Electronic Structure Simulations of Uranium Dioxide

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Reliable simulations for actinide materials are important as a complementary alternative to experimental investigations, because experiments with such usually hazardous materials are difficult and costly. During the recent decades density functional theory (DFT) has proven to be such a method for condensed phase actinide systems. However, the accurate description of the strong correlation of the 5f electrons still poses a challenge for current density functionals and in fact a plain DFT method predicts uranium dioxide (UO_2) to be metallic. As a remedy Anisimov *et al.* [1] proposed the addition of a Hubbard-like U term to the DFT functional. This term introduces an energy penalty for the delocalized 5f electrons which "encourages" the 5f electrons to localize. This so-called DFT+U method improves indeed many physical properties with respect to the experiment, but, unfortunately, it creates also a manifold of possible localization patterns for the 5f electrons at each uranium site which causes the occurrence of metastable states. Several recipes have been devised in the literature to tackle this problem to ensure a convergence to the true electronic ground state for a given atomic configuration [2-5]. In this work fully unconstrained cell optimizations of UO_2 bulk model systems are presented using the DFT+U implementation in the CP2K code [5,6]. Different effective U_{eff} values are employed in the framework of the DFT+U approach proposed by Dudarev [7] for various electronic density guesses. The detected low-lying states are presented and their properties are analyzed.

References

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