

Systematic improvement of the correlation energy of solids and molecules within the ACFDT

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Quantum mechanics provides a comprehensive description of the properties of matter at the atomic scale. Accordingly, the Schrödinger equation could be used as a powerful tool to predict and interpret the properties of materials of technological interest or biological systems, for example. However, the precious information contained in this equation can be hardly extracted even for few electrons. The main theoretical/computational challenge in the solution of the Schrödinger equation is the accurate and efficient evaluation of the correlation part of the energy for realistic many-electron systems. The development of density functional theory constitutes a major breakthrough toward the solution of the many-body problem: The fully interacting electronic system is mapped into a non-interacting Schrödinger equation with the same electronic density, leading to a considerable computational simplification. While DFT provides rather accurate results for several molecular and extended systems, the “semi-empirical” approximations used for the exchange and correlation functional fail systematically to treat certain classes of problems, such as, e.g., the weakly interacting systems. The adiabatic connection fluctuation and dissipation (ACFDT) theorem represents a promising way to systematically improve the precision of DFT. Until now, this approach has been mostly applied within the so-called random phase approximation (RPA) that actually poorly describes the correlation energy on the short range.

The goal of this thesis project is to develop and apply new methods based on the ACFDT. Among the possible ways to proceed, the accuracy of the response functions used within the ACFDT framework will be improved by applying time-dependent density functional theory (TDDFT). Different approximations of the TDDFT kernel will be tested to understand their influence on the accuracy of the correlation energy. The comparison of different approaches will be performed both for extended and molecular systems and the analysis of the results might lead to the development of new and more accurate kernels. Alternatively, it might be possible to exploit in the ACFDT framework ideas that have been developed in the context of accurate quantum chemistry theories, such as the coupled cluster (CC) approach. It has been recently shown that the RPA-ACFDT approach is equivalent to the ring-CC approximation and the analogies between ACFDT and CC have been used to develop the so-called ‘second order screened exchange correction’. Very likely, the comparison of CC and ACFDT will lead to improved approximations.

Future tests and applications will include molecular crystals, layered materials, and weakly bound biomolecules, which are all poorly described within tradition DFT.