

Impact of Spin–Orbit Density Functional Routines for the Prediction of Actinide Thermochemistry.

Lucas E. Aebersold¹, Angela K. Wilson¹

¹ *Department of Chemistry, Michigan State University, East Lansing, Michigan*

The majority of electronic structure calculations done on actinide compounds only account for scalar relativistic effects. The most common literature values utilize relativistic effective core potentials (RECPs), especially for larger actinide complexes. However, vector effects, such as spin–orbit coupling (SOC), are often neglected which can have a significant impact on the results obtained. There are routines capable of incorporating spin–orbit effects into standard RECPs, without much increase in computational cost, specifically for density functional theory (DFT). These spin–orbit DFT (SODFT) routines, however, are not widely used, and their potential effectiveness for computing properties needs more investigation, especially for the actinides. In this study 18 common density functionals are evaluated using DFT and SODFT with the Stuttgart class of small core RECPs. To assess performance, the enthalpies of formation for 66 small actinide (Th–Am) compounds for which experimental data exists are computed for each functional. The chosen compounds included actinide halides, oxides, and oxohalides in a general form, AnO_mX_n , where $n = 0 - 6$, $m = 0 - 3$, and $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{or I}$. The analysis includes the impact of SODFT on the accuracy and consistency of the predicted enthalpies of formation. In addition, the differences between Stuttgart general and segmented contracted atomic natural orbital (ANO) basis set for the RECP. Results from all-electron (AE) calculations using the third-order Douglas-Kroll-Hess method are also shown for further comparison.