

Ab-initio investigation of Graphane

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ABSTRACT

First-principles calculations employing the hybrid exchange functional B3LYP are used to determine the structural parameters, electronic structure and associated properties of a graphene sheet, graphane chair and graphane boat conformations. Graphane is found to have a band gap corresponding to an electronic insulator at room temperature. The relative performance of the B3LYP functional in comparison to calculations employing generalized gradient approximations (PBE) is also assessed. The B3LYP functional finds the band gap to be almost double that predicted by PBE methods. The choice of functional is found to be insignificant in the determination of the structural parameters

Keywords: dft, hybrid-exchange, graphane, electronic structure,

1 INTRODUCTION

Graphene is a two dimensionally periodic sheet of carbon atoms arranged in an hexagonal lattice. The recent development of relatively simple techniques for isolating such sheets by exfoliation from graphite¹ has lead to a significant increase in interest in the control of mechanical and electronic properties. Graphene has been proposed for use in a wide variety of applications².

An area of graphene research that shows great promise is the altering of its structure and composition to create graphene derivatives which have distinct electronic and magnetic properties comparative to the parent material. The graphene lattice can be considered as a single chemical entity, which could potentially react with specific adsorbates resulting in particular arrangements of patterns. The control of such patterns could give the ability to tune its properties. The simplest example of an adsorbate is the hydrogen atom and consequently the mechanisms behind hydrogen adsorption have been extensively researched^{3,4,5}. The possible existence and stability of a structure comprised of hydrogen atoms periodically bound to each carbon atom in the graphene lattice was theoretically predicted in 2007⁶. This structure was termed graphane and is thought to have two favorable confirmations; the chair and boat conformers (figure 1). An

interesting feature of graphane is the significant changes in the electronic structure of the graphene sheet that are predicted to be induced by periodic hydrogenation. Hydrogenation of graphene, a semimetal, to form graphane leads to an opening of a band gap and a thus a transition to an insulating state⁶. Graphane was recently synthesized by exposing an annealed graphene sample to cold hydrogen plasma for two hours⁷. This example demonstrates the potential of chemically altering graphene to create functional derivatives. In the case of graphane this functionality arises via the introduction of a band gap, which has far reaching consequences, for example in prospective applications in the electronics industry. The example also highlights the importance of the predictive power of electronic structure methods, which have a particularly important role to play in graphene research as properties are very sensitive to composition and long range structure, and experimental control of these factors is particularly challenging⁷.

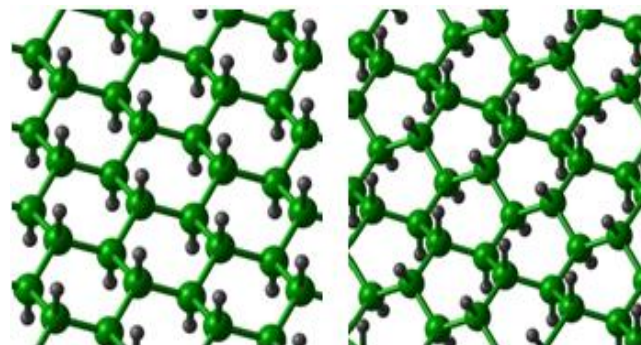


Figure 1-Graphane Chair (left) and Boat (right) conformations. Green atoms represent carbon atoms of graphene lattice and the black atoms correspond to adsorbed hydrogen

From a theoretical perspective the predominant method utilized in the quantum mechanical simulation of periodic systems such as graphene is density functional theory (DFT) as it provides a tractable theory of the ground state energetics while not relying on empirical parameterization. For example the work by Sofo et al and other more recent theoretical studies^{6,8,9} investigating the material have all employed DFT. A crucial component of a DFT calculation

is the choice of functional employed to treat electronic exchange and correlation. All the above mentioned studies employed functionals based on the generalized gradient approximation (PBE)¹⁰. The purpose of this work is to perform similar calculations using DFT, with a particular focus on computing the electronic structure and associated properties, along with the structural parameters, of the material. For this reason, in contrast to previous investigations, the functional of choice for this work is the hybrid exchange density functional in the B3LYP form^{11, 12, 13}. The mixing of nonlocal and semilocal exchange present in hybrid exchange functional overcomes the major flaws of the local spin-density approximation (LSDA)¹⁴ and, more pertinently, generalized gradient approximations (PBE) in the prediction of electronic and magnetic ground states for strongly correlated systems¹⁵. Specifically the B3LYP functional is thought to predict binding energies, geometries and frequencies systematically more reliably and with substantially improved performance compared to PBE methods¹⁶. Furthermore it is expected that band gaps calculated using B3LYP will be more accurate than those derived from PBE calculations, where the non analytic dependence of the effective potential¹⁷ on the density often leads to calculated gaps which are less than half their actual value¹⁵.

2 METHODOLOGY

The first-principles calculations in this work have been performed using the hybrid exchange density functional B3LYP in the CRYSTAL package¹⁸. In CRYSTAL the crystalline wavefunctions are expanded as a linear combination of atom centred Gaussian orbitals (LCAO) with *s*, *p*, *d* or *f* symmetry. The calculations reported here all electron, i.e. with no shape approximation to the ionic potential or electron charge density.

Basis sets of double valence quality (6-21G* for C and 6-31 G* for H) are used. A reciprocal space sampling on a Monkhorst-Pack grid of shrinking factor equal to 24 is adopted. The Gaussian overlap criteria which control the truncation of the Coulomb and exchange series in direct space are set to 10⁻⁷, 10⁻⁷, 10⁻⁷, 10⁻⁷ and 10⁻¹⁴. Typically linear mixing of 80% and an Anderson second-order mixing are used to guide the convergence of the SCF procedure

3 RESULTS AND DISCUSSION

Calculations were performed on graphene sheet, graphane chair and graphane boat confirmations. The geometries of all three structures were fully optimized. The respective structural and electronic data are presented in table 1.

Table 1-Structural parameters, total energy, formation energy and band gaps of three graphene and graphane

	Graphene Sheet	Graphane Chair	Graphane Boat
d_{C-C} (Å)	1.42	1.54	(a) 1.538 (b) 1.569
d_{C-H} (Å)	0.00	1.11	1.10
Lattice Parameter (Å)	2.46	2.54	(a) 2.53 (b) 4.32
Total Energy (per unit cell) (eV)	-2,071.49 (per C ₂)	-2,104.09 (per C ₂ H ₄)	-2,103.86 (per C ₂ H ₄)
Formation energy (per unit cell)		-0.70	-0.48
Band Gap (eV)	0.00	6.93	6.84

Firstly focusing on the structural data, optimization of the graphene sheet gave a lattice constant value of 2.46 Å with a corresponding C-C bond length of 1.42 Å. These optimized parameters were subsequently used as a starting geometry for the two graphane confirmations, with the initial C-H bond length set to 1.1 Å. In the graphane chair confirmation each carbon atom has a hydrogen atom bound to the opposite side of the graphene sheet in relation to its 3 nearest neighbors. While in the graphane boat confirmation this only applies to two nearest neighbors, with the remaining nearest neighbor having a hydrogen atom bound to the same side of the graphene sheet (figure 1). This difference has a notable effect on their respective structural parameters. After optimization the calculated C-C bond length of the graphane chair confirmation was 1.54 Å, which is significantly larger than that of the graphene sheet. This is due to the fact that each carbon in graphane is attached to a hydrogen atom and hence is sp³ hybridized, in comparison to the non-hydrogenated graphene sheet where all the atoms are sp² hybridized. This graphane C-C bond length is comparable to that in the sp³ carbon allotrope diamond which also has a C-C bond length of 1.54Å. In the boat confirmation H-H repulsion between neighboring carbon atoms with hydrogens bound to the same side of the graphene sheet leads to an extension of that particular C-C bond length leading to two distinct C-C bond lengths, this also breaks the hexagonal symmetry and lattice parameter values. As the (b) lattice parameter (table 1) lies parallel to the extended C-C bond it is extended relative to (a) and hence there are two different lattice parameter values.

In comparison to similar theoretical studies^{6, 8, 9} all of which employed GGA functionals, there are some slight differences in the structural parameters but no qualitative changes. This indicates that the detailed treatment of electronic exchange and correlation does not have a significant effect on structural properties. The small remaining differences could arise from the numerical

details of the calculations. For a quantitative comparison the data above (table 1) should be compared to table I in ref 6, 8, 9.

Comparing total energies (table 1), the graphane boat is a higher energy confirmation than the graphane chair. This instability is due to the aforementioned unfavourable repulsion between hydrogen atoms bound to adjacent carbon atoms on the same side of the lattice. The formation energy of each graphane confirmation was also calculated, this was defined as the total energy of a graphane structure minus the total energy of a plain graphene sheet minus the total energy of an individual hydrogen molecule. Following this the difference between the formation energies of each confirmation was computed, thus enabling a direct comparison of the calculated energies with those of other relevant theoretical investigations^{6, 8}. The calculated difference between the formation energy of the graphane chair confirmation and the graphane boat confirmation was found to be 0.225 eV per C_2H_2 , i.e. per unit cell, in favour of the chair confirmation. Sofo et al⁶ calculated what they term to be the “binding energy” difference between the two confirmations, which we assume is the same as what is defined as the formation energy in this study. Their binding energy difference is given as 0.055 eV/atom, also in favour of the chair confirmation. Assuming by units per atom they are referring to the energy required to bind a single hydrogen atom to a single carbon atom, and considering our value is defined per C_2H_2 , in order to make them directly comparable our calculated formation energy difference was halved to yield a value of approximately 0.1125 eV/atom. This is close to being exactly twice as large as the Sofo et al value. Initially this was believed to be a direct consequence of the choice of functional, as this study employed a B3LYP functional while Sofo et al a PBE functional. In order to test whether this was case, we repeated the calculations on the chair and boat confirmations but using a PBE as opposed to a B3LYP functional and computed the formation energy difference just as before. The formation energy difference between the two confirmations using the PBE functional was computed to be 0.222 eV per C_2H_2 in favour of the chair confirmation; which is almost exactly the same as the value that was calculated originally using the B3LYP functional. This therefore means that the observed difference is not a consequence of the functional used.

Looking at graphene’s electronic structure, it is termed a zero gap semiconductor because the highest occupied and lowest unoccupied bands become degenerate at a single point in k-space, the K point of the hexagonal lattices first Brillouin zone, and yet it still has a zero density of states at E_F (figure 2). This can be explained by the fact that graphene has two inequivalent carbon atoms per unit cell (denoted C1 and C2 in figure 2). As each of these atoms is sp^2 hybridised, they both have p_z orbitals perpendicular to the lattice plane, which combine to form the π interactions in graphene. In the periodic sheet the bands of those p_z

orbitals combine to form the π and π^* bonding and antibonding bands. As each band can hold up to two electrons and two electrons are donated from the two p_z orbitals per unit cell, the lower band is full and the upper band is empty. As a result the density of states at E_F is zero.

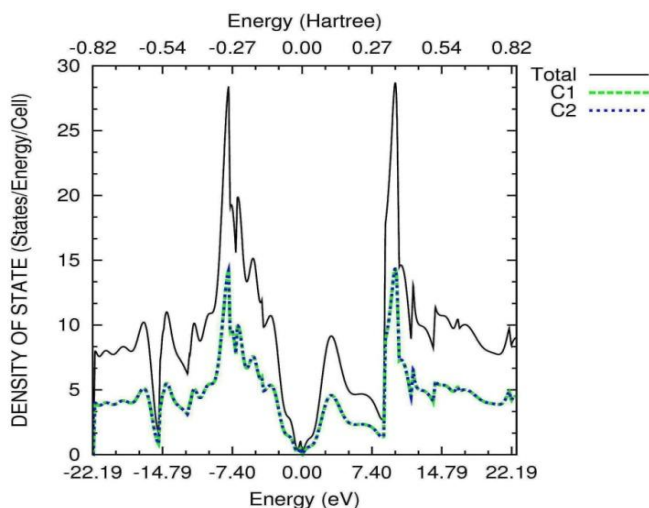


Figure 2-Total and projected density of states of graphene sheet. Projection is onto two inequivalent carbon atoms of the unit cell termed C1 and C2.

Hydrogenation of the graphene sheet to form graphane, results in a change in hybridization from sp^2 to sp^3 for each carbon atom. This therefore removes all π interactions and importantly the π conducting bands, thus opening an energy gap. The computed DOS displaying this band gap, with projections onto the carbon and hydrogen atoms of the unit cell is shown below (figure 3). As the electronic structures of both confirmations are qualitatively the same, only the DOS of the boat confirmation is presented. As the DOS shows the top of the valence band is comprised mainly of carbon p orbitals, while the bottom of the conduction band is more populated by hydrogen s orbitals (figure 3).

The calculated values of the band gaps (E_g) are displayed in table 1, the chair confirmation has a band gap of 6.93 eV, while the boat confirmation has band gap of 6.84 eV. This contrasts with the study by Sofo et al⁶ which found the chair confirmation to have an E_g of 3.5 eV while the boat confirmation has an E_g of 3.7eV. Two points that stand out are that firstly the boat confirmation has a higher E_g than the chair, the opposite is true in this work. Secondly and more importantly the band gaps are much reduced in comparison to those calculated in the current work. This also true of the E_g values computed by Samarakoon et al⁸ which found the band gaps to be 3.5 eV for both graphane confirmations. A probable reason for such a significant discrepancy is the choice of functional employed in the respective calculations. Both Sofo et al⁶ and Samarakoon et al⁸ use PBE functionals, while this investigation utilizes the B3LYP functional. In DFT the potential is computed from the total density and as each

electron contributes to this density, this means that self interaction of an electron with itself is always included. Band widths are usually overestimated and band gaps underestimated in PBE calculations for this reason. In the hybrid exchange functional the mixing of non-local Fock exchange corrects for the self interaction, and thus provides a much more reliable first order description of band gaps than PBE theory. It is therefore likely that the graphane structures described here will behave as electronic insulators at room temperature rather than semiconductors as previously predicted.

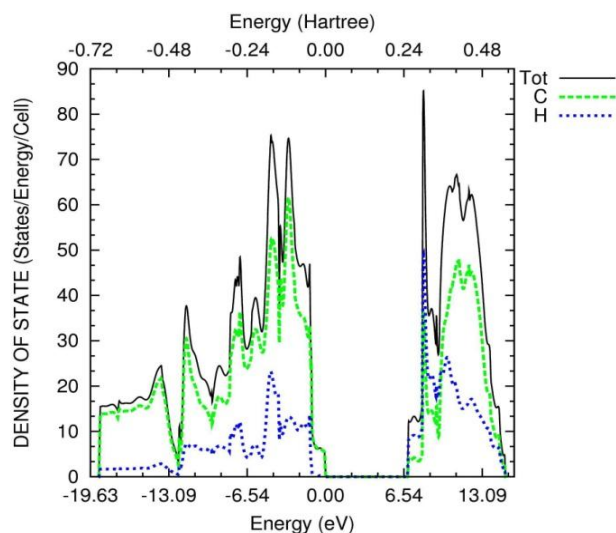


Figure 3-Total and projected density of states of graphane boat confirmation. Projection onto C and H

4 CONCLUSION

First-principles calculations using the hybrid exchange density functional B3LYP have been used to compute the electronic structure and band gaps of two confirmations of graphane. The size of these band gaps, 6.93 eV and 6.94, indicate that graphane is electrically insulating at room temperature. This is contrary to similar investigations^{6, 8} which through the size of their computed band gaps seem to indicate that graphane will be semiconducting at room temperature. As both 6, 8 treated the electronic exchange and correlation terms using PBE functionals, the observed results corroborate with the idea that the inclusion of the fock exchange when computing band gaps corrects for self interaction present in PBE functionals. The relative performance of the B3LYP hybrid exchange functional against PBE functionals in determining structural parameters and energies was assessed. Results seem to indicate that detailed treatment of electronic exchange and correlation does not have a significant effect on structural properties. Possible future work could involve assessing performance of B3LYP on different hydrogen adsorbed graphane structures, for example graphone. The

performance of B3LYP in treating magnetic graphene based systems could also be investigated.

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