

## REVIEW

# Accounting for van der Waals interactions between adsorbates and surfaces in density functional theory based calculations: selected examples

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This article reviews the different density functional theory (DFT) methods available in the literature for dealing with dispersion interactions and recent applications of DFT approaches including van der Waals corrections in the study of the interaction of atoms and molecules with several different surfaces. Focus is given to the interaction of atoms and molecules with metal, metal oxide and graphite surfaces or more complex systems. It will be shown that DFT approaches including van der Waals corrections present significant advances over standard exchange correlation functionals for treating systems dominated by weak interactions.

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## 1. Introduction

In the last decades, density functional theory (DFT) has become the preferred method for the electronic structure calculation of molecular and solid systems being applied along the years to increasingly complex and large systems.

In this theory the central object is the electron density instead of the wave function, which is supported by the first Hohenberg and Kohn theorem<sup>1</sup> where it is demonstrated that the electron density uniquely determines the Hamiltonian operator and, in principle, it is sufficient to obtain all the properties of the system. In other words, given a ground state density it should be possible to obtain the corresponding ground state wave function. Based on the latter theorem, which is sometimes considered the holy grail of density functional theory, the same authors derived a second theorem where it is stated that the universal functional delivers the exact energy if and only if the input density is the exact ground state density and that, otherwise, a higher value is obtained. This is nothing else than the variational principle. These theorems are indicating that in principle there is a unique relationship between the ground state density and the ground state energy. However, the Hohenberg and Kohn theorems do not provide any clue on how to build the functional that yields the ground state energy. One year later, Kohn and Sham suggested a way to approach the universal functional.<sup>2</sup> This

was done by the derivation of a model closely related to the Hartree–Fock approach, leading to a set of one-electron equations with which one can obtain the ground-state density. These are the so-called Kohn–Sham equations. Since then, many developments and practical applications of DFT methods have appeared in such a way that nowadays much of what we know in several areas of knowledge, for instance, about the electronic and structural properties of materials, has been extracted from DFT based calculations using a variety of different implementations. Despite its huge success and applicability there are fundamental weaknesses and limitations on its applicability resulting from the approximate nature of the exchange correlation functionals that are at our disposal (for a review please consider Sousa *et al.*<sup>3</sup>). Among these limitations one can refer the incomplete cancellation of Coulomb self-interaction by the exchange functional<sup>4</sup> and, more relevant to the present work, the lack of a correct inclusion of the long-range van der Waals interactions in the correlation functional.<sup>5</sup> A word of caution is in order; in the condensed matter community the term dispersion interactions and van der Waals interactions are interchangeable while in other contexts van der Waals forces includes in addition to the dispersion (London) forces, the induction (Debye) and orientation (Keesom) forces.<sup>6,7</sup> Along this work we will use van der Waals and dispersion forces as synonyms.

Dispersion terms arise from the long range correlated instantaneous electron-electron interactions being an intrinsically nonlocal electron correlation effect. It is a ubiquitous phenomenon being present even if no other type of interaction, *e.g.* covalent bonds, hydrogen bonds, charges or permanent multipole interactions, are present. It is responsible for an enormous variety of phenomena which includes, for instance, the adhesion mechanism that geckos use to

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climb vertical walls and ceilings or the adhesive properties of new synthetic sticky 'gecko tape'.<sup>8,9</sup> The lack of a correct description of the dispersion interaction strongly limits the applicability of DFT to systems characterized for possessing both strong local bonds and weak nonbonding forces like soft matter, nanostructures, adsorption systems and biostructures.

The adsorption of noble atoms or closed shell stable molecules to a surface is a typical example of a system where van der Waals interaction plays a fundamental role, particularly in the case of physical adsorption. Although standard DFT methods cannot describe correctly the van der Waals attractive tail, the short range attraction felt by the adsorbate near the minima and the Pauli repulsion seem to be treated appropriately by these kinds of electronic structure methods.<sup>10–13</sup> In fact, cluster or periodic calculations employing either local density approach (LDA) or generalized gradient approach (GGA) were found to give a correct description of preferred adsorption sites of rare gases on close-packed metal surfaces (see the review of Diehl *et al.*<sup>14</sup> and references there included). The interaction of molecules with solid surfaces also allows the confrontation of theory with experiment since, for instance, adsorption energies can be measured in desorption experiments and molecular structure on the surface and self-assembling can be "visualized" in scanning tunneling microscopy experiments and quantitatively determined by X-ray Photoelectron Spectroscopy (XPS) and similar techniques.

## 2. Computational methods and surface models

A pragmatic method to tackle the problem of inclusion of van der Waals (vdW) interactions in DFT scheme consists simply in adding a semi-empirical term to the bare Kohn–Sham energy

$$E_{Tot} = E_{DFT} + E_{disp} \quad (1)$$

where

$$E_{disp} = s_6 \sum_{i=1}^{N-1} \sum_{j=i+1}^N \frac{C_6^{ij}}{R_{ij}^6} f_d(S_R R_{ij}^0, R_{ij}) \quad (2)$$

Here, the sum extends to all atom pairs and  $C_6^{ij}$  is the mixed dispersion coefficient between atom  $i$  and  $j$  separated by a  $R_{ij}$  distance. Clearly  $C_6^{ij}/R_{ij}^6$  is the leading term in the London series. To match to the DFT potential this term is multiplied by a dumping function  $f_d$  that depends of a suitable cut-off radii  $R_{ij}^0$  and the functional dependent scaling factors  $S_R$  and  $s_6$ . Different parameterization for the atoms coefficients had appeared in the literature the first one due to Ortman *et al.*<sup>15,16</sup> that used the London formula

$$C_6^{ij} = \frac{3}{2} \alpha_i \alpha_j \frac{I_i I_j}{I_i + I_j} \quad (3)$$

to calculate the atomic dispersion coefficients where  $I_i$  is the ionization potential and  $\alpha_i$  is the polarizability of atom  $i$ . This expression applies to pairs of atoms independently of their environment.

Another parameterization, known as DFT-D, was presented by Grimme<sup>17</sup> based on calculations from extended AO basis sets of polarized TZV or QZV quality. In this work atomic  $C_6$  coefficients were presented only for the elements H and C-Ne. Later, the same author introduced the B97-D functional, also known as DFT-D2,<sup>18</sup> where the short range part of the GGA density functional was adjusted to the presence of the long-range correction avoiding in this way double-counting. A less empirical and more accurate method was reported by the same group in 2010, the so-called DFT-D3<sup>19</sup> approach, which has been extended to the most of the periodic table, comprising the description of elements with nuclear charge  $Z = 1–94$ . In this approach, atom-pairwise specific dispersion coefficients and cutoff radii are both computed from first principles. It also includes the eight-order dispersion term  $C_8R^{-8}$ , the three-body term to dispersion energy and dependence on local coordination. The method still maintains two parameters ( $s_6$  and  $s_8$ ) adjusted for each density functional.

A different scheme was presented by Tkatchenko and Scheffler (TS)<sup>20</sup> based on the relation between polarizability and volume<sup>21</sup> that calculates the dispersion coefficients and vdW radii for atoms in molecules as a function of the ground-state electron density, *i.e.*

$$C_6 = C_6[n(\mathbf{r})] \quad (4)$$

and

$$R_{vdW} = R_{vdW}[n(\mathbf{r})] \quad (5)$$

Contrary to other vdW correction methods where the parameters are fixed, here these parameters change in response to changes on the electronic density and naturally includes hybridization effects. There is one single parameter, which appears in the dumping function that connects the  $R^{-6}$  vdW interaction with the DFT functional, and the method can be applied to all elements of the periodic table. This method has been recently extended by self-consistently including long-range screening effects in the effective atomic polarizabilities.<sup>22</sup>

Silvestrelli<sup>23</sup> presented a method (DFT/vdW-WF) where a sum similar to (2) is performed over pairs of fragments instead of pairs of atoms with the pairs coefficients given by

$$C_6^{nl} = \frac{3}{32\pi^{3/2}} \int_{|\mathbf{r}'| < r_c'} d\mathbf{r}' \int_{|\mathbf{r}| < r_c} d\mathbf{r} \frac{\sqrt{\rho_n(\mathbf{r})\rho_l(\mathbf{r}')}}{\sqrt{\rho_n(\mathbf{r}) + \sqrt{\rho_l(\mathbf{r}')}}} \quad (6)$$

In this formula  $r_{nl}$  is the distance between  $n$  and  $l$  fragments and  $\rho_n(\mathbf{r})$  is the electronic density of the fragment  $n$ . The fragment densities are written in terms of maximally localized Wannier functions  $w_n(\mathbf{r})$  and  $\rho_n(\mathbf{r}) = w_n^2(\mathbf{r})$ , which are obtained from the occupied Kohn–Sham orbitals by means of a unitary transformation that conserves the total density by minimizing the functional

$$\Omega = \sum_n S_n^2 = \sum_n (\langle w_n | r^2 | w_n \rangle \langle w_n | \mathbf{r} | w_n \rangle^2) \quad (7)$$

Recently a new implementation (DFT/vdW-WF2) of the method appeared in the literature.<sup>24</sup> In this approach, the calculation of  $C_6$  is based on the London expression instead of considering eqn (6), and includes the intra-fragment charge overlap of the localized Wannier functions.

Pure DFT functionals neglect the long-range electron-electron exchange interaction and Savin<sup>25</sup> and Hirao<sup>26</sup> and their co-workers suggested long-range corrections schemes for the local density approximation (LDA) and the generalized-gradient approximation (GGA), respectively. These authors suggested the separation of the two-electron operator in its short-range and long-range parts by using the standard error function with a parameter  $\mu$  determining the ratio between these two parts. Then, the long-range exchange interaction is described by the Hartree-Fock exchange integral while LDA or GGA, depending on the scheme, is applied to the short-range exchange interaction. In Hirao's *et al.* approach, the parameter  $\mu$ , optimized to give bond lengths of homonuclear diatomic molecules up to the third period, is 0.33 (a value of  $\mu = 0$  yields the original, uncorrected, GGA functional).

A different philosophy on the approach to include dispersion interaction on DFT calculations is the use of dispersion-corrected atom-centered potentials (DCACPs).<sup>27,28</sup> In this approach, instead of an additional atom-atom (or fragment-fragment) interaction of  $C_6R^{-6}$  type being added, the dispersion interaction is modeled by a modified atom-electron interaction. An atom-centered potential, modeled for each element  $k$ , is added to the Kohn-Sham Hamiltonian

$$H = H_0 + \sum_i V_{ik}(R_i - r) \quad (8)$$

where  $H_0$  is the bare Kohn-Sham Hamiltonian and  $V_{ik}$  is the correction potential, centered on atom  $i$ . Then, the electronic problem is solved for this modified Hamiltonian. DCACP have the same analytical form as the Goedecker-Teter-Hutter (GTH) pseudopotentials and have to be generated to be used with different exchange-correlation functionals.

A similar method has been presented by DiLabio and co-workers<sup>29,30</sup> where DFT calculations employing Gaussian basis sets are performed with the use of dispersion-correcting potentials (DCPs), which are used as atom-centered effective-core potentials. Like the previous approach the dispersion interaction is modeled by a modified atom-electron interaction that, by changing the environment in which the valence electrons move, models the dispersion effects. The analytical form of the DCPs is a sum of Gaussian-type functions, originally two,

$$U_i(r) = r^{-2} \sum_{i=1}^2 c_{ii} r^{n_{ii}} e^{-\zeta_{ii} r^2} \quad (9)$$

with the coefficients optimized for several functionals like B971, PBE, PBE1, PW91, B3LYP and BHandLYP with

6-31G(d,p), 6-31+G(d,p), 6-311+G(2d,2p) and aug-cc-pVTZ basis sets. Latter, DCPs for use with smaller basis sets and with the counterpoise corrections were presented.<sup>31</sup> These DCPs include a third long-range Gaussian function and allow the treatment of larger systems.

A different approach is the non-local van der Waals density functional (vdW-DF) of Langreth, Lundqvist and co-workers.<sup>32</sup> In this approach the exchange-correlation energy is given by

$$E_{xc} = E^{GGA} E_c^{GGA} + E_c^{LDA} + E_c^{nl} \quad (10)$$

where the correlation energy  $E_c^{GGA}$  is substituted by the local LDA correlation  $E_c^{LDA}$  and  $E_c^{nl}$  stands for the non-local correlation energy and accounts for the dispersion contribution. Eqn (10) corresponds to keep only the exchange part of the GGA functional while the local correlation  $E_c^{LDA}$  is obtained at LDA level. This scheme avoids to double-counting the non-local contribution to the correlation energy.

The non-local part of the correlation energy  $E_c^{nl}$  is the most challenging term and its particular form is still a subject of research.<sup>33</sup> Formally, the non-local correlation energy is given by

$$E_c^{nl} = \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' n(\mathbf{r}) \phi(\mathbf{r}, \mathbf{r}') n(\mathbf{r}') \quad (11)$$

involving an integration over electron densities on different space locations interacting *via* response function or kernel  $\phi$  given as a function of  $Rf(\mathbf{r})$  and  $Rf(\mathbf{r}')$  where  $R = |\mathbf{r} - \mathbf{r}'|$  and  $f(\mathbf{r})$  is a function of density  $n(\mathbf{r})$  and its gradient. This term is much smaller in magnitude and in sensitivity on the spatial coordinates than the short-range correlation energy  $E_c^{LDA}$  which allows the introduction of approximations in its calculation and has been evaluated in the vdW-DF with a simple model dielectric function. It is also challenging in terms of practical implementation since it involves the calculation of a double spatial integral. The numerical evaluation of this multidimensional integral is particularly problematic for large unit cells, especially for periodic systems, and several publications have appeared with efficient schemes to evaluate the non-local correlation energy.<sup>34-37</sup>

Since revPBE predicts reduced or simply no binding in vdW complexes, it has been originally suggested<sup>32,38,39</sup> to be the best choice for GGA functional to choose in the vdW-DF scheme. There are however cases where the original vdW-DF method is not sufficiently accurate and alternative exchange functionals to the original revPBE, like the optPBE $\kappa$ , optPBE, optB88 and optB86b among others, were proposed and tested.<sup>40,41</sup> In this line, a second version of the van der Waals density functional (vdW-DF2) was proposed<sup>42</sup> that makes use of the semilocal exchange functional PW86<sup>43</sup> in the refitted version rPW86,<sup>44</sup> and a large- $N$  asymptote gradient correction<sup>45</sup> in determining the non-local correlation energy kernel.

As we stressed before, the non-local correlation energy functional (eqn (11)) is still a subject of research and different models with different functional forms appeared in the

literature like the VV09 and VV10 models of Vydrov and van Voorhis.<sup>46–48</sup>

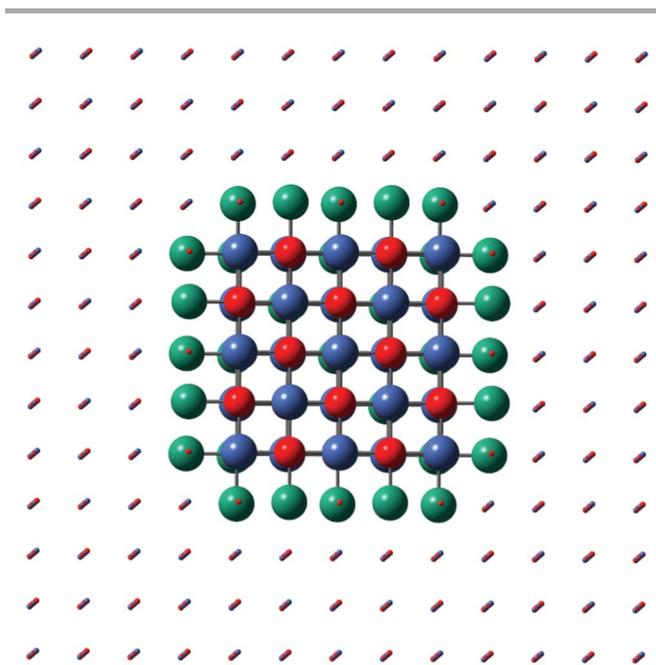
It is also worth mentioning alternative approaches such as fluid density functional theory which have been applied to the study the recognition of polymer at a nanopatterned surface<sup>49</sup> although this type of methodology is more appropriate for soft matter<sup>50,51</sup> and it is only indirectly related to the density functional theory methods of electronic structure. A different way of including dispersion interaction is by employing semilocal or hybrid functionals containing a large number of parameters, which are fitted with data sets including systems with dispersive interactions. Thus, the functional will be able to capture some dispersion interaction effects.<sup>52</sup> This has been done by Zhao and Truhlar<sup>53,54</sup> who developed a set of hybrid *meta*-GGA functionals, the family of M06 functionals, which differs by the amount of exact exchange included, ranging from zero (M06-L,<sup>55</sup>) to one (M06-HF<sup>56</sup>). The fraction of the Hartree–Fock exchange in M06 is 27% and the double amount of the latter value is considered in the M06-2X functional.<sup>54</sup> As an example, the number of optimized parameters in M06 and M06-2X numbers are 35 and 32, respectively. Marom *et al.*<sup>52</sup> studied the accuracy of the M06 family of functionals for evaluating dispersion interactions and found that M06 functionals are able to approximate model dispersion effects at short-range. However, they still miss some long-range contributions and, therefore, they cannot describe correctly long-range dispersion contributions.

Relevant for the interpretation and discussion of the results concerning the adsorption of atoms and molecules on extended surfaces are the strategies used to model such large systems and the quantum mechanical methods employed to describe the electrons in the systems. In order to make the systems tractable computationally, the extended surfaces are modelled either with the finite size cluster or with the periodic slab approaches. In each case the electrons may be treated with localized basis sets such as the familiar Gaussian Type Orbitals basis sets used in Quantum Chemistry or plane-wave basis sets commonly used in Solid State Physics. Also in both cases, the inner electrons are often described with the pseudopotential approach,<sup>57</sup> *i.e.*, they are considered together with the nuclei as rigid non-polarizable ion cores. In the case of the cluster model approach, a finite number of atoms (aggregate) is cut from the bulk material following a specific direction in order to simulate a portion of the surface and a specific Miller index orientation. In the case of small aggregates, this approach enables the consideration of large basis sets but the results are tremendously affected by spurious effects related to the limited size of the model. Furthermore, due to the presence of boundary effects, the results critically depend on the choice of the cluster size, stoichiometry and shape. These problems can be reduced if large cluster models or suitably large nanoparticles are used but these are computationally expensive. Embedding schemes mimicking the effects of atoms at large distances are also often considered to avoid edge effects. For instance, clusters embedded in large arrays of point charges and effective core

potentials (ECP) were proven to be quite useful to study metal oxide surfaces such as those of MgO<sup>58,59</sup> or  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>.<sup>60–62</sup>

An example of an embedded cluster model with three different regions that was used to model the MgO(100) surface is shown in Fig. 1.<sup>58</sup> The inner region, centered on a Mg cation, is composed by 25 magnesium and 25 oxygen atoms which are represented in Fig. 1 as large blue and red spheres. The outermost oxygen positions in the central Mg<sub>25</sub>O<sub>25</sub> cluster are surrounded by a central region composed by 33 ECP which simulate total ion potentials (large green spheres in Fig. 1) and are used to avoid spurious polarization of oxygen atoms at the edge of the cluster model. The inner and central regions are further embedded by an external region comprising a large number of point charges with values of +2 and –2 for cations and anions, respectively. The latter region is essential for a satisfactory representation of the Madelung potential at the center of the cluster model.

In the periodic model, a simple portion of atoms—unit cell—is expanded periodically, usually in the three spatial dimensions (XYZ). The repetition in the three spatial dimensions is ideal for the representation of homogeneous bulk materials but surfaces can be also modelled by the introduction of a vacuum region as shown in the top of the unit cell in Fig. 2a. In the repeated slab mode, as can be seen in Fig. 2, the unit cell is composed by several MgO layers with the vacuum region in the direction normal to these layers. Usually, metal surfaces are well represented by four or five metal layers while, for instance, the surfaces of ionic oxides, *e.g.* alumina or



**Fig. 1** Normal to the surface view of the embedded cluster used to model the MgO(100) surface. The central Mg<sub>25</sub>O<sub>25</sub> cluster (large blue and red spheres are Mg and O atoms, respectively, treated with an all electron basis set) are surrounded by 33 total ion potentials (large green spheres treated with ECPs mimicking Mg cations at the edge and by 280 positive (+2.0, small blue spheres) and 313 negative (–2.0, small red spheres) point charges.

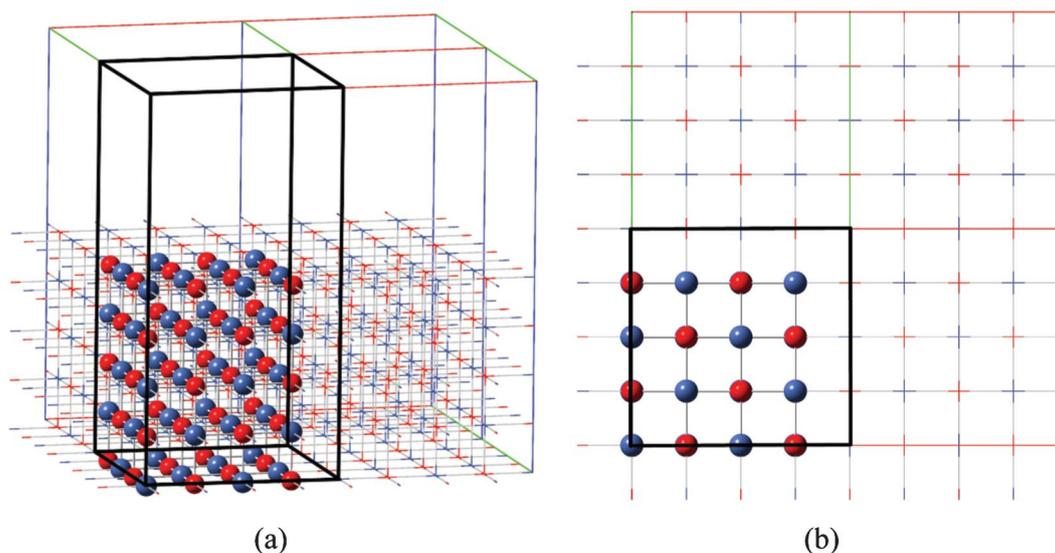


Fig. 2 Side (a) and top (b) views of a periodic model representation of the MgO(100) surface. The unit cell is highlighted in black. Color code as in Fig. 1.

titania,<sup>62,63</sup> have to include several metal and oxygen layers for a good representation. Note, however, that in case of using GTO basis sets, as in the CRYSTAL code,<sup>64</sup> it is possible to make use of periodicity in two directions only. Spurious effects affecting the cluster models are absent in the case of the periodically boundary conditions. It is important to notice that the periodicity of the slab model approach reduces computational costs because the periodicity of the unit cell allows for a reduction of the infinite number of basis functions needed to represent the infinite system to a finite number of orbitals that are needed to represent the electrons of the atoms in the unit cell (Bloch's theorem).<sup>65</sup> The computational cost is thus directly linked with the number (size) and the symmetry of the elements in the unit cell, *i.e.*, small crystalline systems such as bulk metals are treated at very low computational cost. However, when studying adsorption on surfaces modelled with the periodic slab approach, the sizes of the vacuum region and of the edges of the slabs in the directions normal to the surface have important impact in the computational cost of the calculations. On the other hand, the size of the slab unit cell may be employed to study the effects of surface coverage. When using the repeated slab model it is important to ensure that the size of the vacuum region is sufficiently large as to prevent unphysical interactions with the lowermost layers in the replica above. However, a compromise should be reached since the larger the unit cell, the more expensive the calculations are. Vacuum regions of approximately 10 Å are enough for the study of small adsorbates but larger regions are likely to be necessary for large adsorbates, especially those weakly bound to the surface. Note that the dispersion effects covered in the present review may be felt at considerably large distances and the effects of the cell vectors length in the calculated energies should be carefully studied *a priori*.

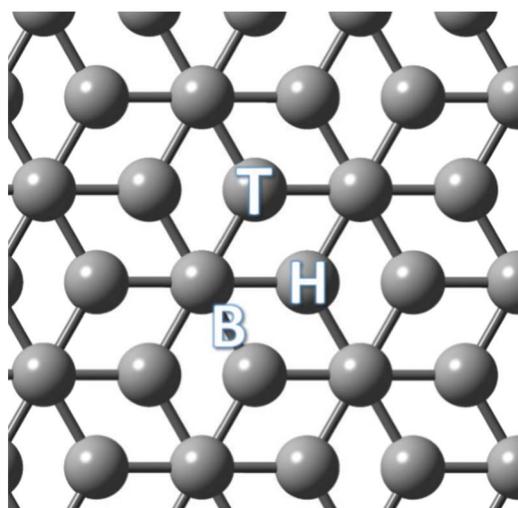
### 3. Adsorption of noble gas atoms

Noble gas adsorption is the prototypical example of the importance of the van der Waals interactions on adsorption where the weak dispersion interactions are responsible for the physical adsorption of the noble gas on a surface. As the noble gas possesses a close-shell electronic structure the interaction of the noble gas with a surface results from the balance between the van der Waals attraction and the Pauli repulsion resulting from the superposition of the atom and surface electronic charge densities. The interaction of rare gas atoms with single crystal surfaces has been the subject of many studies over the last years.<sup>66</sup>

Tkatchenko and von Lilienfeld<sup>67</sup> have used the semiempirical dispersion calibrated atom-centered potential (DCACP), added to the BLYP functional Kohn–Sham Hamiltonian, to study the adsorption of Ar on graphite (Fig. 3). They calculated the same system at LDA level and with the BP, PBE and BLYP exchange–correlation functionals.

They found that GGA BP, PBE and BLYP fail to predict the adsorption of Ar on graphite while reasonable (and probably fortuitous) results of equilibrium distance and energy were obtained with LDA. The BLYP + DCACP calculations, on the other hand, gave results in very good agreement with the literature, predicting the hollow site as the energetically favorable.

The family of methods that makes use of maximally localized Wannier functions have been used for several studies of noble gas atoms weakly bonded onto different surfaces. Silvestrelli *et al.*<sup>68</sup> have studied the adsorption of Ar on graphite and of Ar, He (and also H<sub>2</sub> molecule) on the Al(100) surface. A representation of Al(100) and the adsorption sites on this surface are shown in the topmost panel of Fig. 4. They added the vdW correction to the revPBE functional and compared results with the data calculated with the bare DFT



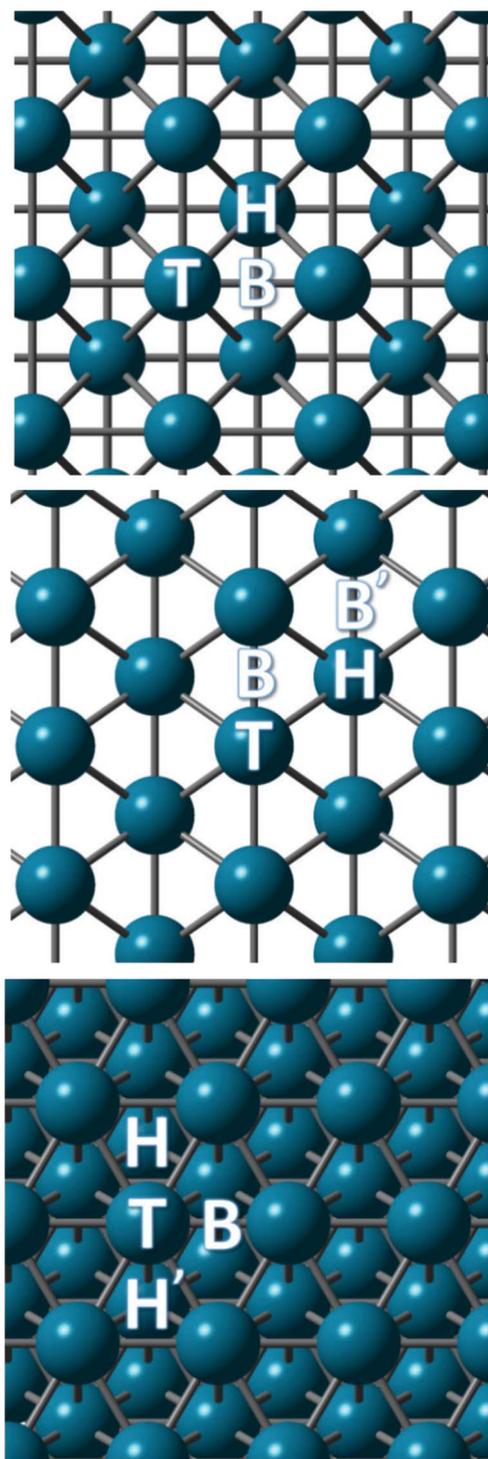
**Fig. 3** Adsorption sites on the graphite surface. T denotes direct adsorption on top of the outermost atoms in the surface, B is used for adsorption at positions bridging two outermost atoms, and H is used to label adsorption at hollow sites.

and with the LDA functionals. The revPBE functional gave completely unphysical results with an extremely small binding energy and with the atoms adsorbed very far from the surface. The binding energies produced by the LDA scheme were reasonable, although the agreement could be accidental since LDA tends to overbind which could mimic the missing vdW contribution. Regarding the equilibrium distances, LDA gave too short values.

Among the most studied surfaces, many close-packed metal surfaces have been extensively studied by DFT methods, including the adsorption of Ne, Ar, Kr and Xe on the Pb(111) and Cu(111). General representations of these (111) surfaces, together with available adsorption sites on the surface, are shown in the lowermost panel of Fig. 4. For this study Silvestrelli *et al.*<sup>69</sup> used the DFT/vdW-WF method. These authors have found similar adsorption energies for the different adsorption sites for Ne, Ar and Kr adsorption on the Cu(111) surface, while for Xe the energetically preferred site for Xe is on top of a Cu atom. For the Pb(111) case the preferred adsorption site is the *hollow* site in all cases. In all studied cases the vdW energy represents the most important contribution of the binding energy but apparently doesn't play an important role in the adsorption site preference.

The DFT/vdW-WF method has been also applied to the study of the adsorption of rare-gas atoms (He, Ar, and Xe) on graphite and graphene surfaces and the results compared to previous theoretical calculations and experimental data.<sup>70</sup> The adsorption of Ar on graphite has been addressed previously by the same authors with the DFT/vdW-WF method in the revPBE + vdW version and also by Tkatchenko *et al.*<sup>67</sup> and by Bichoutskaia and Pyper.<sup>71</sup>

Also in order to test the applicability of the DFT/vdW-WF2, Ambrosetti and Silvestrelli<sup>24</sup> presented results for the adsorption of an Ar atom on graphite and of a Ne atom on the



**Fig. 4** Adsorption sites on the (100), top, (110), middle, and (111), bottom, Miller index surfaces of face center cubic (fcc) metals with labels as in Fig. 3. Note that in the case of the (110) index, the bridge sites may be divided in short bridge (B) and long bridge (B') sites, and that in the case of the (111) index, the hollow sites may be divided in octahedral (H) and tetrahedral (H') sites.

Cu(111) surface. Calculating the binding energy as function of the distance from the surface, the C3 vdW-coefficient that characterizes the atom-surface vdW interaction, can be

obtained. These results showed a good improvement when compared with results obtained with the previous DFT/vdW-WF scheme

The importance of van der Waals interactions on the Xe adsorption on Cu(111) and Pt(111) has been addressed by Lazić *et al.*<sup>72</sup> that concluded the necessity of inclusion of van der Waals interactions in DFT calculations for a correct description of weak adsorption system like Xe adsorbing on metal surfaces.

Recently Chen *et al.*<sup>73</sup> addressed the study of Ar, Kr and Xe adsorption on Pt(111), Pd(111), Cu(111), and Cu(110) metal surfaces comparing LDA, PBE functionals and the vdW-DF1, vdW-DF2, DFT-D2 approaches. For general representations of the (110) and (111) Miller indices of these transition metals and adsorption sites labelling, the reader is referred to Fig. 4. They have found the vdW-DF2 functional to give the best results when compared with experimental data for adsorption energies, equilibrium distances and vibrational energies. The DFT-D2 results generally gave too short equilibrium distances and too high adsorption energy values and the wrong adsorption site preference for four of the nine systems studied by these authors.

Besides metal surfaces the van der Waals interactions have been included in the study of atoms on oxide surfaces. Gomes *et al.*<sup>74</sup> studied the adsorption of Xe on the clean surface of rutile TiO<sub>2</sub>(110) using the PBE and PW91 exchange–correlation functional,<sup>75,76</sup> and analyzed the importance of the van der Waals energy term in the adsorption. Top and side views of the rutile TiO<sub>2</sub>(110) surface are depicted in Fig. 5. From that study it is clearly seen that the adsorption of Xe on the rutile surface is dominated by the dispersion terms and the corrected interaction energies are much larger, from 3.5 times in the case of the O1 site to almost 5 times in the case of the Ti2' site, than those calculated only with the bare DFT approach. As an example the calculated interaction energy in the case of the

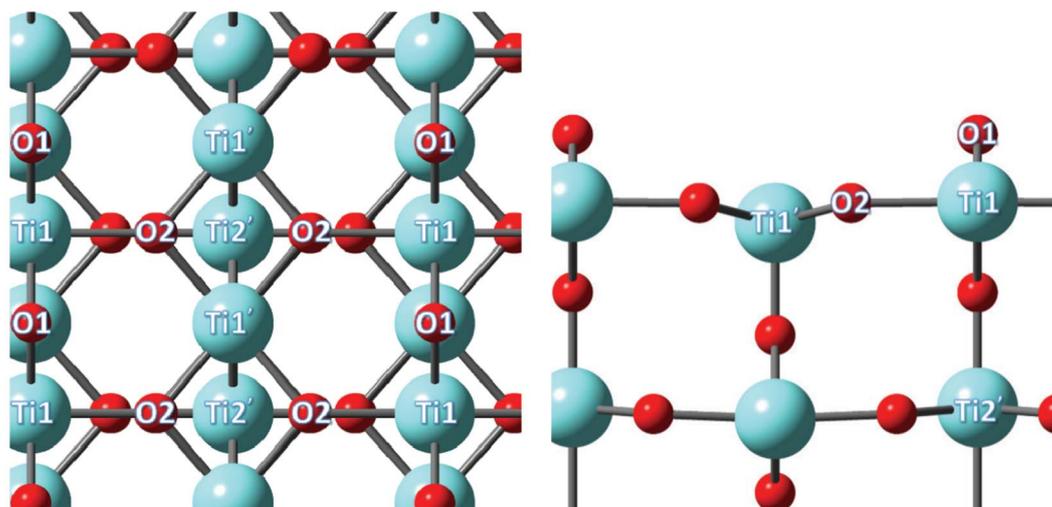
Ti1' site changes from 60 meV to 280 meV when dispersion is added to the PBE calculation. Furthermore, the minimum of the interaction energy curves are shifted to smaller Xe-surface distances as should be expected from the stronger interaction with the surface.

Other atoms than noble gases have been studied. Amft *et al.*<sup>77</sup> calculated the adsorption of Cu, Ag, and Au adatoms on a rather inert support such as graphene by employing the vdW-DF and PBE + D2 methods. They have found the adsorption energies calculated with the PBE + D2 approach systematically higher than those obtained with vdW-DF while PBE + D2 underestimated the equilibrium distances when compared with those calculated with the vdW-DF method but no comparison with benchmark results is made in that work.

## 4. Molecular adsorption

There is a large number and variety of studies of adsorption of molecules that includes in different ways vdW interactions. Differently to atoms, molecules can acquire different conformations upon interaction with the surface and vdW interactions promote the spread conformations of the molecule over the surface as a way to maximize dispersion interactions. The energetic cost due to molecular distortion contributes now, together with the attractive van der Waals dispersion forces, electrostatic, covalent bonding, the Pauli repulsion and surface distortion to the overall interaction of the molecule with the surface.

Adsorption of the adenine molecule (Fig. 6) was studied with the vdW interactions described by the semiempirical scheme of Ortman *et al.*<sup>78</sup> on the (110) surfaces of Cu, Ag, and Au.<sup>79</sup> In all cases the molecule bonds the surface *via* two nitrogen atoms and shows analogous configuration. The interaction with the surface is stronger in the case of Cu and also stronger in covalent character than for Ag and Au. The



**Fig. 5** Top (left) and side (right) views of the rutile TiO<sub>2</sub>(110) surface. Cyan and red spheres are Ti and O atoms, respectively. The positions of the top (O1 and Ti1'), bridge (Ti1) and hollow (O2 and Ti2') sites are shown.

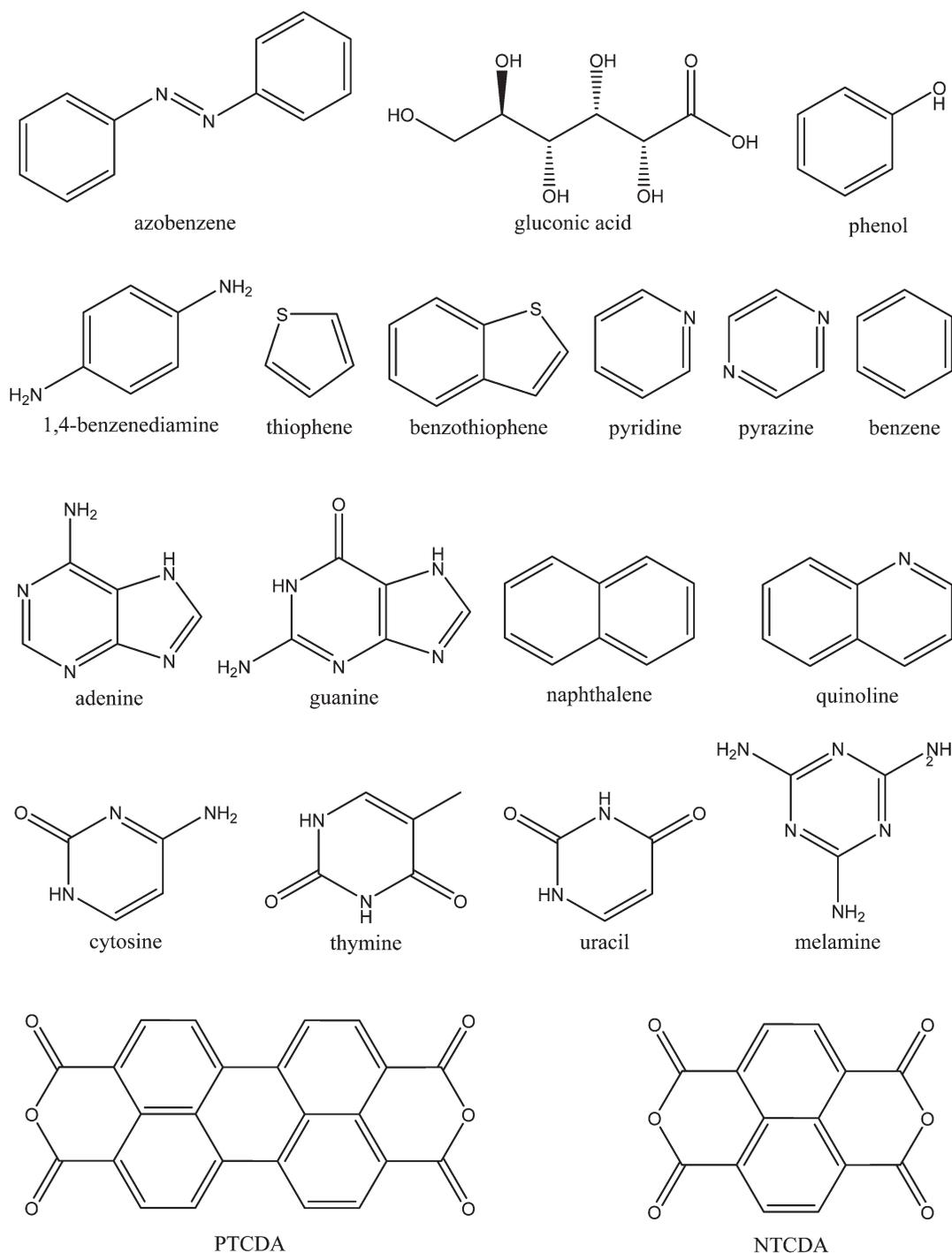


Fig. 6 Structures of different molecules studied on surfaces.

inclusion of vdW effects does not have a marked effect on the binding energies, presumably because the interaction through the N atoms is already quite strong, and is more important for the more planar orientation of the adsorbate.

Prates Ramalho and Illas<sup>80</sup> studied the adsorption of azobenzene (Fig. 6) on the rutile TiO<sub>2</sub>(110) surface. In this study it was found that, contrary to the gas phase case where the *trans* conformation is the most stable, the *cis* isomer is the

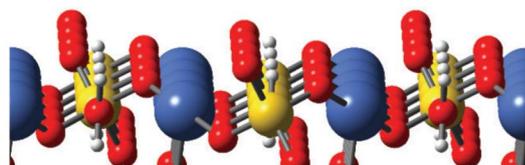
most stable form on the rutile surface. A similar arrangement but on the Pt(111) surface was found also for azomethane.<sup>81</sup> To estimate the magnitude of these interactions, the authors employed the semi-empirical van der Waals correction term proposed by Grimme<sup>18</sup> which was simply added to the total energy at different distances from the surface with the molecular geometry fixed at the optimum predicted by the calculations with the PBE exchange–correlation potential. This

allowed the authors to obtain an estimate of its effect on the equilibrium distance from the molecule to the surface and of its contribution to the adsorption energy. It was found that the additional dispersion term pulls the molecules toward the surface and increases the binding energy from 0.47 eV to 1.78 eV in the case of the *trans* isomer and from 1.31 eV to 2.10 eV for the *cis* isomer. However, including the dispersion term does not qualitatively affect the relative adsorption energies of the both isomers of the species although the energy difference between the two adsorbed species becomes smaller. In a subsequent study, the authors included the same vdW term correction in the geometry optimization of the adsorption systems.<sup>82</sup> This contribution of dispersion to the adsorption energy was found to be major, contributing to 74% to the adsorption energy in the case of the *trans* isomer and 39% in the case of the *cis* one. Both PBE and PBE-D predict that the interaction with the surface only slightly distorts the structure of azobenzene, for both isomers, but essentially maintains their geometrical identity.

Azobenzene and also 1,4-benzenediamine (BDA, Fig. 6) adsorption on Ag(111) has been studied recently<sup>83</sup> with vdW-DF and the semi-local Perdew–Burke–Ernzerhof functional. The inclusion of vdW effects strongly increases the binding energy producing results consistent with experimental findings. It also changes the BDA adsorption geometry stabilizing flat adsorption geometries. For the azobenzene case, the vdW-DF gives better results when compared with other dispersion corrected functionals, although it slightly overestimates by around 16% the equilibrium distance of the adsorbate from the surface.

The adsorption of an example of a hydroxy acid, gluconic acid, Fig. 6, was studied with the PBE-D scheme on the  $\text{MgSO}_4 \cdot \text{H}_2\text{O}(100)$  surface,<sup>84</sup> which is depicted in Fig. 7. Nearly identical adsorption geometries were found when PBE-D or bare PBE were employed except that the dispersion force pulls the molecule 0.1 Å closer to the surface suggesting that while the adsorption geometry does not depend on the inclusion of dispersion terms, the distance of the molecule to the surface is essentially conducted by short-range interactions. The authors also found that vdW interaction does not play a principal role in the adsorption of gluconic acid on  $\text{MgSO}_4 \cdot \text{H}_2\text{O}(100)$  since it is responsible for 20%–25% of the adsorption energy.

In order to study the role of an heteroatom like N in the interaction of several flat  $\pi$ -conjugated molecules like benzene, pyridine and pyrazine on the Cu(110) surface, Fig. 6, Atodiresei



**Fig. 7** Side view of the  $\text{MgSO}_4 \cdot \text{H}_2\text{O}(100)$  surface. Blue, yellow, red and white spheres are Mg, S, O and H atoms, respectively.

*et al.*<sup>85</sup> performed a study where they used vdW-DF and DFT-D. They found that the inclusion of vdW forces is crucial to attain the right geometry of the adsorbed molecules. More important, they found that the inclusion of vdW changes *qualitatively* the nature of adsorption of pyridine on Cu(110) surface from physisorption to chemisorption while is the driving force which binds the molecule to the surface for the benzene and pyrazine adsorption. The adsorption energies were in all cases more negative for vdW-DF than for vdW-D.

In order to assess the accuracy of semiempirical methods for inclusion of vdW interactions on DFT, Mercurio *et al.*<sup>86</sup> performed normal-incidence X-ray standing wave study and temperature programmed desorption spectroscopy of azobenzene on Ag(111) to obtain structural parameters and adsorption energy of the system. Calculations have been made with the Grimme (DFT-D2)<sup>18</sup> and Tkatchenko and Scheffler (TS)<sup>20</sup> schemes. While bare DFT-PBE strongly overestimates the distance between the adsorbed molecule and the surface and produces only a weak binding when compared to the experimental data, they found good agreement on the structural properties when using the DFT-D2 and the TS schemes, but, the latter, lead to a sizeable overbinding.

The adsorption of several flat molecules, namely, melamine, naphthalene tetracarboxyldianhydride (NTCDA) and perylene-3,4,9,10-tetracarboxylic-3,4,9,10-dianhydride (PTCDA), on the Au(111) surface was studied with the vdW-DF method.<sup>87</sup> PBE calculations show weak physisorption for these molecules, with very small binding energies of the order of 0.1/ 0.2 eV while much larger energies (up to ~ 1.9 eV) are obtained with vdW-DF. The vdW-DF adsorption energies increase dramatically with the size of the molecule, which is not observed in the case of PBE. The importance of self-consistency in the calculation of the binding energy by the vdW-DF method has also been highlighted since the results of non-self-consistent calculations can, in some cases, differ by up to 20%.

The role of vdW interactions on organic/inorganic interfaces was addressed by Tkatchenko *et al.*<sup>88</sup> in their rather recent study of perylene-3,4,9,10-tetracarboxylic-3,4,9,10-dianhydride (PTCDA) molecule at surfaces of Ag(111) using the vdW-DF approach. They verified that vdW-DF gives realistic adsorption energies but overestimates adsorption distances. The results were also compared with those obtained by different semi-empirical methods<sup>86,89</sup> and EX + cRPA.<sup>90</sup> The difference between the different methods is sizable with adsorption energies extending between 2 to 4 eV and adsorption distances between 3 and 3.5 Å, values which have to be compared to an estimated experimental adsorption energy of PTCDA of around 2.4 eV and an experimental adsorption distance of 2.86 Å. For the bare PBE functional, the adsorption energy as function of the distance between the molecule and the surface is always positive and, hence, no stable adsorption complex is predicted.

To establish the performance of different approaches to account for the contribution of dispersion terms to surface-adsorbate interactions, benzene is often chosen as a case study system. A study of the adsorption of benzene, and also of

naphthalene (Fig. 6), has been conducted by Chakarova-Käcket *et al.*<sup>91</sup> on a sheet of graphite using the vdW-DF approach.<sup>32</sup> As experimental results for these systems are available, comparisons were performed with the vdW-DF calculations, which gave results for geometry and energetics in good agreement with experiment. In particular, for benzene, it was found a binding energy of 495 meV, to be compared with  $500 \pm 80$  meV<sup>92</sup> and 480 meV,<sup>93</sup> for the equilibrium separation of 3.6 Å between the molecule and the surface, while, for naphthalene, they have found a binding energy of 763 meV, to compare with the experimental values  $800 \pm 100$  meV and  $900 \pm 70$  meV.<sup>92</sup> The same vdW-DF method was also used for the study of benzene adsorption on the Si(001) ( $2 \times 1$ ) surface.<sup>94</sup> Two configurations of the adsorbed benzene, namely the tight-bridge and butterfly configurations (Fig. 8) were studied and different exchange–correlation functionals compared. The PBE and revPBE approaches find the tight-bridge configuration as the most stable for all coverages, while the vdW-DF calculations predict that, for some surface coverages, the butterfly is more stable.

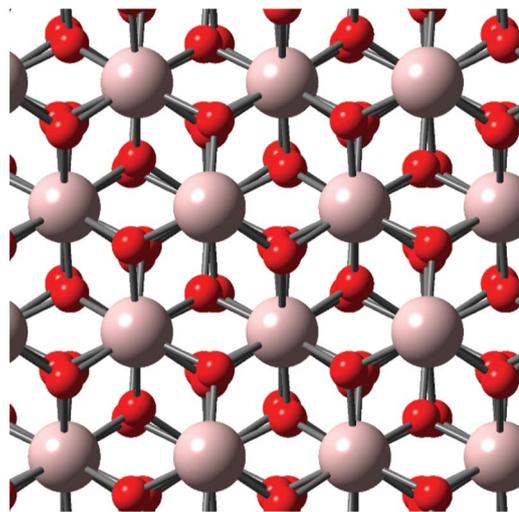
A related molecule, phenol, Fig. 6, adsorbed on graphite (0001) and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(0001), Fig. 9, was studied by using the same approach, *i.e.*, vdW-DF, to include vdW interactions.<sup>95</sup> The nature of the adsorption on these surfaces is different, while the adsorption of phenol on graphite occurs essentially due to dispersion interactions, for the alumina there is an important covalent contribution to bonding. The authors found that even in the case of alumina vdW interaction plays an important and non-negligible role.

Adsorption of butadiene, thiophene, benzothiophene, pyridine, quinoline, benzene, and naphthalene (Fig. 6) on the basal plane of MoS<sub>2</sub> (Fig. 10) has been studied by Moses *et al.*<sup>96</sup> The study has been made with the vdW-DF approach and good agreement with experimental adsorption data was found. The equilibrium geometry predicted for all adsorbed molecules corresponds to an orientation with the molecular plane parallel to the Mo/S rows (*e.g.* Fig. 10b) and  $\sim 3.5$  Å above the basal plane of MoS<sub>2</sub>. This is due to the fact that the adsorbate–substrate interaction is dominated by vdW forces and the parallel orientation maximize this type of interaction.

The vdW-DF scheme has been applied to the adsorption of small n-alkanes, from methane to n-decane, and also H<sub>2</sub> and polyethylene, on graphene<sup>97</sup> and compared to experimental data. The linear dependence of the desorption energy barrier with respect to the alkane chain length was found in the



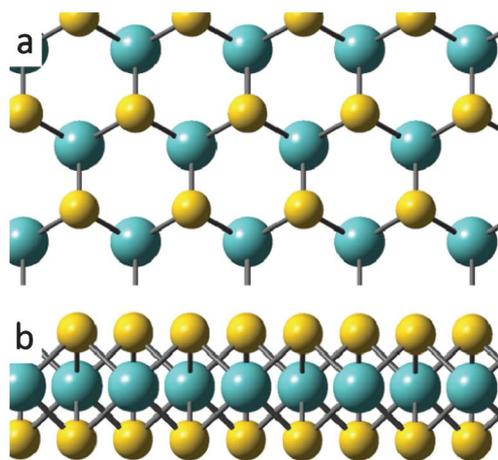
**Fig. 8** Side views for tight bridge (left) and butterfly (right) configurations of benzene adsorbed on the Si(001) surface. Gray and white spheres are C and H atoms, respectively. Adapted from ref. 94.



**Fig. 9** Top view of the Al terminated corundum Al<sub>2</sub>O<sub>3</sub>(0001) surface. Pink and red spheres are Al and O atoms, respectively.

calculations. The same approach and the same substrate were chosen in a recent study of chloroform (CHCl<sub>3</sub>) and other trihalomethanes adsorbed on graphene.<sup>98</sup> Chloroform was found to adsorb with the H atom pointing away from the graphene surface with an adsorption energy of 357 meV whereas the values for fluorform and bromoform were 206 meV and 404 meV, respectively. This is in agreement with the increasing polarizability of the trihalomethanes along the series.

A comparative study of the performance of several approaches aimed to account for vdW terms in DFT has been reported recently for the physisorption of nucleobases (adenine, cytosine, guanine, thymine and uracil) on graphene.<sup>99</sup> Although the calculated adsorption energies predicted by different methods are different, they all predict the same order of the strength of the interactions of the



**Fig. 10** Top (a) and side (b) views of the basal plane (0001) of MoS<sub>2</sub>. Blue and yellow spheres are Mo and S atoms, respectively. Adapted from ref. 96.

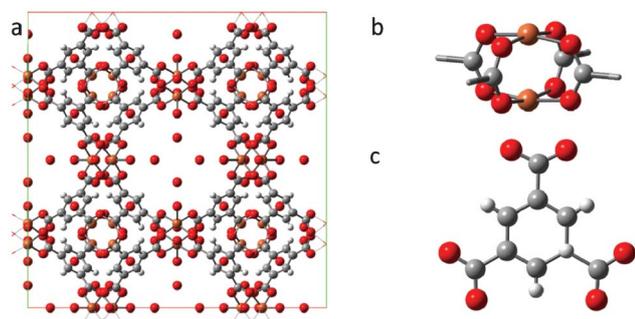
nucleobases with graphene. However, this agreement does not hold for the binding distances that are found to be different within different approaches. Finally, these authors have found that, for this class of problems, DFT-D3 constitutes a good compromise between accuracy and computational cost and suggest combining the DFT-D and vdW-DF schemes to study systems with vdW interactions.

Other important benchmark of different approaches to deal with vdW interactions on DFT adsorption studies have been performed recently.<sup>100</sup> Here the authors compared the vdW-DF, vdW-DF2, DFT-D3 and TS-vdW methods on the study of potential energy curves of H<sub>2</sub> on Cu(111), Cu(100) and Cu(110) surfaces with physisorption data extracted from reflection-diffraction experiments. Qualitative resemblances were found for the vdW-DF and vdW-DF2 functionals results. With the vdW-DF2 functional, potential energy curves were obtained in qualitative and quantitative agreement with the experimental data, while significant differences in the positioning of the minimum of the separation distance and in the well depth were obtained with the DFT-D3 and TS-vdW approaches.

The description of the interaction of molecules with the surfaces of metal organic frameworks (MOFs), is also an important issue. MOFs are a new family of porous materials which are based on metal ions or clusters of metal ions linked by an organic mono-, bi-, tri-, or tetravalent, molecule. Several MOFs present open (unsaturated) metal sites on which some molecules are preferentially adsorbed and this is one of the reasons why these materials are being heavily studied. It was found that standard DFT methods are inadequate for describing the interaction of organic molecules with those metal sites very probably due to difficulties in the correct description of the dispersion interactions between the adsorbate and the MOF organic parts. In fact, in recent studies by Grajciar *et al.*<sup>101</sup> it was found that BLYP, PBE, TPSS and B3LYP underestimate significantly the interaction energies for water with HKUST-1, a MOF with copper open metal sites based on copper “paddle-wheels” connected by benzene 1,3,5-tricarboxylate linkers (Fig. 11). Based on a benchmark CCSD(T)/CBS interaction energy for the water / HKUST-1 system, these authors proposed a combined DFT/CC method,

which includes a correction function to account for the discrepancy between DFT and CCSD(T) energies, to treat the adsorption of water in HKUST-1. They obtained a benchmark result for the interaction enthalpy at  $T = 0$  K in the water / HKUST-1 system of  $-49.0$  kJ mol<sup>-1</sup>. They suggested that DFT approaches based on the GGA are not able to handle this type of systems. The DFT/CC method was also employed by Grajciar *et al.*<sup>102</sup> to describe the interaction of carbon dioxide with HKUST-1. Very recently, some of us have been involved in a comparative study on the applicability of DFT methods to treat the interaction of water with HKUST-1 using a copper formate cluster identical to the paddle-wheel in Fig. 11.b) but where the tubes are hydrogen atoms. This cluster was found to provide identical results to those obtained with much larger cluster models.<sup>103</sup> It was found that the combination of the Hirao's *et al.*<sup>26</sup> long-range correction scheme to the GGAs PBE or BP86, *i.e.*, LC-PBE or LC-BP86 together with triple zeta basis set, yields water to copper distances and interaction enthalpies in good agreement with the benchmark results of Grajciar *et al.*,<sup>101</sup> suggesting that the LC- scheme is suitable for handling these very difficult systems.<sup>104,105</sup> Interestingly, the functionals from the hybrid *meta* M06 family<sup>53</sup> including 0%, 27% or 54% fractions of the Hartree-Fock exchange, more precisely the M06-L,<sup>55</sup> M06<sup>54</sup> and M06-2X approaches,<sup>54</sup> predicted interaction enthalpies in very good agreement with the benchmark result calculated by Grajciar *et al.*<sup>101</sup> The water to Cu and the Cu-Cu distances are quite different from functional to functional. The fact that the M06-2X yields almost as good results as the M06-L or M06 functionals is surprising since the latter were suggested to be better than the former for systems containing transition metal elements.<sup>53</sup> The M06 family of functionals seems to be a good choice for handling molecular systems where weak intermolecular interactions exist. We have confirmed the adequacy of these approaches in the past for two difficult systems, *e.g.* CO adsorption on MgO(100)<sup>58</sup> and CO and NO adsorption on Ni-doped MgO(100),<sup>59</sup> which are also corroborated by the quite encouraging results from recent works concerning the interaction of CO with the (111) surfaces of Rh, Pt, Cu, Ag and Pd<sup>106</sup> or the interaction of benzene, pyridine, thymine and cytosine with Au(111),<sup>107</sup> where the M06-L method and a periodic model approach were used.

Another very hot topic where DFT approaches including van der Waals corrections are being used is in the study of the interaction of graphene with adsorbates<sup>70,77,97–99,108</sup> or with a substrate.<sup>109,110</sup> This is mostly due to the fact that graphene presents unique electronic and mechanical properties, with many thought applications, but graphene is also interesting in part since it constitutes an interesting playground for the testing of dispersion-corrected DFT methods.<sup>19,111,112</sup> In the studies of Kozlov *et al.*,<sup>108–110</sup> the semi-empirical vdW correction due to Ortmann *et al.*<sup>15</sup> was used to correct the calculations performed with the PBE exchange–correlation functional and a periodic approach. Despite the simplicity of the correction scheme (see Eqn (3)), the calculations predicted successfully the coexistence of two different surface struc-



**Fig. 11** The structures of the a) copper benzene 1,3,5 tricarboxylate, HKUST 1 or CuBTC, and of the b) activated copper paddle wheel and of the c) benzene 1,3,5 tricarboxylate fragments. Orange, red, grey and white spheres are Cu, O, C and H atoms, respectively.

tures<sup>109</sup> identified experimentally by high-resolution X-ray photoelectron spectroscopy for graphene on Ni(111). According to the dispersion corrected DFT studies, there are two structures for graphene on Ni(111), namely, a bridge-top and a top-fcc structure, that have almost identical energies, which is in consonance with the experimental simultaneous detection of these two structures.

The adsorption of CO<sub>2</sub> in the interior and exterior walls of clean and nitrogen-doped single-walled carbon nanotubes was studied by Mackie and DiLabio<sup>113</sup> with the dispersion-correcting potentials (DCPs) approach with the nanotubes being modeled as hydrogen-terminated cluster models. The calculation found a relatively strong interaction for the CO<sub>2</sub> with the single-walled nanotubes with binding energies between 4.2 and 11.1 kcal mol<sup>-1</sup>. Gibbs energies of binding have also been calculated and it was found to be much lower in the exterior of the nanotubes compared with the binding inside the tubes.

## 5. Conclusions

Dispersion interactions are ubiquitous in nature and are responsible for an enormous variety of phenomena. The lack of a correct description of the dispersion interaction limits the applicability of density functional theory to a variety of systems in particular those where noble atoms or closed-shell stable molecules interact with rather inert surfaces. The introduction of dispersion interactions in density functional theory calculations is, naturally, an intense field of research and, in the last years, many approaches, with different degrees of empiricism, have appeared in the literature.

For large molecules, or systems where the adsorbate interacts weakly with the substrate, the introduction of a correct description for van der Waals interactions proves to be essential to attain adsorption energy values comparable to experimental values. Their introduction is also fundamental to correctly describe the adsorption geometry. The direct confrontation of theory with experiment allows to check the performance of different functionals. As reviewed above, important advances were made in the recent years on the development of new density functional methods for describing weakly bound systems. The results obtained so far are very encouraging but one must admit that an exchange–correlation functional able to calculate different properties for different molecular systems is still lacking.

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