Impact of Solvent on State-to-State Population Transport in Multistate Systems Using Coherences

Amartya Bose^{*,¶} and Peter L. Walters^{*,¶}

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ABSTRACT: Understanding the pathways taken by a quantum particle during a transport process is an enormous challenge. There are broadly two different aspects of the problem that affect the route taken. First is obviously the couplings between the various sites, which translates into the intrinsic "strength" of a state-to-state channel. Apart from these inter-state couplings, the relative coupling strengths and timescales of the solvent modes form the second factor. This impact of the dissipative environment is significantly more difficult to analyze. Building on the recently derived relations between coherences and population derivatives, we present an analysis of the transport that allows us to account for both the effects in a rigorous manner. We demonstrate the richness hidden behind the transport even for a relatively simple system, a



4-site coarse-grained model of the Fenna–Matthews–Olson complex. The effect of the local dissipative media is highly nontrivial. We show that while the impact on the total site population may be small, there are noticeable changes to the pathway taken by the transport process. We also demonstrate how an analysis in a similar spirit can be done using the Förster approximation. The ability to untangle the dynamics at a greater granularity opens up possibilities in terms of design of novel systems with an eye toward quantum control.

1. INTRODUCTION

Simulating complex chemical reactions in the condensed phase has been the holy grail of computational and theoretical chemistry. This already difficult task becomes even more arduous when the reaction involves the purely quantum mechanism of tunneling. However, this is ubiquitous in various processes like exciton transport in photosynthetic complexes, charge (especially electron and proton) transfer, etc. Furthermore, many exciton and charge-transfer processes happen in extended systems where there can be multiple pathways for the quantum "particle" to follow. A thorough understanding of the contribution of these various pathways is necessary to facilitate a more clear picture of the dynamics.

The simulation of the basic dynamics of quantum particles in a condensed phase is quite challenging in and of itself. Approximations like Redfield and Förster,¹ though often used, are not universally applicable, especially in the nonperturbative regime. For numerically exact simulations of dynamics of extended systems, approaches based on tensor networks have been gaining a lot of popularity. Most notable among them are the density matrix renormalization group $(DMRG)^{2-4}$ and its time-dependent variant.⁵ The family of multiconfiguration time-dependent Hartree $(MCTDH)^{6,7}$ can also be thought of as being based on tree tensor networks. However, these approaches often fail to account for the effects of (a possible continuum of)

translational and vibrational degrees of freedom contributed by the solvent.

Methods based on simulating the reduced density matrix provide a lucrative alternative to the above-mentioned methods. Of these, the quasi-adiabatic propagator path integral $(QuAPI)^{8,9}$ and hierarchical equations of motion $(HEOM)^{10-12}$ are the most widely used. The development of small matrix decomposition^{13,14} of QuAPI has made it especially viable for simulating large systems. Additionally, tensor networks have also been shown to be exceptionally useful in increasing the efficiency of path integral methods.¹⁵⁻¹⁸ These tensor network-based ideas have very recently been successfully extended to a multisite framework capable of simulating the quantum dynamics of extended systems coupled with local dissipative media.¹⁹⁻²¹

Studies of population dynamics conducted with these methods, while very rich in information, are unable to provide a clear and unambiguous insight into the mechanism of

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transport. Consider an extended system with a nontrivial topology allowing for long-ranged couplings between sites, and assume we are interested in the transport of an exciton. For a given initial location of the exciton, one would traditionally focus on the time-dependent population of the exciton on each of the sites. We would have no further information on the route or "pathway" that the exciton took to get to a particular site. Such information, however, is crucial to optimization of materials for guided quantum transport. An extremely naive approach to analyzing the pathways would be to track the route of the strongest couplings in the system Hamiltonian that leads from the "source" to the "sink". Such an approach would obviously miss out on the effects of the dissipative media. A different approach has been recently used to understand these pathways under a Lindbladian model Hamiltonian by evaluating the transport of the base system vis-à-vis a system with a particular chromophore dropped.²² The idea is that dropping a chromophore that is a part of the primary pathways would lead to a large decrease of transport efficiency. Alternatively, Wu et al.²³ have used flux networks constructed on integrated flux between sites and the flux balance method²⁴ to analyze the pathways in the Fenna-Matthews-Olson complex (FMO).

Recently, Dani and Makri²⁵ have shown that the instantaneous rate of change of the site population is related to the offdiagonal terms of the reduced density matrix (also called the "coherences") and rigorously derived the rate constants specific to the various state-to-state channels. "Coherence maps" are visual representations of the time evolution of the off-diagonal terms of the reduced density matrix and have recently been shown to capture important features of the structure of the Hamiltonian.²⁶ Building on these insights, we show how one can efficiently leverage the dynamical information in the off-diagonal terms to understand the effect of dissipative media in modulating the direct transport between sites as a function of time. While rates and kinetic models can often offer deep insights, 23,24,27,28 in many ultrafast chemical systems, the shorttime dynamics, often called the transients, may be very important. Rate theory and steady-state analysis generally fail for such processes and ones with more than one primary timescale. In these cases, it becomes crucial to shift our attention from rates to population transfer.

The paper is organized as follows. The method of analysis is outlined in Section 2. Thereafter, we explore the excitation dynamics in a coarse-grained four-site model of the Fenna– Matthews–Olson complex (FMO) with a focus on how this information can be used in a directed manner to gain detailed insights into the same. In Appendix A, we also develop a similar site-to-site transport analysis based on the incoherent Förster theory. Unlike this approximate approach, we would like to point out at the outset that the coherence-based analysis that is the primary focus of this paper is more general and can be applied to problems beyond exciton transport. Finally, some concluding remarks and future outlook are presented in Section 4.

2. IMPORTANCE OF COHERENCES IN DIRECT UNMEDIATED POPULATION TRANSPORT

Consider a system with N sites or states coupled with arbitrary harmonic baths. These baths may or may not be site-local. The Hamiltonian of such a problem is generally of the form

$$\hat{H} = \hat{H}_0 + \hat{H}_{\rm SB} \tag{1}$$

where \dot{H}_0 is the Hamiltonian corresponding to the system and $\hat{H}_{\rm SB}$ is the Hamiltonian corresponding to the system-bath coupling. (It is assumed that the system is represented in a basis that diagonalizes $\hat{H}_{\rm SB}$.) Under Gaussian response, the harmonic baths are often obtained from a simulation of the bath response function.^{29,30} Usually, one simulates the time-dependent population of each of the states. Here, we define the direct "state-to-state" population transfer from state k to state j as the population transfer between them without any intermediate state, also denoted by $P_{j\leftarrow k}$. The objective is to be able to simulate $P_{j\leftarrow k}$ as a function of time. Given that a "pathway" or "route" of transport is nothing but a sequence of these state-to-state population transfers, it should be possible to assemble a picture of the important pathways using them as the building blocks.

If $\tilde{\rho}(t)$ is the time-evolved reduced density matrix and $P_j = Tr(\tilde{\rho}(t) |j\rangle|\langle j \rangle$ is the population of the *j*th site, it is trivial to show that the time derivative of this population can be expressed as²⁵

$$\frac{\mathrm{d}P_j}{\mathrm{d}t} = \mathrm{Tr}[\tilde{\rho}(t)\hat{F}_j] \tag{2}$$

where

$$\hat{F}_{j} = \frac{i}{\hbar} [\hat{H}_{0}, |j\rangle \langle j|]$$
(3)

so long as the system—solvent coupling is diagonal in the system space. This commutator, \hat{F}_{ij} is exactly the same flux operator that is used for rate theory.^{31,32} Though generally, rate theory is formulated in terms of the equilibrium correlation functions, it has been shown that the rate for a two-state problem can be obtained as a "plateau" value of the time-dependent non-equilibrium flux, eqs 2 and 3, as well.³³ However, here we are not interested in a rate perspective. We rather want to understand the full time dynamics with additional information about the channel-dependent contributions. Following Dani and Makri,²⁵ we expand eq 2 to get

$$\frac{\mathrm{d}P_{j}}{\mathrm{d}t} = \frac{i}{\hbar} \sum_{k} \langle j | \tilde{\rho}(t) | k \rangle \langle k | \hat{H}_{0} | j \rangle - \langle j | \hat{H}_{0} | k \rangle \langle k | \tilde{\rho}(t) | j \rangle \tag{4}$$

For a real symmetric time-independent system Hamiltonian

$$\frac{\mathrm{d}P_{j}}{\mathrm{d}t} = -\frac{2}{\hbar} \sum_{k} \langle j | \hat{H}_{0} | k \rangle \mathrm{Im} \langle j | \tilde{\rho}(t) | k \rangle \tag{5}$$

Equations 4 and 5 can be interpreted in terms of the rates along the different state-to-state channels.²⁵ By comparing eqs 5 with 4, one can, for any k, interpret the term with Im $\langle k|\tilde{\rho}(t)|j\rangle$ as the rate of flow from site k into j and the term with Im $\langle j|\tilde{\rho}(t)|k\rangle$ as the rate of flow from site j to k. The time evolution of the individual coherences, $\langle j|\tilde{\rho}(t)|k\rangle$, as captured through coherence maps, also shows very interesting features reflecting the system dynamics and equilibrium.²⁶

Often the full population dynamics is a fruitful interrogative tool for understanding the system. However, when it comes to ideas of quantum design and understanding transport pathways involved in complex processes such as excitation energy transport (EET) or multicharge transport, it seems to be helpful to think in terms of site-to-site population transfer. The coherences allow us a crucial ability to express the direct and unmediated transfer of population between different sites. One can directly use eq 4 to partition the total population change at a site into the contributions from each state-to-state channel. We define the time-dependent population flow from the *k*th site to the *j*th site as

$$P_{j \leftarrow k}(t) = \frac{i}{\hbar} \int_{0}^{t} dt'(\langle j | \tilde{\rho}(t') | k \rangle \langle k | \hat{H}_{0} | j \rangle - \langle j | \hat{H}_{0} | k \rangle \langle k | \tilde{\rho}(t') | j \rangle)$$
(6)

For a real symmetric time-independent system Hamiltonian, using eq 5, this reduces to

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

Notice that the state-to-state population flow between two sites is proportional to the Hamiltonian matrix element between them. This is what we would have naïvely concluded. However, the proportionality constant is related to the time integral of the coherence. This captures the solvent effect on the system dynamics. These state-to-state populations are independent of how the simulation was done and therefore can be applied to any level of simulation as desired. There are no further approximations over and above the ones used for simulating the time-dependent reduced density matrix of the system. Additionally, eqs 6 and 7 uphold detailed balance in the sense that $P_{j \leftarrow k}(t) = -P_{k \leftarrow j}(t)$ and that $P_{j \leftarrow j}(t) = 0$ for all *j*, encoding the fact that there cannot be any population transfer from a site to itself.

Finally, the time-dependent population of the *j*th site can be expressed as

$$P_j(t) = P_j(0) + \sum_{k \neq j} P_{j \leftarrow k}(t)$$
(8)

The ability to partition the time-dependent population on a site into the components along various channels is important for understanding the effects resulting from the nontrivial interactions between specific changes in the dissipative media and the system Hamiltonian. If the system is thought of as a graph, with the sites being the vertices and the edges being the various inter-site connections, then the time-integrated coherences decompose the time evolution of the population on a site (vertex) along all of the edges that are incident on it. The only assumption in this analysis is that it requires the environment to interact with the system through an operator, which is diagonal in the system space. Even if the solvent is anharmonic or atomistically described, mixed quantum-classical methods like quantum-classical path integral^{34,35} can be used to simulate this information.

3. RESULTS

To demonstrate the utility of this analysis of the state-to-state population transfers leveraging the information of the coherences, consider a coarse-grained system modeled on the FMO complex. FMO is a naturally occurring light-harvesting complex with eight bacteriochlorophyll monomeric sites. It is ubiquitous as a model for excitonic transport and provides a very rich set of dynamical features owing to the nonlinear inter-site couplings. We would like to note that here, FMO is a convenient example problem. The coherence-based state-to-state analysis that is the subject of this paper is not limited to exciton transport. It can help generate direct insight into the complex dynamics of any quantum particle undergoing transport across multiple "sites". The most common examples of such transport processes are exciton or charge-transfer systems. To enable a thorough exploration of the impact of the vibrational modes on the transfers through various state-to-state channels, we simplify the system by coarse-graining it to include the four most relevant sites. For FMO, it is known that if bacteriochlorophyll site 1 is initially excited, the primary pathway is $1 \rightarrow 2 \rightarrow 3$, and the secondary pathway leads from $1 \rightarrow 6 \rightarrow 5 \rightarrow 4 \rightarrow 3$. Thus, in our coarse-grained model, we keep sites 1, 2, and 3 as is, reduce sites 4, 5, and 6 into a new renormalized 4th site, and omit sites 7 and 8 entirely. This is shown in Figure 1. Similar to the full FMO, we expect the model to have a primary pathway of $1 \rightarrow 2 \rightarrow 3$ and a secondary pathway of $1 \rightarrow 4 \rightarrow 3$.



Figure 1. Fenna–Matthews–Olson complex with the bacteriochlorophyll units colored by the coarse-grained units used. Blue: Coarsegrained site 1. Orange: Coarse-grained site 2. Green: Coarse-grained site 3. Red: Coarse-grained site 4. Gray: Ignored.

The coarse-grained FMO model, along with its interactions with the local vibrational baths, is described by the following Hamiltonian

$$\hat{H} = \hat{H}_0 + \hat{H}_{\rm SB} \tag{9}$$

$$\hat{H}_{0} = \sum_{k=1}^{4} \epsilon_{k} |k\rangle \langle k| + \sum_{j \neq k} h_{j,k} |j\rangle \langle k|$$
(10)

$$\hat{H}_{\rm SB} = \sum_{k=1}^{4} \sum_{j=1}^{N_{\rm esc}} \frac{p_{kj}^2}{2m_{kj}} + \frac{1}{2} m_{kj} \omega_{kj}^2 \left(x_{kj} - \frac{c_{kj} |k\rangle \langle k|}{m_{kj} \omega_{kj}^2} \right)^2$$
(11)

where ω_{kj} and c_{kj} are the frequency and coupling of the *j*th harmonic mode of the bath corresponding to the *k*th site. The mass of the bath mode, m_{kj} , is generally taken to be unity. The electronic excitation energies are given by ϵ_{k} , and the inter-site couplings are given by $h_{j,k}$. The frequencies, ω_{kj} , and couplings, c_{kj} , of the *k*th bath are characterized by the spectral density defined as

$$J_k(\omega) = \frac{\pi}{2} \sum_j \frac{c_{kj}^2}{m_{kj}\omega_{kj}} \delta(\omega_{kj} - \omega)$$
(12)

This can be calculated as the Fourier transform of the energy-gap autocorrelation function simulated using molecular dynamics.

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Figure 2. Site-dependent and average spectral densities for the first four bacteriochlorophyll units in FMO obtained from Maity et al.³⁶

The site-dependent spectral densities and Hamiltonian for FMO have been recently obtained using the TD-LC-DFTB density functional.³⁶ We use these parameters as the starting point for our exploration. The Hamiltonian corresponding to this coarse-grained model is given in the Supporting Information. The average and the site-dependent spectral densities are shown in Figure 2 for reference. In our exploration of the FMO model, we will change the spectral densities in various ways that shall be described. However, the parameters for the system Hamiltonian will always remain the same to ensure that the effects that we see arise solely out of the vibrational baths.

Figure 3 shows the excitonic population corresponding to each of the sites for the site-specific and average spectral



Figure 3. Excitonic population on different sites as a function of time. Solid line: average spectral density. Dashed line: different spectral densities.

densities. (This information can, in principle, be calculated using many methods. Here, the simulations have been conducted using the tensor network path integral method¹⁷ based on Feynman–Vernon influence functional. Details of the method are provided in the Supporting Information.) We notice that changing the average spectral density to the site-specific spectral densities has minor effects on the dynamics of bacteriochlorophyll sites 1 and 2 and negligible effects on the populations of sites 3 and 4. A key drawback of this population picture is that it washes away a lot of details. At this level, one cannot answer questions such as how does the transfer from site 1 to site 2, $P_{2\leftarrow 1}(t)$, change in switching between the two descriptions. Or what happens to the various contributions to the site 3 population?

The analysis of the imaginary part of coherences allows us to answer these questions. In Figure 4, we show the population



Figure 4. Transfer pathways of excitonic population corresponding to each site. Solid line: average bath. Dashed line: different spectral densities. Black: Total change of population of the site. Yellow: change due to site 1 ($P_{*-1}(t)$). Red: change due to site 2 ($P_{*-2}(t)$). Green: change due to site 3 ($P_{*-3}(t)$). Blue: change due to site 4 ($P_{*-4}(t)$).

dynamics of specific sites along with the individual contributions. The first thing that one immediately observes is that the primary flow of excitonic population happens along $1 \rightarrow 2 \rightarrow 3$. To see this, consider that the excitation starts on site 1. The biggest transport happens from 1 to 2 in Figure 4a (red line). Then looking at where the population goes from site 2, we see that the maximum amount goes to 3 in Figure 4b (green line). By a similar analysis, we find a secondary, slower pathway that leads from site 1 to site 3 via site 4 $(1 \rightarrow 4 \rightarrow 3)$. Additionally, one sees a non-insignificant contribution from $1 \rightarrow 2 \rightarrow 4 \rightarrow 3$. The direct transfer from site 1 to site 3 is the least important of these. While the ability to analyze the primary pathways

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Figure 6. Population transfer along $1 \rightarrow 2$ and $2 \rightarrow 3$ for components of the primary pathway when the site-specific reorganization energies on site 2 and site 3 are scanned.

immediately is obvious from Figure 4, we would like to emphasize the power of the method in terms of disqualifying unimportant pathways as well. Notice that though site 1 transfers population into site 4, site 4 only transfers population into site 3. Therefore, a path like $1 \rightarrow 4 \rightarrow 2 \rightarrow 3$ is not important.

We notice that with the site-specific spectral densities, the excitonic flow along $1 \rightarrow 2 \rightarrow 3$ is decreased coupled with an increased flow along the $1 \rightarrow 4 \rightarrow 3$ pathway. As for the other

two pathways, the flow along $1 \rightarrow 2 \rightarrow 4 \rightarrow 3$ increases, and the direct transfer $1 \rightarrow 3$ remains the same. These changes in the excitonic pathways are evidenced by the fact that in going from the average to the site-specific spectral densities, the direct transfer from site 2 to site 3 (red curve in Figure 4c) shows a decrease, and the transfer from 4 to 3 (blue curve in the same figure) shows an increase. Furthermore, while there is an increase in both the transfer from site 1 to site 4 (yellow curve in Figure 4d) and site 2 to site 4 (red curve in the same figure), the



Figure 7. Population transfer along $1 \rightarrow 4$ for components of the primary pathway when the site-specific reorganization energies on site 2 and site 3 are scanned.

increase in $1 \rightarrow 4$ is much larger. An explanation for these changes can be made by looking at $P_{3\leftarrow 2}(t)$ (red curve in Figure 4c). We notice that for the site-specific spectral densities, the direct transfer from site 2 to 3 seems to be somewhat restricted, causing a rerouting of the excitation through site 4. Despite all of these subtle changes brought in by spatial inhomogeneity, the ranking of the main pathways still remains unperturbed. Apart from this rather broad overview of the pathways of excitation dynamics, a state-to-state analysis can uncover a wide variety of other features. For example, we can determine that the actual direct transfer from site 1 to site 2, $P_{2\leftarrow 1}(t)$, shows two different timescales. There is a fast transfer of population from site 1 to site 2 up to around 0.5 ps, which is followed by a significantly slower transfer of population. Thus, the red line in Figure 4a and the yellow line in Figure 4b show a much slower gradient starting around that time.

To explore the effect of the site dependence of the spectral density, we systematically change the reorganization energies on single sites using the average bath as a starting point. We scale the reorganization energies on site 2 and site 3 with factors ranging from 0.25 and 1.75 in steps of 0.25. Figure 5 shows the change in the population dynamics of site 3 under such a scan. Notice that in Figure 5b, on scanning the reorganization energy on site 3, the population curve initially increases very quickly when the scaling factor is increased from 0.25 to 0.5. It then seems to stabilize and for scaling factors greater than 1 seems to show a decreasing trend. This behavior is very reminiscent of the inverted region in Marcus theory of electron transfer.³⁷ The trends seem to become different when we consider the scan of the reorganization energy on site 2 (Figure 5a). In the regime scanned, on increasing the reorganization energy on site 2, the population on site 3 seems to grow slower. The analysis based on coherence allows us to investigate these changes in a much greater depth.

Let us consider the primary pathway, $1 \rightarrow 2 \rightarrow 3$. Figure 6 demonstrates the changes in the population dynamics along this pathway on scanning the reorganization energies on sites 2 and 3. (Figure 6a,b shows the change in dynamics for a scan on site 2 and Figure 6c,d shows the change in dynamics for a scan on site 3.) First notice that the curves in Figure 5b are very similar to those in Figure 6d. Also, the direct transfer from site 1 to 2, Figure 6c, shows very little change on scanning the reorganization energy on site 3. This implies that the main cause of change of the population dynamics of site 3 when its

reorganization energy is scanned is the change in the transfer from site 2 to site 3. Things get slightly more complicated when the reorganization energy on site 2 is scanned (Figure 6a,b). Both the transfers from site 1 to 2 and site 2 to 3 change with the reorganization energy, showing a non-insignificant slow-down of the dynamics. Interestingly, only the fast timescale transfer from site 1 to site 2 (Figure 6a) is affected by the increase of the reorganization energy. The transport at later times seems to remain relatively invariant.

Finally, before concluding this discussion, we turn our attention to the $1 \rightarrow 4$ transport when the reorganization energies on sites 2 and 3 are scanned. This is shown in Figure 7a,b, respectively. Notice that though the reorganization energy is being changed on a site that is not even involved in this direct transport, both the scans affect the $1 \rightarrow 4$ transfer. While the pattern is unclear when the scan is on site 3 (Figure 7b), there is a very clear monotonic increase of the population transfer on scanning on site 2 (Figure 7a). (The data corresponding to the other channels, though not explored here, have been reported along with these plots in the Supporting Information for completeness.)

4. CONCLUSIONS

Many exact and approximate methods exist that can simulate the dynamics of complex systems coupled with solvents and vibrational modes. However, it is a significantly more difficult challenge to understand the exact routes that the transport process takes. The naïve approach of looking at the inter-site couplings falls short because of its failure to account for the nontrivial effects of the solvent modes. In this paper, we have presented a novel technique for analyzing the dynamics that yields the contribution of each state-to-state channel. Unlike previous works, the current coherence-based approach is able to generate a dynamical picture of the transport pathways.

There has been a recent realization of the importance of the coherences or off-diagonal terms, especially in the steady state, in understanding the dynamics.^{23,28} It has been shown that the time derivative of the site populations can be written as a linear combination of the imaginary part of the coherences.²⁵ Based on this relation of the time derivatives with the imaginary parts of the coherences, we show that the change in the population of a site can be trivially decomposed into the contributions coming from different channels. Thus, one can, using the coherences, study the effects of the solvent and temperature on the direct and

unmediated transport between any pair of sites as a function of time. We have also derived a similar approach based on the incoherent Förster rate theory. While the coherence-based approach is totally general and can be used to analyze a variety of dynamics, the approach based on Förster rate theory is limited to cases where the latter is applicable, in particular to exciton transfers.

Employing this coherence-based analysis, we can start to untangle the dynamics of systems with complicated inter-site couplings. We use a 4-site model based on the FMO as an example, which enables a comparison of the Förster theorybased approach. For this particular problem, we show that the latter approach also works quite well even in estimating the dynamical state-to-state transfers. As demonstrated, the insights uncovered can often be very nontrivial. From a fundamental perspective, just because the total population on a site has a relatively regular pattern, it is not necessary that the regularity is there in all of the individual contributions. Similarly, the total population showing some strange feature does not imply the existence of the weirdness in each of the contributory dynamics. What is possibly equally important to a fundamental understanding is the fact that changing the vibrational profile on a single site affects not only the pathways involving that site but other pathways as well. This has important implications in trying to design materials to engineer specific outcomes in complex open quantum systems.

An analysis of the coherences reveals a wealth of information that lay hidden in the dynamics of the reduced density matrix. Extending the explorations in ref 26, it is now possible to associate causes with the various changes that happen in the total population dynamics. In the near future, we will utilize these ideas in understanding other processes beyond exciton transport, especially complex reactions with multiple pathways like proton-coupled electron transfer and multi-proton transfers. The fact that the various analyses of coherence done here and earlier elsewhere^{23,25,26,28} are not dependent on any single method of simulation of the time-evolved reduced density matrix makes these ideas universally applicable. Finally, for cases where approximate Förster theory is applicable, we have also derived an approach to obtain similar dynamical state-to-state transfer information. We believe that the combination of these two complementary approaches, and the idea of dynamical stateto-state transport, will be useful in the future for studying the dynamics in a variety of complex systems.

APPENDIX A COMPARISON WITH INCOHERENT FÖRSTER THEORY

Förster theory¹ is a perturbative theory formulated to describe resonant energy transfer between two electronic states. It works especially well if (1) the electronic couplings between two sites are smaller than the strength of the system-bath coupling between the chromophoric units on the one hand and the vibrational modes and protein scaffold on the other, and (2) the chromophoric sites can be thought of as point dipoles.³⁸ The reorganization energies of the baths are 304.77, 442.45, 1004.79, and 405.96 cm⁻¹, which are all greater than the electronic couplings listed in the system Hamiltonian given in the Supporting Information. Consequently, this is a case where the approximate Förster theory should be applicable.

The Förster results for the time evolution of the molecular excitations are shown in Figure 8. Exact results reported in Figure 3 are also reproduced as Figure 8b for convenience. The site-based population dynamics is practically identical, showing



Figure 8. Förster and exact simulations of excitonic population on different sites as a function of time. Solid line: average spectral density. Dashed line: different spectral densities.

the power of the incoherent Förster in simulating the excitonic dynamics in these situations. Now, Förster simulations typically only give the excitonic population on the different sites. We can however build a similar time-dependent site-to-site picture by using the Förster rate matrix and the incoherent populations by identifying that the time derivative of the site-to-site population transfer is given as

$$\dot{P}_{j\leftarrow i}(t) = k_{j\leftarrow i} P_i(t) - k_{i\leftarrow j} P_j(t)$$
(13)

Consequently, we can obtain the population transfer by integrating the right-hand side

$$P_{j\leftarrow i}(t) = \int_0^t \mathrm{d}t' k_{j\leftarrow i} P_i(t') - k_{i\leftarrow j} P_j(t')$$
(14)

The integrated population flux used by Wu et al.²³ is equivalent to the long-time limit of eq 14. Using this, we can estimate the site-to-site population transfer, and in Figure 9, we show a comparison between the Förster results and the exact numerical results. Just as the total site-based population was simulated very



Figure 9. Comparison of transfer pathways of excitonic population corresponding to each site under Förster theory and exact dynamics. Solid line: average bath. Dashed line: different spectral densities. Black: total change of population of the site. Yellow: change due to site 1 $(P_{*-1}(t))$. Red: change due to site 2 $(P_{*-2}(t))$. Green: change due to site 3 $(P_{*-3}(t))$. Blue: change due to site 4 $(P_{*-4}(t))$.

accurately by Förster theory, the site-to-site transfers are also reproduced properly.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jctc.3c00200.

Description of the tensor network path integral method; the coarse-grained FMO model; complete data for the state-to-state transfers (PDF)

AUTHOR INFORMATION

Corresponding Authors

- Amartya Bose Department of Chemical Sciences, Tata Institute of Fundamental Research, Mumbai 400005, India; orcid.org/0000-0003-0685-5096; Email: amartya.bose@ tifr.res.in
- Peter L. Walters Department of Chemistry and Biochemistry, George Mason University, Fairfax, Virginia 22030, United States; Email: peter.l.walters2@gmail.com

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.jctc.3c00200

Author Contributions

[¶]A.B. and P.L.W. contributed equally to this work.

Notes

The authors declare no competing financial interest.

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