Exciton-Phonon Information Flow in the Energy Transfer Process of Photosynthetic Complexes

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Exciton-phonon information flow in the energy transfer process of photosynthetic complexes

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Non-Markovian and non-equilibrium phonon effects are believed to be key ingredients in the energy transfer in photosynthetic complexes, especially in complexes which exhibit a regime of intermediate exciton-phonon coupling. In this work, we harness a recently developed measure for non-Markovianity to elucidate the information flow between electronic and vibrational degrees of freedom. We study the measure in the hierarchical equation of motion approach which captures strong system-bath coupling effects and non-equilibrium molecular reorganization. We find that, for a model dimer system and the Fenna-Matthews-Olson complex, non-Markovianity is significant under realistic physiological conditions. A first step towards experimental quantification is provided by the study of four-wave mixing initial states.

The initial step in photosynthesis involves highly efficient excitonic transport of the energy captured from photons to a reaction center [1]. In most higher plants and other organisms such as green sulphur and purple bacteria this process occurs in light-harvesting complexes which are electronically coupled chlorophyll molecules embedded in a solvent and a protein environment [2]. Several recent experiments show that excitonic coherence can persist for several hundreds of femtoseconds even at physiological temperature [3–6]. These experiments suggest the hypothesis that quantum coherence may be biologically relevant for photosynthesis. The results have motivated a sizeable amount of recent theoretical work regarding the reasons for the long-lived coherences and their role to the function. It was shown that the transport efficiency is enhanced by the interplay of the excitonic dynamics with the vibrational environment [7–11]. Employing entanglement measures, defined in the site basis, can lead to further insights [12,13].

The challenging regime of intermediate coupling of the electronic to the vibrational degrees of freedom motivates the study of sophisticated master equations with non-Markovian effects. Several approaches have been taken, ranging from a polaron transformation [15], quantum state diffusion [16], non-Markovian quantum jumps [17,18], quantum path integrals (QUAPI) [19], to density matrix renormalization group (DMRG) [20]. After photoexcitation, the nuclear coordinates of a molecule will relax to new equilibrium positions, a phenomenon that is borne out by the time-dependent Stokes shift, that is the frequency shift between absorption and emission spectra. Redfield theory assumes that the phonon bath is always in thermal equilibrium and thus cannot capture this effect [21]. Ishizaki and Fleming employed the hierarchical equation of motion (HEOM) approach [22,23], which interpolates between the usual weak and strong (singular) exciton-phonon coupling limits and takes into account non-equilibrium molecular reorganization effects.

In this work, we study the non-Markovianity of the exciton transfer process by means of numerical simulation. Quantum mechanical time evolution under decoherence leads to transfer of information encoded in the electronic excited state to the vibrational degrees of freedom. In this context, non-Markovianity can be characterized as the return of information to the electronic degrees of freedom. To quantify this information flow, we employ the state-of-the art master equation approach by Ishizaki and Fleming and a newly developed measure for non-Markovianity. The central question we will answer is how much information is exchanged between excitonic and phononic degrees of freedom in that process and, specifically, how much information returns from the phonons to the exciton. Additionally, we provide a step towards the experimental characterization of this effect by investigating the preparation of optimal initial states.

Measure for non-Markovianity—A recent area of research is the study of measures to characterize non-Markovianity [24,25]. We utilize the readily applicable measure developed by Breuer and co-workers [25]. It is based on the quantum state trace distance:

$$D (\rho_1 (t), \rho_2 (t)) = \frac{1}{2} \text{Tr} |\rho_1 (t) - \rho_2 (t)\rangle\langle 1 \rangle,$$

where $|A| = \sqrt{A^\dagger A}$. This measure quantifies the distinguishability of two quantum states $\rho_1$ and $\rho_2$. For a completely positive trace-preserving map $E$ the trace distance is contractive, i.e. $D (E (\rho_1), E (\rho_2)) \leq D (\rho_1, \rho_2)$ [28]. Time intervals in which $D$ increases indicate non-Markovian information flow [25], in our case from the vibrational degrees of freedom back to the electronic degrees of freedom. In terms of the slope of $D$, i.e. $\sigma (\rho_1 (t), \rho_2 (t)) = \frac{d}{dt} D (\rho_1 (t), \rho_2 (t))$, this implies that $\sigma > 0$ for these time intervals. Formally, a measure for non-Markovianity is defined by the following [25]:

$$\text{NM-ity} = \max_{\rho_1 (0), \rho_2 (0)} \int_0^\infty dt \alpha (\sigma (t)) \sigma (\rho_1 (t), \rho_2 (t)).$$

Here, $\alpha (x > 0) = 1 (\alpha (x < 0) = 0)$, to only monitor an increasing trace distance i.e. information backflow. The optimization of the initial states in Eq. (2) obtains the maximally possible non-Markovianity of a particular quantum evolution. In the case of photosynthetic energy transfer, initial states are given by the particular physical situation and lead to smaller values for the non-Markovianity. We use both physical and optimized initial states in this work.

Hierarchy equation of motion—The Hamiltonian describing a single exciton in a complex with $N$ molecules is given
by:
\[ H_e = \sum_{m} (\epsilon_m + \lambda)|m\rangle\langle m| + \sum_{m<n} J_{mn} \left( |m\rangle\langle n| + |n\rangle\langle m| \right), \]
where the site energies \( \epsilon_m \), and couplings \( J_{mn} \) are obtained from detailed quantum chemistry studies and/or fitting of experimental data. The set of states \( |m\rangle \) denotes the site basis. The reorganization energy \( \lambda \) is the energy difference of the non-equilibrium phonon state after Franck-Condon excitation and the equilibrium phonon state and is assumed to be the same for each site. The superoperator corresponding to \( H_e \) is \( \mathcal{L}_e \rho = [H_e, \rho] \). The Hamiltonian for the phonon environment is \( H_{ph} = \sum_i \hbar \omega_i \left( p_i^2 + q_i^2 \right) \), where \( \omega_i \), \( p_i \), and \( q_i \) are the frequency, dimensionless momentum and position operators of the phonon mode \( i \). The coupling of the electronic degrees of freedom to the phonons is given by the Hamiltonian \( H_{ex-ph} = \sum_m V_m \left( \sum_i g_i q_i \right) \rho_m \), with \( V_m = |m\rangle\langle m| \) and where we assume that site-energy fluctuations dominate, the bath degrees of freedom at each site are uncorrelated, and the coupling constants to the respective modes are given by the constants \( g_i \). The spectral density, which describes the coupling strength of exciton to particular phonon modes, is given by \( J(\omega) = 2\lambda \gamma / (\omega^2 + \gamma^2) \). Perhaps the most relevant parameter, the bath dissipation rate \( \gamma \), is related to the bath correlation time by \( \tau_c = 1/\gamma \). The open systems dynamics of the exciton is described by an equation of motion for the reduced excitonic density matrix \( \rho \). It can be obtained by tracing out the less relevant phonon degrees of freedom and utilizing Wick’s theorem for the Gaussian fluctuations. The resulting non-perturbative equation of motion can be expressed as a hierarchy of system and auxiliary density operators (ADOs):

\[
\frac{\partial}{\partial t} \sigma^n(t) = - \left( i\mathcal{L}_e + \sum_i n_i \gamma \right) \sigma^n(t) + \sum_i \phi_i \sigma^{n+1}(t) + \sum_i n_i \theta_i \sigma^{n-1}(t).
\]

The system density matrix is the first member of the hierarchy \( \rho(t) = \sigma^0(t) \). The other members of the hierarchy are arranged in tiers and indexed by \( n = (n_1, ..., n_N) \), with the notation \( n_{j=1} = (n_1, ..., n_j \pm 1, ..., n_N) \). The superoperators in the high temperature regime \( \hbar \gamma \beta < 1 \) are \( \phi_i \sigma^n = i[V_i, \sigma^n] \) and \( \theta_i \sigma^n = i(2\lambda/\beta h^2[V_i, \sigma^n] - i\lambda/\hbar \{V_i, \sigma^n\}) \) act on system and ADOs, where \( \{,\} \) is the anticommutator. Initially, all the hierarchy members are zero, which corresponds to the electronic ground state phonon equilibrium configuration. For numerical propagation, the hierarchy is truncated based on the criterion \( \sum_i n_i \gg \frac{1}{\gamma} \). We assume that this condition is satisfied when the \( \sum_i n_i \) is by a factor 5 larger than \( \frac{1}{\gamma} \).

**Results for a dimer**—In this section, a two-molecule system, or dimer, is studied in terms of the measure for non-Markovianity using the hierarchy equation of motion approach and scanning over the parameters of the model. As standard parameters, we use the site energies \( \epsilon_1 = 0, \epsilon_2 = 120/\text{cm} \), and the coupling \( J = -87.7/\text{cm} \). This corresponds to the strongly-couple bacteriochlorophyll site 1 and 2 subsystem of the Fenna-Matthews-Olson complex. For the molecular reorganization energy, the standard value of \( \lambda = 35/\text{cm} \) is employed. Along the lines of the discussion in [2], the standard bath correlation time is taken from 50 fs to 150 fs. We assume ambient temperature \( T = 288 \text{K} = 200/\text{fs} \). The main results use 40 tiers (819 ADOs), and Eq. (4) is integrated up to maximally 20 ps.

First, in Fig. 1, we investigate the time evolution of the trace distance in Eq. (1) for the dimer system. We choose the two initial states \( \rho_1 = |1\rangle \langle 1| \) and \( \rho_2 = |2\rangle \langle 2| \), and the standard parameters given above, while varying the bath dissipation rate. One can see clear non-Markovian revivals in the time intervals at around 150 fs and around 300 fs, borne out by increases in the trace distance. For larger correlation time of the bath of \( \tau_c = 150 \text{ fs} \) these revivals are more pronounced. A bath excitation is more likely to return to the system instead of being dissipated away rapidly, as occurs in the case of smaller correlation time \( \tau_c = 50 \text{ fs} \).

The NM-ity measure involves an optimization of the initial states. On the one hand, the following results use the two initial states \( \rho_1 = |1\rangle \langle 1| \) and \( \rho_2 = |2\rangle \langle 2| \) as above but, one the other hand, compare to a systematically optimized pair of initial states. One initial state is chosen out of 50 pure states on the Bloch sphere. This leads to a total number of 1225 independent pairs of states in the optimization. (The state optimization itself is done with 20 tiers of ADOs.)

We now proceed to scan over the parameters of the model, beginning with the system parameters, the site energy difference and the chromophoric coupling. First, the NM-ity is strongly dependent on the chromophoric coupling, see Fig. 2 (a). At zero coupling, the molecules are independent and the
In Fig. 2 (d), we show the NM measure as a function of the electronic degrees of freedom. Second, the other significant bath longer and the information is able to return back to the electronic system, a-i, for the dimer system, see Fig. 2 (b). As the energy difference increases, the NM-ity becomes maximal, showing a value of around 0.2. At large $\lambda$, the regime of incoherent transport [23], the NM-ity vanishes.

Results for the Fenna-Matthews-Olson complex— We now study the exciton-phonon information flow in the Fenna-Matthews-Olson complex. The FMO complex is found in green sulphur bacteria, where it connects the antenna complex with the reaction center. It is a trimmer with seven bacteriochlorophyll (BChl) molecules in each subunit and with one additional BChl molecule shared between the units. We implement the hierarchy equation of motion for the seven sites ($N = 7$), using a method for rescaling the auxiliary systems as in [29].

Redefining the ADOs as $\tilde{\sigma}^n (t) = (\prod_{i=1}^n |n_i\rangle \langle c_0| - |n_i\rangle \langle c_i|)^{-1/2} \sigma^n (t)$ and rescaling the superoperators as $\phi_0 \sigma \phi_0^{-1} = \sqrt{(n_i + 1)} |c_0\rangle \langle c_0| \sigma n_i = 150 \text{fs}$ and $|c_i\rangle \langle c_0| \sigma n_i = 150 \text{fs}$. At large $\lambda$, the regime of incoherent transport [23], the NM-ity vanishes.

In Fig. 2 (e), we show the NM measure as a function of the bath dissipation rate $\gamma$. The solid lines are calculations done with the initial states being $\rho_1 = |1\rangle \langle 1|$ and $\rho_2 = |2\rangle \langle 2|$ while the dots are computations done with optimized initial states. The dashed part of the lines indicates that the respective parameter was scanned beyond the validity of the model based on the truncation condition. For the FMO complex: e) bath dissipation rate and f) reorganization energy. In all figures, except in c) and e), we use the different bath correlation times: 50 fs (blue), 100 fs (purple), and 150 fs (red).

NM-ity is zero; the two initial states remain perfectly distinguishable. At non-zero coupling, the dynamics shows increasing NM revivals, while both initial states converge to the same thermal equilibrium state. Second, with respect to the site energy difference, the dependence of the NM-ity weakly slopes downward, see Fig. 2 (b). As the energy difference increases the coupling becomes less significant and the molecules become more independent. This leads to decreased NM-ity.

Next, we investigate the role of the bath parameters. First, as mentioned before, the bath correlation time crucially affects the memory of the bath and the information back flow to the system. In Fig. 2 (c), we show the NM-ity measure as a function of the inverse bath correlation time, i.e. the bath dissipation rate. A longer $\tau$, leads to more non-Markovianity, because a sluggish bath keeps the memory of excitations much longer and the information is able to return back to the electronic degrees of freedom. Second, the other significant bath parameter, the reorganization energy, is a measure of the non-equilibrium character of the phonon bath in the excited state. In Fig. 2 (d), we show the NM measure as a function of the reorganization energy. At zero $\lambda$, which essentially means no coupling to the phonons, the dynamics obviously shows zero non-Markovianity. At weak $\lambda$, we observe a NM-ity of around 0.1 at $t_c = 150 \text{fs}$, which is completely negated by Redfield theory. At intermediate $\lambda$ of around 40/cm, close to the physiological values of the Fenna-Matthews-Olson complex, the NM-ity is maximal, showing a value of around 0.2. At large $\lambda$, the regime of incoherent transport [23], the NM-ity vanishes.

Experimental characterization— In principle, the recently proposed ultrafast quantum process tomography protocol extracts a full characterization of the quantum map [31], and could thus be used to determine information about the vibrational environment experimentally. Experiments specifically designed to extract a particular observable, such as in our case the NM-ity measure, could be done with a smaller number of experimental configurations. We provide a first step towards a resource efficient characterization of non-Markovianity and focus on the optimization of the non-Markovianity as a function of relevant experimental input parameters. Experiments on photosynthetic complexes are usually realized with ultrafast four-wave mixing to monitor excited state dynamics. The setup consists of three incoming laser pulses and one phase-matched outgoing pulse (which interferes with a local oscillator). The first two pulses at times $t_1$ and $t_2$, separated by the controllable coherence time $t_{coh} = t_2 - t_1$, prepare the initial state in the single exciton manifold while the third pulse at $t_3$ probes the time-evolved state after a time interval called the...
considerable non-Markovian information flow between elec-

tronic and phononic degrees of freedom of light-harvesting chromophoric systems under physiological conditions, utilizing a realistic model for systems such as the Fenna-Matthews-Olson complex. The results suggest that non-Markovianity plays a significant role in photosynthetic energy transfer. We have provided a first step towards the experimental quantification of non-Markovianity by studying a class of initial states obtained in a four-wave mixing experiment. Future work will investigate analytically and numerically how to efficiently extract the non-Markovianity from the phase-matched signal.

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\[ \text{Coherence time [fs]} \]

\[ \text{Detuning [1/cm]} \]

\[ 0 \leq t \leq 100 \]

\[ -50 \leq -100 \]

\[ 0 \leq 100 \]

\[ \text{FIG. 3: Scan of the non-Markovianity during the population time (1 ps) of a simulated ultrafast experiment for a dimer system. The normalized quantity } N M^-i t y_{\text{ex}}^{\text{exp}}/N M^-i t y_{\text{ex}}^{\text{max}} \text{ is shown as a function of the detuning } \Omega - \Omega_{\text{ref}} \text{ and the coherence time } t_{\text{coh}}. \text{ The maximum is observed at } \Omega - \Omega_{\text{ref}} = -950/\text{cm and } t_{\text{coh}} = 100 \text{ fs.} \]

population time \( t_{\text{pop}} = t_3 - t_2 \). We use the direct simulation method in [32] [33], including the rotating wave approximation. The excited state dynamics is governed by the hierarchy equation of motion, as before. The system parameters are again inspired by the site 1 and 2 dimer of the Fenna-Matthews-Olson complex with \( \lambda = 35/\text{cm} \) and an intermediate bath correlation time \( \tau_c = 100 \) fs.

We study the NM-ity during the population time as a function of two basic parameters that play a crucial role in determining the initial state: the coherence time \( t_{\text{coh}} \) and the color of the laser pulses \([4, 32, 33]\). The Hamiltonian for the light-matter interaction is given by \( H_{L-\text{M}} = E(t) \hat{\mu} \), where the electric field is \( E(t) = eA(t) \exp[i \Omega t + \phi] \), with the amplitude \( A(t) \), polarization \( \hat{\epsilon} \), and the frequency \( \Omega \). The dipole moment is given by \( \hat{\mu} = \sum_m \hat{\mu}_m (\langle 0 \rangle \langle m \rangle + \langle m \rangle \langle 0 \rangle) \).

We assume that the effective dipoles are \( \hat{\mu}_1/\sqrt{\epsilon} = 1 \) \([32, 33]\). The weak Gaussian pulses have a standard deviation of \( 5 \) fs and an amplitude of \( 100/\text{cm} \). The experimentally relevant non-Markovianity during the population time is schematically determined by \( \text{NM-ity}_{\text{ex}}^{\text{exp}}(\Omega, t_{\text{coh}}) = \int_{t_2}^{t_2 + t_{\text{pop}}} dt \alpha(\sigma(t)) \sigma(\rho_{\Omega, t_{\text{coh}}}(t), \rho_{\text{ref}}(t)) \), which is investigated in Fig. 3.

Here, \( t_{\text{pop}} = 1 \) ps and \( \rho_{\text{ref}} \) is a reference state with \( \Omega_{\text{ref}} = 12370/\text{cm} \) (centered at the higher exciton frequency) and \( t_{\text{coh,ref}} = 30 \) fs (to avoid pulse overlap effects). The maximal value is given by \( \text{NM-ity}_{\text{ex}}^{\text{max}} = \max_{\Omega, t_{\text{coh}}} \text{NM-ity}_{\text{ex}}^{\text{exp}}(\Omega, t_{\text{coh}}) \). The maximum is observed at a detuning \( \Omega - \Omega_{\text{ref}} \) of around \(-950/\text{cm} \) and at \( t_{\text{coh}} = 100 \) fs (and a second maximum is at around \(-850/\text{cm} \) and \( 220 \) fs). The optimal pulses create an initial state as different as possible from \( \rho_{\text{ref}} \) in terms of NM-ity, with a detuning that leads to enough frequency overlap to populate the excited states and with a \( t_{\text{coh}} \) that harnesses the time evolution between the two state-preparation pulses.

\text{Conclusion—} We have shown numerically that there is a considerable non-Markovian information flow between elec-

\text{tronic and phononic degrees of freedom of light-harvesting chromophoric systems under physiological conditions, utiliz-

\text{ing a realistic model for systems such as the Fenna-Matthews-Olson complex. The results suggest that non-Markovianity plays a significant role in photosynthetic energy transfer. We have provided a first step towards the experimental quantification of non-Markovianity by studying a class of initial states obtained in a four-wave mixing experiment. Future work will investigate analytically and numerically how to efficiently extract the non-Markovianity from the phase-matched signal.

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