

Abstract Submitted  
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**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 ( $\text{MO}_2$  where  $M = \text{Mn, Fe, or Co}$ ), for which equilibrium structural (eg bent or linear geometry) and electronic (eg 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  $3d$  manifold, leading to incorrect bond elongation and, in turn, poor equilibrium geometries for  $\text{MO}_2$  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  $M(3d)$ - $O(2p)$  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.

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