

Dispersive interactions in water bilayers at metallic surfaces: a comparison of the PBE and RPBE functional including semi-empirical dispersion corrections

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The accuracy and reliability of the DFT-D approach to account for dispersion effects in first-principles studies of water-metal interfaces has been addressed by studying several water-metal systems. In addition to performing periodic DFT calculations for semi-infinite substrates using the popular PBE and RPBE functionals, the water dimer and water-metal atom systems have also been treated by coupled-cluster calculations. We show that indeed semi-empirical dispersion correction schemes can be used to yield thermodynamically stable water bilayers at surfaces. However, the actual density functional needs to be chosen carefully. Whereas the dispersion-corrected RPBE functional yields a good description of both the water-water and the water-metal interaction, the dispersion-corrected PBE functional overestimates the energies of both systems. In contrast thereto, the adsorption distances predicted by the PBE functional is hardly changed due to the additional dispersion interaction, explaining the good performance of previous DFT-PBE studies of water-metal systems.

I. INTRODUCTION

Processes at water-solid interfaces play a very important role in many different areas, in particular in the field of electrochemistry, but they are also relevant in corrosion or atmospheric sciences [1], just to mention a few. The relevance of these processes, also from a fundamental point of view, has led to a growing number of first-principles studies addressing the structure of water-solid interfaces, especially of the water-metal interface [2–7], and reactions at such interfaces [8–12]. These studies are mainly based on periodic density functional theory (DFT) calculations within the generalized gradient approximation (GGA) to account for the exchange-correlation effects. This means that the London dispersion or van der Waals (vdW) interaction is not properly accounted for in these studies. Still, in particular the PBE-GGA functional [13] is able to reproduce water properties reasonably well [5, 14–16] since PBE gives a reliable description of the hydrogen-bonding which is obviously crucial for a proper treatment of water.

However, several studies have already shown that dispersive forces contribute significantly to the stability of water on metal surfaces [17–19]. Feibelman pointed at the important role of van der Waals forces in water structures at metallic surfaces. Based on the similar polarizability of Ar and H₂O, he estimated the vdW energy of the water-metal systems to be similar to the vdW interaction of an Ar-atom with the respective metal surface [17]. In more recent studies, different flavours of the van der Waals density functional (vdW-DF) [20, 21] have been applied to the adsorption of water on Cu(110), Ru(0001) [19] and Rh(111) [18], showing that thermodynamically stable water structures on certain metal surfaces can be obtained, if dispersion forces are accounted for. Furthermore, for describing the adsorption of organic molecules at surfaces in an aqueous environment, the inclusion of dispersive effects is also required [22, 23].

Yet, there is also quite a different, numerically effi-

cient approach of including dispersion effects into DFT, termed DFT-D, that simply adds a C_6R^{-6} -type correction to the Kohn-Sham Hamiltonian. Such popular semi-empirical correction schemes have proven to yield satisfactory results for systems involving classical organic molecules [24–32] and adsorption phenomena on graphite surfaces [33, 34]. In particular, due to their computational efficiency, they represent an appealing alternative to the more laborious vdW-DF and have been successfully applied to larger systems [34]. Although details of the application of DFT-D methods to metallic surfaces are still debated [31, 32], promising results have been obtained for such systems as well, if certain approximations for screening effects of the conducting surface are included [35–38].

Hence, there is a need to assess the accuracy and reliability of the DFT-D approach for the description of the water-metal interface. We have studied the performance of the DFT-D ansatz proposed by Grimme *et al.* [27] for several water-metal systems focusing on the PBE [13] and RPBE [39] functionals which are both rather popular for periodic DFT calculations of metallic systems. In the analysis of the results, we also address one fundamental issue: While extended water bilayers have been observed experimentally on different surfaces under ultra-high vacuum (UHV) conditions [40, 41], common DFT-calculations do not predict such water layers to be thermodynamically stable [2]. Although this long-standing, widely discussed [42, 43] discrepancy between experiment and theory might be explained by kinetically trapped structures, there might also be a significant influence of dispersive interactions that is neglected in most of the DFT-calculations discussed so far.

II. METHODS

Periodic DFT calculations have been performed using the Vienna ab initio simulation package (VASP) [44, 45]. In order to account for electron-ion interactions, the pro-

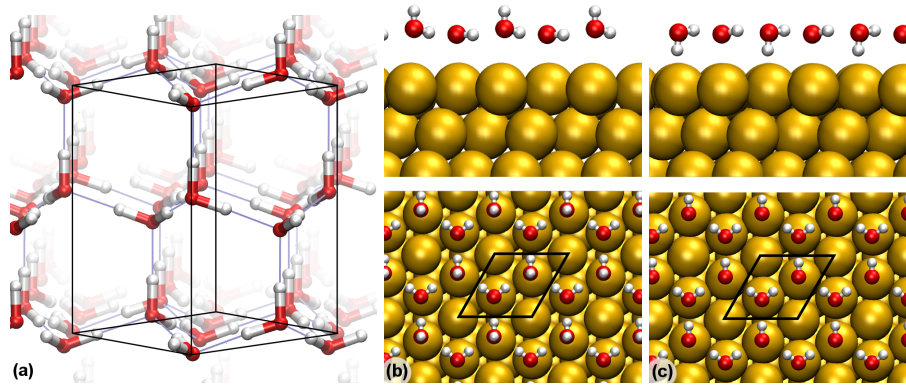


FIG. 1: Models used for the calculations: panel (a) shows the Bernal-Fowler model of the hexagonal phase of bulk ice (I_h), whereas (b) and (c) depict the simple H-up and H-down model assumed for the ice layers on metallic surfaces.

jector augmented wave (PAW) method [46, 47] has been used. The electronic one-particle wave functions were expanded in a plane wave basis set up to an energy cut-off of 400 eV. Electron-electron exchange and correlation interactions have been described within the generalized gradient approximation (GGA) by employing the Perdew, Burke and Ernzerhof (PBE) functional [13] or its revised version (RPBE) of Hammer, Hansen and Nørskov [39].

The metal surfaces were modeled by a slab consisting of five atomic layers that were separated by a vacuum region of about 20 Å. The geometry of the adsorption complex was optimized by relaxing all atoms of the adsorbate and the metal atoms of two uppermost layers of the surface. The layer spacing of the lower layers were taken from the theoretical lattice parameters calculated for bulk metals. A $9 \times 9 \times 1$ Monkhorst-Pack k point mesh [48] with a Methfessel-Paxton smearing of 0.1 eV was used for the integration over the first Brillouin zone. Isolated molecules in the gas phase were treated employing a large cell ($20 \text{ Å} \times 21 \text{ Å} \times 22 \text{ Å}$), the Γ -point only and a Gaussian smearing of 0.1 eV.

Dispersion effects that are missing in current DFT-functionals have been accounted for according to Grimme's correction scheme of 2010 (DFT-D3) [27]. In this approach, the total energy is given by

$$E_{\text{DFT-D}} = E_{\text{DFT}} + E_{\text{disp}} \quad (1)$$

where E_{DFT} is the energy obtained from the DFT calculation. The dispersion energy E_{disp} is calculated as a sum over the multipolar expansion of the dispersive interaction of all atom pairs AB in the system:

$$E_{\text{disp}} = - \sum_{AB} \sum_{n=6,8,10\dots} s_n \frac{C_n^{AB}}{R_{AB}^n} f_{\text{damp}}(R_{AB}) \quad (2)$$

The dispersion coefficient C_6^{AB} is deduced from the Casimir-Polder formular and with the help of an interpolation scheme adjusted to the chemical environment

of the respective atoms. Higher-order coefficients are estimated according to empirical formulas. Finally, the damping function $f_{\text{damp}}(R_{AB})$ makes the dispersion correction vanish at small interatomic distances R_{AB} where the electronic densities overlap and a good description is ensured by the GGA-functional.

The screening of the metal, which is rather problematic in such approaches, was crudely approximated by including only the uppermost layer of the metal in the evaluation of the dispersion energy, as suggested in Refs. [35, 36].

The adsorption energy has been defined as

$$E_{\text{ad}} = E_{\text{tot}} - (E_{\text{surf}} + E_{\text{mol}}) \quad (3)$$

where E_{tot} , E_{surf} and E_{mol} are the total energy of the relaxed adsorption complex, the energy of the clean surface and the energy of the isolated water molecule, respectively.

For comparison, the lattice energy of bulk ice has been calculated. Therefore, the Bernal-Fowler model [49] of the hexagonal phase of bulk ice is employed. Its unit cell containing 12 H_2O molecules is depicted in Figure 1a. The structure has been optimized in connection with a $4 \times 4 \times 4$ mesh of special k-points [48] and a Gaussian smearing of 0.1 eV. Analogously to the adsorption energy, the lattice energy of bulk ice per molecule has been calculated as

$$E_{\text{coh}} = E_{\text{bulk}}/12 - E_{\text{mol}} \quad (4)$$

where E_{bulk} denotes the bulk ice total energy per unit cell.

Calculations of water-water or water-metal dimers were also performed using the GAUSSIAN03 code [50] employing coupled cluster methods or mixing exact exchange to the PBE density functional (PBE0) [51]. The LANL2TZ effective core potential [52] has been used for the metal atom, whereas the atoms of the water molecule are described by the augmented correlation consistent

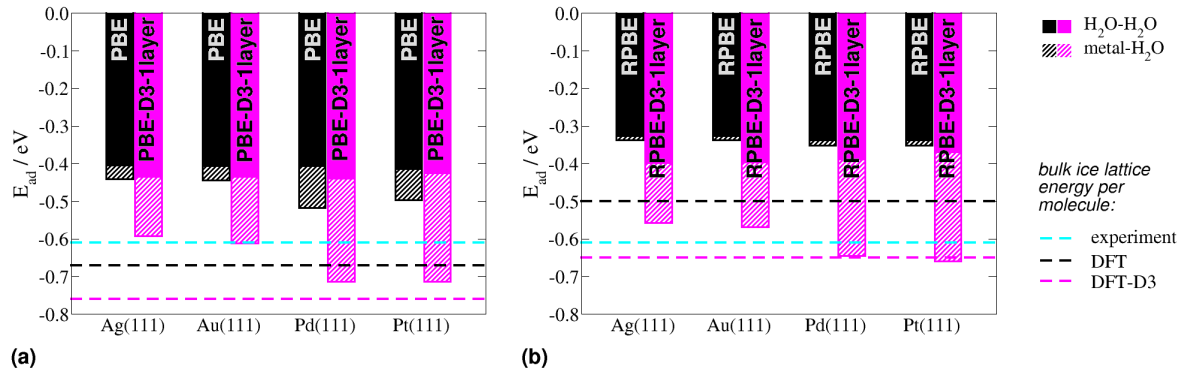


FIG. 2: Calculated adsorption energies of the H-down structure on closed packed surfaces of different metals employing the PBE (a) and the RPBE (b) density functional. The adsorption energies obtained by taking dispersive interactions into account (D3) are included as well. For comparison the lattice energies of bulk ice (per molecule) are shown.

triple zeta basis set of Dunning [53, 54]. To account for the basis set superposition error the counterpoise method was applied [55]. The interaction energy of the dimers has been defined analogously to the adsorption energy.

III. RESULTS AND DISCUSSION

In order to study the influence of dispersive interactions within water bilayers at metal surfaces (Ag(111), Au(111), Pd(111), Pt(111)) the H-down and the H-up structures shown in Fig. 1b,c have been taken as simple models. Figure 2 compares the adsorption energies of water in the more stable H-down structure on different metal (111) surfaces calculated with different methods. For all surfaces the adsorption energies obtained with the PBE functional are by 0.10-0.17 eV larger than the corresponding values deduced with the RPBE functional. Yet, both pure GGA-functionals show the same qualitative behaviour that has been observed before [2–5, 7]: they yield adsorption energies that are considerably smaller than the bulk ice lattice energy per molecule. This finding suggests that ice layers on all of the studied metal surfaces are thermodynamically unstable. In experiments however, only the noble metal surfaces were found to be non-wetting surfaces, whereas both the Pd and the Pt (111) surface were found to be wetted by H₂O [1].

By adding dispersive interactions to both GGA-functionals, adsorption energies that are in the range of the bulk ice lattice energy per molecule are obtained both for the Pd and the Pt (111) surface, whereas the interaction energies of the adsorption on non-wetting noble metal surfaces are still remarkably smaller. Hence, for both PBE-D3 and RPBE-D3 an important contribution to the total adsorption energy stems from van der Waals interactions (26-30% for PBE and 40-47% for RPBE).

Furthermore, due to the additional energy of dispersive interactions, the differences between the adsorption

energies of the two flavours of the GGA-functional diminish ($\Delta E_{ad} < 0.07$ eV). However, while PBE-D3 yields adsorption energies that are still smaller than the bulk lattice energy, RPBE-D3 suggests the H-down structure to be of comparable stability as bulk ice.

In order to get a deeper insight into the interactions occurring at the surface according to PBE and RPBE, the total adsorption energy (see eq. (3)) is split into energetic contributions stemming from the water-metal interaction

$$E_{\text{int}}(\text{Me} - \text{H}_2\text{O}) = \frac{1}{2}(E_{\text{tot}} - (E_{\text{surf}} + E_{\text{layer}})) \quad (5)$$

and the water-water interaction

$$E_{\text{int}}(\text{H}_2\text{O} - \text{H}_2\text{O}) = E_{\text{layer}}/2 - E_{\text{mol}}. \quad (6)$$

Here E_{layer} denotes the energy of the water-layer in its geometry obtained by optimizing the metal-water system.

Firstly, such an analysis shows that the dispersion correction mainly influences the water-metal interaction (enhancement by a factor of 2.5 to 5 for the PBE and by a factor of 17 to 23 for the RPBE functional), whereas it has less influence on the water-water interaction (enhancement by a factor of 1.03 to 1.08 for the PBE and a factor of 1.10 to 1.22 for the RPBE functional).

Additionally, the energetic contributions reveal some more details about the differences in the adsorption energies obtained by the non-dispersion corrected PBE and RPBE functional. The PBE functional predicts a slightly stronger H₂O-H₂O interaction within the H-down layers (about -0.40 eV vs. -0.33 eV for RPBE) and a much stronger interaction between the water molecule and the surface. The latter is in particular obvious for the adsorption of water on the more reactive Pd and Pt (111) surfaces. Here, the absolute value of the molecule-metal interaction energy calculated by means of the PBE-functional is an order of magnitude larger than the corresponding values obtained by using the RPBE-functional.

In order to get further insight into the DFT-D description of water-metal systems, we have also considered molecule-molecule or metal-atom-molecule dimers

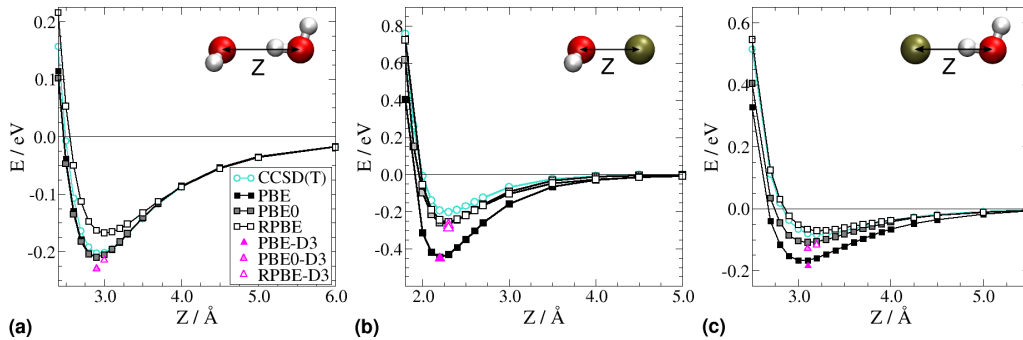


FIG. 3: Interaction energy of a water-dimer (a) and between a water molecule and a Pd atom in different configurations (b+c). The Pd atom was restricted to the singlet state. The calculations have been done using either GAUSSIAN03 (for CCSD(T), PBE0) in connection with the local basis set aug-cc-pVTZ and LANL2TZ or VASP (for RPBE, PBE) in connection with the PAW method.

as model systems (see Figure 3), as the different behaviour of the two GGA-functionals for these finite systems can be compared to coupled cluster calculations.

As far as the water-water interaction is concerned, both by applying PBE and mixing exact exchange to PBE (PBE0), the CCSD(T) potential energy curve is almost perfectly reproduced (deviation < 4%), whereas the RPBE functional underestimates the water-water interaction by about 17%. However, as dispersive interactions are not included so far, the agreement between PBE (or PBE0) and CCSD(T) seems to be accidentally. If Grimme’s D3 correction scheme is applied both PBE-D3 and PBE0-D3 slightly overestimate the water-water interaction (by about 13%), whereas RPBE-D3 agrees well with the CCSD(T) interaction energy (overestimation by about 6%).

The performance of different GGA-functionals in describing hydrogen bonds in larger water systems can also be judged from the comparison to experimental data: the experimental lattice energy per molecule of bulk ice (-0.61 eV [2], the zero-point energy is removed to allow direct comparison) is almost perfectly reproduced by PBE (-0.67 eV). The RPBE-functional, by contrast, underestimates the absolute amount of the interaction energy per molecule by 0.11 eV (see Figure 2). These results are in the range of previously published values (0.64-0.71 eV for PBE and 0.45-0.52 eV for RPBE [18, 56]) that have been obtained by more/less stringent calculational setups. If dispersive interactions are accounted for, the RPBE-D3 method yields a lattice energy of -0.65 eV, that is remarkably close to experiment, and the PBE-D3 method leads to a lattice energy of -0.76 eV and thus, again overestimates the interaction by about 25% (see Figure 2). These findings on the water-water interactions are in accordance with a study of Santra *et al.*, who showed that for several small water clusters PBE tends to overestimate linear hydrogen bonds [57] and thus compensates the missing contribution of dispersion [19].

Regarding the interaction between a Pd-atom in the singlet state and a water-molecule, the PBE functional

largely overestimates the interaction energy by 0.24 (Figure 2b) or 0.08 eV (Figure 2c), corresponding to a factor of 2, independent of the orientation of the water molecule relative to the metal atom. The performance of both PBE0 and RPBE is much better: For the orientation in which the oxygen atom of the water molecule is facing the Pd atom they overestimate the interaction energy by 50-60 meV (25-30%). In the “H-down” orientation of the water molecule the performance of the pure GGA-functional (RPBE) is even slightly better: here, the interaction is *underestimated* by 14 meV (16%). As all other non-dispersion corrected functionals already overestimate the interaction, the addition of dispersive interactions, that are in the range of 7-35 meV for those systems, slightly worsens the agreement between quantum chemical calculations and DFT calculations. However, concerning the RPBE-D3 method, the error amounts to only 0.09 or 0.03 eV (for the respective orientation of H₂O shown in Figure 2b and c) and is therefore considerably smaller than the error of the PBE or PBE-D3 method.

Finally, adding dispersive interactions alters not only the adsorption energy but also the adsorption distance. As shown in Figure 4a, it shifts the molecules by about 0.07-0.44 Å (PBE) or 1.26-1.87 Å (RPBE) closer to the surface. In accordance with the overbinding of the water-metal interaction by the pure PBE-functional described above, the corresponding adsorption distances are already very close to the adsorption distances obtained with DFT-D methods. In contrast thereto, RPBE does not yield such a strong interaction and the adsorption distances are much larger (> 1 Å). However, if dispersion forces are accounted for, both methods (PBE-D3, RPBE-D3) end up with very similar adsorption distances.

Due to their impact on adsorption distances, the semi-empirical dispersion correction schemes indirectly influence the electronic properties of the structures as well and thus also affect workfunction changes, i.e. the difference of the workfunction of the adsorption complex and the workfunction of the clean surface. Despite their spurious long-range behaviour, common GGA-functionals are able

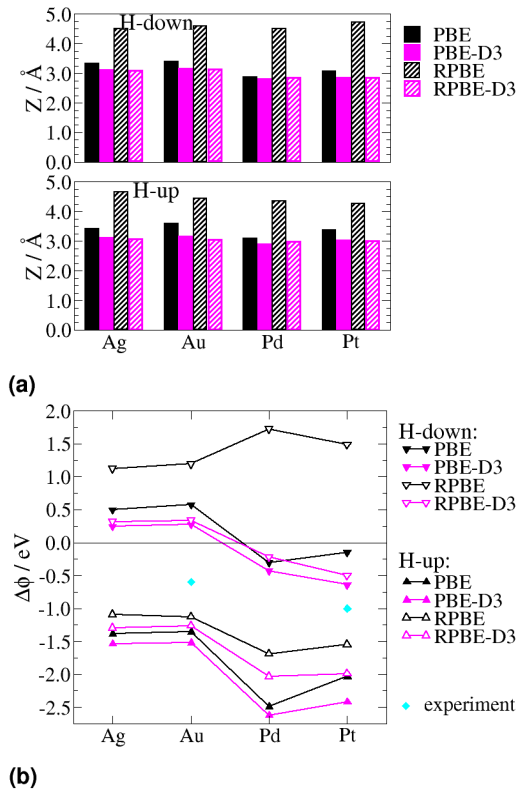


FIG. 4: Calculated adsorption distances (a) and workfunction changes $\Delta\phi = \phi_{metal} - \phi_{ice-metal}$ (b) of the H-up and H-down structures on closed packed surfaces of different metals employing PBE, RPBE and their analoga augmented with Grimme’s semi-empirical dispersion correction of 2010 (D3). For comparison experimental workfunction changes [58–60] are included as well.

to describe workfunction changes rather accurately, as long as the adsorption distance is correct [61–64]. Consequently, the pure GGA-functionals PBE and RPBE have been employed to calculate the workfunction changes at the equilibrium distances obtained by the various methods (see Figure 4b). Consistent with the respective adsorption distances, the workfunction changes are at first glance pretty alike for the distances deduced from the PBE, PBE-D3 and RPBE-D3 methods. A closer look reveals that the workfunction changes of the more stable H-down structures get even slightly closer to experiment, if they are evaluated at the distances obtained by the DFT-D methods. Still, the experimental values cannot be reproduced, most probably because the models used to describe the water layers are too simple [3] and temperature effects, leading to the dissolution of the ideal structures [7, 65], are not accounted for. Nevertheless, this analysis shows, that also calculated electronic properties of such systems can be improved with the help of

semi-empirical correction schemes.

IV. CONCLUSIONS

Addressing the adsorption of water on metal surfaces by periodic DFT calculations, it could be shown that the dispersion-corrected DFT-D approach can be used as a computationally inexpensive, but still reliable alternative to the more costly vdW-DF method in order to reproduce the thermodynamical stability of experimentally observed extended water bilayers at metallic surfaces. However, the PBE functional is only suitable to a limited extend. Actually, only the RPBE-D3 method was able to yield a reasonable description of both the intermolecular water-water interaction and the interaction between the water molecule and a metal atom. In total, using RPBE-D3 water bilayers on Pd and Pt(111) surfaces are predicted to be as thermodynamically stable as bulk ice with the calculated lattice energy of bulk ice being comparable to the experimental value.

By contrast, the pure PBE functional already predicts the right water-water interaction, obviously for the wrong reason. Adding any dispersion correction deteriorates that apparent agreement with high quality ab initio calculations. The water-metal interaction is already largely overestimated by the pure PBE functional and the application of semi-empirical dispersion correction schemes only leads to a further worsening. Since the additional overestimations due to the dispersion correction scheme affect bulk ice and water bilayers to varying degrees, the total adsorption energy and the lattice energy are again comparable. Yet, as comparison with the experimental lattice energy of bulk ice shows, their absolute values are much too large.

As far as the adsorption distances are concerned, both PBE-D3 and RPBE-D3 result in very similar values. Remarkably, also the equilibrium distances of the pure PBE functional are comparable to the interaction distances obtained by dispersion corrected calculations. This explains why many experimentally measured properties of water-metal systems, such as the workfunction changes, could be nicely reproduced or predicted by applying pure PBE calculations, although dispersion effects were missing. Thus, for pure water-metal systems, the PBE functional yields acceptable results. If additional adsorbates are taken into account that require the consideration of dispersion effects, then DFT-D calculations with the RPBE functional seem to be the proper choice.

Acknowledgments

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