

Exciton transfer dynamics and quantumness of energy transfer in the Fenna-Matthews-Olson complex

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We present numerically exact results for the quantum coherent energy transfer in the Fenna-Matthews-Olson molecular aggregate under realistic physiological conditions, including vibrational fluctuations of the protein and the pigments for an experimentally determined fluctuation spectrum. We find coherence times shorter than observed experimentally. Furthermore, we determine the energy transfer current and quantify its “quantumness” as the distance of the density matrix to the classical pointer states for the energy current operator. Most importantly, we find that the energy transfer happens through a “Schrödinger-cat-like” superposition of energy current pointer states.

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I. INTRODUCTION

Recent experiments on the ultrafast exciton dynamics in photosynthetic biomolecules have brought a long-standing question again into the scientific focus whether nontrivial quantum coherence effects exist in natural biological systems under physiological conditions and, if so, whether they have any functional significance. Photosynthesis [1] starts with the harvest of a photon by a pigment and the formation of an exciton, followed by its transfer to the reaction center, where charge separation via primary electron transfer is initiated. The transfer of excitations has traditionally been regarded as an incoherent hopping between molecular sites [2].

Recently, Engel *et al.* [3,4] have reported long-lasting beating signals in time-resolved optical two-dimensional (2D) spectra of the Fenna-Matthews-Olson (FMO) [5,6] complex, which have been interpreted as evidence for quantum coherent energy transfer via delocalized exciton states. It transfers the excitonic energy from the chlorosome to the reaction center and consists of three identical subunits, each with seven bacteriochlorophyll molecular sites (the existence of an eighth site is presently under investigation). Quantum coherence times of more than 660 fs at 77 K [3] and about 300 fs at physiological temperatures [4] have been reported.

Together with recent experiments [7] on marine cryptophyte algae, these reports have boosted ongoing research to answer the question how quantum coherence can prevail over such long times in a strongly fluctuating physiological environment of strong vibronic protein modes and the surrounding polar solvent. Theoretical modeling of the real-time dynamics is notoriously complicated due to the large cluster size and strong non-Markovian fluctuations. It relies on simple models [8] of few chromophore sites which interact by dipolar couplings and which are exposed to fluctuations of the solvent and the protein [1,2]. A calculation of the 2D optical spectrum assuming weak coupling to the environment does not reproduce the experimental data [9]. It also became clear that standard Redfield-type approaches fail even for dimers [10,11].

In connection with molecular exciton transfer, extensions beyond perturbative approaches, such as the stochastic Liouville equation [8], extended Lindblad approaches [12], or small polaron approaches [13], have been formulated. Two recent

approaches have included parts of the standard FMO model. A second-order cumulant time-nonlocal quantum master equation found coherence times [14] as observed experimentally for the FMO complex. However, they employed an Ohmic bath in which the relaxation time is not uniquely fixed by experiments and strong vibrational protein modes are excluded. On the other hand, a variant of a time-dependent density-matrix renormalization group scheme [15] has been applied to a dimer in a realistic FMO environment [16]. The solution of the full state-of-the-art FMO model with seven localized sites and a physical environmental spectrum [16] including a strongly localized Huang-Rhys mode [2] is still missing. In particular, it has not been clarified whether a strong vibronic mode still allows for the observed quantum coherence times.

In this paper we close this gap and present numerically exact results for the full FMO model with seven sites and the spectral density of Ref. [16], determined from optical spectra [17]. Upon adopting the iterative real-time quasiadiabatic propagator path-integral (QUAPI) [18,19] scheme, we find coherence times shorter than observed experimentally. For comparison we recalculate also the dynamics employing the same Ohmic fluctuation spectrum as Ishizaki and Fleming [14]. To quantify quantum effects for energy transfer, we calculate the energy current associated with the transfer dynamics and its “quantumness.” It has been argued that quantum entanglement could be created *in a single excitation subspace* during the energy transfer [20], but this form of entanglement cannot be used to violate a Bell inequality [21] and its role for the transfer efficiency is therefore unclear. Wilde *et al.* [22] used the Leggett-Garg inequality to discuss whether quantum effects are relevant but they applied a phenomenological Lindblad approach. Here we use a recently developed measure of quantumness based on the Hilbert-Schmidt distance of the density matrix to the convex hull of classical states [23], taken as the “pointer states” [24] of the energy-current operator. We show that energy transfer starts with large current out of the initial site and then small currents flow between all seven sites. All currents show substantial quantumness. Interestingly enough, this implies that the energy transfer happens through a largely coherent “Schrödinger-cat-like” superposition of pointer states of the energy current operator.

In the next section we shortly recapitulate the Hamiltonian and the fluctuation spectrum of the site energies for the Fenna-Matthews-Olson complex. Then we determine the population dynamics within the single excitation subspace. In the fourth section we calculate the energy currents between any two sites in the FMO complex and then introduce a measure for the quantumness of these currents. Finally we conclude with a short summary of our results.

II. FMO MODEL

The FMO complex is a trimer consisting of identical, weakly interacting monomers [16], each containing seven bacteriochlorophyll *a* (BChl*a*) molecular sites which transfer excitons. The pigments are embedded in a large protein complex. Each of them can be reduced to its two lowest electronic levels, and their excited states are electronically coupled along the complex. Recombination is negligibly slow (\sim nanoseconds) compared to exciton transfer times (\sim picoseconds). Thus, the excitation dynamics is reliably described within the one-exciton subspace. The coupling of the seven excited levels gives rise to the Hamiltonian

$$H_{\text{FMO}} = \begin{pmatrix} 240 & -87.7 & 5.5 & -5.9 & 6.7 & -13.7 & -9.9 \\ & 315 & 30.8 & 8.2 & 0.7 & 11.8 & 4.3 \\ & & 0 & -53.5 & -2.2 & -9.6 & 6.0 \\ & & & 130 & -70.7 & -17.0 & -63.3 \\ & & & & 285 & 81.1 & -1.3 \\ & & & & & 435 & 39.7 \\ & & & & & & 245 \end{pmatrix} \quad (1)$$

in units of cm^{-1} in site representation [16] for an FMO monomer of *C. tepidum*. We define the lowest site energy of pigment 3 as reference.

The vibrations of the BChl*a*, the embedding protein, and the surrounding polar solvent are too complex for a pure microscopic description and are thus treated within the framework of open quantum systems. They induce thermal fluctuations described by harmonic modes [2] and lead to the total Hamiltonian [16]

$$H = H_{\text{FMO}} + \sum_{j=1}^7 |j\rangle\langle j| \sum_{\kappa} v_{\kappa}^{(j)} q_{j,\kappa} + \sum_{j=1}^7 \frac{1}{2} \sum_{\kappa} (p_{j,\kappa}^2 + \omega_{j,\kappa}^2 q_{j,\kappa}^2) \quad (2)$$

with momenta $p_{j,\kappa}$, displacement $q_{j,\kappa}$, frequency $\omega_{j,\kappa}$, and coupling $v_{\kappa}^{(j)}$ of the environmental vibrations at site j . We assume that fluctuations at different sites are identical but spatially uncorrelated [25].

The key quantity which determines the FMO coherence properties is the environmental spectral density $G(\omega) = \sum_{j,\kappa} (|v_{\kappa}^{(j)}|^2 / 2\omega_{j,\kappa}) \delta(\omega - \omega_{j,\kappa})$. The most detailed identification of the bath properties to date has been achieved by Adolphs and Renger [16]. They used an advanced theory of optical spectra, a genetic algorithm, and excitonic couplings from electrostatic calculations modeling the dielectric protein environment to derive the currently most detailed spectral

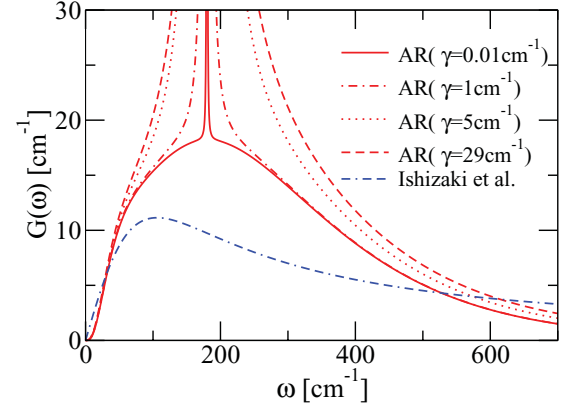


FIG. 1. (Color online) Bath spectral densities of the FMO complex of *C. tepidum*: The most realistic form as determined to the present [16,17] is given by Eq. (3) [AR, red (top four) lines]. The bottom (blue) dash-dot-dashed line shows the Drude form $G_D(\omega)$ used in Ref. [14].

density

$$G_{\text{AR}}(\omega) = \omega^2 S_0 g_0(\omega) + \omega^2 S_H \delta(\omega - \omega_H). \quad (3)$$

Here, $S_0 = 0.5$, $S_H = 0.22$, $\omega_H = 180 \text{ cm}^{-1}$, and

$$g_0(\omega) = 6.105 \times 10^{-5} \times \frac{\omega^3}{\omega_1^4} e^{-\sqrt{\frac{\omega}{\omega_1}}} + 3.8156 \times 10^{-5} \times \frac{\omega^3}{\omega_2^4} e^{-\sqrt{\frac{\omega}{\omega_2}}}$$

with $\omega_1 = 0.575 \text{ cm}^{-1}$ and $\omega_2 = 2 \text{ cm}^{-1}$. It includes a broad continuous part [see top four (red) lines in Fig. 1] which for $\omega \rightarrow 0$ behaves as super-Ohmic, $G_{\text{AR}}(\omega) \sim \omega^5$, and which describes the protein vibrations with the Huang-Rhys factor S_0 . It was determined from temperature-dependent absorption spectra [17]. In addition, a vibrational mode of the individual pigments with the Huang-Rhys factor S_H is included. We have added a broadening to the unphysical δ peak, which is justified since the protein is embedded in water as a polar solvent which gives rise to an additional weak Ohmic damping of the protein vibrations. We fix its width to $\gamma_p = 29 \text{ cm}^{-1}$ which was found for the lowest energy peak of protein vibrations in the LH2 complex [26].

In order to recover known results for the transfer dynamics of excitations in the FMO complex embedded in an Ohmic bath [14], we additionally consider the spectral density used in Ref. [14] given by

$$G_D(\omega) = \frac{2\lambda\omega\omega_c}{\pi(\omega_c^2 + \omega^2)} \quad (4)$$

with a Debye cutoff at frequency ω_c [see bottom (blue) dash-dot-dashed line in Fig. 1]. It includes the reorganization energy $\lambda = 35 \text{ cm}^{-1}$ and the environmental time scale $\omega_c^{-1} = 50 \text{ fs}$.

III. POPULATION DYNAMICS IN THE FMO

To understand whether the vibrational fluctuations of the protein and the pigments allow for the observed coherence times, we apply the numerically exact QUAPI scheme to simulate the real-time exciton dynamics in the FMO complex

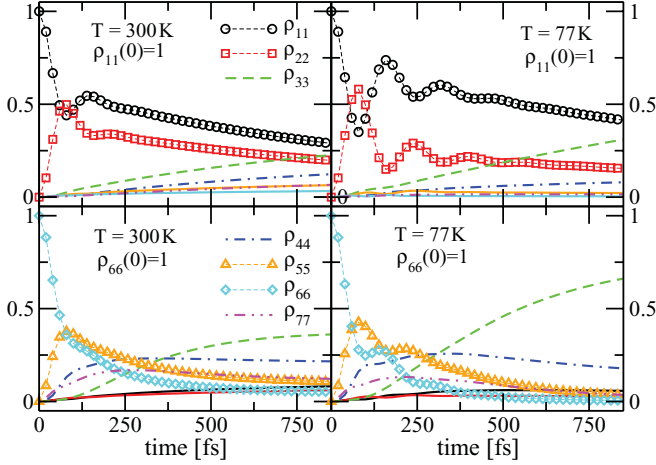


FIG. 2. (Color online) Time-dependent occupation probabilities of all seven FMO sites for $T = 300$ and 77 K with $\rho_{11}(0) = 1$ and $\rho_{66}(0) = 1$ for the measured FMO spectrum Eq. (3) [16].

for the realistic bath spectral density (3). QUAPI is well established [18,19] and allows us to treat nearly arbitrary spectral functions at finite temperatures. We extended recently the original scheme to treat multiple environments, i.e., separate environments for each chromophore site [27].

We calculate the time-dependent populations of the FMO pigment sites for the spectral density of Eq. (3). We choose $T = 300$ K (physiological temperature) and $T = 77$ K (typical experimental temperature). Both the pigments BChl 1 and BChl 6 are oriented toward the baseplate protein and are thus believed to be initially excited (entrance sites) [28]. Thus, we consider two cases, i.e., $\rho_{11}(0) = 1$ and $\rho_{66}(0) = 1$. We focus on the transient coherence effects and thus do not include an additional sink at the exit site BChl 3. In Fig. 2, we show the time-dependent pigment occupation probabilities $\rho_{jj}(t)$. Identical simulations using smaller widths, i.e., $\gamma_p = 5$ cm⁻¹ and $\gamma_p = 1$ cm⁻¹, for the vibrational mode yield identical results for the populations (not shown). For $\rho_{66}(0) = 1$ at room temperature, coherent oscillations are completely suppressed and at 77 K they last up to about 250 fs. For $\rho_{11}(0) = 1$, coherence is supported longer due to the strong electronic coupling between sites 1 and 2. At room temperature, it survives for up to about 200 fs and for 77 K up to 500 fs at most. Thus, coherence times are shorter than experimentally observed. We emphasize that coherence features are a transient property and, hence, not only the low-frequency bath modes but also the discrete vibrational modes are relevant (100 fs corresponds to ~ 333 cm⁻¹).

We additionally calculate the time-dependent populations of the FMO pigment sites for $T = 300$ K (physiological temperature) and $T = 77$ K (typical experimental temperature) for the FMO with the bath spectrum $G_D(\omega)$ [see Eq. (4)]. As above we consider two choices of initial conditions, i.e., $\rho_{11}(0) = 1$ and $\rho_{66}(0) = 1$, and focus on the transient coherence effects and thus do not include an additional sink at the exit site BChl 3.

Figure 3 shows the occupation probabilities of all seven sites at $T = 300$ K versus time. For both initial conditions, coherent oscillations of the populations of the initial site and its neighboring site [$j = 2$ for $\rho_{11}(0) = 1$ and $j = 5$ for $\rho_{66}(0) = 1$] occur due to the strong electronic couplings. They last up

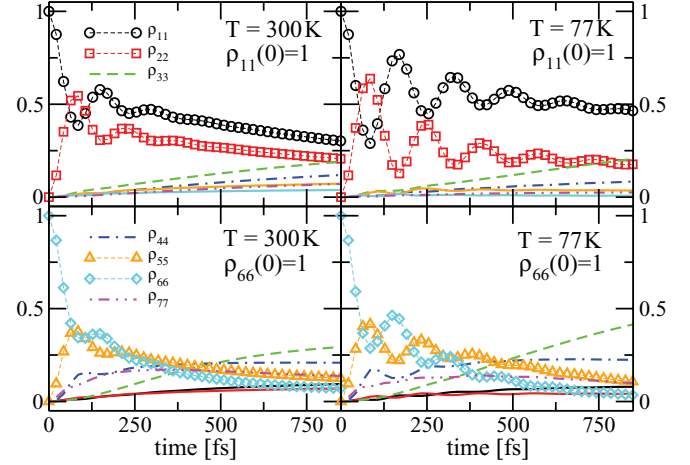


FIG. 3. (Color online) Time-dependent occupations of the seven FMO sites for $T = 300$ K and $T = 77$ K with $\rho_{11}(0) = 1$ and $\rho_{66}(0) = 1$ for the Ohmic spectrum $G_D(\omega)$.

to ~ 350 fs. At $T = 77$ K, as shown in Figs. 3(b) and 3(d), the oscillations persist up to ~ 700 fs. Our results coincide with those of Ref. [14]. Tiny deviations at short times arise since the full FMO trimer is considered in Ref. [14]. The coherence times, however, are not affected.

IV. QUANTUMNESS OF ENERGY TRANSFER THROUGH FMO

Next, we discuss whether energy transfer dynamics is a quantum coherent process. Classical coupled dipoles can show oscillatory energy currents identical to quantum mechanical dipole-coupled systems provided that the interaction between the dipoles is weak enough to be treated via linear response [29]. In FMO [see Eq. (1)], however, off-diagonal couplings are on the same order of magnitude as site energy differences. We use a physically well motivated measure of quantumness which can be found by first identifying the most classical pure states in the problem. In quantum optics, for instance, coherent states are considered “(most) classical” due to their minimal uncertainty and their stability under the free evolution of the electromagnetic field [30]. Next, one identifies the set of all classical states with the convex hull (i.e., all mixtures) of the pure classical states, as mixing cannot increase quantumness. This leads in quantum optics and for spin systems to the well-established notion that classical states are those with a well-defined positive P function [23,31–33]. Finally, one defines “quantumness” as the distances to the closest classical states.

For FMO we are interested in the “quantumness” of the energy current since energy transfer constitutes the main function of the FMO complex. A measurement of the energy current would yield that for any measurement result the state of the system would collapse onto a pointer state. In general, pointer states are the states einselected by the interaction with its environment [24], being here the hypothetical measurement apparatus for measuring energy current. Pointer states are the most classical states in that they arise via decoherence and are those that persist when a quantum system interacts strongly and for a long time with its environment. In our case of a projective von Neumann measurement, they are the eigenstates of the

quantum mechanical operator corresponding to the energy current measurement.

A. Energy currents in FMO

An energy current operator can be derived for a general multisite Hamiltonian [34]. The expression for an energy current operator $\mathbf{j}(\mathbf{x})$ can be obtained from a continuity equation

$$\dot{H}(\mathbf{x}) + \nabla \cdot \mathbf{j}(\mathbf{x}) = 0, \quad (5)$$

where $H(\mathbf{x})$ is the local energy density. This is a well-established procedure introduced by Hardy [34] and which was largely adopted by a large number of subsequent papers (see, e.g., Refs. [35–39]). There is some freedom in the definition of local energy density, but for a Hamiltonian of the form $H = \sum_i T_i + (1/2) \sum_{i \neq k} V_{ik}$, where T_i and V_i are kinetic energy and interaction energy (of possibly a large number of particles) in region i , and V_{ik} is the interaction between the particles in regions i and those in region k , a natural decomposition is given by $H = \sum_i h_i$, $h_i = T_i + (1/2) \sum_{k \neq i} V_{ik} \equiv v_i H(x_i)$, where v_i is a volume of region i .

For the FMO complex, precise information about the the single-excitation sector of the macromolecule with sites $i \in \{1, \dots, N\}$ is known ($N = 7$). The Hamiltonian $H = H_{\text{FMO}}$ is given in tight-binding approximation as

$$H = \sum_{i,k} h_{ik} |i\rangle \langle k|, \quad (6)$$

where $|i\rangle$ is a state with the excitation localized on site i [see Eq. (1)]. The natural decomposition of that Hamiltonian in terms of local excitations is

$$H = \sum_{i=1}^N h_i \quad \text{with} \quad h_i = \frac{1}{2} \sum_{k=1}^N (h_{ik} |i\rangle \langle k| + \text{H.c.}). \quad (7)$$

In order to deduce an energy-current operator from this Hamiltonian, consider first a linear chain in one dimension, where \mathbf{j} has only one component, denoted by j , with values j_i on sites i , taken as equidistant with lattice constant a . The discretized form of Eq. (5) reads

$$\frac{\partial h_i}{\partial t} \frac{1}{a} = \frac{j_i^l - j_i^r}{a}, \quad (8)$$

where $j_i^{l,r}$ denote the energy flux in the positive x direction on the left of site i and on the right of site i . It is convenient to think of j_i^l (j_i^r) as being evaluated halfway between sites $i-1$ and i (between sites i and $i+1$), respectively. Current j_i^l arises from the balance of the currents $s_{i-1 \rightarrow i}$ from site $i-1$ to site i and $s_{i \rightarrow i-1}$ from site i to site $i-1$. The latter two currents are always defined positive and in the direction indicated by the indices, whereas j_i can be positive or negative, depending on which current component dominates. Inserting these expressions into Eq. (8), we find

$$\frac{\partial h_i}{\partial t} = \sum_{k=i \pm 1} (s_{k \rightarrow i} - s_{i \rightarrow k}). \quad (9)$$

This equation is valid for the one-dimensional tight-binding model with only nearest neighbor couplings. It has the natural

interpretation that the change of energy density at a given site is given by the difference between the sum of incoming energy currents and the sum of outgoing energy currents. As such, the expression generalizes in straightforward fashion to a general tight-binding model on a graph, where each site can be connected to an arbitrary number of other sites. Each link can support an energy current, and one has thus

$$\frac{\partial h_i}{\partial t} = \sum_{k \neq i} (s_{k \rightarrow i} - s_{i \rightarrow k}). \quad (10)$$

The left-hand side of Eq. (10) is easily calculated by using Heisenberg's equation of motion,

$$\frac{\partial h_i}{\partial t} = \frac{i}{\hbar} [H, h_i]. \quad (11)$$

A short calculation leads to

$$\frac{\partial h_i}{\partial t} = \frac{i}{2\hbar} \sum_{k \neq i} \sum_l (h_{ki} h_{il} |k\rangle \langle l| - h_{ik} h_{kl} |i\rangle \langle l| - \text{H.c.}). \quad (12)$$

Comparing this expression with Eq. (9), we identify the directed energy current

$$s_{i \rightarrow k} = \frac{i}{2\hbar} \sum_l (h_{ik} h_{kl} |i\rangle \langle l| - \text{H.c.}). \quad (13)$$

The (positive or negative) energy current attributed to link $i-k$ on the graph is $j_{ik} = s_{i \rightarrow k} - s_{k \rightarrow i}$. The dimension of all these energy currents is energy/time. A corresponding classical energy current phase space function can be derived in classical mechanics, if a corresponding classical Hamilton function can be established, in a completely analogous way by using Hamilton's equation of motion to derive a continuity equation for energy transport.

We have calculated all energy currents $\langle j_{ik}(t) \rangle = \text{tr}[j_{ik} \rho(t)]$ for all sites i and k . The currents out of the entrance site toward its strongest coupled neighbor [j_{12} for $\rho_{11}(0) = 1$ and j_{56} for $\rho_{66}(0) = 1$] have by far the largest amplitude. All currents show initial oscillations which are more pronounced at 77 K than at 300 K (see Figs. 4 and 5) on time scales comparable to coherent oscillations discussed above. The currents out of

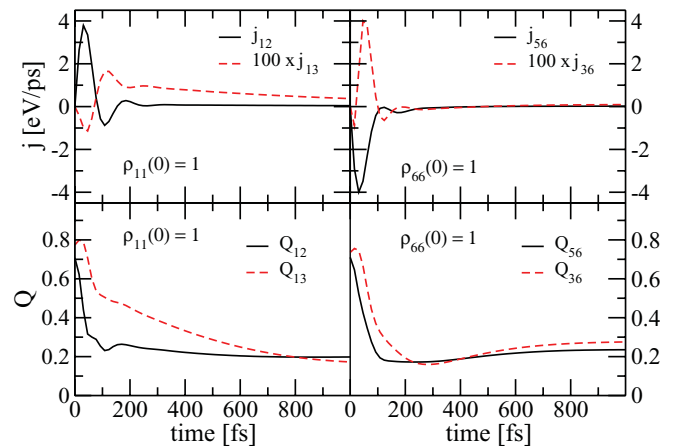


FIG. 4. (Color online) Selected average energy currents j_{ik} (top) and corresponding quantumness Q_{ik} (bottom) for FMO spectral density of Eq. (3) and $T = 300$ K. Notice the rescaling of the currents for better visibility.

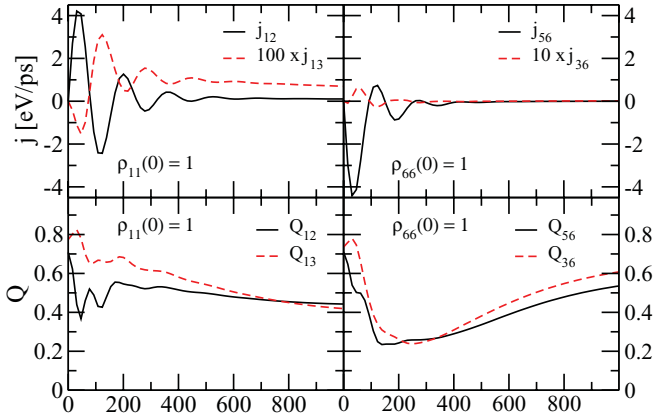


FIG. 5. (Color online) Same as Fig. 4, but at $T = 77$ K.

the entrance site toward its strongest coupled *neighbor* [j_{12} for $\rho_{11}(0) = 1$ and j_{56} for $\rho_{66}(0) = 1$] have by far the largest amplitude. After this initial phase, energy currents between all sites are small but finite (as exemplary shown by j_{13} and j_{36}) and persist up to 1000 fs. Energy transfer, thus, starts by quantum coherent population exchange mainly between sites 1 and 2 (or sites 6 and 5, respectively) and some transfer to other sites. After this initial phase, in which a preliminary redistribution of energy takes place, small currents between all sites will slowly bring the system into thermal equilibrium and result in an according population and energy distribution.

B. Classical states of energy transport

It has long been appreciated that the most classical states corresponding to a given quantum mechanical observable are the so-called pointer states. These states are “einselected” by the decoherence process due to the interaction of an environment with the system. In the case of a measurement, the environment is given by the measurement instrument, and the pointer states are in this case simply the eigenstates of the operator representing the quantum mechanical observable [24,40]. It is in the eigenbasis of these pointer states that the density matrix becomes diagonal due to the decay of the off-diagonal matrix elements. The remaining diagonal matrix elements correspond to the probabilities of finding one of the possible outcomes of the measurement.

As eigenstates of a Hermitian operator, pointer states are pure states. The most general classical states can be obtained by classically mixing the pointer states; i.e., one chooses pointer states randomly with a certain probability. As this is a purely classical procedure, it cannot increase the “quantumness” of the system. This definition of “classicality” is well established in quantum optics and leads to a criterion of classicality based on a well-defined positive-definite P function [41,42]. It was recently extended to spin systems [23,31].

C. Quantumness

Thus, if one wants to decide whether the energy current between two different sites in FMO has to be considered “quantum,” one has to (i) find the pointer states of the corresponding energy current operator and (ii) check whether the state of the system $\rho(t)$ can be written as a convex

combination of these pointer states. A more quantitative statement is possible by measuring the distance of $\rho(t)$ to the convex set of classical states [23,31,43], i.e., here the convex hull of the pointer states. The pointer states are the eigenvectors $|v_{ik}^l\rangle$ of j_{ik} . They define the relevant pure classical states for the energy transfer along link $i-k$. Their classical mixtures form the convex set of all classical states for the energy current on link $i-k$. Any distance measure in Hilbert space is in principle suitable, and we use the Hilbert-Schmidt distance for simplicity, leading to our definition of quantumness of the current j_{ik} ,

$$Q_{ik}(\rho) = \min_{\{p_l | p_l \geq 0, \sum_l p_l = 1\}} \left\| \rho - \sum_l p_l |v_{ik}^l\rangle\langle v_{ik}^l| \right\| \quad (14)$$

with $\|A\| = (\text{tr}AA^\dagger)^{1/2}$. Note that this measure of “quantumness” is completely analogous to and on the same level of abstraction as the measure of entanglement based on the distance of a state to the convex set of separable states (see p.363 in Ref. [44]), but it has the advantage of being meaningful even in the single-excitation sector, and without artificially separating the system into two subsystems.

A finite value of Q_{ik} means that the state cannot be written as a convex sum of pointer states of the energy current operator j_{ik} ; i.e., there are coherences left in $\rho(t)$ written in the pointer basis. This means, essentially, that the system is in a Schrödinger-cat-like state of different energy-current pointer states at a given time t .

By definition, $Q(\rho) \geq 0$, and $Q(\rho) = 0$ if ρ is classical. An upper bound is given by $Q(\rho) \leq Q_{\max} \equiv \sqrt{\text{tr}\rho^2 - 1/d}$, where d is the dimension of the Hilbert space [23] ($Q_{\max} \simeq 0.925$ for pure states and $d = 7$). We have calculated the quantumness $Q_{ik}(t)$ for all energy currents $\langle j_{ik}(t) \rangle$. As discussed above, the currents out of the entrance site toward its strongest coupled *neighbor* [j_{12} for $\rho_{11}(0) = 1$ and j_{56} for $\rho_{66}(0) = 1$] have by far the largest amplitude and all currents show initial oscillations which are more pronounced at 77 K than at 300 K (see Figs. 4 and 5) on time scales comparable to coherent oscillations discussed above. These oscillations go hand-in-hand with substantial quantumness: Q_{12} and Q_{13} are initially of the order of $Q \simeq 0.6-0.8$, but drop within ~ 100 fs to $Q \simeq 0.2-0.4$, with the exception of the case $\rho_{11}(0) = 1$, $T = 77$ K, where Q_{13} drops slowly over 1000 fs, much more slowly than the oscillations of the energy current, and the rapid decay of coherences in the site basis notwithstanding. After this initial phase, energy currents between all sites are small but finite (as exemplary shown by j_{13} and j_{36}) and persist up to 1000 fs and, noteworthy, a substantial amount of quantumness of the order $Q \simeq 0.2-0.4$ still persists at 1000 fs as well. In the last graph ($\rho_{66}(0) = 1$, $T = 77$ K), the quantumness even rises again after the initial drop.

This implies that the superposition of the pointer states of the energy current operator remains largely coherent even after population dynamics does not show coherence anymore. Nature has apparently engineered the environment of the FMO complex in such a way that it is rather inefficient in decohering superpositions of energy currents. Thus, even though the actual currents, which bring the system into thermal equilibrium, are rather small (after the initial oscillatory phase), they turn out to have a finite *quantumness*. This is further illustrated by

comparing with the quantumness of the thermal equilibrium state $\rho_T = \exp(-H_{\text{FMO}}/k_B T)$ at $T = 77$ K and $T = 300$ K, which is of the orders 0.01 and 0.002, respectively. Altogether, our data quantitatively show the nonclassical nature of the energy transfer in FMO and provide a clear physical picture of the quantumness: energy transport in FMO happens largely through a coherent Schrödinger-cat-like superposition of pointer states of the energy current operator.

V. CONCLUSION

To summarize, we have obtained numerically exact results for the real-time exciton dynamics of the FMO complex in the presence of realistic environmental vibronic fluctuations. We have used the most accurate form of the spectral density

realized in nature. It includes vibronic effects via a strongly localized Huang-Rhys mode. The resulting coherence times of the populations are shorter than observed experimentally. The energy transfer dynamics is also intrinsically quantum mechanical on the time scales of several hundred femtoseconds. This has been shown by calculating the quantumness as the distance to the convex hull of pointer states of the energy current. The energy transport in FMO is to a large extent through a coherent Schrödinger-cat-like superposition of the pointer states.

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