

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

### **Project title: Ab initio DFT - practical tool for computational chemistry**

#### **1.1. Project goals**

The density functional theory (DFT) has become a method of choice in computational chemistry and in application to solid state physics, bio- and nanotechnology, as well as to atomic and molecular systems. The DFT is an exact theory in principle, but 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 a more sophisticated, orbital-dependent functionals in the KS-DFT, constituting so-called *ab initio* DFT, lead to potentially an extremely powerful 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 OEP method, another one is the effective implementation of the new OEP correlation functionals in KS-DFT methods.

In this project, which is directly connected to the phd student, we aim at facing these problems, in order to transform *ab initio* DFT into a really practical 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**

In order to transform *ab initio* DFT methods into a really practical 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 art quantum chemical computational systems e.g. ACES and/or PSI4. And 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 the verification of 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 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 of the calculations with newly derived methods (correlated OEP-KS) for several realistic molecular systems .

#### **1.4 Literature**

- [1] 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 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