Density-Functional Theory and Tight-Binding Studies of the Geometry of Hydrogen Adsorbed on Graphynes

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Using density-functional theory and a tight-binding approach we investigate the physical origin of distinct favourable geometries of adsorbed hydrogen atoms in various graphyne structures, and the relation with electronic properties. In particular, H atoms are adsorbed in-plane for α-graphyne, and they assume an oblique configuration in all other graphynes, including 6,6,12-graphyne. The origin of different configurations is identified by means of a simple tight-binding model and it is controlled by the tuning of the hopping between sp2-bonded C atoms and sp-bonded C atoms hybridized with the H atoms. We discuss in details how the geometry change of the attached H atom tunes the electronic properties like energy gap.

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I. INTRODUCTION

The synthesis of graphene, a two-dimensional atomic layer of carbon atoms on a honeycomb lattice, has generated a new area of condensed-matter physics in which basic physics associated with the existence of Dirac cones is intertwined with a huge potential for applications such as electronic devices, hydrogen storage materials, and lithium-ion battery materials.1–4

Device-oriented applications of graphene are based on the possibility to open and tune a band gap from the semimetallic Dirac states5–7. This can be realized by breaking the sublattice symmetry or the chiral symmetry8–11 and by chemical functionalization of adsorbing hydrogen or fluorine on graphene12,13. Even if the functionalization could in principle open the gap, the adsorbed atoms tend to segregate in clusters, strongly limiting the applicative potential of these phases.

A different route to gap-tuning in graphene-like structures is recently offered by graphynes14–18. Graphynes can be ideally obtained inserting carbon atoms with triple bonds (C≡C) between pairs of sp2-bonded carbons in graphene, forming a sp-sp2 hybrid carbon network on a two-dimensional hexagonal lattice.19 Different graphyne structures have been proposed according to position and number of added C≡C units. In Figs. 1 (a), (b), (c), and (d) we show the so-called α-, β-, γ-, and 6,6,12-graphynes. Density functional theory (DFT) calculations predict a semimetallic state with Dirac cones in α- and β-graphyne and a semiconductor with a band gap of 0.47 eV in γ-graphyne.16,17 More recently, a semimetallic state with double Dirac cones has been predicted for 6,6,12-graphyne.18

Just like in graphene, one can in principle open and tune a band gap in the different graphyne structures. Some of us have shown by means of DFT calculations that adsorbed hydrogen atoms prefer different geometries according to the type of graphyne, leading in turn to different electronic properties. For instance, H atoms in α-graphyne (C1H0.75), where each sp-bonded C atom accommodate one H atom, prefer an in-plane configuration and the electronic structure remains semimetallic regardless of the attached H atoms, while H atoms adsorbed on γ-graphyne prefer an oblique configuration with respect to the plane, and the energy band gap dramatically widens to 2.19 eV from the 0.47 eV of the pure compound16.
These results confirm the possibility to tune the electronic properties via hydrogenation also in view of applications. As opposed to graphene, H atoms are able to diffuse in graphynes, opening a path towards application opportunities in devices and and hydrogen storage.

![Graphyne Bandstructures](image)

**FIG. 2**: (Colour online) Bandstructures along the M-Γ-K-M directions of (a) α-, (b) β-, and (c) γ-graphynes calculated by DFT and tight-binding calculations with in-plane H atoms. The energies are in unit of eV and referred to the Fermi energy. α and β-graphyne behave as semimetal, while the γ-graphyne is an insulator with a gap of 0.34 eV.

Here we performed DFT calculations with more k-points than former DFT ones for hydrogenated α- and γ-graphynes, and we newly carried out DFT calculations for hydrogenated β- and 6,6,12-graphynes. In order to identify the physical origin of these different arrangements, we use a tight-binding approach based on the DFT results, and we connect the angle between the C-H bond and the graphyne plane (i.e., the geometry of the adsorbed H) to the hopping between neighbouring sp²-bonded C atom and sp-bonded C with attached H.

Our tight-binding calculations confirms that in α-graphyne the energy is minimized by the hopping which corresponds to in-plane H atoms, while for β- and γ-graphynes tuning the above-defined hopping parameter leads to a lower energy for a finite angle, identifying the physical mechanism behind the different geometrical arrangements.

Finally, we find that adsorption of one H atom per C in 6,6,12-graphyne turns the semimetal into a semiconductor and we discuss the geometric and electronic properties of hydrogenated compound.

The paper is organized as follows: in Sec. II and III we describe the computational detail of the electronic structure calculations and the tight-binding model, respectively. In the first and second parts of the Sec. IV we discuss the DFT as well as TB results of hydrogenated α-, β-, and γ-graphynes in in-plane and optimal configurations of the attached H atom in C atoms, respectively. In the last part of the Sec. IV we analyse geometrical and electronic structures of the optimal 6,6,12-graphyne using the DFT calculations. In Sec. V we summary our findings.

**II. COMPUTATIONAL DETAILS**

Our calculations were performed using a first-principles method based on density functional theory as implemented in the Vienna Ab-initio Simulation Package with a projector-augmented-wave (PAW) method. The exchange correlation energy functional was used with the generalized gradient approximation in the PerdewBurkeErnzerhof scheme, and the kinetic energy cutoff was set at 400 eV. Our model graphyne systems were a 1 × 1 hexagonal cell. A geometrical optimization of H-adsorbed α-graphyne was carried out within a fixed 1 × 1 cell obtained from the equilibrium lattice constant of the isolated graphyne until the Hellmann-Feynman force acting on each atom was less than 0.01 eV/A°. The first Brillouin zone integration was done using the Monkhorst-Pack scheme. A 8 × 8 × 1 k-point sampling was done for the 1 × 1 graphyne cell. To remove spurious interactions between image structures due to periodic calculations, a vacuum layer of 12 Å was taken in each of all nonperiodic directions.

**III. TIGHT-BINDING MODEL**

We performed DFT calculations on hydrogenated α-, β-, and γ-graphyne in the configuration where each sp-bonded C atom accommodates one in-plane H atom. We chose Nc = 8, 18, and 12-sites in the unit cell for α-, β-, and γ-graphynes, respectively and we optimized the lattice parameters. The blue circles in Figs. I (a), (b), and (c) show the position of sp-bonded C atoms hybridized with the H atoms on α-, β-, and γ-graphynes with chemical formula C1H0.75, C1H0.67, and C1H0.5, respectively. We obtained that α- and β-graphynes are semimetal and γ-graphyne is semiconducting with a band gap of 0.34 eV. These results are qualitatively and also quantitatively similar to those of pure graphyne.

Based on these DFT results we have derived a tight-binding Hamiltonian. Our parameterization neglects the...
hybridization effects between the sp-bonded C atoms and the attached H atoms because the DFT results do not show significant differences in the electronic structures of pure and hydrogenated graphynes. Consequently, we assume that the bonding configuration among the p_e orbitals of different sites still form \( \pi - \pi^* \) bands, like pure cases without H atoms.

Our tight-binding Hamiltonian has therefore the form

\[
H = - \sum_{\langle ij \rangle, \sigma} t_{imn'} (c_{im, \sigma}^\dagger c_{jmn', \sigma} + H.c) - \mu_{m'} \sum_{im', \sigma} n_{im', \sigma},
\]

where the site index \((i \text{ or } j)\) runs over all the carbon atoms, which can be either sp^2-bonded (labelled as “2”) and sp-bonded (labelled as “1”) hosting a H atom. The two carbon atoms have different local energies \( \mu_m \) with \( m = 1, 2 \). The hopping is restricted to nearest neighbours, but different hopping amplitudes are associated to bonds connecting (i) two sp-bonded C atoms \((t_{11})\), (ii) one sp^2-bonded carbon with one sp-bonded hydrogenated carbon \((t_{12})\) and (iii) two sp^2-bonded C atoms \((t_{22})\). The hoppings and local energies are obtained simply by fitting the DFT bands.

### IV. RESULTS

#### A. In-plane absorption on hydrogen atoms

As mentioned above, we start from DFT calculations with in-plane H atoms. The hopping parameters \( t_{imn'} \) and on-site energies \( \mu_{m'} \) that we obtain by fitting results for \( \alpha-, \beta-, \text{and } \gamma\)-graphynes are presented in Table 1 (the energy unit is eV). Since \( \alpha\)-graphyne is topologically equivalent to graphene, we can estimate an effective hopping between carbon atoms in the graphene honeycomb lattice. We obtain a value of 0.7 eV, which is slightly smaller than that of graphene and pure \( \alpha\)-graphyne without the absorbed H atoms.

In principle one may expect that both \( \beta\) and \( \gamma\)-graphynes should become insulating with a charge-density-wave ordering because of the broken symmetry between the two sublattices, as it has been observed recently in quasi-neutral molecular graphene with an additional CO molecule. Our calculations confirm this expectation only for \( \gamma\)-graphyne, while the \( \beta\)-graphyne configuration remains semimetallic.

#### TABLE I: \( t_{22} \) is the hopping between sp^2-bonded C atoms, \( t_{12} \) is the hopping of between the sp^2-bonded C atoms and sp-bonded C atoms with adsorbed H atoms, and \( t_{11} \) is the hopping between sp-bonded C atoms with the absorbed H atom. \( \mu_1 \) and \( \mu_2 \) are on-site energies in C and C atoms with the attached H atom, respectively.

| Graphynes  | \( t_{22} \) | \( t_{12} \) | \( t_{11} \) | \( \mu_1 \) | \( \mu_2 \) |
|------------|---------------|---------------|---------------|---------------|---------------|
| \( \alpha \) graphyne | 0.0 | 2.458 | 2.561 | -0.0781 | 0.0987 |
| \( \beta \) graphyne | 3.1772 | 2.6670 | 2.4369 | -0.2046 | 0.11081 |
| \( \gamma \) graphyne | 2.3964 | 2.3833 | 3.1987 | 0.4844 | -0.4491 |

#### FIG. 3: (Colour online) The calculated tight-binding energy gap (Energy gap) as a function of \( \eta \) for \( \alpha-, \beta-, \text{and } \gamma\)-graphynes. The renormalization parameter \( \eta \) is related to geometrical configuration of H atoms attached in sp-bonded C atoms.

In order to account for why the Dirac cone is still present in \( \beta\)-graphyne but absent in \( \gamma\)-graphyne, we write the simple \( 2 \times 2 \) Hamiltonian on honeycomb structure with different hopping \( \tau_1 \) and \( \tau_2 \) along the inequivalent directions. The Hamiltonian is given as

\[
H = \begin{pmatrix}
0 & f(k) \\
\bar{f}^*(k) & 0
\end{pmatrix}
\]

with \( f(k) = \tau_1 e^{ik_x} + \tau_2 (e^{i(-\frac{2\pi}{3} + \frac{2\eta \mu_2}{\sqrt{3}})} + e^{i(-\frac{2\pi}{3} - \frac{2\eta \mu_2}{\sqrt{3}})}) \) and the lattice constant between sites is set into one for simplicity. The \( 2 \times 2 \) matrix structure is associated to inequivalent lattice sites on the two sublattices. It is easy to verify that a Dirac dispersion is present only if \( |\tau_1| \) is smaller than \( 2|\tau_2| \). The DFT results can be therefore rationalized in terms of the effective hopping between C atoms on the sites of the honeycomb lattice. The semimetallic state in \( \beta\)-graphyne is therefore explained by an effective \( \tau_1 \) smaller than \( 2t_{22} \), while the charge-density-wave insulating state with a band gap of 0.23 eV of \( \gamma\)-graphyne is a consequence of a larger effective hopping on the ideal honeycomb lattice, which satisfies \(|\tau_1| > 2t_{22}| \).

#### B. Optimal configurations of the attached H atoms

DFT calculations show that the in-plane configuration of the attached H atoms is stable only in semimetallic \( \alpha\)-graphyne, while \( \beta\) and \( \gamma\)-graphynes choose a finite-angle configuration with a band gap of 0.27 eV and 2.19 eV, respectively. Here we elaborate on the physical origin
We denote with $t$ the value of the hopping element. We define a renormalization parameter $\eta$ for $\alpha$, $\beta$, and $\gamma$-graphyne systems. Therefore, a finite angle between the C-H bond and the $\pi$ and sp-bonded C with H atom would be reduced, because the H atom attracts the sp hybridization between sp$^2$-bonded C with H atom would be reduced, because the H atom attracts the $\pi$ orbital in sp-bonded C atom. Thus, a finite angle between the C-H bond and the graphyne plane reflects in a reduced hopping element $t_{12}$. We denote with $t_{12}^{\text{inplane}}$ the DFT-derived value for an in-plane H adsorption and we perform calculations tuning the value of $t_{12}$ to effectively take into account a finite angle. We define a renormalization parameter

$$\eta = \frac{t_{12}^{\text{inplane}} - t_{12}}{t_{12}^{\text{inplane}}}$$

so that $\eta = 0$ and 1 describe the in-plane configuration and the complete separation between the hexagons, respectively.

In Fig. 3 we plot the energy gap as a function of $\eta$ for our tight-binding representations of $\alpha$, $\beta$, and $\gamma$-graphyne. For $\alpha$-graphyne the system remains semimetallic increasing $\eta$. On the other hand, in $\gamma$-graphyne the gap increases linearly with $\eta$, reaching the DFT value of 2.19 eV for $\eta = 0.33$, which corresponds to $t_{12} = 1.58$ eV. For $\beta$-graphyne, the gap opens for $\eta = 0.23$.

In Figs. 4 (a) and (b) we compare the DFT bandstructures of $\beta$- and $\gamma$-graphyne with those obtained in the tight-binding model for the value of $t_{12}$ which reproduces the DFT gap at the M-point of the Brillouin zone, namely 2.41 eV ($\beta$) and 1.58 eV ($\gamma$). This comparison measures to what extent our simple idea to model the geometrical character of the adsorbed H atoms reproduces the actual DFT calculations. The agreement is extremely good over the whole Brillouin zone for $\gamma$-graphyne, while some discrepancies are visible in $\beta$-graphyne. We conjecture that the discrepancy is most likely due to next nearest neighbour hopping term, which we neglect here in order to keep the model as simple and transparent as possible.

Finally, we plot the band energies as a function of $\eta$ including the four lowest-energy bands around Fermi level at each graphyne in Fig. 5 for $\alpha$-graphyne the energy is minimized by $\eta = 0$, confirming that the adsorbed H atoms prefer to sit in the plane, as in DFT. On the other hand, for $\gamma$-graphyne the energetically favoured configuration is $\eta = 1$, which corresponds to separated hexagons, while in the actual DFT calculation a given configuration with oblique H configuration is stabilized by lattice deformation and hybridization between C and H atoms, which are not included in our very simple tight-binding model. As mentioned above, if we compare energy band, a coefficient $\eta = 0.33$ reproduces the correct gap amplitude and the overall bandstructure.

C. Hydrogenated 6,6,12-graphyne

In this section we investigate within DFT the electronic properties of hydrogenated 6,6,12-graphyne with a concentration of C$_1$H$_{56}$, where each sp-bonded C atoms hosts one H atom. Recent calculations have revealed a double Dirac cone for pure 6,6,12-graphyne. We start our analysis by optimizing the H positions within the in-plane configuration. Here the Dirac cones are found to be replaced with a small band gap opening of 0.03 eV as a consequence of the broken sublattice symmetry in x+y directions.

![Graphene Band structures](image-url)
and x-y directions.

Next, we find the optimal lattice structure releasing the in-plane constraint for the H atoms. The optimal lattice structure with an oblique configuration of the H atoms attached in sp-bonded C atom and the electronic structure with an energy gap of 1.17 eV are shown in upper and lower parts of Fig. 6, respectively. The attached H atoms in the oblique configuration determine a larger symmetry breaking potential with respect to the in-plane configuration in the 6,6,12-graphyne. Therefore, the energy gap becomes much larger and the oblique state is energetically stabilized, just like in γ-graphyne.

V. SUMMARY

In conclusion, we have explored the geometrical configurations of H atoms absorbed on sp-bonded C atoms of α-, β-, γ-, and 6,6,12-graphynes and the consequent electronic properties. In the latter case we show for the first time that adsorption of hydrogen removes the Dirac cones of pure 6,6,12-graphyne leading to a semiconductor with a gap of 1.17 eV which strongly depends on the H atom configuration.

Using DFT calculations, we first studied the electronic properties of the cases with in-plane configurations of the adsorbed H atoms in α-, β-, and γ-graphynes. And then, we established a simplified tight-binding model with lattice parameters based on the in-plane configurations of attached H atoms. Starting from the tight-binding model, we mimicked the p\textsubscript{z}-p\textsubscript{z} hybridization associated to an off-plane oblique configuration by means of a tuned hopping parameter. This simple picture allows to understand why the in-plane configuration of H atom is stable in α-graphyne, while oblique configurations are favoured in β- and γ-graphynes. Moreover, we find that these different geometrical configurations strongly affect the opening and the size of the energy gap, suggesting possible directions to control it in view of applications.

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