Dispersion corrected RPBE studies of liquid water

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The structure of liquid water has been addressed by ab initio molecular dynamics simulations based on density functional theory. Exchange-correlation effects have beed described by the popular PBE and RPBE functionals within the generalized gradient approximation as these functionals also yield satisfactory results for metals which is important to model electrochemical interfaces from first principles. In addition, dispersive interactions are included by using dispersion-corrected schemes. It turns out that the dispersion-corrected RPBE functional reproduces liquid water properties quite well in contrast to the PBE functional. This is caused by the replacement of the over-estimated directional hydrogen-bonding in the PBE functional by non-directional disperse interactions.

Keywords: density functional theory, liquid water, dispersion corrections, ab initio molecular dynamics

I. INTRODUCTION

Water and water/solid interfaces are important in many diverse fields of science and technology [1–4]. Thus numerous theoretical studies of liquid water have been performed [5, 6] ranging from force field based molecular dynamics [7] to ab inito molecular dynamics (AIMD) simulations [8]. Regarding AIMD simulations based in particular on density functional theory (DFT) calculations, it turned out that among different density functionals based on the generalized gradient approximation (GGA) hybrid functionals perform best and are necessary to get the band gap and thus the optical excitations more correctly [9, 10]. They also perform well in describing the intramolecular water potential energy surface, as a comparison with quantum Monte Carlo (QMC) simulations indicates [11]. However, in order to describe electrochemical interfaces, i.e. especially water at metal surfaces, affordable density functionals that are able to describe adequately both the metal surface, the liquid water and the interactions between the two subsystems are needed [12–16]. Unfortunately, hybrid functionals are not applicable for metal surfaces [7, 17] which can be rationalized by the fact that Hartree-Fock fails to describe the electronic structure of metals properly. Therefore mostly non-hybrid GGA-functionals have been employed so far to describe water-metal interaction [12–16, 18–22].

However, functionals based on the GGA that describe metallic systems correctly most often fail to reproduce liquid water properties appropriately: popular GGA-functionals such as PBE lead to an overstructuring of liquid water systems [23–25]. Besides the self-interaction error inherent in all GGA-functionals leading to the underestimation of the electronic band gap, their short-range nature is causal to their lack of describing dispersion interactions. This failure could be one of the reasons why water systems are not described correctly.

The impact of van der Waals forces on water-water interactions has been studied in quite some detail [6, 26–33]. The studies conclude that nondirectional dispersion interactions indeed play a crucial role for the interactions between small water clusters and in bulk water. Moreover, it has been shown, that including dispersion interactions in DFT studies of liquid water leads to a remarkable improvement of the structuring [29–33].

DFT studies including dispersion interactions also showed that van der Waals interactions contribute substantially to the water-metal bond [34–39]. The impact on the water-metal interaction largely exceeds the impact on the water-water interaction. In general, the inclusion of dispersion-corrections has significantly improved the reliability of first-principles studies of molecular adsorption at surfaces [28, 40–43]. Still, none of the studies mentioned so far had addressed the wetting of water on the electrode materials Ag, Au, Pd and Pt which are rather important in electrochemistry.

Recently we have shown that the combination of Grimme's dispersion correction of 2010 (DFT-D3) [44] and the revised PBE-functional (RPBE) [45] outperforms the PBE functional as RPBE-D3 is able to reproduce the correct wetting behavior of water on (111) metal electrodes made of Ag, Au, Pd and Pt [46]. Still, AIMD studies of liquid water favour dispersion corrected hybrid functionals [30–33]. In this study we address the performance of RPBE-D3 regarding the pure liquid water system, which has to the best of our knowledge not been done yet. In addition to PBE [23–25], only the revPBE functional [47] has been used in water simulations together with van der Waals density functional (vdW-DF) [26] or dispersion corrections [33]. This is unfortunate as the RPBE functional is a popular functional for the description of molecular interactions with metal surfaces [48, 49] which are relevant for electrochemistry and electrocatalysis.

We will show that the RPBE-D3 properly describes liquid water properties, similar to dispersion-corrected hybrid functionals [30–33]. However, as already mentioned, the latter are not suited to properly reproduce metal properties. Therefore we propose to use the RPBE-D3 method for the first-principles description of water/metal interfaces.

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II.   COMPUTATIONAL DETAILS

The properties of bulk water from first principles have been addressed by performing ab initio molecular dynamics simulations in a standard setup as typically used in this kind of simulations [23–26, 29–33, 47]. Bulk water has been modelled by a cubic box containing 64 randomly distributed water molecules at a density of 1 g/cm^3. The size of the unit cell and a snap shot of a water configuration are illustrated in Fig. 1

Density functional theory calculations have been performed using the periodic code VASP [50]. Electron-core interactions are accounted for by the projector augmented wave method [51, 52]. An energy cutoff of 400 eV is used to restrict the number of plane waves. Two different types of exchange-correlation GGA-functionals are employed: the PBE-functional [53] and its revised version of Hammer et al. (RPBE) [45]. Corrections for dispersion effects have been added to the Kohn-Sham Hamiltonian according to the method of Grimme of 2010 (DFT-D3) [44].

rm The calculations are restricted to the gamma point only. After an initial geometry optimization to end in the nearest local minimum, AIMD simulations within the microcanonical ensemble have been performed using a time step of 1 fs. Trajectories have been calculated for 22 ps of which the first 5 ps have been regarded as thermalization period. The convergence of the results with respect to these run times was checked by performing simulations with longer thermalization and production run times of up to 5 ps. As the total energy in the numerical microcanonical simulations is typically not exactly fulfilled, average temperatures during the production run time deviate from room temperature. We obtained temperatures of 334 K for PBE, 348 K for PBE-D3, 295 K for RPBE and 314 K for RPBE-D3 which are within the range typical for this kind of simulations [29, 33].

Furthermore vibrational frequencies of an isolated water molecule have been calculated using the NW-CHEM code. For the purpose of comparison not only the density functionals PBE and RPBE but also the BLYP functional and the CCSD(T) method have been employed in connection with Dunning's correlation consistent basis set aug-cc-pVTZ [54].

III.   RESULTS AND DISCUSSION

As usual, we analyze the results of our water simulations using pair distribution functions. In Fig. 2, the oxygen-oxygen radial distribution function of water at room temperature is shown. As observed in many studies before, the PBE functional leads to a distribution that is too structured when compared to the experimental result [55]. The first two peaks are much higher than those corresponding to the experimental structure, indicating that the shell structure is overestimated and that the simulated water structure is too much crystalline-like.
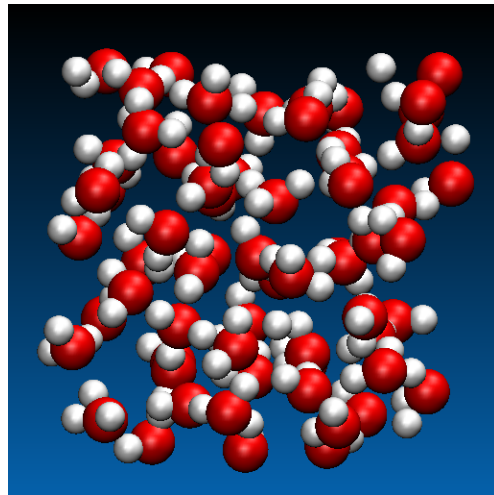

FIG. 1. Illustration of the size of the unit cell used for the water simulations containing 64 water molecules.
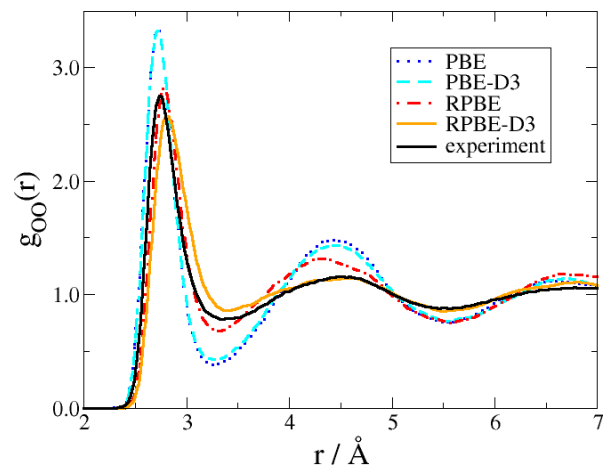

FIG. 2. Oxygen-oxygen (g_{OO}(r)) radial distribution functions obtained from AIMD simulations at room temperature using different xc-functionals with and without semiempirical dispersion corrections. The raw data have been interpolated using cubic splines. Experimental results [55] are shown for comparison.

Obviously, already by going from PBE to its revised version (RPBE) the first peak decreases remarkably. This has also been found in previous water studies using the RPBE [56] and the revPBE [57] functionals which in fact often yield similar results [45]. Furthermore, water simulations with the revPBE functional yield a diffusion coefficient in reasonable agreement with experiments [57]. According to Ref. [58] RPBE even outperforms BLYP, which has been found to be superior to PBE regarding the performance of different GGA-functionals in describing liquid water. Santra et al. [59] explained this apparent predominance of BLYP above PBE by an analysis of the interaction energy of water dimers taken from the liq-
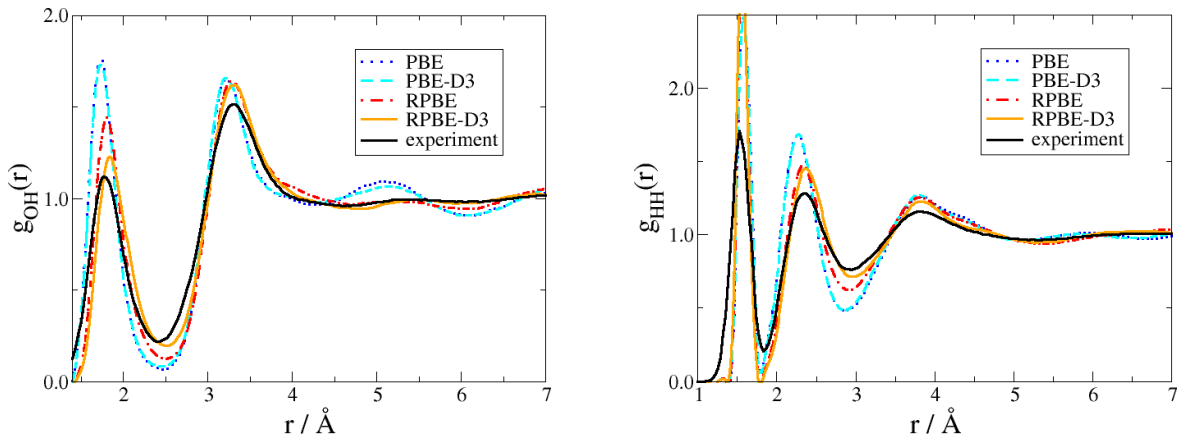
FIG. 3. Oxygen-hydrogen ($g_{OH}(r)$) and hydrogen-hydrogen ($g_{HH}(r)$) radial distribution functions obtained from AIMD simulations at room temperature using different xc-functionals with and without semiempirical dispersion corrections. The raw data have been interpolated using cubic splines. Experimental results are shown for comparison.

uid with respect to the monomers in their equilibrium gas phase geometry. Therefore they divided this interaction energy into the energy needed to deform the monomer from its equilibrium gas phase geometry to its geometry in the liquid (E_{1b}) and into the interaction energy of a dimer with respect to their deformed structures in the liquid (E_{2b}). Both PBE and BLYP were found to underestimate E_{1b}. Whilst PBE gives by chance a good description of E_{2b}, BLYP underestimates these interactions as well. Adding the two there is a fortious cancellation of errors for the BLYP functional whereas PBE overestimates the total interaction energy, leading to the known effect of overstructuring. In that article the authors already speculated that a similar effect could explain the success of RPBE in the first peak of the oxygen-oxygen radial distribution function.

In order to strengthen this assumption made for the RPBE functional we followed the suggestion of Santra et al. [59] and analysed simple accessible estimates for E_{1b} and E_{2b}. First, the deformation energy of a monomer can be estimated by looking at the harmonic vibrational frequencies of the gas phase molecules. These frequencies are shown in Table I.

All GGA-functionals underestimate the energy needed to excite these vibrations by about 6-16 meV compared to

the CCSD(T) result. The differences among the different GGA-flavors only amounts 6 meV, 5 meV and 1 meV for ν_1, ν_2 and ν_3 respectively. Thus all functionals underestimate the energy needed to deform the water molecule from the gas phase structure to possible structures by approximately the same amount of energy. Furthermore Santra et al. also showed that the monomer deformation energy of its structure in the liquid is almost two order of magnitudes larger and the underestimation error of the GGA-functionals indeed become significant but still comparable to each other.

Second, a rough estimate for the interaction energy between two water molecules in the liquid could be the interaction energy of the dimer in the gas phase. Mattsson and Mattsson [56] have shown that the interaction energy of a water dimer is underestimated to a larger extend by RPBE (underestimation of 44 meV) compared to BLYP (underestimation of 36 meV).

Consequently the total error compensation is even more favorable in case of RPBE than in case of BLYP leading to a less structured liquid. This way the good agreement of RPBE with experiment regarding the first peak of the O-O distribution function can be rationalized.

The missing energy contribution of RPBE and BLYP to the interaction energy of a water dimer can be attributed to the lack of dispersion interactions. This way the failure of PBE becomes obvious: without being able to describe the van der Waals interaction it already leads to the correct value of the water-water interaction energy. By adding dispersion corrections the energetics even worsens. On the other hand, by adding dispersion corrections to the RPBE functional, that in its pristine form underestimates the water-water interaction energy, the agreement with CCSD(T) calculations improves [46] and thus RPBE seems to outperform its predecessor. The dispersion contribution of about 40 meV to the water dimer interaction energy is in good agreement with corresponding findings based on QMC calculations [60].

TABLE I. Harmonic vibrational frequencies (in cm^{-1}) for the asymmetric and symmetric O-H stretching modes (ν_1 and ν_2) and the H-O-H bending mode (ν_3) of an isolated water molecule.

	ν_1	ν_2	ν_3
CCSD(T)	3890	3788	1650
PBE	3802	3697	1592
BLYP	3757	3656	1595
RPBE	3791	3688	1604

However, in order to estimate water-water interactions within the liquid not only the interaction energy of a water dimer is important but also the interaction energy of small water clusters should be considered. For such systems Morawietz and Behler used the RPBE-D3 method to calculate the interaction energies [6]. Indeed RPBE-D3 is able to improve the description of interactions in water clusters. Regarding the vibrational properties of isolated water molecules, the dispersion correction should have only a minor impact.

So it seems promising that the RPBE-D3 method could also improve the liquid water system. As shown in Fig. 2, adding dispersion corrections to any of the two density functionals has hardly any impact on the first peak of the oxygen-oxygen radial distribution function. As far as PBE is concerned neither the height nor the position of this peak changes. In case of the RPBE functional the peak is slightly reduced and shifted to larger distances if dispersion effects are included. However, although the RPBE-D3 method slightly deteriorates the agreement of RPBE with experiment regarding the first peak of the oxygen-oxygen distribution function it still outperforms PBE or PBE-D3. The second peak of the O-O distribution is located at around 4.5 Å. This corresponds to a spatial region where van der Waals interactions get important. Indeed by adding the semiempirical correction of Grimme of 2010 distinct changes of the radial distrubitions in this region can be observed. In particular the RPBE-D3 method ends up with a radial distribution function that is remarkably close to the experimental result, even at larger O-O distances.

To sum up ,these results of the O-O distribution function show that replacing the strong directional H-bonds, as described by PBE, by weaker ones, as described by RPBE, and adding nondirectional van der Waals interactions leads to a less structured liquid comparable to the experimental result.

For the sake of completeness, we also included the radial distribution functions of O-H and H-H (Fig. 3). The RPBE-D3 method leads to good results for these distribution functions as well. However, van der Waals interactions are less crucial in these cases due to the lower polarizability of H (and thus a lower van der Waals coefficient) compared to O.

Finally, we like to comment on possible nuclear quantum effects on the water energy and structure. Quantum corrections to the total energy can be estimated by applying quantum statistics to the calculated vibrational frequencies. Thus a quantum correction of about $0.04\,\mathrm{eV}$ per water molecule was estimated [61]. Quantum effects on the water structure can be addressed using, e.g., the path-integral (PI) formalism. A PI Car-Parrinello molecular dynamics (CPMD) study found that nuclear quantum effects soften the structure of liquid water [62]. This result is, however, in conflict with a previous PI CPMD work [63] which arrived at the opposite conclusion, namely that nuclear quantum effects harden the structure of liquid water. In contrast, a very recent path-integral study found that the O-O radial distribution function is hardly affected by nuclear quantum effects [64]. As far as the proton transfer in liquid water is concerned, quantum delocalization effects apparently play an important role [65]. Still, it is fair to say that the exact role of nuclear quantum effects on the water structure is still not fully clarified yet. As the comparison between classical and quantum H_2 dynamics on the same potential energy surface shows, quantum tunneling effects and zero-point effects can to a certain extent cancel each other [66, 67]. Hence it seems justified, at least on a semi-quantitative level, to ignore nuclear quantum effects, in particular if MD simulations of water at interfaces are performed which typically include heavier atoms such a metal atoms.

IV. CONCLUSIONS

Motivated by the good performance of the dispersion corrected RPBE-D3 functional with respect to the wetting behavior of water on metal electrodes, we have studied the bulk water properties using this functional. Compared to the PBE functional, the intermolecular interactions within water are less attractive for pure RPBE, leading to worse agreement with both experiment and high-quality ab initio calculations, as far as the energetics are concerned. However, by adding dispersion corrections to the RPBE functional, the energetics are significantly improved. The directional H-bond, overestimated by PBE, is replaced by weaker H-bonds described by RPBE and amended by adding non-directional van der Waals interactions. Thus the total intermolecular energy gets close to high quality ab initio results. Importantly, the bond is now of a different type: there are no longer directed bonds, but they are replaced by non-directional dispersive interactions. This heals the over-structuring observed for PBE water and results in a less structured liquid, in agreement with the experiment. Hence we propose the RPBE-D3 method as suitable method to describe the structure of liquid water systems, in particular in connection with metal surfaces where hybrid functionals are not appropriate and RPBE-D3 has proven to be an adequate method.

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