

# Lanthanide Covalency in Simple and Complex Oxides – A Combination of Theory and Experiments

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Lanthanide containing complex oxides, especially the  $ABO_3$  perovskite and  $A_{(n+1)}B_nO_{(3n+1)}$  Ruddlesden-Popper series, attract much interest as promising catalytic materials in many renewable energy applications such as electro-chemical energy conversion and hydrogen production. Recent experimental and theoretical studies on some members of these materials, e.g.  $La_2NiO_4$ , revealed that the La-O terminated surfaces are catalytically active under operational conditions. These findings suggested that the conventional understanding of such oxides being fully ionized, and composed of catalytically inert  $La^{3+}$  ions needs to be revised. In this study, generalized gradient approximation and hybrid density functional theory methods were used to study and compare the electronic structures of La and Sr in related oxides. The results were bench-marked across multiple different DFT approaches, including both LCAO and plane-wave based methods, and consistent results were. Density of states plots and charge analysis results showed that La exhibits a partially occupied d-orbital and an atomic charge of +2 instead of its nominal valence number (+3) in the oxides, while Sr does not show similar characteristics. Electron density maps obtained from synchrotron X-ray diffraction experiments directly confirmed the simulation findings. The presence of available d-orbital electron on La and associated partial covalency was postulated as being responsible for the catalytic behaviour observed in experiments. In addition, other elements like Pr and Ba electronic structures in related oxides were also calculated. A similar trend like the La and Sr charges was observed. This observed partial covalency is possibly a common characteristic of all Lanthanide elements.