Examining the Performance of DFT Methods in Actinide Chemistry

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We wish to develop a rigorous theoretical treatment that can be used to model the behaviour of systems that contain actinides, such as the uranyl ion, in aqueous solution. These solutions will contain coordinating anions such as sulphate, carbonate, or halides. For reasons of computational efficiency, DFT methods seem to be essential, as does the use of an ECP. But which version of DFT is the most suitable? How many electrons need to be treated explicitly on the actinide?

To answer these questions, we have examined the performance of many different functionals and two different ECP. The experimental test data include geometries, vibrational frequencies, reaction enthalpies and NMR chemical shifts.

We present below two representations of the uranyl ion in aqueous solution: 17 or 26 water molecules have been included in an ONIOM-type treatment. It is clear that 26 molecules are not sufficient for a balanced description of the aqueous solution.