Coverage of dynamic correlation effects by DFT functionals: Density-based analysis for atoms

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A density-based approach [1] directly hinged on difference radial density (DRD) distributions defined with respect the Hartree-Fock radial density has been employed for analyzing the impact of dynamic correlation effects on the density. Those effects has been analyzed for the Ne and Ar atoms, for which non-dynamic correlation effects play a negligible role.

The DRD-distributions calculated by several ab initio methods have been compared with their DFT counterparts generated for representatives of all generations of broadly used exchange-correlation functionals and for the orbital-dependent OEP exchange-correlation functionals (OEPx, OEP2-f, OEP2-sc, OEP-ccpt2) [2,3]

The impact of correlation effects on the electron density is relatively weak. But the DRD distribution curves provide a reliable description of the impact of these effects both at the WFT and DFT levels

For the local, generalized-gradient, and hybrid functionals it has been found that the dynamic correlation effects are to a large extend accounted for by densities resulting from exchange-only calculations. So, widely used popular exchange-only functionals, in addition to their nominal role, represent dynamic correlation effects. Removal of self-interaction errors does not eliminate the representation of correlation effects by exchange functionals.

It has been demonstrated that the VWN5 and LYP correlation functionals do not represent any substantial dynamical correlation effects on the electron density, whereas these effects are well represented by the orbital dependent OEP2 correlation functionals. Some attention has been paid to demonstrating the differences between the energy- and density-based perspectives. They indicate the usefulness of density-based criteria for developing new exchange-correlation functionals.

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