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Accurate electronic band gap of pure and functionalized graphane from GW calculations

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Using the GW approximation, we study the electronic structure of the recently synthesized hydrogenated graphene, named graphane. For both conformations, the minimum band gap is found to be direct at the Γ point, and it has a value of 5.4 eV in the stable chair conformation, where H atoms attach C atoms alternatively on opposite sides of the two-dimensional carbon network. In the metastable boat conformation the energy gap is 4.9 eV. Then, using a supercell approach, the electronic structure of graphane was modified by introducing either a hydroxyl group or an H vacancy. In this last case, an impurity state appears at about 2 eV above the valence-band maximum.

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I. INTRODUCTION

After the discovery of graphene[1] and of its extraordinary electronic properties[2–4] the chemical functionalization of graphene has become the focus of special interest in contemporary materials science. Being first a truly two-dimensional crystal and demonstrating high-electron mobility,[1] graphene is ideal for modern electronics which is essentially two dimensional.[2] At the same time, the peculiar gapless "ultrarelativistic" energy spectrum of graphene[3,4] makes the creation of a "carbon transistor" based on *p*-*n* junctions highly nontrivial, due to the anomalous transparency ("Klein tunneling").[5] Nanoscale graphene single-electron transistor has been demonstrated already[6] but it has a relatively restricted domain of potential applications. Therefore, to transform graphene into a semiconductor with a conventional electron spectrum keeping its two dimensionality is a real challenge in the field, and chemical functionalization is considered as one of the most promising ways to solve the problem.

A new derivative of graphene was recently synthesized,[7] where hydrogenation turned graphene into what now is called graphane. Previously this compound was studied theoretically, and it is actually an excellent example of a new and interesting material which was predicted from first-principles theory[8,9] before it was synthesized experimentally. In the calculations of the electronic structure it was found that graphane is a semiconductor with a rather wide energy gap.[8,9] In the experiment[7] the adsorption of hydrogen on graphene was indeed observed to result in that a gap opened up in the electron states. Hence the adsorption of hydrogen turned the highly conductive graphene into insulating graphane, in accordance with the theoretical predictions.[8,9] However, the exact value of the band gap is still experimentally unknown. Previous theoretical calculations giving values from 3.5 (Ref. 8)–3.8 eV (Ref. 10) use a standard density functional with generalized gradient approximation (GGA). It is well-known that, in general, this approach is not reliable to calculate energy gaps in semiconductors often giving inaccurate results (the so-called "gap problem").[11] However, the value of the energy gap is of crucial importance for many applications of semiconductors. For instance, the energy gap of graphane will determine tunneling through graphane regions in graphene-graphane nanostructures.

The reason for a band gap opening up when hydrogen is adsorbed on graphene is that sp^2-bonded C atoms become sp^3-bonded atoms, where three of the four covalent sp^3 bonds are saturated by C atoms and the fourth covalent bond is saturated by an H atom. This is for instance illustrated in the theoretical part of Ref. 7 and is also known from the adsorption of single-hydrogen atoms on graphene.[12] In accordance to expectations this change in chemical binding is also reflected in the electronic structure, where sp^3-bonded C atoms do not display a so-called π^* peak in the x-ray absorption spectrum.[12] Hence the basic reason for the drastic change in conductivity is in accordance to expectations for sp^3-bonded carbon (i.e., diamond), with an insulating behavior. There is of course no reason to expect that the size of the band gap of graphane should be similar to that of diamond, even though there are similarities in the nature of the chemical binding. Hence measurements or accurate theoretical calculations are needed, and in this article we present a calculation based on the GW approximation.

II. METHODS

Due to the well-known deficiencies of the density functional theory (DFT) (Ref. 13) to treat excited states (for example, the band gaps in the local density approximation or generalized gradient approximation are much smaller than the experimental values), we have used the GW approximation (GWA) of Hedin[14,15] to study the electronic structure of graphane. In this formalism, the Kohn-Sham equations[13] are replaced by the quasiparticle (QP) equation

$$(T + V_{\text{ext}} + V_h)\psi_{\mathbf{k}n}(\mathbf{r}) + \int d^3r' \Sigma[\mathbf{r},\mathbf{r}',E_n(\mathbf{k})]\psi_{\mathbf{k}n}(\mathbf{r}') = E_n(\mathbf{k})\psi_{\mathbf{k}n}(\mathbf{r}),$$

where T is the free-electron kinetic-energy operator, V_{ext} the external potential due to the ion cores, V_h the Hartree potential, Σ the self-energy operator, and $E_n(\mathbf{k})$ and $\psi_{\mathbf{k}n}(\mathbf{r})$ are, respectively, the quasiparticle energy and wave function.

An adequate approximation for the self-energy operator is to write it as the product of Green's function and the screened Coulomb-interaction W, which yields to the so-called GW approximation.

$$\Sigma(\mathbf{r},\mathbf{r}',\omega)=\frac{i}{2\pi}\int d\omega' G(\mathbf{r},\mathbf{r}',\omega+\omega')e^{i\delta\omega'}W(\mathbf{r},\mathbf{r}',\omega').$$

Then, since the difference $\hat{\Sigma}-\hat{V}_{\rm xc}$ between the self-energy and the Kohn-Sham exchange and correlation potential is small, a perturbation theory is used to write the QP Hamiltonian,

$$\hat{H}^{\rm qp}=\hat{H}_{\rm KS}+(\hat{\Sigma}-\hat{V}_{\rm xc})$$

Finally, the QP energies are obtained by expanding the real part of self-energy to first order around $\epsilon_n^{\rm DFT}(\mathbf{k})$ and assuming that the QP wave-function $\psi_{\mathbf{k}n}$ and Kohn-Sham wave-function $\Psi_{\mathbf{k}n}$ are identical,

$$\begin{aligned}\mathrm{Re}\, E_n(\mathbf{k})] = \epsilon_n^{\rm DFT}(\mathbf{k}) + Z_{n\mathbf{k}} \times \{\langle\Psi_{\mathbf{k}n}^{\rm DFT}|\mathrm{Re}\,\Sigma[\mathbf{r},\mathbf{r}',\epsilon_n(\mathbf{k})]\\ \times|\Psi_{\mathbf{k}n}^{\rm DFT}\rangle - \langle\Psi_{\mathbf{k}n}^{\rm DFT}|V_{\rm xc}^{\rm DFT}(r)|\Psi_{\mathbf{k}n}^{\rm DFT}\rangle\},\end{aligned}$$

where the QP renormalization-factor $Z_{n\mathbf{k}}$ is given by

$$Z_{n\mathbf{k}}^{\rm DFT}=\left\{1-\langle\Psi_{\mathbf{k}n}^{\rm DFT}|\frac{\partial}{\partial\omega}\mathrm{Re}\,\Sigma[\mathbf{r},\mathbf{r}',\epsilon_n(\mathbf{k})]|\Psi_{\mathbf{k}n}^{\rm DFT}\rangle\right\}^{-1}.$$

Therefore, it appears that the DFT eigenvalues $\epsilon_n(\mathbf{k})$ are corrected by the GW approximation, giving a practical scheme to compute reliable excited-state properties.[16–18]

Here we have used the code VASP[19] (Vienna Ab-initio simulation package), implementing the projector augmented waves (PAW) method[20] to compute the ground-state and excited-state properties of graphane. First, we obtained a reliable geometry of the structure by optimizing it for the two possible conformations (see below), using the generalized gradient approximation.[21] Contrary to Sofo *et al.*,[8] we have chosen to simulate completely isolated sheets of graphane, although the resulting band structure is very close to that other.[8] For all the calculations, we have used the default cutoff for the wave function. During the optimization of the structures, a *k*-point grid[22] of $10\times10\times1$ was used. Then, using the relaxed geometries, a final run was performed with a $16\times16\times1$ grid. Finally, these ground-state calculations were used to compute the quasiparticle band structure with VASP, following the method described in Ref. 23. Two hundred bands were used for the summation over bands in the calculation of the polarizability and the self-energy, and a cutoff of 150 eV was used for the size of the polarizability matrices. For details about the implementation of the GW approximation within the PAW formalism, see also Refs. 24 and 25. Notice that the GW approximation was applied successfully to study the properties of graphene nanoribbons,[26,27] of graphene,[28] and of carbon nanotubes.[29]

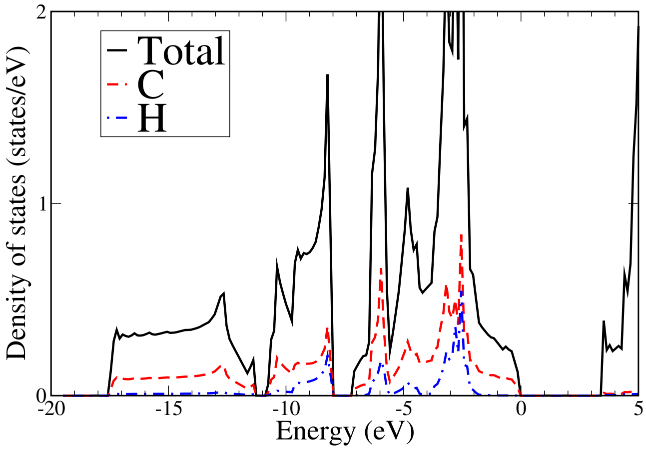

FIG. 1. (Color online) The total (in black) and partial (in red and dashed for carbon and in blue and dotted-dashed for hydrogen) density of states of graphane in the chair conformation. The top of the valence bands is chosen as the zero energy.

III. RESULTS AND DISCUSSION

Graphane is made of a hexagonal network of carbon atoms, with the orbitals being of the sp^3 kind and bonded to hydrogen atoms, with a carbon/hydrogen ratio of one. It exists in two conformers,[8] the chairlike conformer and the boatlike conformer. In the chair conformer, all C-C bonds are equivalent and the hydrogen atoms are bonded alternatively on each side of the carbon plane (see Fig. 1 of Ref. 8). The boat conformer has two types of C-C bonds, depending on whether the carbons atoms are bonded to hydrogen atoms which are on the same side of the carbon plane or not. Our calculations indicate that the chairlike conformer is favored by about 0.051 eV/atom, in very good agreement with the value of Sofo *et al.*,[8] who found 0.055 eV/atom. Also, for the chairlike conformer the bond lengths are 1.53 Å (for the C-C bonds) and 1.11 Å(for the C-H bonds), while for the boatlike conformer, the C-C bonds are 1.57 and 1.54 Å long, and the C-H bonds are 1.10 Å long. These values are essentially identical to the one in Ref. 8. In Fig. 1 we show the partial density of states (pDOS) for the stable chair conformer, and it is clear that the occupied H states are located over an energy interval starting from the valence-band maximum and extending some 10 eV below. As regards to the unoccupied states, the H and C states are also extended and cover a wide energy range.

Being confident about the reliability of our ground-state calculations, we now turn to the calculation of excited-state properties. The GGA (full lines) and GW (dots) band structures for both conformers are presented in Figs. 2 and 3. First, our calculated GGA band structure for the chair conformation agrees well with the one of Sofo *et al.* (notice that the band structure of the boat conformation was not reported in this paper). The minimum band gap is direct at the high-symmetry point Γ and has a value of 3.5 eV. However, this value is dramatically changed when using the more reliable GW approximation, in this case the value is 5.4 eV. The transitions at the high-symmetry points *M* and *K* are also significantly increased, from 10.8 and 12.2 eV with the GGA

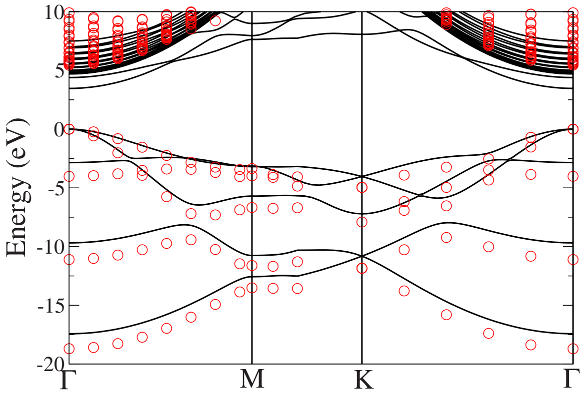

FIG. 2. (Color online) The GGA band structure (full lines) and the GW band structure (red dots) of graphane in the chair conformation. The top of the valence bands is chosen as the zero energy.

approximation, to 13.7 and 15.9 eV with the GW approximation (see Table I). For the boat conformation (Fig. 3), the band gap is also found to be direct at the Γ point, with a value given by the GW approximation of 4.9 eV, whereas the GGA gives only 3.3 eV. The values of the transitions at the *X*, *S*, and *Y* high-symmetry points are also notably corrected, see Table I. Our calculations show that graphane, in both conformers, can be qualified as a large band-gap insulator, and the electronic properties are expected to be quite different from the ones of graphene. This is qualitatively in agreement with observations.

Since graphane is a wide band-gap material it is relevant to ask if defect states can be introduced easily, and manipulated for electronics applications. We have here considered two examples of defects in graphane, in the chair conformation: replacement of an H atom by a hydroxyl group (OH), and H vacancies. We have calculated the electronic structure of such systems using a 3×3 supercell, taking fully into account the relaxation of the structure due to the hydroxyl group or the H vacancy. For both cases, a $2\times2\times1$ *k*-points mesh was used to obtain reliable geometry, and a final calculation with $8\times8\times1$ *k*-points mesh was conducted to obtain well-converged density of states.

In Fig. 4, we present our density of states for graphane +OH. The partial density of states of oxygen is presented for "*s*" and "*p*" states. It appears that the electronic structure of graphane is not significantly modified by the replacement of an H atom by the hydroxyl group. While the O-*s* states are very widely distributed in energy, the O-*p* states appear mainly as a peak close to the maximum of the valence band, between -1 and -2 eV.

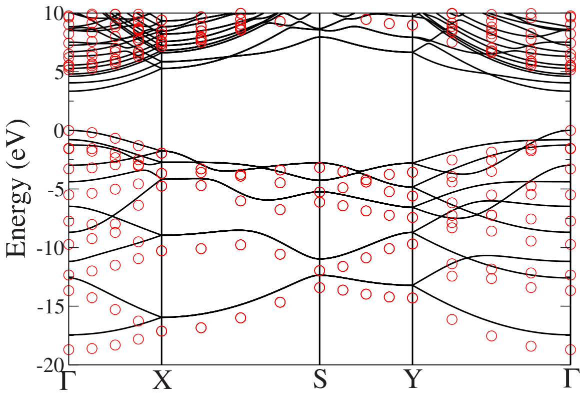

FIG. 3. (Color online) The GGA band structure (full lines) and the GW band structure (red dots) of graphane in the boat conformation. The top of the valence bands is chosen as the zero energy.

TABLE I. Values in eV of the transition energies of graphane at some high-symmetry points of the Brillouin zone for both conformers (chair or boat). The minimum band gap occurs at the Γ point. The last two lines refer to calculations performed with a 2×2 supercell, in which either a hydroxyl group (OH) or an H vacancy was introduced.

Conformation	Transition	GGA value (eV)	GW value (eV)
Chair	$\Gamma_v\rightarrow\Gamma_c$	3.5	5.4
	$M_v\rightarrow M_c$	10.8	13.7
	$K_v\rightarrow K_c$	12.2	15.9
Boat	$\Gamma_v\rightarrow\Gamma_c$	3.3	5.1
	$X_v\rightarrow X_c$	7.0	9.0
	$S_v\rightarrow S_c$	10.7	13.9
	$Y_v\rightarrow Y_c$	9.4	12.6
Chair+OH	$\Gamma_v\rightarrow\Gamma_c$	3.3	5.0
Chair+H vacancy	$\Gamma_v\rightarrow\Gamma_c$	3.7	5.4

Among the extra electrons brought by the oxygen atom, one electron is involved in a bond with the neighboring C atom, another electron is participating in the bond with H, and the two remaining electrons are forming a doublet on the oxygen atom. This is confirmed by the fact that the geometry of the network of carbon atoms, driven by sp^3 hybridization, is almost unaffected by the addition of the hydroxyl group. The band gap (from GGA) is slightly decreased, from 3.5 eV for pure graphane, to 3.3 eV here. Here as well, the band gap is underestimated by GGA, so we have applied the GW approximation to get a meaningful value. However, since the

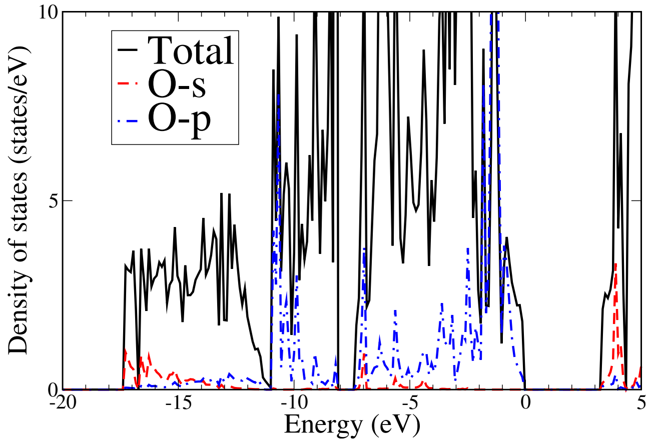

FIG. 4. (Color online) The total (in black) and partial (in red for O-*s* states and in blue for O-*p* states) density of states of graphane+OH. The top of the valence bands is chosen as the zero energy. To be visible on this graph, the O-*s* PDOS has been multiplied by 10, and the O-*p* PDOS has been multiplied by 5.

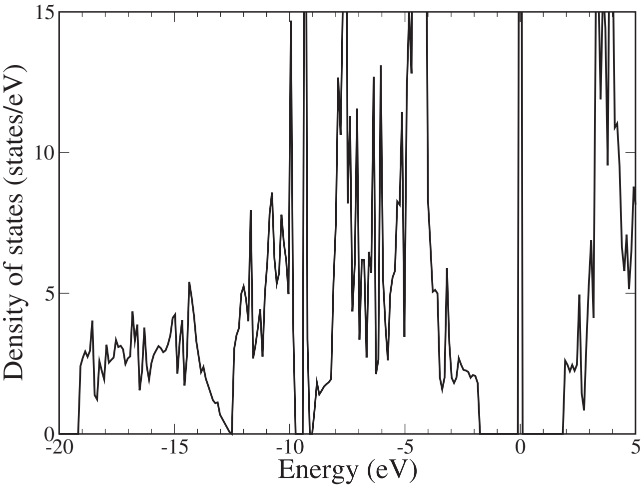

FIG. 5. The total density of states of graphane with an H vacancy, without spin polarization. The Fermi level is put at zero energy.

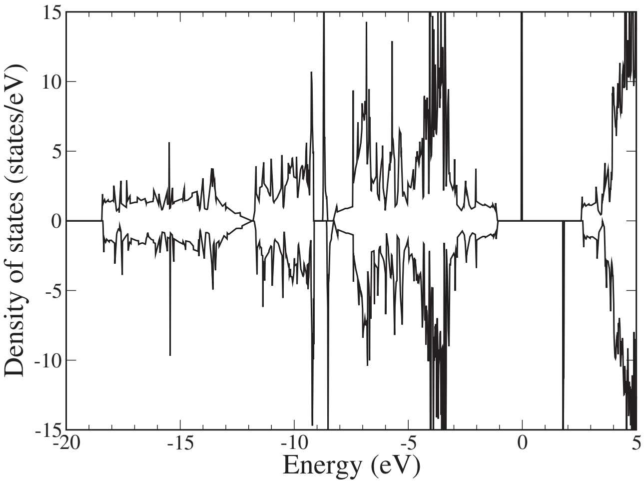

FIG. 6. The spin-polarized total density of states of graphane with an H vacancy. The Fermi level is put at zero energy.

numerical cost of the GW approximation is quite high, we had to reduce the size of the supercell to 2×2. In this case, the GW band gap is about 5.0 eV (see Table I) which is in line with the band gap of pure graphane (5.4 eV).

Next we introduced a single-hydrogen vacancy in graphane. Then, not every C atom of the graphane layer is saturated with an H atom. From inspection of the relaxed geometry, it appears that the bonds between the carbon neighboring the H vacancy and the carbon network have gained a significant part of sp^2 hybridization, such as in graphene, with bond lengths here of 1.49 Å (1.42 Å in graphene). The resulting total density of states is shown in Fig. 5. An impurity state develops close to 2 eV above the valence-band maximum, at the Fermi level, changing significantly the overall picture of the DOS. Also, using the GW approximation (for a 2×2 supercell), the difference in energy between the valence-band maximum and the conduction-band minimum is increased from 3.7 to 5.4 eV, but the impurity state at the Fermi level is not affected by the GW correction.

Since the impurity state at the Fermi level provided by the H vacancy is very narrow, we checked the possibility for the system to be spin polarized. This is indeed the case, as shown by the corresponding spin-polarized total density of states (Fig. 6). The impurity state is now split in an up and down component, each one lying on a different side of the Fermi level, and therefore the system is now insulating. A magnetic moment of about $0.4\mu_B$ is carried by the carbon atom which is the closest to the H vacancy, but the magnetic moments on neighboring atoms are almost negligible.

IV. CONCLUSION

To summarize, in this article, results concerning the electronic structure of graphane have been presented using the GW approximation. It was found that for both conformers, the minimum band gap is direct and located at the Γ point. For the stable chair conformation, the most stable one, it has a value of 5.4 eV, while for the boat conformation, it has a value of 4.9 eV. We also found that defects in graphane, in the form of H vacancies, provide some impurity states in the band gap, which can be checked, e.g., by measurements of optical conductivity of nonstoichiometric graphane.

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