A note on the accuracy of KS-DFT densities

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ABSTRACT

The accuracy of the density of wave function methods and Kohn-Sham density functionals are studied using moments of the density, $\langle r^n \rangle = \int \rho(r) r^n d\tau = \int_0^\infty 4\pi r^2 \rho(r) r^n dr \ \ where\, n = -1, -2, 0, 1, 2, and\ 3$ provides information about the short- and long-range behavior of the density. CCSD(T) is considered the reference density. Three test sets are considered; boron through neon neutral atoms, two and four electron cations, and 3d transition metals. The total density and valence only density are distinguished by dropping appropriate core orbitals. Among density functionals tested CAMQTP00 and ωb97x show the least deviation for the boron through neon neutral atoms. They also show accurate eigenvalues for the HOMO indicating that they should have a more correct long-range behavior for the density. For transition metals, some density functional approximations outperform some wavefunction methods, suggesting that the KS determinant could be a better starting point for some kinds of correlated calculations. By using generalized many-body perturbation theory (GMBPT) the convergence of second, third, and four-order KS-MBPT for the density is addressed as it converges to the infinite-order coupled cluster result. For the transition metal test set, the deviations in the KS-DFT methods depend on the amount of exact exchange the functional uses. Functionals with exact exchange close to 25% show smaller deviations from the CCSD(T) density.