Highly accurate atomization reference energies for pseudpotential benchmarking

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Pseudopotential calculations aim at reproducing all-electron calculations within a chosen exchange correlation functional with errors that are less than the errors arising from the exchange correlation functional itself. Since exchange correlation functionals are approaching the much sought after chemical accuracy of 1 kcal/mol, pseudopotentials should not give rise to errors that are not much larger than this value (The Journal of chemical physics 138, 104109 (2013)). To assess the accuracy of pseudopotential calculations highly accurate all-electron reference values are needed. Obtaining in all electron calculations guaranteed errors lower than the chemical accuracy is impossible with standard atom centered basis sets. Using a novel multi-wavelet basis set we were however able to calculate the atomization energies of some 250 molecules with an accuracy of 0.001 kcal/mol. (The Journal of Physical Chemistry Letters 8, 1449-1457 (2017)). These reference values allow for the first time to check in a reliable way the accuracy of pseudopotentials for atomization energies. It will be shown that pseudopotentials that perform well in the Delta test do not necessarily also give low errors in atomization energies.