

# Car-Parrinello Investigation of Acid/Base and Electronic Properties of Oxide-Water Interfaces

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Surfaces of main group and transition metal oxides are covered by a layer of adsorbed water molecules when exposed to water vapour or immersed in bulk water. The interactions can be strong enough to dissociate some or even all adsorbed water molecules. The resulting surface dipole potential shifts the energy levels of the oxide changing the electronic work function. The energetics, geometry and electronic structure of hydrated solid-gas interfaces have been investigated in great detail using the Density Functional Theory (DFT) based electronic structure calculation methods of computational surface science leading to a number of useful insights. It would appear that application of similar methods could be equally instructive for interfaces with bulk water. However, surfaces in contact with an aqueous phase can lose protons to solution or attract protons building up a net surface charge. The surface charge is compensated by counter ions in solution (electrical double layer) establishing an interfacial potential which must be added to the surface potential due to the adsorption. This is the realm of electrochemistry and colloid science where dynamical simulation methods (“Car-Parrinello”) and related schemes for free energy computation are more appropriate than the in essence static methods of computational surface science.

This talk is an overview of recent work in the group on oxide water interfaces using DFT based molecular dynamics (DFTMD) methods as implemented in the CP2K code (<http://www.cp2k.berlios.de>). The systems that have been investigated to date include  $\text{TiO}_2$ ,  $\text{SiO}_2$  and  $\text{SnO}_2$  water interfaces, while an investigation of aqueous  $\text{MnO}_2$  is under way. The central computational tool is a method for reversible insertion of protons in a DFTMD model of an aqueous solution[1, 2]. The corresponding free energy

enables us to compute Brønsted acidities of surface groups[3] and align the electronic density of states of the solid with the normal hydrogen electrode (NHE)[4]. The talk will focus on the results for the rutile (110)  $\text{TiO}_2/\text{H}_2\text{O}$  interface for which we computed the pH at which the surface carries no net proton charge (the PZC)[3], the energy position of the conduction band bottom and valence band top under flatband conditions relative to the NHE at the PZC[4] and the response to (de)protonation (see paragraph above) from which we obtain an estimate of capacitance of the compact electrical double layer. The most notable result of these calculations, which use the PBE functional, is that the position of the conduction band bottom ( $-0.6$  V versus NHE) is in fair agreement with experiment ( $-0.3$  V). Converting these values to absolute energies relative to vacuum using the experimental solvation free energy of the proton as reference we find  $-3.7$  eV compared to the experimental value of  $-4.1$  eV. Hydration appears to have little effect on the bandgap in our calculation. The well-known underestimation of the bandgap in PBE is therefore largely manifested in the position of the valence band top (minus the ionization potential) which ends up  $1.6$  eV too high. We conclude the presentation with some general comments on the potential and limitations of the application of DFTMD methods to interfacial electrochemistry.

## References

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