First-principles study of bandgap effects in graphene due to hydrogen adsorption

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Abstract

Hydrogen adsorption on graphene in commensurate periodic arrangements leads to bandgap opening at the Dirac point and the emergence of dispersionless midgap bands. We study these bandgap effects and their dependence on periodicity for a single hydrogen adsorbate on periodic graphene supercells using spin-polarized density-functional theory calculations. Our results show that for certain periodicities, marked by a scale factor of three, the bandgap is suppressed to a great extent, and has a special level structure around the neutrality point. We present explanations for the origin of the changes to the band structure in terms of the \textit{ab initio} Hamiltonian matrix. This method may be used to obtain a more accurate tight-binding description of single hydrogen adsorption on graphene.

(Some figures may appear in colour only in the online journal)

1. Introduction

The isolation/discovery of graphene [1], a single layer of graphite, and the demonstration of its unusual electronic properties [2, 3] has attracted a lot of attention in the condensed matter physics community. The origin of the novel phenomena which were observed in these works lies in the special band structure of graphene that was studied theoretically several decades ago [4]. The theoretical analysis showed that the valence and conduction bands in graphene touch at only the two inequivalent corners of the hexagonal Brillouin zone (BZ), known as the Dirac points. The energy dispersion in the neighbourhood of these points is linear and the energy surfaces are in the shape of Dirac cones. The implication of all this is that the charge carriers would behave as two-dimensional (2D) massless chiral Dirac fermions [5] and possess their rich physical properties. Recently device engineers are also showing interest in graphene, because of its exceptional two-dimensional character and high-carrier mobility [6]. However, the zero-gap spectrum renders graphene a semimetal, which is a limitation for applications in logic circuits.

Hydrogen interaction with graphene is of diverse interest and has been the subject of many theoretical and experimental investigations. As recent studies have shown, hydrogen functionalization may induce a metal–insulator transition in graphene [7] and open a bandgap in its electronic spectrum [8–10]. Another interesting property, with potential applications in spintronics, is the emergence of magnetism in graphene materials due to interaction with hydrogen [11]. In addition, hydrogen adsorbates are believed to be a dominant source of scattering in graphene that limits its electron mobility [12, 13]. These and other fascinating properties provide the motivation to study and understand hydrogen interaction with graphene.

Much of the understanding of hydrogen adsorption on graphene has come through density-functional theory (DFT) calculations [14–19]. Thus it has been shown that hydrogen chemisorbs on graphene in an atop position, causing partial $sp^2$ to $sp^3$ rehybridization, and creating a $p_z$ orbital vacancy in the process (figure 1). This implies that hydrogen and vacancy defects have some common properties, such as magnetic moments and resonant scattering. The effect on the electronic structure, calculated by DFT on $n \times n$ graphene supercells with a single hydrogen adsorbate, is the appearance of a pair of spin-polarized states within a bandgap opened around the Dirac point. Other changes include the appearance of spin densities in the graphene plane in a characteristic $\sqrt{3} \times \sqrt{3}R30^\circ$ texture centred on the adsorption site which can be resolved by scanning tunnelling microscopy (STM) [16].
The midgap state is a universal feature of resonant scatterers shared by other covalently bonded adsorbates, including CH$_3$, NH$_2$, OH and F [20], making H/graphene a prototype of a wider class of systems. DFT calculations have been supplemented by a semiempirical tight-binding (TB) model to extend to larger numbers of atoms than can be handled in first-principles calculations. This model has been used in the study of an isolated hydrogen adsorbate [21] and random distributions of hydrogen adsorbates [22].

Recently, it was shown that bandgap opening has a strong dependence on the periodicity of the hydrogen arrangement on graphene [23], so that the bandgap is much smaller for certain periodicities than expected. The existence of different cases with respect to bandgap opening can be explained on the basis of the geometrical relationship between the Brillouin zones of graphene and its periodic superstructures (figure 2), although the precise changes to the band structures would require numerical calculations. In this paper, we focus on DFT calculations of the band structure of graphene with a single hydrogen adsorbate on periodically repeated unit cells in order to study the predicted dependence of bandgap effects on periodicity. We find that for the special periodicities the bandgap is suppressed to a great extent, particularly when spin polarization is neglected. Within spin-polarized calculations, the bandgap is somewhat wider and has a distinct and notable structure, not predictable within the commonly used simple tight-binding model. We attempt to explain the origin of these effects based on tight-binding models extracted from \textit{ab initio} Hamiltonian matrices. This approach is similar to the one used for an accurate tight-binding description of graphene [24]. We remark that the alternative semiempirical TB parameters, obtained by fitting to DFT-derived band structures, turn out to be very different from the \textit{ab initio} parameters. It seems, therefore, necessary to compare more closely the results obtained from semiempirical models and first-principles calculations wherever possible.

The rest of the paper is organized as follows. In section 2 we describe the computational details. In section 3 we present the results and discuss their salient features. In section 4 we present a summary and our conclusions.

2. Computational method

For the choices of $n \times n$ and $n\sqrt{3} \times n\sqrt{3}R30^\circ$ unit cells of graphene with a hydrogen atom adsorbed on top of one of the carbon atoms, as shown in figure 1, we obtain the electronic structure using DFT calculations. For all the calculations we used the SIESTA DFT code, an efficient code that allows us to study relatively low adsorbate coverages of H/graphene, with supercells of up to a few hundred carbon atoms. The
calculations use a basis set of numerical atomic orbitals [25],
norm-conserving pseudopotentials [26] and the generalized
gradient approximation (GGA) of the exchange–correlation
density functional [27]. The use of localized atomic orbitals in
SIESTA makes it convenient to extract tight-binding matrix
elements from the Hamiltonian matrix. Our calculations use
the diagonalization-based method of solving the Kohn–Sham
equations and include both restricted and unrestricted spins.
We chose a separation of 20 Å between repeated slabs, to
represent the 2D systems, and for k-point sampling we used
various Monkhorst–Pack grids [28] typically corresponding
to 36 × 36 × 1 points in the graphene Brillouin zone (Γ
included). The systems were fully relaxed, until the atomic
forces were smaller than 0.01 eV Å−1, before calculation of
the band structure and density of states. We used basis
sets of double-ξ plus polarization (DZP) quality for most of
the results reported, and also single-ξ (SZ) quality, to reduce
computing time, for some of the data involving larger systems.

3. Results

Our systems consist of periodically repeated supercells
containing one hydrogen adsorbate and an integral number of
graphene unit cells (figure 1). This configuration is commonly
used to describe single hydrogen adsorption on an infinite
graphene, under the assumption that if the n × n supercell
is large enough, say n ≥ 4, H adsorbates may be considered
as isolated from each other. Various properties, however, do
depend on the scale of the supercell, as we demonstrate in this
section.

Figure 1 shows two samples of hydrogenated graphenes,
√3 × √3R30° and 3 × 3, which show the periodic arrangement and
also happen to represent special periodicities, to be
explained below. Since it has been established that covalently
bonded hydrogen chemisorbs on top of a carbon atom we
simply used this placement in our calculations and allowed
our DFT code to perform structural relaxation to find the
bond lengths and angles. We found results in agreement with
previous calculations, where the H–C bond is 1.13 Å and the
C–C bond elongates from 1.42 to 1.51 Å as a result of sp2
hybridization. The bond angles do not form the perfect
tetrahedral angles of 109.5°, but have a mixed character
between the two types of hybridization and, furthermore, they
may depend on hydrogen concentration.

Our focus is on the changes made to the band structure
as a result of hydrogen adsorption and on the understanding of
their underlying causes. Towards this end it is useful to compare with the simple spinless tight-binding model that describes hydrogen adsorption on graphene and includes only π bands:

\[ \mathcal{H} = -\gamma_{CC} \sum_{i,j} c_i^\dagger c_j + \varepsilon_H d^\dagger d + \gamma_{HC}(c_i^\dagger d + d^\dagger c_0). \]  

Typical values are χCC = 2.7 eV for hopping between the
carbon 2pz orbitals, \varepsilon_H = −0.2 eV for the hydrogen 1s orbital
on-site energy relative to that of carbon 2pz, and \gamma_{HC} =
−5.2 eV for hopping between H and C orbitals [20]. This is a
semiempirical model whose parameters were derived
by fitting particular DFT band structure calculations and it
provides a useful description of the midgap resonance.

If we use the tight-binding model given by (1) to calculate
the band structures for 4 × 4 or 5 × 5 hydrogenated graphenes we
find bandgap openings at their respective K-points and an
almost dispersionless midgap band. On the other hand, if we
use it to calculate the band structure for √3 × √3R30° and
3 × 3 coverages no bandgap opens, while the degeneracy
point shifts to the Γ-point with the additional low-dispersion
midgap band passing through it. These √3 and 3 structures,
which have unit cells that contain three and nine unit cells
of graphene, respectively, are somewhat exceptional because the
hydrogen adsorption fails to open an expected gap in their
band structure. The difference between these and the ordinary
cases can be deduced from the Brillouin zone structures drawn in
figure 2. As shown in figures 2(a) and (b), related to √3 ×
√3R30° and 3 × 3, respectively, both K-points of graphene
coincide with the Γ-point of the hydrogenated graphene for
these structures. As a result there is a fourfold degeneracy at
the Γ-point in the centre of the Brillouin zone. On the
other hand, for the other structures, 4 × 4 and 5 × 5, shown in
figures 2(c) and (d), the K-points of graphene coincide with the K-points of hydrogenated graphene at the corner
of the Brillouin zone. As bandgap opening due to periodic
perturbations occurs on the boundaries of the Brillouin zone,
the above observation accounts for the dependence of bandgap
opening on periodicity. Such a phenomenon can also be
seen in alkali metal adsorption, which has different bonding
properties and most notably adsorbs on the hollow sites of
graphene instead of the top sites [29]. For alkali metals,
however, the situation is reversed in that bandgap opening is
absent for the regular cases and occurs instead for the
periodicities that involve a multiple of three.

We can now examine band structures for the coverages
discussed above calculated numerically using spin-polarized
DFT. All four band structures, shown in figure 3, have
spin-polarized bands, indicating a magnetic moment of 1 μB
per unit cell, with the exchange splittings that decrease as H
concentration is reduced. Figures 3(a) and (b) for √3 ×
√3R30° and 3 × 3 coverages show small, but finite, bandgap
openings at the Γ-point. The shift of the neutrality point and
gap opening to the Γ-point is in agreement with the analysis in
terms of the Brillouin zones. But in contrast with the simple
TB model which gives zero bandgap, here there is a small
bandgap due to additional symmetry breakings induced by
H adsorption. Figures 3(c) and (d) show the regular cases of
4 × 4 and 5 × 5 coverages where graphene bands open a gap
at the K-point and there is a pair of spin-polarized midgap
bands. The projected densities of states corresponding to the
4 × 4 band structure are also shown in figure 4(a). The energy
bands around the gap in figures 3(a) and (b) have an intricate
structure. The majority up-spin midgap state is degenerate
with the top of the graphene π band at the Γ-point below
the Fermi energy, and the same is mirrored for the minority
down-spin midgap state and the bottom of π∗ band above
the Fermi energy. The origin of this structure must be an
additional symmetry breaking not accounted for in the TB
model of (1).
Figure 3. Band structures of hydrogenated graphene shown for a window surrounding the neutrality point for (a) $\sqrt{3} \times \sqrt{3}R30^\circ$, (b) $3 \times 3$, (c) $4 \times 4$ and (d) $5 \times 5$ structures. The bands are split into pairs due to spin polarization. In (a) and (b) graphene $\pi$ bands open at $\Gamma$, while in (c) and (d) they open at $K$. The points $\Gamma$, $K$ and $M$ represent the centre, corner and middle of the side of the hexagonal Brillouin zones of the corresponding structures, respectively.

An AB sublattice symmetry breaking can be expected on account of the formation of spin and charge textures due to hydrogen chemisorption (see figure 4(b) and [16]). We can uncover it by examining the ab initio Hamiltonian matrix [24], of which we list the most important elements in table 1. If we use a tight-binding model based on this table, we can reproduce the bandgap level structures of figures 3(a) and (b). The AB symmetry breaking is clearly seen in the spin-dependent on-site energies, which are tabulated for the $1s$ orbital of H, and a set of $2p_z$ orbitals of C atoms, indexed with 0–3, which includes the adsorption site and its three nearest neighbours (they occupy the triangular shape in figure 4(b)). Note that the even indices refer to the sublattice of the adsorption site and the odd indices to the complementary sublattice. Setting aside the singular $C_0$ for the time being, the AB sublattice symmetry breaking is manifested in the on-site energies for the three $C_1$, the six $C_2$ and the three $C_3$ sites. In particular, for up-spin parameters the energy of $C_2$ is higher than those of $C_1$ and $C_3$. For the down-spin parameters the sense of symmetry breaking is reversed with the energy of $C_2$ lower than that of $C_1$ and $C_3$. It is precisely this ordering that lifts the degeneracies of $\sqrt{3} \times \sqrt{3}R30^\circ$ and $3 \times 3$ coverages in the manner shown in figure 3.

Returning to the case of $C_0$, we note that its on-site energy has been shifted down by more than 2 eV relative to the other carbon atoms. We also see that the $C_0$–$C_1$ hopping is suppressed by nearly 1 eV relative to its value for clean graphene, which is $-2.96$ eV for the basis set used in our calculation. The usual description of the effect of hydrogen chemisorption on the electronic structure of graphene is that it removes a $p_z$ orbital from the $\pi$ system of graphene [11, 16]. As a consequence a quasi-localized state is formed which populates the complementary lattice. This in turn gives rise to a midgap energy level near the Fermi energy which makes the system unstable with respect to spin polarization. The shifted values of the on-site energy and the hoppings in table 1 that make $C_0$ different from other C atoms provide quantitative parameters for this description.

Finally, from table 1 we note that the on-site energy of H is a few electron-volts below that of the carbon atoms, which is what we expect when we think in terms of atomic orbitals. This is another important difference with the semiempirical model of (1), where $\varepsilon_H = -0.2$ eV. The TB model (1), however, provides a better description of a dispersionless midgap band near the Fermi energy. The shortcoming of the present ab initio model is that next-neighbour hoppings and

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1 Obtaining the ab initio tight-binding parameters does not need any extra calculations, because the Hamiltonian, overlap matrices, etc, are printed by SIESTA to special files, SystemLabel.HSX in binary format, and DMHS.NC in NetCDF format. Our task is only to open either of these files with the appropriate tools and read the selected elements.
Figure 5. Bandgap openings at K-point for a number of structures up to 11 × 11 coverage, 242 atoms, as a function of the number of carbon atoms in the unit cell. n. Special structures, 3 × 3, etc, which have very small bandgaps and do not follow the trend, have been left out. Exchange splittings are plotted for the whole sequence and are seen to be about a third of the corresponding bandgaps. The trend for both curves is $\propto 1/n$.

4. Conclusions

We have made density-functional theory calculations of graphene with periodic arrangements of hydrogen adsorbates. Our focus was to explore and explain the changes made to the electronic band structure of graphene as a result of hydrogen adsorption. The important features include bandgap opening and the emergence of spin-polarized midgap bands, which we have collectively described as bandgap effects. Our primary purpose was to examine the dependence of bandgap effects on hydrogen periodicity, or coverage, within spin-polarized density-functional theory. We showed that for periodicities divisible by three or a $\sqrt{3}$ bandgap opening has a different behaviour than for four, five and, in general, for periodicities not divisible by three. We illustrated that the existence of different classes has purely geometrical reasons. In addition, the changes to the band structures have special features, which we explained on the basis of the AB sublattice symmetry breaking that is caused by hydrogen adsorption. A secondary purpose was to gain a deeper understanding of bandgap effects by examining the ab initio Hamiltonian matrix elements. The tight-binding parameters obtained by this approach reveal the AB sublattice symmetry breaking, as well as the origins of the midgap bands. These parameters are physically more meaningful than those of the simple semiempirical model and may be developed into a more accurate tight-binding description of hydrogen adsorption on graphene.

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