Power series approximation for the correlation kernel leading to Kohn-Sham methods combining accuracy, computational efficiency, and general applicability

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Kohn-Sham KS) methods based on the adiabatic-connection fluctuation-dissipation (ACFD) theorem can overcome limitations of conventional KS methods based on the local density or generalized gradient approximations. Most ACFD approaches invoke the random phase approximation, i.e., take into account only the Hartree kernel in the construction of the required response functions via time-dependent density-functional theory. Recently, ACFD methods were introduced that consider the exchange kernel in addition to the Hartree kernel. [1,2] Here in a further step a power series approximation for the correlation kernel of time-dependent density-functional theory is presented. [3] Using this approximation in the ACFD theorem leads to a new family of KS methods. The new methods yield reaction energies of unprecedented accuracy and enable a treatment of static (strong) correlation with an accuracy of high-level multireference configuration interaction methods but are single-reference methods allowing for a black-box-like handling of static correlation. The new methods exhibit a better scaling of the computational effort with the system size than rivaling wave-function-based electronic structure methods. Moreover, the new methods do not suffer from the problem of singularities in the response functions plaguing previous ACFD methods [4] and therefore are applicable to any type of electronic system, ranging from dissociating molecules to the homogeneous electron gas.

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