

Which is more ionic? UO₂ or PuO₂

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The electronic structure of many of the oxides containing *d*- and *f*-elements has long been a challenge for theory. For example, the traditional workhorses of density functional theory, the local density approximation (LDA) and the generalized gradient approximations (GGA), predict most of these systems to be metallic, when in fact they are insulators with band gaps of several eV. These problems reflect the localization/delocalization dilemma faced in systems with weak overlap and seem to be largely overcome by the new generation of hybrid density functionals developed for molecular studies. Only fairly recently has it been possible to apply these functionals to solids but in the cases studied thus far we find a distinct improvement when comparing with experiment. Hybrid functionals have also made a counterintuitive prediction: that of significant covalency in PuO₂, as opposed to UO₂; a prediction that has now been addressed by experiment. I will review predictions of the theory and recent experimental work on the first single-crystal quality samples of PuO₂.

Covalency in the actinides probed with ligand K-edge X-ray absorption spectroscopy

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I will discuss experimental and theoretical investigations of ligand K-edge X-ray absorption spectroscopy for a number of actinide complexes and solids. Evidence for *f*-orbital – ligand bonding interactions will be presented, and the ramifications of this for actinide electronic structure discussed.