

Research Article

Influence of Electric Field in the Adsorption of Atomic Hydrogen on Graphene

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The influence of external electric field (EF) in the adsorption of atomic hydrogen on graphene (H/G) was studied by means of electronic structure calculations based on spin-polarized density functional theory with generalized gradient approximation (GGA). The changes in atomic hydrogen physisorption-chemisorption on graphene owed to EF (which ranged between -1.25 V/\AA and 0.75 V/\AA) were determined. Analysis of the electronic charge density for an H/G system explained the EF influences on the adsorption properties (analyzing changes in electronic charge density for H/G system). A decrease of more than 100% in the chemisorption barrier for an EF of -1.25 V/\AA was found. The changes in the electronic charge density confirm the possibility of manipulating the physical-chemical adsorption of hydrogen on graphene by applying electric fields.

1. Introduction

Hydrogen (H) is the simplest element known and is one of the most abundant elements in the earth and is expected to have a highly relevant role in the energetic infrastructure of the future, as it has many important advantages over other fuels such as oil [1]. H is an energy carrier and can be stored in various solid materials via reversible sorption processes or chemical reactions. Hydrogen storage technologies have attracted considerable attention because of demands for cleaner and safer energy sources. However, there are several problems with hydrogen storage systems in terms of portability and safety that must be overcome before hydrogen is feasible for use as a green technology [2]. Among these, the most difficult challenge is to find materials that can store hydrogen with large gravimetric and volumetric density and operate under ambient conditions (thermodynamic properties). One important requirement regarding storage materials is weight; they must preferably be made from light elements. Another is the need for hydrogen binding energy between physisorption and chemisorption. To overcome the above problems and to balance both binding energies and weight percentage, recent efforts have been

devoted to studying carbon materials as promising candidates for hydrogen storage [1, 3–6].

Carbon nanomaterials offer different structural arrangements classified by their dimensionality and the type of hybridization presented among their chemical bonds. Graphene (G) is associated with a graphite monolayer and is constituted by hexagonal structures of carbon atoms, bound strongly by covalent bonds characterized by a sp^2 hybridization, occurring in great abundance in nature. The initial studies on G were highly influenced by predictions that Wallace made in 1947, who examined its particular linear electronic dispersion relation with $E(\mathbf{k})$ [7]. Later in 1961, the first reports of its synthesis as graphite oxide appear [8]. In recent years, G has attracted the attention of theoretical and experimental researchers because of synthesis developments and also because of interesting electronic and quantum properties that could be employed in future and present technologies [9–16].

The interactions between adatoms and G are important because they imply a wide range of possible applications of this bidimensional nanomaterial: catalysis, batteries, transistors, and spin filters, among others [17–19]. In this context, adsorption of H atoms on graphene (H/G) can be used to

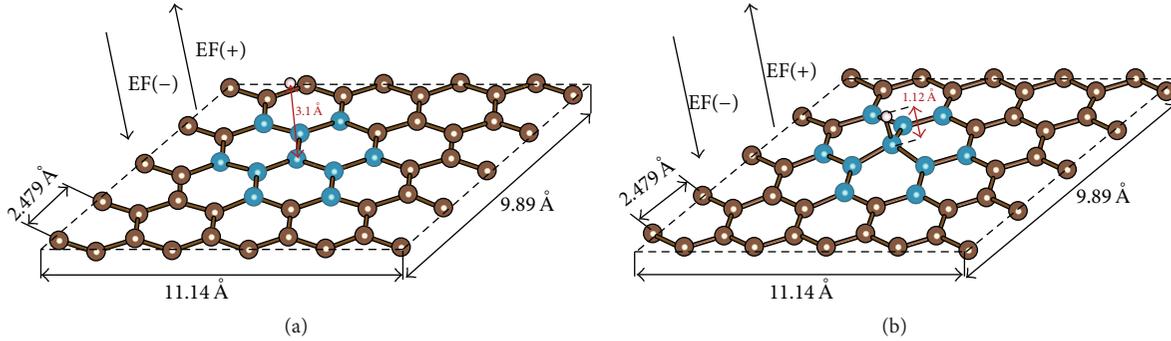


FIGURE 1: Structural parameters of the graphene supercell, with the two directions of the electric field (EF), for physisorption (a) and chemisorption (b). The unconstrained carbon atoms are represented in blue.

tailor physical and chemical properties. Reaction in H/G produces changes in electronic and phonon properties [4]. Through such hydrogen loading, a tunable band gap can be induced in G [20]. In addition, experimental and theoretical studies on the hydrogen storage of G have been carried out to identify the storage mechanisms, capacity, and structure required to estimate the hydrogen storage in other carbon nanostructures [21]. Such studies envision a storage capacity greater than 14 wt% at room temperature under ambient pressure [22]. Thus, hydrogen storage using G is an important research topic and deserves more attention. One possible method of hydrogen storage is an efficient and controllable adsorption/desorption system. The implementation of an external electric field (EF) on carbon nanostructures appears promising for such purposes. In 2006, Ohta and collaborators proposed that the carrier density in G, the occupation of electronic states near to Fermi level, and the magnitude of band gap could be manipulated by means of an EF [23]. Ao and Peeters reported that an EF can have an important catalytic impact on the suppression of reaction energy barriers in the dissociative adsorption of H_2 on G [24]. Some experiments confirm a band gap control in G [25] and also an improvement of hydrogen adsorption on carbon samples thanks to an applied electric field [26].

The combination of physical and chemical methods results in greater improvement of the material properties regarding hydrogen storage in G [27]. The presence of EF has a strong influence on H/G chemical reactivity and its adsorption properties can be modulated through the intensity and direction of EF. Studying hydrogen adsorption in graphene under an external electric field can help us to understand how it could increase graphene's viability as a hydrogen store. In this work we study the influence of an electric field in the hydrogen adsorption on graphene.

2. Methodology

To study the interactions between the hydrogen (H) atom and graphene (G), calculations were performed in the framework of density functional theory (DFT), by means of total energy calculations using the SIESTA code [35, 36]. SIESTA is a self-consistent DFT code based on pseudopotentials and a

basis set of numerical atomic orbitals. For the exchange-correlation potential, the generalized gradient approximation (GGA) proposed by Perdew, Burke, and Ernzerhof (PBE) was used [37]. The pseudopotentials were generated according to the Troullier-Martins procedure [38]. For the numerical atomic orbitals an optimized basis set with soft confinement was considered for carbon (C) atoms and a standard DZP basis set for the H atom. A uniform grid in real space with a mesh cutoff of 450 Ry was used, whereas the reciprocal space was sampled with 98 k-points [39].

First, all C atoms of the G were allowed to interact and relax without constraints until the interatomic forces were lower than $0.02 \text{ eV}/\text{\AA}$, in order to obtain a relaxed structure with a lattice parameter equal to 2.47 \AA . Subsequently the atoms of G in a supercell (5×5) were restricted, except for the first and second neighbors of the C atom that binds to the H atom; this consideration is named here as the reduced structural constraint, as shown in Figure 1. To suppress the electronic interactions between neighboring graphene surfaces (graphite monolayers) as a result of periodicity, a distance of 15 \AA between planes was considered. This theoretical implementation has been successfully applied in the study of structural, elastic, and electronic properties of carbon systems [40], including systems within external electric fields [41–43].

The external electric fields (EF) were applied in two different perpendicular directions relative to G, with a direction from H to G (negative) and a direction from G to H (positive), as shown in Figure 1. The EF values ranged between -1.25 and $0.75 \text{ V}/\text{\AA}$ with increments of $0.25 \text{ V}/\text{\AA}$ keeping the cell periodicity. Here the distance between H and G varied from 1 \AA to 5 \AA , covering physisorption to chemisorption conditions and allowing structural relaxation for first and second neighbors in the supercell at each step, as shown in Figure 1.

3. Results

3.1. Hydrogen Atoms Adsorbed on Graphene. The splitting of hydrogen molecule could be a result of charge transfer between H and C atoms. The dissociative adsorption of hydrogen on the surface of graphene has been already investigated by means of ab initio molecular dynamics based on

DFT [2], reporting a value of 3.33 eV for the activation energy in the dissociative adsorption of H_2 above the graphene surface. This result agrees with a previous study with DFT of Miura and collaborators [44], which reports values close to the latter (3.3 and 3.9 eV).

Hydrogen atoms can be physically and chemically adsorbed on graphite surfaces or graphene (H/G). Physisorption is the first binding state reached, when H atoms approach the graphene or graphite surface, with an experimental measure of the binding energy around 39.2 meV [45]. The theoretical studies used different methodologies and technical implementations to provide values for physisorption energy (E_p) between 8 and 60 meV, with physisorption bond distances (d_p) in the range of 2.0 Å to 3.07 Å [28, 29, 46, 47]. Some of these previous theoretical works could describe the physisorption characteristics with the GGA approximation and found that the size of system and basis set have an important contribution in their results [28, 29, 46]. Inside of our calculations for the physisorption regimen, a benchmarking process was considered. The physisorption state of H/G was characterized with values calculated of 36.5 meV and 3.1 Å for E_p and d_p . From a comparison with previous theoretical studies, we found E_p value within the range of values predicted, while d_p value showed a light increment (0.91%) with respect to the higher value reported [28, 29, 46, 47]. Additionally one recent theoretical study about the contribution of the van der Waals forces and quantum effects in the physisorption properties helped to understand a bit more about of this type of interaction [48]. Inside of this context, the van der Waals interactions were evaluated in our physisorption predictions and showed limited influence on the results, with differences of 0.54% and -1.93% for E_p and d_p , respectively (taking the GGA results as reference point).

The chemisorption of H on G does not spontaneously occur at low temperatures, because there is an energy barrier (E_B) of 0.2 eV, which must be overcome from a physisorption state [33]. The chemical binding of H on G promotes an outside movement of the surface plane localized at the bonded carbon atom, changing its hybridization to a sp^3 -like state [49–51]. Several experimental [33, 45, 52] and theoretical [44–46, 51–54] studies agree on the fact that hydrogen chemisorption on a graphite surface (as with graphene) occurs on top of a carbon atom and requires substantial lattice reconstruction. This superficial impurity induces electronic and magnetic changes in G, producing a band gap and a magnetic moment [31, 49].

The geometrical deformation owed to the chemisorption of H/G is shown in Figure 2, representing the structural parameters which measure deformation. The distance between the hydrogen atom and the bonded carbon atom, the relative position of the bonded carbon atom to the graphene plane, and the chemisorption bond distance are represented by d , d_{puck} , and d_c , respectively.

In our calculation of the structural relaxation for the chemisorption state, the values of 1.12 Å and 0.45 Å for d and d_{puck} were obtained, respectively, with a value for chemisorption energy (E_c) of 0.81 eV, after overcoming an energy barrier (E_B) of 0.2 eV. These last energy and structural results are compared in Table 1 with previous experimental and

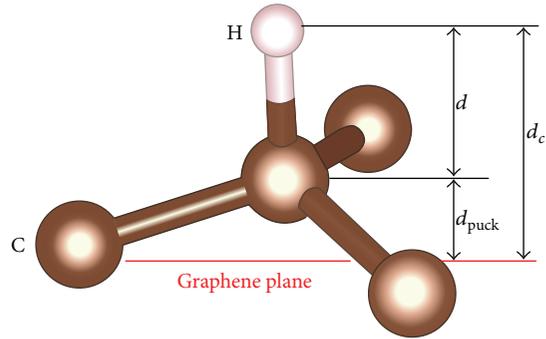


FIGURE 2: The geometrical and structural parameters to quantify deformation in the chemisorption state.

TABLE 1: Comparison with previous works of the distance between the hydrogen atom and the bonded carbon atom (d), the outside plane distance of the bonded carbon atom (d_{puck}), the energy barrier (E_B), and chemisorption energy (E_c).

Reference	d (Å)	d_{puck} (Å)	E_B (eV)	E_c (eV)
[28]	1.15	0.35	0.15	0.57
[29]	1.14	0.36	0.22	0.67
[30]	1.13	—	—	0.86
[31]	1.10	0.36–0.59	0.14	0.75–0.84
[32]	1.13	0.45	—	0.86
[33]	—	—	0.20**	0.60*
[34]	—	—	0.20	—
This work	1.12	0.45	0.20	0.81

*Experimental value of activation desorption energy.

**Energy calculated from experimental data.

theoretical studies. Table 1 shows that all values calculated for E_c , E_B , and structural parameters (d and d_{puck}) are within the respective range of predicted values reported in the literature.

3.2. Electric Field Effect in the Adsorption of Hydrogen Atom on Graphene. The electric field (EF) modifies the physical and chemical properties of carbon structures with low dimensionality [23–25]. Simulation methods are viable alternatives for understanding the changes induced by an EF in carbon nanostructures. In this section, we analyzed the energetic steps of a reaction path when an H atom approaches G in the presence of an EF.

3.2.1. H Physisorption on G inside an EF. The influence of the EF on the physisorption regimen (bond distance > 2.2 Å) of an H/G system was analyzed with the condition of the reduced structural constraint. Figure 3 presents the EF influence on the relationship between total energy (E_T) and the distance between H and G, under physisorption conditions (d_p) localized from 2.2 Å to 5 Å. For distances between H and G lower than 2.6 Å, an influence of the chemisorption barrier can be observed. For purposes of normalization, the value of $d_p = 3.1$ Å and its respective value of physisorption energy ($E_p = 36.5$ meV) for a zero EF were taken as reference points for the calculation of

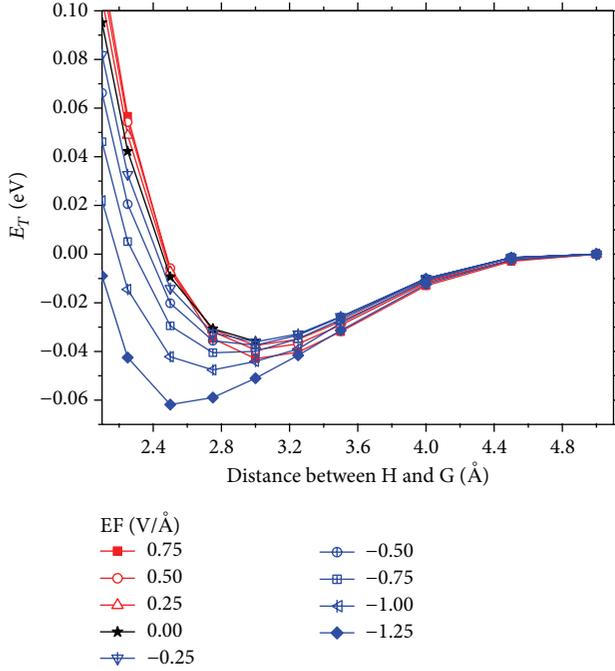


FIGURE 3: Total energy (E_T) versus distance between H and G, with some electric fields (EF) applied ($E_T = 0$ eV for $d_p > 5$ Å).

percentage changes (Δd_p and ΔE_p) when different values of EF are applied. The location and magnitude of the barrier energy can be altered by the EF presence, as well as d_p and E_p (see Figure 3). Therefore, when H and G are largely separated ($d_p > 4.8$ Å), E_T is practically the energy addition of the isolated subsystems with a value assigned to zero for normalization purposes, as shown in Figure 3.

Calculations of positive values of EF at 1.00 and 1.25 V/Å were performed, but the physisorption state was not found, indicating that the intensity of EF required for the suppression of the physisorption state must be higher than 0.75 V/Å. This was mainly due to the loss of capacity in the Coulomb interactions between hydrogen atom and graphene in a polarized condition, which could not counteract the expel force exerted on the hydrogen atom; in this way the physisorption state was not reached for the strong EF in positive direction. Figure 4 presents the percentage change in the physisorption energy (ΔE_p) and the physisorption bond distance (Δd_p) when different intensities of EF are applied.

The physisorption bond distance does not vary significantly ($\Delta d_p \sim 0$) for positive values of EF. However, a decrease in the physisorption bond distance ($\Delta d_p < 0$) appears when the negative values of EF are increased, showing a decrease around 14.3% in Δd_p for the most negative value of EF (-1.25 V/Å). In general, the EF presence regardless of the direction on H/G system induces an increment (with non-linear behavior) in the depth of the physisorption potential ($\Delta E_p > 0$), indicating a reinforcement of the physisorption state. It should be noted at this point that the values of ΔE_p may increase by up to 74.5% for a value of -1.25 V/Å of EF.

To further elucidate EF's strengthening of physisorption interactions, an additional analysis of the electronic structure

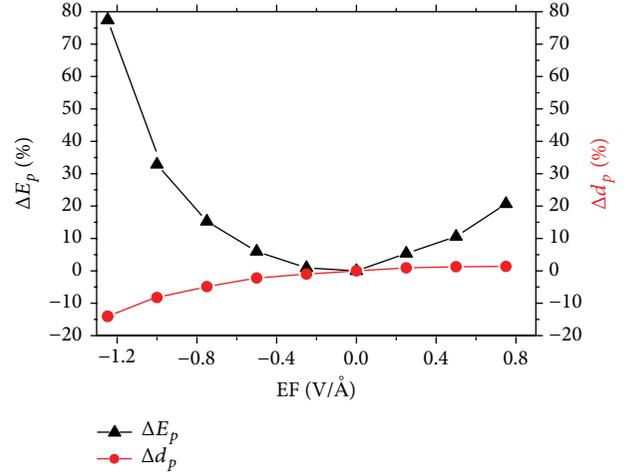


FIGURE 4: Effects of EF on physisorption energy and physisorption bond distance.

was conducted by investigating the change in distribution of charge density. As shown in Figure 5, we analyzed the change in the electronic structure by means of a comparison between the charge densities of the H/G systems (the same structural configuration) with and without EF. The results presented in Figure 5 for the distribution of charge density correspond to an EF value of -1.25 V/Å with $d_p = 2.75$ Å (b), and an EF value of 0.75 V/Å with $d_p = 3.036$ Å (c). Here the red and blue colors represent regions with increases and decreases in the charge density, respectively. From close inspection of Figures 5(b) and 5(c), it can be observed that, under negative and positive values of EF, the resulting charge density between H and G tends to be redistributed as the result of a strong polarization effect. The EF induced an increase in the Coulomb interactions between H and G inside the physisorption regimen, changing the charge density and equilibrium state.

3.2.2. H Chemisorption on G inside an EF. Once the energy barrier is overcome from the physisorption state in H/G, the H atom may achieve a chemisorption state, still under the influence of the EF. Here the chemisorption bond distance (d_c) is defined as the sum of d and d_{puck} values, representing the position of the H atom with respect to the graphene surface. The depth of chemisorption potential or minimum value of total energy (E_T) in Figure 6 represents the chemisorption energy (E_c). Values between 1.4 Å and 1.7 Å for the distance between H atom and G are located for the chemisorption state in the presence of an EF. In Figure 6, a trend in the increase and decrease of the depth of chemisorption potential for positive and negative directions of EF is found, respectively, showing a clear dependence between the chemisorption conditions and EF values.

A more precise analysis is shown in Figure 7, which presents the percentage change in the chemisorption energy (ΔE_c) and the chemisorption bond distance (Δd_c) when different values of EF are applied. The value of 1.57 Å for the chemisorption bond distance (d_c) and its respective value of

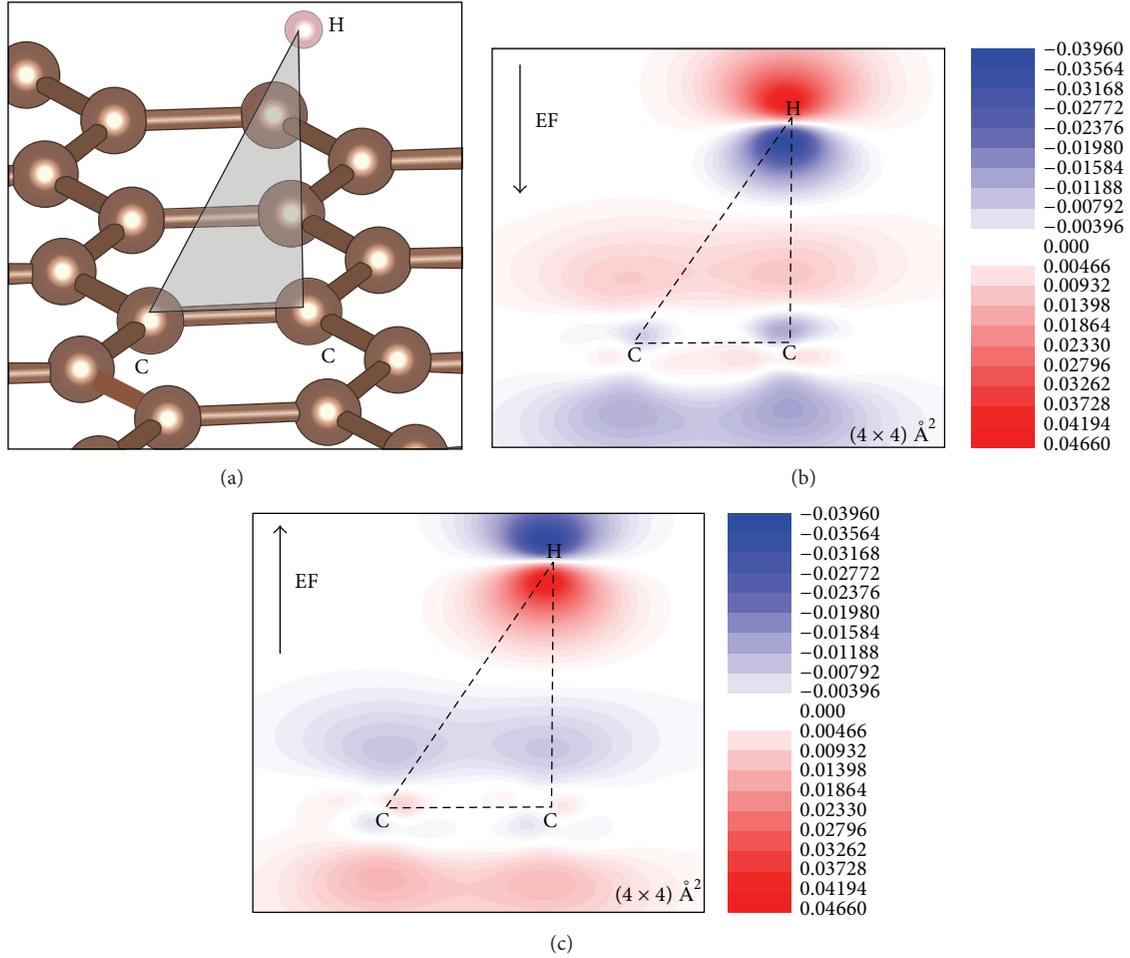


FIGURE 5: (a) Planar projection of the physisorption state; (b) charge density ($e/\text{\AA}^3$) resulting from the subtraction of H/G charge without EF to the systems with an EF of -1.25 V/\AA intensity and (c) 0.75 V/\AA . The density changes are represented by a colored scale, with red and blue representing increases and decreases, respectively.

chemisorption energy ($E_c = 0.81 \text{ eV}$) for a zero EF were taken as reference points for the calculation of percentage changes (Δd_c and ΔE_c). Here the chemisorption bond distance showed no significant variation ($\Delta d_c \sim 0$) when any value of EF was applied. However, for the relationship between ΔE_c and EF a linear behavior was found, with a decrease of 18.3% and increase of 10.6% in ΔE_c for EF values of -1.25 V/\AA and 0.75 V/\AA , respectively. The increases in the chemisorption energy present a linear dependence with the intensity of the EF, unlike the chemisorption bond distance which did not show a significant variation, remaining near its value without EF (1.57 \AA).

The relationships between chemisorption state and EF intensities can be studied by means of a comparison of the electronic charge densities from the H/G systems (with the same structural configuration) with and without EF. The results are presented as a planar projection (see Figure 8(a)), for EF values of -1.25 V/\AA (Figure 8(b)) and 0.75 V/\AA (Figure 8(c)), with the same value of $d_c = 1.57 \text{ \AA}$. Here, red and blue represent regions with increases and decreases

in the electronic charge density, respectively. Similar to that presented in the physisorption state under an EF, polarization in the H atom and G was found too for the chemisorption state. However, the effects of the EF on the H/G system were focused around chemical bonding.

From Figure 8, we can see that positive EF mainly moves the electronic charge of H and G toward the chemical bond, thereby increasing the chemisorption energy. However, negative EF concentrates the electronic charge around the H atom, thus weakening the chemical bond between the H atom and the C atom of graphene. From the electronic charge density analysis, we can see that negative EFs with the highest intensities can help to desorb H atoms in the H/G system from the chemisorption state.

By means of an atomic Mulliken population analysis, we show in Table 2 the charge of H and C atoms for three intensities of electric field (EF), when the hydrogen atom is in an adsorption state (physisorption or chemisorption).

The chemical bonding is confirmed in terms of the charge increment of the hydrogen atom with respect to the

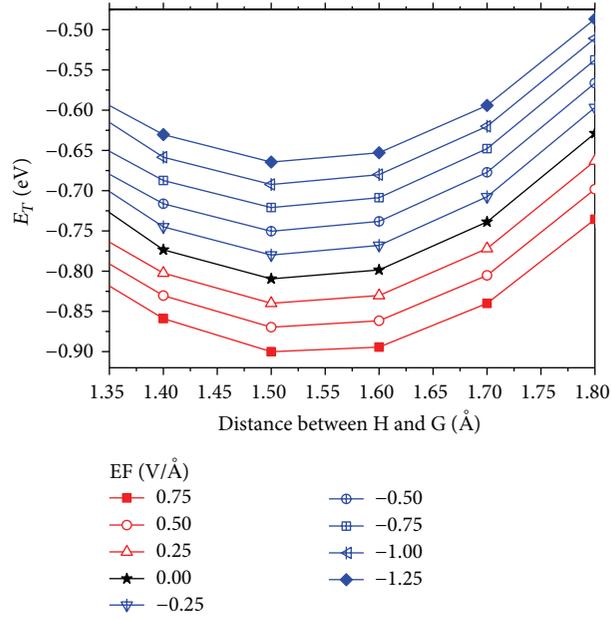
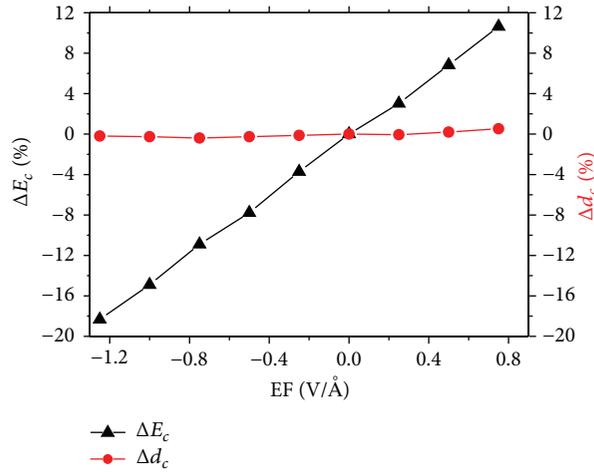
FIGURE 6: Total energy (E_T) versus distance between H and G.

FIGURE 7: Effects of EF on chemisorption energy and bond distance of chemisorption.

TABLE 2: H and C atomic charges (in electrons) for hydrogen physisorption or chemisorption (phys./chem.) under influence of three intensities of electric field (EF).

EF (V/Å)	Charge (e) of H atom (Phys./chem.)	Charge (e) of C atom (Phys./chem.)
-0.75	1.000/1.164	4.000/3.870
0.00	1.000/1.134	4.000/3.867
0.75	1.000/1.106	4.000/3.930

physisorption state without EF. Also, the effect of the EF in the charge of the H atom can be observed for two different values of EF (0.75 V/Å and -0.75 V/Å).

The change in the electronic charge density in the H/G system owed to EF presence can help us to elucidate one

modulation mechanism of the chemisorption energy. In general, the magnitude and direction of the EF have a substantial influence on the charge redistribution of the chemical bond between the H atom and G.

3.2.3. Effect of EF on Chemisorption Barrier. The EF also modifies the chemisorption barrier location (d_B) with respect to the G plane and the magnitude of energy barrier (E_B) for the H/G system. The values of d_B are localized between 1.89 Å and 2.1 Å, whereas for E_B extreme values of -8.9 meV (less energy compared to the system with H and G largely separated) and 216 meV were found for the EF of -1.25 V/Å and 0.75 V/Å, respectively. Figure 9 shows the percentage change in the energy barrier (ΔE_B) required to reach the chemisorption state and its location (Δd_B) when different values of EF are applied. The values of $E_B = 0.2$ eV and

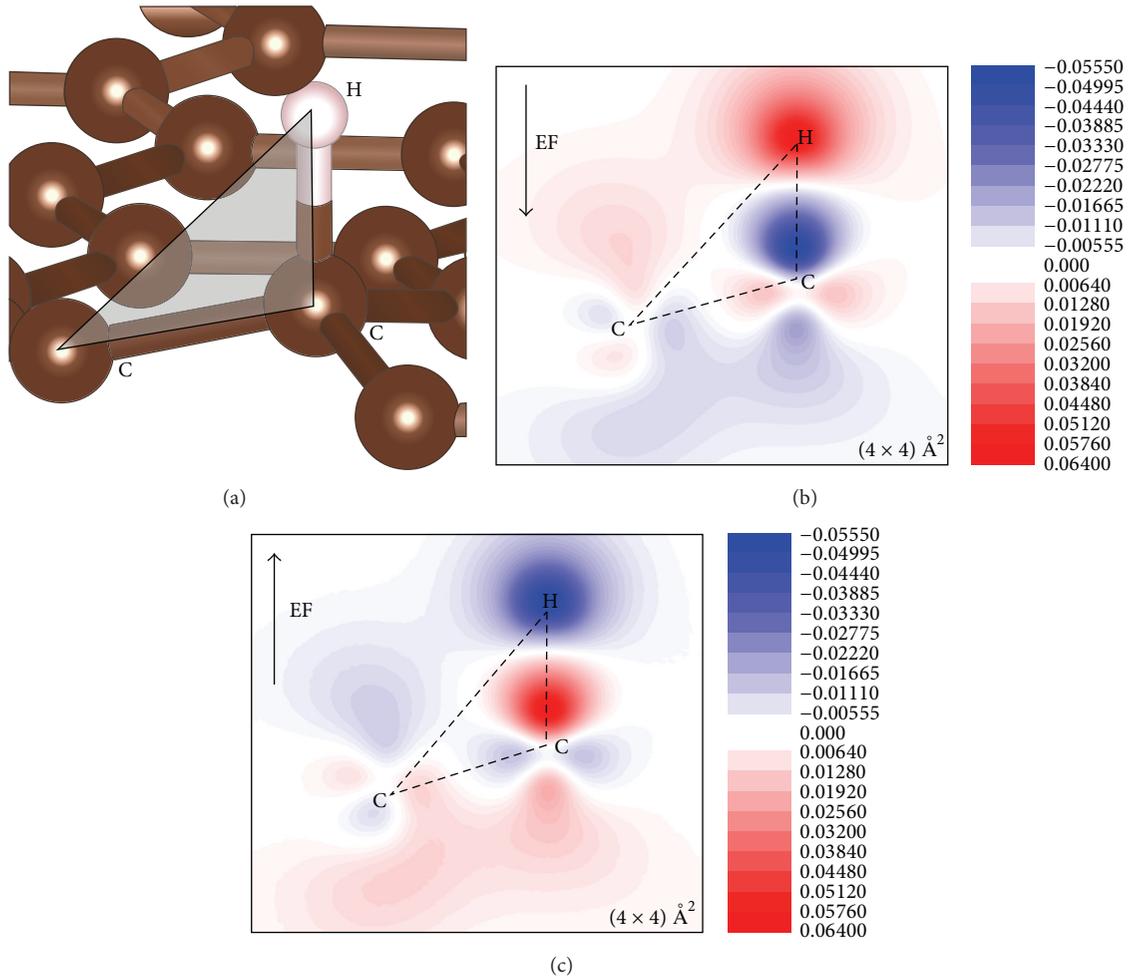


FIGURE 8: (a) Planar projection of the chemisorption state; (b) charge density ($e/\text{\AA}^3$) resulting from the subtraction of H/G charge without EF to the systems with an EF of -1.25 V/\AA intensity and (c) 0.75 V/\AA . The density changes are represented on a colored scale, with red and blue relating to increases and decreases, respectively.

$d_B = 1.87 \text{ \AA}$ without EF as a point of reference were considered for the calculation of ΔE_B and Δd_B . Here, ΔE_B and Δd_B achieved increases of 5.8% and 1.6%, respectively, when an EF value of 0.75 V/\AA was applied (see Figure 9).

Figure 9 shows that, as negative values of EF increase in magnitude, the Δd_B initially decreases to 1.2% before achieving a maximum increase of about 12.3%. However, as the magnitude of negative EF increases, the ΔE_B values decrease. The changes in E_B and d_B were also originated by the electronic charge redistribution between H and G as a result of EF presence. A significant decrease of more than 100% in ΔE_B for an EF value of -1.25 V/\AA was found. This behavior regarding the values of E_B and d_B suggests the possibility of manipulating the chemical adsorption of atomic hydrogen by applying electric fields in graphene.

4. Conclusions

The influence of an electric field (EF) on hydrogen (H) adsorption into graphene (G) was studied by means of density functional theory. The relationship between the

physisorption-chemisorption properties and EF was examined by considering values from -1.25 to 0.75 V/\AA .

The EF shows a substantial influence on the physisorption energy of H into G, with an enhancement of 74.5% for an EF of -1.25 V/\AA . However, only negative values of EF significantly affect the physisorption bond distance (d_p), providing a maximum reduction of 14.3% at a field intensity of -1.25 V/\AA . A linear relationship between the EF intensities and chemisorption energies was found. The chemisorption energy values increased when the EF intensity increased. The chemisorption bond distance did not show a significant change when different intensities of EF were applied.

The value and location of the chemisorption barrier can be modified by means of the EF presence. The EF effect on the redistribution of the charge density between H and G is induced by polarization. A decrease of more than 100% in the energy value of the chemisorption barrier when H/G system is inside an EF of -1.25 V/\AA was found. The changes in the electronic charge density of the H/G system confirm the possibility of manipulating the physical-chemical adsorption of H on G by applying electric fields.

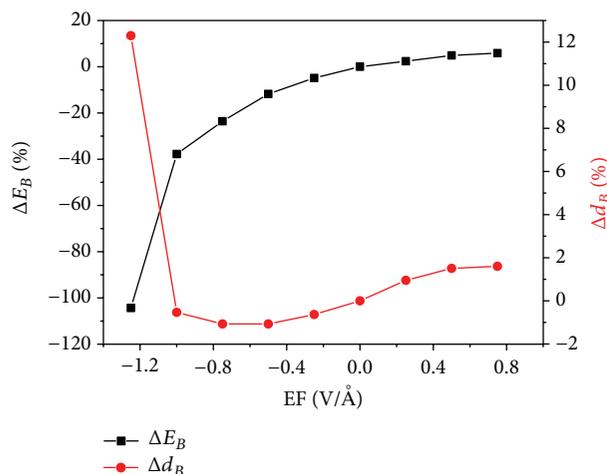


FIGURE 9: Effects of EF on the energy barrier and its location with respect to G.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

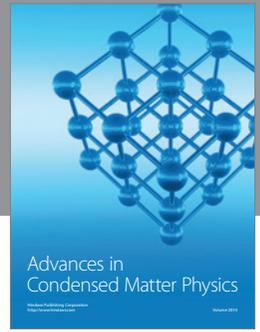
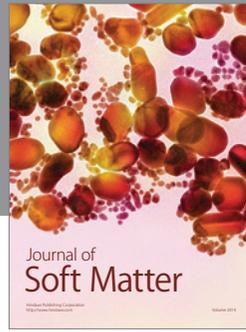
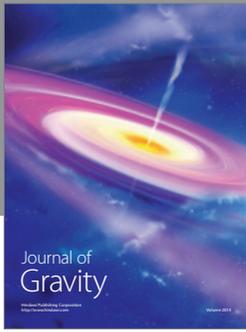
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