

Investigating actinide compounds within a hybrid MCSCF-DFT model

Emmanuel Fromager^a, Pernilla Wåhlin^b, Florent Réal^b, Hans Jørgen Aa. Jensen^a and Ulf Wahlgren^b

^a*Department of Physics and Chemistry, University of Southern Denmark, Odense, Denmark.*

^b*AlbaNova University center, Institute of Physics, Stockholm University, Stockholm, Sweden.*

Investigations of actinide chemistry with quantum chemical methods still remain a complicated task since it requires an accurate and efficient treatment of the environment (crystal or solvent) as well as relativistic and electron correlation effects. Concerning the latter, the current correlated methods, based on either Density-Functional Theory (DFT) or Wave-Function Theory (WFT), have their advantages and drawbacks. On the one hand, Kohn–Sham DFT (KS-DFT) calculates the dynamic correlation quite accurately and at a fairly low computational cost. However, it does not treat adequately the static correlation, which is significant in some actinide compounds because of the near-degeneracy of the 5*f* orbitals: a first example is the bent geometry obtained in KS-DFT(B3LYP) for the neptunyl ion NpO_2^{3+} , which is found to be linear within a *Multi-Configurational Self-Consistent Field* (MCSCF) model [1]. A second one is the stable and bent geometry obtained in KS-DFT(B3LYP) for the plutonyl ion PuO_2^{4+} , which disintegrates at the MCSCF level [1]. On the other hand, WFT can describe the static correlation, using for example a MCSCF model, but then an important part of the dynamic correlation has to be neglected. This can be recovered with perturbation-theory based methods like for example CASPT2 or NEVPT2, but their computational complexity prevents large scale calculations.

It is therefore of great interest to develop a hybrid MCSCF-DFT model which combines the best of both WFT and DFT approaches. The merge of WFT and DFT can be achieved by splitting the two-electron interaction into long-range and short-range parts [2]. The long-range part is then treated by WFT and the short-range part by DFT. We use the so-called "erf" long-range interaction $\text{erf}(\mu r_{12})/r_{12}$, which is based on the standard error function, and where μ is a free parameter which controls the long/short-range decomposition. The newly proposed recipe for the definition of an optimal μ_{opt} parameter [3], independent of the approximate short-range functional and the approximate (MCSCF) wave function, is applied in this work. Recently reviewed calculations on light elements yielded $\mu_{\text{opt}} \approx 0.4$ a.u [3], which is in agreement with previous calibration studies. A new numerical investigation of μ_{opt} is now presented for actinides. A test set consisting of ThO_2 , PaO_2^+ , UO_2^{2+} , UCO and UN_2 (representing cases without significant static correlation) as well as NpO_2^{3+} and PuO_2^{4+} (representing cases with significant static correlation) has been considered. The bending problem of NpO_2^{3+} and PuO_2^{4+} observed in KS-DFT(B3LYP) is then addressed within the hybrid MCSCF-DFT approach. Calculations have been performed at the scalar relativistic level with the MCSCF-DFT code [4] implemented in a development version of the DALTON program package [5], using short-range LDA and PBE-type functionals [3].

References

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