

Effect on hydrogen adsorption due to a lonely or a pair of carbon vacancies on the graphene layer.

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Abstract. The influence on the hydrogen molecule adsorption on a pristine and a defective graphene layer is compared. The different lengths for the C-C bonds on the graphene layer with one vacancy are visualized and compared respect to pristine graphene. The energy of formation of one vacancy is calculated and a comparison of the binding energy for the hydrogen molecule is presented when the molecule is adsorbed on pristine graphene or on the defective graphene layer. The adsorption is studied for a single vacancy and at least for two different pairs of carbon vacancies. The qualitative general result, and contrary to the expected effect of the carbon vacancies on the hydrogen adsorption is that the rearrangement of the carbon atoms on the defective graphene layer allows only a relatively small increase in the magnitude of the binding energy for the hydrogen molecule.

1. Introduction

The hydrogen adsorption by graphitic materials has been studied from the theoretical point of view at least since the 2000 year. Now we look for the effect of some carbon vacancies at the graphene layer, on the possible new results for the hydrogen molecule adsorption compared with those obtained previously for pristine graphene. In the next section a resume of the pristine graphene calculation is given. Then the one carbon vacancy graphene layer is designed and relaxed. The hydrogen molecule is added above the defective graphene layer and the entire system formed by the hydrogen molecule and the mono vacancy graphene layer is relaxed and the results are studied and discussed. There are discussions for at least two initial and different configurations, both with a pair of vacancies. The principal difference is that the initial distances between the vacancies are different for those configurations. These can be compared with the given figures. They allow appreciating that due to the differences in the sizes of the cavities it could be find some differences for the final hydrogen adsorption energies for the studied configurations. These results can be compared with those obtained for a lonely or a pair of vacancies on the BN layer [1]. For that case the studied systems were the entire BN layer, B vacancy, N vacancy and B and N vacancies (a pair of vacancies). As it was expected the hydrogen adsorption energy was in some cases greater for the BN systems mentioned above, respect to the defective graphene layer.

2. Pristine graphene layer.

Quantum espresso computer code was used for all the computer calculations given here. The pristine graphene layer has been designed with the equilibrium cell parameter $a = 4.6117$ a.u., that was obtained before [2]. Again c.fhi.UPF and h.cpi.UPF, LDA pseudopotentials were used for all the calculations. The pristine graphene supercell is formed with 32 atoms, with C-C distance 2.6626 a.u. (1.4090 Å). The total static energy, (E_{tot}) for the pristine supercell is -365.58814088 Ry, with Fermi energy of -1.4977 eV. The cell parameter is the distance between any pair of second neighbor carbon



atoms. There is a distance of 25 a.u. (13.2294 Å), between adjacent graphene layers. This distance is close to that used in a similar study [3] and it is big enough to assume there is no interaction between the images of the graphene layers.

3. One vacancy graphene layer.

To obtain the relaxed system with a vacancy on the graphene layer, schematically illustrated in figure 1, it was simply removed in the pristine configuration one carbon atom that in the final and relaxed configuration appears as an empty space between carbon number 14 and 15 along the horizontal axis of the supercell. By symmetry the vacancy site is equidistant to carbon atoms with number 8, 15 and 21 on figure 1. A repetition of the supercell shows that there are at least two entire hexagonal cavities in any direction around the cavity of the vacancy. One interesting thing to point out is about the calculation of the energy of formation (E_f) of a single vacancy for the graphene layer. To calculate that energy, it is necessary to take into account three energies: a) the total static energy E_{tot} , obtained from the final coordinates for the relaxed entire graphene layer system, b) the non-relaxed initial energy for the defective layer (E_{iwr}) and c) the relaxed final energy (E_{fr}) for the vacancy graphene layer. The calculated values for those energies are $E_{iwr} = -353.54841261$ Ry and $E_{fr} = -353.56568555$ Ry. Following the examples of defects in solids given by Alessandra Satta [4], to calculate the energy of formation of a single vacancy in silicon, here the energies 0.6150 and 0.5978 Ry were obtained for the unrelaxed and relaxed energies of formation of a single vacancy for the graphene supercell. Those energies are 8.368 and 8.133 eV, respectively, and are in good agreement with the formation energy obtained in other work, [5], for single and double vacancy on graphene. Compared with the corresponding energies in silicon, 3.27 and 3.26 eV, it can be seen that the energies are close to 2.5 times larger for carbon in graphene than for the silicon structure. For silicon and for the graphene vacancy, the relaxed energies are more negative than for the non-relaxed systems. Figure 2 shows the distortions of the relaxed graphene layer due to the carbon vacancy. The energy for pristine graphene layer is 12.039728 Ry more negative than for the graphene layer with one vacancy. This energy difference is equal to 163.8088 eV. Something similar occurs for silicon energy because this is around 8.1626018 Ry (111.05784 eV) more negative than for the system with a single vacancy.

There are some differences for C-C bond lengths and angles between the carbon atoms when one compares the pristine graphene layer and the final relaxed vacancy system. To clarify this, take into account the correspondence between the positions of each one of the carbon atoms on figure 1, and their positions in the final configuration for the relaxed defective layer, shown on figure 2. Numbers from 1 to 31 are assigned consecutively from left to right and from above to below the array of carbon atoms. Because the symmetry above and below the line joining the more left carbon atom (number 13) and the righter carbon atom (number 19) along the horizontal axis of the supercell, it is expected equal results for lengths of C-C bonds and for angles between 3 adjacent carbon atoms if they are in symmetrical positions respect to the horizontal axis of the supercell. This is confirmed with measured distances given in table 1, for different pairs of neighboring carbon atoms. The distance d (angstroms), between the carbon atoms C_i and C_j , is denoted by $d(C_i, C_j)$.

Here we comment about the lengths of the C-C bonds for the relaxed vacancy graphene layer. There are nine different distances between pairs of closer carbon atoms; the smaller (bigger) is 1.3802 Å (1.4328 Å). There are for example, six (two) pairs of bonds with the smaller (biggest) bond length. Above the horizontal axis of the supercell the smaller bond length is for the pairs of atoms (3, 8), (7, 8)

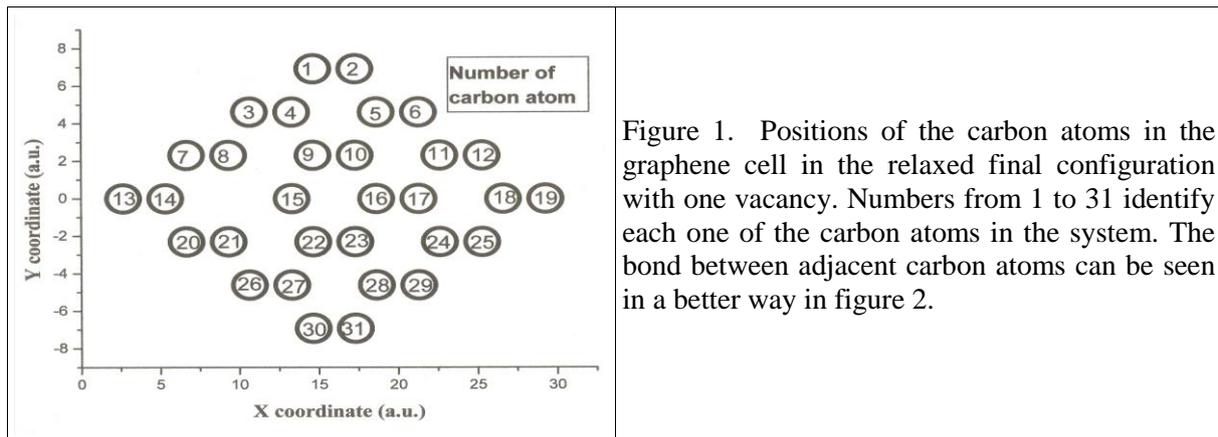


Figure 1. Positions of the carbon atoms in the graphene cell in the relaxed final configuration with one vacancy. Numbers from 1 to 31 identify each one of the carbon atoms in the system. The bond between adjacent carbon atoms can be seen in a better way in figure 2.

and (9, 15). It was used Xcrysden [6] to build figure 2. Displaying the final coordinates of the atoms, it could be seen that the biggest bonds were between carbon atoms pairs (9, 10) and (22, 23). Those are respectively the two horizontal bonds of the central hexagonal cavity on that figure. The angles around the cavity are (in the clockwise direction, beginning at carbon site 14), 116.717° , 123.197° , 123.110° , 123.197° , 116.717° , 123.196° , 123.108° , 123.196° , 116.717° , 123.197° , 123.111° , and 123.197° . The first angle, 116.717° , has as vertex the site for carbon number 14 and is defined by the bonds formed by carbon number 20 and 14 and between carbon number 14 and 7. The angle with vertex at site 7 is the next one, 123.197° , and so on. In the pristine graphene layer all the angles are 120° . The maximum angular deviation respect to that angle is 3.197° or -3.283° . The relatively small differences of lengths and angles respect to the pristine graphene layer will have some perhaps little change on hydrogen adsorption that is discussed in the next section.

4. Hydrogen adsorption on a single vacancy graphene layer.

The hydrogen adsorption energy is obtained using equation (1)

$$E_{\text{ad}}(\text{H}_2) = E(\text{H}_2 \text{ on gl-1v}) - E(\text{gl-1v}) - E(\text{H}_2) \quad (1)$$

$E(\text{H}_2 \text{ on gl-1v})$ is the total energy for the relaxed system formed by one H_2 molecule and the graphene layer (gl) with one vacancy (1v): (gl-1v), $E(\text{H}_2)$ is the total energy of only the hydrogen atoms in the final configuration and in a similar way, $E(\text{gl-1v})$ is the total energy of only the carbon atoms in their final positions corresponding to the final stage of the relaxation of the entire system. With the calculated values, $E(\text{H}_2 \text{ on gl-1v}) = -355.83591945 \text{ Ry}$, $E(\text{H}_2) = -2.26356214 \text{ Ry}$ and $E(\text{gl-1v}) = -353.56555313 \text{ Ry}$, the hydrogen adsorption energy is $E_{\text{ad}}(\text{H}_2) = -0.00680418 \text{ Ry}$ (-0.09257 eV). These data are given on table 2. This adsorption energy is a small energy, is less than one tenth of one electronvolt. The hydrogen molecule was adsorbed on pristine graphene with an energy around -0.070 eV [2]. The negative sign for the energy means the hydrogen molecule is adsorbed to the defective graphene layer. Panels a, b and c of figure 3 are different views for the final configuration of the hydrogen molecule above the vacancy graphene layer. The initial position of the molecule was parallel to the layer. As can be seen in the final configuration the right hydrogen atom is closer to the layer than the left one. The H-H distance is 1.4704 a.u. , a little bigger than for the hydrogen molecule in equilibrium. The distances of the hydrogen atoms to the layer are around 4.49 and 5.79 a.u.

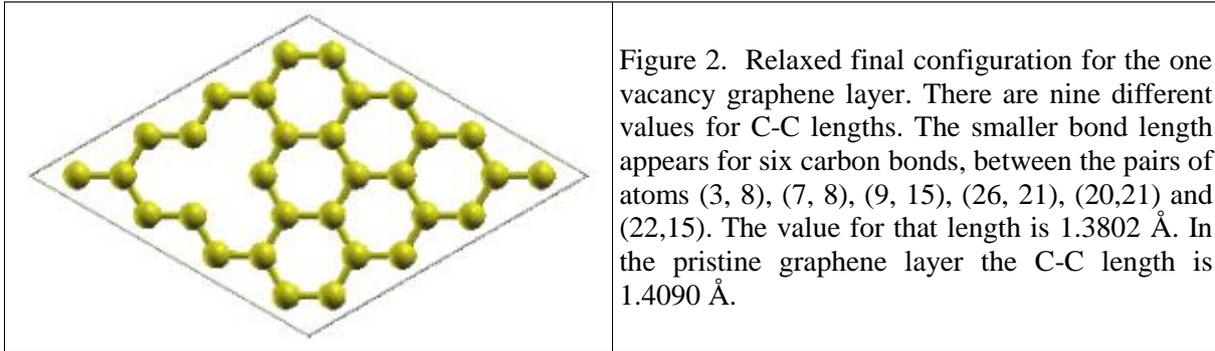


Table 1. Distances d , (angstroms), between pairs of carbon atoms. Distances goes from the smaller, 1.3802 to the biggest, 1.4328 Å. The differences for these distances respect to the theoretical equilibrium distance $d(\text{C-C})$ for the pristine graphene layer, 2.6626 a.u. (1.4090 Å), are -2.044 and 1.689 % respectively.

$d(\text{angstroms})$	Distance between pairs of carbon atoms, $d(\text{C}_i, \text{C}_j)$		
1.3802	$d(7, 8) = d(20, 21)$	$d(3, 8) = d(21, 26)$	$d(9, 15) = d(15, 22)$
1.3940	$d(13, 14)$	$d(1, 4) = d(27, 30)$	
1.4038	$d(18,19)$	$d(2, 5) = d(28, 31)$	
1.4056	$d(11, 12) = d(24, 25)$	$d(10, 16) = d(16,23)$	$d(6, 11) = d(24, 29)$
1.4071	$d(3, 4) = d(26, 27)$	$d(7, 14) = d(14, 20)$	$d(4, 9) = d(22, 27)$
1.4104	$d(1, 2) = d(30, 31)$		
1.4128	$d(16,17)$	$d(11, 17) = d(17,24)$	
1.4180	$d(5, 6) = d(28, 29)$	$d(5, 10) = d(23, 28)$	$d(12, 18) = d(18,25)$
1.4328	$d(9, 10) = d(22, 23)$		

Table 2. The hydrogen adsorption energy on the single vacancy graphene layer, $E_{ad}(\text{H}_2)$, is the sum of the energy for the hydrogen molecule on the graphene layer with one vacancy, $E(\text{H}_2 \text{ on gl-1v})$ minus the sum of the energies of the graphene layer with one vacancy, $E(\text{gl-1v})$, and the energy of the hydrogen molecule, $E(\text{H}_2)$. Energies in Ry units.

$E_{ad}(\text{H}_2)$	$E(\text{gl-1v})$	$E(\text{H}_2)$	$E(\text{H}_2 \text{ on gl-1v})$
-0.0068042	-353.566	-2.2636	-355.8359195

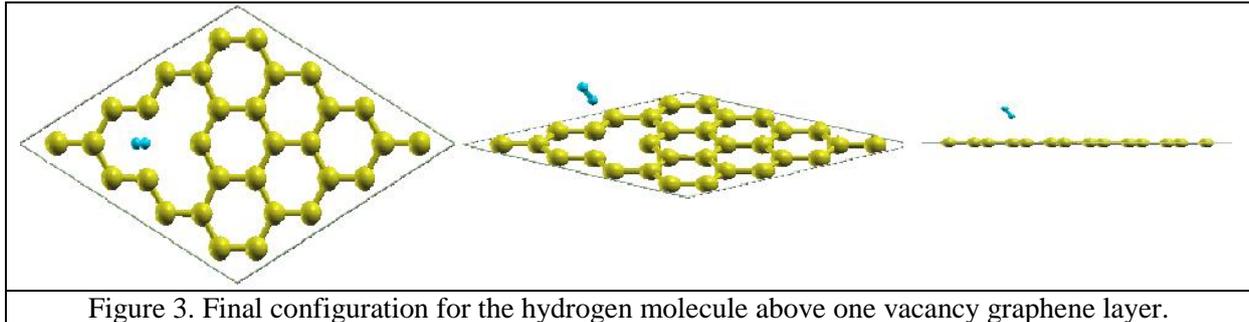


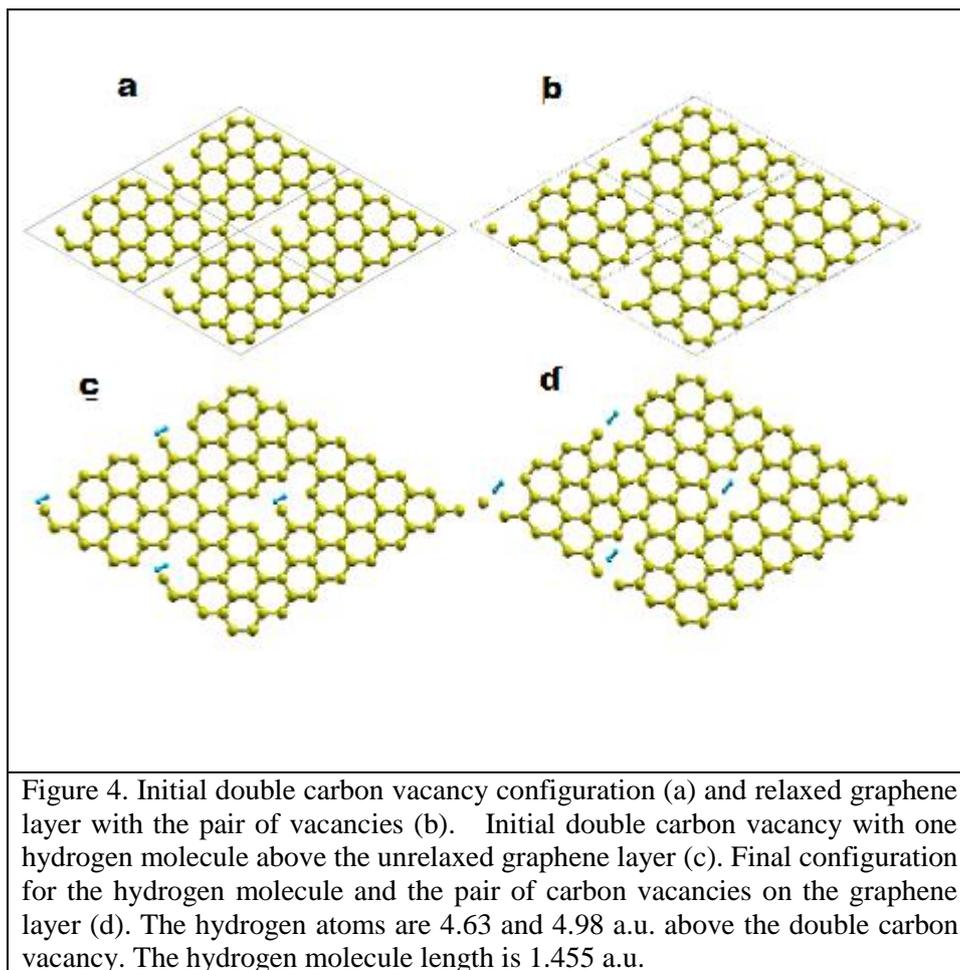
Figure 3. Final configuration for the hydrogen molecule above one vacancy graphene layer.

5. Hydrogen adsorption on two vacancies of the graphene layer.

Next we see if a second carbon vacancy can increase the adsorption energy for the hydrogen molecule. There are several possible elections for the second carbon vacancy. The selected pair of vacancies discussed here is only one of the possibilities. The initial and relaxed graphene layer with double vacancy is those of figure 4a and 4b. The total energy becomes 0.533 Ry more negative for the relaxed configuration respect to the initial one, without relaxation. Greater distortion of the graphene layer is obtained for this relaxed configuration with two carbon vacancies. When the hydrogen molecule is added and placed above the graphene layer with that pair of vacancies, the initial and final relaxed configurations are those of figure 4c and 4d. Besides the differences of this system with the lonely vacancy configuration and contrary to the expected, the adsorption energy for the hydrogen molecule is now -0.0917 eV, very close as the obtained with only one carbon vacancy. When the second vacancy is close to the first one, and both on the principal axes of the graphene supercell a high symmetry is obtained for the relaxed configuration. Relaxing the system with one hydrogen molecule above this new double vacancy, the hydrogen molecule is adsorbed and still remains parallel to the graphene layer with an interatomic distance $d(\text{H-H})$ of 1.47 a.u. The distance between the hydrogen molecule and the double vacancy layer is reduced to 4.5 a.u. This can be compared with the corresponding distance 5.07 a.u., obtained for the pristine graphene layer [2]. Then, the double vacancy allows an approach much closer between the hydrogen molecule and the defective layer compared with the entire graphene layer without vacancies. Table 3 contains the different energy contributions to obtain the hydrogen energy adsorption, $E_{\text{ad}}(\text{H}_2)$. This is the energy of the hydrogen molecule on the graphene layer with two vacancies, given by $E(\text{H}_2 \text{ on gl-2v})$ minus $E(\text{gl-2v})$, the energy of the graphene layer with two vacancies, and minus $E(\text{H}_2)$, the energy of the hydrogen molecule. The hydrogen energy adsorption is close to -0.0076 Ry. This means that there is a relatively small increase (10.5%) in the hydrogen adsorption energy obtained from the value -0.0068 to -0.0076 Ry, for one and two vacancies. Some other configurations, not shown here, but that have been studied, show in general that the hydrogen adsorption energies are very close to those given before even the final orientation for the hydrogen molecule could be very different between one and other. For one of those configurations the hydrogen adsorption energy was -0.0075 Ry (-0.103 eV). Contrary to the expected and the bigger size of the cavity created by the pair of carbon vacancies, still the adsorption energy is too low, and almost the same as with only one vacancy.

Table 3. The hydrogen adsorption energy on the double vacancy graphene layer, $E_{\text{ad}}(\text{H}_2)$, is the sum of the energy for the hydrogen molecule on the graphene layer with two vacancies, $E(\text{H}_2 \text{ on gl-2v})$, the negative of the energy of the graphene layer with two vacancies, $E(\text{gl-2v})$ and the negative of the energy of the hydrogen molecule, $E(\text{H}_2)$. Energies in Ry units.

$E_{\text{ad}}(\text{H}_2)$	$E(\text{gl-1v})$	$E(\text{H}_2)$	$E(\text{H}_2 \text{ on gl-1v})$
-0.00757685	-342.11511875	-2.26356367	-344.38625927



5. Conclusions.

A general trend about the adsorption of hydrogen by defective graphene layer and BN layer [1] is that there is only a small increase of around 10% in the adsorption energy.

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