An electronic structure descriptor for oxygen reactivity at metal and metal-oxide surfaces

Identifying and understanding relationships between the electronic and atomic structure of surfaces and their catalytic activity is an essential step towards the rational design of heterogeneous catalysts for both thermal and electrochemical applications. Herein, we identify a relationship between the atom-projected density of states of surface oxygen and its ability to make and break bonds with the surrounding metal atoms and hydrogen. This structure-property relationship is shown to hold across different classes of materials (metals, rutile metal-oxides, and perovskite metal-oxides) and for different oxygen binding sites (i.e. different oxygen coordination numbers). We utilize understanding from the d-band model and the simple two-level quantum coupling problem to shed light on the physical origin of this relationship for transition metal surfaces and we hypothesize similar principles extend to the other materials considered. Finally, we demonstrate the utility of the identified descriptor to serve as a tool for high throughput screening of oxygen active sites for large systems where many unique oxygen sites exist and can be computationally expensive to probe individually. As an example, we predict the reactivity of 36 unique oxygen atoms at a kinked RuO$_2$ extended surface from a single self-consistent DFT calculation.