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Ionizations of Liquid Water from Charged-cell Periodic Subsystem DFT and Embedded Coupled Cluster Simulations

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Abstract

Modeling the ionization potential (IP) and electron affinity (EA) of liquid water is challenging for two reasons: (1) the bulk-like nature of the liquid imposes the use of periodic boundary conditions (PBCs), which pose roadblocks when considering charge systems; (2) quantitative electronic structure methods, such as coupled cluster, are generally not available in PBCs. In this work, we tackle both challenges by employing subsystem DFT to split the extended system into a collection of finite subsystems embedded by extended, infinite subsystems. This is achieved by an impurity model [?] where coupled cluster wavefunctions can be introduced to evaluate the water molecules' energy functionals.

The liquid's electronic structure is expressed in subsystem contributions by invoking nonadditive density functionals whereby the total energy of the liquid is expressed as the sum of molecule-additive and nonadditive contributions [?]. The inter-molecular interaction is split into Coulomb interactions, and such nonadditive terms as the noninteracting kinetic energy and the noninteracting exchange-correlation [?]. These contributions represent interactions related among others to exchange, van der Waals and Pauli repulsion and are all bifunctional of the subsystem densities [?].

Embedding potentials are computed with the embedded Quantum ESPRESSO (eQE) [?] software employing ultrasoft pseudopotentials. The ground state calculation of each subsystem with the corresponding neutral and polarized embedding potential was carried out with DIRAC [?] and ADF [?]. The final IP/EA values reproduce the experimental values to within 0.5 eV and are determined averaging over 256 water molecules (or subsystems) considered in the simulation cell, calculated by the energy difference of the neutral and the polarized system (Called SCF method) [?] [?].

1 Introduction

2 Theoretical Background

2.1 Mapping a perdic system into a collection of non-periodic subsystems and one periodic subsystem

2.2 Evaluating the Coulomb interaction energy

2.3 Embedding potential scheme

2.4 Impurity Model

3 Computational Section

4 Results

4.1 IPs of Bulk water

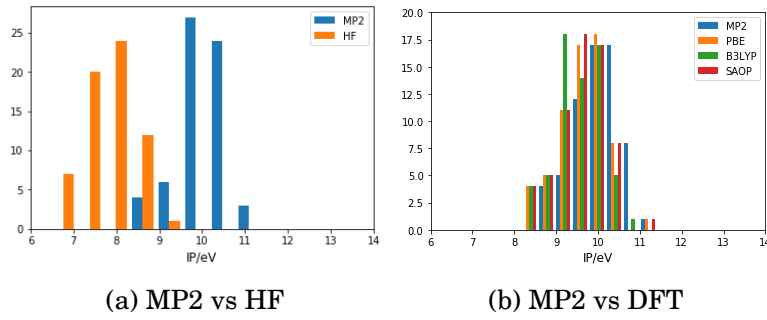


Figure 1: Distribution of IPs of bulk liquid water. The area subtended by the lines sums up to 64 (ie, the number of subsystems). Left: Comparison between MP2 and HF. Right: Comparison between MP2 and DFT

Table 1: average IPs

	IP average (eV)
MP2	9.9941
HF	7.8250
PBE	9.6089
B3LYP	9.5147
SAOP	9.5897

5 Conclusions

6 Acknowledgments