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Impact of Spatial Inhomogeneity on Excitation Energy Transport in the Fenna–Matthews–Olson Complex

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ABSTRACT: The dynamics of the excitation energy transfer (EET) in photosynthetic complexes is an interesting question both from the perspective of fundamental understanding and the research in artificial photosynthesis. Over the past decade, very accurate spectral densities have been developed to capture spatial inhomogeneities in the Fenna–Matthews–Olson (FMO) complex. However, challenges persist in numerically simulating these systems, both in terms of parameterizing them and following their dynamics over long periods of time because of long non-Markovian memories. We investigate the dynamics of FMO with the exact treatment of various theoretical spectral densities using the new tensor network path integral-based methods, which are uniquely



capable of addressing the difficulty of long memory length and incoherent Förster theory. It is also important to be able to analyze the pathway of EET flow, which can be difficult to identify given the non-trivial structure of connections between bacteriochlorophyll molecules in FMO. We use the recently introduced ideas of relating coherence to population derivatives to analyze the transport process and reveal some new routes of transport. The combination of exact and approximate methods sheds light on the role of coherences in affecting the fine details of the transport and promises to be a powerful toolbox for future exploration of other open systems with quantum transport.

1. INTRODUCTION

Light-harvesting complexes play an important role in the photosynthesis in a host of plants, bacteria, and algae. The socalled "antenna complexes" capture solar energy, convert it into an electronic excitation, and carry it to the reaction center where charge separation leads to further chemistry. Crucially, these systems form the basis and inspiration for attempts at artificial photosynthesis. Thus, understanding the mechanisms that allow for the efficient transport of molecular excitation from the point of creation to the reaction center is of fundamental importance. A lot of work has been done in simulating the excitation energy transfer (EET) and characterizing the vibronic couplings. Early experiments^{9,10} seemed to provide evidence of quantum beating. Theoretical studies were performed around the same time to shed light on the origins of these long-lived electronic oscillations.¹¹⁻¹⁵ It was hypothesized that this oscillatory dynamics could be the reason behind the efficiency of EET in biosystems. However, more recent experimental investigations^{16,17} have shown that the optical 2D photon echo spectra at ambient temperature do not show long-lived electronic quantum coherence.

Theoretical studies have been widely performed using Redfield¹¹ and Förster theory.¹⁸ However, the applicability of these approximate perturbative techniques is not always guaranteed a priori. Simulations of thermal dynamics at ambient temperature are optimally performed using reduced density matrix-based approaches like the hierarchical equations of motion^{19,20} (HEOM) or path integrals using the Feynman–Vernon influence functional.²¹ While the quasi-adiabatic

propagator path integral^{22,23} (QuAPI) method has been used to study the Fenna–Matthews–Olson (FMO) complex,^{24,25} almost all other contemporary and more recent studies of the exact dynamics seem to have focused on using HEOM as the method of choice.^{8,13,26–28} EET problems have also been studied using semiclassical methods.^{29–33} Advances in path integral-based methods^{34,35} have recently made them lucrative for studying EET systems.^{36–40} Among these advances, there have been developments that combine ideas from the tensor network and influence functional to help alleviate the cost of path integral calculations in different ways.^{38,41–46}

The methods that simulate the time evolution of the reduced density matrix, typically, require the calculation of spectral densities to characterize the effect of the protein scaffolding and the localized vibrations of the chlorophyll molecules. The spectral density can be calculated as the Fourier transform of the energy-gap correlation function.^{47,48} In case of an EET, this is equivalent to the autocorrelation function of excitation energy fluctuations of individual chromophores. While a lot of work has been done trying to characterize the site-dependent spectral densities for the FMO,^{49–52} there seem to be significant

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disagreements on the best way of obtaining them. Zerner's intermediate neglect of differential orbital method (ZINDO) and time-dependent density functional theory (TD-DFT) have been used to calculate the excited-state energy fluctuations along classical molecular dynamics (MD) trajectories run on the ground Born–Oppenheimer (BO) surface.^{50,53,54} Extensive analysis has been done over the past decade on how to best and most consistently capture the fine interplay of dynamics and electronic structure that goes into these spectral densities. Because of the so-called "geometry mismatch" problem stemming from the inconsistencies between the conformations obtained from these purely classical MD trajectories and the subsequent quantum mechanical calculations, mixed QM/MM dynamics simulations on the ground BO surface have also been performed.^{54,55}

In this work, we simulate the EET dynamics in the FMO complex of the wild-type *Chlorobaculum tepidum* with accurate descriptions of the vibrational degrees of freedom.⁵⁴ While the usual practice is to focus the numerical studies on the time evolution of the population in the excited states of each of the chromophores, the population pathways are more rarely studied.⁵⁶ There has been a recent resurgence of the use of coherences and their relation to fluxes to gain greater insight into the dynamics.^{56–60} Here, we use the recently developed coherence-based analytic technique⁶⁰ to unravel the pathways that the excitation takes and the impact of the vibrational modes. Additionally, all of this analysis is also done under the incoherent Förster approximation⁶⁰ in order to better understand the importance of coherences and the non-Markovian nature of the dynamics.

The paper is organized as follows. In Section 2, we outline the simulation methods used. For the exact dynamics, we used the tensor network path integral representation⁴³ of the time-evolving matrix product operators⁴¹ (TEMPO) method. We also summarize the ideas of using coherences in exploring transport pathways and a similar approach based on the Förster theory.⁶⁰ The results for the FMO system with various spectral densities followed by a thorough analysis are done in Section 3. Finally, some concluding remarks and future directions are outlined in Section 4.

2. METHODS

Under physiological conditions, FMO exists as a trimer, with each monomer consisting of eight bacteriochlorophyll-*a* (BChl *a*) units. The structure of the complex is shown in Figure 1. The Hamiltonian describing the EET process in one 8-unit monomer can be expressed by a Frenkel model

$$\hat{H}_{0} = \sum_{j=1}^{8} \epsilon_{j} |j\rangle \langle j| + \sum_{k \neq j} h_{k,j} |j\rangle \langle k|$$
(1)

where e_j is the electronic excitation energy of the *j*th BChl molecule in the absence of the protein environment, and $h_{k,j}$ represents the electronic couplings. The state where only BChl *j* is excited is denoted by $|j\rangle = \prod_{k \in j}^{\infty} |g_k\rangle \otimes |e_j\rangle \otimes \prod_{l>j}^{\infty} |g_l\rangle$. Here, $|g_j\rangle$ and $|e_j\rangle$ represent the local ground and excited states of the *j*th BChl unit. The full dissipative environment including contributions from both the local, rigid vibrations and the dynamical environment of the protein scaffolding is characterized by a harmonic bath on each site, *j*



(a) FMO trimer with protein scaffold

(b) FMO monomer with bacteriochlorophyll molecules labeled.

Figure 1. Fenna–Matthews–Olson complex in its trimeric and monomeric forms. Blue: BChl 1. Orange: BChl 2. Green: BChl 3. Red: BChl 4. Purple: BChl 5. Brown: BChl 6. Pink: BChl 7. Gray: BChl 8.

$$\hat{H}_{\rm B}^{j} = \sum_{\xi} \frac{p_{j\xi}^{2}}{2m_{j\xi}} + \frac{1}{2}m_{j\xi}\omega_{j\xi}^{2} \left(x_{j\xi} - \frac{c_{j\xi}\hat{s}_{j}}{m_{j\xi}\omega_{j\xi}^{2}}\right)^{2}$$
(2)

where $\omega_{j\xi}$ and $c_{j\xi}$ are the frequency and coupling of the ξ th mode on BChl *j*. The bath interacts with the *j*th BChl unit through the diagonal operator \hat{s}_j specified by $\hat{s}_j | g_j \rangle = 0$ and $\hat{s}_j | e_j \rangle = | e_j \rangle$. The frequencies and couplings of the bath are related to the spectral density as follows

$$J_{j}(\omega) = \frac{\pi}{2} \sum_{\xi} \frac{c_{j\xi}^{2}}{m_{j\xi}\omega_{j\xi}} \delta(\omega_{j\xi} - \omega)$$
(3)

Thus, the full universe including the system and the bath is defined by the following Hamiltonian, which has a Frenkel– Holstein structure

$$\hat{H} = \hat{H}_0 + \sum_{j=1}^8 \hat{H}_B^j$$
(4)

In many cases, the system Hamiltonian, \hat{H}_0 , is specified in terms of the site energy (a.k.a., the optical excitation energy), E_j . This optical excitation energy is however dependent upon the environment. Therefore, ϵ_j is obtained after shifting the optical excitation energy by the corresponding reorganization energy.¹²

Under the influence of the thermal vibrational baths, the reduced density matrix corresponding to the EET system at time $t = N\Delta t$ is given by a path integral expression

$$\tilde{\rho}(S_{N}^{\pm}, N\Delta t) = \sum_{S_{0}^{\pm}} \sum_{S_{1}^{\pm}} \cdots \sum_{S_{N-1}^{\pm}} \tilde{\rho}(S_{0}^{\pm}, 0) P_{S_{0}^{\pm}, S_{1}^{\pm} \dots S_{N}^{\pm}}$$
(5)

$$= \sum_{S_0^{\pm}} \sum_{S_1^{\pm}} \cdots \sum_{S_{N-1}^{\pm}} \tilde{\rho}(S_0^{\pm}, 0) P_{S_0^{\pm}, S_1^{\pm} \cdots S_N^{\pm}}^{(0)} F[\{S_n^{\pm}\}]$$
(6)

where $P_{S_0^{\pm},S_1^{\pm},...,S_N^{\pm}}$ is the path amplitude tensor, which represents the amplitude of the system corresponding to its motion along the specified sequence of forward–backward states in the presence of the solvent. In the notation used here, S_n^{\pm} represents the collective forward–backward state of the system at the *n*th time point (i.e., $S_n^{\pm} = \{s_{1,n}^{\pm}, s_{2,n}^{\pm}, ..., s_{8,n}^{\pm}\}$, where $s_{j,n}^{\pm}$ is the forward– backward state of the *j*th site at the *n*th time point). The path amplitude tensor is a product of the "bare" path amplitude tensor, $P_{S_n^{\pm},S_n^{\pm},...,S_n^{\pm}}^{(0)}$, representing the amplitude of the isolated system's motion along the same path and the Feynman–Vernon influence functional,²¹ F, representing the impact of the solvent degrees of freedom on the system. The dynamics of the isolated system is Markovian. It is the presence of the influence functional, F, that induces non-Markovianness in the dynamics. While, formally, this expression depends on the entire history of any path going back to time step 0, in condensed phases, the memory dies out and is calculated only till a finite number of time steps, L. This L is a convergence parameter.

The dimensionality of the path amplitude tensor grows as d^{2L} where the system is *d*-dimensional (in this case, d = 8), and *L* is the memory length. In the TEMPO⁴¹ method, this exponential growth is heavily compressed by recognizing that the correlations between points separated by large time spans become negligible even in the presence of a non-Markovian bath. This suggests that one can use a matrix product state (MPS) to efficiently represent the path amplitude tensor. An MPS or a tensor train form is obtained by performing sequential truncated singular value decompositions so that each of the indices on the original tensor can be attributed to separate low-ranked tensors. In this representation, the terminal tensors are rank-2 and the intermediate tensors are rank-3, as shown in Figure 2a. The common indices between any two neighboring



Figure 2. Matrix product representations of the path amplitude tensor and the influence functional operators. The bond indices are denoted by α_i and β_i , while the site indices are s_i^{\pm} .

tensors and their dimension are called the bond index and the bond dimension, respectively. In such a representation, it can be shown that the influence functional can similarly be analytically written as a matrix product operator (MPO),⁴³ which is shown in Figure 2b. This analytic form optimizes the representation, accounting for the multiple baths and the symmetries in the influence functional expression.⁴³ While the bare path amplitude has zero long-distance correlations, and consequently a very compact MPS representation, subsequent applications of the influence functional MPO build up these correlations, leading to an increase in the bond dimension. However, efficient algorithms exist to minimize the growth of the bond dimension of the MPS on the application of an MPO based on convergence parameters.⁶¹ This, combined with an optimal representation of the influence functional MPO, makes the tensor network approach especially efficient at simulating these systems.

Generally, an iterative procedure^{22,23,43} is used to propagate the reduced density matrix beyond the non-Markovian memory length (for N > L). While it stops the exponential growth of complexity, the computations still scale with the number of paths within the memory length. The transfer tensor method⁶² (TTM) has demonstrated the possibility of using the augmented forward—backward system propagators as dynamical maps to simplify the propagation in the iterative regime. While the TEMPO with the analytical influence functional MPO allows us to access unprecedented memory lengths for large systems like the FMO, the TTM allows us to speed up the propagation beyond the memory length without incurring further numerical errors from the filtering involved in the tensor network simulations.⁶³

Crucial to an exploration of EET dynamics is an understanding of the pathway-dependent population transfer for each of the cases. Baker and Habershon⁶⁴ have explored these pathways in FMO using the Lindblad master equation. Their approach is based on knocking particular chromophores out of the system and evaluating the resulting change in the transport properties. More rigorous approaches can be built on ideas based on population fluxes. Wu et al.⁵⁶ have built flux networks to analyze the flows along different pathways. More recently, Dani and Makri have shown that the time derivative of the onsite populations is related to linear combinations of the offdiagonal terms of the reduced density matrix⁵⁸ and visualized the coherences in the forms of maps that encode information about the dynamics of the system.⁵⁹ We have extended these ideas to partition the time-dependent population change on a site in terms of transport along different state-to-state channels, which is useful for understanding the instantaneous population transfer in these systems with complex interconnects.⁶⁰ The dynamic site-specific populations can be partitioned into transfers between particular chromophoric sites

$$P_{k\leftarrow j}(t) = -\frac{2}{\hbar} \langle k | \hat{H}_0 | j \rangle \int_0^t dt' \, \mathrm{Im} \langle k | \tilde{\rho}(t') | j \rangle \tag{7}$$

where $P_{k \leftarrow j}(t)$ is the direct population transfer from site *j* to site *k* and is related to the imaginary part of the corresponding coherence. To explore the overall importance of the different pathways using this coherence-based analysis, here we define a time-averaged state-to-state transfer

$$\overline{P}_{k\leftarrow j} = \frac{1}{T} \int_0^T \mathrm{d}t P_{k\leftarrow j}(t) \tag{8}$$

In their work, Wu et al.⁵⁶ have used the integrated population flux to capture the amount of flow along a particular state-tostate channel. This amounts to using $\lim_{t\to\infty} P_{k\leftarrow j}(t)$ in the fully quantum mechanical treatment of the problem. Equivalent ideas have been developed in approximate rate theoretical schemes. The main benefit of using a time average (eq 8) instead of simple integration of the flux is that by using the average, one can capture the relative speeds of transfer as well. (The coherences are more difficult to converge than the populations. Consequently, we employed a scheme that approximately compensates for the errors coming from lack of convergence. This scheme has been detailed in the Supporting Information.)

Finally, incoherent Förster rate theory is often used to study the EET dynamics. In fact, Wilkins and Dattani²⁸ have argued that it is enough to capture the essential features of the excitonic dynamics in FMO and that the role of coherences is minimal. We use our exact path integral simulations to benchmark the incoherent Förster results using the QM/MM-based spectral densities. Like the formalism for state-to-state transport discussed in the previous paragraphs, we have also developed a similar formalism based on the approximate Förster theory.⁶⁰ In terms of the Förster transfer rates $(k_{k \leftarrow j})$, the dynamic sitespecific populations are given by The Journal of Physical Chemistry B

$$P_{k\leftarrow j}(t) = \int_0^t \mathrm{d}t' k_{k\leftarrow j} P_j(t') - k_{j\leftarrow k} P_k(t') \tag{9}$$

where the populations, $P_k(t)$, are obtained by solving the Förster rate equation. This is used to explore the changes that are brought about in the transport pathways due to the neglect of coherences.

3. RESULTS AND DISCUSSION

For the purpose of this exploration, we use the spectral densities calculated via QM/MM trajectories. The two cases considered correspond to energy-gap autocorrelation functions calculated using the TD-LC-DFTB method (average reorganization energy of $\lambda = 572.976 \text{ cm}^{-1}$) and the ZINDO/S-CIS semi-empirical method (average reorganization energy of $\lambda = 839.032 \text{ cm}^{-1}$) reported by Maity et al.⁵⁴ In this study, the site energies for the system Hamiltonian were calculated using the same QM/MM MD trajectories, and the off-diagonal terms were calculated using TrESP.54 A comparison of the dynamics under these recent spectral densities with that under the influence of a spectral density calculated using classical trajectories and ZINDO/S-CIS⁵⁰ is also shown. In many of the later studies, the spectral densities were resolved for each BChl unit and for each of the FMO monomers, effectively leading to 24 spectral densities. However, for simplicity, we are using the BChl sitespecific spectral densities averaged across the three monomers in FMO. As discussed, the optical excitation energies include influence from the solvents. Consequently, the electronic excitations, ϵ_{ii} in the system Hamiltonian, H_{0i} are obtained from the site energies in ref 54 by subtracting the site-specific reorganization energy. We used the correct system Hamiltonian corresponding to the QM/MM MD spectral densities.

The various spectral densities, averaged across all the BChls, are plotted in Figure 3. We also show a spectral density obtained using classical MD trajectories on ZINDO. The classical MD simulation of the spectral density suffers from a significant blue shift of the high-frequency vibrations. Both the QM/MM spectral densities alleviate this problem. Though the alignment of the peaks is not perfect even when using QM/MM MD simulations, it is quite close to the experimental fluorescence line-narrowing spectral density.^{65,66} (Note that the spectral density obtained using classical MD and ZINDO is far smoother than the more recent spectral densities. This is a result of a fitting procedure that was used by Olbrich et al.⁵⁰)

There are a few questions that we want to focus our exploration on: (1) How important is the choice of the density functional for characterizing the vibrations and the protein scaffolding vis-à-vis the EET dynamics? (2) What is the impact of the spatial inhomogeneity on the EET dynamics? (3) How does one analyze the individual pathways and routes of energy flow using exact dynamics? (4) Given that BChl 3 is the sink of the EET process, how much of the excitation energy goes into BChl 3 and how quickly? The last two questions, and their connection with the features of spectral densities, are especially important in terms of the efficiency of the EET process.

First, let us consider the population dynamics corresponding to an initial excitation of a single BChl unit. In Figures 4 and 5, we show the dynamics that happen from each of the different QM/MM MD spectral densities (both the average and sitespecific versions) at an ambient temperature of T = 300 K with initial conditions $\tilde{\rho}(0) = |1\rangle\langle 1|$ and $\tilde{\rho}(0) = |6\rangle\langle 6|$, respectively. (It should be noted that the convergence of the population requires a relatively short time step of 6 fs and a long memory



(a) Comparison with ZINDO-based classical MD spectral density whose parameters are reported in Ref.50



(b) Comparison with experiment 65,66

Figure 3. Comparison of spectral densities simulated using different methods averaged across all the eight BChl molecules obtained from Maity et al.⁵⁴ and Olbrich et al.⁵⁰

length of approximately 300 fs. The memory length spans close to 50 time steps, implying that a naive path integral simulation would require a prohibitively large $64^{51} \approx 10^{92}$ number of paths. The tensor network decomposition⁴³ is indispensable in making the computational load practically feasible. A detailed discussion of these parameters is reported in the Supporting Information. The coherences are not completely converged at these parameters; however, as described in the Supporting Information, we opt to rescale the values to compensate for the slight inadequacies of convergence.) The solid lines correspond to site-specific spectral densities, and the dashed lines correspond to the average spectral densities. The Förster theory seems to underestimate the difference in dynamics for site 3 between average and site-specific spectral densities for both methods. However, the differences are clearly manifest in the exact simulations. It seems that for TD-LC-DFTB, the transfer into site 3 is less efficient in the presence of the average spectral density than in the presence of the site-specific densities. This difference is minimal when the initial excitation is on $\tilde{\rho}(0) = |1\rangle\langle 1|$, but it is significantly more noticeable when $\tilde{\rho} = |6\rangle\langle 6|$. The trend is reversed for the ZINDO spectral densities, where for both initial excitations, the transfer is more efficient in the presence of the average spectral density. However, it has been seen that ZINDO leads to unphysically large reorganization energies.⁵⁴ Consequently, one cannot discount the possibility that spatial inhomogeneity is associated with greater efficiency of excitonic transport into the reaction center. Despite this indication, it should be noted that any such



Figure 4. Comparison of dynamics starting from $\tilde{\rho}(0) = |1\rangle\langle 1|$ for the different ab initio methods and with or without the spatial inhomogeneities. Dashed line: average spectral density. Solid line: site-specific spectral densities. Left column: exact dynamics. Right column: Förster theory.

conclusion requires caution and further investigation because the observations are highly dependent on the initial condition and spectral densities used.

The second aspect to consider from Figures 4 and 5 is the effect of changing the method of calculating the energy gap on the timescales. The most prominent difference between the spectral densities corresponding to the two approaches is the higher intensity and consequently a larger reorganization energy of the ZINDO spectral density.^{54,67} This leads to a slowing down of dynamics under ZINDO. It is noteworthy that despite this slowdown of the dynamics, the transfer from site 1 to site 2 in Figure 4 is increased from the TD-LC-DFTB functional to the ZINDO semi-empirical method. In addition, note that the dynamics predicted by Förster theory seems to be pretty close to the exact dynamics for both initial conditions when the system is described by TD-LC-DFTB. In case of ZINDO, it seems to consistently overestimate the transport into the third site irrespective of the initial conditions $(\tilde{\rho}(0) = |1\rangle\langle 1|$ or $\tilde{\rho}(0) = |6\rangle\langle 6|$) or the presence or absence of spatial inhomogeneities.

While it is known that resorting to classical MD trajectorybased simulations generally leads to geometry mismatch problems, the actual impact of these errors on the dynamics in this case has not been evaluated. The spectral density of the classical ZINDO bath⁵⁰ is shown in Figure 3a. The resultant spectral densities are clearly different from the QM/MM ones. However, the effect of these differences on the dynamics is far from obvious. In Figure 6, we show the dynamics corresponding to the system coupled to site-local baths described by the classical ZINDO spectral density. The system Hamiltonian corresponding to the ZINDO QM/MM MD simulation is used with the classical spectral density as well. This has been done to ensure that the effects we see are only coming from the spectral density. In fact, it is surprising that despite the enormity of the differences at the spectral density level, the dynamics is relatively similar to the QM/MM calculation. The differences are quite subtle. In fact, it is arguable whether the differences in dynamics caused by doing a qualitatively incorrect calculation are greater than the ones seen by using a different method of estimating the energy gap.

It is interesting to probe more deeply into the mechanism behind these behaviors. Such a probe will reveal subtler features of the dynamics than what was seen through the population dynamics. To facilitate such a deeper inquiry into the routes of EET, we resort to the recently developed coherence-based analysis.⁶⁰ The complete information about the average population transfer (eq 8) along each of these channels for the different initial conditions is presented in Figure 7. This data corresponds to the TD-LC-DFTB spectral density though the main trends carry over to the ZINDO spectral density as well. The data was integrated over simulations spanning T = 5 ps. Notice that for the case when $\tilde{\rho}(0) = |1\rangle\langle 1|$, the most important pathway is clearly $1 \rightarrow 2 \rightarrow 3$, with a secondary component coming from the $1 \rightarrow 6 \rightarrow 5 \rightarrow 4 \rightarrow 3$. This is known in the literature. We discover that additional non-insignificant contributions also happen along $1 \rightarrow 5 \rightarrow 4 \rightarrow 3$ and $1 \rightarrow 2$ \rightarrow 4 \rightarrow 3, both short-circuiting site 6. On the other hand, if $\tilde{\rho}(0) = |6\rangle\langle 6|$, the principal pathway is $6 \to 5 \to 4 \to 3$, with very tiny proportions of $6 \rightarrow 1 \rightarrow 2 \rightarrow 3$ and $6 \rightarrow 2 \rightarrow 3$. All the basic inferences remain valid even when the analysis is done

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Figure 5. Comparison of dynamics starting from $\tilde{\rho}(0) = |6\rangle\langle 6|$ for the different ab initio methods and with or without the spatial inhomogeneities. Dashed line: average spectral density. Solid line: site-specific spectral densities. Left column: exact dynamics. Right column: Förster theory.

using the Förster theory. This is likely related to how well it performed for the TD-LC-DFTB. One would surmise that the Förster pathways will not be as consistent with the exact simulations for the ZINDO spectral density. However, despite the apparent similarities, there is one significant distinction. When $\tilde{\rho}(0) = |1\rangle\langle 1|$, Förster seems to eliminate the direct transfer from site 1 to site 3 in favor of the transfer from site 1 to site 4.

Now, let us concentrate on the contributions of the most important pathways to the sink site, site 3. For our analysis, we divide the population transfer from 1 to 3 into three components: (1) direct transport from 1 to 3 $(\overline{P}_{3\leftarrow 1})$; (2) transport via 2 to $3(\overline{P}_{3\leftarrow 2})$; and (3) transport from all other sites combined, which includes the possibility of transport in the $1 \rightarrow 6 \rightarrow 5 \rightarrow 4 \rightarrow 3$ pathway (represented as $\langle \text{rest} \rangle$). The contributions of these three pathways to site 3 are shown in Figure 8.

Looking at Figure 8a, we see that the classical MD spectral density completely wipes out the direct transfer of excitation from sites 1 to 3. Though this direct route, $\overline{P}_{\overline{3}\leftarrow 1}$, is not exceptionally important, for the newer QM/MM-based spectral densities, it gives a non-negligible contribution to the total population of site 3. Also, note that the biggest impact of the spatial inhomogeneities is on the $1 \rightarrow 2 \rightarrow 3$ pathway. More specifically, the transfer from 2 to 3 is noticeably promoted by the absence of different site-specific spectral densities. Interestingly, for the TD-LC-DFTB-based spectral densities, the increase along the $1 \rightarrow 2 \rightarrow 3$ pathway is almost exactly countered by a decrease along the $\langle \text{rest} \rangle$ pathways. Due to this counterbalancing, the overall transfer is practically the same in

the two cases. For the ZINDO spectral densities, there is no counterbalancing, so the overall transfer is dramatically inhibited by the presence of different site-specific spectral densities.

In order to further explore the effect of the spatially inhomogeneous spectral densities, let us consider in a bit more detail the percentage contribution of the different components to the total transport. We have already mentioned the overall increase in the transport to the third site for the average spectral densities. We notice that another effect that is consistently reproduced is the fact the percentage contribution of the channel $\overline{P}_{3\leftarrow 2}$ consistently goes up from the sitedependent bath to the average bath. (The percentage contribution of $\overline{P}_{3\leftarrow 2}$ goes up from approximately 74 to 86% for TD-LC-DFTB and from approximately 76 to 84% for ZINDO. It is interesting that the increases in the percentages are very similar. However, this is likely no more than a coincidence, given that the reference with which the percentage is calculated changes quite dramatically in the case of ZINDO.) In contrast, the proportion of the population along $\langle rest \rangle$ is decreased quite significantly by the average bath (close to 20 to 9% for the TD-LC-DFTB spectral density and from around 19 to 10% for ZINDO). Surprisingly, the direct transport along $\overline{P}_{\overline{3}\leftarrow 1}$ remains constant (at roughly 5%) for all four cases. (While here we have been talking in terms of percentage contributions, the story is slightly different when it comes to the absolute transfers along these channels. While $\overline{P}_{\overline{3}\leftarrow 2}$ and $\overline{P}_{\overline{3}\leftarrow 1}$ both increase, the former increases much more significantly than the latter.) These subtle features would have been inaccessible in the absence of a method to probe the pathways of EET.



Figure 6. Comparison of dynamics corresponding to ZINDO QM/MM MD spectral density versus ZINDO classical MD spectral density. Colors used are the same as those used in Figure 4.

A similar analysis can be done for an initial excitation on the sixth monomer, $\tilde{\rho}(0) = |6\rangle\langle 6|$. Notice that in Figure 9, the patterns are even more convoluted than before. First, consider the comparison of exact quantum dynamics across the different spectral densities shown in Figure 9a. The most obvious thing that one can report is that the major contributor to site 3 is site 4. From Figure 7, we realize that this must be coming from the major pathway of $6 \rightarrow 5 \rightarrow 4 \rightarrow 3$. Contributions of $6 \rightarrow 4 \rightarrow 3$ is minimal. The direct transport from site 2 to site 3 is minimal in all cases, and negligible for ZINDO average spectral density. The conclusions with any degree of universality stop there. Transport from 6 directly to 3 may be an important factor; however, its importance seems to be dependent on the particular excitedstate method used. Whereas the average spectral density gives a smaller transfer into site 3 for the TD-LC-DFTB spectral densities, the reverse is true for ZINDO. Additionally, note that the magnitude of differences between the TD-LC-DFTB and the ZINDO bars in Figures 8 and 9 is larger than that between the ZINDO and the classical MD bars. Thus, the change between the spectral densities is probably significantly less important than that of changing the electronic excitation energies in the system Hamiltonian. This once again demonstrates the growing need for accurate parameters for these complex systems.

It is understood that probably the TD-LC-DFTB spectral densities are more realistic.⁵⁴ Consequently, we have also shown a comparison between the contributions for the various pathways obtained using Förster theory and the path integral calculations for this spectral density in subfigures (b) and (c) of Figures 8 and 9. Consider Figure 8b,c: while the total amount of

transfer is extremely similar, Förster seems to consistently eliminate the $1 \rightarrow 3$ direct transport, which is consistent with what we saw in Figure 7. This is coincidentally the same effect that the classical MD spectral density has. For $\tilde{\rho}(0) = |1\rangle\langle 1|$, the total amount of transfer into site 3 seems to be correctly reproduced by Förster. However, in Figure 9b,c, when $\tilde{\rho}(0) = |6\rangle\langle 6|$, Förster seems to slightly overestimate the transport into site 3. This is primarily because of an overestimation of the $4 \rightarrow 3$ direct transfer. Therefore, for TD-LC-DFTB, not only is Förster good for the population dynamics of the sites but it is also quite reliable for analyzing the energy transport pathways. However, the same cannot be said for the case of ZINDO, where it failed to reproduce the exact nature of excitonic dynamics. Thus, while the rough timescales are reliably reproduced, the details of the dynamics can be quite incorrect under the Förster theory. One should be careful while using it for an in-depth analysis.

4. CONCLUSIONS

In this paper, we have evaluated and compared the exact and Förster dynamics of the EET process in the FMO complex when the rovibrational modes of the molecules and the protein scaffold are described by accurate ab initio MD computations. We have tried to shed light on the effects of the inhomogeneities in the solvent by comparing the dynamics with the ones corresponding to the average bath. Surprisingly, the effects of changing the excited-state method seem to be possibly of a larger magnitude than that of removing spatial inhomogeneities or even that of changing from QM/MM simulations to classical MD simulations. Therefore, the noticeable differences in the



Figure 7. State-to-state population transfer in the presence of the TD-LC-DFTB baths for different initial conditions. The (j, k)th cell in the image represents the average population transferred directly from site k to site j, $\overline{P}_{i \leftarrow k}$.

spectral density must be washed out when it comes to the dynamics. Additionally, this seems to imply that estimating the correct electronic excitation energies of the BChl monomers is more important than simulating an accurate spectral density.

There is a limit to the amount of information that can be extracted from the direct population dynamics. We have used the recently introduced ideas of relating the coherence to the population transport $^{58-60}$ to explore the routes of transfer that the molecular excitation takes. Given the very complex interactions between these chromophores, it is not trivial to use an exact numerical computation to attribute the excitation transport to the different directed pathways that exist. This analysis is uniquely capable of answering these questions, and we have used this technique to present a static picture of the transport as it happens. In doing so, we have uncovered a couple of previously unnoticed transport pathways for the FMO. An analysis of the pathway-specific contributions to the transport problem has yielded further evidence to support the greater importance of the system Hamiltonian and electronic excitation energies as opposed to the spectral density.

Incoherent Förster rate theory is a commonly used approximation for studying excitonic dynamics. We have conducted a detailed comparison of the Förster results with the numerically exact path integral simulations. Consistent with earlier studies, we notice that the timescales of the transport are predicted quite accurately by the approximate theory. For TD-LC-DFTB, the approximate and the numerically exact results are practically identical. However, there are noticeable differences in the ZINDO parameters. Additionally, we have explored the transport pathways associated with the TD-LC-DFTB parameters under the Förster approximation and have found that they replicate the exact results remarkably well. While Förster is an incoherent theory, it is interesting that it is able to replicate the results of a coherence-based pathway analysis. Because of the non-systematic nature of the incoherent approximation, one needs to exercise caution in its usage. There are cases where it performs remarkably well but other places where it fails dramatically. However, in terms of a very crude understanding of the processes, Förster theory does seem to give similar timescales while having differences in the detail.



(a) Comparison of path integral results for different spectral densities.



Figure 8. Time-integrated transport to the third site, $\overline{P}^{(3)}$, when $\tilde{\rho}(0) = |1\rangle\langle 1|$. Dark blue: $\overline{P}_{\overline{3}\leftarrow 2}$. Light blue: $\overline{P}_{\overline{3}\leftarrow 1}$. Red: (rest).



(a) Comparison of path integral results for different spectral densities.



Figure 9. Time-integrated transport to the third site, $\overline{P}^{(3)}$, when $\tilde{\rho}(0) = |6\rangle\langle 6|$. Dark blue: $\overline{P}_{3\leftarrow 2}$. Dark red: $\overline{P}_{3\leftarrow 6}$. Red: $\overline{P}_{3\leftarrow 4}$.

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Ultimately, we have brought together a comprehensive suite of numerically exact and approximate results to bear upon the excitonic dynamics and related pathways in the FMO complex. In combination with the latest and most accurate descriptions of the protein environment and the molecular vibrations, these tools provide deep insight into the mechanism of excitonic transport. Such a toolbox promises to be exceptionally important in future studies of other open systems with quantum transport as well.

ASSOCIATED CONTENT

③ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcb.3c03062.

Description of the rescaling procedure and convergence parameters (PDF)

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Notes

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