

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

**Project title: Orbital-Dependent Functionals in Kohn-Sham DFT - Practical Realization of *ab initio* DFT.**

### 1.1. Project goals

The density functional theory (DFT) has become a method of choice in computational chemistry and application to solid state physics, bio-, nanotechnology, and atomic and molecular systems. The DFT is an exact theory in principle. Still, in practice, the final quality of the results strongly depends on the approximations of the so-called exchange-correlation (XC) functional used in the Kohn-Sham DFT calculations. In general, the standard semi-local XC functionals give satisfactory results only in some areas of applications, and often the quality of the results obtained is not good enough and even unpredictable. Utilization of more sophisticated, orbital-dependent functionals in the KS-DFT, constituting so-called *ab initio* DFT, leads to potentially a compelling approach to electronic structure theory. Combining the efficiency of DFT with the accuracy and systematic improvement of wave function theory it promises to bring computational chemistry to a new level, allowing the accurate description of the electronic properties. However, to date, this possibility is hindered by technical limitations that prevent the efficient and widespread use of *ab initio* DFT methods in computational chemistry applications. One of the main problems is related to the need to find a reliable and cheap basis set to expand the optimized effective potential (OEP), which is crucial for the OEP method. Another one is implementing the new OEP correlation functionals effectively in KS-DFT methods. In this project, which is directly connected to the Ph.D. student, we aim to address these problems and transform *ab initio* DFT into an efficient tool for computational chemistry. Thus, we will propose a solution to the long-standing problem of developing numerically stable OEP methods based on Gaussian basis sets. We will also implement a new version of the correlation functionals, which will allow applying *ab initio* DFT to new problems in computational chemistry.

### 1.2. Outline

To transform *ab initio* DFT methods into an efficient tool (black box type) for computational chemistry, we will develop different approaches to the basis set expansion of the OEP potential (necessary

in solving integral OEP equations) using e.g., Information from localized effective exchange-correlation methods, regularization methods and also different approaches to the auxiliary and orbital Gaussian basis sets OEP implementation

All solutions will be implemented in state-of-the-art quantum chemical computational systems, e.g., ACES and PSI4. Then, they will be tested for systems for which accurate reference results are known. We will study the numerical stability of the methods, their basis set dependence, and implementation dependence. Additional research will also focus on verifying the representation of the correlation effects by ab initio DFT and standard DFT correlation functionals, potentials, electron density, and other properties like energy, IPs, reaction and atomization energies, enthalpies, and more.

### 1.3. Work plan

- i. Design and development of new methods and theoretical mathematical and numerical tools, based on the single and dual basis set implementation, for solving the correlated OEP-KS equations.
- ii. Development of stable/universal basis set for solving correlated OEP equations, allowing to perform calculations for any system
- iii. Numerical implementation of developed methods.
- iv. Performing test calculations for small and medium-sized atomic and molecular systems. Optimizing programs for large-scale calculations.
- v. Performing the calculations with newly derived methods (correlated OEP-KS) for several realistic molecular systems

### 1.4. Literature (*max. 10 listed, as a suggestion for a PhD candidate*)

- ] R. J. Bartlett , I. Grabowski, S. Hirata, S. Ivanov, J. Chem. Phys. **122**, 034104, (2005)  
[2] I. Grabowski, E. Fabiano, S. Śmiga, A. Buksztel, A. M. Teale,, F. Della Sala *J. Chem. Phys.* **141** (2014), 024113-1  
[3] S. Śmiga, F. Della Sala, A. Buksztel, I. Grabowski, E. Fabiano *J Comput Chem* **37** (2016), 2081-2090

### **1.5. Required initial knowledge and skills of the PhD candidate**

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

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

- Deep knowledge and understanding of quantum-chemical methods ranging from ab initio (HF, CC, PT) up to DFT methods
- Acquiring extensive knowledge of the description of 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