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Reprint of "The effect of site-specific spectral densities on the high-dimensional exciton-vibrational dynamics in the FMO complex" ☆

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ABSTRACT

The coupled exciton-vibrational dynamics of a three-site model of the FMO complex is investigated using the Multi-layer Multi-configuration Time-dependent Hartree (ML-MCTDH) approach. Emphasis is put on the effect of the spectral density on the exciton state populations as well as on the vibrational and vibronic non-equilibrium excitations. Models which use either a single or site-specific spectral densities are contrasted to a spectral density adapted from experiment. For the transfer efficiency, the total integrated Huang-Rhys factor is found to be more important than details of the spectral distributions. However, the latter are relevant for the obtained non-equilibrium vibrational and vibronic distributions and thus influence the actual pattern of population relaxation.

1. Introduction

The spectral density (SD) is central to the theory of dissipative quantum dynamics [1]. It describes the coupling of the relevant system to particular modes of the environmental bath. There is a number of model SDs (Ohmic, Debye-Drude or Multi-Mode Brownian Oscillator) [2–4], whose general influence on the dynamics of model systems has been extensively studied. The actual definition of the SD is linked to an assumption concerning the system-bath coupling. For vibrational dynamics, the Caldeira-Leggett model, i.e. a bilinear form in system and bath coordinates, is typically assumed, although its applicability in general has recently been challenged [5]. For problems involving an electronic excitation coupled to nuclear dynamics, the Huang-Rhys (HR) model is commonly applied. It assumes that vibrational degrees of freedom (DOFs) are described in harmonic approximation with the equilibrium positions of the oscillators being linearly shifted upon electronic excitation [4]. Recently, SDs beyond simple models have attracted considerable attention in the context of Frenkel exciton dynamics in photosynthetic light-harvesting complexes. Here, the electronic excitation of the chlorophyll molecules is coupled to both, intramolecular and protein vibrations. While the SD for the latter is essentially structureless and often well described by model functions, intramolecular vibrations give rise to distinct features in the SD, whose spectral positions and weights might be relevant for the exciton dynamics [6].

Under the assumptions of the HR model, SDs can in principle be reconstructed from spectroscopic data such as site-selective fluorescence [7]. For the widely discussed Fenna-Matthews-Olson (FMO) complex of cyanobacteria, Wendling et al. [8] have determined a SD by focussing on the lowest energetic bacteriochlorophyll *a* (BChl *a*) pigment at 4 K. Although their assumption that this particular BChl *a* molecule is electronically decoupled from the other BChl *a* molecules of the complex has been critically discussed [9], the Wendling SD has become a standard for the discussion of FMO dynamics [10–13]. In Ref. [10] the low-frequency phonon part had been found to be rather similar to that of the B877 monomer complex studied in Ref. [14]. However, the Wendling SD, in contrast to the bare phonon wing, contains structured features due to discrete vibrations. In Ref. [10] this effect was modeled by adding an isolated delta-like peak to the SD. Such sharp features are a notorious problem for density matrix approaches to the dynamics. It can be circumvented by including the related vibrational mode into the relevant system [15,16]. For the case of the FMO complex, this approach has been used to perform path integral [17] and Quantum Master equation [18] simulations.

The computational determination of SDs for specific pigment-protein complexes usually employs sampling of the fluctuations

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of local electronic energy gaps using ground state equilibrium classical molecular dynamics. In a pioneering work, Schulten and coworkers have calculated the SD for BChl *a* in the light-harvesting antenna LH2 of purple bacteria [19]. Due to the limited trajectory length only the high-frequency part of the SD was accessible. Concerning the FMO complex there are essentially as many different SDs as there are published papers on this topic, although most of them agree in gross features. For instance, Kleinekathöfer and coworkers have determined site-specific FMO SDs using the semiempirical ZINDO/S approach to calculate electronic excitation energies [20,21]. A comparison of the effect of different force fields and electronic structure methods has been provided in Ref. [22]. Further, the use of the classical approximation has been scrutinized in Ref. [23]. A different strategy has been followed by Renger et al., who used the shifted harmonic oscillator model directly by employing a normal mode analysis of the pigment-protein complex [24]. The latest SD comes from the group of Coker et al. [25,26] and will also be used in the present work. The Coker SD combines both ideas mentioned above, i.e. the phonon wing is modeled using general gap correlation functions, whereas for the intramolecular vibrations a harmonic approximation is assumed [25,26].

In view of the many different FMO SDs, the question arises whether the details really matter for the dynamics of excitation energy transfer. In other words, are there any vibrational mode specific effects in a system as complicated as the FMO complex? Previously, we have shown that, in principle, an answer can be provided based on the propagation of the full exciton-vibrational wavepacket [12,13], which becomes possible by using the ML-MCTDH approach [27–33]. Given an exciton Hamiltonian and a discretized SD, ML-MCTDH provides a numerical solution to the time-dependent Schrödinger equation, whose convergence to a desired accuracy can be monitored.

In the present contribution, ML-MCTDH is applied to FMO dynamics using different SDs, i.e. the Wendling [8] and the Coker SD [26]. This will allow us to highlight the sensitivity of the dynamics with respect to the details of the SD model. The paper starts with a brief outline of Frenkel exciton theory and ML-MCTDH in Section 2. Here, we will also introduce the different SD models. Results of numerical simulations are discussed in Section 3 and a summary is provided in Section 4.

2. Theoretical methods

2.1. Exciton-vibrational Hamiltonian

The Frenkel exciton Hamiltonian describes an aggregate with N_{agg}sites (site index m), each site having the excitation energy E_m, and different sites being coupled by the Coulomb interaction J_{mn}[1]

$$H_{\mathrm{ex}} = \sum_{m,n=1}^{N_{\mathrm{agg}}} (\delta_{mn}E_m + J_{mn})|m\rangle\langle n|. \tag{1}$$

Here, we used the Frenkel one-exciton states $|m\rangle = |e_m\rangle\prod_{n\neq m}|g_n\rangle$, which are defined in terms of the local electronic ground, $|g_m\rangle$, and excited, $|e_m\rangle$, states. For the site energies and Coulomb interactions, we will use the FMO values reported by Moix et al. [34]. They are based on a combination of site energies obtained from quantum chemical/electrostatic calculations [35] and Coulomb couplings described within the dipole–dipole approximation. Previously, it has been shown that the dynamics is essentially confined to the sites 1 to 3 [13,34]. This justifies the restriction to these three sites in the following. Thus the Hamiltonian matrix is given by (in units of cm^{-1}, off-set is 12195 cm^{-1}) [34]:

$$\mathbf{H}_{\mathrm{ex}} = \begin{pmatrix} 310 & -98 & 6 \\ -98 & 230 & 30 \\ 6 & 30 & 0 \end{pmatrix}. \tag{2}$$

Note that the labeling of the sites follows the structure of the Hamiltonian matrix, e.g., site $m=3$ is the energetically lowest site, which is connected to the cytoplasmic membrane containing the reaction center complex.

Diagonalization of this matrix yields the (in the following called adiabatic) one-exciton eigenstates $|\alpha\rangle = \sum_m c_m(\alpha)|m\rangle$ with energies E_α. The related transition energies are given in Fig. 1. The decompositions into the local (in the following called diabatic) states $|m\rangle$ are as follows (in order of decreasing energy): $\mathbf{c}(3) = (-0.83, 0.56, 0.03)$, $\mathbf{c}(2) = (0.56, 0.81, 0.16)$, and $\mathbf{c}(1) = (-0.06, -0.15, 0.99)$.

The local vibrations at site m are described in harmonic approximation by the set of dimensionless normal mode coordinates $\{Q_{m,\xi}\}$ with frequencies $\{\omega_{m,\xi}\}$, i.e. the vibrational Hamiltonian reads

$$H_{\mathrm{vib}} = \sum_m \sum_{\xi\in m} h_{m,\xi}, \tag{3}$$

with the harmonic oscillator Hamiltonian

$$h_{m,\xi} = \frac{\hbar\omega_{m,\xi}}{2}\left(-\frac{\partial^2}{\partial Q_{m,\xi}^2} + Q_{m,\xi}^2\right). \tag{4}$$

EVC is accounted for within the linearly shifted oscillator model, i.e.

$$H_{\mathrm{ex-vib}} = \sum_m \sum_{\xi\in m} \hbar\omega_{m,\xi}\sqrt{2S_{m,\xi}}Q_{m,\xi}|m\rangle\langle m|. \tag{5}$$

The coupling of a particular mode to the electronic transition is characterized by the Huang-Rhys (HR) factor $S_{m,\xi}$.

Frequencies and HR factors can be obtained from the SD, $J_m(\omega)$, of the monomeric BChl *a* molecule [1]

$$J_m(\omega) = A\sum_{\xi\in m} S_{m,\xi}\delta(\omega - \omega_{m,\xi}), \tag{6}$$

where A is a constant that will be used to adjust the total HR factor for site m for a finite discretization according to $S_{\mathrm{tot}} = A^{-1}\int d\omega J_m(\omega) = \sum_{\xi\in m} S_{m,\xi}$.

Since the reported SDs differ considerably, we have used the experimentally determined SD of Wendling et al. [8] in our previous investigation (cf. Fig. 1) [12,13]. In the present study, the Wendling SD will be taken as a reference and will be called *model I*. Specifically, it is discretized into 74 modes within the interval $[2:300]$ cm^{-1} as shown in Fig. 1. The amplitudes of the individual HR factors have been adjusted homogeneously via the constant A such as to preserve the total HR factor, $S_{\mathrm{tot}} = 0.42$, upon summation.

The results of model I will be compared to those obtained using the site-specific Coker SDs of Ref. [26], called *model II*. In Fig. 1 these SDs are decomposed into a phonon wing and a discrete intramolecular part. The former has been fitted to a log-normal distribution, i.e. ($S_{\mathrm{ph}} = (0.33, 0.68, 0.37)$ for sites $(1,2,3)$ and $\sigma = 0.7, \omega_c = 38$ cm^{-1})

$$J_{\mathrm{ph}}(\omega) = \frac{\pi S_{\mathrm{ph}}\omega}{\sqrt{2\pi}\sigma}\exp\left\{-\frac{[\ln(\omega/\omega_c)]^2}{2\sigma^2}\right\}. \tag{7}$$

Note that in Ref. [25] a different definition of the SD had been used. The present J_{ph} are chosen such as to give the same reorganisation energies. The J_{ph} have been discretized in the interval $[2:160]$ cm^{-1} into 32 modes. The intramolecular part was taken directly from Ref. [26]. This results in a total of 81 modes for each site. In the Coker model II the total HR factors are site-specific, i.e.