Structure and charge transfer at the hematite(001)-water interface from all-QM DFT molecular dynamics

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Hematite (Fe₂O₃) has attracted much attention as an anode material for photoelectrochemical water splitting for many years. However, the atomistic surface structure of the material in contact with liquid water and the nature of the excess hole that oxidizes water are not well understood. Our aim is to characterize these properties using large-scale all-QM DFT molecular dynamics simulation of the hematite(001)-water interface. The complex electronic structure of haematite and the large system sizes required to model a realistic aqueous interface make this work extremely challenging, in particular in terms of the computational resources required. We found that a modified HSE06 functional containing 12% exact exchange reproduces electronic and geometric properties with relatively high accuracy, in particular the antiferromagnetic and band ordering. The terminating surface hydrogens are arranged in an unexpected, alternating pattern, 1 proton shared between two surface oxygens and 1 proton protruding in the aqueous solution. These protons are found to easily dissociate from the hematite surface upon injection of an excess hole in the hematite layer giving a possible explaining why water splitting experiments are typically carried out at very high pH. Finally, we outline a possible way to compute charge transfer rates across such interfaces from "first principles" all-QM DFT molecular dynamics.