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The Effect of Nitrogen on the Structural and Electronic Properties of Graphene Sheet using Density Functional Theory

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Abstract: *The present research focuses on a theoretical study of structural and electronic properties of pure graphene sheet and then adding different number of N_2 atoms. The calculations are carried out using the density functional theory (DFT) with hybrid functional B3LYP/6-31G level to investigate the proposed structures. Gauss View 5.0.8 program is used to design the structures of pure and doped graphene sheets. These structures are relaxed by employing the PM6 semi-empirical method with the hybrid functional B3LYP-DFT at Gaussian 09 package. The results of the structural properties of the studied graphene sheets showed that good relaxation of the structures, the constant bonds values in the pure graphene sheets in the same ranges of the carbon rings structures. We calculate the total energy, High Occupied Molecular Orbital (HOMO) and Low Unoccupied Molecular Orbital (LUMO) energies and forbidden energy gap. The result of the total energy of that doping graphene sheets is result of the binding energy of each structure and indicates that these structures have relaxation, and the effect of adding N_2 atoms in pure graphene sheet on the total energy of the molecule is effective. All doping graphene sheets have small forbidden energy gap, but it vibrates depending on the length and number of each sheet and the position of N_2 atoms in the sheets.*

Keywords: Density functional theory (DFT), Graphene sheets, Gauss program

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Introduction

Andre Geim and Konstantin Novoselov at the University of Manchester won the Nobel Prize in Physics in 2010 for ground breaking experiments regarding the two-dimensional material graphene [1, 2]. The carbon atoms in graphene are compactly crowded in a chicken wire regular atomic-scale pattern. Each atom has four bonds of about 1.42 Å, one type of σ-bond with each of its three neighbours and one type of π-bond in which it is oriented out of plane [3]. Graphene can be considered alternant (only six-member carbon ring) polycyclic aromatic hydrocarbon [4]. To enhancement properties of graphene sheets use the Nitrogen because it has high gap between (higher and lower unoccupied molecular orbitals) and large band gap energy also. It has many important properties like high specific volume area, electrical insulation, and high thermal stability [5]. This work focuses on studying the effect of the length of the sheet and the addition of the Nitrogen atoms on the structural, electronic properties of graphene sheets, using the efficiency density functional theory to determine the paths of the applications of the new constructed structures. Many electronic properties will be calculated, such as, geometrical optimization, total energy, some electronic variables.

Theoretical Parts

The time dependent form of Schrödinger equation is as the following equation [6]:

$$i\hbar\,\partial/\partial t\,\Psi(\vec{r},t)=-\hbar\hat{}2/2m\,\nabla\hat{}2\,\Psi(\vec{r},t)+V(\vec{r},t)\Psi=H(\vec{r},t)\Psi(\vec{r},t) \quad \ldots(1)$$

As

$$H\Psi(\vec{r},t)=E\Psi(\vec{r},t) \quad \ldots(2)$$

where Ψ is the wave function, (H)ˆ is the Hamiltonian operator, and E is the total energy of the system. The Hamiltonian operator, H consists of two terms the kinetic energy of the electrons and the nuclei (T) and potential energy components (V) as follows:

$$\hat{H}=\hat{T}+\hat{V} \quad \ldots(3)$$

Hartree-Fock theory is the basis of molecular orbital Hartree-Fock theory. It is based on a simple approximation to the true many-body wave function [7]. Hartree made such a simplification in 1928 through an iterative self-consistent field 'SCF' method. A basis set is a set of functions used to describe the shape of the orbitals in an atom. When ab initio or density functional theory calculations are done, a basis set must be specified. Molecular orbitals and entire wave functions are created by taking linear combinations of basic functions and angular functions. Polarization functions are functions of higher angular momentum such as d- and f- type functions for heavy atoms and p- and d-type functions for hydrogen and helium atoms [8]. Diffuse functions denoted by '+'. For instance, the 6-31++G (d, p) basis set includes a set of d-type functions on all heavy atoms and p-type functions on hydrogen and helium. The first'+' indicates that diffuse s-and p-type

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functions are included on heavy atoms, while the second '+' indicates that diffuse s-type functions have been included on hydrogen [9]. The density functional theory provides the ground state properties of a system, and the electron density plays a key role. The hybrids functional are very successful in describing a wide range of molecular properties accurately. In the large molecules and solids, however, calculating the exact (Hartree-Fock) exchange is computationally expensive, especially for systems with metallic characteristics. The band gap is the difference of the energies between the two orbitals HOMO and LUMO [10].

$$Egap = ELUMO - EHOMO \quad \ldots(4)$$

Results and Discussion

This study involves the designing zigzag graphene sheets at Nanotube modular program and calculated their properties. All these structures are built by Gaussian View 5.0 and results obtained by Gaussian 09 package for structural and electronic proprieties on basis set (6-31G) at hybrid function (B3LYP). The pure structural with proprieties and then adding (N_2) atom (1, 2, 4, 8) to the pure graphene sheet. The electronic proprieties are calculated for HOMO, LUMO, E_T and Eg. Graphene sheets after adding nitrogen atoms have different behavior for HOMO that for the LUMO's. On the other hand, the addition of nitrogen atoms in the middle instead of the carbon atoms at terminal ends of phenylenes ring in the sheets changes the HOMO and LUMO energies, but the effect of the addition on HOMO is more than on LUMO. These results reflect the linear combination of atomic orbitals in both carbon and hydrogen an atom according to the basis sets that describe the individual components in the structure to construct the molecular orbitals. The result of E_g illustrated that is the variation of E_g for the (1 and 2) in comparison with E_g for the (3 and 4). E_g for sheet 3 was increased with adding the Nitrogen atoms in sheet 4, while for the others, E_g decreased with adding Nitrogen atoms, Eg decreased from (0.97034 eV) for the sheet 1 to (0.57796 eV) for sheet 2, and the E_g decreased with increasing the width of it, and therefore, increasing the number of added atoms in it, as illustrated in figures. These global results gave molecular electronics important.

Table 1 describe the bond length and bond types for pure sheet in Angstrom unit, all these results of bond length are compared with stander model for bond types and their length. The optimization parameters of pure graphene sheet are obtained by DFT calculation of bonds length with an agreement with experimental studies for bonds, the bonds range of (C-C), (C=C), (C⋯C) and (C-H) are (1.45478–1.47808) Å, (1.34793–1.38478) Å, (1.39168–1.44396) Å and (1.08155–1.08633) Å respectively. This results back to symmetrical distributions of carbon atoms and hydrogen in the pure sheet [11]. Figure 1 describes the geometrical structure for sheets under the study.

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Table 1. The bond types and length for stander sheet

Graphene Sheet	Bonds	Values Å
Pure	C⋯C	1.44396
	C-H	1.08633
	C=C	1.38478
	C-C	1.47808

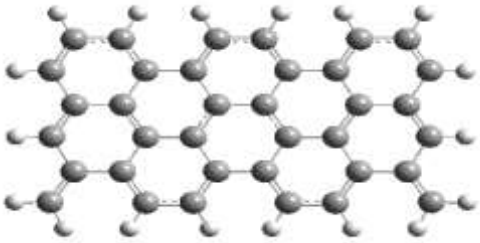


Figure 1. Geometrical Structure for Pure Graphene Sheet

Table 2 contains the total energy (E_T), higher occupation molecular orbital, lowering inoccupation molecular orbital and energy gap (E_g) in electron volt unit (eV).This parameters are important to determine ability of electrons transition and type of materials classification (conductor, semiconductor, and insulator).

Table 2. The Total Energy (E_T), HOMO, LUMO and Energy Gap

Graphene Sheet	HOMO (eV.)	LUMO (eV.)	Eg (eV.)	E_T (eV.)
Pure	-3.73661	-3.46287	0.273743	-37616.3

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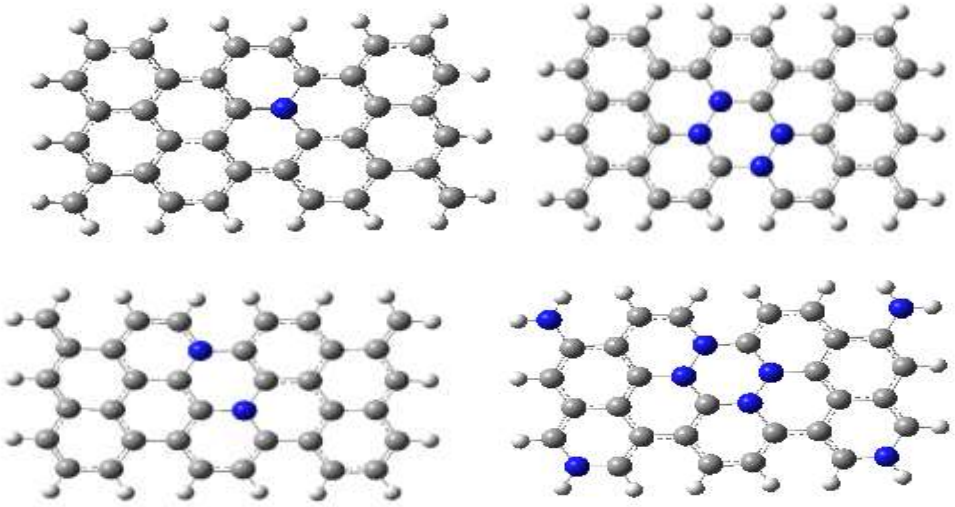


Figure 2. Geometrical structure for doped sheets under study

Table 3 describes E_{total}, E_{HOMO}, E_{LUMO} and E_g in eV of the graphene sheets after adding. The total energy is decreasing with increasing the number of nitrogen atoms of the sheet. The electronic states have small energy gap compared with the pure sheet that refer the ability of translation electrons cross energy band.

Table 3. E_{total}, E_{HOMO}, E_{LUMO} and E_g in eV of the Doped Graphene Sheet

Doped Graphene Sheet	E_{total}(eV)	E_{HOMO}(eV)	E_{LUMO}(eV)	E_g(eV)
1	-38068.35	-3.26831	-2.29797	0.97034
2	-38519.06	-3.62097	-3.04301	0.57796
3	-39419.75	-6.59159	-2.35593	4.23566
4	-41230.76	-2.55258	-1.443	1.10958

Figures 3, 4, 5, and 6 respectively show the total energy, electronic states energies and energy gap for graphene sheet after adding nitrogen atoms. The difference in energy between the structures 1 and 2 is approximately the same as between the structures 3 and 4.

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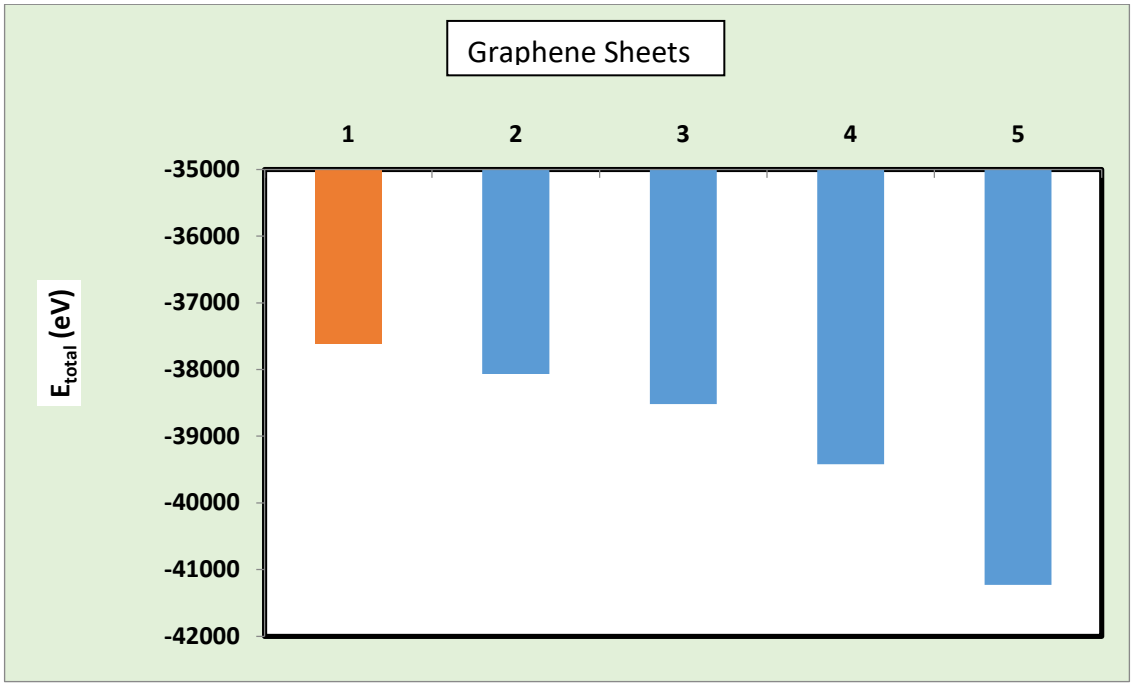


Figure 3. E_{total} in (eV) for Graphene Sheets

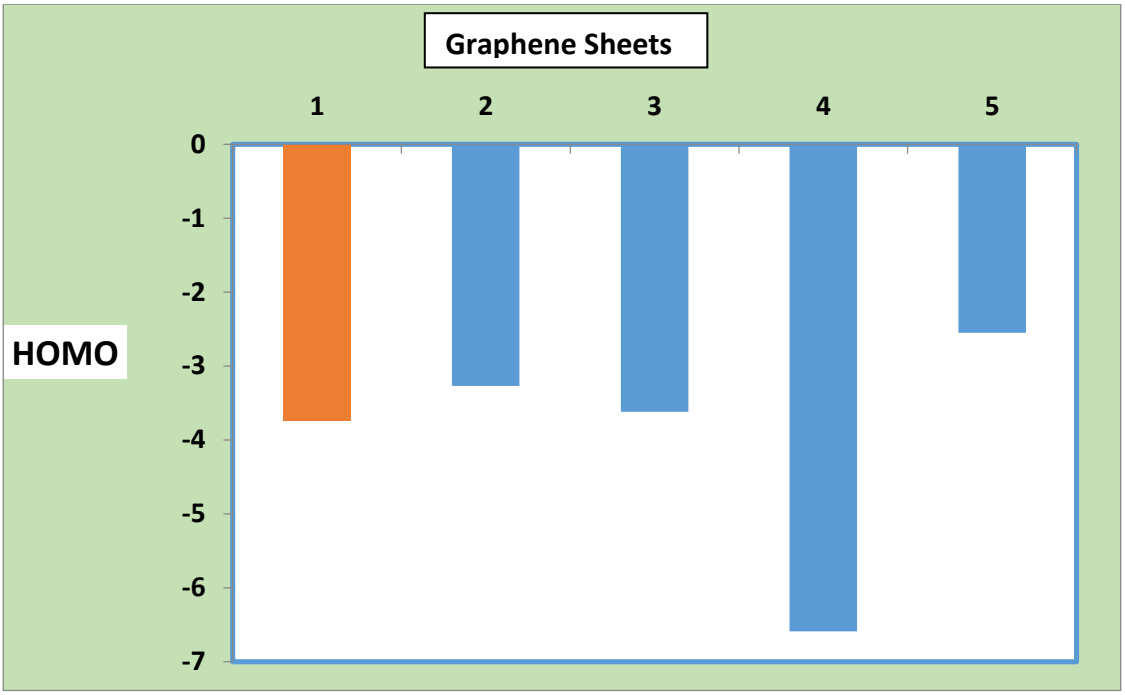


Figure 4. HOMO in (eV) for Graphene Sheet

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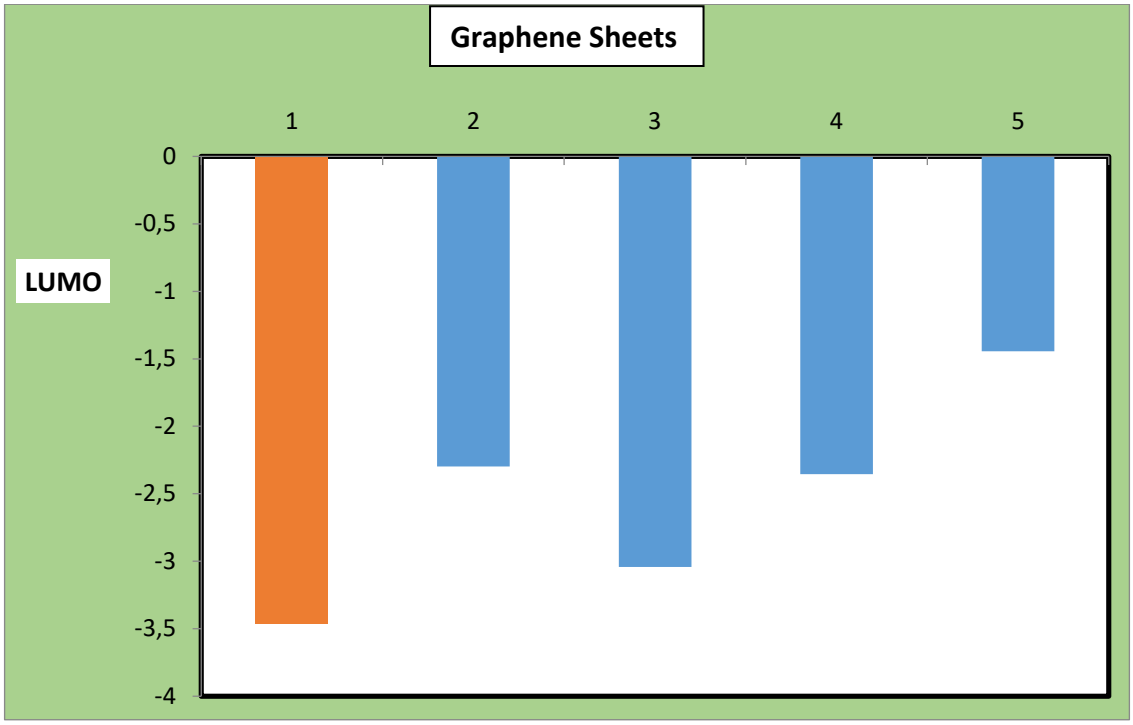


Figure 5. LOMO in (eV) for Graphene Sheet

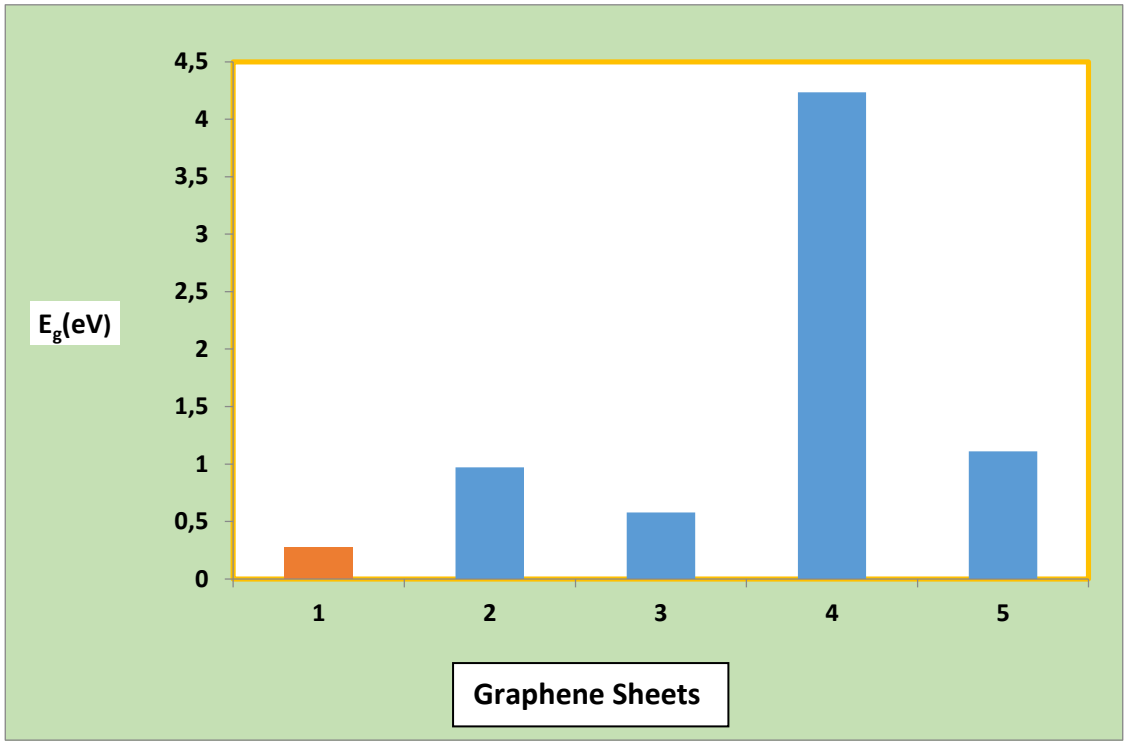


Figure 6. E_g in eV of the Graphene Sheet

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Conclusion

In this research the density functional theory has been concerned. DFT's are dependent on ground state energy, and all other ground state electronic properties are determined uniquely by the density of the electrons. In contrast, the exact ground conditions of the system correlate to the electronic density for minimal total energy. Use a basis set (6-31G) at hybrid function (B3LYP) because is a set of functions used to explain the orbital structure of an atom in assessing the accuracy of the results [12]. Doped graphene sheets are designed here through replacing N_2 atoms in place of Carbon atoms in the terminal ends of pure sheet. The DFT calculations presented result of total energies of all studied systems calculated from the summation of the total energies of the components for each structure and the result compared with literature survey agree with their pure sheets [13]. The total energy is decreasing with increasing the number of N_2 atoms to the sheet, the electronic states have small energy gap compared with pure sheet that refer to ability to translation electrons cross energy band. The relaxation done for the pure, the geometrical parameters (bond lengths) for pure calculated from DFT in current study have been found in agreement with experimental data. Replacing the (C) atoms by N_2 atoms in the sheets leads to a few reducing in the energy gap, this due to the linear combination of atomic orbitals of different atoms to construct the molecular orbitals.

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