

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

Jessica Martinez¹, Pablo Ramos¹, Andre Gomes², Johannes Tölle³, and Michele Pavanello¹

¹*Department of Chemistry, Rutgers University, Newark, New Jersey*

²*Université de Lille, CNRS, UMR 8523 – PhLAM – Physique des Lasers, Atomes et Molécules, Lille, France*

³*Theoretische Organische Chemie, OrganischChemisches Institut and Center for Multiscale Theory and Computation (CMTC), Westfälische Wilhelms-Universität Münster, Corrensstraße 40, 48149, Münster, Germany*

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 η_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 η_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

3 Computational Section

4 Results

4.1 IPs of Bulk water

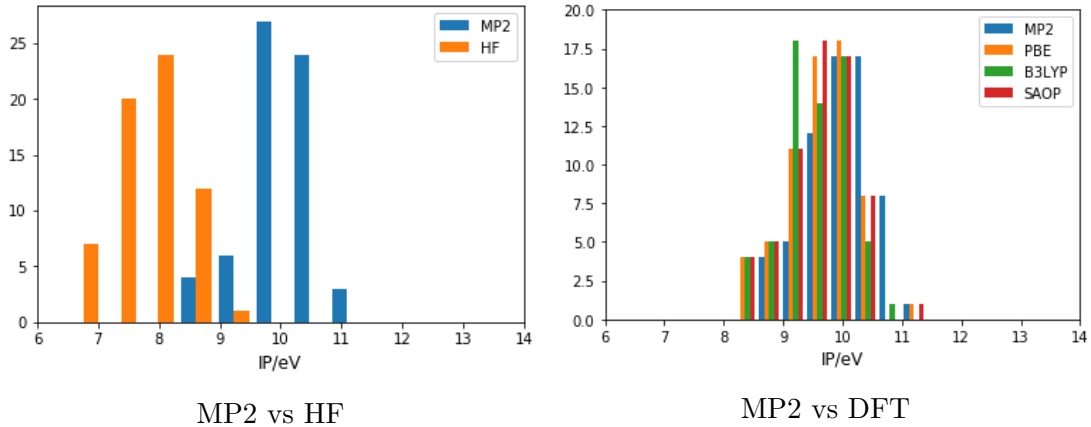


Figure 1: Distribution of IPs of bulk liquid water. The area subtended by the lines sums up to 64 (ie, the number of subsystems). Left: Comparison between MP2 and HF. Right: Comparison between MP2 and DFT

Table 1: average IPs

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

5 Conclusions

References

1. Tölle, J., Severo Pereira Gomes, A., Ramos, P. & Pavanello, M. Charged-cell periodic DFT simulations via an impurity model based on density embedding: Application to the ionization potential of liquid water. *International Journal of Quantum Chemistry* **119**, e25801 (2019).

2. Martyna, G. J. & Tuckerman, M. E. A reciprocal space based method for treating long range interactions in ab initio and force-field-based calculations in clusters. *The Journal of chemical physics* **110**, 2810–2821 (1999).
3. Krishtal, A., Sinha, D., Genova, A. & Pavanello, M. Subsystem density-functional theory as an effective tool for modeling ground and excited states, their dynamics and many-body interactions. *Journal of Physics: Condensed Matter* **27**, 183202 (2015).
4. Genova, A. *et al.* eQE: An open-source density functional embedding theory code for the condensed phase. *International Journal of Quantum Chemistry* **117**, e25401 (2017).
5. Saue, T. *et al.* The DIRAC code for relativistic molecular calculations. *The Journal of Chemical Physics* **152**, 204104 (2020).
6. Te Velde, G. t. *et al.* Chemistry with ADF. *Journal of Computational Chemistry* **22**, 931–967 (2001).
7. Bagus, P. S. Self-consistent-field wave functions for hole states of some Ne-like and Ar-like ions. *Physical Review* **139**, A619 (1965).
8. Waskom, M. *et al.* mwaskom/seaborn: v0. 8.1 (September 2017). *Zenodo*, doi **10** (2017).
9. Dal Corso, A. Pseudopotentials periodic table: From H to Pu. *Computational Materials Science* **95**, 337–350 (2014).

6 Acknowledgments