Adsorption of Cu, Ag, and Au atoms on graphene including van der Waals interactions

Martin Amft\textsuperscript{1}, Sébastien Lebègue\textsuperscript{2}, Olle Eriksson\textsuperscript{1} and Natalia V Skorodumova\textsuperscript{1}

\textsuperscript{1} Department of Physics and Astronomy, Uppsala University, Box 516, S-751 20 Uppsala, Sweden
\textsuperscript{2} Laboratoire de Cristallographie, Résonance Magnétique et Modélisations (CRM2, UMR CNRS 7036) Institut Jean Barriol, Nancy Université BP 239, Boulevard des Aiguillettes 54506, Vandoeuvre-lès-Nancy, France

E-mail: martin.amft@physics.uu.se

Received 18 May 2011, in final form 8 July 2011
Published 2 September 2011
Online at stacks.iop.org/JPhysCM/23/395001

Abstract

We performed a systematic density functional (DF) study of the adsorption of copper, silver, and gold adatoms on pristine graphene, especially accounting for van der Waals (vdW) interactions by the vdW-DF and PBE+D2 methods. In particular, we analyze the preferred adsorption site (among top, bridge, and hollow positions) together with the corresponding distortion of the graphene sheet and identify diffusion paths. Both vdW schemes show that the coinage metal atoms do bind to the graphene sheet and that in some cases the buckling of the graphene layer can be significant. Only the results for silver are qualitatively at variance with those obtained with the generalized gradient approximation, which gives no binding in this case. However in all three cases, we observe some quantitative differences between the vdW-DF and PBE+D2 methods. For instance the adsorption energies calculated with the PBE+D2 method are systematically higher than the ones obtained with vdW-DF. Moreover, the equilibrium distances computed with PBE+D2 are shorter than those calculated with the vdW-DF method.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

As of today, it is still a challenge for theory to correctly predict the binding of atoms and molecules on coinage metal surfaces [1]. Recently reported studies, employing a variety of methods, showed the importance of non-local correlations for the correct description of the physisorption of aromatic molecules on copper, silver, and gold surfaces [2–5]. Furthermore, the reverse setup of coinage metal atoms and clusters on carbon-based materials, such as graphite, is a long-standing and not yet completely resolved issue. Already Darby et al [6] have speculated that dispersion forces, i.e. van der Waals forces, significantly contribute to the adsorption energies of gold atoms on graphite.

In recent years graphene, the two-dimensional building block of graphite, has gained much attention in its own right [7–10]. The gapless ultrarelativistic energy spectrum of graphene [11] as well as effects such as Klein tunneling [12] are of fundamental interest from a theoretical point of view. Moreover, graphene shows the quantum Hall effect at room temperature [13], and its conductive properties correspond to ballistic transport. Also, graphene offers enormous possibilities for applications in electronics, sensors, biodevices, catalysis, energy storage, etc [11, 14] that often involve adsorbed coinage metal clusters. For the utilization of these systems a deeper understanding of their stability and electronic properties is needed. From experiments, it is known that adatoms and small clusters of coinage metals bind weakly to graphite and graphene and are highly mobile [15–21].

A wide range of theoretical studies have been performed for small coinage metal clusters on graphite and graphene [22–28]. We are not aware of any experimental study of the adsorption sites or energies of coinage metal adatoms on pristine graphene. However, there exists, to our knowledge,
just one theoretical study that attempted to evaluate the importance of non-local correlation effects on the binding of silver and gold nanoclusters on graphite [29]. The authors of [29] used a number of different semi-empirical methods, based on pair potentials, and concluded that the obtained results are in fact strongly dependent on the choice of method, calling for more studies on these systems.

To fill this gap, we undertook a systematic investigation of the adsorption of copper, silver, and gold adatoms on graphene, based on density functional theory (DFT) and accounting for van der Waals (vdW) interactions by the vdW-DF method [30–32] as well as by the PBE + D2 method [33]. In principle, more advanced schemes such as the random phase approximation [34–36] (RPA) or the quantum Monte Carlo (QMC) method [37, 38] could also be used to take the van der Waals interaction into account: recently, the vdW-DF and PBE + D2 methods have been compared to the RPA for the case of graphite [39, 40]. It was found that vdW-DF and PBE + D2 appeared to be quantitative methods to take dispersive interactions into account. Although these two methods do not reach the accuracy of advanced quantum chemistry methods, they are at the moment the only computational tools that allow us to treat the dispersive interaction in such a large system as a sheet of graphene with a metallic adatom, together with periodic boundary conditions.

2. Methods

We calculated the total energies of Cu, Ag, and Au on either of the top (t), bridge (b), or hollow (h) position on a 5 × 5 graphene sheet, i.e. 50 carbon atoms, using the calculated equilibrium C–C bond length of 1.42 Å.

These scalar-relativistic ab initio DFT calculations were performed using the projector augmented wave (PAW) [41, 42] method as implemented in VASP [43, 44]. The exchange–correlation interaction was treated in the generalized gradient approximation (GGA) in the parameterization of Perdew, Burke, and Ernzerhof (PBE) [45] and, for comparison, also in the local density approximation (LDA) in the parameterization of Perdew and Zunger [46]. A cut-off energy of 600 eV was used and a Gaussian smearing with a width of σ = 0.05 eV for the occupation of the electronic levels. Spin-polarization was taken into account for all the calculations. The repeated images of the graphene sheets were separated from each other by 20 Å of vacuum. A Monkhorst–Pack Γ-centered 5 × 5 × 1 k-point mesh (13k-points in the irreducible wedge of the Brillouin-zone) was used for the structural relaxations of the carbon atoms. We also tested a finer k-point mesh, i.e. a 16 × 16 × 1 k-point mesh (130 k-points), and found the changes in the geometry and the charge density distribution of the systems to be negligible.

We accounted for the non-local correlation energies by employing two different methods: the van der Waals density functional (vdW-DF) method [30–32] as implemented in the Jülich non-local (JuNoLo) code [47], and the density functional theory plus long-range dispersion correction (DFT+D2) method [33] in the implementation of [40]. From a practical computational point of view, these methods differ significantly. While vdW-DF is implemented as an ab initio post-processing method in the JuNoLo code, the PBE + D2 method allows the inclusion of the vdW interactions in the self-consistency cycle, i.e. during structural relaxations. In [48] it has been shown, for instance for a set of small molecular systems, that the total energies and binding distances obtained with the vdW-DF as a post-processing method and in a self-consistent implementation agree very well.

As an input to the vdW-DF calculations one uses the charge density of the relaxed structure obtained in DFT with PBE. In PBE + D2, as well as in PBE, we started from the same initial configuration, i.e. a flat graphene sheet with an adatom above one of the three studied adsorption sites. While the positions of the adatoms were fixed during all calculations, the carbon atoms in the graphene sheet, except those in the rim of the supercell, were free to relax. The relaxation procedure was stopped when the Hellmann–Feynman forces on the carbon atoms that were allowed to relax were smaller than 5 × 10⁻³ eV Å⁻¹. Note that in PBE + D2 the van der Waals forces were taken into account during the relaxation.

Within the vdW-DF method, the missing vdW interactions are accounted for by replacing the correlation energy from the GGA calculation by the sum of a strictly local (E_{c,\text{LDA}}) and a non-local (E_{c,\text{nl}}) correlation energy:

$$E_{0,\text{vdW-DF}}^\text{vdW-DF} = E_{0,\text{PBE}}^\text{PBE} - E_{0,\text{xc}}^\text{x} + E_{0,\text{xc}}^\text{PBE} + E_{0,\text{LDA}}^\text{xc} + E_{0,\text{nl}}^\text{xc},$$  \hspace{1cm} (1)

where $E_{0,\text{PBE}}^\text{PBE}$ and $E_{0,\text{xc}}^\text{x}$ are the total energy and the exchange–correlation energy, respectively, calculated with PBE. The non-local contribution to the correlation energy is calculated as

$$E_{c,\text{nl}} = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' n(\mathbf{r}) \phi(\mathbf{r}, \mathbf{r}') n(\mathbf{r}'),$$  \hspace{1cm} (2)

with $n(\mathbf{r})$ being the charge density. The kernel $\phi(\mathbf{r}, \mathbf{r}')$ depends on the distance $|\mathbf{r} - \mathbf{r}'|$ and the electron densities $n$ in the vicinities of $\mathbf{r}$ and $\mathbf{r}'$, cf equation (14) in [31] for the full functional form of the kernel.

In the PBE + D2 method, on the other hand, the vdW interactions are described by a pair-wise correction ($E_{\text{disp}}$), optimized for some popular DFT functionals, and added to the self-consistent Kohn–Sham energy ($E_{\text{KS–DFT}}$) such that

$$E_{\text{PBE+D2}} = E_{\text{KS–DFT}} + E_{\text{disp}},$$  \hspace{1cm} (3)

with

$$E_{\text{disp}} = -\frac{s_n}{2} \sum_{i=1}^{N_d} \sum_{j=1}^{N_d} \sum_{L} C_6^{ij} f(|\mathbf{r}_L - \mathbf{r}_i whose value is 0.75 for the PBE functional, which was used here. $C_6^{ij}$ is
In this section, we present our results concerning the adsorption energies, preferred binding sites, equilibrium distances, and preferred diffusion paths for Cu, Ag, and Au adatoms on graphene. In order to reach a qualitative conclusion, we used two different schemes to take the dispersive interaction into account. Namely, the vdW-DF and PBE + D2 methods were employed, see section 2 for details. For the sake of comparison, we also report our results obtained with a semi-local (GGA) and a local (LDA) approximation, although none of these methods are able to describe the non-local correlation effects needed to tackle the present problem correctly.

The total energy curves, where vdW interactions were taken into account, are shown in the upper panels of figures 1–6. In the appendix, we also show the PBE and LDA total energy curves, figures A.1–A.6, for completeness. In all of the figures 1–6 and A.1–A.6 the total energy $E_0$ is shown as a function of the initial vertical metal atom–graphene distance. The total energies were calculated for three adorption sites of the metal atom, i.e. the top (t), bridge (b), and hollow (h) position, respectively. The lower panels in figures 1–6 and A.1–A.6 show the maximal vertical distortion ($b_{\text{max}}$) of the carbon atoms closest to the Cu adsorption site.

The calculated adsorption energies $E_{\text{ads}}$ and their corresponding vertical equilibrium distances $h_{\text{eq}}$ are compiled in tables 2, 4, and 6. The equilibrium distances are the differences between the initial vertical metal atom–graphene distance $h_{\text{init}}$ and the vertical buckling: $h_{\text{eq}} = h_{\text{init}} - b_{\text{max}}$. Tables 3, 5, and 7 show the differences between the total energies of adsorption sites, e.g. $\Delta E^{t-b}_{0}$ between the top and

![Figure 1](image1.png)

**Figure 1.** Upper panel: total energy ($E_0$) as a function of the initial vertical Cu adatom–graphene sheet distance ($h$) for three binding sites, calculated in PBE + D2. Lower panel: vertical distortion ($b_{\text{max}}$) of the carbon atoms in the first coordination shell of the Cu adsorption site. Positive values of $b_{\text{max}}$ mean that the carbon atoms buckle toward the adsorbed adatom.

![Figure 2](image2.png)

**Figure 2.** Upper panel: total energy versus initial vertical Cu–graphene distance for three binding sites, calculated in vdW-DF. Lower panel: vertical distortion ($b_{\text{max}}$) of the carbon atoms closest to the Cu adsorption site.

3. Results
All three coinage metal adatoms have an unpaired $s$-electron in the gas phase, which, upon adsorption, gives rise to a total spin moment of between 0.82 and 1 $\mu_B$ of the system, depending of the charge transfer between the adatom and the graphene sheet. In table 1 the Bader charges of the adatoms ($Q[M]$) at their corresponding (method dependent) equilibrium distances to the graphene sheet, see following sections, are summarized. Clearly, the adsorbed Cu adatom becomes cationic, while the Ag adatom stays neutral, and the Au adatom becomes anionic, independently of the adsorption site. The different methods, i.e. PBE + D2, vdW-DF and PBE, predict somewhat different equilibrium distances, see tables 2, 4, and 6, which explains the variations in the charge transfers. Note that our PBE results for $M_s$ compare well with the recent calculations of [54].

### 3.1. Cu on graphene

We begin by presenting our results for copper on graphene. The total energy curves of the PBE + D2 and vdW-DF calculations for this system are shown in figures 1 and 2 (upper panels). For both methods, the top position is energetically most preferable. Especially in the PBE + D2 results, the top position competes within a small but noticeable energy difference with the bridge configuration, while the hollow position is definitively not favorable in either of the two methods. The PBE approximation (figure A.1 in...
corresponding vertical equilibrium distances position being the preferred one. Table 2 also summarizes the three sites are in a competitive energy range, with the bridge the aforementioned vdW and PBE results. In the LDA, the differences in the total energies with the LDA (figure A.2 in the appendix) are in contrast to in table 2. The ordering of the adsorption sites obtained shallow, as one can also see from the adsorption energies ground state, but all the obtained minima are comparatively small. The ordering of the adsorption sites obtained by four different approximations to the exchange–correlation functional, and vertical equilibrium Cu–graphene distances $h_{\text{eq}}$ (Å), at three binding sites, top (t), bridge (b), and hollow (h). Table 2. Adsorption energies of Cu on graphene (eV), calculated by four different approximations to the exchange–correlation functional, and vertical equilibrium Cu–graphene distances $h_{\text{eq}}$ (Å), at three binding sites, top (t), bridge (b), and hollow (h).

|        | Top | Bridge | Hollow |
|--------|-----|--------|--------|
| $E_{\text{ads}}^{t}$ | $h_{\text{eq}}^{t}$ | $E_{\text{ads}}^{b}$ | $h_{\text{eq}}^{b}$ | $E_{\text{ads}}^{h}$ | $h_{\text{eq}}^{h}$ |
| PBE + D2 | −0.909 | 2.11 | −0.901 | 2.13 | −0.706 | 2.00 |
| vdW-DF  | −0.684 | 2.28 | −0.592 | 2.36 | −0.176 | 2.57 |
| PBE     | −0.228 | 2.12 | −0.219 | 2.08 | −0.063 | 2.27 |
| LDA     | −0.842 | 1.96 | −0.874 | 1.93 | −0.802 | 1.76 |

Table 3. The differences in the total energies $\Delta E_{0}$ (meV) at the three adsorption sites (top, bridge, and hollow) allow one to infer the diffusion path of Cu on graphene.

|        | Top to bridge $\Delta E_{0}^{t-b}$ | Top to hollow $\Delta E_{0}^{t-h}$ | Bridge to hollow $\Delta E_{0}^{b-h}$ |
|--------|---------------------------------|---------------------------------|---------------------------------|
| PBE + D2 | 8 | 203 | 195 |
| vdW-DF  | 92 | 508 | 416 |
| PBE     | 9 | 164 | 156 |
| LDA     | 31 | 40 | 71 |

Table 4. Adsorption energies of Ag on graphene (eV), calculated by four different approximations to the exchange–correlation functional, and vertical equilibrium Cu–graphene distances $h_{\text{eq}}$ (Å), at three binding sites, top (t), bridge (b), and hollow (h).

|        | Top | Bridge | Hollow |
|--------|-----|--------|--------|
| $E_{\text{ads}}^{t}$ | $h_{\text{eq}}^{t}$ | $E_{\text{ads}}^{b}$ | $h_{\text{eq}}^{b}$ | $E_{\text{ads}}^{h}$ | $h_{\text{eq}}^{h}$ |
| PBE + D2 | −0.703 | 2.90 | −0.700 | 2.90 | −0.711 | 2.90 |
| vdW-DF  | −0.195 | 3.30 | −0.194 | 3.40 | −0.192 | 3.40 |
| PBE     | No binding | No binding | No binding |
| LDA     | −0.368 | 2.34 | −0.359 | 2.35 | −0.296 | 2.59 |

Table 5. Ag is purely physisorbed on graphene, therefore the differences between the total energies $\Delta E_{0}$ (meV) at the three adsorption sites are less significant.

|        | Top to bridge $\Delta E_{0}^{t-b}$ | Top to hollow $\Delta E_{0}^{t-h}$ | Bridge to hollow $\Delta E_{0}^{b-h}$ |
|--------|---------------------------------|---------------------------------|---------------------------------|
| PBE + D2 | 2 | 8 | 11 |
| vdW-DF  | 1 | 3 | 2 |
| PBE     | | | |
| LDA     | 9 | 72 | 62 |

Table 6. Adsorption energies of Au on graphene (eV), calculated by four different approximations to the exchange–correlation functional, and vertical equilibrium Cu–graphene distances $h_{\text{eq}}$ (Å), at three binding sites, top (t), bridge (b), and hollow (h).

|        | Top | Bridge | Hollow |
|--------|-----|--------|--------|
| $E_{\text{ads}}^{t}$ | $h_{\text{eq}}^{t}$ | $E_{\text{ads}}^{b}$ | $h_{\text{eq}}^{b}$ | $E_{\text{ads}}^{h}$ | $h_{\text{eq}}^{h}$ |
| PBE + D2 | −0.886 | 2.53 | −0.881 | 2.79 | −0.870 | 3.10 |
| vdW-DF  | −0.385 | 2.65 | −0.314 | 2.72 | −0.322 | 3.40 |
| PBE     | −0.099 | 2.54 | −0.081 | 2.72 | No binding |
| LDA     | −0.732 | 2.22 | −0.698 | 2.26 | −0.451 | 2.40 |

Table 7. The differences in the total energies $\Delta E_{0}$ (meV) at the three adsorption sites (top, bridge, and hollow) allow one to infer the diffusion path of Au on graphene.

|        | Top to bridge $\Delta E_{0}^{t-b}$ | Top to hollow $\Delta E_{0}^{t-h}$ | Bridge to hollow $\Delta E_{0}^{b-h}$ |
|--------|---------------------------------|---------------------------------|---------------------------------|
| PBE + D2 | 5 | 16 | 11 |
| vdW-DF  | 71 | 63 | 8 |
| PBE     | 18 | | |
| LDA     | 34 | 281 | 247 |

The differences in the total energies $\Delta E_{0}$ (meV) at the three adsorption sites (top, bridge, and hollow) allow one to infer the diffusion path of Au on graphene.

Figure 6. Upper panel: total energy versus initial vertical Au–graphene distance for three binding sites, calculated in vdW-DF. Lower panel: vertical distortion ($h_{\text{max}}$) of the carbon atoms closest to the Au adsorption site.

Table 4. Adsorption energies of Ag on graphene (eV), calculated by four different approximations to the exchange–correlation functional, and vertical equilibrium Cu–graphene distances $h_{\text{eq}}$ (Å), at three binding sites, top (t), bridge (b), and hollow (h).

Table 5. Ag is purely physisorbed on graphene, therefore the differences between the total energies $\Delta E_{0}$ (meV) at the three adsorption sites are less significant.

Table 6. Adsorption energies of Au on graphene (eV), calculated by four different approximations to the exchange–correlation functional, and vertical equilibrium Cu–graphene distances $h_{\text{eq}}$ (Å), at three binding sites, top (t), bridge (b), and hollow (h).

Table 7. The differences in the total energies $\Delta E_{0}$ (meV) at the three adsorption sites (top, bridge, and hollow) allow one to infer the diffusion path of Au on graphene.
In the cases of PBE + D2 and vdW-DF, i.e. the relaxed PBE structure, the deformation of the graphene sheet is always positive around the equilibrium distance, i.e. the carbon atoms and the copper atom attract each other, see the lower panels in figures 1 and 2. For smaller distances, the buckling becomes negative, which is obviously a steric effect. Also, the buckling is always larger for the top configuration, which is another indicator of the increased stabilization of this site with respect to the hollow and bridge ones. The vertical distortions of the graphene sheet obtained from the PBE and PBE + D2 structural relaxations differ by less than 10% only.

As mentioned above, the binding order from the LDA calculations is different, see figure A.2. The maximum buckling is obtained for a top configuration, although the bridge position is the actual ground state in the LDA. Hence, the energy minimum and buckling do not seem to be correlated in this approximation.

From the differences of the total energies at the different adsorption sites, $\Delta E_0$ in table 3, one can obtain some insight into the diffusion paths of the coinage metal adatoms on graphene, since it has been shown that $\Delta E_0 [\text{top}−\text{bridge}]$ is the height of the diffusion barrier along the carbon–carbon bonds [28]. Although the energy differences vary significantly for $\Delta E^{\text{D2}}_{0}$ in the case of copper, the overall trends are identical in PBE + D2 and vdW-DF: diffusion will take place along the carbon–carbon bonds, since a path over the hollow site is energetically too expensive.

3.2. Ag on graphene

The silver adatom on graphene presents quite a different picture from copper and gold. While PBE + D2 (figure 3) and vdW-DF (figure 4) clearly show binding, $E_{\text{ads}} \approx −0.7$ and $−0.19$ eV, respectively, at large equilibrium distances, i.e. 2.9 Å and 3.3 Å respectively, pure GGA fails completely to predict any binding, see figure A.3. Note that we repeated the PBE calculations with other GGA functionals, i.e. PW91 [51] and RPBE [52], and both failed to predict a minimum as well. As for the other two atomic species, the LDA gives binding for Ag on graphene, with the ordering top–bridge–hollow, see figure A.4, and shorter equilibrium distances than PBE + D2 and vdW-DF.

In contrast to Cu and Au on graphene, where one finds a small hybridization in the density of states, i.e. a chemical contribution to the binding, the PBE + D2 and vdW-DF calculations give a pure physisorption of Ag on graphene [28]. However, the energies of the preferred binding sites are ordered differently in the two methods. The minima in the total energy in PBE + D2 are ordered as hollow–top–bridge, while vdW-DF gives top–bridge–hollow.

The differences in the total energies, listed in table 5, of the three binding sites are smaller than 11 meV in both vdW methods. In combination with the large binding distances, see table 4, we conclude that both methods predict pure physisorption. Also from table 5 one can conclude that Ag is the most mobile of the three coinage metals on graphene and does not have preferred diffusion paths like the other two.

The distortion of the graphene sheet by Ag is negligible for equilibrium distances, see the lower panels in figures 3 and 4, supporting the interpretation that there is pure physisorption in this system. The buckling away from the adatom at smaller distances is again a steric effect, as in the other two cases.

Our PBE + D2 results for Ag on graphene can be compared to the results in [29], where van der Waals interactions also have been included according to the Grimme scheme [33]. In contrast to our PBE + D2 results in table 4, [29] found smaller adsorption energies, i.e. $−0.42$ to $−0.56$ eV, and a different binding order. These calculations predicted that the top site was more favorable than the bridge and hollow sites, in accordance with our vdW-DF results. Two methodological differences which might explain the contradicting results between our PBE + D2 results and those of [29] need to be pointed out. First, the value of the $s_8$ coefficient, cf equation (4), is not clear from [29]. Second, the Grimme method [33] is parameterized for PBE and not for PW91, which has been used in [29] for the initial relaxation.

3.3. Au on graphene

In the last studied case of a gold adatom on graphene all four studied approximations to the exchange–correlation energy predict the top adsorption site to be most favorable, see the upper panels in figures 5 and 6, as well as in figures A.5 and A.6 for comparison. Note that for the bridge site vdW-DF predicts a local minimum and PBE an inflection point at 2.8 Å only. For the hollow site vdW-DF gives a shallow minimum at 3.4 Å which is in fact lower in energy than the local minimum at the bridge site, while PBE fails to predict binding at this site. Although the total energy curve of the PBE + D2 method has a minimum at the hollow site as well, the equilibrium distance is 3.1 Å i.e. even larger than in the case of Ag on silver, which indicates physisorption at this site too. Comparing the binding energies of PBE and PBE + D2, the latter essentially adds $−0.8$ eV to $E_{\text{ads}}$ of the former. This indicates the importance of the vdW interaction to the binding, which is even more pronounced in this system than for Cu on graphene.

For the calculated adsorption energies, table 6, we obtained trends that are similar to those of Cu on graphene, cf table 2. The PBE + D2 method predicts $E_{\text{ads}}$ ranging from $−0.870$ to $−0.886$ eV, which exceeds the LDA results for this system. PBE, on the other hand, predicts significantly lower $E_{\text{ads}}$ of less than $−0.099$ eV only, while vdW-DF gives adsorption energies that lie in between those of PBE and PBE + D2, ranging from $−0.310$ to $−0.385$ eV.

The equilibrium distances $h_{\text{eq}}$ shown in table 6 agree rather well for PBE + D2 and vdW-DF, i.e. with deviations of less than 9%. Note that the buckling of the graphene sheet is 50% smaller in PBE + D2 than in vdW-DF, i.e. in the relaxed PBE structure. Even PBE gives comparable $h_{\text{eq}}$ for the top and bridge sites, while the LDA overbinds and predicts $h_{\text{eq}}$ that are up to 23% shorter than those obtained in PBE + D2.

As in the case of copper, the differences of the total energies between the top and bridge sites vary greatly among the employed vdW approximations. Still, one can conclude that the gold adatom is likely to diffuse along the carbon–carbon bonds. Therefore, the use of PBE is justified.
for studies of, for instance, the mobility and clustering of gold on graphene as in [28].

4. Summary and conclusions

We performed a systematic DFT investigation of the adsorption of copper, silver, and gold adatoms on graphene, especially taking van der Waals interactions by the vdW-DF and the DFT+D2 methods into account. For copper and gold we found that the PBE parameterization to the exchange–correlation energy predicts the same ordering of the adsorption sites as vdW-DF and PBE + D2, i.e. it also favors the top over the bridge and hollow positions. We also found that the non-local interactions increased the calculated adsorption energies of Cu and Au on graphene by up to 0.8 eV (PBE + D2) and 0.45 eV (vdW-DF), respectively. The predicted vertical equilibrium distance calculated with PBE, for Cu and Au adsorption, agrees to better than 13% with the more advanced non-local methods. A Bader analysis shows that the Cu adatom donates approximately 0.15 e\textsuperscript{−} to the graphene sheet, and hence becomes cationic, while the Au adatom receives approximately 0.1 e\textsuperscript{−} from the sheet and becomes anionic. For the adsorption of silver on graphene our calculations predict that it is purely of van der Waals type. Different generalized gradient approximations to the exchange–correlation functional fail to give any binding at all, while the PBE + D2 and vdW-DF predict physisorption at large equilibrium distances of 2.9 and 3.3 Å respectively. Due to these large binding distances the Ag adatom stays essentially neutral. From the differences in the total energies we conclude that diffusion of Cu and Au takes place along the carbon–carbon bonds, while the Ag adatoms can diffuse almost unrestrictedly on the graphene sheet.

Taking vdW interactions into account during the structural relaxations in the PBE + D2 method did not significantly change the buckling of the graphene sheet in the case of Cu compared to PBE calculations. The calculated distortion of the graphene sheet upon adsorption of a silver atom was found to be negligible. Compared to the PBE calculation, we found a 50% smaller buckling of the graphene sheet in the case of gold with the PBE+D2 method that might be related to its parameterization. Ripples in the graphene structure give rise to both effective scalar and vector potentials in the electronic structure of graphene, see e.g. [53]. The adsorption of Cu or Au adatoms may be an important tool to enhance this rippling and hence the strength of these scalar and vector potentials.

Acknowledgments

This research was supported by the Swedish Energy Agency (Energimyndigheten), the Swedish Research Council (Vetenskapsrådet), and Research and Innovation for Sustainable Growth (VINNOVA). OE is grateful to the European Research Council (ERC) for support. SL acknowledges financial support from ANR Grant ANR-07-BLAN-0272 and ANR Grant ANR-06-NANO-053-02. Supercomputer time was granted by the Swedish National Infrastructure for Computing (SNIC) and GENCI (project x2010085106).

Appendix

In the appendix we present calculated total energy curves and vertical distortions of the carbon atoms closest to the adsorption sites for the PBE and LDA functionals. The Cu results are found in section A.1, the Ag results in section A.2 and the Au results in section A.3.

A.1. Cu/graphene (PBE and LDA)

Figure A.1. Upper panel: total energy versus initial vertical Cu–graphene distance for three binding sites, calculated in PBE. Lower panel: vertical distortion of the carbon atoms closest to the Cu adsorption site.

Figure A.2. Upper panel: total energy versus initial vertical Cu–graphene distance for three binding sites, calculated in the LDA. Lower panel: vertical distortion of the carbon atoms closest to the Cu adsorption site.
A.2. Ag/graphene (PBE and LDA)

Figure A.3. Upper panel: total energy versus initial vertical Ag–graphene distance for three binding sites, calculated in PBE. Lower panel: vertical distortion of the carbon atoms closest to the Ag adsorption site.

Figure A.4. Upper panel: total energy versus initial vertical Ag–graphene distance for three binding sites, calculated in the LDA. Lower panel: vertical distortion of the carbon atoms closest to the Ag adsorption site.

A.3. Au/graphene (PBE and LDA)

Figure A.5. Upper panel: total energy versus initial vertical Au–graphene distance for three binding sites, calculated in PBE. Lower panel: vertical distortion of the carbon atoms closest to the Au adsorption site.

Figure A.6. Upper panel: total energy versus initial vertical Au–graphene distance for three binding sites, calculated in the LDA. Lower panel: vertical distortion of the carbon atoms closest to the Au adsorption site.

References

[1] Brivio G P and Triomi M I 1999 The adiabatic molecule-metal surface interaction: theoretical approaches Rev. Mod. Phys. 71 231
[2] Rohlfing M and Bredow T 2008 Binding energy of adsorbates on a noble-metal surface: exchange and correlation effects Phys. Rev. Lett. 101 266106
[3] Romaner L, Nabok D, Puschig P, Zojer E and Ambrosch-Draxl C 2009 Theoretical study of ptcda adsorbed on the coinage metal surfaces, Ag(111), Au(111) and Cu(111) New J. Phys. 11 053010
[4] Mercurio G, McNellis E R, Martin I, Hagen S, Leyssner F, Soubatch S, Meyer J, Wolf M, Tegeder P, Tautz F S and Reuter K 2010 Structure and energetics of azobenzene on Ag(111): benchmarking semiempirical dispersion correction approaches Phys. Rev. Lett. 104 036102
[5] Rauls E, Blankenburg S and Schmidt W 2010 Chemical reactivity on surfaces: modeling the imide synthesis from DATP and PTCDA on Au(111) Phys. Rev. B 81 125401
[6] Darby T P and Wayman C M 1975 Growth of gold thin film dendrites on graphite substrates J. Cryst. Growth 29 98

[7] Novoselov K S, Geim A K, Morozov S V, Jiang D, Katsnelson M I, Grigorieva I V, Dubonos S V and Firsov A A 2005 Two-dimensional gas of massless Dirac fermions in graphene Nature 438 197–200

[8] Novoselov K S, Jiang D, Schedin F, Booth T J, Khotkevich V V, Morozov S V and Geim A K 2006 Two-dimensional atomic crystals Proc. Natl Acad. Sci. USA 102 10451

[9] Geim A K and Novoselov K S 2007 The rise of graphene Nature Mater. 6 183–91

[10] Katsnelson M I 2007 Graphene: carbon in two dimensions Mater. Today 10 20–7

[11] Castro-Neto A H, Peres N M R, Novoselov K S and Geim A K 2009 The electronic properties of graphene Rev. Mod. Phys. 81 109

[12] Katsnelson M I, Novoselov K S and Geim A K 2006 Nature Phys. 2 620

[13] Novoselov K S, Jiang Z, Zhang Y, Morozov S V, Stormer H L, Zeitler U, Maan J C, Boebinger G S, Kim P and Geim A K 2007 Room-temperature quantum Hall effect in graphene Science 315 1379

[14] Geim A K 2009 Graphene: status and prospects Mod. Phys. Lett. B 23 102505

[15] Amft M, Sanyal B, Eriksson O and Skorodumova N V 2011 Small gold clusters on graphene, their mobility and clustering: a DFT study J. Phys.: Condens. Matter 23 205301

[16] Jalkanen J P, Halonen M, Fernandez-Torre D, Laasonen K and Halonen L 2007 A computational study of the adsorption of small Ag and Au nanoclusters on graphite J. Phys. Chem. A 111 12317–26

[17] Rydberg H, Dion M, Jacobson N, Schröder E, Hylgaard P, Simak S, Langreth D and Lundqvist B 2003 Van der Waals density functional for layered structures Phys. Rev. Lett. 91 126402

[18] Dion M, Rydberg H, Schröder E, Langreth D and Lundqvist B 2004 Van der Waals density functional for general geometries Phys. Rev. Lett. 92 246401

[19] Jiang D, Schedin F, Booth T J, Khotkevich V V, Morozov S V, Novoselov K S, Geim A K and Firsov A A 2006 Two-dimensional gas of massless Dirac fermions in graphene Nature Mater. 5 438

[20] Simak S, Langreth D and Lundqvist B 2005 Erratum: Van der Waals density functional for layered structures Phys. Rev. Lett. 95 109902

[21] Grimme S 2006 Semiempirical GGA-type density functional constructed with a long-range dispersion correction J. Comput. Chem. 27 1797

[22] Gunnarsson O and Lundqvist B 1976 Exchange and correlation in atoms, molecules, and solids by the spin-density-functional formalism Phys. Rev. B 13 4274

[23] Langreth D C and Perdew J P 1975 The exchange–correlation energy of a metallic surface Solid State Commun. 17 1425

[24] Langreth D C and Perdew J P 1977 Exchange–correlation energy of a metallic surface: wave-vector analysis Phys. Rev. B 15 2884

[25] Foulkes W M C, Mitas L, Needs R J and Rajagopal G 2001 Quantum Monte Carlo simulations of solids Rev. Mod. Phys. 73 33

[26] Spanu L, Sorella S and Galli G 2009 Nature and strength of interlayer binding in graphite Phys. Rev. Lett. 103 196401

[27] Lebègue S, Harl J, Gould T, Angyán J G, Kresse G and Dobson J F 2010 Cohesive properties and asymptotics of the dispersion interaction in graphite by the random phase approximation Phys. Rev. Lett. 105 196401

[28] Bucko T, Hafner J, Lebègue S and Angyan J G 2010 Improved description of the structure of molecular and layered crystals: ab initio DFT calculations with van der Waals corrections J. Phys. Chem. A 114 11814

[29] Blöchl P E 1994 Projector augmented-wave method Phys. Rev. B 50 17953–79

[30] Kresse G and Joubert D 1999 From ultrasoft pseudopotentials to the projector augmented-wave method Phys. Rev. B 59 1758–75

[31] Kresse G and Furthmüller J 1996 Efficiency of ab initio total energy calculations for metals and semiconductors using a plane-wave basis set Comput. Mater. Sci. 6 15–50

[32] Kresse G and Furthmüller J 1996 Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set Phys. Rev. B 54 11169

[33] Perdew J P, Burke K and Ernzerhof M 1996 Generalized gradient approximation made simple Phys. Rev. Lett. 77 3865–8

[34] Perdew J P and Zunger A 1981 Self-interaction correction to density-functional approximations for many-electron systems Phys. Rev. B 23 5048

[35] Lazic P, Atodiresei N, Alaei M, Caciuc V and Blügel S 2010 Junolo–Jülich nonlocal code for parallel post-processing evaluation of vdW-DF correlation energy Comput. Phys. Commun. 181 371–9
[48] Thonhauser T, Cooper V R, Li S, Puzder A, Hyldgaard P and Langreth D C 2007 Van der Waals density functional: self-consistent potential and the nature of the van der Waals bond Phys. Rev. B 76 125112

[49] Grimme S 2010 private communication

[50] Tang W, Sanville E and Henkelman G 2009 A grid-based Bader analysis algorithm without lattice bias J. Phys.: Condens. Matter 21 084204

[51] Perdew J P and Wang Y 1992 Accurate and simple analytic representation of the electron-gas correlation energy Phys. Rev. B 45 13244

[52] Hammer B, Hansen L B and Nørskov J K 1999 Improved adsorption energetics within density-functional theory using revised Perdew–Burke–Ernzerhof functionals Phys. Rev. B 59 7413

[53] Gibertini M, Tomadin A, Polini M, Fasolino A and Katsnelson M I 2010 Electron density distribution and screening in rippled graphene sheets Phys. Rev. B 81 125437

[54] Yazyev O V and Pasquarello A 2010 Metal adatoms on graphene and hexagonal boron nitride: Towards rational design of self-assembly templates Phys. Rev. B 82 045407