On the Development of Accurate Gaussian Basis Sets for f-Block Elements - Initial Efforts for F12 Correlation Consistent Basis Sets for Uranium

Kirk A Peterson[a] and J. Grant Hill[b]

[a] *Washington State University,* [b] *University of Sheffield*
kipeters@wsu.edu

Over the last few years, the Peterson group has developed sequences of correlation consistent basis sets for the f-block elements La-Lu and Ac-Lr [1-3]. These were mostly all-electron sets based on either the Douglas-Kroll-Hess or eXact 2-component scalar relativistic Hamiltonians, but additional sets based on relativistic effective core potentials were also developed for Th-U. All of these basis sets, which included those for both valence and outer-core correlation, exhibited systematic convergence to both the Hartree-Fock and correlation energy complete basis set (CBS) limits, but exhibited relatively slow convergence, particularly for correlation of the outer-core. Based on our previous experience with explicitly correlated F12 methods [4], these should be very efficient at recovering correlation effects of electrons in the compact inner valence orbitals, e.g., the 5f of the actinides, as well as the important outer-core electrons, e.g., the 5s5p5d of actinides. Initial results for geometries and relative energies will be presented at the CCSD(T)-F12 level of theory using existing cc-pV*n*Z-PP basis sets for selected uranium-containing molecules. Preliminary design of new F12 basis sets for uranium will also be discussed.

References

1. K.A. Peterson, *J. Chem. Phys*. **142** (2015), 074105.
2. Q. Lu and K.A. Peterson, *J. Chem. Phys.* **145** (2016), 054111.
3. R. Feng and K.A. Peterson, *J. Chem. Phys*. **147** (2017), 084108.
4 J.G. Hill and K.A. Peterson, *J. Chem. Phys*. **141** (2014), 094106.