Role of Strong Correlations in Disproportionation of Aqueous Actinides

STEVEN E. HOROWITZ, J.B. MARSTON, Brown University — We study the role of strong electronic correlations in the disproportionation of aqueous actinide complexes An(aq) and AnO$_2$(aq) where An = U, Np, and Pu. Correlations are expected to be important due to the localized nature of the actinide 5f orbitals. We first confirm that relativistic DFT, despite yielding reasonable geometries and bond lengths, fails to reproduce experimentally observed degeneracies of the redox potentials. By using a continuum model for the water beyond the first solvation sphere we are able to construct and diagonalize reduced Hubbard-like models of the actinide complexes, and incorporate the missing physics of strong intra-atomic Coulomb repulsion.

1Supported in part by NSF DMR-0213818.
2ADF2004.01, SCM, Theoretical Chemistry, Vrije Universiteit.
6D. V. Efremov et al., cond-mat/0303414; E. Runge et al., cond-mat/0402124.