

# Electronic Transport Calculation of Graphene with Hexagonal Boron Nitride Substrate Using Maximally Localized Wannier Functions, a First Principle Study

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**Abstract.** In this paper, a first-principle investigation of the electronic properties of graphene on hexagonal boron nitride substrate is presented within density functional theory (DFT). We obtain the most stable orientation of graphene on the substrate, the adsorption energy, the 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 quantum conductivity and current for graphene due to the presence of the substrate. We show that the band gap of 64 meV induced by the BN substrate can greatly improve the electrical characteristics of graphene-based field effect transistors (FETs) and its on/off ratio and decreases the minimum conductance by orders of 3. We identify the substrate is acting as donor for graphene layer.

**Keywords:** Charge transfer, Density functional theory, Density of state, Quantum transport, Wannier function.

## 1. Introduction

Graphene, a one-atom-thick carbon sheet, is a transparent single layer of  $sp^2$  hybridized carbon atoms arranged in a hexagonal honeycomb structure with strong in plane  $\sigma$  and weaker  $\pi$  bonds. It has chemical stability and physical properties like a conductor with high charge carrier mobility. Undoped graphene is a zero-gap semiconductor. Electronic states near the Fermi energy of a graphene sheet at energies close to  $K$  and  $K'$  points in momentum space form Dirac cones. So at low energy, linear energy dispersion relation results zero mass quasiparticles that provide ultrahigh mobility for the graphene carriers and high conductivity. Thus graphene flakes are suitable to construct field effect transistors (FETs) [1]. One of the biggest hurdles for graphene to be useful as an electronic material is the lack of an energy gap in its electronic spectra and its minimal conductivity. Since the Dirac fermions are massless, electrical current does not block by tuning the gate voltage. The lack of a band gap limits the usage of two dimensional graphene for digital switching, where high on/off ratios are necessary.

Considering graphene on a substrate makes the two carbon sublattices inequivalent that opens an energy gap at Dirac points. The origin of this gap is the breaking of sublattice symmetry owing to the graphene-substrate interaction that generates mass for the Dirac fermions that opens an energy gap at Dirac points. By this way one can solve complication of usage of graphene in electronic devices. Here, we show that use of Hexagonal boron nitride (h-BN) as a substrate for graphene produces a gap of  $\approx 64$  meV that is in good agreement with other result [2]. Hexagonal boron nitride (h-BN) is a suitable choice as a substrate for a graphene sheet. It greatly improves the mobility of charge carriers in graphene compared with the corresponding  $\text{SiO}_2$  substrate [1,3,4]. h-BN is a wide gap insulator that has a layered structure very similar graphene. The lattice mismatch of graphene with h-BN substrate is little enough to have least disorders in

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graphene. In this work we have investigated the effects of h-BN substrate on density of states (DOS), band structure of graphene and the charge transfers between graphene sheet on h-BN substrate, using first-principles calculations based on the density functional theory (DFT).

The organization of this paper is as follows: In Section 2 the computational details are discussed. In Section 3 we investigate the electronic structure of the graphene surface with and without h-BN substrate, using density functional theory within the local density approximation. Finally in Section 4 the electrical conductance of pristine graphene and graphene with h-BN substrate are studied.

## 2. Computational details

Our calculations are based on the use of DFT and the *ab initio* pseudopotential plane-wave method using the PWSCF code [5] of the Quantum ESPRESSO distribution. We performed the calculations with LDA Perdew-Zunger (PZ) (non NLCC) pseudopotentials [6]. For the pseudopotential generation Brillouin Zone integrations was performed using a  $4 \times 4 \times 1$  Monkhorst and Pack special point grids [7] using Gaussian smearing technique with a smearing width of 0.01 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 450 Ry. These values are used because of the ultrasoft pseudopotentials for N, B and C and the imposed periodic boundary conditions. A graphene sheet is simulated by a relatively small hexagonal cell of 8 atoms, with lattice parameters  $a = 4.85 \text{ \AA}$ ,  $b = 4.85 \text{ \AA}$  in the  $xy$  planes and  $c = 12 \text{ \AA}$  (Figure. 1). We represent the vacuum above sheet with an empty space of  $12 \text{ \AA}$ .

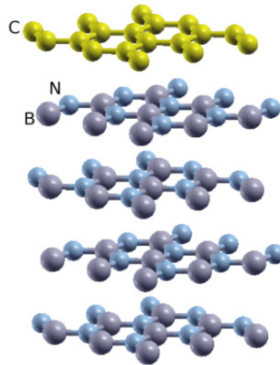


Fig. 1: Configuration of graphene on h-BN

The sampling of the Brillouin zone was done using a  $16 \times 16 \times 1$  grid, and tested to give convergent results for the total energy. To calculate the density of states (DOS) (Figure 2), we use a  $50 \times 50 \times 1$  grid. The charge transfer from B to N is obtained  $0.419 e$  and band gap of a BN sheet is calculated  $4.33 \text{ eV}$  which are in good agreement with other results ( $0.429 e$  and  $4.64 \text{ eV}$ ). Unlike the delocalized  $\pi$  electrons in graphite, the  $\pi$  electrons in BN are distributed more around N, because of its stronger electronegativity. This strong directional effect of bonding confines the motion of the  $\pi$  electrons and thus results in a gap in *h*-BN.

The amount of charge transfer between graphene sheet and BN 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 graphene sheet and graphene sheet with h-BN substrate. From this result one can determine whether the substrate acts as an acceptor or as a donor. The donor behaviour of substrate causes the Fermi level of graphene sheet with substrate to shift upward, and the acceptor behaviour of it causes the Fermi level of graphene sheet with substrate to shift downward with respect to the Fermi level of graphene sheet. There is a small total charge transfer of  $0.014 e$  between graphene surface and the h-BN substrate. Comparing Fermi energy of two cases shows that graphene on h-BN substrate acts as an acceptor.

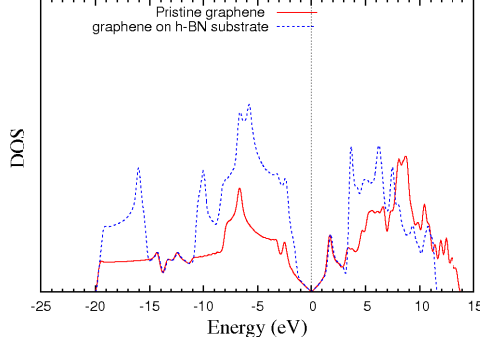


Fig. 2: DOS of graphene with and without h-BN substrate (Fermi energy is set to zero).

h-BN has a hexagonal closed packed structure with weak interaction between layers. The boron atoms in a layer are directly above the nitrogen atoms in its neighbour layer. The orientation of single-layer graphene with respect to the h-BN surface is considered such one carbon takes place over B, and the other carbon centers above a h-BN hexagon. Our calculations show this configuration has minimum of total energy with respect to other possible of configurations. On the basis of this structural information, we construct a unit cell with four layers of *h*-BN and a graphene top layer. Within the local density approximation (LDA), the separation of adjacent h-BN layers and graphene layer is found to be 3.185 Å, which is reasonably close to the experimental value of 3.33 Å and previous work [2]. Here, we show that use of h-BN as a substrate for graphene produces a gap of  $\approx 64$  meV (Figure 3) that is in good agreement with other result [2].

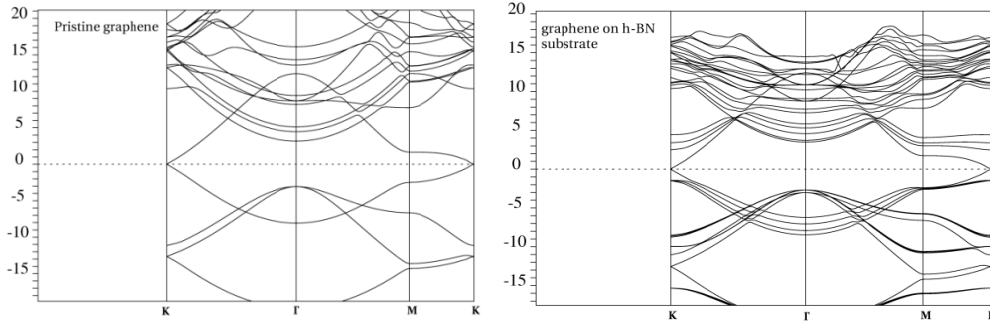


Fig. 3: Band structure of graphene with and without h-BN substrate (Fermi energy is set to zero).

The adsorption energy of this system ( $E_{ad}$ ) is defined as the difference between the energy of the fully relaxed graphene sheet with h-BN substrate ( $E_{total}$ ) and the sum energy of the graphene sheet ( $E_{graphene}$ ) and h-BN in bulk case ( $E_{h-BN}$ ):

$$E_{ad} = E_{total} - (E_{graphene} + E_{h-BN}),$$

the adsorption energy of this system is calculated to be -56.7 meV. The low adsorption energy indicates that the adsorption is a weak physisorption.

### 3. Calculation of electrical conductivity

Calculations of the quantum conductance have been obtained using the WanT package [8] that are performed using the Fisher-Lee formula. The bulk transmittance for the system is considered with homogeneous Monkhorst-Pack grids for Brillouin zone (BZ) summation. We have investigated the electrical transmission of two dimensional pristine graphene with and without h-BN substrate. The wannier functions (WFs)' centers for occupied  $\sigma$  bands are chosen at every bond center and the centers of the WFs for  $\pi$  bands are considered on every carbon atom for graphene and similar for h-BN layers. At first, the WFs and the spreads of the WFs are obtained from the calculations. After calculation in pristine graphene sheet the WFs are symmetric and are centered both at the mid-point of C-C bonds and on carbon atoms, while in the presence of substrate the interactions between substrate and carbon atoms induce a polarization which

modifies the WFs such that their distributions are unsymmetrical near the mid-point of C-C bonds and on carbon atoms Figure 4.

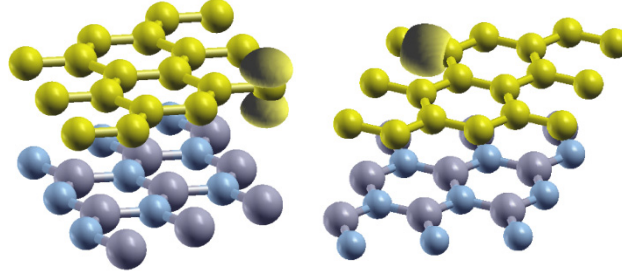


Fig. 4: (Right) Isosurface of  $\sigma$  WF in graphene, (Left) Isosurface of  $\pi$  WF in graphene.

Calculation of quantum conductance and current at low biases are done. As can be seen in Figure 5, at the Fermi level the conductivity of graphene with h-BN substrate is less than that of pristine graphene. This is due to the donor behaviour of the h-BN molecule which causes the Fermi level of graphene with h-BN to shift upward with respect to the Fermi level of pristine graphene. In Figure 5 the I/V curves of the two cases have been depicted. They are linear and ohmic which is in good agreement with other works [9]. Calculating the slopes of these curves, we obtain the conductance of pristine graphene, graphene with the substrate to be 0.58, 0.25 ( $\mu\text{A}/\text{V}$ ), respectively.

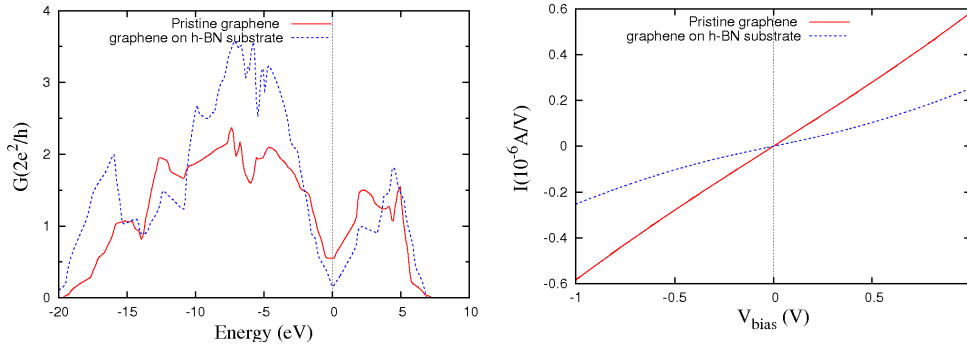


Fig. 5: (Left) Calculated quantum conductance and (Right) current for pristine graphene and graphene on h-BN substrate in terms of bias voltage.

Boardering of bandstructure near Fermi level at K point in momentum space after forming graphene on the substrate induces none zero mass for quasiparticles that provide lower mobility for the graphene carriers and lower conductivity. Minimum conductivities are calculated  $1.1 e^2/h$  and  $0.36 e^2/h$  for graphene and graphene with the substrate that is in good agreement with other work [10]. Minimum current at zero bias voltage is  $3.56 \times 10^{-10} \mu\text{A}$  for graphene that limits the usage of two dimensional graphene for digital switching, where high on/off ratios are necessary. The minimum current is decreased by placing graphene on h-BN substrate,  $1.17 \times 10^{-10} \mu\text{A}$ . As a result, graphene on h-BN substrate has higher on/off ratio respect to pristine graphene.

#### 4. Conclusion

We have investigated the electronic structure and quantum conductance of a graphene sheet on top of a lattice-matched hexagonal boron nitride (h-BN) substrate using first-principles methods. The calculations are done utilizing the density functional theory through the pseudopotentials and plane-waves method within the local density approximation. The most stable configuration has one carbon atom on top of a boron atom, and the other centered above a BN ring. The resulting inequivalence of the two carbon sites leads to the opening of a gap of 64 meV at the Dirac points of graphene and generating a non zero mass for the Dirac fermions that causes decreasing the minimum conductance by orders of 3. The band gap induced by the BN surface can greatly improve the characteristics of graphene-based FETs and its on/off ratio.

## 5. Acknowledgment

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