Basis set limit and systematic errors in local-orbital based all-electron DFT VOLKER BLUM, JÖRG BEHLER, RALF GEHRKE, KARSTEN REUTER, MATTHIAS SCHEFFLER, Fritz-Haber-Institut, Faradayweg 4-6, 14195 Berlin, Germany — With the advent of efficient integration schemes,[1,2] numeric atom-centered orbitals (NAO's) are an attractive basis choice in practical density functional theory (DFT) calculations of nanostructured systems (surfaces, clusters, molecules). Though all-electron, the efficiency of practical implementations promises to be on par with the best plane-wave pseudopotential codes, while having a noticeably higher accuracy if required: Minimal-sized effective tight-binding like calculations and chemically accurate all-electron calculations are both possible within the same framework; non-periodic and periodic systems can be treated on equal footing; and the localized nature of the basis allows in principle for $O(N)$-like scaling. However, converging an observable with respect to the basis set is less straightforward than with competing systematic basis choices (e.g., plane waves). We here investigate the basis set limit of optimized NAO basis sets in all-electron calculations, using as examples small molecules and clusters (N_2, Cu_2, Cu_4, Cu_{10}). meV-level total energy convergence is possible using ≤ 50 basis functions per atom in all cases. We also find a clear correlation between the errors which arise from underconverged basis sets, and the system geometry (interatomic distance).
[1] B. Delley, J. Chem. Phys. **92**, 508 (1990), [2] J.M. Soler *et al.*, J. Phys.: Condens. Matter **14**, 2745 (2002).

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