

# 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 [1] 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 non-additive density functionals whereby the total energy of the liquid is expressed as the sum of molecule-additive and nonadditive contributions [2]. The inter-molecular interaction is split into Coulomb interactions, and such nonadditive terms as the noninteracting kinetic energy and the noninteracting exchange-correlation [3]. These contributions represent interactions related among others to exchange, van der Waals and Pauli repulsion and are all bifunctional of the subsystem densities [1].

Embedding potentials are computed with the embedded Quantum ESPRESSO (eQE) [4] software employing ultrasoft pseudopotentials. The ground state calculation of each subsystem with the corresponding neutral and polarized embedding potential was carried out with DIRAC [5] and ADF [6]. 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) [7, 8].

## 1 Introduction

## 2 Theoretical Background

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

To cast DFT in a subsystem fashion, we invoke nonadditive functionals in which each energy term of the supersystem is expressed as the sum of additive and nonadditive contributions [2]. Therefore, when dealing with a finite subsystem with electron density  $\eta_I$ , and an infinite or extended subsystem with electron density  $\eta - \eta_I$ , the total energy is given by,

$$E_{tot} = E[\eta_I] + E[\eta - \eta_I] + E^{int}[\eta_I, \eta - \eta_I] \quad (1)$$

And the interaction energy can be broken down into the following contributions,

$$E^{int} = E_H^{int} + V_e^{int} N + T_s^{nad} + E_{xc}^{nad} \quad (2)$$

The two Coulombic terms  $E_H^{int}$  and  $V_e^{int} N$  are the electron-electron and electro-nuclear interactions, respectively. And the nonadditive terms  $T_s^{nad}$  and  $E_{xc}^{nad}$ , represent the noninteracting kinetic energy of the system and the noninteracting exchange-correlation functionals, respectively [3]. The two last terms represent interactions related among other to exchange, van der Waals and Pauli repulsion and are all bifunctional of the two subsystem densities.

### 2.2 Coulomb interaction energy determination

### 2.3 Embedding Scheme for the Neutral System

For the neutral system, the Coulomb interaction energy can be expressed as a potential that maps the interaction of an accurately infinitely extended environment onto and isolated subsystem  $I$ ,

$$v'_{int}[\eta](r) = v[\eta](r) - \bar{v}[\eta_I](r) \quad (3)$$

Where  $v[\eta](r)$  is the total Coulomb potential of the system and  $\bar{v}[\eta_I](r)$  the potential of the isolated subsystem  $I$ . The latter was evaluated using the Martyna-Tuckerman method whereby density  $\eta_I$  is assumed to be isolated and not periodic [2]. The embedding potential for the neutral subsystem can also be calculated directly from equation 3.

## 2.4 Impurity Model for the Ionized system

To obtain the embedding potential of a charged subsystem, we consider the system to be composed of an ionized subsystem embedded in a nonionized environment. To assemble the appropriate embedding potential, first was evaluated a screening potential,  $v^{screen}[\eta_I](r) = v[\eta_I](r) - \bar{v}[\eta_I](r)$ , for both charged and neutral subsystems (understood as a self-interaction of the charge in PBC). The embedding potential depends on three densities:  $\eta$ , the total system,  $\eta'_I$ , the neutral subsystem, and  $\eta_I$  the charged subsystem, and has the form,

$$v^I_{emb,imp}[\eta](r) = v[\eta, \eta'_I, \eta_I](r) - \bar{\eta}_I(r) \quad (4)$$

with

$$v[\eta, \eta'_I, \eta_I](r) = v[\eta](r) + \Delta v^{screen}[\eta_I, \eta'_I](r) \quad (5)$$

where  $\Delta v^{screen}[\eta_I, \eta'_I](r) = v^{screen}[\eta'_I] - v^{screen}[\eta_I]$

## 3 Computational Section

All calculations were carried out with embedded Quantum ESPRESSO (eEQ) employing ultrasoft pseudopotentials. The ground state calculation of each subsystem with the corresponding neutral and polarized embedding potential was determined through ADF [6] software. A comparison among Density Functional Theory (DFT), using GGA(PBE), Hybrid(B3LYP), Double-Hybrid (B2KPLYP, B2NCPLYP, and REVDSDBLYP) and Statistical average of orbital potentials(SOAP) models, Møller–Plesset perturbation theory (MP2) and HF methods was made, with the basis QZ4P. The final IP/EA values are calculated using an average for each of the 256 water molecules or subsystems considered in the simulation cell, calculated by the energy difference of the neutral and the polarized system (Called  $\Delta$ SCF method) [7, 8].

## 4 Results

### 4.1 IPs of Bulk water

Table 1: average IPs

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

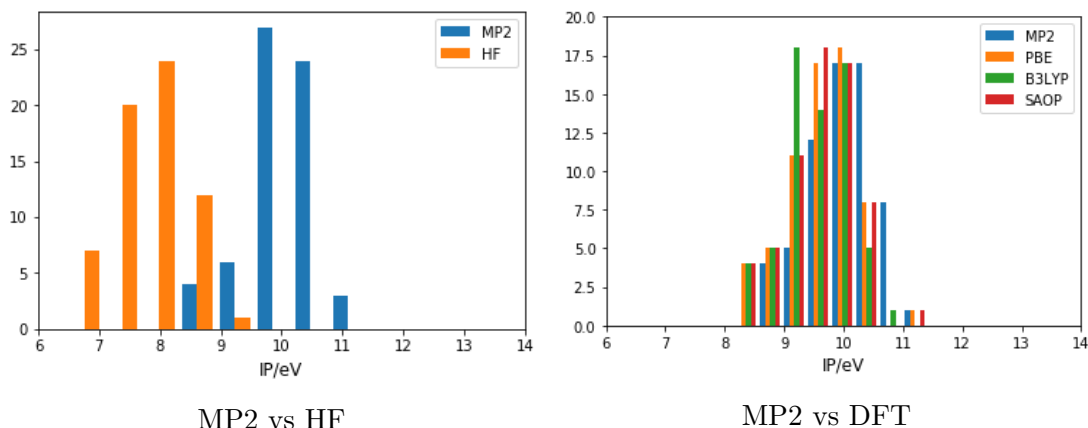


Figure 1: Distribution of IPs of bulk liquid water. The area subtended by the lines sums up to 64 (ie, the number of subsystems). Left: Comparison between MP2 and HF. Right: Comparison between MP2 and DFT

## 5 Conclusions

## References

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## 6 Acknowledgments