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First-Principles Approach to Energy Level Alignment at Aqueous Semiconductor Interfaces[1]

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We have developed a first principles method to calculate the energy level alignment between semiconductor band edges and reference energy levels at aqueous interfaces [1, 2]. This alignment is fundamental to understand the electrochemical characteristics of any semiconductor electrode in general and the potential for photocatalytic activity in particular. For example, in the search for new photo-catalytic materials, viable candidates must demonstrate both efficient absorption of the solar spectrum and an appropriate alignment of the band edge levels in the semiconductor to the redox levels for the target reactions. In our approach, the interface-specific contribution to the electrostatic step across the interface is evaluated using density functional theory (DFT) based molecular dynamics to sample the physical interface structure and the corresponding change in the electrostatic potential at the interface. The reference electronic levels in the semiconductor and in the water are calculated using the GW approach, which naturally corrects for errors inherent in the use of Kohn-Sham energy eigenvalues to approximate the electronic excitation energies in each material. Taken together, our calculations provide the alignment of the semiconductor valence band edge to the centroid of the highest occupied $1b_1$ level in water. The known relationship of the $1b_1$ level to the normal hydrogen electrode completes the connection to electrochemical levels. We discuss specific results for GaN, ZnO, and TiO_2. The effect of interface structural motifs, such as different degrees of water dissociation, and of dynamical characteristics, will be presented together with available experimental data.

[1] N. Kharche, et al., Phys. Rev. Lett. 113, 176802 (2014).

[2] Research done in collaboration with N. Kharche, J. Lyons and J. T. Muckerman.

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