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

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INTRODUCTION

The high-accuracy calculations of ionization potentials (IPs) and electron affinities (EAs) of condensed-phase molecular systems as liquid water has represented a challenge for the last years in both experimental and computational fields [1]. Thus, ionized states of the electrons take part in many crucial processes in electrochemistry and photochemistry[2]. The most recent theoretical report of IPs and EAs [3] using self-consistent GW approach with an implicit vertex correction based on the projector augmented wave (PAW) method are 10.2 and 1.1 eV, for IP and EA of liquid bulk water, respectively. Including the use of periodic boundary conditions (PBC) another method was introduced [1] to determine the ionization potentials (IPs) and electron affinities (EAs) of liquid water, called 'Impurity model'.

This *impurity model* has two remarkable qualities:
1. The charged periodic system is replaced by a non-periodic one which is still truly extended (i.e. of infinite size) using a formally exact density embedding method, subsystem DFT [4].
2. The potentials of the neutral and the charged system are pegged to a common reference finding a consistent choice for the *G=0* component of the Coulomb Kernel in a reciprocal space.

GOAL

Here we present an update of the current state-of-the-art of liquid water IPs and EAs base on an impurity model using an exact density embedding method, subsystem DFT. This may allow us to contribute to the discussion generated about the most accurate value for the EAs of bulk water.
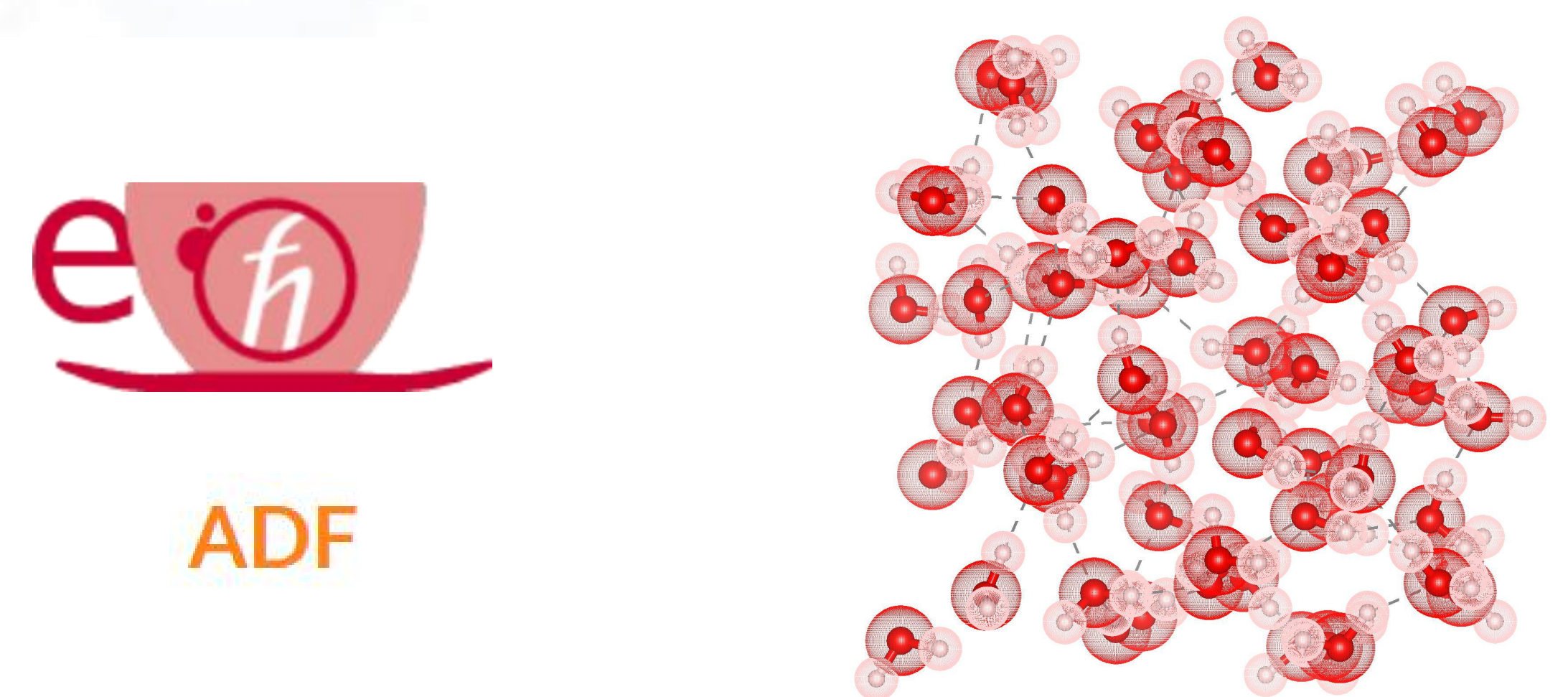

Fig. 1. *Right: Single snapshot with 64 water molecules based on subsystem DFT-based molecular dynamics simulation [5]. Left: Embedded Quantum ESPRESSO (eQE) [6] used to obtain embedding potentials for ionized and nonionized systems, employing ultrasoft pseudopotentials and ADF software [7] for the ground state calculation of each subsystem with the corresponding neutral and polarized embedding potential.*

Theoretical Background

1. *Mapping a periodic system into a collection of non-periodic subsystems* with electron density n_I *and one periodic subsystem* with electron density $n - n_I$,

$$E_{tot} = E[n_I] + E[n - n_I] + E^{int}[n_I, n - n_I] \ (1)$$

$$E^{int} = E_H^{int} + V_{eN}^{int} + T_s^{nad} + E_{xc}^{nad} \ (2)$$

2. *Embedding Scheme for the Nonionized System*, where $v[n](r)$ is the total Coulomb potential of the system and $\overline{v}[n_I](r)$ the potential of the isolated subsystem I

$$v_{emb}^{I}[n](r) = v[n](r) - \overline{v}[n_I](r) \ (3)$$

3. *Impurity Model for the Ionized system*, we first evaluate a screening potential, $v^{screen}[n_I](r) = v[n_I](r) - \overline{v}[n_I](r)$, for both charged and neutral subsystems. The embedding potential depends on 3 densities: n, the total system, n'_I, the neutral subsystem, and n_I the charged subsystem, and has the form,

$$v_{emb, imp}^{I}[n, n'_I, n_I](r) = \boldsymbol{v[n, n'_I, n_I](r)} - \overline{v}[n'_I](r) \ (4)$$

$$\boldsymbol{v[n, n'_I, n_I](r)} = v[n](r) + \Delta v^{screen}[n_I, n'_I](r) \ (5)$$

$$\Delta \boldsymbol{v^{screen}[n_I, n'_I](r)} = v^{screen}[n'_I](r) - v^{screen}[n_I](r) \ (6)$$
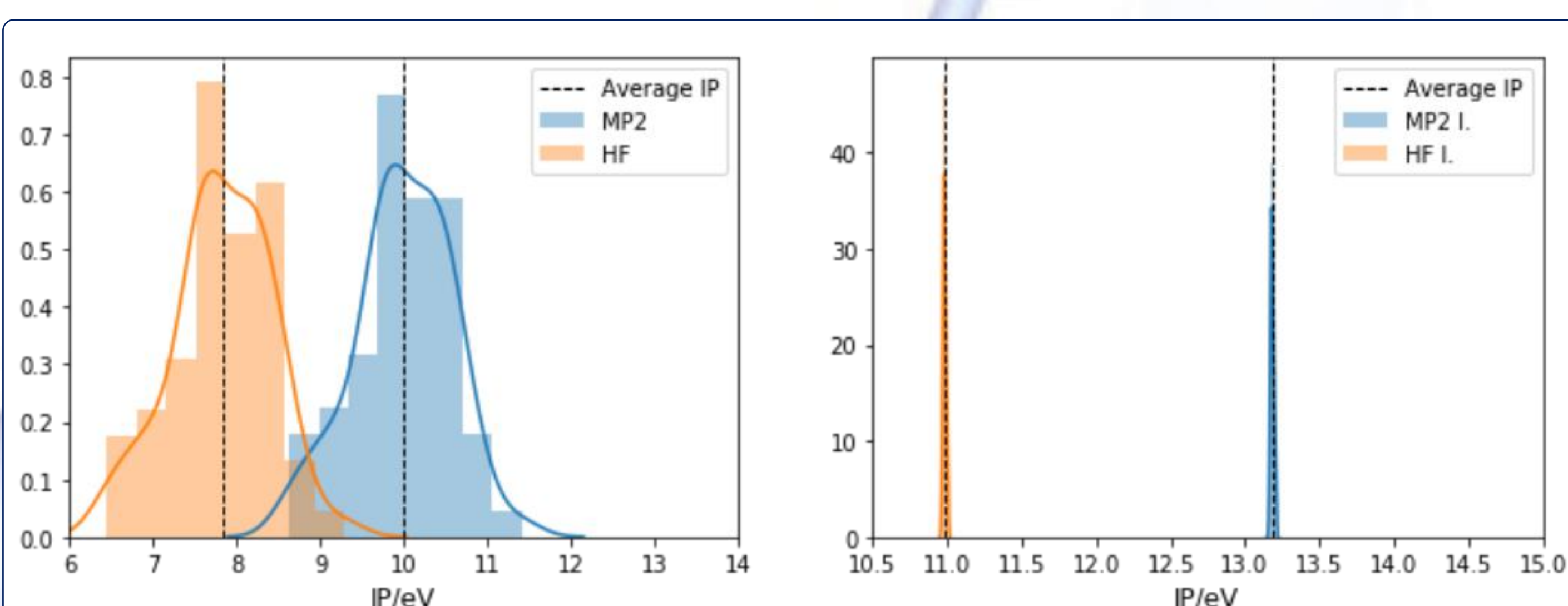
RESULTS

Fig. 2. *Distribution of IPs of bulk liquid water using MP2 and HF methods through ADF [7]. The area subtended by the lines sums up to 64 (i.e., the number of subsystems). Left: Embedded water molecules in the bulk. Right: Isolated water molecules. Dot lines represent the average IP. The lines fitting the underlying distributions are obtained from a kernel density estimation using Seaborn's Gaussian envelopes[8]*
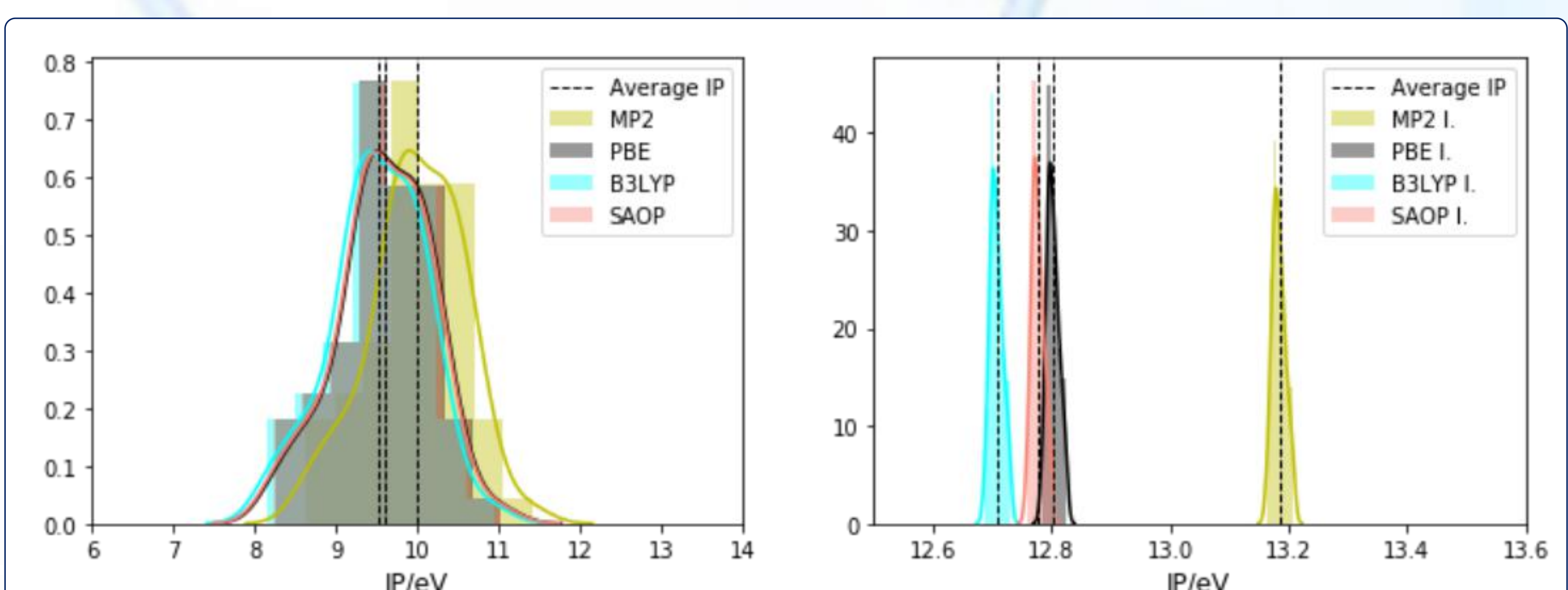

Fig. 3. *Distribution of IPs of bulk liquid water using MP2 and DFT methods through ADF [7]. The area subtended by the lines sums up to 64 (ie, the number of subsystems). Left: Embedded water molecules in the bulk. Right: Isolated water molecules. Dot lines represent the average IP. The lines fitting the underlying distributions are obtained from a kernel density estimation using Seaborn's Gaussian envelopes[8]*

CONCLUSIONS

Taking advantage of the density embedding depiction of the electronic structure of a system under periodic boundary conditions, we were able to compute through an impurity model that incorporates charged and neutral finite subsystems within an extended(infinity) surrounding subsystem, the IPs of bulk liquid water. So far, the best average value is 9.99 eV using the MP2 level of theory which is in complete agreement with liquid experimental reported values (9.9-10.06 eV) and GW recent simulations (10.2-10.55eV). Future applications of the method will be aimed at the implementation of the embedding potential into the calculation of ionization potential and electron affinities a higher level of theory.

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