Signatures of quantum exciton transport in two-dimensional coherent optical signals of photosynthetic complexes

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Oscillatory spectral dynamics has been reported in two dimensional (2D) coherent electronic spectra of the Fenna-Matthews-Olson (FMO) antenna complex at 77 K [1] and more recently at room temperature [2]. Such oscillations could originate from long-lived exciton quantum coherence and may increase the overall light harvesting efficiency via quantum transport by balancing the coherent and dephasing processes [3,4]. However, quantum beats of exciton coherences are not sufficient for quantum transport to occur. The coherences must be coupled to exciton populations in eigenstate representation in order to influence the energy transport. This coupling would then cause oscillatory energy migration. This regime of dynamics is the quantum transport (QT). If coherences are not coupled to populations, the populations (and energy) migrate according to the Pauli master equation. This is the classical transport (CT) regime.

We present a novel exciton dynamics simulation algorithm, which includes the quantum transport starting with the Frenkel exciton Hamiltonian [5]:

$$\hat{H} = \sum_m \varepsilon_m \hat{B}_m^\dagger \hat{B}_m + \sum_{mn}^{m \neq n} J_{mn} \hat{B}_m^\dagger \hat{B}_n \ , \tag{1}$$

where $\hat{B}_m^\dagger$ ($\hat{B}_m$) are exciton annihilation (creation) Pauli operators, ε_m is the excitation energy on chromophore m and J_{mn} is the inter-chromophore resonant interaction. In standard treatment of quantum dissipation, transport is described by coupling the exciton system to a phonon bath and deriving equations of motion for the reduced density matrix, ρ , which include dephasing and transport [5]:

$$\dot{\rho} = -i[\hat{H}, \rho] + K\rho \quad . \tag{2}$$

The tetradic relaxation superoperator, K is calculated to second order in the system-bath coupling in Markovian limit. This Redfield approach couples populations and coherences, but it only works in a weak coupling and short time regime, otherwise populations may become negative or diverge. An additional secular approximation in the system eigenstate basis must be made, that decouples populations and coherences, but ensures physical dynamics of the density matrix, leading to the CT. We employ an alternative Lindblad form of the relaxation parameters, which guarantees a physically adequate density matrix and includes QT [6]. We then demonstrate the effects of the QT in a two-dimensional photon echo signal.

In the Lindblad theory, the relaxation part of equation 2 is [6]

$$K\rho = \sum_\alpha \hat{V}_\alpha \rho \hat{V}_\alpha^\dagger - \frac{1}{2}\rho \hat{V}_\alpha^\dagger \hat{V}_\alpha - \frac{1}{2}\hat{V}_\alpha^\dagger \hat{V}_\alpha \rho \quad . \tag{3}$$

Here $\hat{V}_\alpha$ represents the coupling of the exciton system to the environment. We define

$$\hat{V}_\alpha = \sum_{mn} u_{mn}^{(\alpha)} \hat{B}_m^\dagger \hat{B}_n \ . \tag{4}$$

The tetradic relaxation matrix K can then be given in terms of Lindblad correlation coefficients [6,7]

$$C_{mn,kl} = \sum_\alpha u_{mn}^{(\alpha)*} u_{kl}^{(\alpha)} \ . \tag{5}$$

We next consider exciton eigenstates. The correlation coefficients measure inter-exciton correlations with respect to system-bath interactions, and in the case of local system-bath coupling are related to spatial exciton overlaps, $\xi_{ee'} = \sum_m |\psi_{em}||\psi_{e'm}|$, where ψ_{em} are single-exciton wavefunctions obtained from the Schrodinger equation of the isolated system. If excitons e and e' do not overlap ($\xi_{ee'} = 0$), they are not correlated and the Lindblad correlation coefficients for eigenstates, $C_{e_4 e_3, e_2 e_1}$, are diagonal: $C_{ee',ee'} \neq 0$ - others vanish. The equation of motion then reduces to the secular Redfield equation. Overlapping excitons ($\xi_{ee'} \neq 0$) are correlated and $C_{e_4 e_3, e_2 e_1}$ has off-diagonal elements. This leads to couplings between density matrix populations and coherences, thus, we have QT regime. Based on these assumptions we have developed a practical algorithm for computing the Lindblad relaxation matrix which uses the Hamiltonian parameters ε_m and J_{mn} of eq. (1), the secular transport and dephasing rates for single-excitons, $K_{ee,e'e'}$, $K_{eg,eg}$ (g is the ground state), and the single exciton wavefunctions spatial overlaps, $\xi_{ee'}$.

We applied our theory to describe exciton quantum dynamics in the reaction center (RC) of a photosynthetic complex photosystem II (PS-II). Its structure is shown in fig 1a. Our simulations include the core chlorophyll pigments: the special pair, P_{D1} and P_{D2} and accessory chlorophylls Acc_{D1} and Acc_{D2}. We assume that pheophytin molecules weakly affect exciton dynamics in the core system. The electronic excitations are described by the Frenkel exciton Hamiltonian as optimized by Raszewski et al [8]. This our model is approximate but is sufficient to demonstrate QT effects in 2D spectroscopy.

We calculated the absorption and two-dimensional photon echo k_I (rephasing) spectrum in (Ω_1, Ω_3) representation, as a function of transport time t_2. The QT affects both linear and 2D signals. The entangled evolution of populations and coherences narrows the absorption spectrum (fig. 1b). This suggests that QT leads to long-living quantum coherences. The simulated 2D signal at room temperature is shown in fig. 1c. We mark the main QT peaks by squares. The spectrum has two main diagonal peaks D1 and D2 (blue – negative, red-positive) corresponding to the lowest-energy excitons e_1 and e_2. The strength of a diagonal peak depends on population of the corresponding exciton (note that in k_I (rephasing) 2D spectrum coherences are mapped on the cross-peak area and do not affect the diagonal peaks). The main crosspeak C1 is

related to population transfer from e_2 to e_1. Other crosspeaks can be associated with specific system resonances: blue-negative are induced by excited state emission and ground state bleaching, while yellow-positive come from excited state absorption.
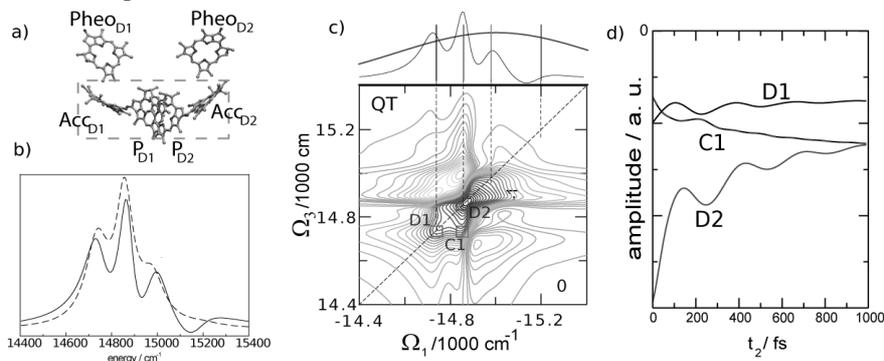
Fig. 1. a) Structure of the RC core. b) absorption spectrum: QT (black solid) and CT (dashed). c) 2D photon echo spectrum: main peaks are marked, absorption (black) as well as 20 fs laser pulse spectrum (red) is shown on top. d) evolution of selected peaks with delay t_2.

The time evolution of the main diagonal peaks (D1, D2) and the crosspeak (C1) with t_2 is displayed in fig. 1d. QT shows strong oscillations of diagonal peaks D1 and D2 lasting for over 600 fs reflecting the non equilibrium oscillating populations (in D1 and D2) and coherences (in C1). The oscillations are correlated to the beating of C1. Corresponding classical transport simulations do not show oscillations of D1 and D2 peaks (not shown).

The population transport in QT regime acquires oscillatory components due to its coupling with coherences. The coherences survive for longer times since they are pumped by non-equilibrium populations. Oscillatory diagonal peaks in photon echo $\boldsymbol{k}_1$ (rephasing) spectrum are thus the major signature of QT.

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