

ON-TOP TWO-ELECTRON DENSITIES COMPUTED WITH ONE-ELECTRON BASIS SETS AND THEIR (MIS)USE IN QUANTUM-CHEMICAL FORMALISMS

Jerzy Cioslowski

Institute of Physics, University of Szczecin, Wielkopolska 15, 70-451 Szczecin, Poland
✉ jerzy.cioslowski@usz.edu.pl

The properties of the approximate on-top two-electron densities $\Phi(\mathbf{r})$ computed with one-electron basis functions are investigated in detail. The key findings of these investigations, which also concern the reduced variant of $\Phi(\mathbf{r})$, i.e. $4 \Phi(\mathbf{r}) / \rho(\mathbf{r})^2$ [where $\rho(\mathbf{r})$ is the one-electron density], are as follows: 1) $\Phi(\mathbf{r})$ converge extremely slowly to the complete basis set (CBS) limits, their errors asymptotically scaling like $N^{-1/3}$ with the number N of basis functions (as contrasted with the N^{-1} error scaling of the electronic energy); 2) this slow convergence results in gross inaccuracies of the approximate $\Phi(\mathbf{r})$ computed with standard basis sets; 3) the errors in these $\Phi(\mathbf{r})$ are in general refractory to reduction with standard convergence acceleration techniques such as the CBS-limit extrapolation; 4) it is essential to make a distinction between the physically meaningful genuine $\Phi(\mathbf{r})$ (such as those produced by highly accurate calculations) and the contrived ones (such as those appearing in some variants of the Kohn-Sham formalism and in overly simplistic models) that are merely auxiliary quantities to which no physical meaning should be attached; 5) due to the presence of spurious features in the contrived $\Phi(\mathbf{r})$, their employment in analysis of electronic structure leads to false and misleading conclusions on chemical bonding and electron correlation; and 6) the MC-PDFT formalism suffers from a hidden "double-counting" problem whose presence is masked for sufficiently small active spaces by its use of the contrived $\Phi(\mathbf{r})$.