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Redox potential of liquid water: A first-principles theory
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Rensselaer Polytechnic Institute — A first-principles molecular dynamic method is proposed to calculate the absolute redox potentials of liquid water. The key of the method is the evaluation of the difference between the vacuum level and the average electrostatic potential inside liquid water, which employs an average over both time and space. By avoiding the explicit use of the Kohn-Sham level, such as the position of the valence band maximum, as the reference energy for the excited electrons, we are able to calculate water redox potentials accurately. The results using the PBE functional are in good agreement with experiment. We attribute the success of the method to the accurate charge density given by density functional calculation under the local or semi-local approximations. This establishes the validity to apply these effective and efficient approximations to study both the energetics and dynamics of the redox processes at more complex systems such as solid/solution interfaces.

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