

Random-phase approximation correlation methods including exchange interactions

The random-phase approximation (RPA) method, which usually is employed to calculate excitation energies, here is used to determine the ground-state correlation energy of molecules. While standard RPA methods typically overestimate the electron correlation energy due to self-correlation errors produced by EPV diagrams in a perturbation expansion of the RPA correlation energy, RPA methods including exchange effects are able to correct this deficiency. It will be shown, however, that the way to include exchange interactions in RPA methods is not unique and that a number of different exchange RPA methods exist. Moreover, arguments will be given why it is advantageous to use Kohn-Sham instead of Hartree-Fock determinants as reference determinants in RPA approaches. Two such Kohn-Sham based RPA approaches will be presented that can be implemented with a moderate scaling of N^5 with respect to the molecular size and which yield accurate results for a number of molecular properties.