Quantum chemistry methods, despite several decades of intensive development, are still struggling with the problem of strong electron correlation. One might think that chemical problems are not associated with strongly correlated electrons and can be described by theoretical methods assuming weak electron correlation. This is not the case, however, because strong electron correlation is, in fact, ubiquitous in chemistry. It governs not only a fundamental problem in chemistry, which is covalent bond breaking, but also numerous photochemical processes, reactions of molecules containing heavy metals or transition metals. The latter are molecules of biological importance.

To describe theoretically the above problems, one needs the so-called multireference wavefunction, which is a linear combination of a number of Slater determinants. In recent years, there has been tremendous progress in the development of multireference methods, applicable to molecules containing dozens of strongly correlated electrons. This progress notwithstanding, accuracy of multireference methods is generically flawed with lack of the so-called dynamic electron correlation.

Accounting for dynamic correlation energy is necessary to make not only quantitative but also qualitatively correct predictions about electronic structure of molecules. In practice, until recently, the only theoretical tool to equip multireference methods with dynamic correlation was perturbation theory. Unfortunately, dynamic correlation energy obtained perturbatively is often too inaccurate, burdened with the so-called intruder state problem or lacking size-consistency. In addition, the high computational cost of perturbation methods constrains their applicability to about 30 strongly correlated electrons.

In our project, we are developing dynamic correlation calculation methods that will not be based on the perturbation theory. Instead, these methods will be derived from the adiabatic connection in the particle-particle approximation. They will be more computationally efficient than perturbation methods and free from the deficiencies of the latter. Combined with state-of-the-art multireference methods, they will allow to overcome the limit of several dozen strongly correlated electrons in the system. In the second part of the project, the development of a novel class of correlation density functionals is planned, which will automatically adapt to a multireference method and recover the missing part of the correlation energy.

The resulting methods will enable accurate calculations for challenging multireference systems whose electronic structure is debated. In the longer term, the newly developed computational approaches will allow one to study molecules inaccessible to existing methods.