

Emission Spectra of LH4 Complex: Full Hamiltonian Model

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Abstract— To be able to create an ideal energy source in the future - an artificial photosynthetic complex, the first step is a detailed understanding of the function of photosynthetic complexes in living organisms. Knowledge of the microscopic structure of some photosynthetic systems and their function invokes during last twenty years long and intensive investigation of many theoretical and experimental laboratories. Photosynthesis starts with the absorption of a solar photon by one of the light-harvesting (LH) pigment-protein complexes and transferring the excitation energy to the reaction center where a charge separation is initiated. The geometric structure of such LH complexes is known in great detail, e.g. for the LH2 and LH4 complexes of purple bacteria. Absorption and steady state fluorescence spectra of exciton states for ring molecular system, which can model the peripheral cyclic antenna unit LH4 of the bacterial photosystem from purple bacteria are presented. The cumulant-expansion method of Mukamel et al. is used for the calculation of spectral responses of the system with exciton-phonon coupling. Dynamic disorder, interaction with a bath, in Markovian approximation simultaneously with uncorrelated static disorder in local excitation energies are taking into account in our simulations. We compare calculated absorption and steady state fluorescence spectra for LH4 ring obtained within the full Hamiltonian model with our previous results calculated within the nearest neighbour approximation model. All calculations were done in software package *Mathematica*.

Keywords—LH4, absorption and fluorescence spectrum, static and dynamic disorder, exciton states, *Mathematica*

I. INTRODUCTION

Solar energy is the primary source of energy on Earth. Its transformation provides the chemical energy ensuring the development of the vast majority of living beings. The effective recovery, processing and storage of solar energy is a major challenge but this energy would

be a perfect answer to current energy needs. Photovoltaic systems can harvest solar energy and transform it into electricity. But this latter form of energy has the disadvantage of being difficult to store.

The natural chemical processes mastered the solar energy through the process of photosynthesis. In photosynthesis, solar energy is converted to chemical energy. The chemical energy is stored in the form of glucose (sugar). Photosynthesis occurs in two stages. These stages are called the light reactions and the dark reactions. The light reactions convert light into energy (ATP and NADHP) and the dark reactions use the energy and carbon dioxide to produce sugar. In the process of photosynthesis (in plants, bacteria, and blue-green algae), solar energy is used to split water and produce oxygen molecules, protons and electrons. The perfect solution of above mentioned problem would be to get the energy produced by photosynthesis in plants or bacteria directly. Or we should be able to copy this process that billions of years of evolution have perfected in order to convert solar energy into chemical energy as hydrogen, which is easier to store than electricity. To be able to copy the process of photosynthesis it is necessary to know in great detail the structure and properties of organisms in which photosynthesis takes place.

Photosynthesis starts with the absorption of a solar photon by one of the light-harvesting pigment-protein complexes and transferring the excitation energy to the photosynthetic reaction center, where a charge separation is initiated. These initial ultrafast events have been extensively investigated. Knowledge of the microscopic structure of some photosynthetic systems, e.g., photosynthetic systems of purple bacteria, invokes during last twenty years long and intensive effort of many theoretical and experimental laboratories. No final conclusion about the character of excited states, energy transfer, etc. can be generally drawn.

A wide variety of pigment-protein complex are used as light-harvesting (LH) antennas to intercept light to meet the demand for energy of photosynthetic organisms. Each type of antenna complex has its own specific absorption spectrum, thereby optimizing the efficiency of light absorption depending on environmental conditions. Light energy that is absorbed by an LH antenna is then rapidly and efficiently transferred to a reaction center (RC), where it is used to drive a transmembrane charge separation. At this point the light energy has been trapped

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and the chemistry begins [1]. The number of antenna complexes per RC depends on light intensity in which the bacterium is grown. When grown under high-intensity conditions, less antenna complexes are required to let the RC operate at a maximal turnover rate. However, at low intensity conditions the ratio of antenna complexes to RC increases significantly [2].

The antenna systems of photosynthetic units from purple bacteria are formed by ring units LH1, LH2, LH3, and LH4. The geometric structure is known in great detail from X-ray crystallography. The general organization of above mentioned light-harvesting complexes is the same: identical subunits are repeated cyclically in such a way that a ring-shaped structure is formed. However the symmetries of these rings are different.

The core antenna LH1 contained in purple bacteria such as *Rhodospseudomonas palustris* consists of approximately 16 structural subunits in which two bacteriochlorophyll *a* (BChl-*a*) molecules are noncovalently attached to pairs of transmembrane polypeptides. These subunits are arranged in a ringlike structure which surround the RC. In the near infrared LH1 absorbs at 870 nm. More about crystal structure of this core complex is possible to find e.g. in [3].

Crystal structure of LH2 complex contained in purple bacterium *Rhodospseudomonas acidophila* in high resolution was first described by McDermott et al. [4] in 1995, then further e.g. by Papiz et al. [5] in 2003. The bacteriochlorophyll molecules are organized in two concentric rings. One ring features a group of nine well-separated BChl molecules (B800) with absorption band at about 800 nm. The other ring consists of eighteen closely packed BChl molecules (B850) absorbing around 850 nm. LH2 complexes from other purple bacteria have analogous ring structure.

Some bacteria express also other types of complexes such as the B800-820 LH3 complex (*Rhodospseudomonas acidophila* strain 7050) or the LH4 complex (*Rhodospseudomonas palustris*). Details of crystal structure for LH3 complex are stated e.g. in [6] and for LH4 in [2]. LH3 like LH2 is usually nonameric but LH4 is octameric. While the B850 dipole moments in LH2 ring have tangential arrangement, in the LH4 ring they are oriented more radially. Mutual interactions of the nearest neighbour BChls in LH4 are approximately two times smaller in comparison with LH2 and have opposite sign. The other difference is the presence of an additional BChl ring in LH4 complex.

The intermolecular distances under 1 nm determine strong exciton couplings between corresponding pigments. Due to the strong interaction between BChl molecules, an extended Frenkel exciton states model is considered in our theoretical approach. Despite intensive study of bacterial antenna systems, e.g. [2], [4], [5], [7], the precise role of the protein moiety for governing the

dynamics of the excited states is still under debate. At room temperature the solvent and protein environment fluctuate with characteristic time scales ranging from femtoseconds to nanoseconds. The simplest approach is to substitute fast fluctuations by dynamic disorder and slow fluctuation by static disorder.

In our previous papers we presented results of simulations doing within the nearest neighbour approximation model. In several steps we extended the former investigations of static disorder effect on the anisotropy of fluorescence made by Kumble and Hochstrasser [8] and Nagarajan et al. [9]–[11] for LH2 rings. After studying the influence of diagonal dynamic disorder for simple systems (dimer, trimer) [12]–[14], we added this effect into our model of LH2 ring by using a quantum master equation in Markovian and non-Markovian limits [15]–[17].

We also studied influence of four types of uncorrelated static disorder [18], [19] (Gaussian disorder in local excitation energies, Gaussian disorder in transfer integrals, Gaussian disorder in radial positions of BChls and Gaussian disorder in angular positions of BChls on the ring). Influence of correlated static disorder, namely an elliptical deformation of the ring, was also taken into account [20]. The investigation of the time dependence of fluorescence anisotropy for the LH4 ring with different types of uncorrelated static disorder [21]–[23] was also done.

Recently we have focused on the modeling of absorption and steady state fluorescence spectra. Our results for LH2 and LH4 rings within the nearest neighbour Hamiltonian model have been presented in [24]–[31]. Very recently we have started to work within full Hamiltonian model and the results for LH2 complex have been presented in [32].

Main goal of the present paper is the comparison of the results for LH4 ring calculated within full Hamiltonian model with the previous results calculated within the nearest neighbour approximation model. In our simulations we have taken into account uncorrelated diagonal static disorder in local excitation energies simultaneously with diagonal dynamic disorder (interaction with phonon bath) in Markovian approximation.

Present paper is the extension of our contribution [33] presented on WSEAS conference ECC'13. The rest of the paper is structured as follows. Section II. introduces the ring model with the uncorrelated static disorder and dynamic disorder and the cumulant expansion method, which is used for the calculation of spectral responses of the system with exciton-phonon coupling. In Section III. the computational point of view for our calculations is discussed. The graphically presented results of our simulations and used units and parameters could be found in Section IV. Finally in Section V. some conclusions are drawn.

II. PHYSICAL MODEL

We assume that only one excitation is present on the ring after an impulsive excitation. The Hamiltonian of an exciton in the ideal ring coupled to a bath of harmonic oscillators reads

$$H^0 = H_{\text{ex}}^0 + H_{\text{ph}} + H_{\text{ex-ph}}. \quad (1)$$

Here the first term,

$$H_{\text{ex}}^0 = \sum_{m,n(m \neq n)} J_{mn} a_m^\dagger a_n, \quad (2)$$

corresponds to an exciton, e.g. the system without any disorder. The operator $a_m^\dagger$ (a_m) creates (annihilates) an exciton at site m , J_{mn} (for $m \neq n$) is the so-called transfer integral between sites m and n . The second term,

$$H_{\text{ph}} = \sum_q \hbar \omega_q b_q^\dagger b_q, \quad (3)$$

represents phonon bath in harmonic approximation (the phonon creation and annihilation operators are denoted by $b_q^\dagger$ and b_{-q} , respectively). Last term in (1),

$$H_{\text{ex-ph}} = \frac{1}{\sqrt{N}} \sum_m \sum_q G_q^m \hbar \omega_q a_m^\dagger a_m (b_q^\dagger + b_q), \quad (4)$$

describes exciton-phonon interaction which is assumed to be site-diagonal and linear in the bath coordinates (the term G_q^m denotes the exciton-phonon coupling constant).

Inside one ring the pure exciton Hamiltonian can be diagonalized using the wave vector representation with corresponding delocalized "Bloch" states α and energies E_α . Considering homogeneous case with only the nearest neighbour transfer matrix elements

$$J_{mn} = J_0(\delta_{m,n+1} + \delta_{m,n-1}) \quad (5)$$

and using Fourier transformed excitonic operators (Bloch representation)

$$a_\alpha = \sum_n a_n e^{i\alpha n}, \quad (6)$$

where

$$\alpha = \frac{2\pi}{N} l, l = 0, \pm 1, \dots, \pm \frac{N}{2}, \quad (7)$$

the simplest exciton Hamiltonian in α - representation reads

$$H_{\text{ex}}^0 = \sum_\alpha E_\alpha a_\alpha^\dagger a_\alpha, \quad (8)$$

with

$$E_\alpha = -2J_0 \cos \alpha \quad (9)$$

(see Fig. 1 - left column). In case of the full Hamiltonian model (dipole-dipole approximation), energetic band structure slightly differs (Fig. 1 - right column). Differences of energies in lower part of the band are smaller and in upper part of the band are larger in comparison with the nearest neighbour approximation model.

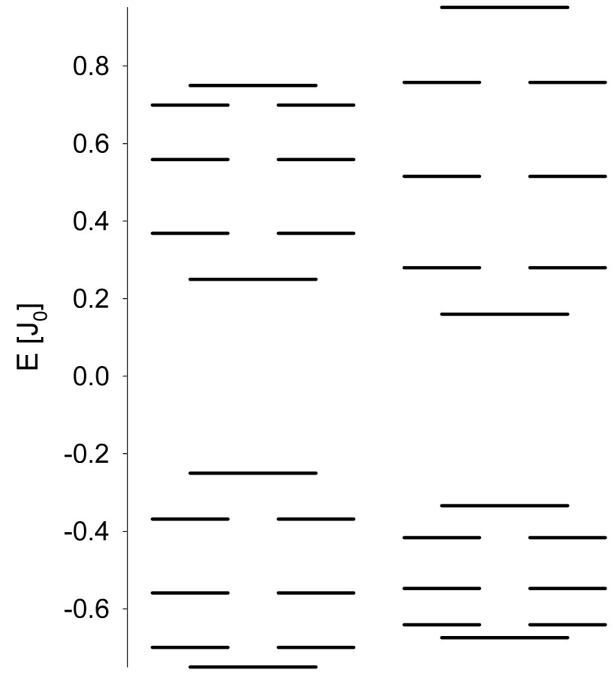


Fig. 1. Energetic band structure of the ring from LH4 (left column - the nearest neighbour approximation model, right column - full Hamiltonian model).

Influence of uncorrelated static disorder is modeled by the local excitation energy fluctuations $\delta\varepsilon_n$ with Gaussian distribution and standard deviation Δ

$$H_s = \sum_n \delta\varepsilon_n a_n^\dagger a_n. \quad (10)$$

The Hamiltonian H_s of the uncorrelated static disorder adds to the Hamiltonian H_{ex}^0 .

The cumulant-expansion method of Mukamel et al. [34], [35] is used for the calculation of spectral responses of the system with exciton-phonon coupling. Absorption $OD(\omega)$ and steady-state fluorescence $FL(\omega)$ spectrum can be expressed as

$$OD(\omega) = \omega \sum_\alpha d_\alpha^2 \times \text{Re} \int_0^\infty dt e^{i(\omega - \omega_\alpha)t - g_{\alpha\alpha\alpha\alpha}(t) - R_{\alpha\alpha\alpha\alpha}t}, \quad (11)$$

$$FL(\omega) = \omega \sum_\alpha P_\alpha d_\alpha^2 \times \text{Re} \int_0^\infty dt e^{i(\omega - \omega_\alpha)t + i\lambda_{\alpha\alpha\alpha\alpha}t - g_{\alpha\alpha\alpha\alpha}^*(t) - R_{\alpha\alpha\alpha\alpha}t}. \quad (12)$$

Here

$$\vec{d}_\alpha = \sum_n c_n^\alpha \vec{d}_n \quad (13)$$

is the transition dipole moment of eigenstate α , c_n^α are the expansion coefficients of the eigenstate α in site representation and P_α is the steady state population of the

eigenstate α . The inverse lifetime of exciton state $R_{\alpha\alpha\alpha}$ is given by the elements of Redfield tensor $R_{\alpha\beta\gamma\delta}$ [36]. It is a sum of the relaxation rates between exciton states,

$$R_{\alpha\alpha\alpha} = - \sum_{\beta \neq \alpha} R_{\beta\beta\alpha\alpha}. \quad (14)$$

The g-function and λ -values in (12) are given by

$$g_{\alpha\beta\gamma\delta} = - \int_{-\infty}^{\infty} \frac{d\omega}{2\pi\omega^2} C_{\alpha\beta\gamma\delta}(\omega) \times \left[\coth \frac{\omega}{2k_B T} (\cos \omega t - 1) - i(\sin \omega t - \omega t) \right], \quad (15)$$

$$\lambda_{\alpha\beta\gamma\delta} = - \lim_{t \rightarrow \infty} \frac{d}{dt} \text{Im}\{g_{\alpha\beta\gamma\delta}(t)\} = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi\omega} C_{\alpha\beta\gamma\delta}(\omega). \quad (16)$$

The matrix of the spectral densities $C_{\alpha\beta\gamma\delta}(\omega)$ in the eigenstate (exciton) representation reflects one-exciton states coupling to the manifold of nuclear modes. In what follows only a diagonal exciton phonon interaction in site representation is used (see (1)), i.e., only fluctuations of the pigment site energies are assumed and the restriction to the completely uncorrelated dynamical disorder is applied.

In such case each site (i.e. each chromophore) has its own bath completely uncoupled from the baths of the

other sites. Furthermore it is assumed that these baths have identical properties [16], [37], [38]

$$C_{mnmm'n'}(\omega) = \delta_{mn}\delta_{mm'}\delta_{nn'}C(\omega). \quad (17)$$

After transformation to the exciton representation we have

$$C_{\alpha\beta\gamma\delta}(\omega) = \sum_n c_n^\alpha c_n^\beta c_n^\gamma c_n^\delta C(\omega). \quad (18)$$

Various models of spectral density of the bath are used in literature [39]–[41]. In our present investigation we have used the model of Kühn and May [40]

$$C(\omega) = \Theta(\omega) j_0 \frac{\omega^2}{2\omega_c^3} e^{-\omega/\omega_c} \quad (19)$$

which has its maximum at $2\omega_c$.

III. COMPUTATIONAL POINT OF VIEW

To have steady state fluorescence spectrum $FL(\omega)$ and absorption spectrum $OD(\omega)$, it is necessary to calculate single ring $FL(\omega)$ spectrum and $OD(\omega)$ spectrum for large number of different static disorder realizations created by random number generator. Finally these results have to be averaged over all realizations of static disorder. Time evolution of exciton density matrix has to be calculate also for each realization of static disorder. That is why it was necessary to put through numerical integrations for each realization of static disorder (see (12)).

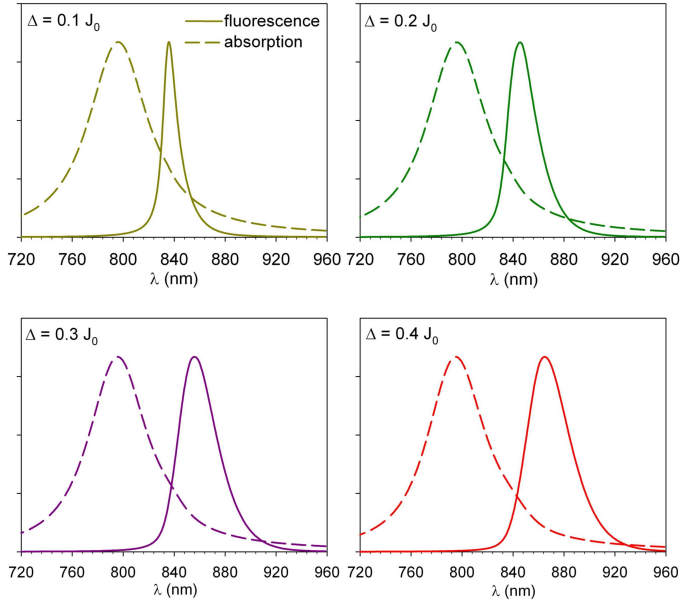


Fig. 2. Calculated fluorescence (FL) and absorption (OD) spectra of LH4 ring (full Hamiltonian model) averaged over 2000 realizations of static disorder in local excitation energies $\delta\varepsilon_n$ (low temperature $kT = 0.1 J_0$, four strengths $\Delta = 0.1, 0.2, 0.3, 0.4 J_0$).

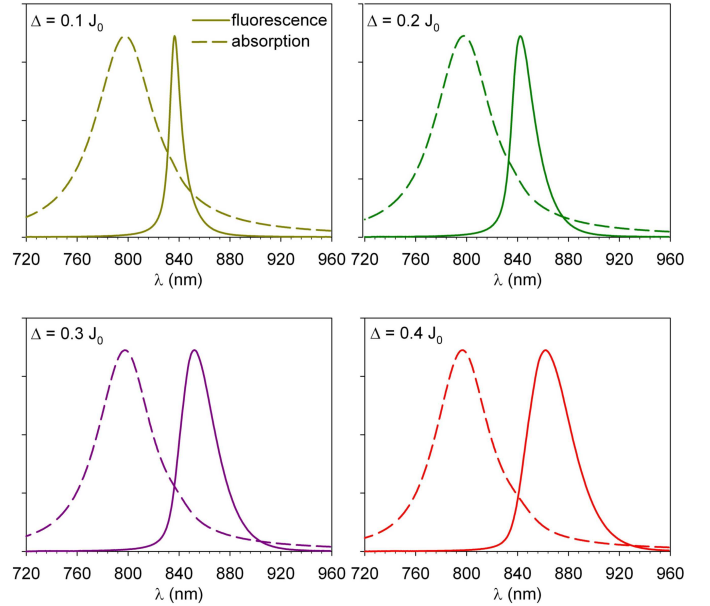


Fig. 3. Calculated fluorescence (FL) and absorption (OD) spectra of LH4 ring (the nearest neighbour approximation model) averaged over 2000 realizations of static disorder in local excitation energies $\delta\varepsilon_n$ (low temperature $kT = 0.1 J_0$, four strengths $\Delta = 0.1, 0.2, 0.3, 0.4 J_0$).

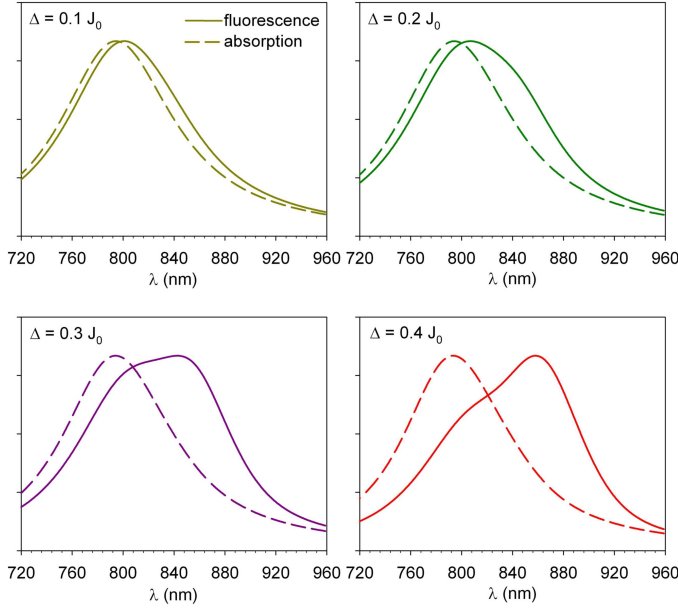


Fig. 4. Calculated fluorescence (FL) and absorption (OD) spectra of LH4 ring (full Hamiltonian model) averaged over 2000 realizations of static disorder in local excitation energies $\delta\epsilon_n$ (room temperature $kT = 0.5 J_0$, four strengths $\Delta = 0.1, 0.2, 0.3, 0.4 J_0$).

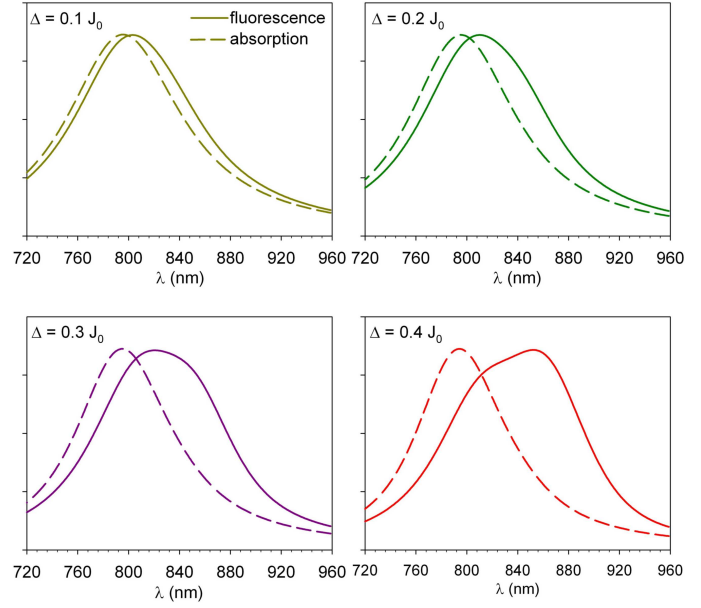


Fig. 5. Calculated fluorescence (FL) and absorption (OD) spectra of LH4 ring (the nearest neighbour approximation model) averaged over 2000 realizations of static disorder in local excitation energies $\delta\epsilon_n$ (room temperature $kT = 0.5 J_0$, four strengths $\Delta = 0.1, 0.2, 0.3, 0.4 J_0$).

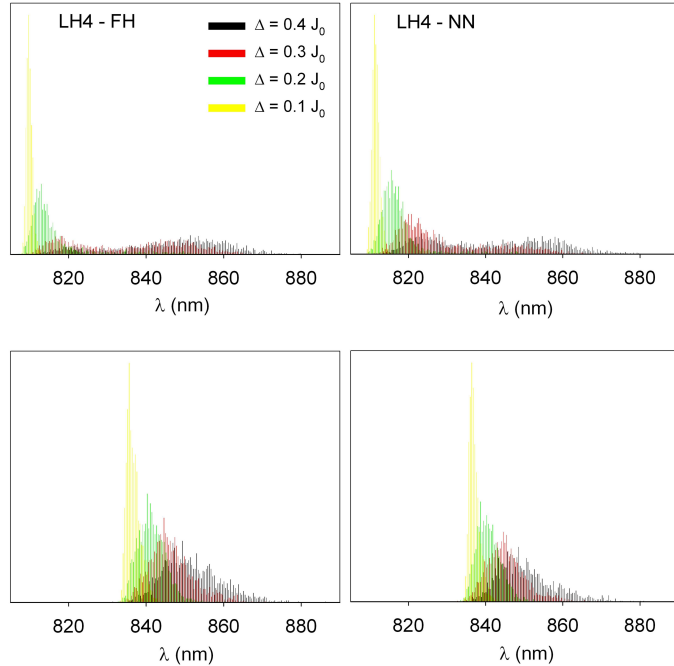


Fig. 6. Peak position distributions of calculated steady-state single ring fluorescence (FL) spectra of LH4 ring at room temperature $kT = 0.5 J_0$ (first row) and low one $kT = 0.1 J_0$ (second row) for 2000 realizations of Gaussian uncorrelated static disorder in local excitation energies $\delta\epsilon_n$ – four strengths $\Delta = 0.1, 0.2, 0.3, 0.4 J_0$ (full Hamiltonian model – left column; nearest neighbour approximation model – right column).

Mathematica [42] was used. This package is very convenient not only for symbolic calculations [43] which are needed for expression of all required quantities, but it can be used also for numerical ones [44]. That is why the software package *Mathematica* was used by us as for symbolic calculations as for numerical integrations and also for final averaging of results over all realizations of static disorder.

IV. RESULTS

Above mentioned type of uncorrelated static disorder, e.g. fluctuations of local excitation energies, has been taken into account in our simulations simultaneously with diagonal dynamic disorder in Markovian approximation. Resulting absorption $OD(\omega)$ and steady state fluorescence $FL(\omega)$ spectra for LH4 ring obtained within the full Hamiltonian model are compared with our previous results calculated within the nearest neighbour approximation model.

Dimensionless energies normalized to the transfer integral J_0 ($J_0 = J_{12}$ in LH2 ring) have been used. Estimation of J_0 varies in literature between 250 cm^{-1} and 400 cm^{-1} . The transfer integrals in LH4 ring have opposite sign in comparison with LH2 ring and differ also in their absolute values. Furthermore, stronger dimerization can be found in LH4 in comparison with LH2 [2]. Therefore we have taken the values of transfer integrals in LH4 ring as follows: $J_{12}^{LH4} = -0.5 J_{12}^{LH2} = -0.5 J_0$, $J_{23}^{LH4} = 0.5 J_{12}^{LH4} = -0.25 J_0$. All our simulations of

For the most of our calculations the software package

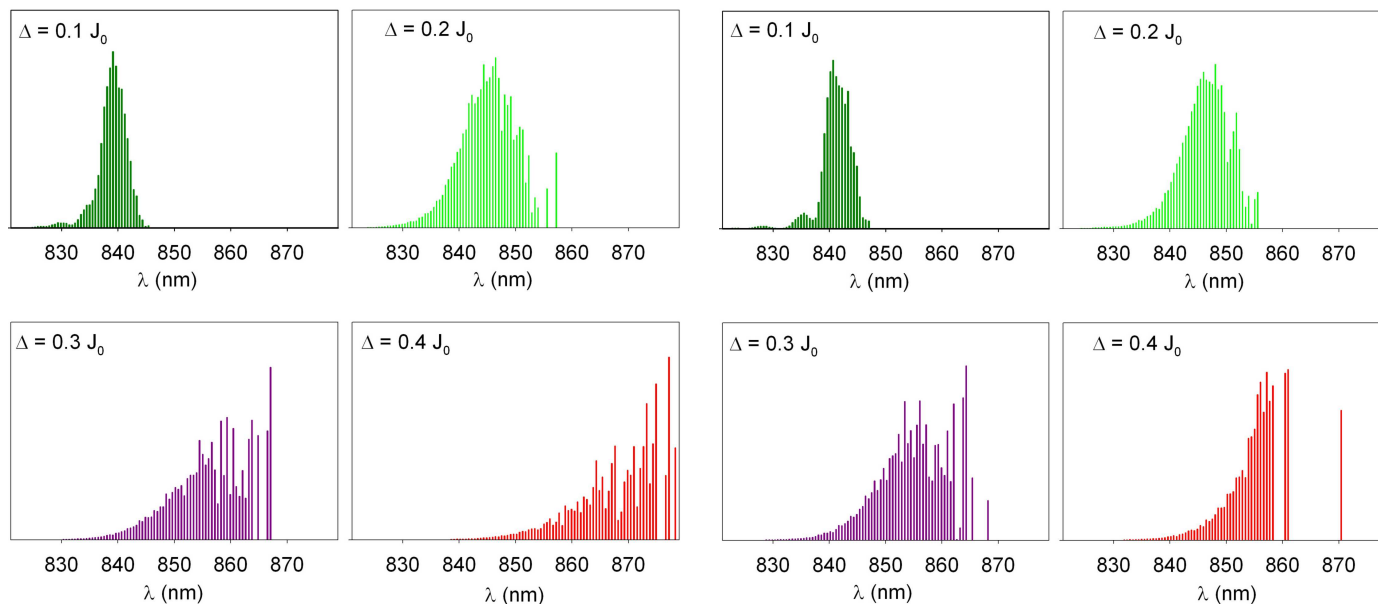


Fig. 7. Distributions of the quantity $\sum_{\alpha} P_{\alpha} d_{\alpha}^2$ as a function of wavelength λ in room temperature $kT = 0.5 J_0$ for four strengths of Gaussian uncorrelated static disorder in local excitation energies (full Hamiltonian model).

LH4 spectra have been done with the same values of $J_0 = 370 \text{ cm}^{-1}$ and unperturbed transition energy from the ground state $E_0 = 12280 \text{ cm}^{-1}$, that we found for LH2 ring (the nearest neighbour approximation model) [24].

The model of spectral density of Kühn and May [40] has been used in our simulations. In agreement with our previous results [18], [23] we have used $j_0 = 0.4 J_0$ and $\omega_c = 0.212 J_0$ (see (19)). The strengths of uncorrelated static disorder has been taken in agreement with [19]: $\Delta = 0.1, 0.2, 0.3, 0.4 J_0$.

Resulting absorption spectra $OD(\omega)$ and steady state fluorescence spectra $FL(\omega)$ averaged over 2000 realizations of static disorder in local excitation energies $\delta\epsilon_n$ for full Hamiltonian model can be seen in Figure 2 (low temperature $kT = 0.1 J_0$) and in Figure 4 (room temperature $kT = 0.5 J_0$). The same but for the nearest neighbour approximation model can be seen in Figure 3 (low temperature $kT = 0.1 J_0$) and in Figure 5 (room temperature $kT = 0.5 J_0$).

Peak position distributions of steady state fluorescence spectrum for single LH4 ring depend on the realization of static disorder and also on the temperature. The results of our simulations for both models (the nearest neighbour model and full Hamiltonian model) are presented in Figure 6.

For clarification of fluorescence line splitting appearance in case of full Hamiltonian model, the quantity $\sum_{\alpha} P_{\alpha} d_{\alpha}^2$ (P_{α} is the steady state population of the eigenstate α , d_{α}^2 is the dipole strength of eigenstate α , see

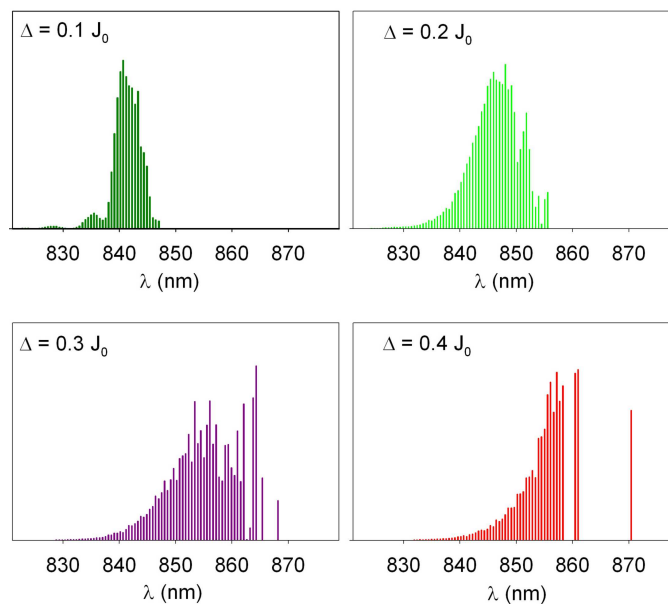


Fig. 8. Distributions of the quantity $\sum_{\alpha} P_{\alpha} d_{\alpha}^2$ as a function of wavelength λ in room temperature $kT = 0.5 J_0$ for four strengths of Gaussian uncorrelated static disorder in local excitation energies (nearest neighbour approximation model).

12) as a function of wavelength λ has been investigated. The distributions of this quantity for room temperature $kT = 0.5 J_0$ and 2000 realizations of static disorder are presented in Figure 7 (full Hamiltonian model) and in Figure 8 (the nearest neighbour approximation model).

V. CONCLUSIONS

Software package *Mathematica* has been found by us very useful for the simulations of the molecular ring spectra. From the comparison of our simulated FL and OD spectra for LH4 ring within full Hamiltonian (FH) model (Figures 2, 4) with our previous results calculated within the nearest neighbour approximation (NN) model (Figures 3, 5) we can make following conclusions.

No significant differences between the results calculated within FH model and NN one can be seen in case of low temperature $kT = 0.1 J_0$.

On the other hand the resulting spectra differ in case of room temperature $kT = 0.5 J_0$. The absorption spectra $OD(\omega)$ for FH model in case of room temperature $kT = 0.5 J_0$ are slightly wider in comparison with NN model.

For both models we can see indication of fluorescence spectra splitting especially for higher strengths of static disorder Δ . In case of FH model the splitting appears already for $\Delta = 0.2 J_0$, while in case of NN model the splitting is visible just for $\Delta = 0.3 J_0$. This effect is caused by different energetic band structures for both models (see Fig. 1). The optically active states in case of LH4 complex are the upper states $\alpha = \pm 7$ (unlike LH2 with lower optically active states $\alpha = \pm 1$). In case

of room temperature $kT = 0.5 J_0$ upper states are more probably occupied and that is why the splitting can be seen only in this case (unlike LH2, where the splitting is visible only in case of low temperature $kT = 0.1 J_0$ and FH model).

As concern the peak position distributions (see Figure 6), we can conclude that the distributions are wider for full Hamiltonian model in comparison with the nearest neighbour approximation model. The distributions of the quantity $\sum_{\alpha} P_{\alpha} d_{\alpha}^2$ presented in Figure 7 and Figure 8 are shifted to higher wavelengths in case of full Hamiltonian model in comparison with the nearest neighbour approximation model.

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