Effects of the self-interaction error in Kohn-Sham calculations: A DFT + U case study on penta-aqua uranyl(VI)

Using the LCGTO-DFT + U methodology, we analyze the potential effect of self-interaction artifacts in standard Kohn-Sham (KS) density functional calculations on geometries, vibrational frequencies, and bonding for the example of the uranyl (VI) dication, both without and with explicit aqua ligands. We attribute the bent structure of the uranyl moiety in the penta-aqua complex to the limited accuracy of the Coulomb interaction of the U 5f orbitals afforded by common local or gradient-corrected exchange-correlation functionals. In particular, with scalar relativistic, all-electron Douglas-Kroll-Hess calculations we demonstrate that the distorted geometry of the uranyl penta-aqua complex is essentially rectified by the inclusion of a small positive on-site repulsion parameter, U(\text{eff}), for the 5f shell of the uranium atom. (C) 2010 Elsevier B.V. All rights reserved.

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