Developing Standardised Modelling Workflows for the QM/MM Simulation of Metal Oxides

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Modelling plays a key role in advancing our understanding of materials, assisting in both the discovery of novel condensed phase systems and development of their applications. Thus, models of solid state materials need to be both accurate and efficient, yet there is often a compromise between accuracy and computational cost. QM/MM (Quantum Mechanical/Molecular Mechanical) simulations achieve high accuracy with good computational efficiency by limiting the full quantum mechanical calculation to a small region of interest where preserving physicality is critical; the interactions with the quantum region are then modelled though coupling to an environment of classical charges.[1] QM/MM has advantages over periodic density functional theory (DFT) simulations; the latter method can be resource inefficient, scale poorly with increasing sizes of cells and require corrections for nonphysical interactions, such as defect interactions, due to limitations in cell size.[2] The advantages of QM/MM methods for modelling point defects come from eliminating the simulation cell altogether, fully isolating defects as we would expect to find them in nature.

We have performed calculations on neutral and charged point defects in bulk MgO, employing QM/MM simulations (validating these against periodic DFT calculations) to develop a full workflow for producing accurate and realistic simulations. Our initial methodology is based on the simple system of bulk magnesium oxide (MgO) to facilitate accurate model development, allowing us to design heuristics for easily setting up embedding simulations.[3-6] Currently, we have been exploring how to best define an optimal size/shape of the QM and MM regions for accurate and efficient simulation, building on previous work in this area that suggests a unit cell based partitioning approach is superior to the simpler radial partitioning method.[7, 8] A study by Shushko, Shluger and Catlow explored MgO surfaces with a similar but distinct embedding method, and we hope to be able to replicate their results using our newer models.[9] Our investigation into MgO is now being extended into surface models to achieve this goal, utilising the same methodologies as seen in the bulk studies – comparison of QM/MM results with those generated by periodic DFT, observing the efficacy of this methodology for modelling point defects in the solid state. The outcomes of both these studies will show if the best method of partitioning can be rigorously identified from chemical observables of the periodic bulk or surface systems.

In the future, we hope to use this work to investigate species that are more challenging to model for their applications in catalysis such as rocksalt structure MnO and CoO as well as expanding the scope to materials for photocatalytic hydrogen production such as TiO_2.

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