Transition metal dioxides: a case for the intersite term in Hubbard-model functionals

HEATHER KULIK, Stanford University, NICOLA MARZARI, Oxford University — Triatomic transition-metal oxides in the “inserted dioxide” (O-M-O) structure represent one of the simplest examples of systems that undergo qualitative geometrical changes via subtle electronic-structure modulation. We discuss three transition-metal dioxide molecules (MO$_2$ where M = Mn, Fe, or Co), for which equilibrium structural (e.g., bent or linear geometry) and electronic (e.g., spin or symmetry) properties have been challenging to assign both theoretically and experimentally. Augmenting a standard density-functional theory (DFT) approach with a Hubbard term (DFT+$U$) occasionally over-localizes the 3$d$ manifold, leading to incorrect bond elongation and, in turn, poor equilibrium geometries for MO$_2$ molecules, while preserving good spin-state splittings. We recover a proper description of both geometry and energetics for these molecules through either calculating DFT+$U$ relaxations at fixed M-O bond lengths or by inclusion of an inter-site interaction term $V$ that favors M(3$d$)-O(2$p$) interactions. In the latter case, both $U$ and $V$ are calculated fully from first-principles and are not fitting parameters. Finally, we present an approach that more accurately determines the Hubbard $U$ over a coordinate in which the character of bonding varies.