

Inducing energy gaps in monolayer and bilayer graphene: Local density approximation calculations

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In this paper we study the formation of energy gaps in the spectrum of graphene and its bilayer when both these materials are covered with water and ammonia molecules. The energy gaps obtained are within the range 20–30 meV, values compatible to those found in experimental studies of graphene bilayer. We further show that the binding energies are large enough for the adsorption of the molecules to be maintained even at room temperature.

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I. INTRODUCTION

Graphene is a two-dimensional system made solely of carbon atoms arranged in a honeycomb lattice. Since its isolation^{1,2} in late 2004, it has attracted a great deal of attention due to its unconventional physical properties. Together with this wonderful system it was also possible to produce its layered relatives, such as the graphene bilayer, trilayer, etc.

The physical properties of single layer graphene are governed by the elementary excitations around the Fermi surface, which in graphene is made of only six points in the Brillouin zone, located at momenta values denominated \mathbf{K} and \mathbf{K}' points.³ These elementary excitations are massless Dirac particles, described by the 2+1 Dirac equation. The unusual properties of graphene are therefore a consequence of the fact that the emergent physical theory of this system is not the usual Schrödinger equation but instead a relativistic problem. For the layered systems the situation is also equally interesting. For example for the bilayer case, although the low-energy spectrum is parabolic, the effective theory is that of massive chiral particles^{4–6} and again not the usual Schrödinger equation.

Both graphene and its bilayer are expected to integrate the next generation of nanoelectronic devices.⁷ However, both graphene and its bilayer do not present an energy gap in the spectrum, preventing large on-off signal ratios in possible electronic devices. In the case of graphene, there is also a finite conductivity value^{1,2,8} at the neutrality point, which prevents the pinch off of the field effect transistor. Clearly, what is necessary for having full working devices made of graphene is an energy gap in the spectrum, as in the usual semiconductor devices.

There are at the moment two different proposals for producing energy gaps in the spectrum of graphene. The first is by producing graphene nanoribbons.^{9–11} The theoretical studies^{9,10} show that depending on the type of terminations a graphene ribbon may have, the mechanisms for the opening of a gap will be different. For zigzag nanoribbons, the existence

of edge states^{12–14} would prevent the existence of an energy gap. However, the system finds a way out by inducing magnetization⁹ at the edges and by opening a gap in the spectrum. The same happens in a graphene bilayer with zigzag edges.^{14,15} For nanoribbons with armchair edges, the gaps are formed due to quantum confinement, and the value of the gap depends on the width of the ribbon. For ribbons smaller than 10 nm on/off ratios as large as 10^6 have been demonstrated.¹¹

Another method of producing a gap in the spectrum of graphene is by depositing graphene on top of a boron nitride (BN).¹⁶ This material is a band-gap insulator with a boron to nitrogen distance of the order of 1.45 Å (Ref. 17) (in graphene the carbon-carbon distance is 1.42 Å) and a gap of the order of 4 eV. It was shown that in the most stable configuration, where a carbon is on top of a boron and the other carbon in the unit cell is centered above a BN ring, the value of the induced gap is of the order of 53 meV. Depositing graphene on a metal surface with a BN buffer layer leads to *n*-doped graphene with an energy gap of 0.5 eV.¹⁸

The existence of energy gaps in the spectrum of graphene also prevents the occurrence of the Klein paradox,^{19,20} which would be another limiting source to the effective pinch off of the field effect transistor.

The situation in bilayer graphene is also being unveiled experimentally. It has already been demonstrated that it is possible to open a gap in the spectrum of the bilayer when this material is deposited on top of silicon carbide (SiC) and its exposed face is covered with potassium atoms.²¹ The value of the gap is, in this case, connected to the amount of doping the potassium atoms induce. Using a similar method, it was experimentally demonstrated the opening of a gap in a bilayer deposited on top of silicon oxide, by covering its exposed face with ammonia molecules.²² In both these methods, the value of the gap and the amount of doping are interconnected. Recently,²³ a device with both top-gate and back-gate setups became available, which allows one to control the value of the gap in the bilayer spectrum and the amount of charge carrier independently.

From the above experimental studies it is clear that covering the bilayer system with some atomic species will lead to a gap in the spectrum. These results motivated first-principles studies²⁴ of gap formation in graphene bilayer leading to calculated gaps in the interval 0.64–3 eV.

In this paper we study the effect of covering both graphene and its bilayer with water and ammonia, showing that in both cases this covering leads to a gap in the spectrum, albeit smaller than those reported in Ref. 24. Our results for the induced gaps in the graphene bilayer are compatible with those determined for this system by measuring the cyclotron masses of the charge carriers.²²

II. THEORETICAL METHOD

We are interested in describing the effect that covering graphene and its bilayer with water and ammonia has in their electronic spectra and in particular in the appearance of an energy gap in the spectrum. There is strong experimental evidence for the presence of water in graphene,²⁵ and there are working graphene devices based on covering one of the surfaces of the graphene bilayer with ammonia.²² Therefore our motivation is to understand from first principles how these two types of molecules change the electronic spectrum near the Dirac point.

The method we use in our investigation rests upon the local density approximation (LDA). In particular, the calculations were performed using the density-functional code AIMPRO.^{26,27} In what follows we give the relevant details of our calculations.

The Brillouin zone (BZ) was sampled for integrations according to the scheme proposed by Monkhorst-Pack.²⁸ A grid of $8 \times 4 \times 1$ \mathbf{k} points was generated and folded according to the symmetry of the BZ. An increase in the number of points did not result in a significant total energy change.

We use pseudopotentials to describe the ion cores. Lower states (core states) are accounted for by using the dual space separable pseudopotentials by Hartwigsen *et al.*²⁹ The valence states are expanded over a set of s -, p -, and d -like Cartesian-Gaussian Bloch atom-centered functions, and Fermi filled using a value of $k_B T = 0.01$ eV. Kohn-Sham states are expressed as linear combinations of these basis functions. The basis functions were optimized for graphene, water, and ammonia separately. The calculation of potential terms is more efficient in reciprocal space, and therefore the electron density is Fourier transformed by using plane waves with kinetic energy of up to 300 Ry.

Graphene was modeled in a slab geometry by including a vacuum region in a supercell containing eight carbon atoms. Different sizes were also tested, as well as several water or ammonia molecules concentrations per supercell, leading to very different molecular surface densities but to only small changes in the gap values. In the normal direction (z direction), the vacuum separating repeating slabs has more than 30 Å. The size of the supercell in the z direction was optimized to make sure there was no interaction between repeating slabs.

In the calculations, all the atoms were fully relaxed to their equilibrium positions. That is to say that the final struc-

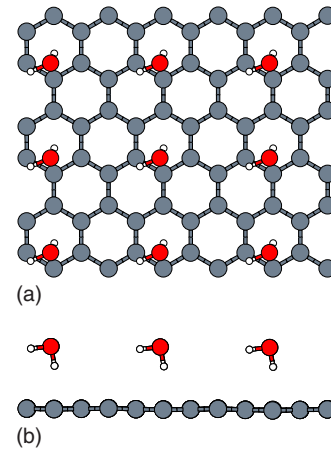


FIG. 1. (Color online) Water on the top of graphene: top and side views.

ture of the system is that obtained by energy minimization and is not imposed externally. Consequently all the distances found below are a consequence of energy minimization of the full structure.

The electronic band structure for the path $\mathbf{K}-\Gamma-\mathbf{M}$ was calculated for all the structures. Since the supercell is much larger than the primitive cell, the bands appear folded in the graphs. The electronic density of states (DOS) was calculated by sampling 12 800 points in the BZ and broadened with a 0.1-eV Gaussian width.

The binding energies were calculated by subtracting the total energies of the graphene sample and the molecule calculated separately from the total energy of the graphene plus molecule.

III. RESULTS

A. Structure

Figure 1 shows the relaxed water molecule on the top of the graphene. In this calculation, water concentration is very low (one water molecule per eight carbon atoms or a density of about 6 nm^{-2}) and this results in low interaction between the water molecules, meaning that each water molecule acts like an independent scattering center. One of the hydrogen atoms binds to a carbon atom, and the carbon atoms move from their initial positions, especially in the z direction (as much as 0.05 Å). The presence of water therefore breaks the A - B symmetry of the graphene lattice structure. This, as we shall see, will affect the electronic states (see Sec. III B), especially close to the Dirac point. The same happens when we add ammonia.

The ammonia in the top of the graphene (Fig. 2) has a higher binding energy (see Table I) since it binds through two hydrogen atoms, and not through one, as the water molecule. Table II shows the distances between the heaviest atom of the water and the ammonia molecules and the closest carbon atom. We choose the position of the heavier atoms of the molecules as a reference because their position can usually be measured using techniques such as low-energy electron diffraction (LEED), x-ray photoemission spectroscopy

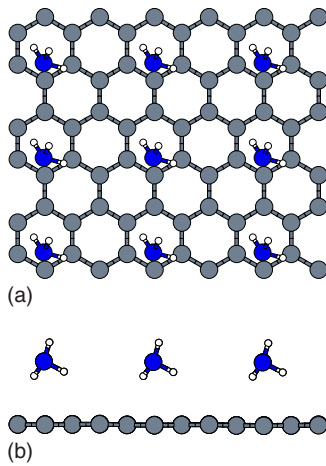


FIG. 2. (Color online) Ammonia on the top of graphene: top and side views.

copy (XPS), ultraviolet photoemission spectroscopy (UPS), and electron-energy-loss spectroscopy (EELS).³⁰ Our results show a much higher binding energy than the ones obtained by other authors.³¹ We believe this is because those authors impose restrictions to the rotation of the molecules on the top of graphene; we observed that our molecules never relaxed to those positions but rotate instead to more favorable orientations.

When a second layer of graphene is added, a bilayer is obtained. The usual stacking of the graphene bilayer is the Bernal stacking although there are situations where rotational defects may also be present.³² In the Bernal stacking two of the carbon atoms, each belonging to different layers, are positioned exactly on top of each other. For these atoms we have found that they move away from the plane as much as 0.004 Å. The distance between layers (measured as the distance between two carbon atoms that are superimposed in the Bernal stacking) is 2.6 Å. This is lower than the interplan distance on graphite. We believe this is due to the absence of layers on both sides of the bilayer.

The bilayer has a binding energy per carbon atom of 0.21 eV, and both the water and the ammonia molecules are less bound to the bilayer than to graphene. This is because in the bilayer the carbon atoms near the molecules also have to share electrons with the underlying carbon layer. In fact, the hydrogen of the molecule that is closer to the surface binds to a carbon atom that has no other carbon atom below. In

TABLE I. Binding energies for the adsorbed molecules of ammonia and water (per molecule), and for the bilayer (per carbon atom).

System	Binding energy (eV)
Graphene+H ₂ O	1.94
Graphene+NH ₃	3.58
Bilayer	0.21
Bilayer+H ₂ O	1.30
Bilayer+NH ₃	2.86

TABLE II. Distances between oxygen and nitrogen and the closest carbon atom of graphene.

System	Atoms	Distance (Å)
Graphene	O—C	2.79
Graphene	N—C	2.91
Bilayer	O—C	2.83
Bilayer	N—C	2.97

every case the binding energy is high and so desorption by thermal evaporation at room temperature is not expected. This is consistent with the experimental finding that graphene usually has adsorbed water.²⁵ Figures 3 and 4 show the water and the ammonia molecules, respectively, on their equilibrium positions on the top of the bilayer.

We also have done calculations for higher molecular concentrations. In these cases, there is a strong interaction between the molecules that causes their reorientation, in such a way as to align some of the hydrogen atoms to the oxygen/nitrogen in order to make hydrogen bonds. For water, two molecules per eight carbon atoms covers the graphene surface; one molecule more and a second water layer starts to form. For ammonia, two molecules per eight carbon atoms is enough for a second layer to be formed.

B. Electronic structure

The electronic band structure for the graphene with water and ammonia molecules on the surface is shown in Fig. 5. Since we are using a supercell, the Brillouin zone is different from the standard one, and that is reflected on the shape of the bands. But the absolute location of points **K** and **M** are the same. In both cases, a localized band appears distinctly above the valence band of the graphene. It corresponds to the highest occupied molecular orbital (HOMO) level of the

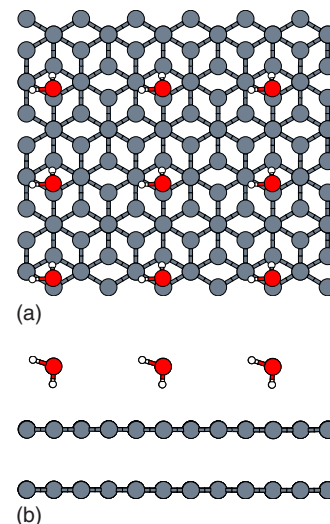


FIG. 3. (Color online) Water on the top of bilayer graphene: top and side views.

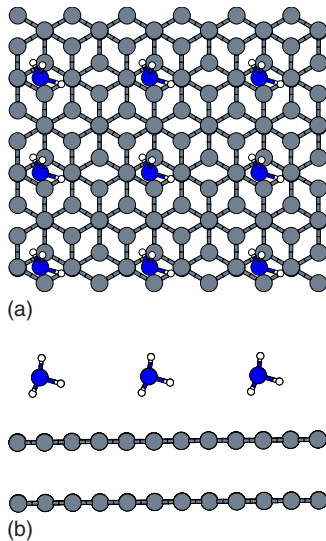


FIG. 4. (Color online) Ammonia on the top of bilayer graphene: top and side views.

molecules, which is clearly below the Fermi level. The lowest unoccupied molecular orbital (LUMO) of the molecules is very much above the Fermi level. This means that the charge transfer in the interaction between the molecules and the surface of graphene will be small, and the interaction must be of dipole or van der Waals type.

The bands near the Dirac point can be seen in detail in Fig. 5 and have a similar form for both types of molecular coverage of the carbon layers. A gap opens and it is shifted to one side of the \mathbf{K} point. This happens because there is a symmetry lost due to the displacement of the carbon atoms interacting with the molecules.

Table III shows the calculated values for the band gap. It is well known that local density-functional theory, while expected to give a realistic account of the ground state structure, only gives an approximate description of unoccupied states in a system. In particular the energy gap is underestimated, being typically 60% off the real value. This should be taken into account when analyzing the bands and the gap values in detail. In principle a gap in the graphene spectrum is not expected, except when the A - B symmetry of the lattice is broken. As our calculations show, there is a vertical distortion of the graphene lattice, which leads precisely to the breaking of the A - B symmetry and therefore to the opening of a gap. This breaking of the symmetry lattice translates in a spectrum that is hyperbolic near the Dirac point, where the bands are still linear for finite energies, except close to the Dirac point, where they become parabolic in shape.

The electronic band structure for the bilayer with water and ammonia molecules on the surface are shown in Fig. 6. Since in our calculations we have the two layers much closer than in graphite, which is the distance usually considered in other calculations, it is natural that we have the second band at higher energies than what other authors had, due to an increase in the tight-binding parameters in the direction perpendicular to the graphene layers. In the case of water on the top of the bilayer there is no flat band above the bilayer valence band while there is one in the case of ammonia.

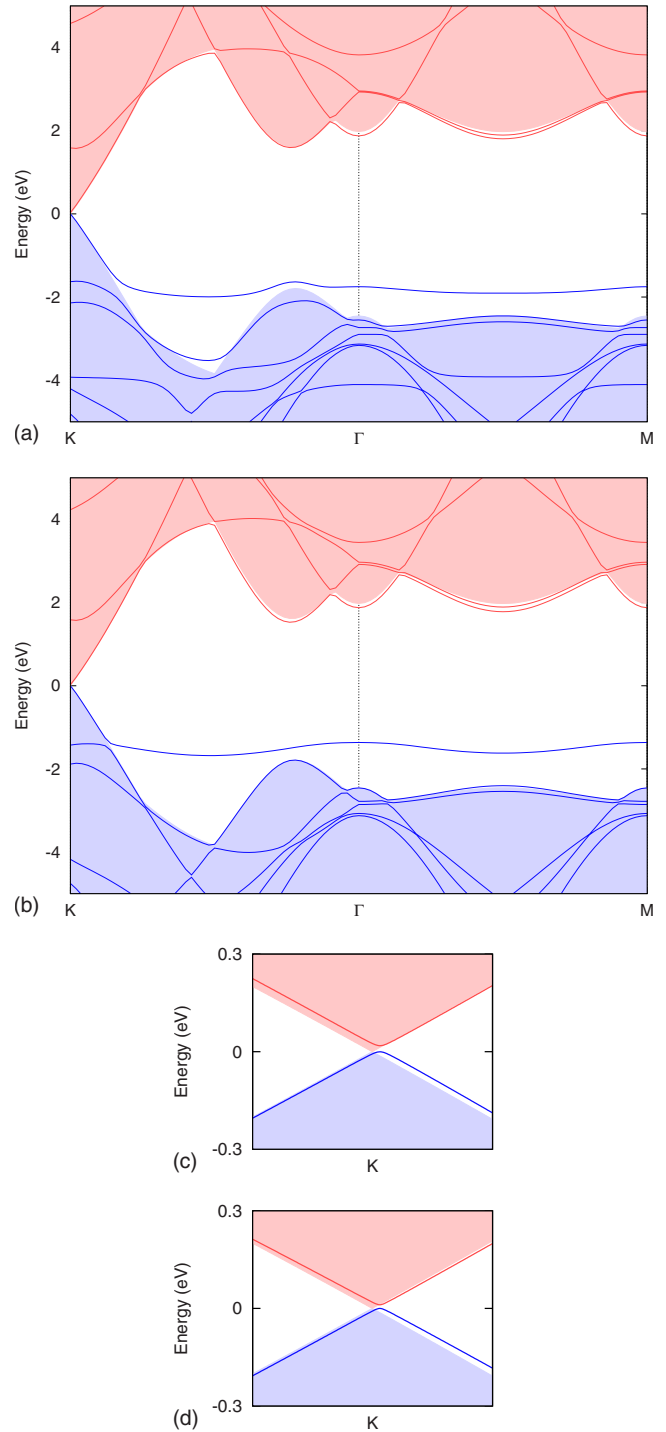


FIG. 5. (Color online) Electronic band structure for the system (a) graphene plus water, (b) graphene plus ammonia, (c) detail near the Dirac point, and (d) detail near the Dirac point. The clean graphene band structure appears as a shadow in the background.

As in graphene, covering the bilayer with either water or ammonia leads to the opening of gap that is shifted to one side of the \mathbf{K} point, which is consistent with the results obtained by Guinea *et al.*³³ These authors found that the gap in bilayer graphene does not reach a minimum at the \mathbf{K} point due to a “Mexican hat” dispersion at low energies. Although the resolution of our figures is not enough to see the Mexican

TABLE III. Calculated band gaps for the systems considered. The gap shown for the bilayer+NH₃ is indirect.

System	Band gap (meV)
Graphene+H ₂ O	18
Graphene+NH ₃	11
Bilayer+H ₂ O	30
Bilayer+NH ₃	42

hat, its presence in the band structure was verified by the authors. The gaps (see Table III) that the molecules generate on the bilayer are much larger than the ones on graphene.

It is known that the unbiased bilayer has parabolic bands at the Dirac point, with the valence and the conducting band touching each other. Presence of the molecules opens up a gap in the spectrum, but while in the case of water, the gap is very near the Dirac point. In the case of ammonia the gap is indirect and far from the **K** point. This last result is a direct consequence of the type of molecule used and cannot be obtained within tight-binding calculations.

It is known²² that a difference in potential along the *z* direction induces a gap in the electronic band structure for the bilayer. The water and the ammonia molecules have both an electric dipole, which will produce an electric field on the bilayer. In this case, the difference in electric potential between the layers is 0.198 V for the system with ammonia and 0.027 V for the system with water.

The gap we obtained with ammonia is consistent with the gap calculated using tight-binding and a self-consistent determination of the electric potential.²² Yet, our calculations lead to a electric potential between graphene layers interacting with the ammonia molecule of 0.198 V. This value, when included in the equation,²²

$$\Delta_g = [e^2 V^2 t_{\perp}^2 / (t_{\perp}^2 + e^2 V^2)]^{1/2}, \quad (1)$$

gives a much larger gap. The discrepancy may be explained by the fact that the expression is not valid for indirect gaps and it does not include the distortion of the bilayer lattice. The gap for the bilayer with water estimated from the electric potential between the layers and using Eq. (1) (based on a tight-binding model) gives consistent results with those determined from the band-structure calculation.

In our case, besides the electric potential induced by the molecule, there is also a distortion in lattice both in the case of graphene and its bilayer. Our calculations show that the distortion of the lattice in the bilayer tends to counteract the molecule's dipole but still leading to a band gap.

The electronic DOS of the systems considered is shown in Fig. 7. The molecules create a lot of structure in the density of states, the most relevant are the strong peaks that correspond to very flat bands localized around the molecule. Except for the water on the bilayer, the molecules generate a very high peak on the DOS at higher energies than the first peak of the occupied states for the clean surfaces. The presence of these peaks leads to an increase in the absorption at energies of a few electron volts.

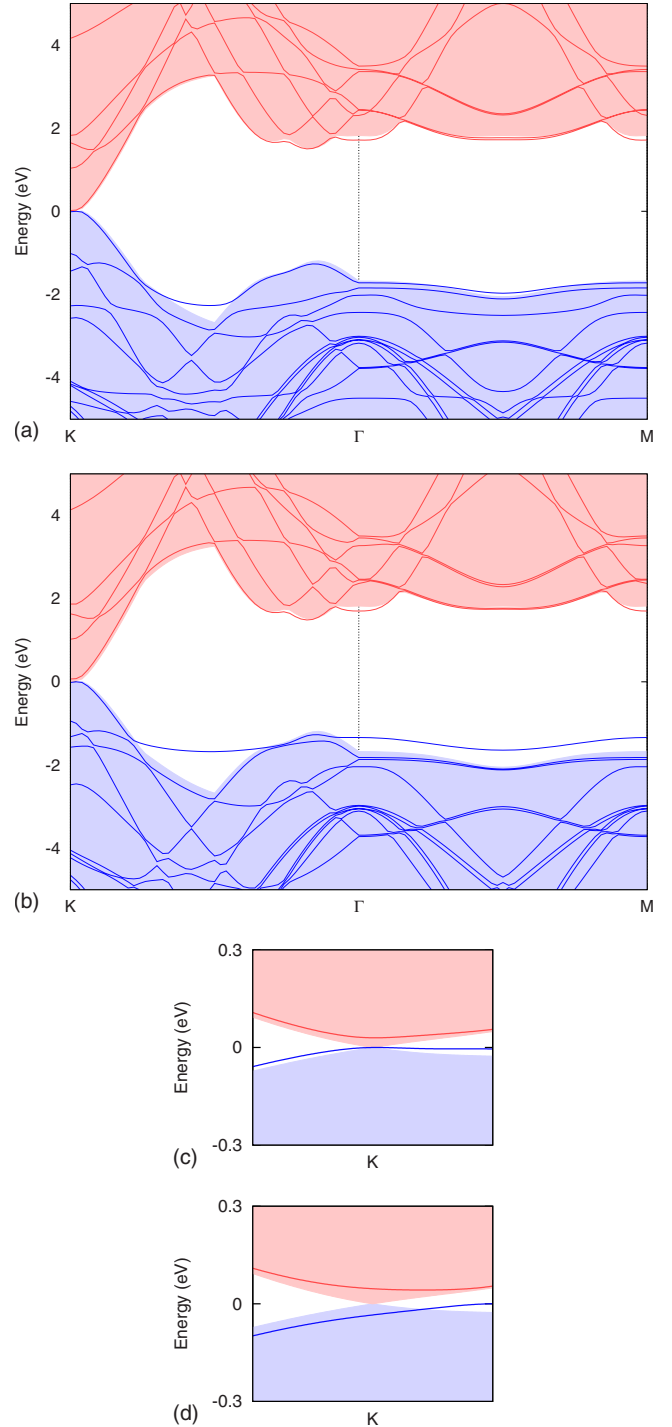


FIG. 6. (Color online) Electronic band structure for the system (a) bilayer plus water, (b) bilayer plus ammonia, (c) detail near the Dirac point, and (d) detail near the Dirac point. The clean bilayer graphene band structure appears as a shadow in the background.

IV. CONCLUSIONS

The adsorption of water and ammonia on the top of the graphene and graphene bilayer was studied. The position and orientation of these molecules relative to the surfaces was obtained as well as the binding energies. The high values of the binding energies (of the order of the electron volt) indi-

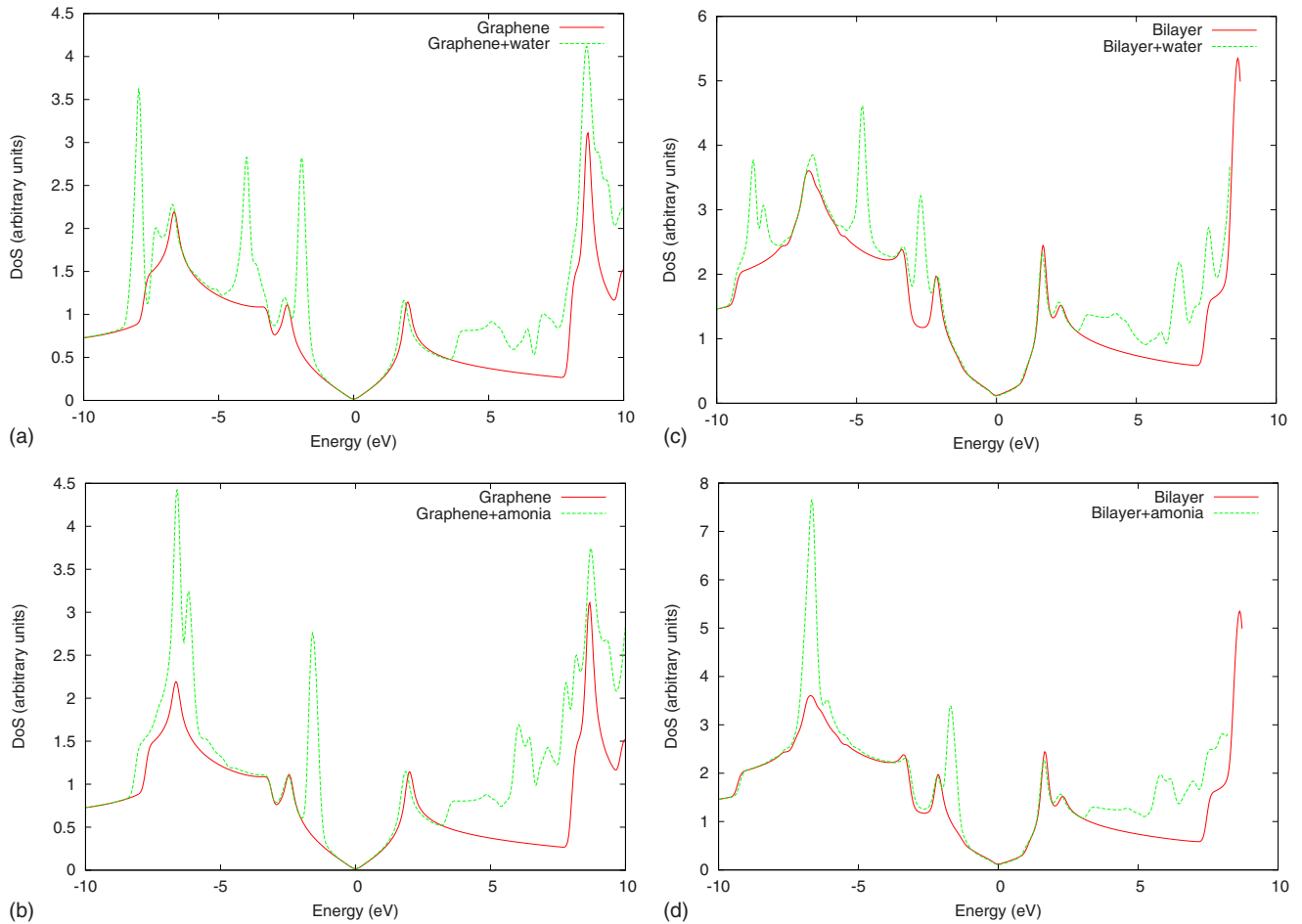


FIG. 7. (Color online) Electronic density of states for the system (a) graphene plus water, (b) graphene plus ammonia compared with graphene, (c) bilayer plus water, and (d) bilayer plus ammonia compared with bilayer.

ates that desorption of these molecules cannot be obtained at room temperature and a surface coverage is expected if the surfaces are exposed to water or ammonia.

We have showed that a gap opens up in the band structure when molecules adhere to the surface, both on graphene and on the bilayer, and its value is of the order of a few tens of millielectron volts. The mechanism for opening an energy gap may be different for the graphene single and bilayer since the random distribution of the molecules on the single layer may not break the *A-B* symmetry in average while the gap opening in the bilayer is related to the symmetry between top and bottom layers.

We therefore have showed the existence of a feasible method to produce graphenes with gaps in their spectrum, which is not restricted to the manipulation of nanoribbons.

We found that the gap is in general displaced away from the Dirac point.

An increase in the absorption coefficient for energies above about 2 eV due to the presence of the molecules is predicted from the electronic density of states.

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