Vilnius University **Faculty of Physics**
Sauletekio 9, b. 3, 10222 VILNIUS, Lithuania Dean, tel. + 370 5 236 6001

Report of Leonas Valkunas as a referee of the doctoral thesis „Theory of Relaxation and Energy Transfer in Open Quantum system“ by Jan Olšina

Upon light absorption, molecules undergo a transition from the ground state to one of the excited states. The energy levels of these molecules, and thereby their absorption spectrum depend on the chemical structure but they are also influenced by the molecular environment, for instance a solvent or a protein (in the case of the photosynthetic pigment-proteins); the energy levels are usually both shifted and broadened as compared to the vacuum situation. When there is another molecule in its direct environment with similar optical properties/energy levels, both molecules can (strongly) interact through electrostatic interactions in such a way that spectroscopically they behave as one supermolecule, although they might not even be in "physical" contact. New energy levels are created, transitions to these levels will be (partly) allowed and/or (partly) forbidden and excitations become intimately shared. Such collective excitations are called excitons and corresponding absorption and fluorescence properties depend on the relative orientations and positions of the interacting molecules. Intermolecular interactions are also the main factors determining excitation energy transfer dynamics while excitation relaxation is caused by the interaction with vibrational degrees of freedom. To describe excitation evolution in molecular systems both types of interactions have to be taken into account simultaneously. The exciton concept is widely used to explain both steady-state and time-resolved spectroscopic properties of strongly coupled pigments.

The study of the system response to the electromagnetic field in various types of the resonance conditions is the main objective of various spectroscopic methods. Nonlinear optical techniques usually performed using ultra-short laser pulses in regions from IR to visible wavelengths, are capable of probing various dynamical phenomena on microscopic/nanoscopic scale. In the time domain this type of experiments are performed by applying either two-pulses (pump-probe) or three-pulses (homodyne three-pulse photon echo), or four-pulses (coherent heterodyned signals) to generate and detect the desired signal due to the light-induced third order polarization as a parametric function of the delays between incident laser pulses. The polarization dynamics with respect to these parameters reflects wide variety of ultrafast molecular processes. Recent development of nonlinear spectroscopies, such as two-dimensional photon echo (2D PE) spectroscopy, is getting widely available for studies of exciton coherence in various molecular systems. 2D PE spectroscopy was the key tool demonstrating a complex pathway network of the energy transfer and long-lasting coherence in a photosynthetic Fenna-Matthews-Olson (FMO) complex. These oscillations observed in the 2D spectroscopy of FMO complexes as well as other molecular systems stimulated a huge interest to the problem of the excitation dynamics especially by considering a possible role of the quantum coherence in the excitation energy transfer.

The core of the spectroscopy experiment is the semiclassical approximation. Interaction between the field and the system is usually is considered perturbatively. Thus, the complexity of the problem is mainly related to the excitation behavior in the system due to its interaction with the environment. Jan Olšina considered this complex problem of the excitation dynamics and relaxation in his thesis. The first chapter, where he presented the description of basic theoretical approaches taking into account the system-bath interaction is well and clearly written, quatum master equations in the local-time and nonlocal-time description are well formulated and justified. Theoretical description of the nonlinear spectroscopic methods based on the perturbative approach by considering the light-matter interaction is presented in the second chapter. The remaining three chapters contain his original results. Initially he studies the possible role of non-secular terms in the quantum master equations. Since these terms are responsible for mixing of the coherence and population in the density matrix formalism, such type of consideration is naturally related to the problem of long-lasting oscillations as observed in the 2D PE spectra. It is convincingly demonstrated that in this sence the non-secular effects are rather small. Moreover, it is demonstrated that non-local time description provides the longer lifetime of the coherence and is comparable with the results obtained from the hierarchical equations.

Most realistic systems are not isolated, the coupling of the system to its environment cannot be considered as a negligible factor. Therefore, the theory of open quantum systems is the main approch in determining the dynamics and relaxation of excitations induced by the external electromagnetic field. A novel approach using the projection operator technique, so-called parametric projection in determining the relevant master equation, is formulated in the subsequent chapter of the original results of Jan Olšina. Applicability of this description is based on the correspondence of this description with the results, which follow from the second order cumulate method in the case of the absence of the resonance interaction. And finally the method based on stochastic unraveling of resonance interaction by cumulant expansion is proposed in the final chapter. This method is demonstrated by considering the excitonically coupled molecular dimer.

According to the said above I have to admit that the structure of the thesis is acceptable. By reading the thesis I got the impression that Jan Olšina understands the complexity of the problems related to the excitation dynamics and relaxation in molecular systems by considering them as open quantum systems. I can also conclude that the original results compose a good basis to study the problems of temporal evolution in other systems, which are characterized by other set of parameters. Indead, there is not much specificity of pigment-proteins by demonstrating the results in the thesis, this approach might be directly applied to other type of systems, which could be considered as resonantly coupled two-level systems interacting with the bath.

Thus, I have to conclude that I have a positive impression about the thesis of Jan Olšina.

Prof., habil. dr. Leonas Valkunas
18-03-2014, Vilnius