UMA NOVA GEOMETRIA FRACTAL DOPING PARA NANOFIBRAS DE GRAFENO E A OTIMIZAÇÃO DE CRISTAL: UM ESTUDO DA TEORIA DA DENSIDADE FUNCIONAL (DFT)**A NOVEL FRACTAL GEOMETRY DOPING FOR GRAPHENE NANORIBBON AND THE OPTIMIZATION OF CRYSTAL: A DENSITY FUNCTIONAL THEORY (DFT) STUDY**JABBAR, Mohammed L.^{1*}; AL-SHEJAIRY, Kadhum J.²¹ Physics Department, Science College, University of Thi- Qar, Nassiriya – Iraq.² Physics Department, Science College, University of Mustansiriyah – Iraq.**Corresponding Author**E-mail: mohammed25382@gmail.com*

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RESUMO

A dopagem química é uma rota promissora para projetar e controlar as propriedades eletrônicas de nanofibras de grafeno em zigue-zague (ZGNR). Utilizando os primeiros princípios dos cálculos da teoria funcional da densidade (DFT), no B3LYP / 6-31G, implementado no software Gaussian 09, várias propriedades, como a estrutura geométrica, o espectro de infravermelho DOS, HOMO, LUMO e o gap de energia do ZGNR foram investigadas com vários locais e concentrações de fósforo (P). Observou-se que o ZGNR pode ser convertido da dimensão linear para a fractal usando impurezas de fósforo (P). Também se destaca a árvore binária fractal das estruturas ZGNR e P-ZGNR. Os resultados demonstraram que a diferença de energia possui valores diferentes, localizados nessa faixa de 0,51eV a 1,158 eV para estruturas ZGNR e P-ZGNR intocadas. Essa faixa de gap de energia é variável de acordo com o uso de GNRs em qualquer aparelho. Então, o P-ZGNR tem comportamento semicondutor. Além disso, não há números de onda imaginários no espectro vibracional avaliado, confirmando que o modelo corresponde à energia mínima. Então, esses resultados fazem com que o P-ZGNR possa ser utilizado em várias aplicações, devido a essa estrutura ter se tornado mais estável e com menor reatividade.

Palavras-chave: *Nanofibras de grafeno, diferença de energia, Densidade de estado, espectros de infravermelho.***ABSTRACT**

Chemical doping is a promising route to engineering and controlling the electronic properties of the zigzag graphene nanoribbon (ZGNR). By using the first-principles of the density functional theory (DFT) calculations at the B3LYP/ 6-31G, which implemented in the Gaussian 09 software, various properties, such as the geometrical structure, DOS, HOMO, LUMO infrared spectra, and energy gap of the ZGNR, were investigated with various sites and concentrations of the phosphorus (P). It was observed that the ZGNR could be converted from linear to fractal dimension by using phosphorus (P) impurities. Also, the fractal binary tree of the ZGNR and P-ZGNR structures is a highlight. The results demonstrated that the energy gap has different values, which located at this range from 0.51eV to 1.158 eV for pristine ZGNR and P-ZGNR structures. This range of energy gap is variable according to the use of GNRs in any apparatus. Then, the P-ZGNR has semiconductor behavior. Moreover, there are no imaginary wavenumbers on the evaluated vibrational spectrum confirms that the model corresponds to minimum energy. Then, these results make P-ZGNR can be utilized in various applications due to this structure became more stable and lower reactivity.

Keywords: *Graphene Nanoribbon, energy gap, Density of State, Infrared spectra.*

1. INTRODUCTION:

Graphene nanoribbon (GNR) may be a sheet of graphite (monolayer) comprising of atoms sp^2 hybridized C making a daily honeycomb (hexagonal) lattice. GNR has attracted considerable importance within the industry and research community thanks to its outstanding properties like structural, electronic, and optical. Recently, there has been outsized importance towards the realization, and studying of nanoribbon graphene supported devices of electronic design through the accurate structure of electronic tailoring that exploiting the electrical field effect and other fields of application as strain. In other words, the GNR has stimulated enormous outburst of experiment and theoretic fields an investigation (Aliofkhazraei *et al.* 2016); (Moghaddam *et al.* 2011); (Abbott's 2007); (Sahoo and Dutta 2012); (Banerjee and Sahoo 2013); (Bryan 2013).

Many reports (theoretical) proposed an electronic property (band structure) must appear that's presumed to account upon the shape and width (Oliveira Jr *et al.* 2015), additionally to the precise orientation for crystallographic of nanoribbon (Morozov *et al.* 2005); (Ezawa 2006); (Brey and Fertig 2006); (Shemella *et al.* 2007); (Son, Cohen, and Louie 2006a). GNRs with edges of shaped of zigzag are assumed to possess gaps of the direct band, where the gap lowers with width increasing, while edges of armchair-shape are often either semiconducting or metallic counting at widths (Nakada *et al.* 1996); (Wakabayashi *et al.* 1999); (Celis *et al.* 2016); (Neto *et al.* 2009); (Geim and Novoselov 2010); (Son, Cohen, and Louie 2006b); (Ajeel, Mohammed, and Khudhair 2019). One is aware that the stability of Hydrogen terminated GNR (Okada 2008); (Wassmann *et al.* 2008).

Benoit Mandelbrot (Mohammed Lateef Jabbar 2015); (Vass 2014); (Jebbar 2007); (Mohammed L Jabbar 2017) suggested the existence of geometries, referred to as geometry. A natural sort of fractal tree is represented by a binary fractal tree (BFT). Four factors specify a binary fractal tree (θ_1 , θ_2 , r_1 , and r_2). Where, the primary two factors (belong the angle) are the branching angles θ_1 and θ_2 , which may take any real values between 0° and 360° while the last two factors are the scaling ratios r_1 and r_2 , which may take any real values between 0 and 1 (Taylor 2005); (Pons 2013).

An intuitive explanation of a binary fractal

tree is as follows. Every tree features a trunk, which may be a closed vertical line segment of unit length. This trunk divides into two new branches at the highest. The primary branch has length r_1 and makes of θ_1 angle with the affine trunk hull, and therefore the second branch has length r_2 and makes of θ_2 angle with the affine trunk hull. Each of those two branches procedures the trunk of a sub-tree, i.e., it splits into two more branches, following an equivalent method. BFT is that the object obtained by applying the branching process to Infinitum (Taylor 2005); (Mandelbrot and Frame 1999); (Koch and Holthausen 2015) (Baughman, Zakhidov, and De Heer 2002) (Pons 2013). The density functional methods supply a strong instrument in quantum physics and computational nanoscience of atoms, (Parr 1980) molecules and other finite structures (Martin and Martin 2004). It proposes the density function rather than the wave function to explain the quantum systems (Wysokiński, Kuduk-Jaworska, and Michalska 2006). Born interpretation is one among methods that represent the theoretical basis of density functional theory (Tozer and De Proft 2005). It offers a chic formulation of the N electron system and computational efficiency (Young 2004). Electron density plays an important role in molecular structure, electrostatic potential, and contours (Koch and Holthausen 2015) (Koch and Holthausen 2015). Density functional theory (DFT) is additionally an approximation for the outline of the properties of the bottom state of insulators, metals, and semiconductors. The base state is unequivocally defined by the electron density (Mohammed L Jabbar 2018); (H Muzel, Alwan, and Jabbar 2017).

The main purpose of this paper was to study the binary fractal trees structure (with a scaling ratio $r=r_1=r_2=1$ to make some structures of zigzag graphene nanoribbon (ZGNRs) doping by phosphorus atoms), and electronic properties of the graphene systems. Based on the first-principles of the density functional theory calculations, frontier orbital (highest occupied molecular orbital, HOMO, and lowest unoccupied molecular orbital, LUMO) distributions, the energy gaps, density of state and infrared spectra have been investigated.

2. MATERIALS AND METHODS:

Herein are hydrocarbons chains of aromatic polycyclic (PAHs) that are occupied as ZGNRs models of finite-size. The treated ZGNRs contain edges of zigzag shape on each side with passivation hydrogen to decrease the boundary

effects (Figure 1). The GNR may be a rectangular $[n,m]$ with width $m=4$ (in direction of armchair) and length $n=6$ (in direction of zigzag).

2.1. Details of computation

All ZGNRs computations were carried out utilizing the method of DFT as applied within the Gaussian 09W software (Frisch *et al.* 2009). B3LYP (Stephens *et al.* 1994), as a functional hybrid that informs the exchange of Becke (Becke 1992) and correlation of Lee, Yang, and Parr's (Lee, Yang, and Parr 1988) the 3-21G (or 6-31G) means set of basis (Petersson and Al-Laham 1991), were utilized for the computation of quantum-chemical (H Muzel, Alwan, and Jabbar 2017); (Zandler and D'Souza 2006); (Rad 2016); (Yoosefian, Raissi, and Mola 2015). Before energy calculations for pristine ZGNR and with addition different atoms levels of P, whole systems are relaxed. This process is named geometry optimization. The GNR electronic characteristics such as DOS of analysis, energies of molecular highest occupied orbital (HOMO), molecular energies of lowest unoccupied orbital (LUMO), and gaps of energy (the eigenvalues difference the of the maximum valence band and therefore the band of minimum conduction or mathematically through express $E_g = E_{LUMO} - E_{HOMO}$) are theoretically investigated along few impurities structures P by using fractal binary tree method as novel mathematically model for doping.

3. RESULTS AND DISCUSSION:

As a primary task, the researchers started by building a pristine, a ZGNR. It consists of 48 atoms. GNR rectangular $[4, 6]$ (rectangular $[n, m]$ with width equally ($m = 4$ atoms) (in the armchair direction) and length equally ($n = 6$ atoms)) of width adequate to 4 (in the trend of an armchair) and length appropriate to 6 (in the trend of zigzag), is GNR designated $[4, 6]$. The ZGNRs treated contain edges of a zigzag for a single side along with the passivation of Hydrogen to minimize the effects of the boundary. Method of DFT was used to optimize the structure geometrically along with the B3LYP functional of hybrid. The structure of the pure GNR $[4, 6]$, as elucidated in Figure 2, is consistent with GNRs are nowadays illustrious: their characters of electronic predicted to be considered upon the shape and width, additionally to the precise crystallographic orientation of the nanoribbon. However, it is not possible to observe the visible deformation of pure GNRs along its zigzag direction.

The model BFT can be applied in the doping process to get a new structure. An intuitive description of a BFT is as follows. Each tree features a trunk, which may be a closed vertical line segment of unit length (Figure 3a). This trunk divides into two new branches at the highest. One branch has length r_1 and yields θ_1 angle with affine trunk hull, and therefore other branch has length r_2 and yields θ_2 angle with affine trunk hull as illustrated in Figure 3b. Those 2 branches yields subtree trunk as elucidated in Figure 3c, i.e., it splits into two more branches, following an equivalent method., a pristine GNR was then doped with different impurities of phosphorus atom ($P=2, 4, 8$). This addition of impurities obeyed to mathematically model. It's been wont to create nanostructures involving phosphorus element, theoretically, by using the geometry to urge a replacement structure to replace some carbon atoms within the pristine structure by the number of phosphorus atoms to offer the model binary fractal tree. Also, the models are geometrically optimized and need final arrangements (Figures 3 and 4).

As the fractal binary tree retains branching and splitting from 0 into 1 into 2 and so on., the binary tree is doing so, during this case, in base two and a scaling ratio $r=r_1=r_2=1$. The primary step of binary fractal tree does not have any value of angle with vertical line in other word, the angle value will adequate to zero. The second step branch trunk has one angle with a vertical line, while the third step has two angles on each side (Table 1).

Current surface is often expressed by high orbital's molecular occupation (HOMO) and low orbital's molecular occupation (LUMO). The abbreviations HOMO and LUMO occasionally ask the frontier orbitals in frontier molecular orbital theory. Figure 5 appears schematic HOMO, LUMO surfaces for pure GNR $[4,6]$, and GNR with P. The resulting orbitals could also be interpreted consistent with a molecular orbital theory, which considers the orbitals of the molecule because of the combination of linearity to the orbitals of molecule. The green color in figure 5 mentions positive a part of the function of the wave, whereas red color mentions the negative a part of the function of the wave. The energy gap may be a vital property in solids because it allows the prediction of the fabric, whether it's conductor or insulator or semiconductor. The bandgap is defined because of the difference in energy between the upper region of the valence band edge (VBE) and,

therefore, the lower region of conduction band edge (CBE).

Table 2 demonstrates the values of LUMO, HOMO, and energy gap for GNR and GNR with impurities (P=2, 4, and 8), respectively. During this work, the worth of the energy gap is calculated for pristine GNR following others obtained results (Son, Cohen, and Louie 2006a). Here energy values gap for both GNR and GNR with dopants performed by Gaussian 09 package. One note that the structures have different values of energy gap thanks to the various numbers and positions of dopants. Whereas, the electronic properties of GNR are quite different due to these different interfacial Interactions.

Figure 5 demonstrates that states density (DOS) versus energy according to the chemical structure of the material; naturally when the chemical structure is modified, at least, in theory, the DOS distribution should change. Generally, those impurities are called dopants, so the chemical composition changes by doping. The change within the energy distribution of the allowed states cannot have a general rule such as the bandgap will increase after the introduction of impurities from phosphorus.

The infrared spectral range is extensive, approximately from 12800 to 10 cm^{-1} spectral region. In the IR spectrum, a molecule to be absorbed by the moment of the molecules should be expected to vary as a result of vibration and rotation frequencies. There are two sorts of stretching variations. The primary type is named symmetric stretching, which occurs when the vibration of atoms of equivalency occurred within an identical phase. The opposite last type is called stretching of asymmetric, which takes place when vibrations of bonds occur in different phases. IR spectrum shows information about the structure of a molecule. The frequencies of harmonic vibration are studied for pure P-GNRs and GNR. Figure 6a shows the peaks shape for pure GNR, while figures 6b – 6d elucidate that there is a peak replacement; a single peak denotes the bond between 2 atoms neighboring to each other. Figure 6a demonstrates some peaks in the 800-900 cm^{-1} region (c-c single bond - aromatic atoms), whereas the peaks in 1200 - 1550 cm^{-1} region are the (c=c double bond - aromatic atoms). The obtained results are following the experimental results (Dykstra *et al.* 2017). New bonds inform new modes of specific numbers wave, whereas spectra of infrared are effected by coordinates of geometry and topological characters. Figure 6 shows C-P and P-P bond, which is cause to point

out a replacement peak. These new peaks show thanks to strange atoms. Then the structure will become asymmetric.

4. CONCLUSIONS:

The structures were extremely useful in making up apply devices because they need hetero-junction of band gap (the ability to fabricate P- and n-type regions is required). The calculations demonstrated that this work might be an example to use the mathematical model to make nanostructures involving phosphorus element by using the fractal geometry method to exchange some atoms in the pristine structure by phosphorus atoms. The model binary fractal tree can apply in doping process to get a new structure. The non-existence of imaginary wavenumbers on the evaluated vibrational spectrum confirms that the model corresponds to minimum energy.

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Figure 1. Grapheme of nanoribbon rectangular with width $m = 4$ (in direction of armchair) and length $n = 6$ (in direction of zigzag) of GNR designing [4, 6].

Figure 2. Pure GNRs structure of geometry

Figure 3. Structure of geometry after and before optimized of (a) two atoms of impurities P with GNRs (b) four atoms of impurities P with GNRs (c) eight atoms of impurities P with GNRs.

Figure 4. Fractal binary tree (a) the first step of doped. (b) the second step of doped. (c) the third step of doped.

(a)

(b)

(c)

(d)

Figure 5. HOMOs scheme of the (left) and LUMOs (right) and density of state (DOS) of (a) pristine GNR [4, 6], (b) 2 P-GNR, (c) 4 P-GNR, and (d) 8 P-GNR.

(a)

(b)

(c)

(d)

Figure 6. Infrared spectra of (a) pristine GNR (b) 2 P-GNR, (c) 4 P-GNR, and (d) 8 P-GNR

Table 1. Geometrical parameters optimized for S-GNR some selected branch order (Z) and angles (°).

System	Branch order Z	2^Z	Branch level	Angle θ (degree)	
2-P	0	2^0	1	0	
4-P	1	2^1	2	51.181	
8-P	2	2^2	4	L=26.955	R=41.371

Note: L: point out the left branch, and R: point out the proper branch on each side.

Table 2. The electronic states for pure GNR and nP- GNR (where n=2, 4, and 8)

System	HOMO (eV)	LUMO (eV)	E_g (eV)
Pristine GNR	-3.76768989	-4.286611212	0.518921322
2 P- GNR	-3.37666213	-3.86211343	0.485451305
4 P- GNR	-3.469997218	-4.62838634	1.158389128
8 P - GNR	-3.943475508	-4.55382712	0.610351612