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Probability-current analysis of energy transport in open quantum systems

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We introduce a probability-current analysis of excitation energy transfer between states of an open quantum system. Expressing the energy transfer through currents of excitation probability between the states in a site representation enables us to gain key insights into the energy transfer dynamics. In particular, the analysis yields direct identification of the pathways of energy transport in large networks of sites and quantifies their relative weights, as well as the respective contributions of unitary dynamics, coherence, dephasing, and relaxation and dissipation processes to the energy transfer. It thus provides much more information than studying only excitation probabilities of the states as a function of time. Our analysis is general and can be readily applied to a broad range of dynamical descriptions of open quantum system dynamics with coupling to non-Markovian or Markovian environments.

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I. INTRODUCTION

In the description of electronic excitation energy transport in systems of coupled sites—such as molecular aggregates, biological and artificial light-harvesting systems, coupled quantum dots—knowledge about the contributions of the different processes involved is important both for understanding and modeling of the energy transport mechanisms in nature, as well as for design of artificial and biomimetic systems that enable efficient transport. The key processes involved in the energy transfer that are essential for this analysis are unitary dynamics, dephasing, and relaxation and dissipation. It has been found that the right balance between these processes can enable highly efficient, directed energy transport [1–4]. Another key aspect in the investigation of design-function relationships in natural and artificial light-harvesting systems is the identification of the specific pathways of energy transport in large networks of sites and the quantification of their relative weights [4–9]. In such systems and for open quantum systems in general, it has long been appreciated that coherent dynamics play a role in the overall energy transfer, and the coherent features of transport have been intensively studied in a broad range of open quantum systems [10–18]. In recent years, experimental evidence for long-lasting coherence in biological photosynthetic systems obtained from ultrafast spectroscopies has also sparked questions and discussions about the contribution of coherence to the energy transport that drives photosynthesis [16,18–28].

To address these aspects of energy transfer in natural and artificial systems, we introduce here an analysis in which the energy transfer between the states of an open quantum system is expressed through excitation probability currents. In this paper the analysis is carried out in a site basis consisting of states in which the excitation is localized on single sites. This is the most convenient basis for applying the probability current analysis to spatial energy transport, which is the focus of a subsequent paper [4]. However, we emphasize that the excitation probability current analysis itself is general and independent of basis. It is thus applicable to description of excitation transport in any basis.

Describing excitation or charge transport by means of probability currents is commonly encountered in a number of situations in condensed matter [29–31] and in electron transfer reactions [32]. However, such a description is usually not applied in the study of light-harvesting systems, where energy transfer has instead usually been evaluated in terms of time-dependent populations of excited states (see, e.g., Refs. [6,16,22,33–38]). For such systems, and for other systems, a large amount of additional information about the system dynamics in terms of pathways, etc., can be gained from an analysis of the probability currents. This is also demonstrated in a companion paper [4], where the analysis developed in this paper is applied to numerical simulations investigating excitation energy transfer and design-function relationships in the Photosystem II protein complex that drives photosynthesis in higher plants.

In our analysis, we obtain the probability currents from a continuity equation for the excitation probability of the sites. Since the total excitation probability inside the (open) system is usually conserved, such a treatment based on continuity equations and probability currents is widely applicable. In this paper we show that this analysis enables us to address the following tasks in a straightforward manner:

(1) Calculate the excitation probability currents between the individual sites, i.e., their direction and magnitude, thus revealing the pathways of transport. This can be performed for a large, complicated network of sites, where the excitation of the sites couples to either a Markovian or a non-Markovian environment.

(2) Quantify the respective contributions of unitary dynamics, dephasing, and relaxation and dissipation to the currents.

(3) Quantify the contribution of coherence (versus the contribution of populations) to the currents, i.e., to the energy transfer.

Here we shall understand coherence to be quantified by the off-diagonal elements of the system's density matrix in the basis under consideration. The system's density matrix can be obtained from a quantum master equation or other kinds of quantum dynamical equations such as (stochastic) Schrödinger

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equations, and can be transformed to study populations and coherences in different bases. For the probability-current analysis, this flexibility of the density matrix also allows us to obtain the currents between states in the desired basis. As noted above, in this work we employ the site basis in order to study the spatial transport of energy. While the currents between individual sites can be obtained from a density matrix approach, they may not be evident from an (effective) rate equation approach, such as generalized Förster transfer, that provides only the time-dependent populations of effective delocalized states, but no explicit coherence.

Our treatment is applicable to the tight-binding and Holstein-like models—whether described as open or closed quantum systems—that are typically used for modeling excitation transfer systems of the form of biological or artificial light-harvesting systems [39–44]. In the probability-current framework, we obtain formulas for the contribution of the different processes—coherence, dephasing, relaxation—to the currents (i.e., to the excitation energy transport) from the evolution equation for the system's density matrix. Inserting the elements of the time-dependent system density matrix into these formulas, where the matrix elements are obtained either from a numerical simulation or a tomographic reconstruction from experimental measurements, one can then numerically evaluate the contributions to the currents for specific model situations.

In the following, we first briefly review the description of energy transport in an open quantum system by means of a non-Markovian quantum master equation (Sec. II). This will provide the underlying dynamical basis for our probability-current analysis. Then, in the main part of the paper in Sec. III, we introduce our probability-current analysis, where we express the energy transport through probability currents and derive the different contributions of unitary evolution, dephasing, and relaxation to the currents based on the quantum master equation. Using this framework, we then explicitly analyze the contribution of coherence to the energy transport. To illustrate the interplay between the probability current and the coherence, we analyze the dynamical equations for the case of a Markovian environment, for which the equations are particularly simple and yield useful general insights. A quantitative analysis for a (33-site) system with a more general non-Markovian environment is given in Ref. [4]. Throughout the paper we shall illustrate the analysis with application to the case of electronic energy transport, but we emphasize that the formalism is quite general and can be readily applied to other forms of energy transfer. Concluding remarks are given in Sec. IV.

II. QUANTUM MASTER EQUATION DESCRIPTION OF ENERGY TRANSFER

In this section we briefly outline the quantum master equation approach to generating the open quantum system dynamics that constitute the focus of the probability-current analysis in Sec. III.

Energy transport is often described by means of an open quantum system approach in order to be able to treat the large number of degrees of freedom involved in the dynamics. In this description, the problem is divided into three components—the "system" degrees of freedom that are most relevant for the energy transport, other "environmental" degrees of freedom, and the "system-environment coupling."

For example, in electronic energy transport, the system may be the set of ground and excited electronic states of the sites supporting the excitations, while the vibrational degrees of freedom (commonly termed a "bath") constitute the environment and the electron-vibration coupling constitutes the system-environment interaction [42,45]. In many important electronic energy-transfer processes, the energy is carried by molecular electronic excitations that are coupled to intramolecular and/or intermolecular vibrational modes. Thus, in pigment-protein complexes in photosynthetic systems, the electronic excitation of the molecular pigments is coupled to internal vibrational modes of the molecules and to vibrational modes of the protein scaffold in which the pigments are embedded [46,47]. This coupling to vibrations is often crucial in the design-function relationship of such biological systems, since it induces dephasing and vibrational relaxation, which help to efficiently direct the energy transport to a target location (in photosynthesis the energy might be directed from an antenna complex to a reaction center complex), where the energy is trapped and transformed [1,4,37,48]. It is therefore important to include such vibrational degrees of freedom in the modeling and simulation of the excitation transport, in order to take these important dephasing and relaxation effects into account.

In this open quantum system approach one then solves an effective evolution equation in the small space of the system degrees of freedom, where the system degrees of freedom are treated explicitly and the environment degrees of freedom are taken into account only implicitly. This approach makes even large networks of sites numerically manageable [38,49]. One widely used class of effective evolution equations derived from an open quantum system approach is represented by quantum master equations. These describe the time evolution of a reduced density matrix of the system, which formally corresponds to tracing out the environment degrees of freedom in the density matrix of the total problem (see, e.g., [22,45,50–53]). In simulations of molecular electronic energy transfer, the reduced density matrix may contain just the electronic degrees of freedom, i.e., where formally the partial trace over the vibrational degrees of freedom was carried out [6,42,54], or alternatively, both the electronic and selected vibrational degrees of freedom [55], where the latter are chosen to reflect the most strongly coupled or resonant vibrations.

As a dynamical model for electronic excitation energy transport in a system of coupled sites, we consider here a quantum master equation of the form

$$\partial_t \rho(t) = \mathcal{P}[\rho(t)] = -i[H,\rho(t)] + \mathcal{L}_{\text{nonunitary}}[\rho(t)], \qquad (1)$$

describing the time evolution of the electronic reduced density matrix $\rho(t)$ of a system composed of a finite number of sites each possessing two electronic states, with initial condition ρ_0. Here H is the system Hamiltonian that contains the energies of the sites and the couplings between these. (Here and throughout the paper we set $\hbar \equiv 1$.) The first term in Equation (1) describes the unitary dynamics of the system. The second term describes the nonunitary contribution to the system dynamics due to interaction of the system with the environment. We shall restrict our attention here to the density matrix components in the single excitation sector, which is spanned by the states $|n\rangle$, where $|n\rangle$ is the state in which only site n is excited and all other sites are in the ground state. The probability to find the electronic excitation localized on site n at time t is then given by

$$\rho_{nn}(t) = \langle n|\rho(t)|n\rangle. \tag{2}$$

Transport of electronic excitation energy between the sites following an initial injection of a single excitation into the system will manifest itself in the time-dependent behavior of these excitation probabilities $\rho_{nn}(t)$ of the sites.

We assume that the nonunitary term of Eq. (1) is a sum of two contributions, one of dephasing and one of dissipation and relaxation between electronic states due to the coupling to the environment:

$$\mathcal{L}_{\text{nonunitary}}[\rho(t)] = \mathcal{L}^{\text{Dephas}}[\rho(t)] + \mathcal{L}^{\text{Relax}}[\rho(t)]. \tag{3}$$

We shall realize Eq. (1) by a time-convolutionless, non-Markovian quantum master equation [50–53,56], which are well suited to describe energy transfer in molecular systems where the electronic excitation couples to non-Markovian vibrational modes of the environment [38,54]. In this description the dephasing contribution can be written in the form

$$\begin{aligned}\mathcal{L}^{\text{Dephas}}[\rho(t)] = \sum_n \big[&L_n^{\text{D}}\rho(t)A_n^{\text{D}\dagger}(t) + A_n^{\text{D}}(t)\rho(t)L_n^{\text{D}\dagger}\\ &-L_n^{\text{D}\dagger}A_n^{\text{D}}(t)\rho(t) - \rho(t)A_n^{\text{D}\dagger}(t)L_n^{\text{D}}\big],\end{aligned} \tag{4}$$

with $L_n^{\text{D}} = |n\rangle\langle n|$ the system operator coupling electronic excitation of site n to the environment and $A_n^{\text{D}}(t)$ a time-dependent auxiliary operator. The operators $A_n^{\text{D}}(t)$ follow a separate evolution equation that is independent of the density matrix $\rho(t)$, which captures the non-Markovian influence of the environment (see Refs. [4,53,54]). We note that the non-Markovian coupling to the environment described by Eq. (4) not only induces dephasing, but can also induce vibrational relaxation [55]. In the remainder of the paper we shall nevertheless continue to refer to the term Eq. (4) as "dephasing," in order to distinguish it from the *electronic* relaxation described below, which constitutes direct relaxation of the system degrees of freedom.

Electronic dissipation and relaxation between electronic states is analogously described by the operator

$$\begin{aligned}\mathcal{L}^{\text{Relax}}[\rho(t)] = \sum_{l,n\neq l} \big[&L_{nl}^{\text{R}}\rho(t)A_{nl}^{\text{R}\dagger}(t) + A_{nl}^{\text{R}}(t)\rho(t)L_{nl}^{\text{R}\dagger}\\ &-L_{nl}^{\text{R}\dagger}A_{nl}^{\text{R}}(t)\rho(t) - \rho(t)A_{nl}^{\text{R}\dagger}(t)L_{nl}^{\text{R}}\big],\end{aligned} \tag{5}$$

with system coupling operators $L_{nl}^{\text{R}} = |l\rangle\langle n|$ describing relaxation from a state $|n\rangle$ to a state $|l\rangle$, and time-dependent auxiliary operators $A_{nl}^{\text{R}}(t)$ that similarly include the non-Markovian effects of the coupling to the environment.

In the Markovian limit, where the correlation time of the environment is assumed to be short compared to the relevant system time scales of the dynamics, both the time-dependent auxiliary operators for dephasing and relaxation become independent of time [53]:

$$A_n^{\text{D}}(t) \rightarrow \tfrac{1}{2}\gamma_n^{\text{D}} L_n^{\text{D}}, \tag{6}$$

$$A_{nl}^{\text{R}}(t) \rightarrow \tfrac{1}{2}\gamma_{nl}^{\text{R}} L_{nl}^{\text{R}}, \tag{7}$$

with system-environment coupling parameters γ_n^{D} and γ_{nl}^{R}, respectively. In this limit, the non-Markovian quantum master equation Eq. (1) becomes the well-known Markovian-Lindblad equation [53], as can be seen by inserting Eqs. (6) and (7) into Eqs. (4) and (5), respectively.

III. PROBABILITY-CURRENT ANALYSIS OF ENERGY TRANSFER

We now develop the analysis of probability currents for dynamics generated by the non-Markovian quantum master equation description of the previous section.

Energy transfer between the sites occurs when the electronic excitation is transferred between the sites, driven by the intersite coupling. Since the overall excitation probability in the system is conserved, $\sum_n \rho_{nn}(t) = 1$, even if the system is open (i.e., it couples to an environment and $\rho(t)$ is identified with the reduced density matrix of the system), and a continuity equation holds:

$$\partial_t \rho_{nn}(t) = \sum_{l\neq n} j_{ln}(t), \tag{8}$$

where $j_{ln}(t)$ is the net probability current at time t that transports excitation probability from a site l to site n, i.e., the net flow of probability along the link between the two sites, with dimensions 1/time [57]. When $j_{ln}(t)$ is positive, excitation is transported from site l to site n, while when $j_{ln}(t)$ is negative, there is transport from site n to site l. These currents can be identified with the energy transfer between the sites. (We note that instead of the probability currents considered in the present work, others have considered *energy* currents to quantify excitation energy transfer [58]. However, this can be problematic in open systems, since the energy inside an open system is *not* a conserved quantity, and therefore there is no corresponding continuity equation.)

By making use of the additivity of currents $j_{ln}(t)$ between the sites, we may also calculate the currents between subcomplexes that consist of a number of sites. Specifically, the current $J_{AB}(t)$ between a subcomplex A and a subcomplex B is given by

$$J_{AB}(t) = \sum_{l\in A}\sum_{n\in B} j_{ln}(t). \tag{9}$$

Similar to the currents between sites, when the current $J_{AB}(t) > 0$, there is a net flow from A to B, and when $J_{AB}(t) < 0$, there is a net flow from B to A.

We now analyze the energy transfer dynamics given by the quantum master equation Eqs. (1)–(5) of Sec. II in terms of these probability currents. We find that this quantum master equation leads to changes of the site populations in time given by

$$\begin{aligned}\partial_t \rho_{nn}(t) &= -i\langle n|[H,\rho(t)]|n\rangle + \langle n|\mathcal{L}^{\text{Dephas}}(\rho(t))|n\rangle \\ &\quad +\langle n|\mathcal{L}^{\text{Relax}}(\rho(t))|n\rangle \\ &= \sum_{l\neq n} 2H_{ln}\,\text{Im}(\rho_{ln}(t)) + \sum_{l\neq n} 0 \\ &\quad + \sum_{l\neq n} 2\,\text{Re}\big\{\langle l|\big(\rho(t)A^{\text{R}\,\dagger}_{ln}(t) - A^{\text{R}}_{nl}(t)\rho(t)\big)|n\rangle\big\}.\end{aligned} \tag{10}$$

Here $H_{ln} = \langle l|H|n\rangle$ are the intersite couplings, which may be assumed to be real. Comparing Eq. (10) with the continuity equation Eq. (8), shows that the population currents from sites l to sites n ($l \neq n$) are

$$j_{ln}(t) = j^{\text{Unitary}}_{ln}(t) + j^{\text{Dephas}}_{ln}(t) + j^{\text{Relax}}_{ln}(t), \tag{11}$$

with

$$\begin{aligned}j^{\text{Unitary}}_{ln}(t) &= 2H_{ln}\,\text{Im}[\rho_{ln}(t)], \\ j^{\text{Dephas}}_{ln}(t) &= 0, \\ j^{\text{Relax}}_{ln}(t) &= 2\,\text{Re}\left[\sum_k \rho_{lk}(t)A^{\text{R}\,*}_{ln,nk}(t) - A^{\text{R}}_{nl,lk}(t)\rho_{kn}(t)\right].\end{aligned} \tag{12}$$

The currents are seen to be a sum of three contributions, which we label by the corresponding terms in the quantum master equation: a unitary term, a dephasing term, and an electronic relaxation term. These terms can be expressed in terms of the coherences between the sites, $\rho_{ln}(t)$, and the populations of the sites, $\rho_{nn}(t)$. $A^{\text{R}}_{nl,lk}(t) = \langle l|A^{\text{R}}_{nl}(t)|k\rangle$ are the site-basis matrix elements of the time-dependent auxiliary operators $A^{\text{R}}_{nl}(t)$ describing relaxation between states n and l ($*$ denotes complex conjugation). Given a system density matrix $\rho(t)$ and the relaxation auxiliary operators $A^{\text{R}}_{nl}(t)$, one can then use Eq. (12) to calculate the currents between the sites at all times. We now discuss the three different contributions to the total current.

A. Unitary term

Equation (12) shows that the unitary contribution to the total current, $j^{\text{Unitary}}_{ln}(t)$, is caused *entirely* by the coherence between the sites, in particular by the imaginary components of this. This is an important result, since it shows that without coherence the unitary contribution to the spatial energy transfer would be zero. As might be expected, this contribution is proportional to the intersite couplings H_{ln}. While this unitary contribution does not explicitly depend on the diagonal elements of H, i.e., the energies of the sites, it does *implicitly* depend on the site energies through the time evolution of the coherence. The above result for the unitary contribution $j^{\text{Unitary}}_{ln}(t)$ is well known for closed quantum systems; see, e.g., Ref. [29].

An important property of this unitary contribution $j^{\text{Unitary}}_{ln}(t)$ is that, because the coherence $\rho_{ln}(t)$ is limited by the Cauchy-Schwarz inequality for the coherence and population of a density matrix $\rho(t)$,

$$|\rho_{ln}(t)|^2 \leqslant \rho_{ll}(t)\,\rho_{nn}(t), \tag{13}$$

the unitary contribution to the current is also bounded:

$$\begin{aligned}\left|j^{\text{Unitary}}_{ln}(t)\right| &= 2|H_{ln}\text{Im}[\rho_{ln}(t)]| \\ &\leqslant 2|H_{ln}|\sqrt{\rho_{ll}(t)\,\rho_{nn}(t) - \{\text{Re}[\rho_{ln}(t)]\}^2}.\end{aligned} \tag{14}$$

Thus, the larger the real component of the coherence between two sites, the more limited is the unitary current between these sites.

This analysis of the unitary contribution illustrates the important complementary roles that the imaginary and the real components of the coherence play in the spatial energy transfer. While the imaginary component of the coherence constitutes the actual transport current, the real component does nevertheless have a constraining effect on the energy transfer. Because of these two different roles, it can be useful to study the real and imaginary components of the coherence involved in energy transfer dynamics separately. In Sec. III G we do this explicitly for the special case of system-environment coupling in the Markovian limit.

B. Dephasing term

In Eq. (11), the dephasing term of the current is zero, regardless of the specific form of the dephasing, i.e., the specific behavior of the time-dependent auxiliary operators $A^{\text{D}}_n(t)$ that describe the non-Markovian influence of the coupling to the environment. (Here we have assumed that $\langle n|l\rangle = \delta_{nl}$, i.e., the states are orthonormal.) This finding is important, because it means that the dephasing does not influence the currents and hence the energy transfer explicitly. Thus, in a model that only includes unitary dynamics and non-Markovian dephasing, but no electronic relaxation between some or all of the sites—a model often applied [6,54,59]—the currents between the respective sites would be given entirely by the unitary contribution $j^{\text{Unitary}}_{ln}(t)$. Nevertheless, Eq. (4) shows that the dephasing term $\mathcal{L}^{\text{Dephas}}[\rho(t)]$ does act on the coherence between the sites, via the terms

$$\begin{aligned}\langle l|\mathcal{L}^{\text{Dephas}}(\rho(t))|n\rangle &= \langle l|\big[\rho(t)A^{\text{D}\,\dagger}_l(t) - \rho(t)A^{\text{D}\,\dagger}_n(t) \\ &\quad - A^{\text{D}}_l(t)\rho(t) + A^{\text{D}}_n(t)\rho(t)\big]|n\rangle\,(1-\delta_{ln}).\end{aligned} \tag{15}$$

Thus, the dephasing term can, e.g., cause the coherence to decay. As a consequence of this, the dephasing can indirectly influence the unitary contribution $j^{\text{Unitary}}_{ln}(t)$ to the current that is driven by the coherence, and thus implicitly influence the energy transport. Since the action of the dephasing terms on the coherence depends on the time-dependent auxiliary operators $A^{\text{D}}_n(t)$, the precise way in which coherence is influenced by these terms will depend on the details of the non-Markovian dynamics of the environment.

In the Markovian limit, however, the action of the dephasing terms on the coherence is simple. Here $A^{\text{D}}_n(t) \rightarrow \frac{1}{2}\gamma^{\text{D}}_n L^{\text{D}}_n$ [Eq. (6)] and the dephasing is described by Lindblad terms

$$\langle l|\mathcal{L}^{\text{Dephas}}_{\text{Lindbl}}[\rho(t)]|n\rangle = -\tfrac{1}{2}\big(\gamma^{\text{D}}_l + \gamma^{\text{D}}_n\big)\,\rho_{ln}(t)\,(1-\delta_{ln}). \tag{16}$$

These simply cause the coherences between the sites to decay on a time scale given by the coupling parameters γ^{D}_n. In the Markovian limit, dephasing will therefore diminish or inhibit the unitary contribution $j^{\text{Unitary}}_{ln}(t)$ that is driven by the coherence. It is well known that for dephasing fast compared to the other timescales of the dynamics, the energy transfer is inhibited (Quantum Zeno effect) [1].

C. Relaxation term

Equation (12) shows that the third term, $j_{ln}^{\mathrm{Relax}}(t)$, the contribution of electronic relaxation to the total current, depends on both the coherences and populations of the sites and on the time-dependent auxiliary operators. The contribution of this term to the total current can therefore have a complicated dependence on the interplay of electronic coherence and populations with the environment.

In the Markovian limit, the situation is again relatively simple. Inserting $A_{nl}^{\mathrm{R}}(t) \to \frac{1}{2}\gamma_{nl}^{\mathrm{R}} L_{nl}^{\mathrm{R}}$ [Eq. (7)] into the $j_{ln}^{\mathrm{Relax}}(t)$ term of Eq. (12), yields the Markovian relaxation contribution

$$j_{ln}^{\mathrm{Relax,Lindbl}}(t) = \gamma_{ln}^{\mathrm{R}} \rho_{ll}(t) - \gamma_{nl}^{\mathrm{R}} \rho_{nn}(t). \tag{17}$$

This contribution has the character of a purely classical rate equation (see, e.g., Ref. [60]), in which γ_{ln}^{R} specifies the rate of electronic relaxation transport from a state $|l\rangle$ to a state $|n\rangle$ and γ_{nl}^{R} the rate for the reverse process. This relaxation contribution to the excitation transfer relies entirely on the populations; coherence between the sites does not enter into this process. Since this contribution does not depend on coherence between the sites, it will not be destroyed by site dephasing. Such *Markovian* Lindblad terms for electronic relaxation and dissipation have been used together with non-Markovian dephasing terms in quantum master equations describing both energy transfer and trapping in pigment-protein systems [3,4,22,59].

D. Energy-transfer analysis in basis of system Hamiltonian eigenstates

For the above analysis we have considered the elements of the system density matrix in the basis of states $|n\rangle$ representing local excitations of the sites. Another basis of interest is the one given by the eigenstates of the system Hamiltonian, i.e., $H|k_\mu\rangle = E_\mu|k_\mu\rangle$. Using the unitary transformation between site and energy bases, $|n\rangle$ and $|k_\mu\rangle$, respectively, we have $\rho_{ln}(t) = \sum_{\mu\lambda} a_l^\mu a_n^{\lambda *} \widetilde{\rho}_{\mu\lambda}(t)$, where $\widetilde{\rho}_{\mu\lambda}(t) = \langle k_\mu|\rho(t)|k_\lambda\rangle$ and $a_l^\mu \equiv \langle l|\, k_\mu\rangle$. The unitary term of the population currents in Eq. (12) is then given by

$$j_{ln}^{\mathrm{Unitary}}(t) = 2H_{ln} \sum_{\mu,\lambda\neq\mu} a_l^\mu a_n^\lambda \,\mathrm{Im}[\widetilde{\rho}_{\mu\lambda}(t)], \quad l \neq n, \tag{18}$$

where we have assumed that the Hamiltonian H is real and symmetric so that its eigenvectors can be chosen to be real, and thus the coefficients a_l^μ are real. Equation (18) shows that in the energy eigenbasis $|k_\mu\rangle$ the energy transfer is entirely driven by the imaginary parts of the coherences, just as was found above in the site basis $|n\rangle$.

E. Quantifying the contribution of coherence to energy transfer

The above analysis has shown that in the absence of electronic relaxation, excitation transfer during a time interval Δt depends entirely on the coherence between the sites, given by the off-diagonal elements of the density matrix $\rho(t)$ in this time interval. According to Eq. (12), this constitutes the unitary contribution $j_{ln}^{\mathrm{Unitary}}(t)$ to the current. If this site coherence is zero, there will be no excitation transfer during this time interval.

We can quantify the contribution of coherence to the energy transfer, i.e., to the currents $j_{ln}(t)$, by writing the currents as a sum of the two contributions of the populations of the sites and the coherence between the sites,

$$j_{ln}[\rho(t)] = j_{ln}^{\mathrm{pop}}[\rho^{\mathrm{d}}(t)] + j_{ln}^{\mathrm{coher}}[\rho^{\mathrm{nd}}(t)]. \tag{19}$$

Here the first term contains the diagonal elements of the density matrix at time t in the site basis (populations) and the second term contains the off-diagonal elements (coherences), i.e., $\rho(t) = \rho^{\mathrm{d}}(t) + \rho^{\mathrm{nd}}(t)$. This partitioning is possible because the propagator $\mathcal{P}$ of the evolution equation Eq. (1) is linear in $\rho(t)$. The same partitioning can be applied to the changes $\partial_t \rho_{nn}(t)$ of the populations of the sites, which are just the sums of the currents to/from the sites [see Eq. (8)]:

$$\begin{aligned}\partial_t \rho_{nn}(t) &= \sum_{l\neq n} j_{ln}^{\mathrm{pop}}[\rho^{\mathrm{d}}(t)] + \sum_{l\neq n} j_{ln}^{\mathrm{coher}}[\rho^{\mathrm{nd}}(t)] \\ &= \langle n|\mathcal{P}[\rho^{\mathrm{d}}(t)]|n\rangle + \langle n|\mathcal{P}[\rho^{\mathrm{nd}}(t)]|n\rangle. \end{aligned} \tag{20}$$

Here the contributions of population and coherence can be readily calculated by (numerically) applying the propagator $\mathcal{P}$ of the evolution equation Eq. (1) to the diagonal and off-diagonal part of a given density matrix $\rho(t)$ at each point in time, respectively.

In the situation of non-Markovian dephasing combined with Markovian electronic relaxation and dissipation that was described above [see Eq. (17)], we have the simple partitioning

$$\begin{aligned} j_{ln}^{\mathrm{coher}}[\rho^{\mathrm{nd}}(t)] &= j_{ln}^{\mathrm{Unitary}}(t) \quad \text{and} \\ j_{ln}^{\mathrm{pop}}[\rho^{\mathrm{d}}(t)] &= j_{ln}^{\mathrm{Relax,Lindbl}}(t), \end{aligned} \tag{21}$$

since the unitary contribution contains only coherence, the contribution of the electronic relaxation contains only populations, and the dephasing contribution is zero.

The above analysis shows that in the absence of electronic relaxation, energy transfer requires coherence. We note that there are other dynamical models commonly applied to describe energy transfer in which coherence is not explicitly present, e.g., the (generalized) Förster method or other methods using classical master equations (rate equations) [9,61], yet the system Hamiltonian matrix elements H_{ln} do appear in the rate parameters, distinct from the relaxation rates. This is not a contradiction to the aforementioned result that coherence is essential for the occurrence of energy transfer (in the absence of transfer via electronic relaxation between the sites), because such classical rate equations can be seen as *effective* models derived from a general quantum master equation. When this reduction is done consistently, it is evident that such classical rate equations implicitly take coherence into account, even though no coherence terms appear explicitly in the classical rate equation. In such descriptions the key matrix elements H_{ln} appear as parameters in the rate coefficients for transport between sites. A thorough analysis of this reduction is given in Refs. [22,62]. For example, a classical rate equation containing conventional Förster rates for the excitation energy transfer is valid only within a restricted parameter regime where the electronic inter-site coupling is weak compared to the electron-vibration coupling, providing a limiting case of the general quantum master equation where the effect of the intersite electronic coupling H_{ln} may be incorporated by a perturbative calculation of a rate constant within the Golden Rule approximation. Since, as demonstrated above, in the quantum master equation model intersite coherence is necessary for energy transfer regardless of the parameter regime, it follows that an effective Förster model *implicitly* takes this coherence into account, even though no coherence terms appear explicitly in the Förster rate equation. We note that in the literature, Förster transfer is often termed "incoherent" (see, e.g., Refs. [21,63,64]) since it does not contain explicit coherence terms. However, this is somewhat misleading, since Förster transfer does implicitly take coherence within the site-to-site excitation transfer into account.

F. Energy-transfer pathways

The probability-current description is also very useful to identify the pathways of energy transfer in a network of sites and to reveal the relative weights, i.e., the relative importance, of different pathways. This can provide important insight into the design-function relationships of natural biological systems such as light-harvesting complexes, *inter alia*. To reveal the pathways, one can integrate the probability currents between the sites over a certain time interval of interest to obtain both the direction of transport and the net amount of excitation probability that has been transported via each pathway during this time period. Thus, the net amount of probability $\Delta P_{ln}(\Delta t)$ that has been transported between a site l and a site n during the time Δt can be calculated from

$$\Delta P_{ln}(\Delta t) = \int_{t_0}^{t_0+\Delta t} dt\; j_{ln}(t), \tag{22}$$

where the currents $j_{ln}(t)$ are calculated beforehand with Eqs. (11) and (12) from a given time-dependent density matrix $\rho(t)$ obtained from the quantum master equation. We note that this analysis may be made using any underlying dynamical model, provided that time dependence of the density matrix and probability currents are consistently calculated with the same model. This approach is used with a convolutionless non-Markovian master equation in a companion paper [4] to reveal the pathways of energy transport in the Photosystem II super-complex, a light-harvesting apparatus driving photosynthesis in higher plants. For illustration, the resulting transport pathways of Ref. [4] are shown in Fig. 1. These pathways are obtained by time-integrating the probability currents according to Eq. (22), where the probability currents $j_{ln}(t)$ are calculated from the time-dependent electronic density matrix of the sites $\rho(t)$ using the formalism of Eqs. (12) and (17) (see Ref. [4] for more details).

This diagram can help to understand the function of the individual pigments of Photosystem II and their arrangement in the super-complex. For instance, it can reveal which pigments play a crucial role in the long-range transport chain and which ones mainly serve as light absorbers, or, in case of the pigments in the reaction center (RC), which ones serve primarily to create the charge separation states that trap the excitation energy. The diagram identifies the pathways between antenna pigments (LHCII) and inner pigments (CP43, RC).

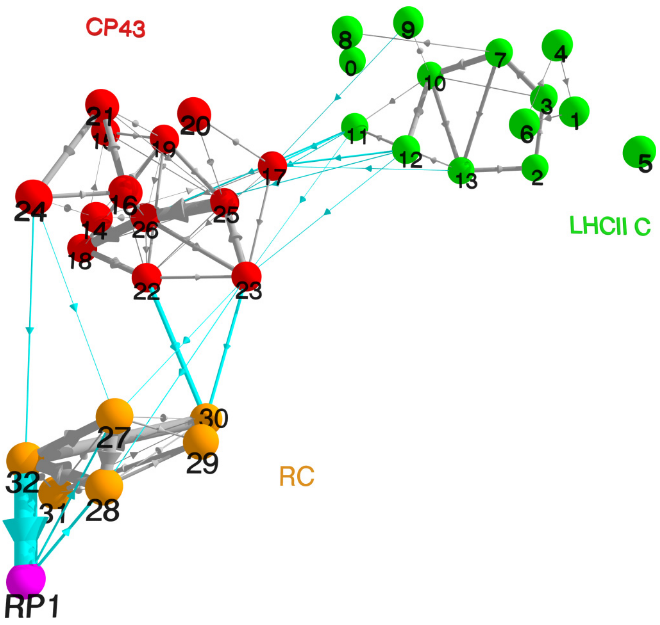

FIG. 1. Time-integrated excitation probability currents between the pigments in a Photosystem II super-complex (over a time period of 1 ns) reveal pathways of excitation transport, based on the numerical propagation of the electronic density matrix in Ref. [4] using a non-Markovian quantum master equation. Initially only pigments 7 and 10 are excited. The arrows show the directions and their thickness the relative magnitude of the integrated currents (see Ref. [4] for details of the calculation).

The arrows in the diagram show the directions and relative importance (magnitude of the integrated current) of the different pathways. From these pathways, it is apparent that there is a distributed network of transport channels rather than single dominant pathways. This observation holds true for the transport between the different complexes (LHCII, CP43, RC), as well as inside the complexes. There are multiple pathways from LHCII to CP43 and from CP43 to the RC. Within complexes, some of the pathways transport a large amount of excitation energy.

The intracomplex transport dynamics also appear to create "loop currents," where the excitation is transported in a loop between sites. For instance, in the reaction center there is a relatively strong loop current from pigment 32 to 27 to 28, and back to 32 (see diagram).

Furthermore, the diagram shows that the transport to and inside the reaction center appears to be mainly via the two pigments 30 and 32, while the other pigments do not contribute much to the net transport to the first state of the charge separation trap (labeled RP1 in the diagram). Even though pigments 27 and 28 are involved in the strong loop current, their contribution to the net current to RP1 seems negligible.

In Ref. [4], we tested this interpretation of the transport in the RC obtained from the diagram by running a simulation where excitation transport is allowed only to the pigments 30 and 32 and transport to the other RC pigments is blocked. It was found that in this restricted simulation the same amount of excitation is transported to the trapping state as before. Thus, it appears that pigments 30 and 32 are crucial for the excitation transport to the trapping states, whereas the other RC pigments seem to be mainly needed for the charge separation (trapping).

This example demonstrates that probability-current diagrams as the one presented in Fig. 1 provide a powerful tool for the analysis of pathways and design-function relationships in transport in quantum systems.

G. Dynamics for Markovian system-environment coupling

When the memory time of the environment is short relative to the characteristic time scale of the system dynamics, the coupling to the environment is Markovian and the energy transfer dynamics are particularly simple, allowing useful analytic insight to be obtained. As described below, we find that in this situation only three quantities are sufficient to fully characterize the dynamics, namely, the probability current between the sites, the real component of the coherence between the sites, and the imaginary component of the coherence.

In the Markovian limit, the quantum master equation of Sec. II reduces to a Lindblad equation, with dephasing and relaxation terms given by Eqs. (6) and (7). From Eqs. (11), (12), and (17), the total population current from site l to site n is

$$\begin{aligned} j_{ln}^{\mathrm{Lindbl}}(t) &= -\partial_t\, d_{ln}(t) = j_{ln}^{\mathrm{Unitary}}(t) + j_{ln}^{\mathrm{Relax,Lindbl}}(t) \\ &= 2V_{ln}\,\mathrm{Im}(\rho_{ln}(t)) + \left[\gamma_{ln}^{\mathrm{R}}\rho_{ll}(t) - \gamma_{nl}^{\mathrm{R}}\rho_{nn}(t)\right], \end{aligned} \tag{23}$$

where $d_{ln}(t) \equiv [\rho_{ll}(t) - \rho_{nn}(t)]/2$ denotes the population difference of sites l and n, and $V_{ln} = H_{ln}$ the intersite electronic coupling. As before, the unitary contribution to the population current is driven by the imaginary component $\mathrm{Im}[\rho_{ln}(t)]$ of the coherence between the sites and the relaxation contribution depends on the population $\rho_{nn}(t)$ of the sites.

Considering the evolution equations for the imaginary and real components of the coherence separately, using the Lindblad dynamics, Eq. (1), with Eqs. (6) and (7) and Eqs. (4) and (5), we obtain for the imaginary component of the coherence

$$\begin{aligned} \partial_t\,\mathrm{Im}[\rho_{ln}(t)] &= 2V_{ln}\,d_{ln}(t) - \Delta_{ln}\,\mathrm{Re}[\rho_{ln}(t)] - \Gamma_{ln}\,\mathrm{Im}[\rho_{ln}(t)] \\ &\quad + \sum_{k\neq l,n}\{V_{kn}\,\mathrm{Re}[\rho_{lk}(t)] - V_{lk}\,\mathrm{Re}[\rho_{kn}(t)]\}, \end{aligned} \tag{24}$$

where $\Delta_{ln} \equiv (H_{ll} - H_{nn})$ is the energy gap between the transition energies of sites l and n. The dephasing and electronic relaxation rates have been combined here into a single decay rate $\Gamma_{ln} \equiv (\gamma_l^{\mathrm{D}} + \gamma_n^{\mathrm{D}} + \sum_{k\neq l}\gamma_{lk}^{\mathrm{R}} + \sum_{k\neq n}\gamma_{nk}^{\mathrm{R}})/2$. For the real component of the coherence, we find

$$\begin{aligned} \partial_t\,\mathrm{Re}[\rho_{ln}(t)] &= \Delta_{ln}\,\mathrm{Im}[\rho_{ln}(t)] - \Gamma_{ln}\,\mathrm{Re}[\rho_{ln}(t)] \\ &\quad - \sum_{k\neq l,n}\{V_{kn}\,\mathrm{Im}[\rho_{lk}(t)] - V_{lk}\,\mathrm{Im}[\rho_{kn}(t)]\}. \end{aligned} \tag{25}$$

The three coupled Eqs. (23)–(25) completely describe the energy transfer dynamics. Since the structure of these equations is relatively simple, some qualitative observations can be made directly from analysis of their forms.

First, we note that the imaginary component of the coherence creates population transport via the first term in Eq. (23), as discussed above. The population transport in turn couples back into the imaginary component of the coherence via the population difference $d_{ln}(t)$ in the first term in Eq. (24). In contrast, the real component of the coherence [Eq. (25)] is not directly coupled to the population transport. Nevertheless, this does indirectly influence the population transport, because it is coupled to the imaginary component of the coherence via both the first and last terms in Eq. (25) and the second and last terms in Eq. (24). These terms coupling the real and imaginary components of the coherence can be divided into two distinct contributions.

(i) Terms depending on the *local* coherence, i.e., the coherence between two sites l and n that affect the population current between the same two sites [second term in Eq. (24) and first term in Eq. (25)]. These terms scale with the energy gaps Δ_{ln} between sites.

(ii) Terms that account for the *nonlocal* influence of the coherence stemming from the coupling to other sites [last terms of Eqs. (24) and (25), respectively]. These terms scale with the electronic intersite couplings V_{kn}.

We note further that the influence of the energy gaps Δ_{ln} on the population current depends on the magnitude of the real component of the coherence since it appears only as a factor in the $\mathrm{Re}[\rho_{ln}(t)]$ term in Eq. (24).

The Markovian dephasing and relaxation leads to a simple decay term for both the imaginary component of the coherence, Eq. (24), and the real component of the coherence, Eq. (25), that is characterized by a single decay time scale which is given by the Γ_{ln}, the sum of dephasing and relaxation rates.

Finally, it is of interest to consider the application of this analysis to the smallest possible coupled site system, namely to energy transfer between the two sites in a molecular dimer. A dimer will possess only local coherence terms but no nonlocal coherence terms [$k \neq l,n$ in Eqs. (24) and (25)]. This leads to a reduction of possible coherence effects, e.g., no long distance transfer and similarly no transfer from a given site to multiple other sites. In this situation the reduction of possible coherence effects leads to significantly simpler dynamics. Furthermore, for the commonly studied example of a homodimer, i.e., $\Delta_{1,2} = 0$, Eq. (25) would be completely decoupled from the other two equations and the real part of the coherence decays with the decay rate given by $\Gamma_{1,2}$.

IV. CONCLUSIONS

In this paper we have introduced an analysis of electronic excitation energy transport using excitation-probability currents. While the analysis is general and independent of basis, our discussion is set in terms of a specific physical focus on spatial energy transport through systems of coupled sites and therefore employs a site basis. We applied the analysis to an open quantum system model for energy transport in which the dynamics are described by a non-Markovian quantum master equation that contains both terms representing unitary dynamics and dephasing and relaxation. We illustrated the analysis for electronic energy transport in systems such as molecular aggregates and biological pigment-protein complexes, for which the electronic degrees of freedom are typically coupled to a vibrational environment and the resulting dephasing and relaxation play an important role. We showed that the probability-current analysis gives instructive insights into key features of the transport, allowing a clear identification and quantification of the contributions of unitary dynamics, coherence, dephasing, and electronic relaxation and dissipation to the transport.

The probability currents representing the energy transport are found to be given by a sum of unitary, dephasing, and relaxation contributions. Each of these have simple forms and can be readily calculated from a given time-dependent electronic density matrix of the system, obtained, e.g., from a numerical simulation of the quantum master equation. An important result of the probability-current analysis is that the unitary contribution to the current is caused entirely by coherence between the sites, i.e., the off-diagonal elements of the electronic system density matrix in the site basis, and has no contribution from the population of the sites (diagonal elements of the density matrix). This means that if there is no coherence between the sites, then the unitary contribution to the current will be zero. It is also noteworthy that only the *imaginary* component of the coherence is involved in the unitary current—not the real component. The same holds for the unitary contribution to the current in the energy eigenstate basis of the system Hamiltonian, i.e., only the imaginary part of the coherence contributes, neither the real part of the coherence nor the energy eigenstate population terms contribute. The analysis shows that it is therefore useful to consider imaginary and real components of the coherence separately when studying energy transport dynamics.

Another key finding is that the contribution of the dephasing term to the currents is always zero, regardless of specific properties of the non-Markovian environment, such as the form of the environment spectral density that describes the strength of the coupling between the electronic excitation and each vibrational mode of the environment. This means that in a model containing only unitary dynamics and non-Markovian dephasing—a commonly used model for energy transfer—the only contribution to the overall energy transfer comes from the unitary contribution to the current and thus from the coherence between the sites. However, even though the dephasing does not contribute *explicitly* to the currents, it is found to affect the coherence that constitutes the unitary contribution to the currents and thereby influence the energy transport *implicitly*. If dephasing is strong, it can completely suppress the intersite coherence and thus remove the unitary contribution to the transport currents (this is the well-known Quantum Zeno effect; see, e.g., Ref. [1]), so that the current derives only from relaxation contributions. In this context, it is important to note that a non-Markovian dephasing term in the quantum master equation can also induce relaxation within the vibrational manifold of the environment [55].

The contribution of the electronic relaxation to the current was seen to be more complicated than the other contributions. In general, the relaxation contribution can depend explicitly on both coherence and population terms in the electronic density matrix, as well as on the non-Markovian dynamics of the environment. In the Markov limit, however, when the memory time of the environment is short compared to the other time scales of the dynamics, the electronic relaxation contribution to the current was found to reduce to a very simple classical rate equation term that depends on the populations of the sites and on the corresponding relaxation rates, but not on the coherence. Note that performing the Markov limit with respect to the electronic relaxation still allows the incorporation of *non-Markovian* dephasing—and hence of *vibrational* relaxation as noted above—caused by a *non-Markovian* environment [4,55,59].

Such nonunitary electronic relaxation is often used to model radiative or nonradiative decay of electronic excitation or trapping of excitation [3,4,22,59]. The transport deriving from this Markovian relaxation is a very distinct process from the unitary, coherent excitation transport mechanisms between sites. The latter derives only from the Hamiltonian terms, e.g., from resonant transition dipole-dipole interaction between molecules [4,6,14]. Since the third possible current contribution (dephasing) does not contribute explicitly to the currents, the probability-current analysis shows that even in the presence of electronic relaxation, the actual excitation transport currents between sites may depend entirely on the coherence between the sites and the Hamiltonian coupling appearing in the unitary contribution. Consequently, if the coherence is zero at a time t, there will be no current, i.e., no energy transport, at this time t and the overall energy transport is dependent on the presence of sustained coherence in the system.

The finding that the energy transport can be entirely determined by the coherence is one of the key insights provided by this probability-current approach. As discussed in the text, this reliance of the transport on coherence does not contradict the fact that the (overall) transport dynamics can often be described reasonably well by classical master equations, such as the rate equations deriving from Förster and modified Redfield models that contain only population terms and no explicit coherence terms, in contrast to the quantum master equations that contain the coherence as off-diagonal elements of the density matrix [4,9,22,61]. This is because such classical rate equations can be interpreted as *effective* descriptions of a full quantum description, in which the effective rate equation *implicitly* takes coherence into account by virtue of derived, effective rate parameters, even though the coherence does not explicitly appear in the equation [22].

Another very useful aspect of the description of energy transport by means of probability currents is that this analysis can reveal the pathways of the transport and their relative importance in a large network of sites. This issue can be addressed by integrating the probability currents between sites over a certain time interval of interest, to show the net amount of excitation probability transported via each pathway and the direction of the transport within this time period. In a concrete example of application, we demonstrated that such a probability-current analysis allows revelation of long-range energy-transport pathways within and between different subcomplexes in the Photosystem II super-complex that drives photosynthesis in higher plants, leading to new insights into the design-function relationship of this photosynthetic apparatus. Details of the application to Photosystem II are given in a companion paper [4].

The interplay between the probability current and the imaginary and real components of the coherence was specifically analyzed for the case of a Markovian environment where the evolution of population and coherence is described by a Lindblad quantum master equation. Here a set of three coupled equations are found to completely describe the energy transfer dynamics, allowing a qualitative analysis of the mutual influence that these quantities have on each other and how they are affected by dephasing, relaxation, and localization due to energy gaps between the sites. These are the effects that play a crucial role in modeling and understanding excitation energy transport in molecular aggregates and pigment-protein complexes [1–3].

Finally, we point out that while the probability-current analysis presented in this paper has focused on a quantum master equation description of electronic energy transfer, the procedure to identify and quantify contributions to probability currents that stem from the different terms of an evolution equation is far more general and can be applied to a broad range of dynamical models and evolution equations. Indeed the approach is not restricted to energy transfer and can in principle be applied to any evolution equation that describes the time-dependence of probabilities or other conserved quantities, including classical master equations that contain probabilities and rates, such as those derived from a generalized Förster or modified Redfield models [9,61], as well as other quantum evolution equations.

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[1] P. Rebentrost, M. Mohseni, I. Kassal, S. Lloyd, and A. Aspuru-Guzik, Environment-assisted quantum transport, New J. Phys. **11**, 033003 (2009).

[2] A. W. Chin, A. Datta, F. Caruso, S. F. Huelga, and M. B. Plenio, Noise-assisted energy transfer in quantum networks and light-harvesting complexes, New J. Phys. **12**, 065002 (2010).

[3] F. Caruso, A. W. Chin, A. Datta, S. F. Huelga, and M. B. Plenio, Highly efficient energy excitation transfer in light-harvesting complexes: The fundamental role of noise-assisted transport, J. Chem. Phys. **131**, 105106 (2009).

[4] J. J. J. Roden, D. I. G. Bennett, and K. B. Whaley, Long-range coherent energy transport in Photosystem II, arXiv:1501.06674.

[5] T. Brixner, J. Stenger, H. M. Vaswani, M. Cho, R. E. Blankenship, and G. R. Fleming, Two-dimensional spectroscopy of electronic couplings in photosynthesis, Nature **434**, 625 (2005).

[6] A. Ishizaki and G. R. Fleming, Theoretical examination of quantum coherence in a photosynthetic system at physiological temperature, Proc. Natl. Acad. Sci. USA **106**, 17255 (2009).

[7] J. Moix, J. Wu, P. Huo, D. Coker, and J. Cao, Efficient energy transfer in light-harvesting systems, III: The influence of the eighth bacteriochlorophyll on the dynamics and efficiency in fmo, J. Phys. Chem. Lett. **2**, 3045 (2011).

[8] Y. Shibata, S. Nishi, K. Kawakami, J.-R. Shen, and T. Renger, Photosystem II does not possess a simple excitation energy funnel: Time-resolved fluorescence spectroscopy meets theory, J. Am. Chem. Soc. **135**, 6903 (2013).

[9] D. I. G. Bennett, K. Amarnath, and G. R. Fleming, A structure-based model of energy transfer reveals the principles of light harvesting in photosystem II supercomplexes, J. Am. Chem. Soc. **135**, 9164 (2013).

[10] H. Haken and P. Reineker, The coupled coherent and incoherent motion of excitons and its influence on the line shape of optical absorption, Z. Physik **249**, 253 (1972).

[11] H. Haken and G. Strobl, An exactly solvable model for coherent and incoherent exciton motion, Z. Physik **262**, 135 (1973).

[12] R. Silbey, Electronic energy transfer in molecular crystals, Annu. Rev. Phys. Chem. **27**, 203 (1976).

[13] V. M. Kenkre, *The Master Equation Approach: Coherence, Energy Transfer, Annihilation, and Relaxation* (Springer, Berlin, 1982).

[14] V. May and O. Kühn, *Charge and Energy Transfer Dynamics in Molecular Systems* (John Wiley & Sons, New York, 2008).

[15] A. Eisfeld, Phase directed excitonic transport and its limitations due to environmental influence, Chem. Phys. **379**, 33 (2011).

[16] S. Hoyer, A. Ishizaki, and K. B. Whaley, Spatial propagation of excitonic coherence enables ratcheted energy transfer, Phys. Rev. E **86**, 041911 (2012).

[17] J. M. Moix, M. Khasin, and J. Cao, Coherent quantum transport in disordered systems: I. The influence of dephasing on the transport properties and absorption spectra on one-dimensional systems, New J. Phys. **15**, 085010 (2013).

[18] A. Eisfeld and J. S. Briggs, Classical master equation for excitonic transport under the influence of an environment, Phys. Rev. E **85**, 046118 (2012).

[19] G. S. Engel, T. R. Calhoun, E. L. Read, T.-K. Ahn, T. Mančal, Y.-C. Cheng, R. E. Blankenship, and G. R. Fleming, Evidence for wavelike energy transfer through quantum coherence in photosynthetic systems, Nature **446**, 782 (2007).

[20] E. Romero, R. Augulis, V. I. Novoderezhkin, M. Ferretti, J. Thieme, D. Zigmantas, and R. Van Grondelle, Quantum coherence in photosynthesis for efficient solar-energy conversion, Nat. Phys. **10**, 676 (2014).

[21] I. Kassal, J. Yuen-Zhou, and S. Rahimi-Keshari, Does coherence enhance transport in photosynthesis? J. Phys. Chem. Lett. **4**, 362 (2013).

[22] S. Jesenko and M. Žnidarič, Excitation energy transfer efficiency: Equivalence of transient and stationary setting and the absence of non-markovian effects, J. Chem. Phys. **138**, 174103 (2013).

[23] A. Chenu and G. D. Scholes, Coherence in energy transfer and photosynthesis, Annu. Rev. Phys. Chem. **66**, 69 (2015).

[24] A. Olaya-Castro, C. F. Lee, F. F. Olsen, and N. F. Johnson, Efficiency of energy transfer in a light-harvesting system under quantum coherence, Phys. Rev. B **78**, 085115 (2008).

[25] C. Kreisbeck and T. Kramer, Long-lived electronic coherence in dissipative exciton dynamics of light-harvesting complexes, J. Phys. Chem. Lett. **3**, 2828 (2012).

[26] A. W. Chin, J. Prior, R. Rosenbach, F. Caycedo-Soler, S. F. Huelga, and M. B. Plenio, The role of nonequilibrium vibrational structures in electronic coherence and recoherence in pigment-protein complexes, Nat. Phys. **9**, 113 (2013).

[27] J. S. Briggs and A. Eisfeld, Equivalence of quantum and classical coherence in electronic energy transfer, Phys. Rev. E **83**, 051911 (2011).

[28] G. D. Scholes, T. Mirkovic, D. B. Turner, F. Fassioli, and A. Buchleitner, Solar light harvesting by energy transfer: From ecology to coherence, Energy Environ. Sci. **5**, 9374 (2012).

[29] Erasmo A. de Andrada e Silva, Probability current in the tight-binding model, Am. J. Phys. **60**, 753 (1992).

[30] D. H. Dunlap, K. Kundu, and P. Phillips, Anderson localization from a generalized master equation, J. Phys.: Condens. Matter **1**, 7883 (1989).

[31] D. Izzo, D. H. Dunlap, and P. Phillips, Calculation of the temperature-dependent mobility transition for small-polaron hopping in one dimension, Phys. Rev. B **44**, 85 (1991).

[32] A. A. Stuchebrukhov, Tunneling currents in electron transfer reactions in proteins, J. Chem. Phys. **104**, 8424 (1996).

[33] S. Jang, S. Hoyer, G. Fleming, and K. B. Whaley, Generalized Master Equation with Non-Markovian Multichromophoric Förster Resonance Energy Transfer for Modular Exciton Densities, Phys. Rev. Lett. **113**, 188102 (2014).

[34] A. Ishizaki and G. R. Fleming, On the interpretation of quantum coherent beats observed in two-dimensional electronic spectra of photosynthetic light harvesting complexes, J. Phys. Chem. B **115**, 6227 (2011).

[35] V. Novoderezhkin, A. Marin, and R. van Grondelle, Intra- and inter-monomeric transfers in the light harvesting LHCII complex: The Redfield-Förster picture, Phys. Chem. Chem. Phys. **13**, 17093 (2011).

[36] D. P. S. McCutcheon and A. Nazir, Coherent and incoherent dynamics in excitonic energy transfer: Correlated fluctuations and off-resonance effects, Phys. Rev. B **83**, 165101 (2011).

[37] A. Kolli, E. J. O'Reilly, G. D. Scholes, and A. Olaya-Castro, The fundamental role of quantized vibrations in coherent light harvesting by cryptophyte algae, J. Chem. Phys. **137**, 174109 (2012).

[38] G. Ritschel, J. Roden, W. T. Strunz, A. Aspuru-Guzik, and A. Eisfeld, Absence of quantum oscillations and dependence on site energies in electronic excitation transfer in the Fenna-Matthews-Olson trimer, J. Phys. Chem. Lett. **2**, 2912 (2011).

[39] Th. Holstein, Studies of polaron motion: Part I. The molecular-crystal model, Ann. Phys. **8**, 325 (1959).

[40] O.-S. Barišić, Calculation of excited polaron states in the holstein model, Phys. Rev. B **69**, 064302 (2004).

[41] A. H. Romero, D. W. Brown, and K. Lindenberg, Converging toward a practical solution of the holstein molecular crystal model, J. Chem. Phys. **109**, 6540 (1998).

[42] Y.-C. Cheng and G. R. Fleming, Dynamics of light harvesting in photosynthesis, Phys. Chem. **60**, 241 (2009).

[43] F. Herrera and R. V. Krems, Tunable holstein model with cold polar molecules, Phys. Rev. A **84**, 051401 (2011).

[44] J. Singh, E. R. Bittner, D. Beljonne, and G. D. Scholes, Fluorescence depolarization in poly [2-methoxy-5-((2-ethylhexyl) oxy)-1, 4-phenylenevinylene]: Sites versus eigenstates hopping, J. Chem. Phys. **131**, 194905 (2009).

[45] F. Petruccione and H.-P. Breuer, *The Theory of Open Quantum Systems* (Oxford University Press, Oxford, 2002).

[46] A. Damjanović, I. Kosztin, U. Kleinekathöfer, and K. Schulten, Excitons in a photosynthetic light-harvesting system: A combined molecular dynamics, quantum chemistry, and polaron model study, Phys. Rev. E **65**, 031919 (2002).

[47] V. I. Novoderezhkin and R. van Grondelle, Physical origins and models of energy transfer in photosynthetic light-harvesting, Phys. Chem. Chem. Phys. **12**, 7352 (2010).

[48] A. W. Chin, S. F. Huelga, and M. B. Plenio, Coherence and decoherence in biological systems: Principles of noise-assisted transport and the origin of long-lived coherences, Philos. Trans. R. Soc., A **370**, 3638 (2012).

[49] C. Kreisbeck, T. Kramer, and A. Aspuru-Guzik, Scalable high-performance algorithm for the simulation of exciton dynamics. Application to the light-harvesting complex II in the presence of resonant vibrational modes, J. Chem. Theor. Comput. **10**, 4045 (2014).

[50] M. Tokuyama and H. Mori, Statistical-mechanical theory of random frequency modulations and generalized brownian motions, Prog. Theor. Phys. **55**, 411 (1976).

[51] F. Shibata, Y. Takahashi, and N. Hashitsume, A generalized stochastic liouville equation. Non-Markovian versus memoryless master equations, J. Stat. Phys. **17**, 171 (1977).

[52] H.-P. Breuer, B. Kappler, and F. Petruccione, Stochastic wave-function method for non-Markovian quantum master equations, Phys. Rev. A **59**, 1633 (1999).

[53] W. T. Strunz and T. Yu, Convolutionless non-Markovian master equations and quantum trajectories: Brownian motion, Phys. Rev. A **69**, 052115 (2004).

[54] G. Ritschel, J. Roden, W. T. Strunz, and A. Eisfeld, An efficient method to calculate excitation energy transfer in light-harvesting systems: Application to the Fenna-Matthews-Olson complex, New J. Phys. **13**, 113034 (2011).

[55] J. Roden, W. T. Strunz, K. B. Whaley, and A. Eisfeld, Accounting for intramolecular vibrational modes in open quantum system description of molecular systems, J. Chem. Phys. **137**, 204110 (2012).

[56] D. Ahn, Time-convolutionless reduced-density-operator theory of an arbitrary driven system coupled to a stochastic reservoir: Quantum kinetic equations for semiconductors, Phys. Rev. B **50**, 8310 (1994).

[57] G. Szabó, T. Tomé, and I. Borsos, Probability currents and entropy production in nonequilibrium lattice systems, Phys. Rev. E **82**, 011105 (2010).

[58] P. Nalbach, D. Braun, and M. Thorwart, Exciton transfer dynamics and quantumness of energy transfer in the Fenna-Matthews-Olson complex, Phys. Rev. E **84**, 041926 (2011).

[59] C. Kreisbeck, T. Kramer, M. Rodríguez, and B. Hein, High-performance solution of hierarchical equations of motion for studying energy transfer in light-harvesting complexes, J. Chem. Theor. Comput. **7**, 2166 (2011).

[60] R. K. P. Zia and B. Schmittmann, Towards a classification scheme for nonequilibrium steady states, Phys. Procedia **7**, 112 (2010).

[61] G. Raszewski and T. Renger, Light harvesting in photosystem II core complexes is limited by the transfer to the trap: Can the core complex turn into a photoprotective mode? J. Am. Chem. Soc. **130**, 4431 (2008).

[62] S. Jesenko and M. Žnidarič, Excitation energy transfer rates: Comparison of approximate methods to the exact solution, arXiv:1405.4156.

[63] D. M. Wilkins and N. S. Dattani, Why quantum coherence is not important in the Fenna-Matthews-Olsen complex, J. Chem. Theor. Comput. **11**, 3411 (2015).

[64] M. Chachisvilis, O. Kühn, T. Pullerits, and V. Sundström, Excitons in photosynthetic purple bacteria: Wavelike motion or incoherent hopping? J. Phys. Chem. B **101**, 7275 (1997).