

Ionization of liquid water: A challenge for electronic structure and free energy calculation

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Water can in first approximation be viewed as a disordered insulating oxide with a valence band (VB) top consisting of non-bonding O2p orbitals and a conduction band (CB) consisting of a superposition of the antibonding (σ^*) orbitals of the bonds to the electropositive component (the H atom). The consensus among experimentalists is that the one-electron gap is 8.7 eV. Optical absorption starts at ≈ 6.5 eV with a first peak at 7.4 eV. Recent progress in photo emission spectroscopy (PES) of liquids enables us also to assign a firm number to the VB maximum, namely -9.9 eV relative to vacuum. This places the CB minimum just under vacuum at -1.2 eV. What makes liquid water unique are the extremely fast relaxation times in response to changes in electronic state due to the small mass of the proton and the molecular nature of the system. Essentially within 100 fs after ionization spin and charge have separated and the excitation has relaxed to a hydroxyl (OH^\bullet) radical and a solvated $\text{H}^+ - \text{e}^-$ ion pair. The free energy of this product defines an adiabatic energy gap, which is equal to 6.9 eV according to electrochemical estimates. This is significantly smaller than the vertical bandgap of 8.7 eV, but mysteriously close to the threshold for optical absorption.

Reproducing these numbers is still a major challenge for computation. The key issue is that the generalized gradient approximation (GGA) to density functional theory (DFT) commonly used for extended systems has a tendency to delocalize holes in O2p orbitals stabilizing ionization products. This is manifested in serious underestimation of both the vertical and adiabatic bandgaps. Exploiting recent gains in efficiency of the implementation of hybrid functionals[1] for extended systems we have been able to make substantial progress. These calculations indicate that the main culprit is indeed the GGA treatment of the occupied states. The empty (virtual) states are comparatively much better described by DFT even at GGA level. This conclusion could be reached by aligning the ionization potential and electron affinity of liquid water with the normal hydrogen electrode and comparing to the experimental PES data. The computational normal hydrogen electrode used in the calculation is based on methods we have developed for the calculation of redox potentials and acidity constants[2,3]. We find that application of hybrid functionals opens up the adiabatic gap to within a few 100meV from the experimental value. The one-electron gap still remains too narrow by 2 eV. Explaining how results were obtained and their interpretation will be the main topic of the talk. The persistent underestimation of the vertical gap probably calls for the more advanced many body perturbation methods as used in solid physics. Our group is not (yet) active in this field. These methods have however already been applied to optical absorption and dielectric response of liquid water by the groups of Olivia Pulci/Lucia Reining and Giulia Galli (see e.g. Ref. 4) and we end the talk with a brief overview of this work.

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