Static polarizabilities at the basis set limit: A benchmark of 128 species

Anders Brakestad[a], Stig Rune Jensen[a], Kathrin H. Hopmann[a], and Luca Frediani[a]

[a]*Hylleraas Centre for Quantum Molecular Sciences, Department of Chemistry,*
UiT The Arctic University of Norway
anders.m.brakestad@uit.no

Multiwavelets have been shown to deliver atomization energies [1] and magnetic properties [2] at the complete basis set limit (CBS). In this work we extend the use of multiwavelets to the calculation of static polarizabilities (StatPol) for a set of 128 small molecular and atomic species. By comparing to highly accurate multiwavelet results, we have quantified the basis set errors present in StatPol calculations with the large GTO basis set aug-pc-4 [3]. With the MRChem program package, we used the finite difference approach to obtain StatPols, and all comparisons were done with the PBE functional. We find that the large GTO basis generally performs well, resulting in relative deviations of less than $0.5\,\%$ for the majority of the species (Figure 1). However, several challenging cases are revealed, especially among the open-shell species, where relative deviations as large as $8\,\%$ are observed. Note that a portion of these larger deviations are likely due to contamination from hyperpolarizabilities, due to the large field strength of $\epsilon = 0.01$ used in the GTO calculations. Further, GTOs seem to overestimate the StatPols, which goes against intuition as analytical StatPols are variationally approached from below. In sum, it cannot be assumed that large GTO basis sets are sufficiently close to the CBS when computing StatPols for open-shell species, and multiwavelets provide the possibility of obtaining quasi-exact results with respect to the CBS. The contributions from hyperpolarizabilities also need to be quantified in order to provide a fair comparison of GTOs and multiwavelets.
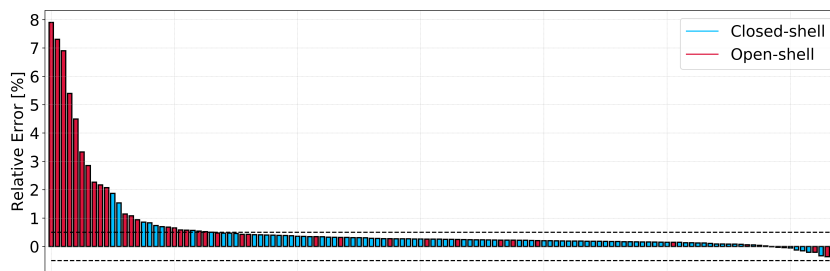

Figure 1: Distribution of relative deviations for all 128 species. The dashed lines are located at $\pm 0.5\,\%$ relative deviations.

References
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