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Interaction of a water molecule with a graphene layer

E. Rangel Cortes[a], L. F. Magaña Solís[a], and J. S. Arellano[b]
[a] *Instituto de Física, Universidad Nacional Autónoma de México,*
Apartado Postal 20-364, México, 01000 D.F., México.
e-mail: jsap@correo.azc.uam.mx
[b] *Universidad Autónoma Metropolitana Azcapotzalco,*
Av. San Pablo 180, Col. Reynosa Tamaulipas, México, 02200 D.F., México.

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Density functional theory was used to obtain total potential energy curves. We performed static calculations for five distinct approaching orientations of the water molecule to the graphene layer. The calculated adsorption energies for those orientations are in the range (-0.0866, -0.1421) eV. Additionally, we made calculations using molecular dynamics with different initial orientations for the water molecule. The resulting mean dipolar moment of this molecule is nearly parallel to the graphene layer. The interaction energy values are consistent with more costly MP2 calculations and experimental results obtained by other groups.

Keywords: Graphene layer; water molecule; density functional theory.

Se utilizó la teoría de la funcional de la densidad para la obtención de curvas de energía potencial total. Realizamos cálculos estáticos para cinco orientaciones preliminares diferentes de la molécula de agua hacia la capa de grafeno. Las energías de adsorción calculadas para las orientaciones mencionadas están dentro del intervalo (-0.0866, -0.1421) eV. Además, realizamos cálculos de dinámica molecular con distintas orientaciones iniciales de la molécula de agua. El momento dipolar promedio resultante de esta molécula es casi paralelo a la capa de grafeno. Los valores de la energía de interacción son consistentes con los obtenidos con cálculos más costosos de MP2 y con resultados experimentales obtenidos por otros grupos.

Descriptores: Grafeno; molécula de agua; teoría de la funcional de la densidad.

PACS: 68:43.Bc; 61.48.De; 81.05.Uw; 61.46.-w

1. Introduction

Ab initio Density functional theory (DFT) calculations for the interaction energy of a water molecule with graphite or a graphene layer is important to meet some technological applications and solve some problems as for airplanes, or the design and building of new humidity sensors for atmosphere studies. In materials science to help, to characterize the presence of water in some carbonaceous systems as fullerenes, nanotubes, and graphene layers. There are different models to study the water molecule adsorption on graphite or upon a graphene layer. Our study helps to clarify the effect on the H_2O molecule adsorption, of other atoms such as hydrogen atoms around a relatively small and flat graphene layer formed by carbon atoms. The results are compared with theoretical calculations from [1], and from other groups. In [1] a value of -0.251 ± 0.017 eV for the electronic binding energy of a water molecule to a graphene layer was estimated. This result comes from a large basis set MP2 calculations on a series of fragment models up to $C_{96}H_{24}$ in size. Wallace et al [2], found for the minimum energy configuration an interaction energy of 0.17 ± 0.017 eV (-4.05 ± 0.406 kcal/mol) and the zero point energy was estimated at 0.0134 eV. Other results for that binding energy, due to Wayan S. and Wallace G. [3], are -0.1036 and -0.1005 eV for two different orientations of the water molecule above the graphite layer. All of these calculations were done using second order Moller-Plesset perturbation theory, MP2, with benzene rings terminated with hydrogen atoms. In this work, we show that DFT calculations within local density approximation (LDA), predict in a very close agreement with experimental results, and with other more consuming time calculations such as MP2, the hydrogen adsorption energy of one water molecule to a graphite layer. This advantage is used now for the study of the system under other circumstances and the presence of other atomic species.

2. Theoretical method

In this section, we review the experimental and theoretical results for water adsorption. The most used method to determine the hydrogen molecule adsorption on graphite is second order perturbation theory MP2. K.V. Pogorelyi and V.V. Turov [4], modeled water adsorption complexes on basal and partially oxidized lateral thermal expanded graphite using 1.42 Å and 3.55 Å for C-C bond length in the basal plane of graphite, and the separation between planes, respectively, with a relative shift between them of 0.142 nm. This means they considered the most typical graphite formed by layers of type A and B, displaced one from another the distance given above. To model the interaction of a water molecule with the basal graphite face, they used a sample cluster with 32 carbon atoms, saturating the peripheral atoms with hydrogen atoms.

The binding energy of water with a center-symmetric fused-benzene ring structure with increasing size was calculated by C. S. Lin and coworkers [5], obtaining for the binding energy 0.125 eV. For a water cluster assembly $(H_2O)_n$, n=1-6 on a graphite surface, they used a density functional tight-binding method complemented with an empirical van der Waals (vdW) force correction with confirmation using second-order Møller Plesset perturbation theory. The binding energy of water clusters interacting with graphite is dependent on the number of water molecules that form hydrogen bonds, but is independent of the water cluster size. They recognize that to obtain qualitative information about the interaction between water molecules and a graphite surface, the effect of vdW interaction should be taken into account. The method used by Lin and coworkers is a less expensive, computationally efficient approximation to density functional theory. The self-consistent charge density functional tight-binding (SCC-DFTB) scheme is complemented by the empirical London dispersion energy term (acronym DFTB-D). This is used to study the energy and geometry structure of water clusters $(H_2O)_n$, n=1-6, interacting and adsorbed on a graphite surface, modeled with a center-symmetric fused-benzene ring structure with increasing size, denoted as $(fbz)_m$, m being up to 51, the number of carbon hexagonal rings. For one water molecule interacting with a benzene molecule, using different basis sets, the binding energy of the benzene-water system predicted with the MP2 method is between 0.086 eV and 0.130 eV. The result of the DFTB-D method is 0.098 eV. This is in good agreement with a pair of experimental results: 0.097±0.0121 eV and 0.105±0.0039 eV. It is convenient to mention that we could not find experimental results for the adsorption of water on graphene. Thus, we take experimental results for similar systems, like graphite or benzene. See Table I, for comparison. Both the experimental and theoretical results show that one of the H-O bonds of the water molecule points to a carbon atom of the benzene ring and the other H-O bond is nearly parallel to the benzene ring. The distance predicted by DFTB-D is 3.257 Å between the oxygen and the center of mass of the benzene ring. The high-level theoretical calculations at both the CCSD(T)/aug-cc-pVDZ and MP2/aug-cc-pVDZ levels of theory yields distances of 3.235 and 3.211 Å, [5]. Lin saw those results are in good agreement with the experimental value of 3.347 ± 0.005 Å, given by Suzuki [6].

With resonant two-photon ionization time-of-flight mass spectroscopy for the neutral complex C_6H_6-H_2O, among others, Gotch and Zwier [7], concluded that the H_2O molecule must be on or near the sixfold axis of C_6H_6, undergoing internal rotation about the sixfold axis. Previous ab initio calculations to Gotch work predict a benzene-H_2O center of mass separation in the range 3.21-3.33 Å, while semi empirical calculations are $\sim$ 0.2 Å smaller. Calculated binding energies are in the range 0.130-0.173 eV. All but one calculation predict that the water molecule lies in a plane perpendicular to the benzene plane. Still, there were more predictions in the orientation of a water molecule within this plane, *i.e.*, whether water is π hydrogen bonded to benzene via one or two hydrogen atoms. The semi empirical potential of Severance and Jorgenson favors a single hydrogen atom down, while others show large amplitude bending motion. Gotch results are in agreement, especially with ab initio calculations. The experimental configuration and structure is for a water molecule's center of mass on, or very near, the six fold axis with the center of mass separation of 3.32 ± 0.07 Å, very close to the calculated one. For two water molecules above the benzene ring, the structure is best described as a water dimmer in witch one of the water molecules is hydrogen bonded to benzene's π cloud. This is also other result obtained by Gotch and Zwier. In other work, Chakarov *et al*., [8], studied the effect of potassium. They remember that water alone adsorbs non dissociatively on the clean graphite surface at 85 K, forming hydrogen bonded aggregates. They found that water coadsorption with potassium is nonreactive or reactive, depending on temperature and potassium coverage. On the other hand, Courty *et al*., [9] made experiment and molecular dynamics simulations to document the ionization behavior of the C_6H_6-H_2O and C_6H_6-D_2O complexes close to the ionization threshold. They deduced the binding energy D_0, for the neutral species: $D_0(C_6H_6\text{-}H_2O)$ = 0.106 ± 0.004 eV and $D_0(C_6H_6\text{-}D_2O)$ = 0.116 ± 0.005 eV. The calculations are based on a semi empirical intermolecular potential. With their potential they found that the water molecule is located just above the benzene ring, in such a way that the oxygen atom stands on the benzene C_6 axis. They obtained 3.16 Å for the distance between the water and the benzene center of masses, in reasonable agreement with ab initio calculations, but a little less than the experimental values. The planes of both molecules (the benzene ring and water molecule), are perpendicular and their configuration is similar to our orientation for the water molecule shown in panel c of Fig. 1. The intersection of the water plane with the graphene layer in our case contains two symmetrically opposite carbon atoms in the hexagonal ring and for them the intersection of the water plane is with the middle and opposite points of two C-C bonds in the benzene ring. The two hydrogen atoms in the water molecule in their configuration are directed toward the benzene ring in a quasi-equivalent way. So, there is a little height difference for the two hydrogen atoms, above the benzene ring. If the water hydrogen atoms were equivalently directed toward the benzene ring, there will be only one attraction well. But, on the contrary, there will be a double well on the potential energy surface if not. Jijum Zhao *et al*., [10] studied the adsorption of gas molecules NO_2, O_2, H_2O, NH_3, CH_4, CO_2, H_2, N_2 and Ar in carbon nanotubes and nanotube bundles. The tube-molecule interaction is physisorption. Most molecules studied (with exception of NO_2, and O_2) are charge donors with small charge transfer ($0.01 \sim 0.035$ electron per molecule) and weak binding (≤ 0.02 eV). For NO_2, and O_2, both of which are charge acceptors, the charge transfer is not negligible. The equilibrium tube-H_2O distance is 2.69, 2.68 and 2.69 Å, for (10,0), (5,5) and (17,0) SWNT respectively. The corresponding adsorption energies were 0.143, 0.128 and 0.127 eV. The charge transfer is 0.035, 0.033 and 0.033 e, for those SWNT, respectively. For those nanotubes the optimal adsorption site was on the top of a carbon atom.

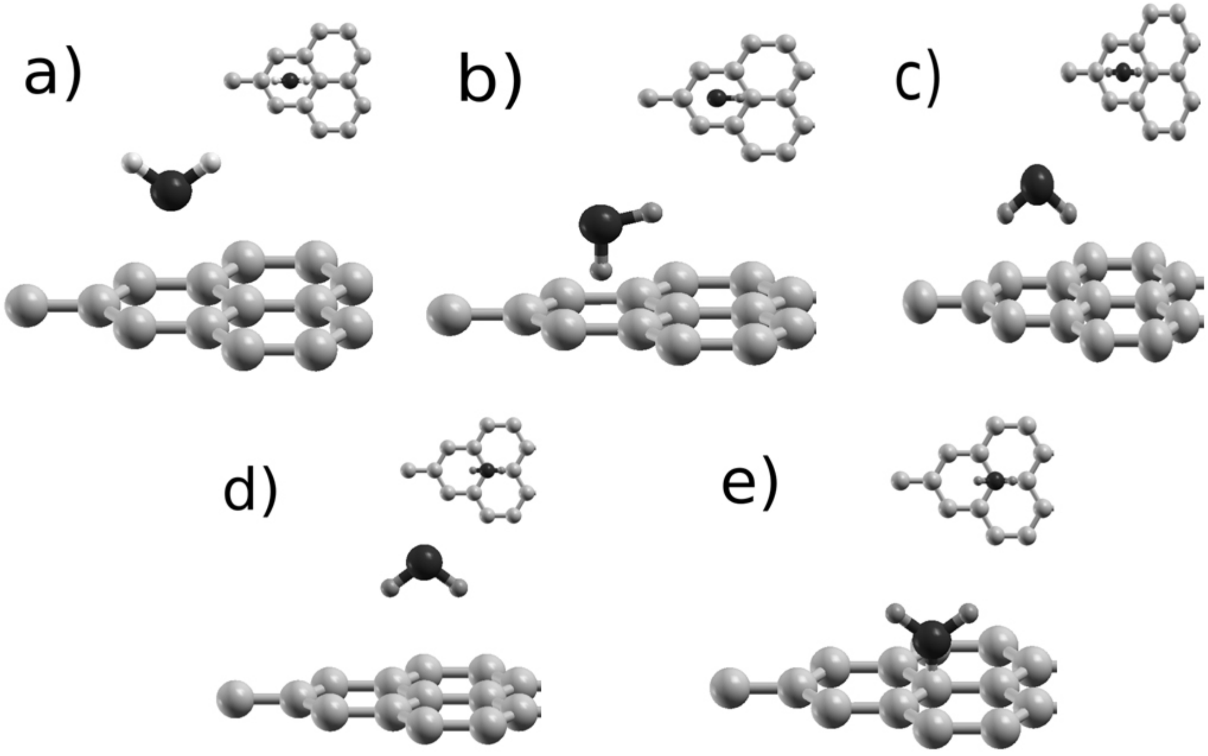

FIGURE 1. Configurations for the water molecule above the graphene layer. The interlayer distance is 35 a.u. In configurations a, b and c, the oxygen atom is above the hexagonal cavity formed by the carbon atoms. The oxygen atom is just above a carbon atom in the configurations d and e.

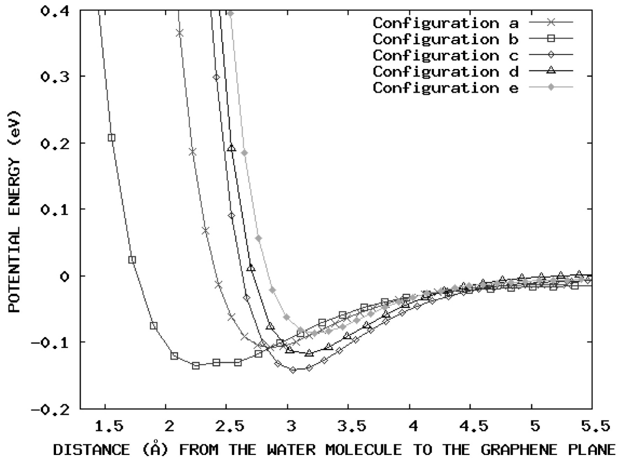

FIGURE 2. Total potential energy (eV) for the water molecule above the graphene layer, for the five configurations shown in Fig. 1. The distance (Å), is measured from the water molecule to the graphene layer.

As it was mentioned above, Feller and Jordan estimated the interaction energy between a water molecule and a single layer of graphite. They obtained 0.251±0.017 eV This value is larger than other reported values, which vary from -0.071 to -0.186 eV [11,12]. Using the Dang-Chang (DC) many body polarizable potential model, Karapetian and Jordan [13] predicted the binding energy of a water molecule and graphite to be 0.1084 eV. DFT was also used by Sanfelix *et al*., [14], with a plane-wave basis set with ultra soft pseudo potentials to evaluate the structure of water layers on the closed packed surface of graphite under low and high coverage. The water molecule was located at least 3.5 Å above the graphitic surface. The vdW force was not taken into account for that calculation.

B. Collignon *et al*., [15] studied, with quantum calculations, the interaction between small water aggregates containing up to five water molecules and hydroxylated graphite surfaces. These surfaces are modeled by anchoring OH groups on the face side or on the edges of a graphite crystallite of nanometer size. The calculations based on the ONIOM approach aim at characterizing the adsorption properties (structure and adsorption energy) of small water aggregates, in order to better understand at a molecular level the role of these OH sites in the hydrophilic properties of graphite surface modeling soot emitted by aircraft. This soot is made of non-crystallites containing graphite-type layers of 20-50 nm size, with hydrophilic sites such as carbonyl, carboxyl, phenol, and hydroxyl groups. Thermodynamics measurements of water adsorption isotherms confirmed that soot particles could acquire a substantial amount of water molecules unlike pure graphite. The OH group can act as a nucleation center for small water aggregates (3-5 molecules), with mean adsorption energies per water molecule between 0.1730 and 0.333 eV above the face, and between 0.200 and 0.354 eV above the edge of the hydroxilated graphite cluster. Wayan

TABLE I. Data obtained in this work for the binding energy of the water molecule. The energies are compared with experimental values and theoretical results obtained by other groups. The last column is the estimated distance from the oxygen atom to the graphene layer. SCC-DFTB means self-consistent charge density functional tight-binding and vdWC is van der Walls correction. DFTB-D means that the calculation includes the empirical London dispersion energy term.

Reference	Methodology	Configuration	ΔE in eV (kcal/mol)	Distance (Oxygen- graphene) (Å)
This work	DFT-LDA	a	-0.1075(-2.479)	2.88
This work	DFT-LDA	b	-0.1348(-3.109)	2.25
This work	DFT-LDA	c	-0.1421(-3.278)	3.06
This work	DFT-LDA	d	-0.1172(-2.704)	3.12
This work	DFT-LDA	e	-0.0866(-1.997)	3.22
Ref. 3	(MP2)	a	(-2.32)	(3.09, 3.12)
Ref. 3	(MP2)	c	(-2.39)	(3.39, 3.45)
Ref. 2	(MP2)		(-4.05 $\pm$ 0.406)	
Ref. 1	(MP2)	b	(-5.8 $\pm$ 0.4)	
Ref. 9	Potential Modeling	c	(-3.30)	~ 3.16
Ref. 9	Experimental		(2.44 $\pm$ 0.09)	$\sim (1.6, 2.7)$
Ref. 7	Experimental		(1.63 , 2.78)	3.32 $\pm$ 0.07
Ref. 5	SCCDFTB+vdWC		(2.9)	
Ref. 5	DFTB-D		(2.28)	3.257
Cited by Ref. 5	Experimental		(2.25 $\pm$ 0.28)	
Ref. 6	Experimental			3.347 $\pm$ 0.005
Ref. 11,12			(-1.65 , 4.3)	
Ref. 13			(-2.5)	
Ref. 14				~ 3.5

and Wallace [3], estimated the interaction energy of a water molecule with a graphitic cluster using ab initio methods at MP2 level of theory and with the 6-31G (d=0.25) basis set. The interaction energy is estimated by extrapolation of two series of increasing size graphitic cluster models ($C^2_{6n}H_{6n}$ and $C^2_{6n}F_{6n}$, n = 1, 3).They studied the effect of using fluorine instead of hydrogen atoms for terminating the cluster model, to clarify the role of the boundary. They considered two fixed orientations of the water molecule: (a) both hydrogen atoms of water pointing toward the cluster (see panel c in Fig. 1), and (b) both hydrogen atoms of water pointing away from the cluster (see panel a in Fig. 1). The interaction energies are found to be -0.1036 and -0.1005 eV, respectively for those orientations, when the cluster is terminated with hydrogen atoms. For fluorine atoms, the corresponding energies were -0.1079 and -0.1057 eV One conclusion of Wayan and Wallace is the following. The terminating atoms for the cluster model affect strongly the interaction energy of the water molecule with a finite cluster and that the uncertainty in the water orientation on a graphitic surface will require larger size of basis sets and a higher level of theory to improve the interaction energies.

The role of the substrate in the water adsorption on graphene was studied by Wehling and coworkers [16]. They used DFT. They calculated the electronic properties of graphene upon water adsorption and the influence of the SiO_2substrate. Perfect suspended graphene is rather insensitive to H_2O adsorbates. They found a different behavior for graphene on a defective SiO_2 substrate. H_2O adsorbates can shift the substrates' impurity bands and change their hybridization with the graphene bands. Then H_2O can lead to doping of graphene for much lower adsorbate concentrations than for free hanged graphene. This effect has a strong dependency on the microscopic substrate properties. Previous DFT calculations found H_2O physisorption but no H_2O induced impurity states close to the Fermi level. Highly oriented water clusters as well as water adsorbates with a defective SiO_2 substrate can lead to doping of graphene. They proposed model systems for water and ice in different concentrations on free standing graphene as well as for water interacting with defective SiO_2 substrates.

Picaud and coworkers [17] used molecular dynamics (MD) simulations to study the adsorption of water molecules on partially oxidized graphite surfaces containing COOH and OH sites. The competition of those sites with respect to water adsorption was characterized at 200, 250 and 300 K. Their results show that the adsorption process is mainly driven by the interaction water-water and the interaction water-COOH sites, at least at low water coverage. The adsorption energy of one water molecule is equal to about -0.39 eV above a COOH site, nearly twice than above a OH site. This is because the formation of two hydrogen bonds between H_2O and COOH instead of only one between H_2O and OH. The MD simulations show that OH in addition to COOH sites can influence the dynamics of the water adsorption process at 300 K. The dynamics of the adsorption process depends on the presence of COOH and on the distribution of OH sites on the surface. The gaps in the formation energy present in the spectrum of graphene and its bi-layer, when both these materials are covered with water and ammonia molecules was studied by Ribeiro *et al.*, [18]. They obtained energy gaps between 0.020 and 0.030 eV. These results are compatible with experimental studies of graphene bi layer. They also show that the binding energies are large enough for the adsorption of the molecules to be maintained even at room temperature. For having full working devices made of graphene, there is an energy gap in the spectrum, as in the usual semiconductor devices. However, both graphene and its bi layer do not present an energy gap in the spectrum. The position and orientation of water and ammonia relative to the graphene and its bi layer surfaces was obtained as well as the binding energies. The highest value of the binding energy was close to 1 eV. This means that the molecules' desorption cannot be obtained at room temperature. A surface coverage is expected if the surfaces are exposed to water or ammonia. The mechanism for opening an energy gap may be different for the graphene single and bi layer surfaces. This is because the random distribution of the molecules on the single layer may not break the A-B symmetry in average; while the gap opening in the bi layer is related to the symmetry between top and bottom layers of typical graphite.

Finally, in a recent study [20], Ma *et al* used Quantum Montecarlo and the random-phase approximation to study the interaction of water molecules with a graphene layer. They found that the water molecules are adsorbed with an energy < 100 meV.

DFT with LDA and the Quantum Espresso code [21] were used to perform all the energy calculations. The results confirm that the approximation used in [21] is good enough to describe the adsorption of the water molecule on a graphite layer. The code requires periodic cells and plane waves. As a first step, Troullier-Martins pseudo potentials were generated with the fhi98PP code [21], for the atoms C, O and H. The valence electrons were C: $1s^22p^2$; O: $2s^22p^4$ and H: $1s^2$. The cutoff radii were respectively r_s = 0.794 and r_p = 0.815 Å, for C; r_s = 0.661, r_p = 0.661 and r_d = 0.661 Å for O and r_s = 0.423 Å, for H atom. For these atoms the s component of the pseudo potential was used as the local one. A total of 34 K points were used in the Monkhorst and Pack convention [23], for the automatic generation of the k points. For exchange and correlation the local density approximation, with the Perdew-Zunger functional [24] was used. The cutoff energy was 1600 eV, and 0.0001 eV was the convergence energy value for the calculated energies.

The carbon pseudo potential was tested for graphite. The relaxed C-C bond length was 1.4076 Å. The optimized interlayer graphene distance was 3.32 Å. The experimental values are 1.415 and 3.350 Å [5], respectively. Next, using the H and O pseudo potentials and by relaxing its structure, a bond length OH of 1.8248 a.u. (0.9657 Å) and an angle OHO of 104.47 degrees were obtained for the water molecule. The experimental values are 0.9578 Å and 104.50 degrees, respectively. In this way our results for these quantities compare very well with the experimental ones. To study the interaction of only one hydrogen molecule with an isolated graphene layer the distance between adjacent graphene layers was fixed at 18.52 Å.

3. Results for water adsorption on graphene

To model the interaction of a water molecule with a graphene layer, a hexagonal, infinite and periodic cell formed by 18 carbon atoms was used. The cell parameters are a = b = 7.31 Å, and C = 18.52 Å. The distance between two adjacent water molecules is 7.31 Å.

The distances are from the oxygen atom to oxygen atom of each molecule. These values assure that there is no interaction between neighboring water molecules. In a first step, we performed static calculations for five different orientations of the molecule respect to the graphene layer. Those orientations or configurations are shown in Fig. 1. They are denoted with labels a, b, c, d and e respectively. On panels a, b, and c, the oxygen atom is above the center of the hexagonal cavity. In panels d and e, the oxygen atom is upon a carbon atom of the graphene layer. Total potential energy curves were obtained for each one of those orientations. To build the energy curve, the distance (H_2O-graphene layer) was changed several times without any change of neither the molecule orientation nor the HO length or in the H-O-H angle. In other words, that length and angle were kept frozen during the calculations. For those values, we used 0.9657Å and 104.47 degrees, respectively. Those values were obtained when an isolated water molecule was relaxed. For all the molecule orientations the total potential energy values are constant when the distance between the center of mass of the water molecule and the graphene layer is close to 10 Å. This let us assign the zero energy value for the distance 10 Å for each orientation.

In Fig. 2 are shown five energy curves. They have the same behavior and converge for distances beyond 4 Å, and correspond to each one of the orientations of the water molecule shown in Fig. 1. It can be seen in Fig. 2 that the binding energy is more negative for the third orientation (panel c in Fig. 1). The water molecule is adsorbed close to 3.1 Å above the hexagonal cavity formed by the carbon atoms, with the hydrogen atoms a little closer to the graphene layer than the oxygen atom. The minimum for the energy curve is around 2.25 Å for orientation b, and near 3.25 Å for orientation e. This means that in a full relaxation for the molecule, in a region between 2.25 and 3.25 Å above the graphene layer, the water molecule may change its orientation and its configuration easily to reach a configuration with the minimal energy. The static equilibrium positions and binding energies (depth of the potential well) are in Table I, with other theoretical and experimental data. The small value of each one of the binding energies, with magnitudes less than 0.15 eV, suggest that the water molecule is physisorbed on the graphene layer.

4. Discussion

The results in Table I, obtained here with DFT and LDA not only are consistent with experimental results. In contrast with other calculations for the binding energy, our results have no boundary contributions to the binding energy due to some hydrogen or fluorine atoms considered by other groups around the carbon atoms used to simulate a piece of a graphene sheet. Our results simulate a periodic and infinite graphene layer alone and the adsorption of a water molecule. Even this process, the adsorption of the molecule, due to the periodicity of the system, is repeated some distance apart (the cell parameter), it has the advantage also, respect to the MP2 calculations, that are well converged and with a relatively low computational cost respect to another type of calculations. The greater energy difference is 0.55 eV, this is for the orientations c and e in Fig. 2. Once more, this confirms the great sensitivity and dependence of the energy calculation upon the orientation of the water molecule respect to the graphene layer. Table I also contains the optimized distances of the oxygen atom to the graphene layer. The smallest distance is for orientation b (2.25 Å) and the largest one is 3.22Å for orientation e. This result can be stated in the following way. It is expected that when the water molecule approaches the graphene layer from approximately 4Å above the graphene layer, its orientation and configuration may change a lot. For example, a trajectory for the water molecule may begin with orientation e (see Fig. 1). Then, the oxygen atom is closer to the graphene layer than the hydrogen atoms of the molecule, and above a carbon atom and may finish with configuration c, changing the relative positions of the atoms of the molecule. Look out that for orientation c (see Fig. 1),the hydrogen atoms are closer to the graphene layer than the oxygen atom and that this atom has been displaced to end just above the center of the hexagonal cavity formed by six carbon atoms of the graphene layer.

All those static calculations were complemented with MD calculations at 0 K, for the initial orientations given by d and by a (see Fig. 1).There are differences in the relative positions of the hydrogen and the oxygen atoms in these configurations. The oxygen atom is above the center of the hexagonal cavity in one case, and it is above a carbon atom in the other case. However, the mean adsorption energy has the same value: 0.117 eV and the mean distance of the oxygen atom to the graphene layer was 3.055 Å, for both configurations. The average dipolar moment of the hydrogen molecule at the end of both MD calculations, remains nearly parallel to the graphene layer. The average angle H-O-H, and length H-O, for the last 25 steps in the MD (time step 1 femtosecond), had the values 103.8058 or 103.9074 degrees, and 0.9722 or 0.9712 Å, for orientations (a) and (d), respectively. The number of steps was 2074 and 1850, respectively for those calculations. These average quantities can be compared with the initial values 104.5328 degrees and 0.9657 Å for angle H-O-H, and length H-O, respectively. Due to the effect of temperature, the inter-atomic distance H-O, is increased in a little less than 1.0 %. The time evolution of the system for both configurations shows the water molecule freedom to displace from one site to another site above the graphene layer, and for the hydrogen atoms to rotate around the oxygen atom. The value of the adsorption energy agrees with that of Gotch *et al.*, [7]. They reported 3.32 ± 0.07 Å for the distance from the center of mass of the water molecule to the benzene ring

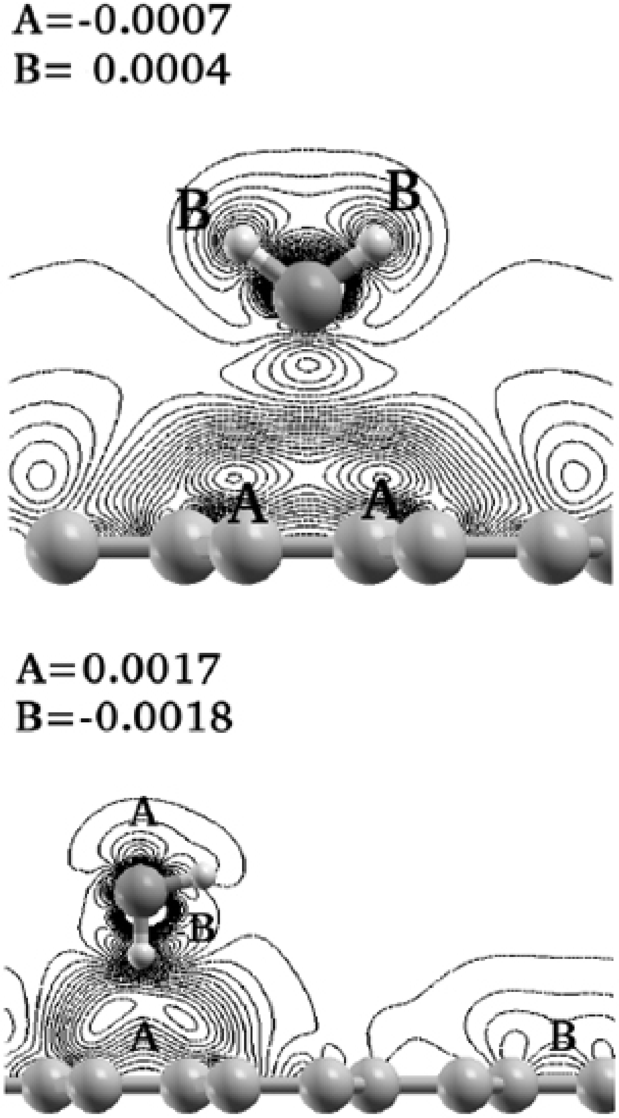

FIGURE 3. (above) and Fig. 4 (below). Charge density difference for the system formed by the graphene layer plus the water molecule in the equilibrium configuration The geometries correspond respectively for the equilibrium configurations a, and b of Fig. 1.

C_6. Our estimation is 3.06 Å for configuration c in our system. They give for their system a binding energy within the large range -0.070, -0.120 eV. We predict a larger binding energy, -0.1421 eV, for configuration c. This is the most favorable of all the studied static configurations.

We also analyzed the charge density difference for all the studied cases. This allowed us to conclude that the charge redistributions between the graphene layer and the water molecule, for all the initial orientations, a through e, are small. This makes evident that the graphene layer-water molecule interaction is small, of the van der Walls type.

In Figs. 3 and 4 we show the charge density difference on the perpendicular plane to the graphene layer. Figures 3 and 4 correspond to the bottom of the total potential energies of configurations named a, and b, respectively from Fig. 2. The oxygen atom in Fig. 3 is located 2.88 Å above the graphene plane. Above the oxygen atom, there is a deficit of electronic charge of magnitude 2.6×10^{-3}e/(Å$)^3$. This zone is denoted as region B in that figure. In contrast, region A, close to the graphene layer, has an excess of electronic charge of magnitude 4.7×10^{-3}e/(Å$)^3$. This means that a net electronic charge transfer occurs from the water molecule to the graphene layer. On the contrary, in Fig. 4, for orientation b of the water molecule, there is an excess of electronic charge just below the oxygen atom. The charge density difference becomes positive in region A of that figure 2.5×10^{-4}e/(Å$)^3$, above the hexagonal ring formed by the carbon atoms of the graphene layer. In this case there is a net electronic charge transfer from the π orbitals of the carbon atoms to the hydrogen atom of the water molecule, just above the hexagonal ring of the graphene layer.

One interesting point is that the minima of the potential energy curve is for a distance of 2.25 Å between the oxygen atom and the graphene layer for orientation b, while the corresponding distance is around 3 Å for other orientations of the water molecule.

5. Conclusions

With an infinite, periodic, hexagonal cell with 18 carbon atoms, and cell parameters a = b = 7.31 Å, and c = 18.52 Å, it was studied the water adsorption on the graphene layer. Total potential energy curves for static calculations for five distinct approaching orientations of the water molecule to the graphene layer, were obtained. The respective binding energies (minima of the energy curves), -0.1075, -0.1348, -0.1421, -0.1172 and -0.0866 eV, are given in Table I.

Molecular dynamics for two different orientations (denoted with label a, and d) of the water molecule, reach the same energy value, -0.117 eV for the binding energy. This value is practically the same as that obtained in the static calculation for orientation d. Wayan Sudiarta and Wallace Geldart studied water adsorption to graphite using Moller Pleset second order perturbation theory (MP2) with cluster models for the graphene layer, terminated with hydrogen or fluorine atoms. They obtained -0.1036 and -0.1005 eV respectively, for the interaction energy of water molecule with the hydrogen terminated carbon cluster, for orientations corresponding to those denoted with labels a and c, in Fig. 1. In resume, using density functional theory with local density approximation, our calculations are very well compared to the experimental available data for water adsorption on graphene. The theoretical method used here, in comparison with the MP2 approach, has no terminating atoms for the carbon cluster model, neither any bordering problem. One more advantage of the LDA calculation is the less computational cost than using the more costly MP2 calculation. This advantage is now used to continue the study of the system but with the presence of other atomic species and taking into account not only the effect of pressure but also temperature as well.

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