

## **1. PHD PROJECT DESCRIPTION (4000 characters max., including the aims and work plan)**

### **Project title:**

Symmetry-adapted perturbation theory for the description of the photophysical properties of fluorophores in the presence of solvent

**1.1. Project goals** The main goal of the project is to provide the consistent methodology for the description of the photophysical properties of fluorophores upon their interaction with solvent within the symmetry-adapted perturbation theory (SAPT). The specific objectives of the project include: benchmarks for the excited-state-solute--solvent interaction, the development of the computational protocols for the description of the excited states within SAPT, the verification of the quality of vertical absorption energies estimated within SAPT for the wide range of fluorophores.

**1.2. Outline** Photophysical properties of organic molecules remain continuously of high importance due to the strong demands from various branches of technology for photooptical devices, sustainable energy sources, biomedical imaging techniques or chemosensors. New materials can be rationally designed, starting from the theoretical chemistry approaches. The photooptical features of the molecules need to be determined in the environment, since intermolecular interactions can drastically change the attributes of the system via solvatochromic shift of absorption bands or aggregation-induced emission quenching. Therefore, the proper description of the excited state in solvent is vital. The description of solute-solvent interactions is mostly limited to their ground state or continuum solvent models. Nevertheless, this approach does not allow for the direct inclusion of the effects from the explicitly considered solvent molecules such as hydrogen bonding in the excited state of the system. Thus, the development of the tools which permit for the routine investigation of the interaction of the excited state of the fluorophore with solvent molecules are invaluable. This project combines development and applications SAPT in studies of optical transitions of fluorophores such as difluoroborate derivatives in solvents of various character (polar protic, polar aprotic or non-polar). SAPT relies on calculations of interaction energies directly, from properties of molecules only. This makes the calculations cheaper and easier, as one controls the state of monomer precisely. Also, the interaction energy provided by SAPT is naturally split into physically meaningful components (electrostatics, induction, exchange, dispersion). They are not only powerful for the interpretation of the results, but can be nowadays used in classifications of systems, "big chemical data" analysis, or in

building machine learning models for interactions and properties.

This project is a stepping stone toward better understanding the excited states in aggregates, molecules in solutions etc. and the minimum plan is to collect sufficient amount of data to test the lowest order SAPT interaction energy which can be obtained from TDHF/DFT density matrices (in excited states) or more sophisticated methods (CASSCF, EOMCC). The hypothesis of the project is that even the first-order SAPT for excited states can provide the reasonably accurate description of the shifts of vertical absorption energy for molecules in solution and provide an improvement with respect to the currently applied methods. The energy-structure relations are to be determined for chromophores with different substituents using SAPT components.

- 1.3. Work plan** 1) Benchmarking the solute-in-excited-state—solvent interactions: studies of vertical absorption energies, landscapes of potential energy surfaces 2) Development of SAPT methodology for determination of vertical absorption energy in solution: low-order SAPT from density matrices obtained with TDHF/TDDFT; 3) Determination of the quality of the results by comparison with ab initio calculations (EOM CCSD, CC2, CC3, ADC(2), TDDFT), data analysis, trends for fluorophores with various functional groups. 4) Verification of the developed methodology for the wide range of model systems; 5) Comparison with experiment for the real-life systems.
- 1.4. Literature:** **1.** K. Szalewicz, Symmetry-adapted perturbation theory of intermolecular forces, *WIREs Comput. Mol. Sci.* 2012, 2: 254–272 doi: 10.1002/wcms.86; **2.** G. Fradelos, J. J. Lutz, T. A. Wesółowski, P. Piecuch, M. Włoch, Embedding vs Supermolecular Strategies in Evaluating the Hydrogen-Bonding-Induced Shifts of Excitation Energies, *J. Chem. Theory Comput.* 2011, 7, 6, 1647–1666, doi: 10.1021/ct200101x; **3.** D. Jacquemin, B. Mennucci, C. Adamo, Excited-state calculations with TD-DFT: from benchmarks to simulations in complex environments, *PCCP* 2011, 13, 16987, doi: 10.1039/c1cp22144b.
- 1.5. Required initial knowledge and skills of the PhD candidate** Basic chemistry and spectroscopy, basic quantum chemistry or quantum physics, experience in application of computational chemistry packages, communicative English written and spoken, programming skills highly appreciated, ability of working both independently and in the team, eager to take on challenges
- 1.6. Expected development of the PhD candidate's knowledge and skills** The candidate will develop the thorough knowledge of the theory of intermolecular interactions and the photophysical properties of molecules in condensed phase. He will obtain the strong background in the widely applied quantum chemistry approaches and program packages

and will be able to plan and perform the advanced theoretical calculations. He will develop the computer skills including the scripting and programming languages and computer cluster administration and management.