Double-Quantum Coherence Spectroscopy of Chromophore Aggregates

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Abstract. Double-quantum four wave mixing signals contain signatures of exciton correlations and can distinguish between couplings arising from transition- and excited-state charge densities. The former (resonant couplings) determine single-exciton properties, while the latter affect the two-exciton manifold.

Photosynthetic antennas consist of coupled pigments embedded in proteins [1]. Their optical properties are strongly affected by the couplings between transition-charge densities of different pigments. These couplings control single-exciton absorption, exciton delocalization and energy transport.

The Frenkel exciton model is widely used to simulate the optical signals of coupled chromophores [1]. The model is based on the Heitler-London approximation, where the wavefunction of the aggregate is constructed out of direct products of wavefunctions of isolated molecules. The Hamiltonian of a complex in this basis reads [1-3]

$$\hat{H}^{(e)} = \sum_m \varepsilon_m \hat{B}_m^\dagger \hat{B}_m + \sum_{m,n}^{m \neq n} J_{mn} \hat{B}_m^\dagger \hat{B}_n + \frac{1}{2} \sum_{m,n}^{m \neq n} K_{mn} \hat{B}_m^\dagger \hat{B}_n^\dagger \hat{B}_m \hat{B}_n, \tag{1}$$

where $\hat{B}_m^\dagger$ is the exciton creation ($\hat{B}_m$ - annihilation) Pauli operators of two-level systems, ε_m is the excitation energy of chromophore m, J_{mn} is the resonant excitonic coupling between transition charge densities of two chromophores and K_{mn} coupling is given by Coulomb interaction between excited state charge densities of two chromophores. In this basis the Hamiltonian is block-diagonal with single-, double-, and higher-exciton manifolds. In the single-exciton manifold, the diagonal elements of the Hamiltonian are the transition energies of individual molecules, ε_m and the off diagonal elements reflect inter-molecular interactions J. Both types of couplings affect the double-exciton manifold. A state with two chromophores m and n excited, (mn), is characterized by the diagonal element, its energy, $\varepsilon_m + \varepsilon_n + K_{mn}$. The off-diagonal elements are induced by J coupling. The J and K couplings thus have different physical significance: J couplings are all off-diagonal elements of the Hamiltonian, mixing exciton states; K couplings represent the shifts of the double-exciton states (also known as bi-exciton binding energies).

In a dipole approximation for the charge densities the couplings are given by:

$$J_{mn} = \frac{1}{4\pi\varepsilon\varepsilon_0} \left(\frac{\boldsymbol{\mu}_m \cdot \boldsymbol{\mu}_n}{|\boldsymbol{R}_{mn}|^3} - 3 \frac{(\boldsymbol{\mu}_m \cdot \boldsymbol{R}_{mn})(\boldsymbol{\mu}_n \cdot \boldsymbol{R}_{mn})}{|\boldsymbol{R}_{mn}|^5} \right), \tag{2}$$

$$K_{mn} = \frac{1}{4\pi\varepsilon\varepsilon_0} \left(\frac{\boldsymbol{d}_m \cdot \boldsymbol{d}_n}{|\boldsymbol{R}_{mn}|^3} - 3 \frac{(\boldsymbol{d}_m \cdot \boldsymbol{R}_{mn})(\boldsymbol{d}_n \cdot \boldsymbol{R}_{mn})}{|\boldsymbol{R}_{mn}|^5} \right), \tag{3}$$

where $\boldsymbol{\mu}_n$ is a transition dipole moment of chromophore n and $\boldsymbol{d}_n$ a corresponding dipole moment in the excited state. Most simulations only include the J couplings: the

permanent dipole moments are neglected. However, electronic structure calculations of Bacteriochlorophyll molecules (BChls), which are the main pigments in photosynthetic complexes, show that their excited state dipole is comparable with the transition dipole [4]. Additional K couplings then affect double-exciton energies: they dominate for pigments with very different energies (like in heteronuclear NMR), where the J couplings are not effective.

To probe the K couplings we propose to use the double-quantum coherence technique $\boldsymbol{k}_{III} = \boldsymbol{k}_1 + \boldsymbol{k}_2 - \boldsymbol{k}_3$ (Fig. 1C) [5,8]. The signal is described by two Feynman diagrams (Fig. 1D). Both involve excited state absorption and monitor the double-exciton resonances during delay t_2; during t_3 single- and double-exciton resonances are mixed. The two diagrams have opposite signs and cancel at $t_3 = 0$. The signal is thus generated by exciton correlations when the double-exciton energies are not additive, i. e. $\varepsilon_f \neq \varepsilon_e + \varepsilon'_e$. Fourier transform with respect to $t_2 \to \Omega_2$ and $t_3 \to \Omega_3$ generates the two-dimensional signal, directly displaying double-exciton resonances along Ω_2. Since during t_1 the evolution of single-exciton coherences is equivalent to phase-rotation, we set $t_1 = 0$. Simulations were based on the response function formalism (Spectron code) as described in ref [6].
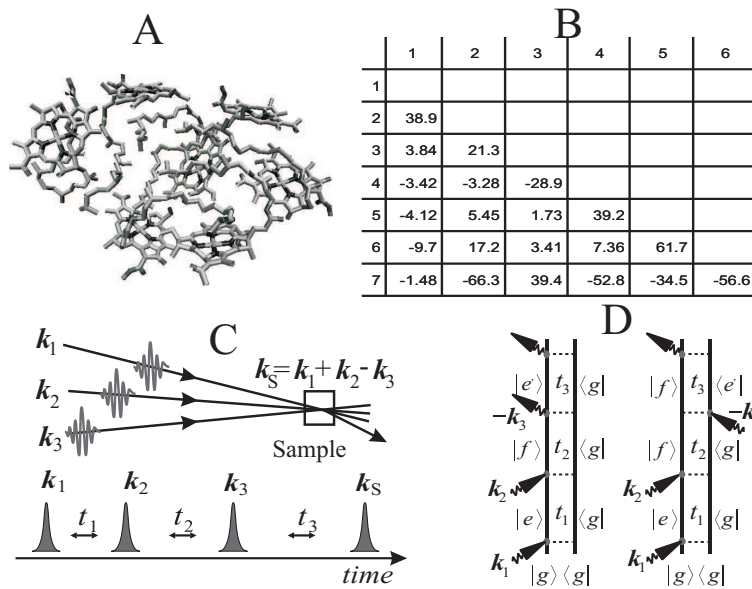

	1	2	3	4	5	6
1						
2	38.9					
3	3.84	21.3				
4	-3.42	-3.28	-28.9			
5	-4.12	5.45	1.73	39.2		
6	-9.7	17.2	3.41	7.36	61.7	
7	-1.48	-66.3	39.4	-52.8	-34.5	-56.6

Fig. 1. A: configuration of BChls in photosynthetic Fenna-Matthews-Olson complex; B: estimated $K = K_0$ couplings of the complex in [cm^{-1}]; C: scheme of the coherent double-quantum technique; D: its Feinman diagrams of the contributing Liouville space pathways.

We apply this technique to the Fenna-Matthews-Olson (FMO) complex of a green sulfur bacteria [1]. This is a trimer of small noninteracting identical subunits, each consisting of seven BChls (see Fig. 1A). A single unit is usually sufficient for simulations of optical signals. The broad absorption band of the complex extends from 11800 cm^{-1} to 12800 cm^{-1}. We use the single-exciton Hamiltonian of ref. [7]. K couplings were calculated by Eq. (3) using dipole moments obtained from charge distributions of ref. [4]; the permanent dipole of a BChl molecule is perpendicular to its N atoms

plane, pointing towards Mg; the dipole amplitude was set to 4.9 D. The calculated K couplings (a set K_0) are given in Fig. 1B.
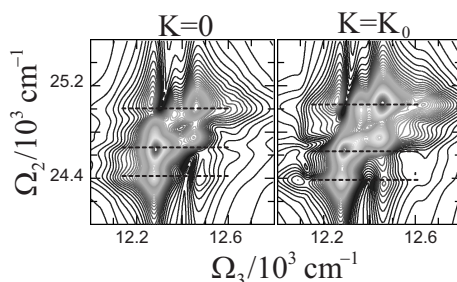

Fig. 2. Simulation results of double-quantum signal of Fenna-Matthews-Olson complex using $K = 0$ and $K = K_0$ as of Fig. 1B.

Fig. 2 compares the two-dimensional signal for $K = K_0$ (Fig. 1B *right*) and for K switched off (*left*). Three main double-exciton resonances along Ω_2 can be observed at $K = 0$ as marked by dashed lines. The peak pattern along both Ω_2 and Ω_3 reveals and elaborate exciton resonances. The $K = K_0$ simulations show a similar peak pattern, while some double-exciton signatures are now blue-shifted as can be seen from the dashed lines. Peak intensities change significantly for $\Omega_3 > 12400 cm^{-1}$.

Recently performed two dimensional photon echo experiments revealed single-exciton dynamics and relaxation pathways [7] This dynamics is governed by the J couplings and is not affected by K. Our simulations address a different class of phenomena, by using a different technique which shows a high sensitivity to K couplings, and thus provides a direct probe of excited state permanent dipole moments. Excited state dipole moments can be extracted by comparing the clear and well-resolved peak pattern with experiment. Both intermolecular J and K couplings can be obtained using a combination of different two-dimensional techniques: $\mathbf{k}_I = -\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3$ is most sensitive to J couplings [7], whereas the presented double-quantum technique is a direct probe of K [5]. By combining these techniques the entire exciton Hamiltonian can be derived from experiment.

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