Orbital-dependent kernels in time-dependent density-functional theory and new correlation functionals

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A Time-Dependent Density-Functional (TDDFT) response equation for the effective Kohn-Sham potential instead of the electron densities is presented that enables the use of orbital-dependent exchange-correlation kernels. In combination with the frequency-dependent exact-exchange EXX kernel the new approach describes long-range charge-transfer excitations qualitatively correctly in contrast to standard TDDFT methods, as shown by formal analysis and applications to molecular systems. [1] The relation of TDDFT response methods based on the EXX kernel to time-dependent Hartree-Fock ist discussed. The fluctuation-dissipation theorem is used to construct new orbital-dependent correlation functionals within a random phase approximation using the EXX kernel. The new correlation functionals yield promising results in comparison with methods employing various other correlation functionals or compared to wave-function-based methods like Moller-Plesset perturbation theory or coupled cluster methods [2].

Literature:

[1] Andreas Heßelmann, Andrey Ipatov, and Andreas Görling, Phys. Rev. A 80, 012507 (2209).

[2] Andreas Heßelmann and Andreas Görling, Mol. Phys., in press.