DFT study of the magnetic ground-state of UO_2

The goal of this study is to describe accurately structural, electronic and magnetic ground-state properties of UO_2, using ab initio electronic structure calculations. Experimental assessment of the magnetic ground-state of UO_2 at low temperature is challenging because of complications posed by radioactive decay, the tendency to oxidize and form non-stochiometric UO_{2+x}, and the toxicity of the material. Computational methods do not suffer from these difficulties, and can provide complementary critical information on the material. What is known from experiments is that UO2 is an antiferromagnet with a fluorite-type ($Fm\bar{3}m$) structure. Below the Néel temperature, however, small oxygen displacements arise, lowering the symmetry. Previous DFT studies had found the magnetic ground state of UO_2 to be (collinear) transverse 1k anti-ferromagnetic, which is not in line with the $Pa\bar{3}$ crystal symmetry suggested by some experiments.[1,2]

This work focuses on ground-state properties of UO_2 and on benchmarking the DFT calculations. We discuss the functionals and parameters needed to describe UO_2 accurately and research the magnetic ground-state of the material. We've established that using PBE+U and HSE06 (using the effective U value derived from experiment,[3] and standard $\alpha = 0.25$) functionals to describe the localised f-states is not enough to create the correct (Mott-) insulating behaviour of the material when it has a non-collinear anti-ferromagnetic ordering. The inclusion of spin-orbit coupling is necessary to shift the f-levels and open the band gap. We also determine the screening parameter α in HSE06 that better describes the effective screening in UO_2 and its electronic properties.

References

[1] Desgranges L et al 2017 Inorg. Chem. 56 321−326.

[2] Faber J and Lander GH 1975 Phys. Rev. Lett. 35 1770.

[3] Kotani A and Yamazaki T 1992 Prog. Theor. Phys. Suppl. 108 117.