Insight from first principles into the stability and magnetism of alkali-metal superoxide nanoclusters

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Alkali-metal superoxides are gaining increasing interest as 2p magnetic materials for information and energy storage. Despite significant research efforts on bulk materials, gaps in our knowledge of the electronic and magnetic properties at the nanoscale still remain. Here we focused on the role that structural details play in determining stability and magnetic couplings of $(MO_2)_n$ (M = Li, Na, and K, with n = 2 - 8) clusters. Using first-principles density functional theory based on the Perdew-Burke-Ernzerhof (PBE) and Heyd-Scuseria-Ernzerhof (HSE06) functionals, we examined the effect of atomic structure (Figure 1) on the relative stability of different polymorphs within each investigated cluster size. We found that small clusters prefer to form planar-ring structures, whereas non-planar geometries become more stable when increasing the cluster size. However, the crossover point depends on the nature of the alkali metal. Our analysis revealed that electrostatic interactions govern the highly ionic M-O_2 bonding and ultimately control the relative stability between 2-D and 3-D geometries.

Additionally, alkali-superoxides have been identified as strongly correlated 2p magnetic materials than can be described by a multi-orbital Hubbard-type Hamiltonian. In this framework we extracted Maximally Localized Wannier Functions from the bands of interest and used them to calculate magnetic exchange couplings between superoxide sites in our nanoclusters. In order to contrast the fidelity of our calculations we compared them with results from very accurate wave function based calculations.

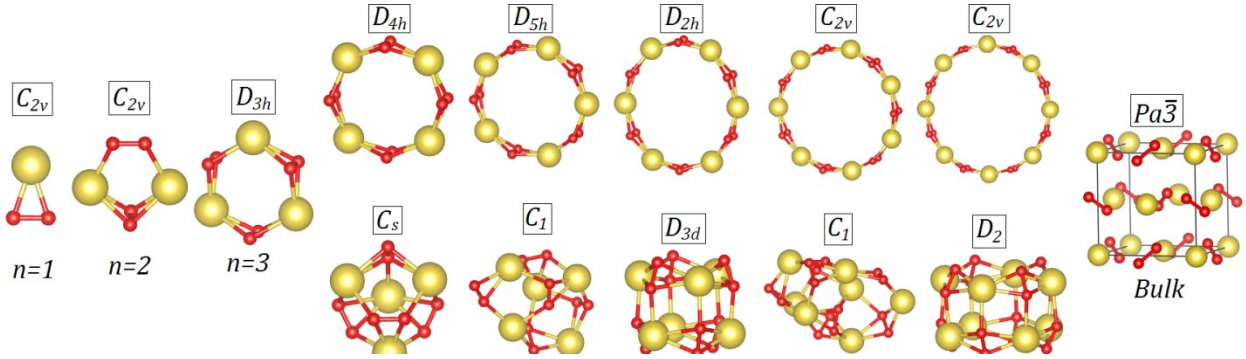

Figure 1. Atomic structure of optimized $(NaO_2)_n$ clusters and $Pa\acute{3}$ NaO_2 bulk (pyrite phase) using HSE06. The point group of each cluster is indicated. Yellow and red spheres are Na and O atoms, respectively.