Modeling electron density changes due to noncovalent interactions using symmetry-adapted perturbation theory

Molecular systems, although in many cases electrically neutral, interact with each other through weak intermolecular forces, also known as van der Waals forces. They arise because the charge density associated with the nuclei and electrons of a given molecule tends to fluctuate and change as a result of the presence of the charge densities of other molecules. These effects play a vital role in many physical, chemical, and biological phenomena. They are responsible for the surface tension of fluids, are essential for the formation of molecular crystals, and govern the interactions of drug-like compounds with biomolecules. These interactions are usually studied through the calculations of the interaction energies. This study, however, focuses on developing an *ab initio* theoretical method for direct calculations of the electron density changes due to the intermolecular interactions.

The main scientific goal of the project is a derivation of a novel theoretical method inspired by the symmetry-adapted perturbation theory (SAPT) and focused not on the calculations of the interaction energies but on the interaction-induced changes in the so-called one-electron reduced density matrices (1-RDMs). These are well-defined quantities appearing in the quantum theory of molecular systems. Based on them, much relevant information about the molecular system can be obtained, e.g., knowing them enables one to calculate molecular properties such as dipole moments. Additionally, they can be used to obtain the electron density of the system itself, which describes the probability density of finding an electron at a given point in space around the molecule's nuclei. Interestingly, the electron density can be visualized in the 3D space by plotting its isosurfaces. The interaction-induced changes in the density developed in this project can be plotted in a similar way, allowing for the visual analysis of the effect of intermolecular interactions on molecular systems.

Moreover, basing the method on the grounds of the SAPT theory brings further benefits, as it enables the collection of additional insights and understanding as the splitting of interaction-induced corrections into physically meaningful terms naturally arises in SAPT and SAPT-based methods. These terms can be categorized into four types of contributions: (i) electrostatic interactions between static multipoles of the monomers, which can be either attractive or repulsive in character; (ii) repulsive exchange interactions – related to valence repulsion; (iii) attractive interactions between static and induced multipoles on the monomers, and (iv) dispersion interactions, which occur due to the formation of instantaneous multipoles. Research developments of this project can allow for direct, *ab initio*, analytical, 3D space visual representations of the corresponding intermolecular interaction contributions.