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A DFT Study of The Sensing and Adsorption of Graphene Nanoribbons for DNA Sequencing

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***Abstract*— Because of its chemical and physical properties, the graphene nanoribbons(GNR) are utilized in the production of accuracy sensors. In this paper, the thickness utilitarian hypothesis Density Functional Theory (DFT) with the B3LYP level, and by utilization of the Gaussian 09 arrangement of projects, was used to explore the adsorptive and detecting ability of DNA on the unblemished nanoribbon. The detecting capacity of these structures was determined as far as a variation of band hole vitality after cooperation among GNR and DNA. Because of counts, it was discovered for GNR that the electronic properties are firmly delicate to the nearness of the DNA particle. In this way, we accept that GNRs can be utilized in sensor gadgets.**

I. INTRODUCTION

Researchers have utilized DNA to investigate life on prior occasions. The DNA is a general fundamental the nearness of life where are on the whole living creatures, the investigation proposes sense the DNA atom by utilizing one of the nanomaterials.

Nanostructures assume a significant job in the progression of logical and designing innovations at the nanoscale. In the course of recent years, nanostructures have inspired a lot of intrigue on account of their particular qualities that impact physical, electrical, substance, natural, and optoelectrical properties. The piece of nanostructures, for example, monometallic, bimetallic, attractive, metal oxide, semiconductor, half and half, composite, and so on., has been utilized habitually as the reason for their characterization. This section surveys the various sorts of nanostructures and nanomaterials, for example, nanowires, nanofibers, nanotubes, nanobelts, nanofluids, nanoribbons, nanosprings, nanocapsules, quantum dabs, nanosheets, nanocomposites, and nanoparticles, thinking about their various directions, morphologies, and qualities. Nanostructures, in the entirety of their structures, establish a functioning zone of innovative work in the fields of nanotechnology and nanoscience.

One of the significant nanostructures is the graphene nanoribbons, which is utilized in clinical and modern applications, one type of graphene will be graphene nanoribbons GNRs.

GNRs have pulled in extraordinary interests from the scholarly community and industry because of its exceptional physical properties: most reduced electrical resistivity, ultrahigh electron portability, high surface territory, great mechanical quality, and high similarity to macromolecules and biomolecules [1-3]. These qualities made graphene nanoribbon has been considered as a promising possibility for cutting edge detecting applications. Up until this point, an assortment of graphene-based sensors has been built for the exceptionally specific or potentially delicate location of mechanical powers, perilous gases, substantial metal particles, physiological signs, and so on.

Among them, biosensors manufactured with graphene have been broadly researched for the recognition of glucose, proteins, H_2 O_2, dopamine, and nucleic corrosive. Specifically, the identification of deoxyribonucleic corrosive (DNA) is particularly huge in quality designing and hereditary illness revelation, because the groupings and deformities of DNA particles firmly influence hereditary and ceaseless sicknesses[1, 3-6].

A sensor is a gadget that identifies the adjustments in a physical improvement and changes over them into an evaluable sign which can be estimated or recorded. It gets a physical amount and changes over it into a sign appropriate for preparing (for example optical, electrical, mechanical1) [7]. A nanosensor is a class of sensor gadgets or frameworks in which a nanoscale collaboration is misused as the premise of recognizing the nearness or level of a known analyte. Size of a few nanometers in two measurements (wires, poles, and so forth.) or every one of the three (groups, particles, and so forth.) is a shortsighted rule for a framework to be considered "nano". Electrochemical nanosensors have as of late discovered broad applications in pharmaceutical and biomedical businesses with certain focal points, for example, lower location limits, more extensive straight reaction extend, affectability, great security, and reproducibility when contrasted and different sensors and strategies. These days, a variety of investigative techniques are utilized in natural, pharmaceutical, or clinical research centers and various business purposes of-care gadgets work utilizing nanosensors in general or a fundamental part)[7].

In this work, one can investigate the graphene nanoribbons as a nanobiosensor for DNA molecule by using the density functional theory (DFT) method. Then, one can use the

variation in the structural and electronic properties, that are resulting from the interaction between GNRs with DNA molecule to use GNRs as a nanobiosensor for DNA molecule.

II. COMPUTATIONAL METHODS

One can use picked a graphene nanoribbons (GNR) as a nanosensor, which are contained of 36 C iotas and 18 hydrogen molecules at the end to diminish the breaking point impacts, show Fig. 1. It depends on the GNR that was performed by using the thickness practical hypothesis (DFT) technique with the crossover useful B3LYP[8] and 3-21G basis set as applied in the Gaussian 09W package [9]. The DFT method with this level have been chosen because of the accuracy associated[10-13], where the DFT method focuses on the electron density function instead of wavefunction was used to study the interaction between GNR and the nitrogenous bases of DNA and calculation of global reactivity indexes by the Koopmans theory-based quantities [14-16]. This hypothesis depends on the contrasts between the most noteworthy involved sub-atomic orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies for the impartial particle [17, 18].

Structurally, individual strands of DNA consist of a phosphate-deoxyribose backbone connecting nitrogenous bases, either purines (adenine and guanine) or pyrimidines (cytosine and thymine). The nitrogenous bases of DNA are composed of aromatic rings with base pairs spaced 3.4 A˚ in the double helix [19], see Fig. 2.

To evaluate the reactivity and the stability of the nanosensor, DFT-based descriptors were calculated [14, 15]:

$$\mu = (\partial E/\partial N)_{V(r),\,T} \quad (1)$$

$$\eta = 1/2(\partial^2 E/\partial N^2)_{V(r),\,T} \quad (2)$$

$$S = \frac{1}{2\eta} \quad (3)$$

$$\omega = \mu^2/2\eta \quad (4)$$

where μ, η, S and ω are the chemical potential, chemical hardness, chemical softness, and electrophilicity, respectively. While *E*, *N*, and *V(r)* are the total electron energy, the number of electrons, and external potential, respectively[17, 18]. Using Koopman's theorem the above equations can be given as :

$$\chi = (E_{HOMO} + E_{LUMO})/2 \quad (5)$$

$$\eta = (E_{HOMO} + E_{LUMO})/2 \quad (6)$$

GaussSum program[28](r24) was used to obtain the density of states (DOS) results, it is worth mentioning that the adsorption energy (E_{ads}) between DNA on GNRs was defined as[18, 20-23]:

$$E_{ads} = E_{DNA/GNR} - (E_{DNA} + E_{GNR}) \quad (7)$$

Where $E_{DNA/GNR}$, $E_{GNR,}$ and E_{DNA} are total energy of the DNA/GNR, the total energy of GNR, and DNA molecules in relax geometry, respectively. Negative adsorption energy refers to the stable formed systems and the positive adsorption energy indicates the local minima, i.e. through this explanation when $E_{ads} < 0$ leads to a stable structure, which corresponds to exothermic adsorption, Sees Fig. 3. [16],

Variation of the conductivity of each structure which determines the performance in DNA sensing is determined in terms of variation band gap energy through Eqs. [20, 24]:

$$\Delta E_g\% = \frac{E_g\ (without\ DNA) - E_g\ (with\ DNA)}{E_g\ (without\ DNA)} \times 100 \quad (8)$$

where, E_g (with DNA) and Eg (without DNA) represent the band gap energy of the substrate after and before interaction with DNA molecule, respectively.

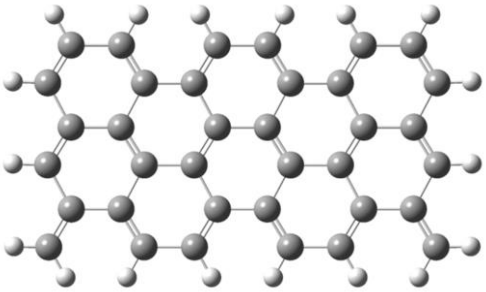


Fig.1. The optimized structure of pristine graphene nanoribbon.

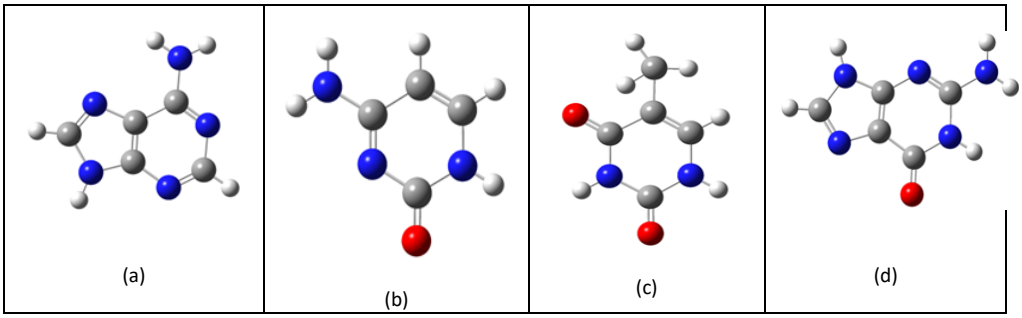


Fig.2. The four nitrogenous bases in DNA,where (a) Adenine, (b) Cytosine, (c) Guanine, (d) Thymine

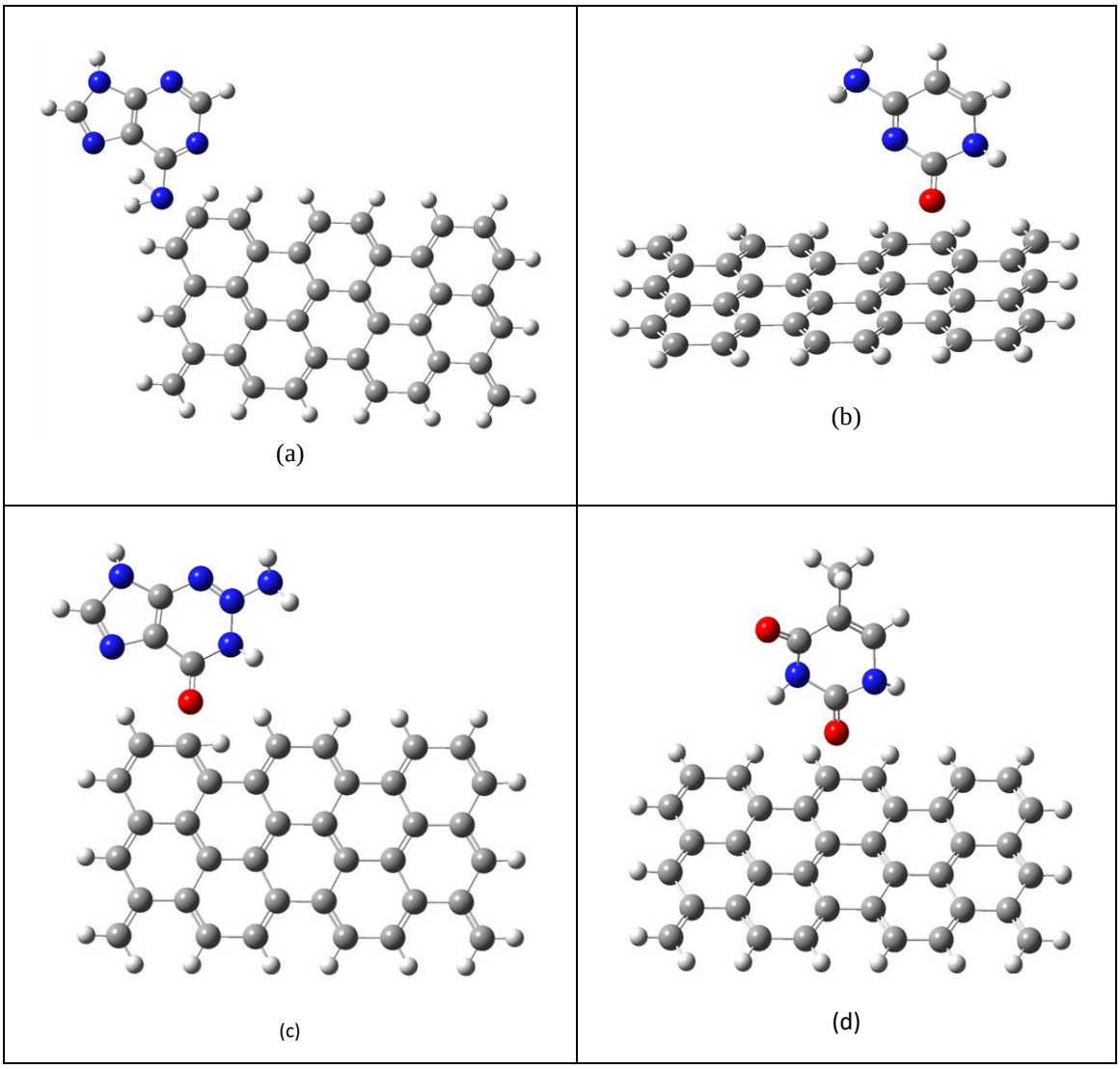


Fig.3. Adsorption of the nitrogenous bases of DNA on graphene nanoribbon,
where (a) Adenine/GNR, (b) Cytosine/GNR, (c) Guanine/GNR, (d) Thymine/GNR.

III. RESULTS AND DISCUSSIONS

In our result, the interactions between the four nitrogenous bases in DNA and GNR, are studied using DFT calculations. After full structure relaxation, the DNA molecule was added to pristine GNR and study the sensing and adsorption capability, the optimized geometries of all structures under study are shown in Figs. 1, 2, and 3.

Table 1: The electronic properties of GNR with the adsorbed nitrogenous bases of DNA.

Structure	Electronic Energy (eV)	E_{ad} (eV)	E_{HOMO} (a.u.)	E_{LUMO} (a.u.)	E_g (eV)	ΔE_g (eV)%
GNR	-37412.19527	–	-0.15254	-0.12221	0.82531	–
Adenine	-12644.05673	–	-0.22540	-0.02454	5.46560	–
Adenine/GNR	-50042.11132	14.14068	-0.13704	-0.12328	0.37442	-54.633
Cytosine	-10686.13312	–	-0.22492	-0.02863	5.34125	–
Cytosine/GNR	-48055.9444	42.38399	-0.13448	-0.11001	0.66585	-19.321
Guanine	-14680.06454	–	-0.21746	-0.00903	5.67159	–
Guanine/GNR	-52073.52294	18.73687	-0.12013	-0.10079	0.52626	-36.235
Thymine	-12281.4545905	–	-0.15980	-0.05061	2.97117	–
Thmine/GNR	-49661.5726662	32.07720	-0.13802	-0.10153	0.99293	20.310

A. *Adsorptive capability*

Adsorption vitality is the primary marker of structures capacity in DNA adsorption, where, minimal estimation of ΔE_{ads} infers the higher liking of GNR structure upon DNA adsorption. From Table 1, the adsorption vitality estimations of the association Adenine with GNR are (14.141 eV) which is the most minimal worth. Appropriately, it very well may be said that the communication among GNR and Adenine is more grounded contrasted with the remainder of the

nitrogenous bases that make up the DNA consecutive. In any case, it is qualified to refer to that the presence of a solid collaboration between the adsorbed atom and adsorbent surface isn't attractive. The large E_{ad} just as solid connection between the adsorbed atom and the adsorbent sheet cause to solidify the desorption procedure and draw out the recuperation time. In any case, it is qualified to refer to again that the positive estimation of E_{ads} shows the exothermic character of the GNR. The customary change state hypothesis shows that the recuperation time (τ) is characterized by[16, 25]

where v_0 is the attempt frequency which in many investigations is taken to be of the request for 109 $^{s-1}$ [18, 26], K_B and T are the Boltzmann's constant and the temperature in Kelvin respectively. As indicated by the above condition, the expansion in E_{ad} worth will draw out the recuperation time in an exponential model.

B. Sensing capability

The detecting capacity of GNR was concentrated by considering the variety of E_g after the expansion of DNA. From Table 1, sees that the $\%\Delta E_g$ esteems for the initial three structures are negative; the negative estimations of ΔE_g % express the hole vitality of structures decline from estimations of GNR because of adsorption (Adenine, Cytosine, Guanine) consequences for the surface it, bringing about higher conductivity for these structures. While, the synthesis with the most elevated $|\% \Delta E_g|$ show up better sensor execution.

A slight change in the E_g of GNR causes to modify the number of conduction electrons. This adjustment in the electrical conductivity can be gone to a discernible electrical signal. In any case, it is qualified to make reference to that changing the value of the bandgap E_g can correct the electrical conductivity in the framework as per the condition [27-29]:

$$\sigma \propto \exp\left((-E_g)/(2K_B T) \right) \quad (9)$$

σ is conductance, T is the temperature, and k_B is the Boltzmann's constant.

From Table 1, one can note that the most elevated estimation of ΔE_g % is (54.63). It relates to the interaction of GNR with Adenine. So, it can be concluded that the GNA is an appropriate sensor for Adenine.

As shown in Figs. 4-12. the HOMO of pristine graphene nanoribbons (PGNR) is generally confined on the C–C bonds and its LUMO on the clashing site. After interacting with DNA, both Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) largely shift on DNA molecule which corresponds to the reduction in the gap of energy (E_g).

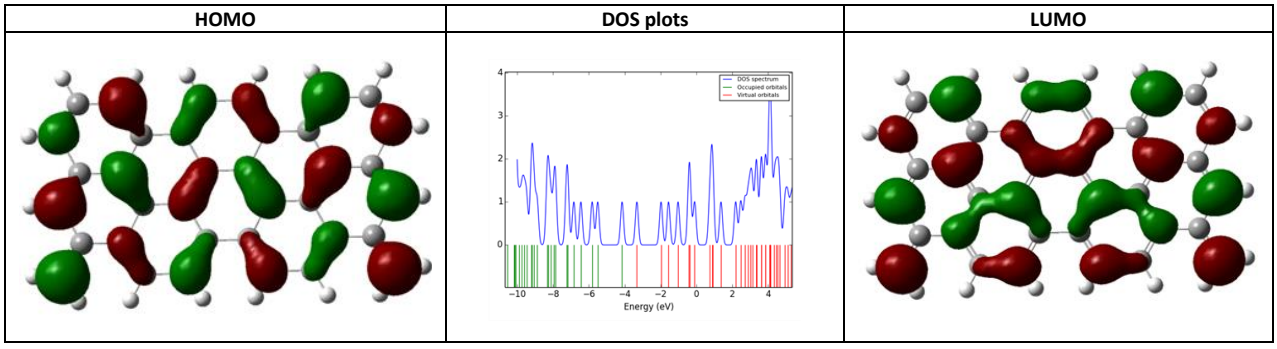


Fig.4. The DOS and HOMO – LUMO distribution of graphene nanoribbon

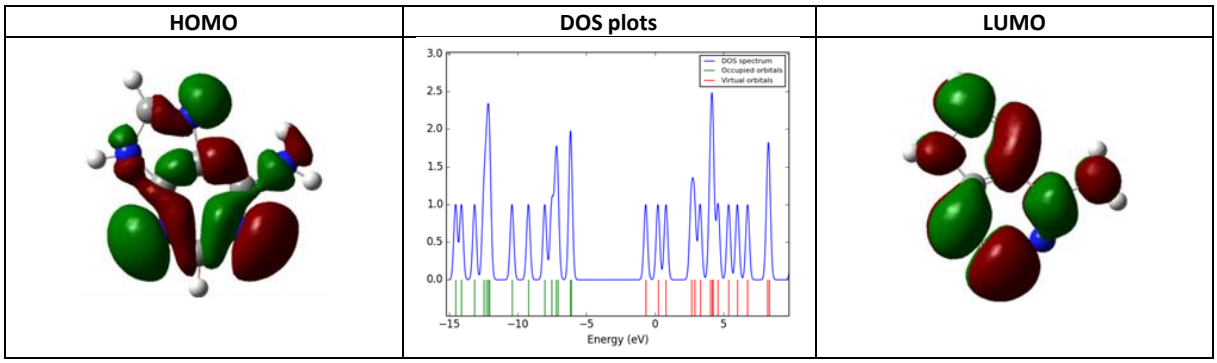


Fig.5. The DOS and HOMO – LUMO distribution of Adenine.

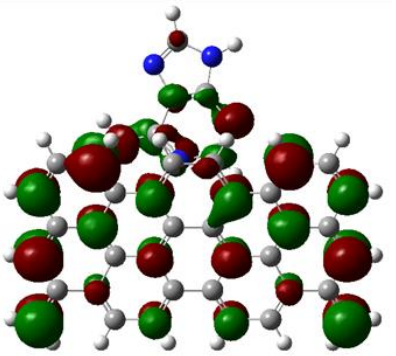
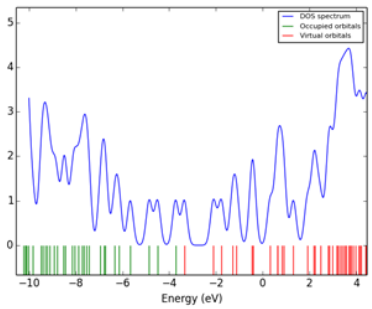
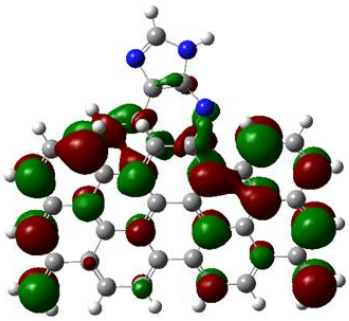
HOMO	DOS plots	LUMO
		

Fig.6. The DOS and HOMO – LUMO distribution of Adenine/GNR

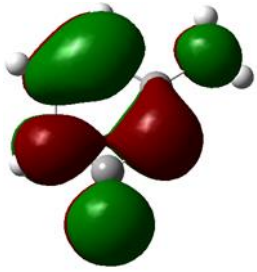
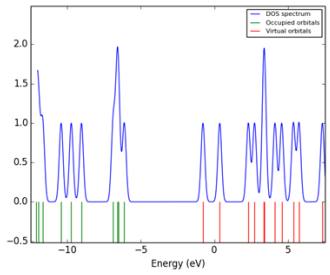
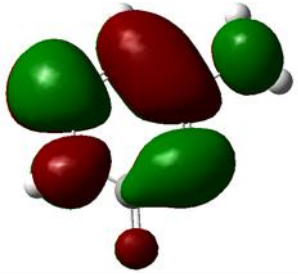
HOMO	DOS plots	LUMO
		

Fig.7. The DOS and HOMO – LUMO distribution of Cytosine

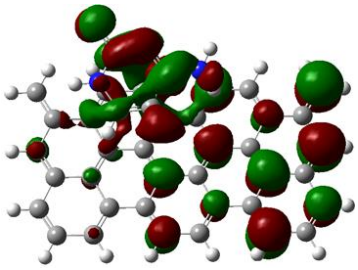
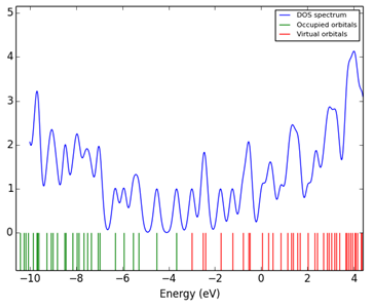
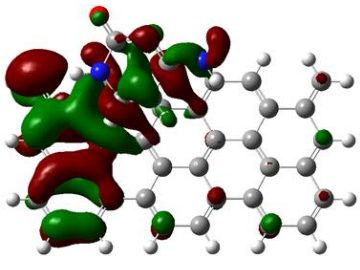
HOMO	DOS plots	LUMO
		

Fig.8. The DOS and HOMO – LUMO distribution of Cytosine/GNR

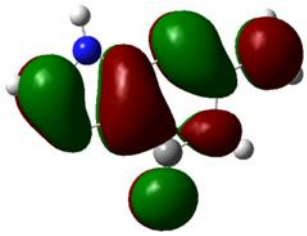
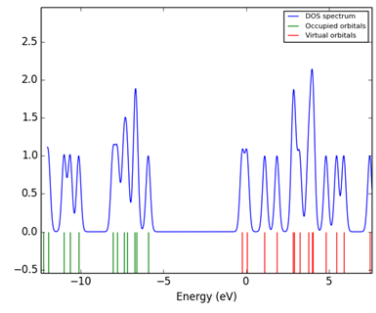
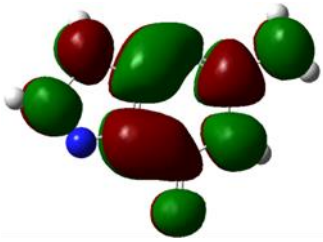
HOMO	DOS plots	LUMO
		

Fig.9. The DOS and HOMO – LUMO distribution of Guanine

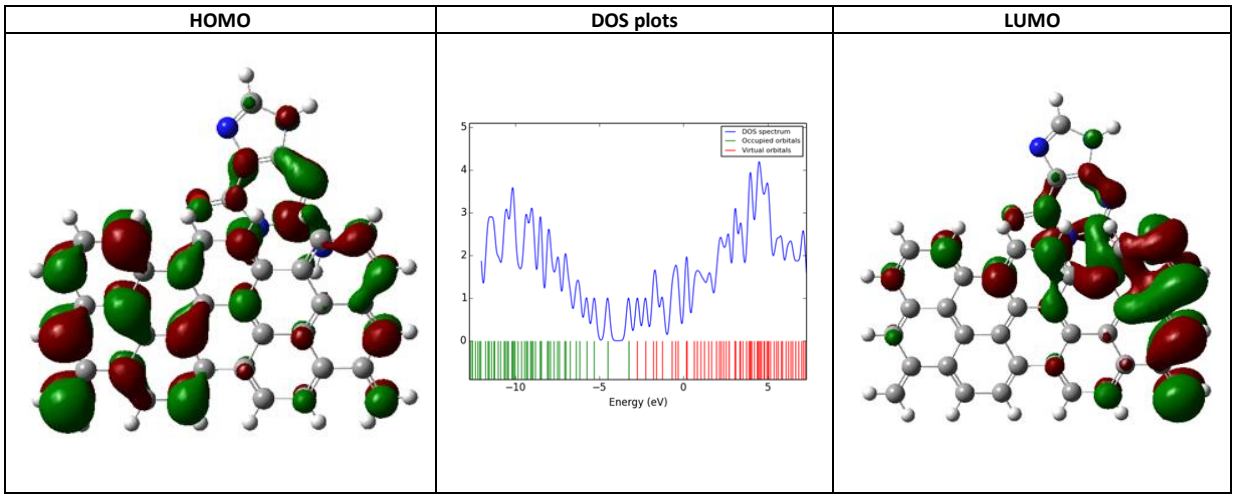


Fig.10. The DOS and HOMO – LUMO distribution of Guanine/GN

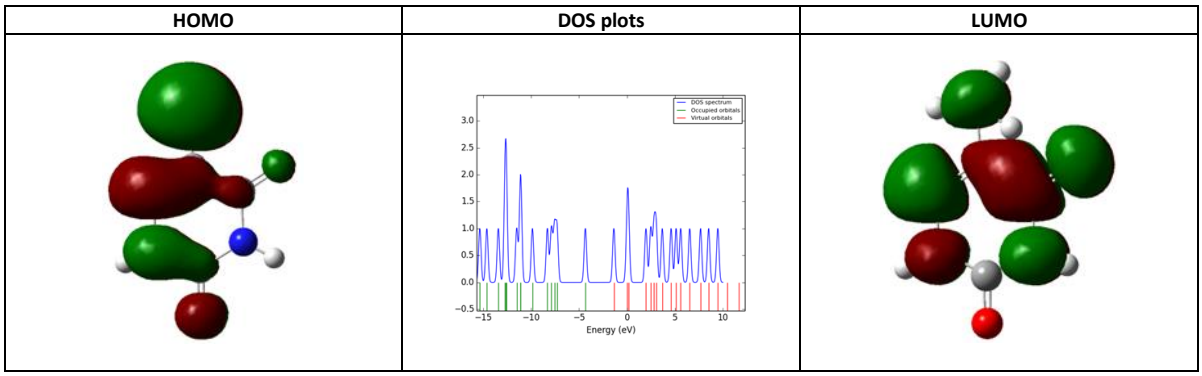


Fig.11. The DOS and HOMO – LUMO distribution of Thymine

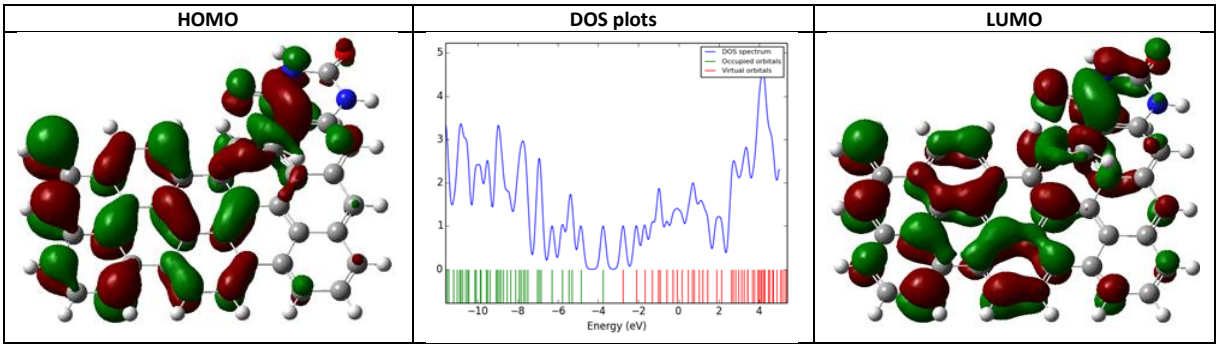


Fig.12. The DOS and HOMO – LUMO distribution of Thymine/GNR

IV. CONCLUSION

In summary, the interaction between GNR and DNA molecules has been studied by using DFT via the energetic data of the GNR.

It was observed that the adsorption energy values of the interaction Adenine with GNR are (14.141 eV) which is the lowest value compared to the interaction with the other nitrogenous bases that make up the DNA sequential. So, the interaction between GNR and adenine is stronger.

Also, we notice that the highest value of $\Delta E_g\%$ is (54.63). It relates to the interaction of GNR with Adenine. So, it can be concluded that the graphene nanoribbon is a good sensor for DNA molecules.

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V.