as constant throughout a system obscures important asymmetries in the sensitivity of efficiency to correlation. We argue that for exciton transport systems embedded in heterogeneous environments, a correct model of the effects of spatial correlation must allow for differences in this function throughout the
system. While previous work has revealed a strong dependence of efficiency on dephasing, this work builds upon this finding to demonstrate that dephasing of coherences between the site coupled to the trap and adjacent sites are most important in mediating the dephasing/efficiency relationship. This relationship between spatial correlation, dephasing and efficiency has important implications for the design of exciton transport systems. We suggest that in system design, the possible heterogeneity of spatial correlation should be considered, and optimization efforts should be focused on the spatial correlation between the site coupled to the trap and its neighboring sites.

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Appendix

This method for calculating dephasing was previously derived by Haken and Strobl [53] and Mukamel [54]. The dephasing parameter for two excited states $m$ and $n$ is derived from the fluctuations in site energies as follows, where $g$ refers to the ground state. $\delta \omega_{mg}$ refers to the difference between the frequency of a particular instantaneous energy gap between states $g$ and $m$ and the frequency of the average energy gap between states $g$ and $m$:

$$D = \langle \delta \omega_{mn} (\tau) \delta \omega_{mn} (0) \rangle$$  \hspace{1cm} (A.1)

$$= \langle \delta (\omega_{mg} - \omega_{ng}) (\tau) \delta (\omega_{mg} - \omega_{ng}) (0) \rangle$$ \hspace{1cm} (A.2)

$$= \langle \delta \omega_{mg} (\tau) \delta \omega_{mg} (0) \rangle + \langle \delta \omega_{ng} (\tau) \delta \omega_{ng} (0) \rangle - 2 \langle \delta \omega_{mg} (\tau) \delta \omega_{ng} (0) \rangle.$$ \hspace{1cm} (A.3)

$\langle \delta \omega_{eg} (\tau) \delta \omega_{eg} (0) \rangle = \Gamma \delta (t)$ for all excited states $e$ where $\Gamma$ is the rate of dephasing. Therefore, for any two excited states $m$ and $n$,

$$D = 2 \Gamma \delta (t) - 2 C_{mn} \Gamma \delta (t)$$ \hspace{1cm} (A.4)

$$= 2 (1 - C_{mn}) \Gamma \delta (t),$$ \hspace{1cm} (A.5)

where $C_{mn}$ refers to the corresponding element of the correlation matrix. The dephasing parameter $\gamma_{mn}$ is derived from the integral over $D$ as follows, using the properties of delta functions:

$$\gamma_{mn} = \int_0^\tau d\tau_1 D (\tau_1)$$ \hspace{1cm} (A.6)

$$= 2 \Gamma \int_0^\tau d\tau_1 (1 - C_{mn}) \delta (\tau_1)$$ \hspace{1cm} (A.7)

$$= \Gamma (1 - C_{mn}).$$ \hspace{1cm} (A.8)
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