Double vacancy on BN layer: A natural trap for Hydrogen Molecule

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Abstract. A pair of vacancies, one of boron and other of nitrogen atom at a flat layer becomes a natural trap to capture a hydrogen molecule at the center of the cavity defined by the empty space left by the lack of a nitrogen and a boron atom at the perfect BN layer formed by 16 N atoms and 16 B atoms. The adsorption of the hydrogen molecule is compared with the equivalent graphene layer with a pair of carbon vacancies. The little increase in the BN cell parameter respect to the graphene cell parameter, besides the differences between N, B and C atoms helps to explain the easier adsorption on the defective BN layer.

1. Introduction

Before the great interest on novel materials containing carbon atoms in systems such as fullerenes, nanotubes and other graphitic systems such as the lonely graphene layer, there were many works about the nature of graphite, one of the allotropic forms of carbon. Some years ago we reported the adsorption of the hydrogen molecule above the graphene layer [1]. The main purpose of this work is to study the adsorption of one hydrogen molecule due to a pair of vacancies on the BN layer. A big difference appears when comparison is made for the adsorption of one hydrogen molecule above an equivalent pair of carbon vacancies on a graphene layer with the same amount of atoms as the BN defective layer. With the work of Geim and Novoselov [2] it was pointed out the great importance of the graphene 2D system. Applications now are everywhere and many of them are very innovative ones. In a publication [3] there is a resume about the number of graphene works and graphene patents for the year 2010. The number of works and patents has been increasing the recent years. To show some other application of the graphitic systems it can be pointed out that there are new desalination water systems using the filtering and porous properties of the graphene [4]. On the other side, the possibility to detect and to eliminate or remove defects in graphene has been announced since 2010 [5]. If this can be applied to control the number of double B-N vacancies in the BN layer, the hydrogen adsorption reported here could be controlled in principle.

2. Computer simulations

The results given here were obtained using the free software package Quantum espresso, in particular program PWSCF v.4.3.2 [6]. The package is formed by open source computer code for electronic structure calculations and materials modeling at the nanoscale. As other computer codes, it is based on density functional theory, planes waves and also on pseudopotentials. To simulate the N, B and H atoms, the corresponding pseudopotentials N.pw-mt_fhi.UPF, B.pw-mt_fhi.UPF and H.pw-mt_fhi.UPF were used for all the calculations.

Before [1] it was used a cutoff energy of 40 Ry. Now, while making proofs for the energy convergence for the BN layer, it was noticed the necessity to increase the corresponding parameter, ecutwfc to 70 Ry for the BN system. It was then necessary to calculate for graphene and BN layers with the same values for other quantities refereeing to convergence for example.

3. Results

For the graphene layer it was obtained the value 4.6117 a.u. for the cell parameter. The value obtained for the BN layer is 4.67 a.u., a little bigger than for the layer with only carbon atoms. There is great similitude for both layers because they form hexagonal cavities. The principal difference as is shown in figure 1, boron and nitrogen atoms alternate around any hexagonal cavity.

Those values for the cell parameters were obtained after making tests increasing the cutoff energy from 30 or 40 until 70 Ry. Also several tests were done to conclude that with 26 k points the calculations are well converged and with the required convergence criteria.

For both layers it was designed a 4x4 supercell, with a total of 32 atoms, all carbon atoms for the graphene layer and 16 boron and 16 nitrogen atoms for the BN layer.

a. Results for graphene layer:

To obtain well converged energies for the graphene layer it was enough to use 40 Ry for the cutoff energy. For the lonely graphene layer, the total energy was -365.74482262 Ry.

b. Results for BN layer:

To obtain well converged energies for the BN layer it was used 70 Ry for the cutoff energy. For the lonely BN layer, the total energy was -429.29958813 Ry.

Next results are given for the total energies when a pair of vacancies is created on the graphene layer and on the BN layer.

c. Results for the double vacancy graphene layer:

The total energy is -341.77284704 Ry, when two carbon atoms along the “diameter” of the perfect hexagonal cavity are pulled out. Figure 2 (a) is a picture of the mentioned system. The distance for those C atoms, in the entire system (Figure 1 (a)), was 5.3251 a.u.

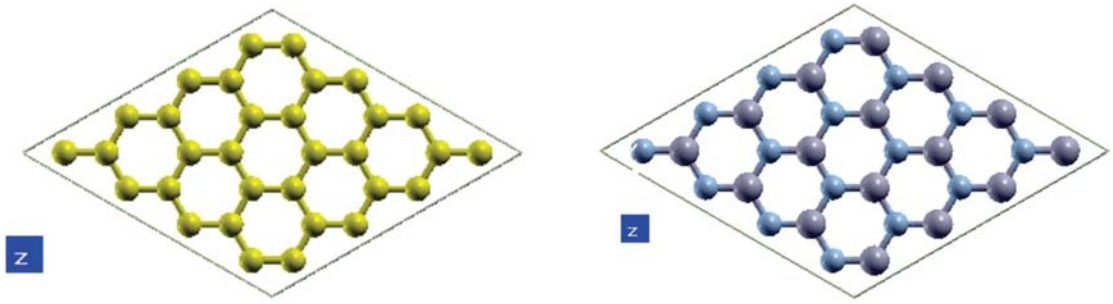
d. Results for the double vacancy on the BN layer:

The total energy is -401.71162699 Ry, when two atoms, boron and nitrogen are omitted respect to the perfect BN layer. Figure 2 (b) shows the corresponding vacancies. In the perfect layer (Figure 1 (b)), those atoms were apart one from another 2.66625 a.u. As can be compared this distance is only around one half of the corresponding distance for the lacking carbon atoms at the defective

graphene layer. This makes clear a bigger empty space in the BN double vacancy in comparison with the double vacancy for the graphene layer.

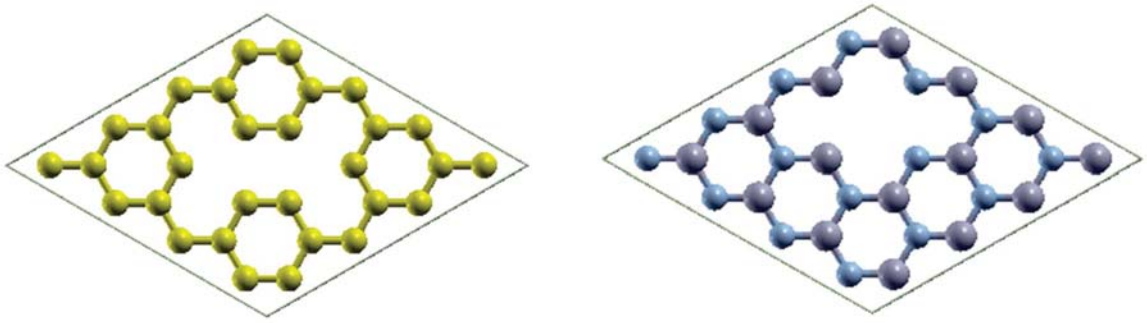
e. Adsorption of hydrogen molecule above the double vacancies layers:

Once both defective layers were studied, the next step was to study the adsorption of only one hydrogen molecule above the double vacancies. Figure 3 (a) is a perspective of the final configuration for the hydrogen molecule relaxed above the defective graphene layer. The equilibrium distance between hydrogen atoms is d (H-H) =1.4374 a.u. and its position is 5.43 a.u. above the center of the defective graphene layer. This result agrees with the result given in reference [1].



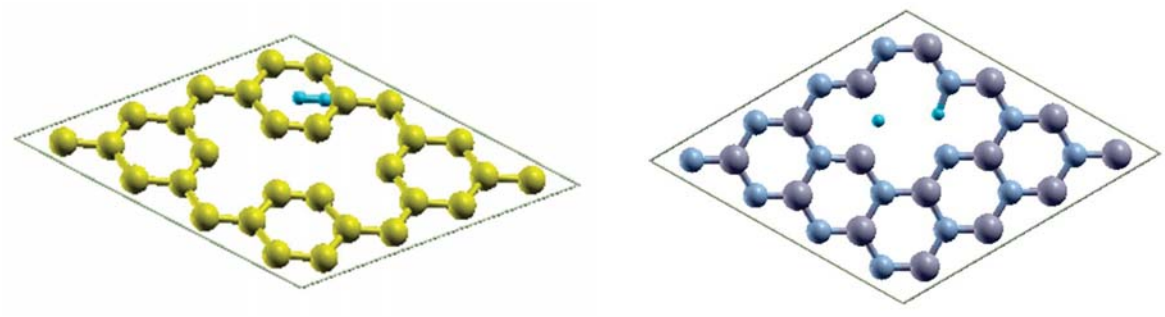
(a) (b)

Figure 1. (a) Graphene layer with 32 carbon atoms. (b) BN layer with 32 atoms. N atoms are smaller than B atoms. The unit cell parameter for both systems is the distance from one atom to the second neighboring atom. The unit cell parameter is 4.6117 a.u. and 4.67 a.u. respectively for graphene and BN layer.



(a) (b)

Figure 2. (a) Graphene layer with 30 carbon atoms. The double vacancy is created at the center of the layer. (b) BN layer with also 30 atoms. The vacancy is created taking out of the perfect BN layer shown on Figure 1 (b), one N atom and one B atom that were initially on a horizontal line.



(a) (b)

Figure 3. (a) Hydrogen molecule adsorbed above the double vacancy graphene layer. The molecule is about 5.43 a.u. above the graphene layer. The H-H distance 1.4374 a.u., close value to 1.48 a.u., the calculated value for the lonely molecule. (b) For the BN layer with the double vacancy, the hydrogen molecule is broken and one of the hydrogen atoms makes a bond with the closer N atom.

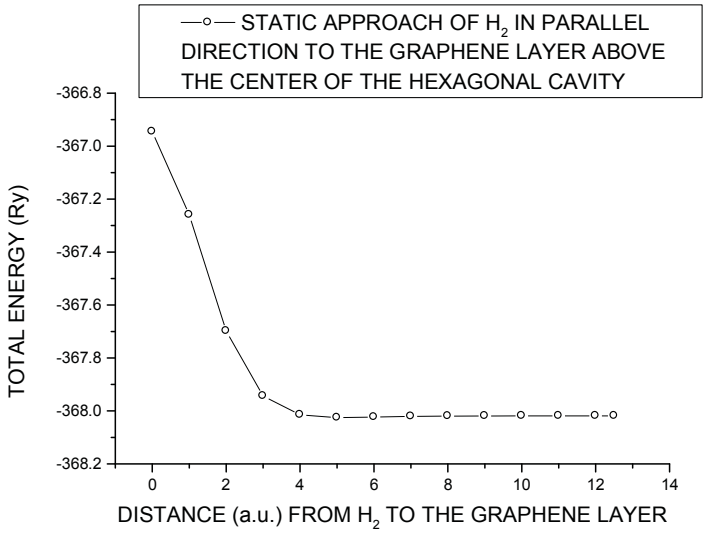


Figure 4. Total energy curve for static calculations with fixed distance H-H equal to 1.48 a.u., the equilibrium interatomic distance obtained for the isolated hydrogen molecule. The maximum separation between the molecule and the perfect graphene layer is z = 12.5 a.u., half of the cell parameter in the perpendicular direction to the layer. The energy difference for z = 12.5 and the minima, around 5.0 a.u. is 0.00639 Ry, close to 0.087 eV.

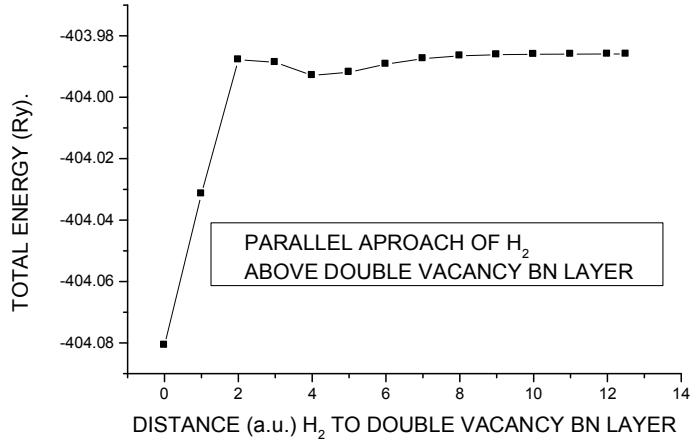


Figure 5. Total energy curve for static calculations with fixed distance H-H equal to 1.48 a.u. The more negative energies for distances less than 2 a.u. means the double vacancy on the BN layer favors the rupture of the hydrogen molecule and at least the bonding of one of the hydrogen atoms with the N atom for example, as shown in figure 3 (b).

In contrast, when the hydrogen molecule is placed above the double vacancy of the BN layer, the most stable configuration is with the hydrogen atoms adsorbed at the same plane of the BN layer and at the middle point of the double vacancy. This was confirmed by a series of static calculations putting the molecule at different distances above the layer, and also making relaxations of the molecule putting it at different distances above the BN layer. All of them finish with the same result: the hydrogen atoms are adsorbed at the center of the double vacancy. This configuration is shown in figure 3 (b). In that panel, the right hydrogen atom makes a bond with an N atom. Their interatomic distance is 2.09 a.u. The left hydrogen is at 2.65 or 2.69 a. u. respect to the boron atom almost above and below this second hydrogen atom, respectively.

4. Discussion

Results show that the hydrogen molecule can be attracted and adsorbed by the BN double vacancy layer at a very short distance, close to 2.0 a.u. This distance is much shorter than the distance close to 5.07 a.u. for the adsorption of the hydrogen molecule by the perfect graphene layer [1] or the distance 5.43 a.u. in the case of the pair of vacancies on the graphene layer. The rupture of the molecule when approaching the layer can be used although there were imperfections in some BN layer synthesized by any method, in such a way that the vacancies can be useful for the purpose of adsorbing hydrogen in a porous material without the presence of any other atomic species. The hydrogen molecule adsorption above the lonely B vacancy or the N vacancy alone also has been studied. The static approach of the hydrogen molecule above one or another of the vacancies for fixed distance H-H = 1.48 a.u. gives very similar results for the total energy curve as a function of the distance from the molecule to de BN defective layer. In both cases the hydrogen molecule is adsorbed at a distance between 5 and 6 a.u. This suggest that carbonaceous planar systems such as the graphene layer with isolated carbon vacancies could be not enough to be able to absorb a good

quantity of molecular hydrogen but perhaps a pair of closer vacancies as shown here for the BN layer could be considered attractive to study experimentally the possibility that hydrogen could be adsorbed in an easier way in such a system.

5. Conclusion

The main conclusion is that a porous system like the BN layer with distributed pairs of B-N vacancies all around the defective material could be a simple and cheaper porous system with a good capacity to adsorb and perhaps to storage an attractive quantity of molecular hydrogen. The proposal is that some experimental groups could study the hydrogen adsorption and desorption hydrogen process to compare with the computer simulations discussed above and compare with other porous systems that are being evaluated as good candidates for hydrogen storage.

References

[1] Arellano J S, Molina L M, Rubio A, and Alonso J A. J. Chem. Phys. 112, 8114, 2000 .
[2] Geim A K and Novoselov K S 2007 *Nature Mater*. **6** 183.
[3] Brumfiel G. Nature 140, V 488, 2012.
[4] http://www.sciencedaily.com/releases/2014/02/140225122504.htm.
[5] http://www.sciencedaily.com/releases/2010/06/100606162131.htm.
[6] P Giannozzi et al. J. Phys. Condens. Matter 21 395502 (2009); URL http://www.quantum-espresso.org".