Electronic Structure Calculation of Adsorbate Gas Molecules on a BN Nanolayer, a First Principle Study

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Abstract—**In this paper, a first-principle investigation of the electronic properties of monolayer hexagonal boron nitride adsorbing gas molecules of gas molecules of H_2O, CO_2, NO, NO_2, NH_3 and H_2 within density functional theory (DFT) is presented. For full geometric relaxation of the molecules in the vicinity of a BN sheet, we obtain the adsorption geometry, the equilibrium cohesive energies, charge transfer and density of states (DOS). We discuss the changes in the density of states as well as the extent of charge transfer, band gap and finally the exchange energies due to the presence of these adsorptions. These absorptions affect electronic structure of 2D BN sheet. We can identify which of the adsorbate molecules is acting as donor or acceptor.**

Keywords-Density functional theory; Density of state; BN nanolayer; Charge transfer.

I. Introduction

Two-dimensional crystals, including graphene and single layer of hexagonal boron nitride (BN), have recently been fabricated [1]. Among them, only graphene has been studied extensively [2]. Unlike graphene, two-dimensional (2D) graphenelike BN [3] is a wide band-gap semiconductor and is a promising material in optics and opto-electronics [4]. The gas molecules, H_2O, CO_2, NO, NO_2, NH_3 and H_2, are all of great practical interests for industrial, environmental and medical applications.

Boron nitride is a binary chemical compound consisting of equal proportions of boron and nitrogen. The hexagonal structure of boron nitride is geometrically similar to that of graphite in carbon structures [5, 6], since in the periodic table, boron and nitrogen are adjacent to carbon [5]. It is second only to diamond in hardness. Boron-Nitride (BN) in ionic honeycomb lattice which is the Group III-V analogue of graphene has also been produced having desired insulator characteristics. Nevertheless, unlike the delocalized π electrons in graphite, the π electrons in BN are distributed more around N, because of its stronger electronegativity. This strong directional effect of bonding confines the motion of the π electrons and thus results in a gap in *h*-BN. BN is the lightest III-V compound of those that are isoelectronic with III-V semiconductors such as GaAs, but with a wider band gap with ionic bonding through significant charge transfer from B to N. , i.e., E_g(BN)=4.0–5.8 eV at room temperature [7], compared with 1.42 eV of GaAs. Moreover, it is believed that the large band gaps in this material may produce better electronic properties than those of carbon

structures [8]. Hexagonal boron nitride sheets are also known as good electrical semiconductors with excellent stability and thermal conductivity which can be used in vacuum technology, the nuclear energy industry, and for the development of x-rays and lubrication [9].

In this work, we perform first principles calculations for the adsorption of H_2O, CO_2, NO, NO_2, NH_3 and H_2 molecules on a Hexagonal boron nitride sheet. After geometrical optimization, we obtain the positions and orientations of the adsorbed molecules. We then calculate the adsorption energies (E_{ad}) and the charge transfers between BN sheet and adsorbate molecules due to bindings between the molecules and atoms in BN layer. By probing the density of states (DOS) of these systems one can find out the direction of charge transfer (from the molecules to the BN sheet or vice versa) and from this one can determine whether the doped molecule acts as a donor or as an acceptor.

The organization of this paper is as follows: In Section II the computational details are discussed. In Section III we investigate the electronic structure of the BN sheet surface with adsorbate molecules, using density functional theory within the local density approximation.

II. Computational Details

Our calculations are based on the use of DFT and the *ab initio* pseudopotential plane-wave method using the PWSCF code of the Quantum ESPRESSO distribution [10]. We performed the calculations with LDA Perdew-Zunger (PZ) [11] (non NLCC) pseudopotentials. For the pseudopotential generation Brillouin Zone integrations were performed using a $8\times8\times1$ Monkhorst and Pack [12] special point grids using Gaussian smearing technique with a smearing width of 0.02 Ry in order to smooth the Fermi distribution. The Kohn-Sham orbitals are expanded in a plane wave basis set. The energy cut-off for the wave function and the charge density are respectively 45 Ry and 300 Ry. These values are used because of the ultrasoft pseudopotentials for N, B, C, O and H and the imposed periodic boundary conditions.

A BN sheet is simulated by a relatively small orthorhombic supercell of 8 atoms, with lattice parameters *a* = 4.92 ˚A, *b* = 4.26 ˚A in the *xy* planes and *c* = 12.01 ˚A (Figure. 1).

Figure 1. The unit cell of BN sheet with 8 atoms.

The sampling of the Brillouin zone was done using a 8×8×1 grid, and tested to give convergent results for the total energy. For calculating the density of states (DOS), we use a $20 \times 20 \times 1$ grid. The charge transfer from B to N is obtained 0.419 e and band gap of BN sheet is calculated 4.33 eV which are are in good agreement with other results (0.429 e and 4.64 eV).

The amount of charge transfer from BN sheet to the molecules can be estimated by projecting the charge density onto the atomic orbitals. We define the charge transfer as the

difference between the Löwdin charges for isolated BN sheet and BN sheet with the adsorbate molecule. From this result one can determine whether the adsorbate acts as an acceptor or as a donor. It is important to note that the size of the charge transfer is slightly dependent on the method chosen for calculations. For each adsorbate molecule, adsorption site is considered on the top of the center of the hexagon. For this position, we relaxed the BN sheet with the molecule adsorbed on it. Then we determined the exact orientation and position of the molecules on the surface.

The adsorption energy (E_{ad}) is defined as the difference between the energy of the fully relaxed BN sheet with the adsorbed molecule on it (E_{total}) and the sum energy of the BN sheet (E_{sheet}) and the isolated molecule ($E_{molecule}$):

$$E_{ad} = E_{total} - (E_{sheet} + E_{molecule}).$$

TABLE I. CALCULATED ADSORPTION ENERGIES (EAD) AND CHARGE TRANSFER (CT) FROM THE GAS MOLECULES TO BN SHEET.

Molecules	NO	NO$_2$	CO	CO$_2$	H$_2$O	H$_2$	NH$_3$
E_{ad} (meV)	-117	-125	-97	-103	-140	-81	-100
CT (e)	0.0054	0.0387	0.0201	0.0259	0.0145	0.0139	0.0169

We find that different gas molecules prefer different geometries in the adsorption. The configurations of the molecule-BN systems were optimized through fully relaxing the atomic structures until the remaining forces were smaller than 0.001 eV/Å. The orientations of gas molecules are adsorbed around the center of the hexagon as shown in Figure 2, 3 and 4. The bond length of the adsorbed CO and NO near the BN sheet are 1.131 and 1.162 ˚A respectively which are a little longer than the bond length of the isolated CO and NO molecule (1.128 and 1.15 ˚A). The molecules take an orientation with its C or N atom pointing at the BN sheet. The low adsorption energy and long distance indicate a weak interaction.
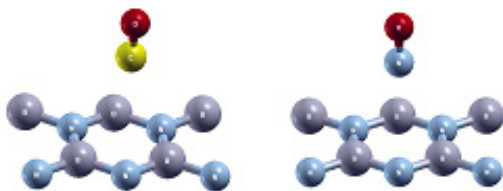

Figure 2. The position of the CO and NO molecules on the BN sheet after full relaxation.

For the adsorbed CO$_2$ and NO$_2$ the length of the C-O and N-O bond are calculated to be 1.166 and 1.202 ˚A and the O-C-O and O-N-O angle 179.7◦ and 133.1◦.The adsorbed NO$_2$ molecule bonded to the sheet surface with both oxygen ends, while the adsorbed CO$_2$ axis aligned parallel to the BN plane The calculated bond length of the adsorbed CO$_2$ and NO$_2$ are a little longer than that of the isolated one which are 1.20 and 1.197 ˚A, and the calculated O-C-O and O-N-O angle is smaller than the one in isolated CO$_2$ and NO$_2$ which are 180 and 134◦.
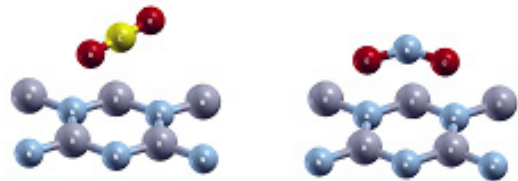

Figure 3. The position of the CO$_2$ and NO$_2$ molecules on the BN sheet after full relaxation.

The calculated bond length of the adsorbed H$_2$, H$_2$O and NH$_3$ are 0.769, 0.98 and 1.02 ˚A are a little longer than that of the isolated one. In these adsorptions, the adsorption configuration of molecules on the BN sheet has one hydrogen atom pointing towards the sheet.
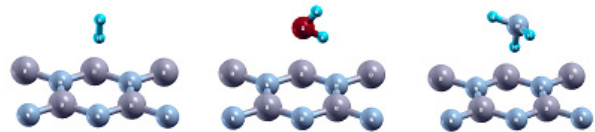

Figure 4. The position of the H$_2$, H$_2$O and NH$_3$ molecules on the BN sheet after full relaxation.

The results show that all these adsorption configurations are energetically favourable (the negative adsorption energy corresponds to the exothermic reaction). The adsorption energies of CO, NO, NO$_2$, CO$_2$, H$_2$, H$_2$O and NH$_3$ are all smaller than 0.5 eV, corresponding to weak physisorption. The adsorptions of H$_2$O, NO and NO$_2$ on BN sheet are stronger than other and the adsorption of H$_2$ is the weakest.

III. THE DENSITY OF STATES OF MOLECULE-BN SHEET SYSTEM

To verify the effects of the adsorption of small molecules on the BN sheet' electronic properties, the total electronic densities of states (DOS) of the molecule-BN adsorption systems are calculated, and figure 5, 6, 7 and 8 show the DOS for representative systems.

The total DOS of the system and PDOS of the molecules show that these molecules modulate the electronic property in different manners: NO molecule adsorption introduces impurity states in the band gap and the Fermi levels of the system crosses these states. Therefore, gas adsorption will decrease the original band gap, and probably have some influence on the optical properties of BN. For CO adsorption, there are p unoccupied states of C and O in the band gap will decrease the original band gap. It would be very difficult for charge carriers to transit between the valence (or conduction) band and impurity states at finite temperature.
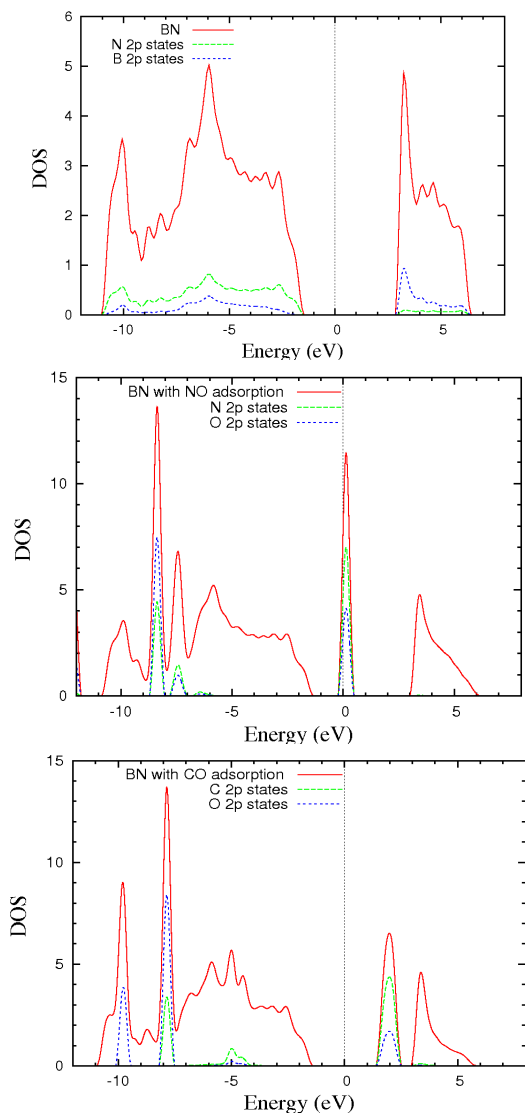

Figure 5.   DOS and PDOS of BN sheet, BN sheet adsorbed NO and BN sheet adsorbed CO. The Fermi level is set to zero.

PDOS analysis (Figure. 6) shows that the states contributed by NO_2 molecules are localized around the top of valence band and hybridize with the original valence band. Because of these half-occupied impurity states being near the top of valence band, the electrons of the valence band can transit into these states and the system will exhibit p-type semiconducting behaviour at finite temperature.

The contribution of the CO_2 electronic levels to the total DOS for both systems is localized between -10.0 and -4.0 eV in the valence bands and around 3.5 eV in the conduction bands, which are far away from the Femi level. This adsorption shows a little change in energy gap respect to BN sheet.
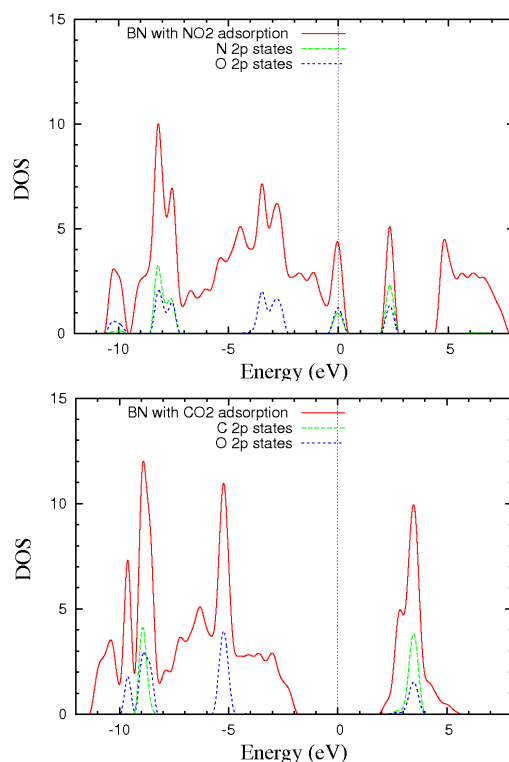

Figure 6.   DOS and PDOS of BN sheet adsorbed NO_2 and BN sheet adsorbed CO_2. The Fermi level is set to zero.

The contribution of the NH_3 electronic level in the NH_3 on BN sheet is localized at -3.0 eV, at top of valence bands, while partial charge density analysis (Figure. 8) for adsorption of H_2 and H_2O on BN sheet show that the states near the Fermi level are mainly contributed by the B and N atoms of the BN sheet rather than H_2 and H_2O molecules. The Fermi energy level shifted towards upper for NH_3 and lower for H_2 and H_2O respect to BN sheet Fermi energy level.
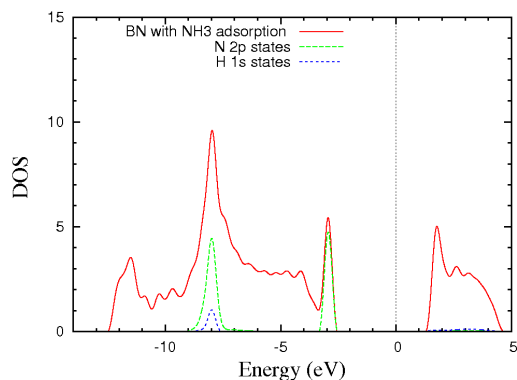
Figure 7. DOS and PDOS of BN sheet adsorbed NH_3. The Fermi level is set to zero.
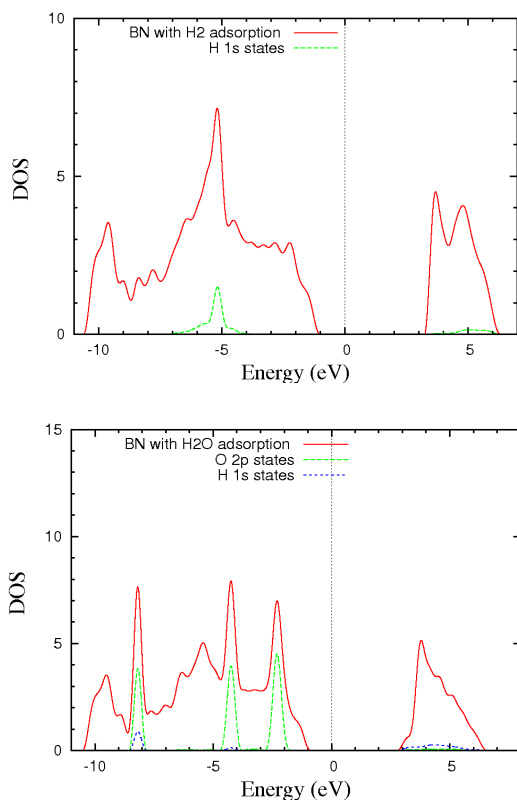

Figure 8. DOS and PDOS of BN sheet adsorbed H_2 and H_2O. The Fermi level is set to zero.

IV. CONCLUSIONS

In this work the adsorption of small molecules on BN sheet was investigated. We optimized the position of the adsorbate molecules on BN sheet. After full relaxation the adsorption energy and the charge transfer properties between the molecules and the BN sheet are determined. The above calculations on the adsorption energies have suggested that the CO_2, H_2 and H_2O on BN sheet have weak interactions between the molecules and the sheet. Such weak interactions

are also evident in their DOS structures (figure. 6, 7 and 8), which show little change after the adsorption. The small charge transfer from the molecules to BN sheet was observed. But charge transfer for NO molecule on BN sheet was very small. The donor behaviour of a molecule causes the Fermi level of BN sheet with adsorbed molecule to shift upward, and the acceptor behaviour of a molecule causes the Fermi level of BN sheet with adsorbed molecule to shift downward with respect to the Fermi level of BN sheet. So, NH_3 and CO_2 act as donor and CO, NO, H_2 and H_2O act as acceptor by the results. The results show that BN sheet is more sensitive to NO_2 and NH_3.

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