Water wetting on representative metal surfaces: Improved description from van der Waals density functionals

Ikutaro Hamada [a,*], Sheng Meng [b,*]

[a] WPI-Advanced Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan
[b] Beijing National Laboratory for Condensed Matter Physics, and Institute of Physics, Chinese Academy of Sciences, 100190 Beijing, China

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ABSTRACT

We present a simple and useful approach based on the van der Waals density functional to investigate water wetting on two representative metal surfaces, Cu(110) and Ru(0001). We found that a mixed van der Waals density functional, by incorporating the Perdew–Burke–Ernzerhof (PBE) exchange for water–metal interactions and the revised PBE (revPBE) exchange of Zhang and Yang for hydrogen bonding, respectively, correctly predicts the wetting of extended water-chains and half-dissociated water layer on Ru(0001), as well as wetting of H-down bilayers on Cu(110), after correcting zero-point energy.

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1. Introduction

The generalized gradient approximation (GGA) is the method of choice in density-functional theory (DFT) [1,2] to study of water and water/solid interfaces [3–15], as it accounts for interwater hydrogen-bonds and metal-surface interactions with balanced accuracy and computational cost. In particular, DFT-GGA has succeeded in determining structures of small water clusters and water overlayers on metal surfaces in conjunction with scanning probe microscopy [16,17]. There is, however, a fundamental problem in GGA to describe water wetting on metal surfaces: water adsorption energy is consistently smaller than that of bulk ice Ih, implying that two-dimensional water wetting of metal surfaces is thermodynamically unstable compared to three-dimensional ice growth. One of the reasons for this failure is considered to be GGA's poor description of van der Waals (vdW) interactions in this system. The vdW attraction is expected to be relatively large, because of the large density of states at the Fermi level of metal surfaces. Moreover, since water–metal and hydrogen bonds are comparable in strength, inclusion of vdW interactions is critical to the delicate balance between water–metal and hydrogen bonding interactions, leading to radically different wetting phenomena. However, there have been only a few attempts to include vdW interactions at water/metal interfaces: Feibelman [18] first estimated the vdW attraction which is missing in GGA by comparing to experiment. Hamada et al. [19] later applied the van der Waals density functional (vdW-DF) of Dion et al. [20], to water bilayer/Rh(111) interfaces and confirmed the importance of vdW interaction at water/metal interfaces. More recently, Poissier et al. [21] used vdW-DF

to study the water–metal interaction on a Pd(111) surface. Despite these efforts, the calculated adsorption energies using standard vdW-DF are still much smaller than the ice binding energy. Very recently, Carrasco et al. [22] used vdW-DF with an optimized exchange functional [23] to study the one-dimensional water pentagonal chain on Cu(110) [24] and the extended water-chains on Ru(0001) [10] and succeeded in obtaining adsorption energies larger than the binding energy of ice Ih within the same level of theory.

In this work, we present a much simplified vdW-DF approach and study the wetting of extended water overlayers on Cu(110) and Ru(0001). This investigation is based on observations by extensively applying vdW-DFs with different exchange functionals, including those of Perdew–Burke–Ernzerhof (PBE) [25], and the revised PBE functional of Zhang and Yang (revPBE) [26], to study the energetics of intact as well as half-dissociated water overlayers on Cu(110) and Ru(0001). These surfaces are believed to be the border lines for water dissociation, and thus could serve as good examples to test the accuracy of vdW-DF for describing interwater hydrogen-bonding and water–metal interactions in intact and dissociated water overlayers. We found that vdW-DFs with these pure exchange energy functionals do not predict water wetting as reported in previous works [19,22]. However, by applying different exchange energies to different interactions, namely, PBE exchange for water–metal interactions and revPBE for hydrogen bonds in vdW-DF, we show that the description of water adsorption is significantly improved. More importantly, this simple modified approach with a mixed vdW-DF correctly predicts the wetting behavior of H-down water bilayers on Cu(110), and the wetting of half-dissociated layer and extended water-chains on Ru(0001), by comparing water adsorption energy of overlayers to the binding energy of bulk ice Ih.

* Corresponding authors.
E-mail addresses: ikutaro@wpi-aimr.tohoku.ac.jp (I. Hamada), smeng@iphy.ac.cn (S. Meng).

2. Methods

All the calculatisons were conducted using the STATE [27] code. Electron–ion interactions were described by the ultrasoft pseudopotentials [28], and wave functions and augmentation charge density were expanded in terms of a plane wave basis set with cutoff energies of 36 Ry and 400 Ry, respectively. For GGA calculations, we used the PBE [25] exchange-correlation energy functional as well as revPBE [26]. The Cu(1 1 0) surface was modeled by using a six-layer slab in a $p(2 \times 2)$ periodicity with a vacuum region equivalent to 12-layer spacing (15.337 Å). The slab was constructed using the experimental lattice constant (3.615 Å). For Ru(0 0 0 1), a five-layer ($\sqrt{3} \times \sqrt{3}$) slab was employed to model the surface, and the experimental lattice constant of 2.70 Å (c/a = 1.584) was used. We verified that the effect of the lattice constant used on the adsorption energy is small. Water overlayers were put on one side of the slab, and spurious dipole as well as multipole interactions with the image slabs [29] are eliminated by making use of the Green's function technique of Otani and Sugino: [30]. In the Green's function technique, a slab is sandwiched by the effective screening medium (ESM) of permittivity. The Green's function is greatly simplified when the slab has a planar boundary condition, and the electrostatic potential is thereby obtained analytically. When ESM of permittivity one is used, the Green's function is solved with an open boundary condition, enabling one to treat an isolated slab. Brillouin zone integration was performed with a 6×6 Monkhorst–Pack [31] special k-point set for Cu(1 1 0) and a 8×8 Γ-centered k-point set for Ru(0 0 0 1). First-order Hermite–Gaussian smearing of the width of 0.03 eV was employed to treat the Fermi surface [32]. When we use a denser (12×12) k-point set for Cu(1 1 0), adsorption energy changes at most 17 meV and difference in adsorption energies of different configurations are within 6 meV. Zero-point energy (ZPE) was calculated using harmonic vibrational frequencies of water molecules.

Within vdW-DF, the exchange-correlation energy is given by

$$E_{xc}[n] = E_x^{GGA}[n] + E_c^{LDA}[n] + E_c^{nl}[n], \tag{1}$$

where n is the charge density self-consistently determined within GGA, E_x^{GGA} is the exchange energy within GGA, and E_c^{LDA} is the correlation energy within the local density approximation, which describes the short-range part of the correlation energy. In the original vdW-DF, the revPBE exchange is employed. In this work, the PBE exchange is also used, as the revPBE exchange is too repul-

sive and it overestimates the intermolecular distance. In what follows, we use a notation vdW-DF^X with X being the flavor of exchange energy functional, to specify the exchange used in vdW-DF explicitly. The nonlocal correlation energy is defined by

$$E_c^{nl}[n] = \frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' n(\mathbf{r}) \phi(\mathbf{r}, \mathbf{r}') n(\mathbf{r}'), \tag{2}$$

where $\phi(\mathbf{r}, \mathbf{r}')$ the nonlocal correlation kernel [20]. To calculate E_c^{nl} for periodic systems within the real-space approach, the integral over $\mathbf{r}$ in Eq. (2) is done in a unit cell, while for $\mathbf{r}'$, the integral should be cutoff at a finite distance. A cutoff radius of 14.29 Å was used to ensure the convergence of adsorption energy within 1 meV with respect to the interaction cutoff. All the vdW-DF calculations were conducted as a post-GGA perturbation, i.e., in a non-self-consistent way. The effect of self-consistency was shown to be small [33,35]. Geometries optimized using revPBE (PBE) were adopted in the vdW-DF^{revPBE} (vdW-DF^{PBE}) calculations. We verified that the relaxation effect is small when vdW forces are taken into account (see Ref. [35], and below).

Adsorption energy of water is calculated as a sum of different contributions as

$$E_{ads} = \frac{1}{n_{H_2O}} \left(E_{int}^{H_2O-M} + E_{int}^{H_2O-H_2O} + E_{rlx}^{H_2O} + E_{rlx}^{M} \right), \tag{3}$$

where n_{H_2O} is the number of water molecules in a unit cell, $E_{int}^{H_2O-M}$ is interaction energy between water layer and M substrate, $E_{int}^{H_2O-H_2O}$ is interaction energy between water molecules in the layer, and $E_{rlx}^{H_2O}$ and E_{rlx}^{M} are energies paid to deform water molecules and substrate upon adsorption (relaxation energy), respectively [33]. $E_{int}^{H_2O-M}$ corresponds to exfoliation energy of water bilayer, which is calculated by subtracting total energy of the combined system from the sum of total energies of isolated water layer and substrate. $E_{int}^{H_2O-H_2O}$ is energy necessary to isolate water molecules (or energy gain by forming water bilayer with a hydrogen-bonding network), which is calculated as the difference between the sum of total energies of
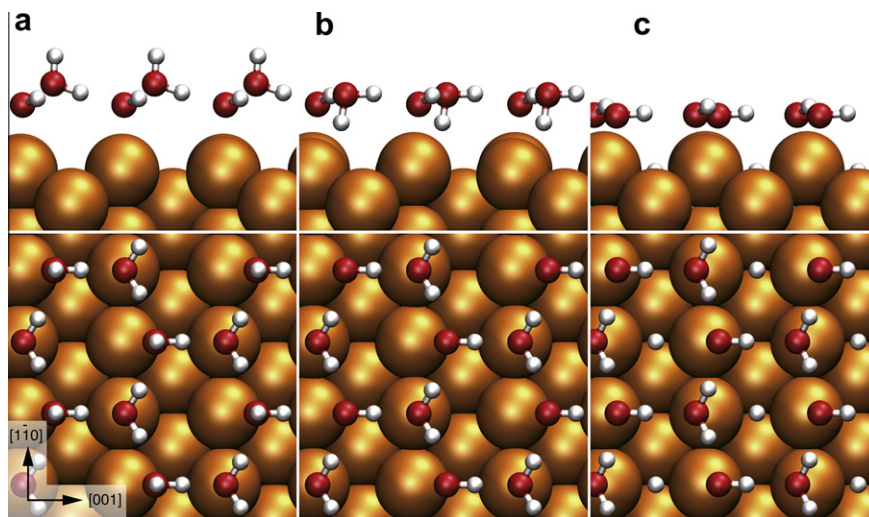
Table 1
Adsorption energy of water bilayer on Cu(1 1 0) using PBE and revPBE exchange-correlation functionals. The unit of energy is eV/H_2O.

	H-up	H-down	Half-dissociated
PBE	0.475	0.528	0.448
revPBE	0.273	0.293	0.147

Figure 1. (a) H-up, (b) H-down, and (c) half-dissociated water bilayers on Cu(1 1 0) (upper, side view; lower, top view). Small, medium, and large balls represent H, O, and Cu atoms, respectively.

isolated water molecules and the energy of the water bilayer. Isolated molecules are calculated in a unit cell elongated by three and two times (four times) in the directions of first and the second lattice vectors for Cu(110) [Ru(0001)]. In the calculations of interaction energies, atomic positions as well as their relative positions to the real-space grid were fixed to their adsorption geometries, to minimize the grid-related error. Relaxation energies are unavailable in the present vdW-DF calculations, as they are implemented in a non-self-consistent way. We used revPBE (PBE) values for $E_{rlx}^{H_2O}$ and E_{rlx}^{M} in vdW-DF^{revPBE} (vdW-DF^{PBE}) adsorption energies as in previous studies [19,34]. It should be noted that in the case of the half-dissociate water bilayer, $E_{int}^{H_2O-M}$ is interaction energy between (OH + H + H$_2$O) layer and substrate, and $E_{int}^{H_2O-H_2O}$ is interaction energy between OH + H complex and H$_2$O. Furthermore $E_{rlx}^{H_2O}$ for a dissociated water molecule is energy paid to dissociate it into OH and H fragments. In order to corroborate such decomposition, we calculated the adsorption energy of (OH + H + H$_2$O) layer on Cu(110) within PBE in a conventional approach, i.e., energy difference between the sum of total energies of isolated water molecules and bare metal substrate, and the total energy of combined system, obtaining identical results.

3. Results and discussion

We first performed GGA calculations for H-up (Figure 1a), H-down (Figure 1b), and half-dissociated (Figure 1c) water bilayers on Cu(110). Calculated E_{ads}'s are summarized in Table 1. Both PBE and revPBE functionals predict that intact H-down water bilayer is stable against dissociated bilayer, and adsorption energies are consistently smaller than the ice binding energy (0.665 eV/H$_2$O with PBE and 0.476 eV/H$_2$O with revPBE) calculated with the same pseudopotentials and similar plane-wave basis set [35]. We also found that RPBE of Hammer et al. [36] yields similar results with those obtained using revPBE. It should be noted that although adsorption of water bilayers is exothermic with revPBE, $E_{int}^{H_2O-M}$ is quite small or even negative (0.034 and −0.021 eV/H$_2$O for H-down and H-up water bilayers, respectively) as seen in water bilayer/Rh(111) systems, [35] suggesting revPBE gives too small interaction energy between water and metal substrate. Apparently, the energetic ordering obtained in the present work seems to be at variance with that in Refs. [11,12], where the half-dissociated water layer is found to be the most stable. Although different pseudopotentials and computational packages are used, we believe that this discrepancy is most likely attributed to insufficient k-point sampling in the previous study. Nevertheless, both the previous and present studies show that intact and half-dissociated water layers are very close in energy (differences ⩽0.08 eV/H$_2$O) on Cu(110), confirming that Cu(110) is a border line case for water dissociation.

We now move to vdW-DF results. Before discussing the water bilayer results, we address the interaction energy of a water monomer with Cu(110). We extracted a water monomer adsorbed on Cu(110) from the bilayer structures obtained with PBE, and calculated interaction energy as a function of surface-oxygen distance with PBE, revPBE, vdW-DF^{revPBE}, and vdW-DF^{PBE}, as shown in Figure 2. We considered water monomer lying parallel to the surface (Figure 2a) and that with its one OH bond directing toward vacuum (H-up, Figure 2b) and that with one OH toward the surface (H-down, Figure 2c). Overall, vdW-DF^{revPBE} underestimates water–substrate interactions compared with PBE, although the former accounts the vdW attraction, suggesting that further improvement of vdW-DF^{revPBE} is required to describe water–substrate interactions correctly. On the other hand, by using the PBE exchange (vdW-DF^{PBE}), interaction energies are 'improved,' i.e., they become larger than the PBE values. We note that by comparison to higher-level

quantum chemistry methods such as CCSD (T), it was found that the PBE functional underestimates adsorption energy of water on a NaCl(001) surface by a large amount (∼0.16 eV) [23]. We also note that it was reported that revPBE as well as PBE predicts adsorption energy of water monomer on a Cu(111) surface, much smaller than the experimental values [37]. Here it should be noted that although the interaction energies become larger by a correct account of vdW attraction, equilibrium water–substrate distances calculated with GGA and vdW-DF are almost identical: The equilibrium distance with vdW-DF^{revPBE} (vdW-DF^{PBE}) is almost identical to that with revPBE (PBE), justifying the use of revPBE- (PBE-) optimized geometries in vdW-DF^{revPBE} (vdW-DF^{PBE}) calculations.
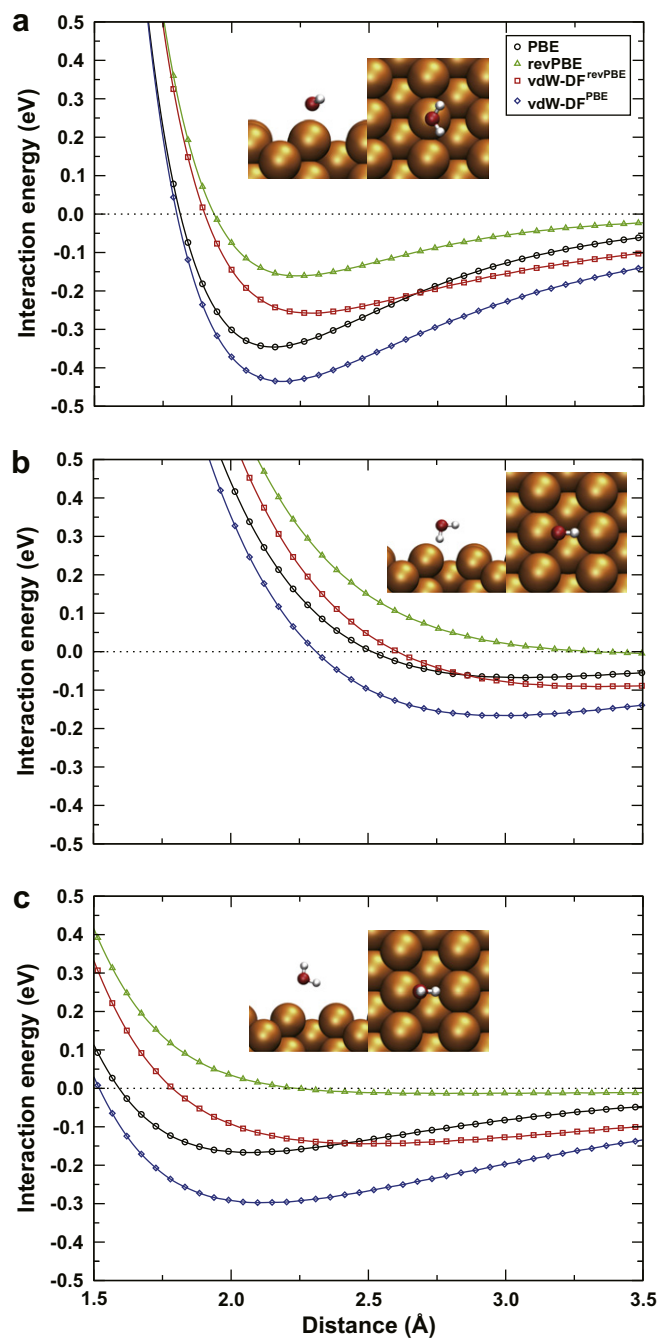

Figure 2. Interaction energies for (a) flat, (b) H-down, and (c) H-up H$_2$O molecules on Cu(110). The geometries for flat and H-down configurations are extracted from the H-down H$_2$O bilayer, and that for H-up one, from the H-up H$_2$O bilayer.

Table 2
Adsorption energy of water bilayer on Cu(110) and its components calculated with PBE and vdW-DFs. Nonlocal correlation contribution to the interaction energy is given in parentheses. E_{rlx} is a sum of E_{rlx}^M and $E_{rlx}^{H_2O}$. In a vdW-DF^{revPBE} calculation with PBE geometry, E_{rlx} obtained using PBE was used. The unit of energy is eV/H_2O.

		PBE	vdW-DF^{revPBE}	vdW-DF^{revPBEa}	vdW-DF^{PBE}
$E_{int}^{H_2O-Cu}$	H-up	0.059	0.109 (0.234)	0.102 (0.264)	0.193 (0.264)
	H-down	0.141	0.153 (0.280)	0.146 (0.303)	0.256 (0.303)
	Half-dissociated	3.294	3.087 (0.471)	3.056 (0.483)	3.261 (0.483)
$E_{int}^{H_2O-H_2O}$	H-up	0.465	0.394 (0.161)	0.398 (0.166)	0.523 (0.166)
	H-down	0.466	0.376 (0.179)	0.383 (0.182)	0.520 (0.182)
	Half-dissociated	0.653	0.557 (0.207)	0.573 (0.213)	0.732 (0.213)
E_{rlx}	H-up	−0.049	−0.040	−0.049	−0.049
	H-down	−0.078	−0.061	−0.078	−0.078
	Half-dissociated	−3.499	−3.443	−3.499	−3.499
E_{ads}	H-up	0.475	0.463	0.458	0.667
	H-down	0.528	0.468	0.451	0.698
	Half-dissociated	0.448	0.201	0.131	0.495

[a] PBE-optimized geometry.

Table 3
Adsorption energy of water layer on Ru(0001) and Cu(110), using the mixed PBE/revPBE exchange energy functional in vdW-DF. Binding energy of ice Ih is presented for comparison. The ZPE corrected value is given in parenthesis. The unit of energy is eV/H_2O.

	H-up	H-down	Half-dissociated	Extended chains
Cu(110)	0.542 (0.450)	0.561 (0.466)	0.336 (0.311)	
Ru(0001)	0.577 (0.487)	0.543 (0.455)	0.581 (0.539)	0.683 (0.585)
Ice Ih		0.588 (0.456)		

We then calculated E_{ads}'s of water overlayers on Cu(110) with the vdW-DFs. E_{ads}'s and their components are summarized in Table 2, together with nonlocal correlation contributions to the interaction energies. For comparison, E_{ads}'s calculated with PBE and vdW-DF^{revPBE} at the PBE-optimized geometries are also shown.

In the cases of intact bilayers, nonlocal-correlation contribution is solely responsible for the adsorption of water bilayer, as it is the dominant contribution in $E_{int}^{H_2O-M}$. This conclusion is unaltered when different exchange energy is used. $E_{int}^{H_2O-H_2O}$'s with vdW-DF^{revPBE} are smaller than those obtained with PBE, while vdW-
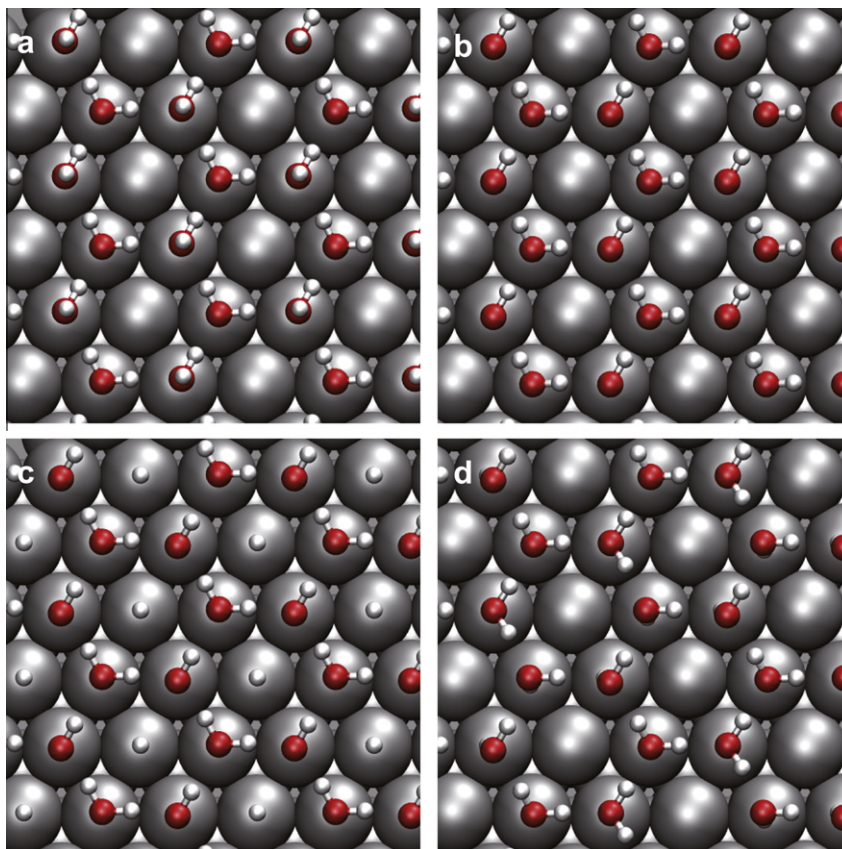

Figure 3. (a) H-up bilayer, (b) H-down bilayer, (c) half-dissociated bilayer, and (d) extended water-chain models on Ru(0001). Small, medium, and large balls represent H, O, and Ru atoms, respectively.

DF^{PBE} gives large values (see discussion below). E_{rlx}'s are small compared with interaction energies, demonstrating the fact that the water adsorption is weak. Resulting E_{ads}'s with vdW-DF^{revPBE} are smaller than the corresponding PBE values, while those with vdW-DF^{PBE} are large, because of dominant contribution of $E_{int}^{H_2O-H_2O}$ in E_{ads}. In both vdW-DF^{revPBE} and vdW-DF^{PBE} cases, difference of E_{ads}'s for both H-down and H-up bilayers is small and they are quasi-degenerated, similar to the Rh(1 1 1) case [19]. The result is supported by the experimental evidence for the coexistence of H-up and H-down bilayers [38].

In the case of the half-dissociated bilayer, $E_{int}^{H_2O-M}$ is significantly larger than those of intact bilayers, as it contains the interaction of hydroxyl radical and hydrogen atom with the substrate. Nonlocal correlation contribution is slightly larger than the intact ones, because distance between bilayer and substrate is smaller. Large $E_{int}^{H_2O-M}$ is compensated for by larger E_{rlx}, which includes energy necessary to dissociate water molecule into hydroxyl and hydrogen species, resulting in E_{ads} comparable to those of intact bilayers.

It is found that similar to the PBE case, intact water bilayer is more stable than the half-dissociated one within vdW-DF, and the latter becomes less stable with vdW-DF regardless of the exchange energy used. Neither vdW-DF^{revPBE} nor vdW-DF^{PBE} predict larger adsorption energies than the ice binding energy [35] (0.588 eV/H$_2$O with vdW-DF^{revPBE} and 0.773 eV/H$_2$O with vdW-DF^{PBE}), meaning that water wetting of the Cu(1 1 0) surface is as obtained thermodynamically unstable in contrast to experiment.

Recently, it was shown [35] that although vdW-DF^{revPBE} underestimates the binding energy of water dimer, the calculated binding energy of crystalline ice Ih with vdW-DF^{revPBE} is more accurate than that obtained using PBE, whereas vdW-DF^{PBE} severely overestimates it. This result implies that vdW-DF^{revPBE} is superior in describing condensed phase of water ice, and hence the interaction energy within a water bilayer may be described more accurately than using PBE. In contrast, from the monomer results (Figure 2), vdW-DF^{revPBE} is insufficient to describe both energy and geometry of water on the substrate accurately, and vdW-DF^{PBE} is more appropriate for water–substrate interactions.

Based on the above consideration and the decomposition of adsorption energy (Eq. (3)), we propose to use different exchange functionals for different interaction energies, i.e., the PBE exchange for water–substrate interactions and revPBE one for water–water interactions. In other word, a mixed exchange energy in vdW-DF is used for an improved description of water bilayer on metal surfaces. In practice, the structure of water bilayer is optimized using PBE. Then water–substrate interactions ($E_{int}^{H_2O-M}$) are calculated with vdW-DF^{PBE} and water–water interactions ($E_{int}^{H_2O-H_2O}$) are obtained with vdW-DF^{revPBE}. Relaxation energies for both water and substrate ($E_{rlx}^{H_2O}$ and E_{rlx}^{M}, respectively) are calculated using PBE, and added to the interaction energies, to obtain the 'total' adsorption energy (Eq. (3)). Calculated adsorption energies are compared with the ice binding energy calculated with vdW-DF^{revPBE}, and are used to discuss the wetting of the metal surface.

Adsorption energies thus obtained are shown in Table 3, with significant improvements over the 'pure' vdW-DFs. They are now comparable to the ice binding energy from vdW-DF^{revPBE}. By including the zero-point energy (ZPE) correction, adsorption energy of H-down bilayer (0.466 eV) is larger than the ice binding energy with ZPE correction (0.456 eV), i.e., water wetting is more stable than three-dimensional ice growth. Furthermore, the wetting water bilayer may become more stable, when we use a larger supercell with (7 × 8) periodicity as observed in low energy electron diffraction (LEED) experiments [38]. Therefore we conclude that intact water layer is thermodynamically stable on Cu(1 1 0) and that our mixed vdW-DF approach is able to describe water wetting of Cu(1 1 0) surfaces at low temperatures.

To further verify the validity of such a mixed vdW-DF approach, we performed calculations for water overlayers on Ru(0001) (Figure 3). The results are summarized in Tables 3 and 4. Within 'pure' vdW-DF, we obtain contradictory results: vdW-DF^{revPBE} predicts stable intact water bilayer, whereas vdW-DF^{PBE} predicts that the half-dissociated bilayer is the most stable. Neither approach predicts wetting of water overlayers on Ru(0001), while in experiment both partially-dissociated [39–41] and intact [39,40] water layers were observed to wet the surface in large areas [10]. Temperature programmed desorption (TPD) experiments also indicate that the partially-dissociated layer binds stronger to the substrate than the intact ones [10]. Accordingly we test our modified vdW-DF approach to resolve this discrepancy. By using the mixed PBE/revPBE exchange, we obtain stable half-dissociated water bilayer (Table 3). Moreover, the obtained energies for intact and dissociated water overlayers are all comparable to the ice binding energy. In the present water/Ru(0001) case, if we include ZPE correction into the energies obtained from the modified vdW-DF treatment, we obtain a very appealing result that is consistent with experimental observations: both the half-dissociated (0.539 eV) and intact H-down layers (0.455 eV) would wet the Ru(0001) surface, and the half-dissociated layers are the most stable. This point is reached by comparison to ice binding energy of 0.456 eV after ZPE correction. Finally, we adopted the energetically more stable extended water-chain model (Figure 3d) [10]. Adsorption energies for the water-chain model without ZPE correction are calculated to be 0.636 and 0.557 eV/H$_2$O with PBE and vdW-DF^{revPBE}, respectively, which are smaller than the ice binding energies calculated with the same functionals. vdW-DF^{PBE} gives the adsorption energy

Table 4
Adsorption energy of water bilayer on Ru(0001) ($\sqrt{3} \times \sqrt{3}$) calculated using PBE and vdW-DFs. Nonlocal correlation contribution to the interaction energy is given in parentheses. E_{rlx} is a sum of E_{rlx}^{M} and $E_{rlx}^{H_2O}$. In a vdW-DF^{revPBE} calculation with PBE geometry, E_{rlx} obtained using PBE was used. The unit of energy is eV/H$_2$O.

		PBE	vdW-DF^{revPBE}	vdW-DF^{revPBE}[a]	vdW-DF^{PBE}
$E_{int}^{H_2O-Ru}$	H-up	0.066	0.124 (0.321)	0.109 (0.348)	0.219 (0.348)
	H-down	0.161	0.160 (0.320)	0.177 (0.371)	0.299 (0.371)
	Half-dissociated	3.333	3.235 (0.569)	3.224 (0.583)	3.402 (0.583)
$E_{int}^{H_2O-H_2O}$	H-up	0.474	0.394 (0.150)	0.406 (0.159)	0.529 (0.159)
	H-down	0.408	0.340 (0.172)	0.326 (0.173)	0.459 (0.173)
	Half-dissociated	0.914	0.754 (0.233)	0.753 (0.237)	0.952 (0.237)
E_{rlx}	H-up	−0.049	−0.035	−0.049	−0.049
	H-down	−0.082	−0.053	−0.082	−0.082
	Half-dissociated	−3.574	−3.536	−3.574	−3.574
E_{ads}	H-up	0.491	0.483	0.466	0.699
	H-down	0.487	0.446	0.421	0.676
	Half-dissociated	0.673	0.453	0.403	0.779

[a] PBE-optimized geometry.

of 0.815 eV/H$_2$O (without ZPE correction), which exceeds the ice binding energy, but it is unable to predict the stable intact water bilayer as discussed above. On the other hand, by using the modified vdW-DF approach, we obtain the adsorption energy of 0.585 eV with ZPE correction, which surpasses well the ice binding energy of 0.456 eV, rendering a perfect wetting phenomena as observed in experiment. We note that the calculated adsorption energy of the extended water-chain is larger than that of the half-dissociated water layer, in apparent contradiction with experimental observations. However, to stabilize the dissociated water layer on Ru(0001), segregation of hydrogen out of the water overlayer is necessary [39]. Thus, adsorption energy of water-hydroxyl overlayer on Ru(0001), in which dissociated hydrogen atoms adsorb on a bare patch of the Ru surface [3] should be greater than that of the extended water-chain.

4. Conclusion

We study the wetting behavior of intact and half-dissociated water layers on two representative metal surfaces, Cu(110) and Ru(0001), based on various vdW-DFs. It is found that neither vdW-DF with standard revPBE/RPBE exchange nor vdW-DF with PBE exchange yields water wetting on these surfaces. Rather, we propose a simple modified vdW-DF approach using a different exchange functional for different type of interaction, namely, PBE exchange for water–substrate and revPBE for interwater hydrogen-bonding interactions. We show that such a simple *ad hoc* vdW-DF approach with a mixed PBE/revPBE exchange significantly improves the description of water adsorption on metal surfaces with GGAs or 'pure' vdW-DFs, and appears to be very successful in describing water wetting: it correctly predicts the wetting phenomena of intact water layers on Cu(110) and Ru(0001), and that half-dissociated water layer wets on Ru(0001). Both are consistent with experimental observations. This approach represents a different strategy to the development of vdW-DFs, where most efforts were devoted to find a general, optimized exchange [42,23,43] and correlation [44–46] functionals for a universal performance. Compared to these popular approaches, the disadvantage of the present method is that it lacks a consistent description of general electronic interactions in different environments, and becomes hard to apply when interactions of very different types are entangled and cannot be separated. Nevertheless, we believe that the present approach is simple, effective, and usable to study water wetting of metal surfaces until more accurate exchange energy for vdW-DF is developed and/or more elaborated methods based on quantum Monte Carlo or random-phase approximation are at hand.

Acknowledgments

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