The quantum-chemical computational methods have become a standard tool to supplement the interpretation of experimental data, being utilized as the first selection of potential candidates for new materials in the future development process. Additionally combined with molecular dynamics simulation can also be used to design new drugs or vaccines for pathogens like viruses. Thus, they became especially attractive for material science and the nano-biotechnology and pharmaceutical industry. Nowadays, to most commonly used quantum chemical methods one can include those developed within density functional theory (DFT), especially due to their very attractive accuracy/computational-cost ratio which allows applying DFT to very large molecular systems. We note that the accuracy of DFT results is strictly related to the quality of so-called exchange-correlation (XC) density functional approximations (DFA) used in the Kohn-Sham (KS)-DFT calculations. To the most sophisticated one, we can include the range-separated hybrids (RSH) functionals where the Coulomb electron-electron interaction is decomposed into the short-range (SR) part (described by the semi-local form of functional) and long-range (LR) part (described by wave function theory (WFT) expression). The RSH functionals have turned out to be especially efficient in reducing some deficiencies of semi-local and hybrid DFAs. They were successfully applied in systems e.g. prone to self-interaction error, to model weakly interacting molecular systems. We note, however, that the obtained results strongly depend on the value of the range-separation parameter μ which basically governments how fast the SR range XC interaction changes into the LR regime. Moreover, the long-range WFT part of DFAs increases the computational cost of the whole method.

The main aim of this project is to resolve above deficiencies by 1) changing the paradigm laying behind the construction of range-separated functionals; 2) to construct a new type of semi-local XC functionals which can be utilized within the proposed scheme (p. 1), as well as standard hybrids, being in the same time more accurate then presently used variants.

In task 1), in the contrary to RSH functionals, we propose that separation will be performed in the occupied orbital space where orbitals will be decomposed into the orbital-short-range (OSR) (eg. core orbitals/electrons) and orbital-long-range (OLR) (eg. valance orbitals/electrons), rather than decomposition of Coulomb electron-electron interaction. This will be performed by the decomposition of the exact WFT XC hole (by truncation of summation) into OSR and OLR parts. In task 2), we will construct a new form of XC functional which will be able to provide the accuracy beyond presently used ones. Starting from WFT total energy expression (e.g. coupled-cluster (CC) or Møller-Plesset (MP) method) we will construct the XC hole and investigate its behavior for several systems. Because this object is six-dimensional and it is difficult to visualize, we will work with the system- and spherically averaged XC holes. The XC hole will be reconstructed using e.g. the KS orbitals and orbital energies, both from occupied and unoccupied levels which inclusion is especially important to accurately model the correlation hole that, in turn, may allow to model e.g. dispersion interactions accurately. We expect that, the inclusion of virtual orbitals and energies can radically the accuracy of results and thus the quality of predictions made by DFT. We expect that new functionals will provide the results which are comparable with approaches such as CC methods (i.e. CCSD(T)) or RSH+WFT method, at much reduced computational cost. We note, that developed at this stage functionals can be directly utilized in the scheme described in p. 1) as well as in regular KS-DFT calculations.

We expect that the outcome of this project will guide new development, and enhance significantly the applicative power of the DFT method, both in chemistry and solid-state physics. Thus, large systems for biology and nanoscience can be described with unprecedented accuracy e.g. non-covalent complexes, which is a fundamental issue in chemistry, biochemistry, and material science. These achievements will have a relevant impact on the field of computational chemistry/physics in Poland and the World.