

The design and characteristics of photoactive materials based on organic compounds, such as organic light emitting diodes or photovoltaic cells, is an active area of research in chemistry. The structure of these materials is governed by noncovalent interactions – intermolecular forces driving the formation and stability of molecular aggregates. Noncovalent interactions are typically by one or two orders of magnitude weaker than covalent ones, the latter leading to rearrangement of chemical bonds and formation of new molecules. Nevertheless, it is these weak intermolecular forces that are responsible for the existence of the liquid phase, folding of proteins and DNA/RNA strands, or molecular-recognition processes.

The strength and character of noncovalent interactions changes upon electronic excitation. In consequence, the material undergoes structural reorganization, such as modification of the hydrogen bonding patterns, which in turn affects its absorption and emission properties. The intense experimental efforts in engineering photoactive materials call for quantum chemistry methods that could guide the synthesis of new compounds with desirable optical properties.

Modern quantum chemistry approaches dedicated to noncovalent interactions between ground state molecules have reached the level of accuracy that provides a direct comparison with the experiment. However, their extension to excited states is non-trivial and much less advanced. One reason is that several fundamental approximations, which facilitate the description of ground states, are no longer valid in the excited state regime. This requires more complex and computationally demanding models. The second reason are the so-called resonance interactions, which occur between two identical monomers in different electronic states. This phenomenon does not exist for ground states and warrants methods capable of handling degenerate electronic states.

The aim of this project is to develop a theoretical method dedicated to noncovalent interactions in excited state complexes. This approach will be based on perturbation theory in which the interaction energy arises directly from properties of the subsystems and is represented as a sum of physically meaningful components: electrostatic, exchange (Pauli repulsion), induction, and dispersion. The method will combine the computational efficiency and accuracy offered by density functional theory with the ability to access excited states using wave function models. In its degenerate formulation, the new approach will allow for the characterization of systems with resonance interactions. These are excimers and exciplexes - complexes that play an important role in modern optoelectronic materials and can be used as chemosensors or molecular beacons.

The developed method will be applicable to large systems such as organic light-emitting crystals and optoelectronic materials. These studies will elucidate the role of noncovalent interactions in light-emitting molecular assemblies.