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

Project title: New adiabatic connection model-based exchange-correlation functionals

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, 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. Often, the quality of the results obtained is not good enough and is even unpredictable. The utilization of more sophisticated, orbital-dependent functionals in the KS-DFT, constituting so-called ab initio DFT, potentially leads to a compelling approach to electronic structure theory. Combining DFT efficiency with the accuracy and systematic improvement of wave function theory promises to bring computational chemistry to a new level, allowing an accurate description of the electronic properties. One of the possibilities in this direction is the construction of a new XC approximation within the adiabatic connection formalism (ACM), which represents a general path for calculating XC energies in electronic systems within the KS-DFT. The existing ACM functionals work efficiently for the strongly correlated regimes. They nevertheless face challenges involving thermochemistry and even the weakly interacting regimes. The main goals of this proposal are twofold: 1) to resolve the above deficiencies by modifying the construction of GL2-based ACM approximations; 2) to create and design the new ACM formula to target accuracy beyond present-day DH and ACMs, both in weakly and strongly correlated regimes. We will also implement a new version in PSI4 quantum chemistry package of the correlation functionals, which will allow applying ACMs to further problems in computational chemistry.

1.2. Outline: We will derive a new class of ACMs by altering the initial slope of W_λ by changing the H0 in the AC Hamiltonian. To this end, we will utilize the natural second-order choices of H0, taking inspiration from ab initio DFT theory, which lead to OEP2-f and OEP2-sc energy expressions. Furthermore, our goal is to better understand and explore all significant aspects (benefits and drawbacks) of the ACM-based approach to increase its high accuracy, efficiency, and future applications. All solutions will be implemented in state-of-the-art quantum chemical computational systems, i.e., PySCF 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 ACMs functionals, potentials, electron density, and other properties like energy, IPs, reaction, and atomization energies,

enthalpies, and more.

1.3. Work plan

- formal derivation of the ACM with our modified H0 Hamiltonian
- implementation of new variants in quantum chemistry packages e.g. PySCF and Psi4
- performing test calculations for small and medium-sized atomic and molecular systems.
- optimizing programs for large-scale calculations.
- performance of the calculations with newly derived methods (correlated OEP) for several realistic molecular systems.

1.4. Literature *(max. 7 listed, as a suggestion for a PhD candidate preliminary study)*

[1] Phys. Rev. B 109, 235129, 2024
[2] J. Chem. Phys. 159, 244111, 2023
[3] J. Chem. Theory Comput., 18, 10, 5936–5947, 2022
[4] J. Chem. Phys. 127, 154111, 2007
[5] J. Chem. Phys. 122, 034104, 2005

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.
- Fundamentals 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