

Electronic Coherence Dephasing in Excitonic Molecular Complexes: Role of Markov and Secular Approximations

Jan Olšina and Tomáš Mančal

*Institute of Physics of Charles University, Faculty of Mathematics and Physics,
Charles University in Prague, Ke Karlovu 5, CZ-121 16 Prague 2, Czech Republic**

We compare four different types of equations of motion for reduced density matrix of a system of molecular excitons interacting with thermodynamic bath. All four equations are of second order in the linear system-bath interaction Hamiltonian, with different approximations applied in their derivation. In particular we compare time-nonlocal equations obtained from so-called Nakajima-Zwanzig identity and the time-local equations resulting from the partial ordering prescription of the cumulant expansion. In each of these equations we alternatively apply secular approximation to decouple population and coherence dynamics from each other. We focus on the dynamics of intra-band electronic coherences of the excitonic system which can be traced by coherent two-dimensional spectroscopy. We discuss the applicability of the four relaxation theories to simulations of population and coherence dynamics, and identify features of the two-dimensional coherent spectrum that allow us to distinguish time-nonlocal effects.

I. INTRODUCTION

Modeling molecular properties related to their non-equilibrium dynamics requires various theoretical approaches depending on the particular microscopic processes related to the observed molecular features. Since the dawn of quantum mechanics, properties of molecules and solids have been studied theoretically in ever greater detail. This has led in recent years to a state in which dynamics of complex systems with multitude of degrees of freedom (DOF) is accessible to quantitative theoretical study [1]. Many properties of molecular systems are directly related to the equilibrium or time dependent conformations of nuclear DOF for which electronic states play the role of a background contributing to the nuclear potential energy surfaces. Problems like these are the realm of molecular dynamics (MD) in its classical, quantum or mixed versions and quantum chemistry (QC), where impressive qualitative and quantitative results have been achieved in recent years. For certain types of dynamical problems, however, less expensive model approaches are the preferred choice due to the scale of studied system or due to the physical nature of studied processes. A good example of such a problem is ultrafast photo-induced excited state dynamics of small molecular systems and their aggregates [2]. Here, most of the relevant experimental information is only available through ultrafast non-linear spectroscopy, and thus the theory has to span the whole distance between the microscopic dynamics of the molecular system, and the macroscopic description of experimental signals [3]. Typical field in which such an approach has yielded deep understanding of the relevant physico-chemical processes is the study of primary processes in photosynthesis. The related quantum mechanical problem is usually formulated

in terms of a model describing the relevant DOF of the system (electronic states of photosynthetic molecules), and a thermodynamics bath (the protein environment). Parameters for such models can be supplied by experiment [4], QC studies [5, 6], MD modeling [7], or are a result of suitable simplified models [3].

Recent advances in non-linear spectroscopy have opened a wide new experimental window into the details of ultrafast photo-induced dynamics of molecular systems. Experimental realization of two-dimensional (2D) coherent spectroscopy in the visible and near IR regions [8–11] has enabled to overcome some of the frequency- vs. time-resolution competition problem otherwise faced by ultrafast spectroscopy, and yielded thus unprecedented experimental details of the time evolution of molecular excitations. Most importantly, it was predicted that the presence of certain oscillatory features in 2D spectra is a manifestation of coherences between molecular excited states [12, 13]. It was also concluded that these oscillations should be present in the 2D spectrum of photosynthetic Fenna-Matthews-Olson (FMO) chromophore-protein complex [12]. Experimental results not only confirmed this prediction [14], but yielded also surprising results such as unexpectedly long life time of these coherences, as compared to the predictions of standard dephasing rate theory. Furthermore, while possible coherence transfer was ignored by the relaxation theory used in Ref. [12], the experiment provided some evidence for its role in excitation energy transfer. It was speculated that photosynthetic systems might use the coherent mode of energy transfer to more efficiently channel excitation energy by scanning their energetic landscape in a process similar to quantum computing [14]. More experiments have recently reported coherent dynamics in photosynthetic systems [15] and conjugated polymers [16], and the field of energy transfer in photosynthesis has seen an increased interest from theoretical researchers from previously unrelated fields [17–20].

*Electronic address: tomas.mancal@mff.cuni.cz

Theoretical basis for the description of the decoher-