Excitation energies from the time-independent ensemble Density-Functional Theory

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In 1988 Gross, Oliveira and Kohn established a Hohenberg–Kohn functional for ensembles consisting of a simple weighted combination of the lowest states of the Born–Oppenheimer Hamiltonian. With a Kohn–Sham ansatz, they also established an appealing expression to calculate excitation energies from Kohn–Sham orbital energies and the derivative of the exchange-correlation energy with respect to the ensemble weight. The ensembles approach is in principle entirely general and could be used to evaluate excitation energies beyond the scope of TDDFT.

We study the definition of the universal ensemble density functional as the convex conjugate of the ensemble energy and evaluate the functional with accurate full-CI input densities. Next we evaluate the ensemble exchange-correlation density functional and its derivative with respect to the ensemble weight. Finally we establish adiabatic-connection curves and probe the weight dependence of the functional.