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

Project title: New exchange-correlation hybrid functionals based on range separation.

1.1 Project goals

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. The semi-local DFAs, although they can provide quite qualitatively correct results, mostly work by mutual error cancellation effect between exchange and correlation part of the functional. Improved results are generally obtained with the more sophisticated DFAs e.g., double-hybrids, random phase approximations, or range-separated hybrids (RSH) functionals where the Coulomb electron-electron interaction v(r) =1/r 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 latter type of DFAs has become 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 or to model weakly interacting molecular systems. We note, however, that the obtained results strongly depend on the value of the range-separation parameter, which governments how fast the SR range XC interaction changes into the LR regime. Moreover, the LR WFT part of DFAs significantly increases the computational cost of the whole method.

The main aim of this project is to resolve the above deficiencies by 1) changing the paradigm laying behind the construction of range-separated functionals in KS-DFT; 2) constructing a new type of XC functional 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) on 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) (e.g. core orbitals/electrons) and orbital-long-range (OLR) (e.g. valance orbitals/electrons), rather than decomposition of Coulomb electron-electron interaction. This will be performed by decomposing the exact WFT XC hole expression (by truncation of summation) into OSR and OLR parts. In task 2), we will construct a new form of XC functional that will provide accuracy beyond presently used DFAs. Starting from WFT total energy expression, we will construct the XC hole from i.e., MP2, CCSD, CCSD(T), etc., methods by investigating its behavior for several systems. The XC hole will be reconstructed using semi-local ingredients, such as reduced gradient, reduced Laplacian, kinetic energy density, and KS orbitals and orbital energies from occupied and unoccupied levels. The inclusion of the latter ingredients is essential to accurately model the correlation hole that may allow modeling e.g. dispersion interactions, accurately. We expect that the inclusion of virtual orbitals and energies can radically impact the accuracy of results and the quality of DFT predictions. We expect that new functionals will provide comparable results with approaches such as coupled cluster CC (e.g., CCSD(T)) or RSH+WFT methods, at much reduced computational scaling.

1.2 Outline

We will derive a new class of range-separated functionals called ORSH based on the decomposition of the occupied orbital space into the OSR and OLR subspaces which will be performed via truncation summation

in XC hole. Furthermore, base on the examination of accurate features of XC hole from WFT methods, we will develop a new XC form of functionals compatible with ORSH scheme as well as applicable in standard KS-DFT calculations. Moreover, we aim at investigating and understanding in detail all important features (advantages and disadvantages) of the ORSH method to elevate their future
applicability, high accuracy, and efficiency. We expect that the outcome of this project will push the knowledge in the field, guide new development, and enhance the applicative power of the DFT method significantly, 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, a fundamental issue in chemistry, biochemistry, and material science.

1.3 Work plan

i. Design and development of new methods and theoretical mathematical and numerical tools
ii. Numerical implementation of developed methods.
iii. Performing test calculations for small and medium-sized atomic and molecular systems.
iv. Optimizing programs for large scale calculations. Performation of the calculations with newly derived methods for several realistic molecular systems .

1.4 Literature

[1] S. Śmiga, I. Grabowski, Mateusz Witkowski, Bastien Mussard, Julien Toulouse, "Self-consistent range-separated density-functional theory with second-order perturbative correction via the optimized-effective-potential method", J. Chem. Theory Comput. 16 (2020), 211-223, DOI: 10.1021/acs.jctc.9b00807

[2] S. Śmiga, Lucian A. Constantin, "Unveiling the physics behind hybrid functionals", *J. Phys. Chem. A* **124** (2020), 5606-5614, DOI: 10.1021/acs.jpca.0c04156

[3] Subrata Jana, Bikash Patra, S. Śmiga, Lucian A. Constantin, Prasanjit Samal, "Improved solid stability from a screened range-separated hybrid functional by satisfying semiclassical atom theory and local density linear response", *Phys. Rev. B.* **102** (2020), 155107-1-155107-16, DOI: 10.1103/PhysRevB.102.155107

1.5 Required initial knowledge and skills of the PhD candidate

- Deep knowledge about quantum mechanics and quantum chemistry.
- Knowledge about quantum chemical methods at the level of exchange and correlation effects.
- Basic knowledge about Density Functional Theory and Wave Function Theory methods.
- Programming skills (FORTRAN, C, Python).
- Basis and/or advanced numerical methods knowledge.
- Using of artificial intelligence algorithms .
- Involvement in scientific work.

1.6 Expected development of the PhD candidate's knowledge and skills

- Deep knowledge and understanding quantum-chemical methods ranging from *ab initio* (HF, CC, PT) up to DFT methods
- Acquiring extensive knowledge of description many-electron systems including electron correlation effects.
- Efficient programming at the advanced level, making parallel code, running quantum chemical

calculations

- Ability to analyze the results and draw conclusions
- General knowledge about calculating different properties of many electron systems