PHD PROJECT DESCRIPTION
(4000 characters max., including the aims and work plan to de published online)

Project title: Advanced correlation methods based on the adiabatic connection formalism

1.1. Project goals

The aim of this PhD project is to develop advanced correlation methods for Kohn-Sham density functional theory based on the adiabatic connection (AC) formalism. The central objective is to construct a new family of nonlinear double-hybrid exchange-correlation functionals that interpolate between the non-interacting Kohn-Sham limit, $\lambda = 0$, and the physical fully interacting system, $\lambda = 1$.
The project will use exact and physically motivated information available at both ends of the AC curve. At $\lambda = 0$, the method will exploit exact exchange and perturbative correlation information, including second- and higher-order contributions. At $\lambda = 1$, the functional will include information from the physical interacting system and constraints related to strong electron correlation. The goal is to obtain a realistic description of the AC integrand over $0 \leq \lambda \leq 1$.
The main objective is to overcome limitations of existing AC-based and double-hybrid functionals, such as overestimation of correlation energies, poor robustness for stretched bonds and near-degenerate systems, and strong dependence on technical details. The final methods should improve the accuracy of DFT while remaining affordable and suitable for implementation in PySCF and Psi4.

1.2. Outline

Density functional theory is one of the most widely used approaches for electronic-structure calculations in chemistry, physics, and materials science. Its accuracy depends mainly on the exchange-correlation functional, which describes the collective motion and interaction of electrons. The adiabatic connection formalism provides a rigorous route to construct such functionals by switching on the electron-electron interaction through the coupling-strength parameter λ.

In this project, the AC formalism will be used as the theoretical foundation for designing nonlinear interpolation models. These models will connect the weak-correlation regime at $\lambda = 0$ with the fully interacting regime at $\lambda = 1$. Unlike standard double-hybrid functionals, which often correspond to simple approximate AC forms, the proposed functionals will use flexible nonlinear expressions constrained by exact endpoint information.

The work will focus on deriving interpolation formulas, analyzing their mathematical and physical properties, and transforming them into practical double-hybrid functionals. Particular attention will be paid to the balance between dynamical and static correlation and to challenging cases such as noncovalent complexes, reaction barriers, stretched bonds, and transition-metal compounds.

1.3. Work plan

- The project will begin with a literature review of Kohn-Sham DFT, hybrid and double-hybrid functionals, Görling-Levy perturbation theory, and existing AC-based models. We will generate the accurate, reference endpoint data to form highly accurate wave-function theory methods.

- Next, new nonlinear interpolation formulas for the AC curve will be developed. Polynomial, rational, and Padé-like expressions will be examined. Their ability to reproduce the weak-correlation limit, the physical interacting limit, and the overall shape of the AC curve will be tested.

- The most promising interpolation models will then be converted into practical nonlinear double-hybrid functionals. These functionals will combine exact exchange, semilocal density-functional components, and perturbative correlation terms. Different parameters and reference quantities will be analyzed to reduce correlation overestimation and improve transferability.

- The developed methods will be implemented in PySCF and/or Psi4, validated on small molecular systems, and tested in limiting cases. Finally, the new functionals will be benchmarked for thermochemistry, noncovalent interactions, barrier heights, bond dissociation, and strongly correlated systems. The best-performing methods will be documented, prepared for publication, and released.

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

- J. Harris, Phys. Rev. A 29, 1648 (1984)
- P. Gori-Giorgi, G. Vignale, and M. Seidl, J. Chem. Theory Comput. 5, 743 (2009)
- M. Seidl, P. Gori-Giorgi, and A. Savin, Phys. Rev. A 75, 042511 (2007)
- S. Śmiga and et al., J. Chem. Theory Comput. 18, 5936 (2022)
- L. A. Constantin and et al., J. Phys. Chem. Lett. 16, 3378 (2025)

1.5. Required initial knowledge and skills of the PhD candidate

- 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, especially related to the adiabatic connection framework and Kohn-Sham Density Functional Theory
- Acquiring extensive knowledge of the description of many-electron systems, including electron correlation effects.
- Efficient programming at the advanced level, making parallel code, and running quantum chemical calculations
- Generating and curating the data, the ability to analyze the results and draw conclusions
- General knowledge about calculating different properties of many-electron systems