Quantum Coherence in Photosynthetic Exciton Dynamics

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Abstract.
We present numerically exact results for the electronic energy transfer dynamics in the Fenna-Matthews-Olson (FMO) molecular aggregate. In particular, we determine its single excitation subspace dynamics within an open quantum dynamics approach which is based on parameters for the dipolar couplings, site energies and their respective fluctuations. We study and compare the dynamics for parameters according to several models available in the literature. Depending on the model used we find quantum coherent dynamics with coherence times exceeding experimentally observed times but also shorter times for other models. Even strongly overdamped decay of the site populations with no coherent population dynamics is observed for model parameters based on atomistic molecular dynamics. Thus, theoretical understanding at the present stage can neither support nor rule out a picture of quantum coherent energy transfer in natural photosynthesis.

1. Introduction
Recently, experiments have been reported in which long-lived coherence effects have been observed in the ultrafast exciton dynamics in photosynthetic biomolecules. These results caused tremendous renewed interest in the longstanding question whether quantum coherence effects have any functional significance in natural biological systems under physiological conditions. Photosynthesis [1] starts with the absorption of a photon by a pigment and the formation of an exciton, followed by its transfer to the reaction center, where charge separation takes place. The excitation transfer has traditionally been regarded as an incoherent hopping between molecular sites [2].

A few years ago, Engel et al. [3, 4] have reported long-lasting beating signals in time-resolved optical two-dimensional spectra of the Fenna-Matthews-Olson (FMO) [5, 6] complex. These have been interpreted as evidence for quantum coherent energy transfer via delocalized exciton states. FMO’s function is to transfer energy from the chlorosome, a large vesicle of pigments, to the reaction center. FMO consists of three identical subunits, each with eight bacteriochlorophyll molecular sites. Quantum coherence times of more than 660 fs at 77 K [3] and about 300 fs at physiological temperatures [4] have been reported. Similar experimental findings were observed in marine cryptophyte algae [7].

The question how quantum coherence can survive over such long times in these biomolecular environments with strong vibronic modes and a surrounding strongly coupled polar solvent is open. Full quantum theoretical modeling of the real-time dynamics is beyond current computer...
powers due to the large cluster size and strong non-Markovian fluctuations. Studies of the excitation dynamics, therefore, rely on simplified models [8] of few chromophore sites which interact by dipolar couplings and which are exposed to environmental fluctuations of the bacteriochlorophyll molecule, the surrounding protein and the solvent [1, 2].

From simple donor-acceptor toy models one realizes that standard Redfield-type or other weak coupling approaches fail for typical environmental fluctuation spectra [9, 10]. Nevertheless, weak coupling approaches including various extensions have been employed to investigate the question whether quantum coherence is functionally relevant for the near unity quantum efficiency of energy transfer [11, 12, 13]. In order to study the origin of the long lived coherence, methods which can describe the non-Markovian behavior exactly have to be employed [14]. Again, donor-acceptor toy model studies showed that either temporal correlations of environmental fluctuations, with time scales exceeding the internal electronic coupling time scale, or spatial correlations which extend between the chromophores, which exchange energy, can cause long lived coherence [15, 16, 17, 18].

In order to study excitonic energy transfer in FMO, model descriptions including an excitonic Hamiltonian and environmental fluctuation spectra are necessary. Based on an analysis of optical experimental data Adolphs and Renger determined site energies, dipolar couplings between pigments and the fluctuation spectrum for the site energies for a subunit of the FMO trimer [19]. The latter includes, besides a broad continuous spectrum resulting from the solvent fluctuations, additionally a single low-frequency vibronic mode. This spectrum goes back to experimental measurements of Wendling et al. [20] who have measured fluorescence line-narrowing at low temperature. Adolphs and Renger, however, only considered the discrete vibronic state with the lowest frequency (besides the continuous background). This Adolphs / Renger (AR) model was further simplified by Cho et al. [21] (CF-model) and also by Ishizaki and Fleming [22] (IF-model) by considering a phenomenological environmental fluctuation spectrum.

Recently, Olbrich et al. have used extensive classical molecular dynamics simulations for the FMO aggregate including the environmental solvent to determine site energies, electronic couplings and their respective fluctuational characteristics [23] (OK-model). In a follow-up paper, Olbrich et al. [24] have analyzed the properties of the fluctuations in more detail and have determined explicitly the environmental fluctuation spectra necessary for the full FMO dynamics. Noteworthy, they obtain different spectra for each site. Each spectrum consists of two continuous solvent contributions and a set of up to 13 vibronic modes. Thus, the OK-model for FMO includes much more details than the IF-, the CF- or the AR-model but is solely obtained from classical MD simulations.

Ishizaki and Fleming used a second-order cumulant time-nonlocal quantum master equation to determine the site population dynamics in the single excitation subspace [22] and found quantum coherent dynamics with coherence times as observed experimentally for the FMO complex. The present authors used the quasi adiabatic path integral approach (QUAPI) to study the dynamics of the AR model [25] where we found coherence times roughly by a factor of two smaller than observed in the FMO complex.

In the present report, we use the OK-model for the FMO and determine the population dynamics numerically exactly using QUAPI for a monomeric subunit of the trimer. We find that the time evolution of the site populations is overdamped at room temperature as well as at 77 Kelvin. Furthermore we study the dynamics in the CF-model where we observe coherence times exceeding experimentally observed ones.

The present work is organized as follows: In the following section we briefly summarize for completeness the various models for FMO and discuss the resulting site energies, coupling strengths and environmental fluctuation spectra. Then, we briefly summarize the numerical method used to solve the dynamics of the FMO model coupled to environmental fluctuations. We then present results for a monomeric subunit of the FMO trimer for each of the introduced...
models. A comparison of the results from the various models shows that we are not able to conclude on an answer to the question whether the excitation transfer is quantum mechanically coherent on time scales up to 500 fs at physiological temperatures.

2. Model

2.1. Model - Hamiltonian

The FMO complex is a trimer consisting of identical, weakly interacting monomers, each containing eight bacteriochlorophylla (BChlα) molecular sites. Excitation energy is transferred between these pigments. They are embedded in a large protein complex. Typically, each of them is reduced to its two lowest electronic levels. Thereby, their excited states are electronically coupled. Recombination is negligibly slow (∼ns) compared to exciton transfer times (∼ps) and multiple excitation is unlikely under natural conditions. Thus, the excitation dynamics is reliably described within the 1-exciton subspace.

Adolphs and Renger [19] have determined the site energies and dipolar couplings leading to the Hamiltonian

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

in units of cm\(^{-1}\) in site representation for an FMO monomer of \textit{C. tepidum}. We define the lowest site energy as reference. Adolphs and Renger give also parameters for a monomeric subunit of the FMO trimer which are rather close to their monomer parameter set (therefore we omit this parameter set in the following discussion completely). Note that the description by Adolphs and Renger is based on seven pigments for each monomeric subunit of the FMO trimer. The existence of the eighth pigment was only realized recently [26]. The eighth pigment has, however, little influence on coherence which is dominated by the strongly coupled pigments 1 and 2.

Olbrich et al. obtain for a monomeric subunit of the trimer

\[ H_{\text{FMO-OK}} = \begin{pmatrix}
185.4 & -80.3 & 3.5 & -4.0 & 4.5 & -10.2 & -4.9 & 21.0 \\
80.6 & 23.5 & 6.7 & 0.5 & 7.5 & 1.5 & 3.3 \\
0 & -49.8 & -1.5 & -6.5 & 1.2 & 0.7 \\
112.8 & -63.4 & -13.3 & -42.2 & 1.2 \\
64.5 & 55.8 & 4.7 & 2.8 \\
88.6 & 33.0 & -7.3 \\
491.7 & -8.7 \\
217.6
\end{pmatrix} \]

in units of cm\(^{-1}\) in site representation. Here, we actually consider the seven chromophores of one monomeric subunit and the eighth chromophore of the one neighboring subunit for which the distance 1 – 8 is minimal. This eighth pigment is rather strongly coupled to the monomeric subunit under consideration whereas the actual eighth chromophore of this subunit is only weakly coupled to it.

In both model Hamiltonians, site 3 has lowest site energy which motivates the fact that site 3 is generally believed to be 'exit' site from which the energy is transferred from the FMO complex into the reaction center. There are, however, two noteworthy differences. Firstly, the AR-Hamiltonian (1) has sites 1 and 6 with highest energy whereas the OK-Hamiltonian (2) has
sites 7 and 8 with highest energy. Secondly, in the OK-Hamiltonian (2) the dipolar couplings tend to be smaller than in the AR-Hamiltonian (1). This already hints towards weaker coherent features in the OK-model.

2.2. Model - Fluctuation spectra

The vibrations of the BChlα, 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

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

(3)

with momentum $p_{j,\kappa}$, displacement $q_{j,\kappa}$, frequency $\omega_{j,\kappa}$ and coupling $\nu_{\kappa}^{(j)}$ of the environmental vibrations at site $j$. Notice that each BChlα has its own fluctuating environment. The key quantity which determines the FMO coherence properties is the environmental spectral density $G_j(\omega) = \sum_{\kappa} (|\nu_{\kappa}^{(j)}|^2/2\omega_{j,\kappa})\delta(\omega - \omega_{j,\kappa})$.

Ishizaki and Fleming [22] used a single Ohmic spectrum with a Debye cut-off function for each site independently

$$G_{IF}(\omega) = \frac{2\lambda}{\pi} \frac{\omega\omega_{c,IF}}{\omega_{c,IF}^2 + \omega^2}$$

(4)

with reorganization energy $\lambda = 35\text{cm}^{-1}$ and Debye relaxation time (or inverse cut-off frequency) $\omega_{c,IF}^{-1} = 50\text{fs}$. This spectrum is depicted in Fig. 1 by the dark green full line (lower left corner). It includes only a continuous part describing the solvent fluctuations and omits all discrete vibronic modes from the BChlα or the embedding protein. The Debye relaxation time (or cut-off frequency) of this spectrum is experimentally only fixed within certain limits.

Cho et al. [21] used an exponentially cut-off Ohmic spectrum

$$G_{CF}(\omega) = \frac{\lambda}{\omega_{c,CF}} e^{-\omega/\omega_{c,CF}}$$

(5)

with $\lambda = 35\text{cm}^{-1}$ but $\omega_{c,CF} = 50\text{cm}^{-1}$ ($\omega_{c,CF}^{-1} = 20\text{fs}$) which is depicted in Fig. 1 by the red dashed line (lower left corner).

Wendling et al. [20] have provided fluorescence line-narrowing measurements at low temperature and have obtained the so far still most detailed experimentally determined fluctuation spectrum for FMO. Adolphs and Renger [19] give an explicit form of this spectrum,
thereby focusing only on the discrete vibronic state with lowest frequency besides the continuous contributions, leading to

\[ G_{AR}(\omega) = \omega^2 S_0 g_0(\omega) + \omega^2 S_H \delta(\omega - \omega_H) \]

with \( S_0 = 0.5 \), \( S_H = 0.22 \), \( \omega_H = 180 \text{cm}^{-1} \) and

\[ g_0(\omega) = 6.105 \cdot 10^{-5} \frac{\omega^3}{\omega_1^4} e^{-\sqrt{\omega/\omega_1}} + 3.8156 \cdot 10^{-5} \frac{\omega^3}{\omega_2^4} e^{-\sqrt{\omega/\omega_2}} \]

with \( \omega_1 = 0.575 \text{cm}^{-1} \) and \( \omega_2 = 2 \text{cm}^{-1} \). This spectrum is plotted in Fig. 1 as the full violet line. There is a continuous underlying contribution plus a single overlying vibronic peak. Again independent but identical fluctuations at each site are assumed. We furthermore broadened the unphysical \( \delta \)-peak and used instead a Lorentzian peak

\[ \pi \omega^2 S_H \delta(\omega - \omega_H) \rightarrow \pi S_H \omega \frac{\omega \gamma_p}{(\omega - \omega_H)^2 + \gamma_p^2} \]

with width \( \gamma_p = 29 \text{cm}^{-1} \) taken as a typical value from the Olbrich et al. [24] spectra (see below).

Recently, Olbrich et al. [24] have determined by extensive molecular dynamical simulations the fluctuations of the site energies in the FMO. This allowed them to extract detailed fluctuation spectral functions \( G_j(\omega) \) for each site \( j \) separately. They observe different spectra for each site. The spectra consist of two continuous contributions resulting from solvent fluctuations and up to 13 discrete vibrational modes. We plot the spectra in Fig. 1.

The spectra show discrete vibrational modes up to energies around 1800 \text{cm}^{-1} \) (see inset in Fig. 1). In the upper left corner (vertical blue) of Fig. 1 the energy differences between the eigenstates in the Hamiltonian (2) are indicated by vertical lines. These energy differences are (at least within a one-phonon picture) the relevant energy quanta which the FMO electronic excitations want to exchange with the environment. These energy differences do not exceed about 500 \text{cm}^{-1} \) and accordingly, we expect little influence of the higher energetic modes for the excitation dynamics. The same holds true for the energy differences of Hamiltonian (1). Nevertheless, some influence by the lower energetic modes could be expected. Remarkably, for the spectra at each site already the continuous solvent contribution (lowest frequency flank in the figures) is higher than for the IF-, the CF- and the AR-spectra. Thus, already from this observation, substantially shorter coherence times for the OK-spectra should be expected. The same argument would not allow to distinguish the effects of the IF-, the CF- and the AR-spectra.
However, the CF-spectra has the shortest high energy tail followed by the IF-spectrum and then the AR-spectrum due to the vibrational mode. Thus, one expects coherence times longest for the CF-spectra.

We apply the numerically exact quasi-adiabatic propagator path-integral (QUAPI) to simulate the real time exciton dynamics, thereby avoiding any approximation within the model.

3. Method

We determine the time dependent statistical operator \( \rho(t) \) of the chromophoric system, consisting of either seven (CF-, IF- and AR-model) or eight (OK-model) energetic sites, using the numerically exact quasi-adiabatic propagator path-integral (QUAPI) [27, 28, 29] scheme. The QUAPI scheme was recently extended to describe quantum systems which are disturbed by multiple separate baths [17], i.e., where each energetic site is subject to its own fluctuations and to describe various environmental initial conditions [30].

For details of this well-established iterative technique, we refer to previous works [27, 28, 29]. In brief, the algorithm is based on a symmetric Trotter splitting of the short-time propagator \( K(t_{k+1}, t_k) \) for the full Hamiltonian into a part depending on the system Hamiltonian and a part involving the bath and the coupling term. The short-time propagator gives the time evolution over a Trotter time slice \( \delta t \). This splitting in discrete time steps is exact in the limit \( \delta t \to 0 \), i.e., when the discrete time evolution goes into the limit of continuous evolution. For any finite time slicing, it introduces a finite Trotter error which has to be eliminated by choosing \( \delta t \) small enough such that convergence is achieved. On the other side, the environmental degrees of freedom generate correlations being non-local in time. For any finite temperature, these correlations decay exponentially fast at asymptotic times, which fixes the associated memory time scale. The QUAPI scheme now defines an object called the reduced density tensor, which lives on this memory time window and establishes an iteration scheme in order to extract the time evolution of this object. All correlations are completely included over the finite memory time \( \tau_{\text{mem}} = K \delta t \) but are neglected for times beyond \( \tau_{\text{mem}} \). We have to increase accordingly the memory parameter \( K \) until convergence is found. The two strategies to achieve convergence, i.e., minimize \( \delta t \) but maximize \( \tau_{\text{mem}} = K \delta t \), are naturally counter-current, but nevertheless convergent results can be obtained in a wide range of parameters, including the cases presented in this work.
4. Results and Discussion

4.1. Population dynamics in the IF-model

At first, we focus on the time-dependent populations of the FMO pigment sites in the Ishizaki-Fleming model with the Hamiltonian (1) and the environmental fluctuation spectra (4) depicted in Fig. 1 by the dark green full line. We choose \( T = 300 \text{K} \) (physiological temperature) and \( T = 77 \text{K} \) (typical experimental temperature). Both pigments, BChl 1 and BChl 6, are oriented towards the baseplate protein and are thus believed to be initially excited (entrance sites) [31] in the natural excitation energy transfer process. However, the dipolar coupling between pigment 1 and 2 is maximal and thus the longest coherent dynamics is expected as population oscillation between these two pigments. Thus, we focus on the initial condition \( \rho_{11}(0) = 1 \) since we are interested in the maximal coherence times in the different FMO models.

In Fig. 2, we show the time-dependent pigment occupation probabilities \( \rho_{jj}(t) \). Our results coincide with results by Ishizaki and Fleming [22]. For both temperatures, \( T = 300 \text{ K} \) and \( T = 77 \text{ K} \), we observe coherent population oscillations between site 1 and 2. After 800 fs half the population is still at these two sites at room temperature but site 3, the exit site, is populated to about \( 1/5 \). At 77 K the occupation of the exit site is almost as large although still about half the population is in site 1.

Coherent dynamics is observed for about 400 fs at room temperature and for about 800 fs at \( T = 77 \text{ K} \).

4.2. Population dynamics in the AR-model

Secondly, we investigate the time-dependent populations of the FMO pigment sites in the Adolphs-Renger model with the Hamiltonian (1) and the environmental fluctuation spectra (6) depicted in Fig. 1 by the violet full line. We choose \( T = 300 \text{K} \) (physiological temperature) and \( T = 77 \text{K} \) (typical experimental temperature) with initial condition \( \rho_{11}(0) = 1 \).

In Fig. 3, we show the time-dependent pigment occupation probabilities \( \rho_{jj}(t) \) (see also [25]). For both temperatures, \( T = 300 \text{ K} \) and \( T = 77 \text{ K} \), we observe coherent population oscillations between site 1 and 2. As in the IF-model, after 800 fs half the population is still at these two sites at room temperature but site 3, the exit site, is populated to about \( 1/4 \) and thus slightly larger than in the IF-model. At 77 K the occupation of the exit site is almost as large but again most of the population is still at site 1.

Coherent dynamics is observed considerably shorter as compared to the IF-model. In detail, coherence is seen for about 250 fs at room temperature and for about 500 fs at \( T = 77 \text{ K} \).
4.3. Population dynamics in the OK-model

Thirdly, we study the time-dependent populations of the FMO pigment sites in the Olbrich-Kleinekathöfer model with the Hamiltonian (2) and the environmental fluctuation spectra for each site as depicted in Fig. 1 by the full lines denoted by a number corresponding to the pigment. We choose $T = 300\text{K}$ (physiological temperature) and $T = 77\text{K}$ (typical experimental temperature) with initial condition $\rho_{11}(0) = 1$.

In Fig. 4, we show the time-dependent pigment occupation probabilities $\rho_{jj}(t)$. For both temperatures, $T = 300\text{K}$ and $T = 77\text{K}$, we observe overdamped dynamics, i.e., no coherent oscillations. In contrast to both previous models more than half the population is still after 800 fs at site 1 and 2 at room temperature and the occupation of the exit site 3 is by far smaller. The population is mainly transferred from site 1 to 2 and then is stuck there. The same holds at 77 K, but surprisingly the occupation of the exit site is larger than at room temperature and actually comparable to values from both previous models.

Coherent dynamics is not observed, neither at room temperature nor at $T = 77\text{K}$.

4.4. Population dynamics in the CF-model

At last we determine the time-dependent populations of the FMO pigment sites in the Choe-Fleming model with the Hamiltonian (1) and the environmental fluctuation spectra (5) depicted in Fig. 1 by the dashed red line. Due to the small cut-off frequency $\omega_{c,\text{CF}} = 50\text{cm}^{-1}$ in the CF-model convergence of the QUAPI scheme can only be achieved by explicitly extrapolating to $\delta t \rightarrow 0$ and $\tau_{\text{mem}} \rightarrow \infty$. Instead of doing so for each population at each give point in time, we use the population $\rho_{11}(t)$ and fit it using

$$f(t) = a_1 \cdot \cos(a_2 t) \exp(-a_3 t) + a_4 \cdot \exp(-a_5 t) + (1 - a_1 - a_4)$$

Seeking convergence for the fit parameters $a_i$ allows us to determine the time-dependent population $\rho_{11}(t)$ at physiological temperature $T = 300\text{K}$ as plotted in Fig. 5. Although we cannot discuss the energy transfer within the FMO complex over the 800 fs, we observe that coherent dynamics is much more pronounced in the CF-model compared to the other models investigated. At room temperature coherence is observed for more than 800 fs.

5. Conclusion

In this work, we present numerically exact results for the electronic energy transfer dynamics based on various models for the Fenna-Matthews-Olson (FMO) molecular aggregate. We determine its single excitation subspace dynamics within an open quantum dynamics approach based on dipolar couplings, site energies and their respective fluctuations from four different models including various degrees of detail, i.e. in the considered environmental fluctuations.
Table 1. Coherence times in [fs] in the various models for $T = 300$ K and $T = 77$ K.

|       | CF | IF | AR | OK |
|-------|----|----|----|----|
| 300 K | 800| 400| 250| 0  |
| 77 K  | 800| 500| 0  | 0  |

The Cho-Fleming model [21] and the Ishizaki-Fleming model [22] both use an Ohmic phenomenological environmental fluctuation spectrum to characterise the site energy fluctuations which originate from solvent fluctuations as well as molecular vibrations. The Adolphs-Renger model [19] adds a single discrete vibrational mode to model the dominant molecular vibration following a detailed analysis of environmental fluctuations by Wendling et al. [20]. All three models were previously used to describe successfully experimental optical data. Nevertheless all three spectra already differ substantially. The Olbrich-Kleinekathöfer model [23, 24] is determined by extensive classical molecular dynamical simulations. It gives different spectra for each site and each spectrum consists of two continuous contributions resulting from solvent fluctuations and up to 13 discrete vibrational modes. Although these spectra are analyzed to fit the optical absorption spectrum of FMO as the other models the OK-model shows much stronger fluctuations than the others.

Investigating the population dynamics in all models we find coherent oscillations for site populations of pigments 1 and 2 in the CF-, IF- and AR-model. In the OK-model we find solely overdamped dynamics. The dynamics of $\rho_{11}(t)$ for all four models in comparison is plotted in Fig. 5. Coherence times are given in Table 1 and are decreasing shifting from the CF-, IF-, AR- to the OK-model. This could be partially expected from a simple one-phonon picture despite the strong non-Markovian charakter of the environmental fluctuations. Experimentally quantum coherence beatings in two-dimensional optical femtosecond spectroscopy were observed on time scales of more than 660 fs at 77 K [3] and about 300 fs at physiological temperatures [4]. Thus we must finally conclude at the present stage that currently the theoretical models can neither support the interpretation of the quantum beatings in the two-dimensional electronic spectra as purely electronic coherence nor can they rule it out.

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References
[1] van Amerongen H, Valkunas L and van Grondelle R 2000 Photosynthetic Excitons (Singapore: World Scientific)
[2] May V and Kühn O 2004 Charge and Energy Transfer Dynamics in Molecular Systems 2nd ed. (Weinheim: Wiley-VCH)
[3] Engel G S, Calhoun T R, Read E L, Ahn T K, Mančal T, Cheng Y-C, Blankenship R E and Fleming G R 2007 Nature 446 782
[4] Panitchayangkoon G, Hayes D, Fransted K A, Caram J R, Harel E, Wen J, Blankenship R E and Engel G S 2010 Proc. Natl. Acad. Sci. USA 107 12766
[5] Fenna R E and Matthews B W 1975 Nature 258 573
[6] Milder M T W, Brüggemann B, van Grondelle R and Herek J L 2010 Photosynth. Res. 104 257
[7] Collini E, Wong C Y, Wilk K E, Curmi P M G, Brumer P and Scholes G D 2010 Nature 463 644
[8] Reineker P 1982 Exciton Dynamics in Molecular Crystals and Aggregates Springer Tracts in Modern Physics, vol. 94 (Berlin: Springer)
[9] Ishizaki A and Fleming G R 2009 J. Chem. Phys. 130 234110
[10] Nalbach P and Thorwart M 2010 J. Chem. Phys. 132 194111
[11] Mohseni M, Rebentrost P, Lloyd S and Aspuru-Guzik A 2008 J. Chem. Phys. 129 174106
[12] Plenio M B and Huelga S F 2008 New J. Phys. 10 113019
[13] Olaya-Castro A, Lee C F, Fassioli F and Johnson N F 2008 Phys. Rev. B 78 085115
[14] Nalbach P, Ishizaki A, Fleming G R and Thorwart M 2011 New J. Phys. 13 063040
[15] Thorwart M, Eckel J, Reina J H, Nalbach P and Weiss S 2009 Chem. Phys. Lett. 478 234
[16] Ishizaki A and Fleming G R 2009 J. Chem. Phys. 130 234111
[17] Nalbach P, Eckel J and Thorwart M 2010 New J. Phys. 12 065043
[18] Chen X and Silbey R J 2010 J. Chem. Phys. 132 204503
[19] Adolphs J and Renger T 2006 Biophys. J. 91 2778
[20] Wendling M, Pullerits T, Przyjalgowski M A, Vulto S I E, Aartsma T J, van Grondelle R and van Amerongen H 2000 J. Phys. Chem. B 104 5825
[21] Cho M, Vaswani H M, Brixner T, Stenger J and Fleming G R 2005 J. Phys. Chem. B 109 10542-56
[22] Ishizaki A and Fleming G R 2009 Proc. Natl. Acad. Sci. 106 17255
[23] Olbrich C, Jansen T L C, Liebers J, Aghtar M, Strümper J, Schulten K, Knoester J and Kleinekathöfer U 2011 J. Chem. Phys. B 115 8609-21
[24] Olbrich C, Strümper J, Schulten K and Kleinekathöfer U 2011 J. Chem. Phys. Lett. 21771-76
[25] Nalbach P, Braun D and Thorwart M 2011 Preprint arXiv:1104.2031v1
[26] Tronrud D E, Wen J, Gay L and Blankenship R E 2009 Photosynth. Res. 100 79-87
[27] Makri N and Makarov D E 1995 J. Chem. Phys. 102 4600
[28] Makri N 1995 J. Math. Phys. 36 2430
[29] Nalbach P and Thorwart M 2009 Phys. Rev. Lett. 103 220401
[30] Nalbach P and Thorwart M 2010 Phys. Rev. B 81 054308
[31] Wen J, Zhang H, Gross M L and Blankenship R E 2009 Proc. Natl. Acad. Sci. 106 6134