Stability of gold atoms and dimers adsorbed on graphene

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Abstract
We report density functional theory (DFT) calculations for gold atoms and dimers on the
surface of graphene. The calculations were performed using the plane wave pseudopotential
method. Calculations were performed for a variety of geometries, and both the graphene surface
and gold atoms were allowed to fully relax. In agreement with experiment, our results show that
the gold–gold interaction is considerably stronger than the gold–graphene interaction, implying
that uniform coverage could not be attained. The minimum energy configuration for a single
gold atom is found to be directly above a carbon atom, while for the dimer it is perpendicular to
the surface and directly above a carbon–carbon bond. Our results are consistent with previous
similar calculations.

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

1. Introduction

Stable and reproducible structures with sizes of the order
of nanometres are hugely important for the development of
nanoelectronics and other nanodevice applications. From the
fundamental science point of view, monoatomic chains [1, 2]
and small clusters of atoms can be used to test simple
physical models of transport at the quantum level and to
understand exotic electronic structures. Recently it has
been shown that nanowires can be synthesized reliably by
deposition on single-walled carbon nanotubes (SWNT) [3, 4].
It is therefore essential to have a good understanding of
the metal–SWNT interaction and the type of coverage to be
expected. SWNT's can be regarded as *rolled up* sheets of
graphene. Therefore a good place to start understanding the
properties of nanowires is to look at the properties of metal
atoms adsorbed on graphene sheets. Gold is a particularly
interesting material in nanoclusters. As a metal it is well
known for its resistance to corrosion and chemical reaction [5].
However, gold nanoparticles have recently been found to be
reactive, and a great deal of interest has arisen in making
gold nanostructures such as clusters [6–8], wires [9, 10] and
shells [11]. Because of their unique properties, such structures
are likely to find application in microelectronics, catalysis,
sensors, gene mapping and many other spheres.

Some of the first experimental work involving gold on
carbon surfaces began in 1973 with Arthur and Cho [12]. They
used mass spectrometry techniques to observe the adsorption

and desorption of gold and copper on the surface of graphite.
From their results they proposed a model to explain the unusual
kinetics of gold on graphite. Their model suggested that the
adsorption of metal atoms occurs through the formation and
growth of two-dimensional clusters from a mobile surface
atom population, which is held weakly by the substrate. The
binding energy for gold was found to be 0.65 eV. The authors
suggest that the binding energy is consistent with a van der
Waals interaction. Gold clusters were found to coalesce into
caps or spheres upon heating. Arthur's data suggested that
the gold was deposited on to the surface of graphite as a
film, but upon heating it formed discrete droplets. This
suggests that gold coatings are discontinuous, with a very low
nucleation density due to a weak gold–graphite interaction. A
low gold–graphite binding energy suggests that there is a low
activation barrier for diffusion. Using transmission electron
microscopy, Heyraud and Metois [13, 14] were able to observe
a superstructure in gold on graphite surfaces. The evolution
of the morphology of gold clusters grown in nanometre-sized
pits on graphite at $T = 623$ K was investigated using scanning
tunneling microscopy (STM) by Irawan *et al* [15] for a broad
range of cluster sizes. They observed a transition from three-
dimensional growth for small cluster sizes (<103 atoms) to a
mainly lateral growth after the formation of hexagonal (111)
facets on top of larger clusters (>104 atoms). Zhang *et al*
[16] have imaged films forming in to gold islands on single-
walled carbon nanotubes. Scanning tunnelling microscopy
data [17] suggests that the diffusion properties of adatoms were

similar to that of clusters. However, adatoms remain at the surface of the substrate for several seconds before migrating to a larger cluster or island [18, 19]. The favoured site of adsorption on graphite is the bridging site. This is contrary to models of physisorption of noble gas atoms which are located above the hole sites. Until now we have only commented on experimental data of gold adsorbed on graphite and carbon nanotubes.

Wang *et al* [20, 21] have investigated the binding orientation, energy landscape and mobility of silver and gold atoms on relaxed graphitic surfaces. Their computational study was based on related systems of Duffy and Blackman [22], who investigated the structure of silver adatoms and dimers on fixed layers of graphite. It is key to mention that in the work of Duffy and Blackman [22] the relaxation of the graphite layers affected the binding site of the adsorbate. Wang *et al* [20] implemented the density functional theory approach through the program PLATO [23]. Their unit cell consisted of a $3 \times 3 \times 2$ primitive unit cell including four atomic layers with vacuum gaps above and below. Their work confirmed the experimental results for the energetic order of binding for a gold adatom on graphite; the bridge site, atop site, a bridging site then the hollow site. As the charge of the gold adsorbate decreases, so does the binding energy. Their results showed that gold atoms are negatively charged when bound at any site and that large surface deformation occurs in regions surrounding the metal adatom. This showed that the greater the charge on the adsorbed species, the greater the polarization of the surface, which resulted in a stronger interaction between the gold atom and the substrate. Da Silva *et al* [24] have performed a series of calculations for gold atoms on carbon nanotubes and also provided a good point of reference for our calculations. Further relevant results have been reported by Yagi *et al* [25], who looked at 3d elements adsorbed on carbon nanotubes, while Moullet [26] reported first-principles calculations for aluminium clusters on a single graphite surface. Pyykko has produced an extraordinarily inclusive database of gold atoms and clusters on a variety of surfaces [27], while the morphology of gold clusters has been discussed in detail by Bravo-Perez *et al* [30]. Jensen *et al* [28] have performed a comprehensive study of gold atoms adsorbed on graphite using different geometries and approximations. They found that gold adatoms easily diffuse over this surface, with a diffusion barrier of 0.05 eV. The adsorption energy was found to be more difficult to quantify within density functional theory. Finally, in a very recent study, Jalkanen *et al* [29] have looked at the adsorption of small gold and silver nanoclusters on the (0001) graphite (actually graphene) surface, including both single atoms and dimers, and we compare our results with them where appropriate.

In this paper we report a systematic study of the properties of small numbers of gold atoms adsorbed on graphene based on density functional theory.

2. Theory

Standard first-principles calculations of the geometry, total energy and electronic structure of gold atoms and dimers
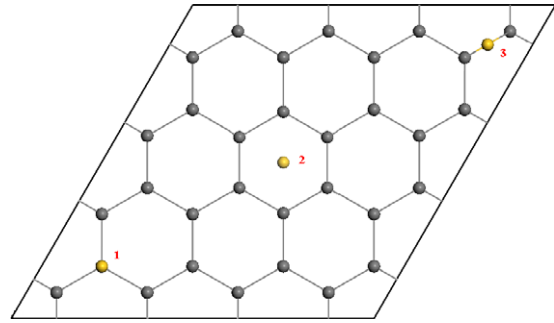

Figure 1. The initial positions of gold atoms on graphene: (1) atop, directly above a carbon atom; (2) hollow, directly above the centre of a hexagon of carbon atoms; (3) bridge, directly above a carbon–carbon bond.

on graphene have been performed using the CASTEP code [31–33]. These were carried out using the plane wave pseudopotential method with the local density approximation (LDA) for the exchange and correlation. A supercell containing 32 atoms in a graphene sheet was employed throughout. The size of the supercell yielded a separation of graphene from its periodic image in the surface normal direction of 15 Å. We used Vanderbilt ultrasoft pseudopotentials to represent the carbon and gold atoms. Plane waves up to an energy cutoff of 350 eV were used, based on validation tests for graphene and for gold atoms and dimers. The Brillouin zone integrations were performed using maximum k-point separations of 0.04 Å^{-1}. The smearing parameter was 0.1 eV when in the ground state. All atomic positions within the graphene and of the gold were fully relaxed, meaning that in the final geometry no forces exceeded 0.03 eV (Å)$^{-1}$. The binding energy was calculated as

$$E_{\mathrm{B}} = -\left(E(\text{system}) - E(\text{graphene}) - nE(\text{Au})\right)$$

where n is the number of gold atoms. This is clearly the difference between the total energy of graphene with a gold atom absorbed and the separate graphene sheet and gold atom(s). A closely related quantity is the adsorption energy, which treats the dimer as a single entity. This is just the binding energy for a dimer rather than for the individual two separate atoms:

$$E_{\mathrm{A}} = -\left(E(\text{system}) - E(\text{graphene}) - E(\text{Dimer})\right).$$

An important reference point for this calculation is the electronic structure of pure graphene, which has been reported many times previously [34, 35]. Of course, in our calculations all arbitrary quantities such as cutoff energy, lattice size etc were thoroughly tested for numerical convergence, and all results in this paper are converged to the accuracy indicated. The calculations were all performed using the LDA, as these were found in testing to be marginally superior to various generalized gradient approximations (GGAs) in reproducing known experimental results for Au and graphene.
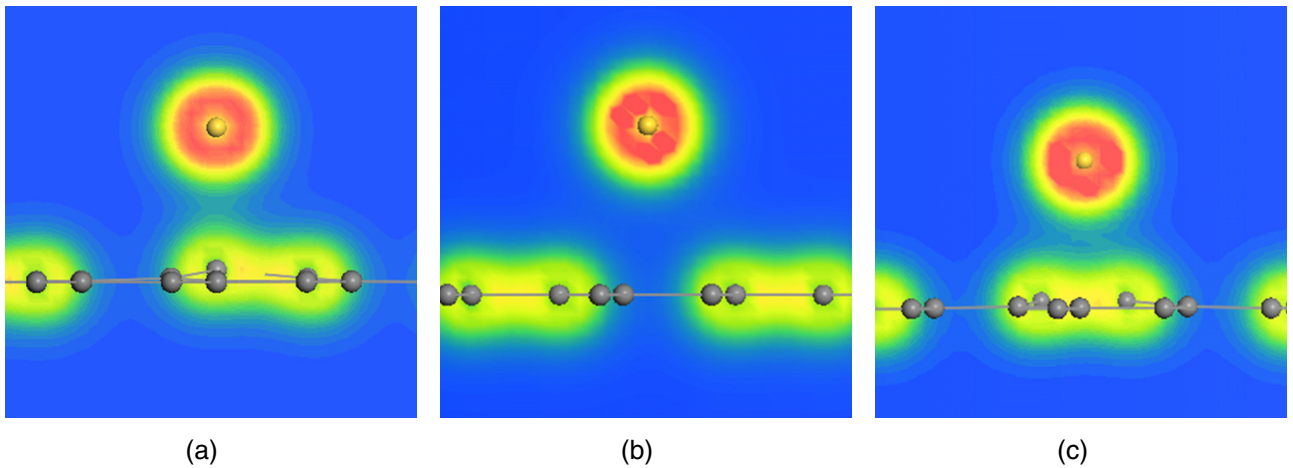
Figure 2. An electron density slice through the gold atom and the graphene sheet for the atom in (a) the atop position, (b) the hollow position, (c) the bridge position.

3. Results

3.1. Gold atoms

Gold atoms were placed 0.2887 nm above the graphene surface at atop, hollow and bridge positions as shown in figure 1. The lattice parameters were fixed and the whole system was allowed to relax during the self-consistency process. A Mulliken population analysis was performed on all relaxed configurations and the energetics and charge transfers were studied. To our knowledge there are no directly analogous calculations with which to compare our results. However, we can discuss our results in comparison with those of Wang *et al* [20, 21], where the substrate was layered graphite rather than a single graphene layer, and those of da Silva *et al* [24], where the substrate was a single-walled carbon nanotube (SWCT) which, for some purposes, may be regarded as 'rolled up' graphene.

The principal results of our calculations are shown in table 1 and figure 2. The atop configuration is marginally favoured over the bridge configuration, and both of those arrangements are significantly more favourable than sitting over a hollow site. This is in agreement with STM results for gold on graphite [17], which showed gold atoms sitting at atop sites on graphite, but not at hollow sites. With the gold sitting at the atop site, 0.15 electrons have transferred from the gold, principally to the carbon directly beneath (0.10 electrons) but also to its nearest neighbours (approximately 0.02 electrons each). There is considerable distortion of the graphene plane with the carbon atom nearest to the gold, rising 0.018 nm above the surface average. When the gold atom sits above the hollow site, approximately 0.11 electrons transfer from the gold and are shared equally between the six carbon atoms on the edge of the hollow. With a gold atom at the bridge site, approximately 0.17 electrons transfer from the gold. Each of the bridging atoms has gained 0.07 electrons and their nearest neighbours have gained approximately 0.01 electrons each. The bridging atoms have a magnetic moment of $0.01\mu_B$. The charge transfer has caused the bridging atoms and their neighbours to move slightly above the plane of the graphene

Table 1. Interaction between a gold adatom and a graphene surface. E_B is the binding energy. h is the height of the gold atom above the nearest carbon atom.

Site	$-E_B$ (eV)	h (nm)	Au charge (e)	Au moment (μ_B)
Atop	0.79	0.244	+0.15	−0.15
Bridge	0.74	0.227	+0.17	−0.17
Hollow	0.52	0.226	+0.11	−0.11

sheet. Comparison of the figures in table 1 with those of Duffy and Blackman [22] and Wang *et al* [20], who performed similar calculations for Ag, show that the trends are similar, but our energies are systematically higher and the charge transfers are lower. Our results are very comparable with those of Wang *et al* [21] (whose calculations were for gold on a graphite (not graphene) substrate). Our trends are the same, although the absolute values of the binding energy are a little greater in our calculation. Da Silva *et al* [24] report results in good agreement with Wang *et al* for the atop site energetics, but there is a 10% difference in the height of the atom between the calculations. Our calculations yield a slightly higher binding energy and agreement with Wang *et al* for the position of the atom. In the hollow site our energies are very similar to those of Wang, and our calculation of the height is also in closer agreement with this calculation than those of da Silva *et al*. Interestingly, all these calculations find the same atop site as the most stable, however Yagi *et al* [25] find that for 3d metals the reverse is true. There, it is the hollow site that is most stable and the atop site is least stable.

3.2. Gold dimers

Calculations were performed for a variety of initial conditions for gold dimers above graphene. All calculational details were the same as in the case of the single atom. For a dimer the calculation contains more degrees of freedom and the initial configuration is not necessarily equal to the configuration after the system has relaxed. The initial and final configurations for gold dimers adsorbed on graphene are as follows and are shown in figures 3(a) and (b):
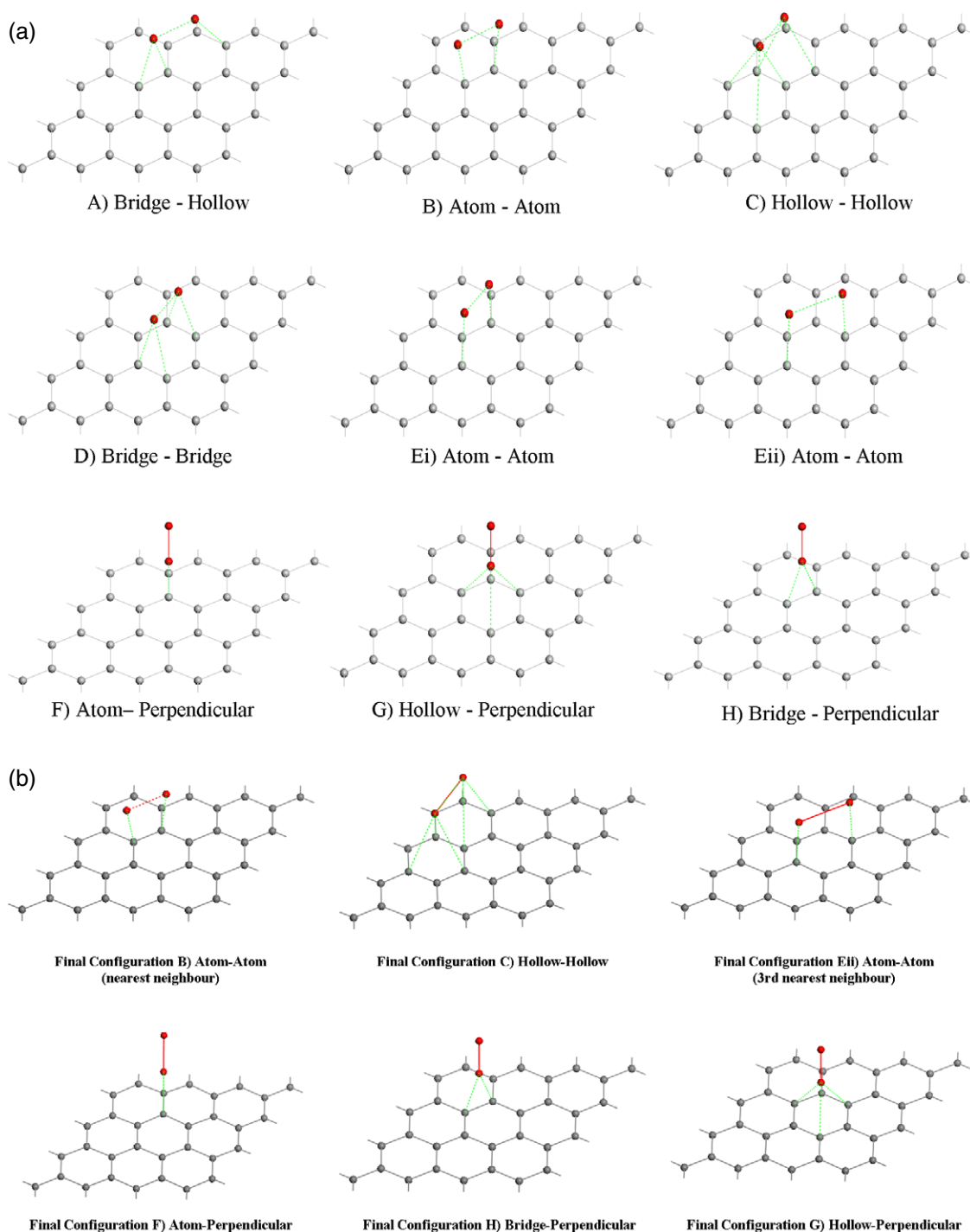
Figure 3. The positions of gold dimers on graphene: (a) prior to relaxation; (b) the relaxed configurations.

A: Bridge–hollow; one end of the gold dimer is adsorbed over a bridge site, with the bond bridging a carbon atom and the other end of the gold dimer is placed over the hollow.

B: Atom–atom nn; each end of the dimer is placed above a carbon atom and the carbon atom's nearest neighbour.

C: Hollow–hollow; each end of the dimer is placed over a hollow.

D: Bridge–bridge; each end of the dimer is adsorbed over a bridging carbon site, and the bridging carbon atoms are separated by one carbon atom.

Ei: Atom–atom 2nn; each end of the dimer is placed over a carbon atom, and the carbon atoms are separated by a single carbon neighbour.

Eii: Atom–atom 3nn; each end of the dimer is adsorbed over a carbon atom, and the carbon atoms are separated by two carbon atoms.

F: Atop; in an atop site perpendicular to the lattice.

G: Hollow; over a hollow site perpendicular to the lattice.

H: Bridge; over a bridging site perpendicular to the lattice.

Table 2. Initial and final configurations of a gold dimer on a graphene surface.

Reference	Initial configuration	Final configuration
A	Bridge–hollow	Bridge-perpendicular
B	Atom–atom nn	Atom–atom nn
C	Hollow–hollow	Hollow–hollow
D	Bridge–bridge	Bridge-perpendicular
Ei	Atom–atom 2nn	Bridge-perpendicular
Eii	Atom–atom 3nn	Atom–atom 3nn
F	Atom-perpendicular	Atom-perpendicular
G	Hollow-perpendicular	Hollow-perpendicular
H	Bridge-perpendicular	Bridge-perpendicular

This selection of initial conditions differs from Wang's [20] because his use of graphite, rather than graphene, as a substrate makes some of the sites chosen by him irrelevant to our considerations.

All of the gold dimers were placed 0.2887 nm above the perfect graphene surface. The initial gold–gold dimer bond length was 0.247 nm (84). The binding energy is the dissociative energy of the dimer from the surface, and the adsorption energy assumes that the dimer bond energy on the surface is identical to its value in the gas phase. In the case of a dimer there are many more degrees of freedom, and the final configuration is not necessarily equivalent to the initial configuration. This is illustrated in table 2.

Six of the final configurations resulted in the adsorbate lying perpendicular to the plane of the graphene sheet and in three cases the dimer found a metastable state where it had adsorbed parallel to the graphene sheet. Now we will review these final configurations, their stability and electronic structure. If the gold atoms are different distances from the surface, then the one nearer is labelled Au1 and the one further away is labelled Au2. Throughout we will compare our results with those of other authors, but the comparison can only be qualitative, because the graphite substrate used by them provides many more routes for charge to move to or from the gold dimer. The central results of the calculations are shown in table 3. The gold–gold distance of the free dimer is 0.250 nm

In the atom-perpendicular configuration the results differ from those of Wang *et al* [21] by at most 3%. The carbon atom below gold atom (Au1) is charged by $+0.14e$. A dipole has been induced on the gold atoms. There is significant s–d and s–p hybridization between the two gold atoms bound to the surface. This hybridization stabilizes the dipole between the

two gold atoms and between the dimer and bonds the dimer to the surface.

In the hollow-perpendicular configuration the results differ from those of Wang *et al* by at most 5%. The carbon atoms surrounding the hollow are each charged by $-0.06e$. The dimer is only very weakly held to the surface and there is no surface deformation. The gold–gold distance is the same as for the free dimer, and this reinforces the idea that the gold–gold bond is much stronger than the gold–carbon bonds. In the atom–atom n configuration the results differ from those of Wang [21] by at most 5%. The extent of the polarization of the carbon atoms is much greater in this case, with half the atoms having a charge between -0.01 and $-0.02e$. The gold atoms have not relaxed to an equal distance above the graphene layer. Au2 is 0.286 nm above the surface and Au1 is 0.294 nm above the surface. This leads to a slightly different magnetic moment on the gold atoms of $0.08\mu_B$ on Au2 and $0.06\mu_B$ on Au1.

In the atom–atom 3nn configuration the results differ from those of Wang [20, 21] by at most 8%. The gold dimer is parallel to the surface in this case. The carbon atoms directly below the gold atoms have gained $0.08e$ each, and the remaining excess charge is distributed among 18 of the remaining 30 atoms.

The hollow–hollow configuration was not examined by Wang *et al*. The adsorption of a gold dimer above two hollows produced one of the highest-energy configurations. This is not unexpected, as the adatom configuration studied previously showed that an adatom adsorbed above a hollow was the highest-energy configuration, and we have found that there is a metastable configuration where the dimer is held above the substrate in this configuration. Similarly to previous systems, the final structure is metallic. Au1 is 0.311 nm from a nearer carbon atom and 0.322 nm from the furthest carbon atom in the hexagon surrounding the hollow. Au2 is the more distant gold atom from the surface, with its closest carbon atom (within the hexagon surrounding the hollow) 0.315 nm and the furthest is 0.320 nm. The dimer is not parallel to the surface, but it does cause noticeable surface deformation and polarization. This is similar to the cases of the other dimers which lay parallel to the surface. The gold–gold bond length is elongated when compared to the free dimer case, hence the low binding energy. The gold–gold bond length is normally favoured over the gold–substrate length, in this situation the gold bond length is forced to stretch due to the repulsion from the hollows and the presence of a carbon–carbon bond below it. The gold dimer has distributed electrons evenly between the two gold

Table 3. The structural and electronic parameters for a gold dimer adsorbed onto graphene in a variety of configurations. E_B is the binding energy, E_A is the adsorption energy, h is the distance of the gold atom above the nearest carbon atom. d_{Au-Au} is the distance between the gold nuclei in the dimer. Au1 is the gold atom nearer to the graphene plane.

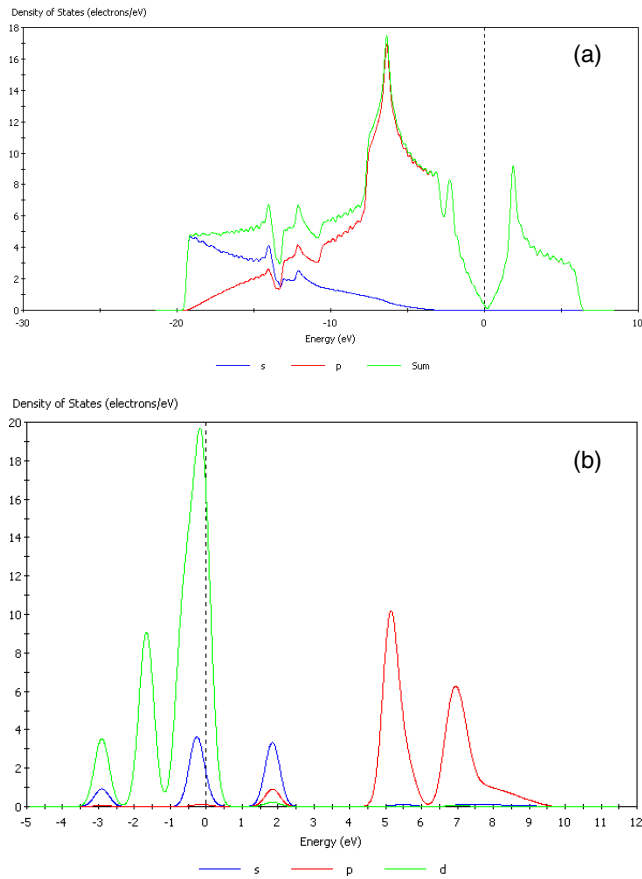| Reference	$-E_B$ (eV)	E_A (eV)	h (nm)	Au1 charge (e)	Au2 charge (e)	Au1 moment (μ_B)	Au2 moment (μ_B)	d_{Au-Au}
B	3.242	0.419	0.286	0.13	0.15	−0.13	−0.15	0.252
C	3.419	0.452	0.311	0.13	0.13	−0.13	−0.13	0.252
Eii	3.382	0.559	0.243	−0.21	0.21	−0.21	0.21	0.257
F	3.979	1.155	0.221	+0.56	−0.21	−0.56	0.21	0.250
G	3.593	0.769	0.267	+0.55	−0.18	−0.55	0.18	0.250
H	4.014	1.191	0.228	+0.59	−0.21	−0.59	0.21	0.250

Figure 4. (a) The partial density of states of a graphene sheet. (b) The density of states of a gold dimer. In both figures, $E = 0$ corresponds to the Fermi energy.

atoms. This charge is transferred to the surface. Unexpectedly, the charge associated with the dimer is not transferred to the carbon–carbon bond over which the dimer's bond is placed. Instead, the charge of $0.03e$ is transferred to carbon atoms that lay parallel to the carbon–carbon bridge site described.

In the bridge-perpendicular configuration the results are in excellent agreement with those of Wang [20, 21]. A dipole is induced in the gold dimer. The bridging site carbon atoms both receive the same contribution of electrons ($0.12e$) from the dimer. Additional charge is then distributed throughout the lattice. Our calculations show that this configuration is indeed the ground state.

4. Discussion

The results for the energetics of the single atom on graphene are in good agreement with the work of da Silva *et al*. Both his study and ours find the atop arrangement to be the most stable.

For the dimer we find qualitative agreement with Wang *et al*, although our binding energies are systematically a few per cent higher than theirs and our values of h show a greater variation than theirs.

In figure 4(a) we show the density of states for a free gold dimer. As expected, there is a substantial density of states at the Fermi level that is dominated by the d-electrons. In
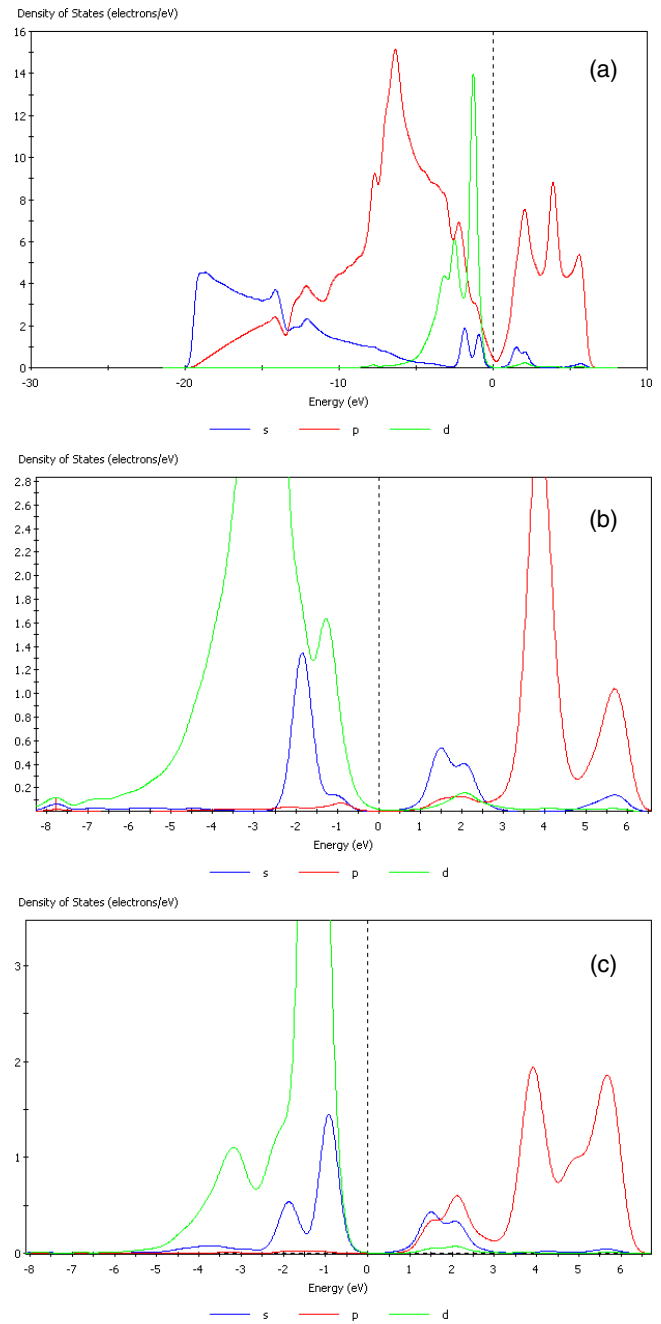
Figure 5. Density of states for the bridge-perpendicular configuration. (a) For the graphene sheet, (b) for the gold atom nearer to the graphene sheet, (c) for the gold atom further from the graphene sheet. All energies are in electronvolts and $E = 0$ corresponds to the Fermi energy.

figure 4(b) we have the density of states for a perfect graphene plane. The Fermi energy sits at a minimum in the p-density of states. This density of states is in excellent agreement with earlier work [35].

In figures 5(a) and (b) we show the density of states of gold atoms closer to and further away from the graphene plane, respectively. We see that the interaction with the graphene plane has opened up an energy gap on the dimer. This is not true of any of the metastable configurations for the gold dimer.

Figure 5(c) shows the density of states for the full bridge-perpendicular system. It is clear that the gold d-states have essentially been filled and have been pushed down below the Fermi energy. The gold s-states have been split into bonding and antibonding bands, while the p-states on the graphene plane remain much the same as in perfect graphene. The magnetic dipole moment and the charge transfer between the gold atoms in the dimer both take on a maximum value for this bridge-perpendicular atomic arrangement.

It is clear from the figures that the peaks in the d-band densities of states on both gold sites coincide and are considerably lower in energy than in the pure dimer case. This indicates that it is the d-electrons that are responsible for holding the dimer together, as would be expected. There is also a strong change transfer effect, in that the Au1 atom has lost about 0.6 of an electron, 0.21 electrons have moved to Au2 and most of the remainder are located on the two carbon atoms closest to the gold dimer. On Au2 this has allowed the s-and d-bands to fill and fall below the Fermi energy, opening up the gap. In Au1 the situation is not so clear, but it appears that the s-band has filled again while a single d-state has been split off from the rest of the d-band by the spin polarization and has opened a gap in that way. The electrons that have been donated to the graphene sheet have led to a small shoulder in the carbon p-electron density of states which hybridizes with the gold d-states and is responsible for the bonding of the dimer to the surface.

The metastable configurations that were of particular interest were those that remained parallel to the surface of the graphene sheet. If there are metastable configurations of dimers on the surface of graphene, then it may be possible to form wires on the surface of graphene, thus enabling us to form a wire around a carbon nanotube where the curvature of the surface affects the carbon–carbon bond. Gold dimers that lay parallel to the surface of graphene are weakly bound, however they induce a large amount of surface deformation and surface polarization, even though they are adsorbed a considerable distance from the surface, as shown in table 3. We have observed that the perpendicular configuration of the gold dimer preserved the gold–gold bond length and that the parallel configuration had increased gold–gold bond lengths, when compared to the free dimer. There was significant charge transfer from the gold atom adsorbed at the surface to the gold atom furthest from the surface, inducing a dipole on the dimer in many cases. The results of this work are fully in support of the statement by Wang *et al* that the greater the charge on an adsorbed species, the higher the polarization of the surface and the stronger the interaction between the gold dimer and the surface.

Comparison of our results with those of Jalkanen *et al* [29] is instructive. Their calculations are comparable to ours in a number of ways, but also contain key differences. They have also performed DFT calculations with periodic boundary conditions and plane wave basis sets. Their work is on a single graphite layer (graphene), so the results can be compared directly. They have also employed a scheme that allows them to approximate the van der Waals energies in these materials, which may be significant. For the single atom on graphene they find the atop position as the lowest-energy state, with a similar charge transfer and height above the plane in good agreement with our work. For the bridge and hollow positions their results differ markedly from ours (and those of Wang). For the dimer our conclusions are in agreement with Jalkanen *et al* [29], in that we find the perpendicular orientation favoured over the parallel orientation and we find that there is only a very small energy difference between the atop and bridge sites while these are substantially favoured over the hollow site. They also find that the Au_2 bond lengths are essentially unchanged from the gas-phase values. However, the absolute numbers for the adsorption energies and distances vary by up to about 30% between our calculation and theirs. The differences between their calculation and ours must be attributable to the fact that our calculation employs the LDA, while theirs uses the GGA, plus their approximate inclusion of van der Waals energies. In general, the LDA is known to overbind, although in our validation tests the LDA produced results in better agreement with experiment than the GGA for both pure graphene and pure gold. Indeed, Jalkanen *et al* themselves point out that there is a very large variation in calculated adsorption energies, as a function of which exchange–correlation approximation is chosen.

Our work is a standard density functional calculation which will have an uncertainty of up to about 1% mainly due to the LDA (in fact, the lattice constant of Au had a 0.9% error and that of graphene a 0.1% error with respect to experiment for lattice data). As stated above, the uncertainty in energetic quantities is a lot greater than this, predominantly due to the uncertainties in the exchange–correlation energy. DFT does not describe van der Waals interactions properly and so these are not included in our calculations. Jalkanen *et al* have evaluated these and have found substantial variations and uncertainties, depending on what approximations are used. Nonetheless, their work does at least indicate the order of magnitude of these energies and they are substantial, of the same order as the energy differences we are seeking. Therefore our, and all previous, DFT work can only form a basis for further more detailed investigations of the energetics of impurities on graphene.

Acknowledgments

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