

# A Study of The Geometrical Optimization and Energies of Carbon Nanoribbons: B3LYP/DFT

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## Abstract

This study deals with the geometrical optimization and energies of three structures of carbon nanoribbon using the B3LYP-DFT hybrid functional. 6-31G basis sets was employed to study the effect of the ribbons length on the energies and electronic properties of the structures. The results showed that the hybrid functional used is suitable for calculations the geometrical parameters of the structures. So, the energy gap was increased with increasing the length of the ribbon due to the change of both the HOMO and LUMO energies of the carbon nanoribbons. The shortest the ribbon the higher electronic softness and the more reactive it is as compared to the long ribbon.

**Key words:** HOMO, LUMO, Koopmans theorem, Energy Gap.

## الخلاصة

يشتمل البحث الحالي على الامثلية الهندسية والطاقات ثلاث تراكيب من شرائط الكربون النانوية باستخدام الهجينة ذات المعاملات الثلاث من طريقة دالية الكثافة. تم تطبيق الدوال الاساس 6-31G لدراسة تأثير طول الشرائط على الطاقات والخواص الالكترونية للتراكيب. بينت النتائج ان الدالة الهجينة المستعملة كانت مناسبة لحسابات المعاملات الهندسية للتراكيب. كما ان فجوة الطاقة قد ازدادت بزيادة طول الشريط نتيجة لتغير طاقات كل من المستوي الجزيئي العلوي المشغول والمستوي الجزيئي السفلي الفارغ لشرائط الكربون النانوية. الشريط الاقصر طولاً يمتلك اعلى مرونة الكترونية وفعالية اكبر من الشريط الاطول.

**الكلمات المفتاحية:** المستوي الجزيئي العلوي المشغول، المستوي الجزيئي السفلي الفارغ، نظرية كوپمان، فجوة الطاقة.

## Introduction

Graphene is an allotrope of carbon in the form of a two-dimensional , atomic-scale, hexagonal lattice in which one atom forms each vertex. It is the basic structural element of other allotropes, and it is a particularly intriguing two-dimensional structure with the quasi-relativistic dispersion law that has recently burst into the solid state physics. In 2004, researchers of Manchester University have succeeded in manufacturing a monoatomic graphite layer graphene on an insulating substrate [Hirsch; 2010; Zheng and Zeng; 2012, Bronner *et al.*, 2013; Kroto, *et al.*, 1985, Hirsch, 2005]. This technological breakthrough has attracted a great deal of attention of leading experimental and theoretical groups over the world. In a very short time, a new area of research in the area of graphene-based structures has emerged and become one of key research directions in the material science and condensed matter physics, The reason for this is the exceptional properties of graphene that make this material highly interesting from the point of view of both fundamental physics and potential applications [Hirsch; 2010; Zheng and Zeng; 2012], most prominently, the carbon-based nanoelectronics. Geim and Novoselov were awarded the Nobel Prize 2010 for the discovery of graphene.

There have been several reviews discussing the topic of graphene in recent years. Many are theoretically oriented, with Castro Neto *et al.*, review of the electronic properties as a prominent example[Died Erich *et al.*, 1991], and a more focused

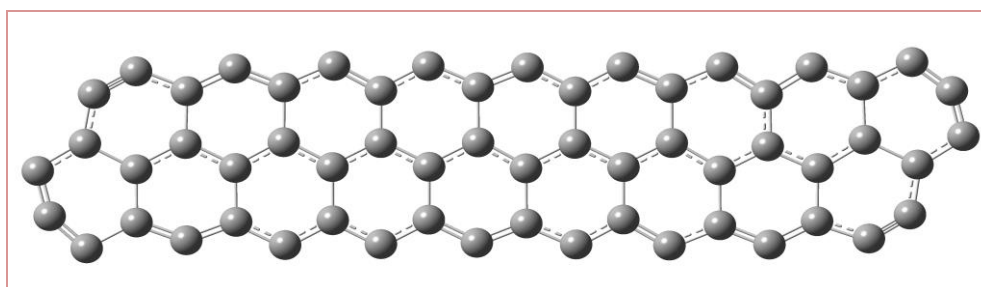
review of the electronic transport properties [Buhl, and Hirsch, 2001]. Experimental reviews, to name only a few, include detailed discussions of synthesis and Raman characterization methods [Kratchmer and Fotinopoulos 1990, Richter, 1997], of transport mechanisms [Taylor *et al.*, 1993; Pope *et al.*, 1993], of relevant applications of graphene such as transistors and the related band gap engineering [Howard *et al.*, 1991], and of graphene optoelectronic technologies [Tremblay, 2002]. However, the literature is lacking a comprehensive overview of all major recent experimental results related to graphene and its applications. This research focuses on the effect of the length of the graphene ribbon, its structural and electronic properties.

## Theory

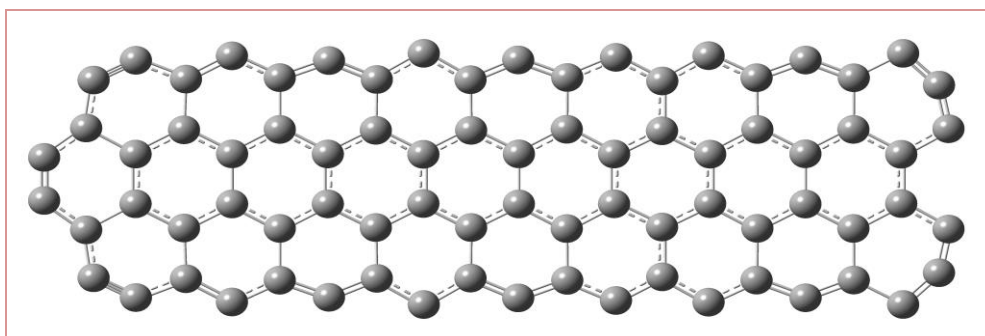
GAUSSIAN 09 [Frisch *et al.*, 2009] package of programs was used to perform the calculations. Full geometry optimizations of three structures of nanoribbons were performed with Berny optimization algorithm [Schlegel, 1982, Becke, 1988]. The gradient corrected density functional methodology employed Becke's exchange function (B) and Becke's three-parameters adiabatic connection (B3) hybrid exchange function in combination with the Lee–Yang–Parr correlation function B3LYP. While the BLYP methodology is a 'pure DFT' one (it includes no HF exchange), the B3LYP contains an admixture of HF exchange. The B3 function contains a linear combination of exact HF exchange, Slater exchange and Becke gradient-corrected exchange [Becke, 1993]. The standard 6-31G basis set was used for orbital expansion to solve the Kohn–Sham equations in all cases [Lee *et al.*, 1988, Peter, 2006]. The computed stationary points for which the structures and force fields are presented correspond to real minima on the molecular potential energy hyper surfaces.

## Results and Discussion

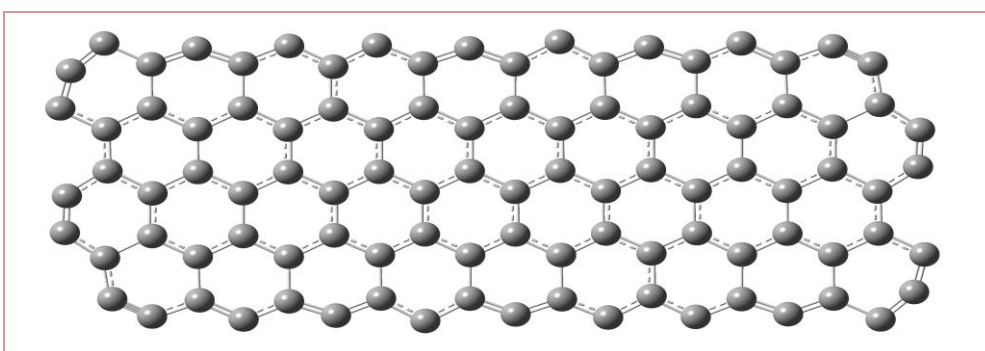
The optimized structures in Figure 1 are relaxed at Berny optimization by employing the DFT-B3LYP/6-31G to investigate the electronic properties of the mentioned carbon nano-ribbon structures. These structures are (0, 8), (0, 10) and (0, 12), and they are labeled molecules 1, 2 and 3, respectively. The results showed a suitable hybrid functional used in the relaxation of the studied structures in which they all satisfy the virial ratio occurs at the value ( $-V/T = 2.0052$ ), and the bonds C=C and C-C lie in the same range of these bonds in the carbon rings structures [Vamathevan, V. *et al.*; 2002]. Table (1) illustrates the minima ground state energy  $E_T$ , electronic states (High Occupied Molecular Orbital Energy  $E_{HOMO}$  and Low occupied Molecular Orbital Energy  $E_{LUMO}$ ) and the forbidden energy gap  $E_g$  in eV.



**Ribbon 0,8**



**Ribbon 0,10**



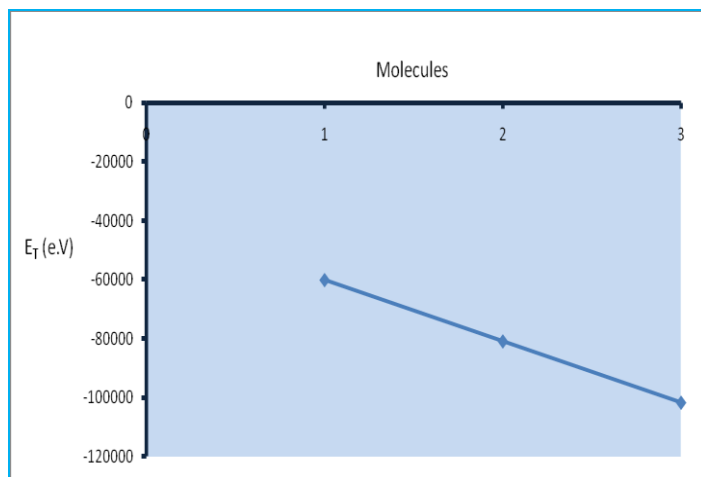
**Ribbon 0,12**

**Figure (1): The relaxed structures of pure nanoribbons from DFT.**

**Table (1) : The ground state energy  $E_T$ ,  $E_{HOMO}$ ,  $E_{LUMO}$  and  $E_g$  in eV of the studied nanoribbons molecules from DFT.**

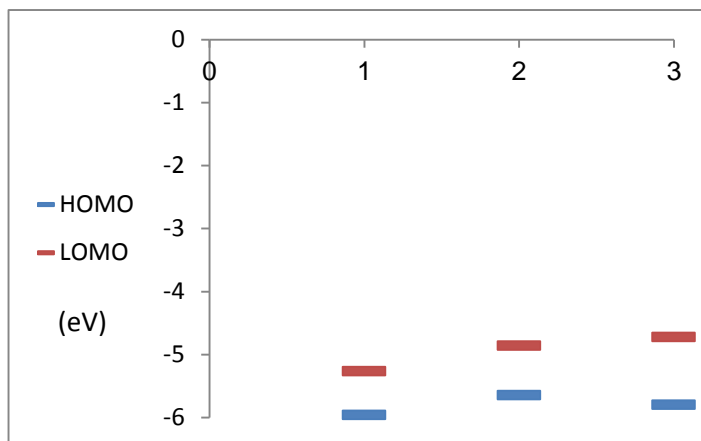
Molecule	$E_T$ (eV)	$E_{HOMO}$ (eV)	$E_{LUMO}$ (eV)	$E_g$ (eV)
1	-60072.1067	-5.95322	-5.26342	0.6898
2	-80807.0615	-5.63539	-4.85335	0.7820
3	-101542.5116	-5.79403	-4.71974	1.0742

Figure (2) shows the calculated total energy  $E_T$  of the studied nanoribbons molecules. The total energy is of the order  $(0, 12) < (0, 10) < (0, 8)$ . The total energy is linearly decreased with the increase of the length of the ribbon.

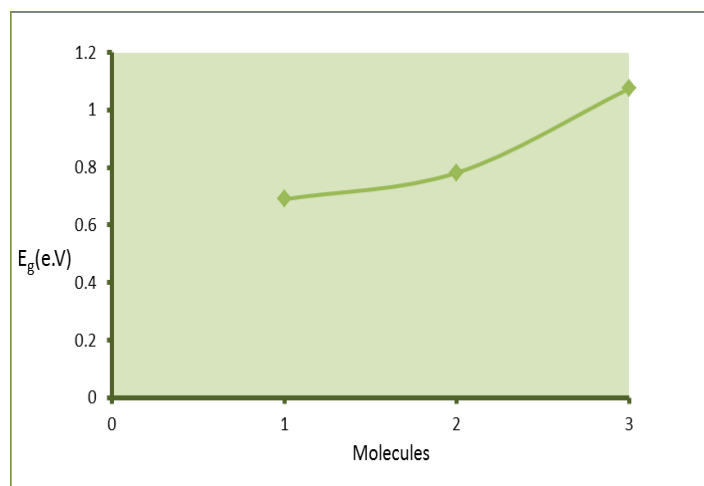


**Figure (2): The total energy of the studied nanoribbons molecules .**

Figure (3) shows the influence of the length of the ribbons on the electronic states  $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$ . As we see, the effect of the ribbon length on LUMO energy is more than the effect on HOMO energy. The increase of the length of the nanoribbon linearly decreases the LUMO energy. Therefore, the results of HOMO and LUMO affect on the calculated value of the energy gap for each ribbon. The energy gap was decrease from (1.0742 eV) for (0, 12) to (0.7820 eV) for (0, 10) and then to (0.6898 eV) for (0, 8). The mode of the variation of the energy gap represents a global result and is a sign that these nanoribbons give semiconducting properties. Figure (4) illustrates the variation of  $E_g$  due to the length of the nanoribbon.

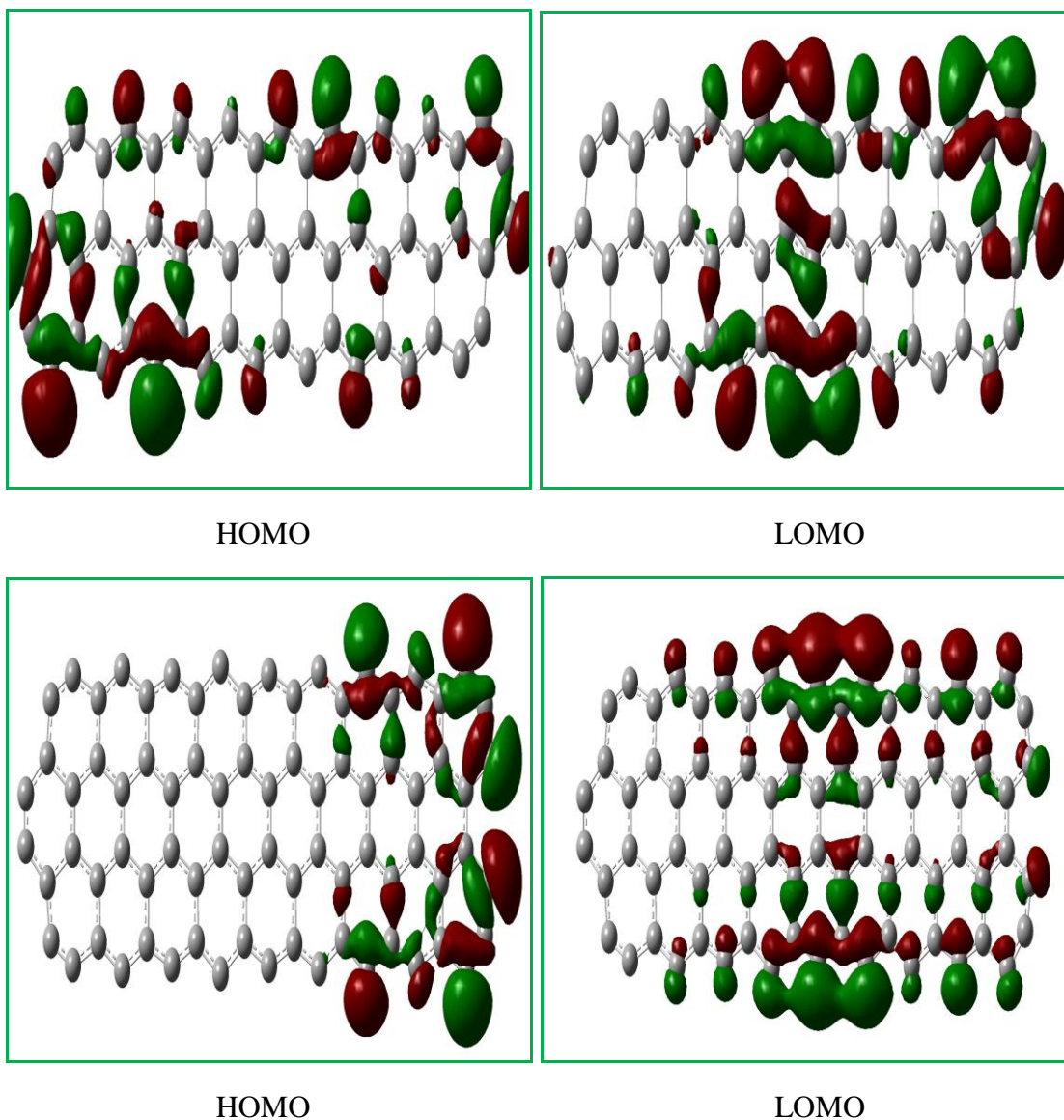


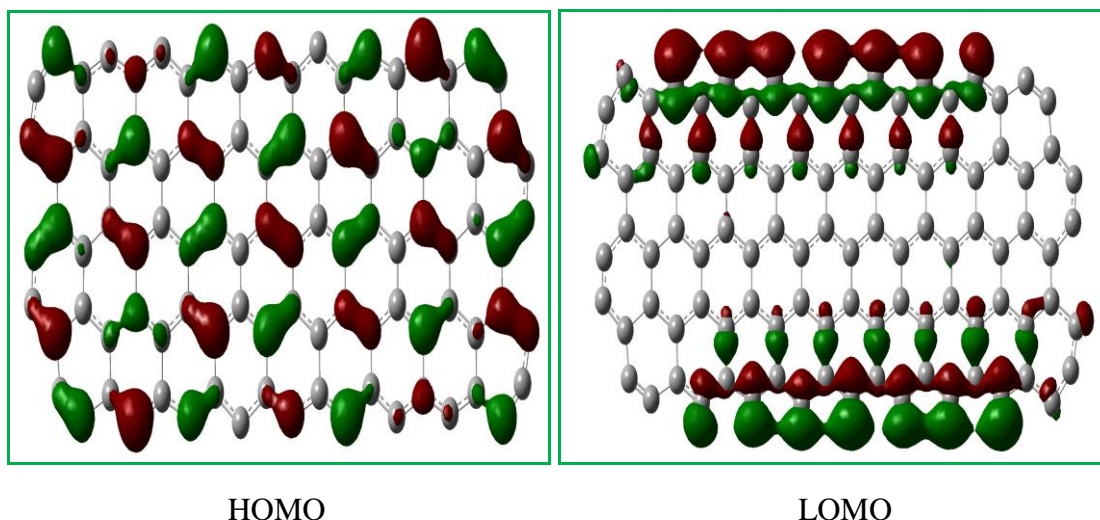
**Figure (3): The  $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$  of the studied nanoribbons molecules.**



**Figure (4): The  $E_g$  of the studied nanoribbons molecules .**

Figure (5) shows the shapes of the HOMO and LUMO distribution of the studied structures.





**Figure (5): The shapes of HOMO and LUMO distribution of the studied nanoribbons molecules.**

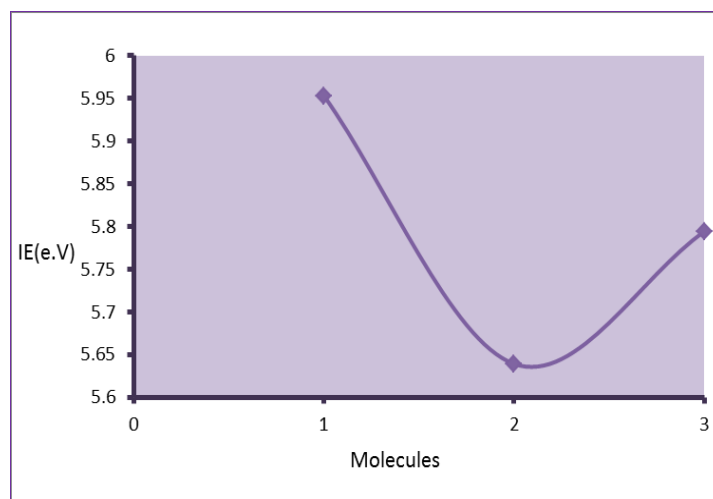
The calculated values of some electronic variables included the ionization energy IE, electron affinity EA, electrochemical hardness H, electronic softness S and electrophilic index W of the studied nanoribbons are listed in Table (2). The results showed that the IE is independent of the increase of the nanoribbon length, (0, 10 ) has IE lower than that for the others, while the smallest one (0, 8 ) has the highest value of IE and EA, one can conclude that this structure has the high ability to accept an electron when the earlier(the structure) interacts with other species. Figures 6 and 7 show the behavior of IE and EA according to the length of the nanoribbon.

One of the main Features of this research is the low values of the electrochemical hardness H with suitable values of electronic softness S. All the ribbons are softer, the lowering values of H indicate to that band gap goes to be rather soft and reduces the resistance of these structures to lose an electron. The electrophilic index W in Table 2 showed that the studied nanoribbons are more active to interact with other species, they have large values of W. Figures 8, 9 and 10 illustrate the results of H, S and W, respectively.

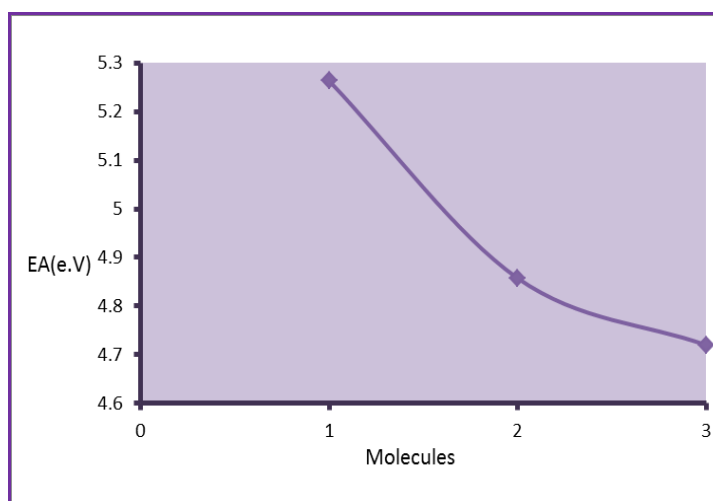
**Table (2) : Some electronic variables of the studied nanoribbons molecules .**

Molecule	IE(eV)	EA(eV)	H(eV)	S (eV) <sup>-1</sup>	W( eV)
1	5.9532	5.2634	0.3449	1.4496	45.597
2	5.6353	4.8533	0.3910	1.2787	35.168
3	5.7940	4.7197	0.5371	0.9308	25.724

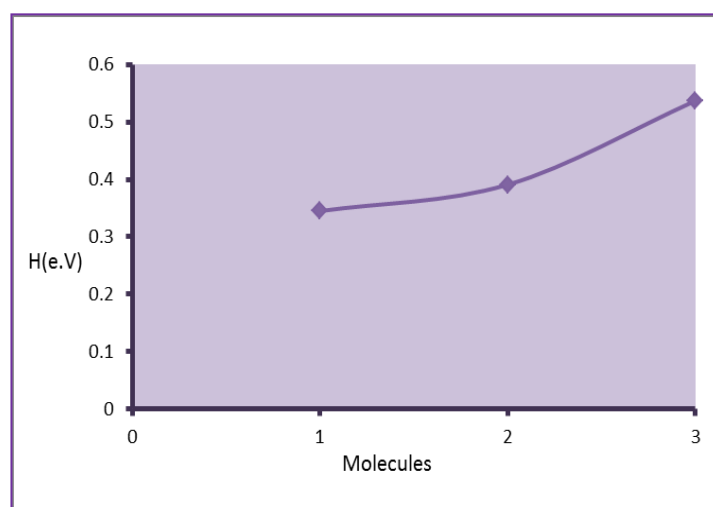




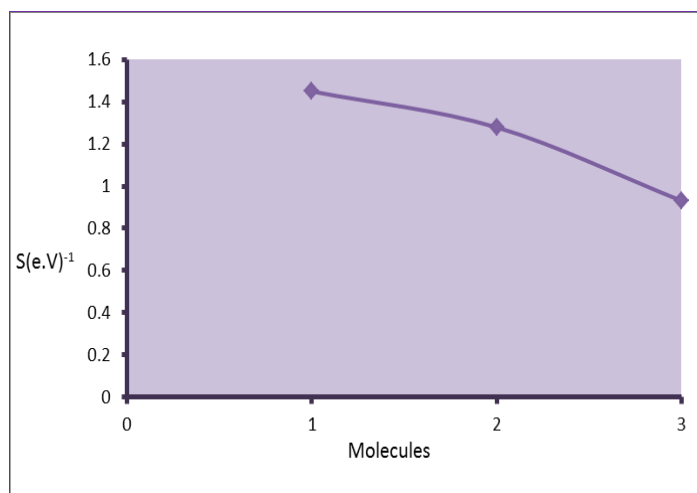
**Figure (6): The IE of the studied nanoribbons molecules .**



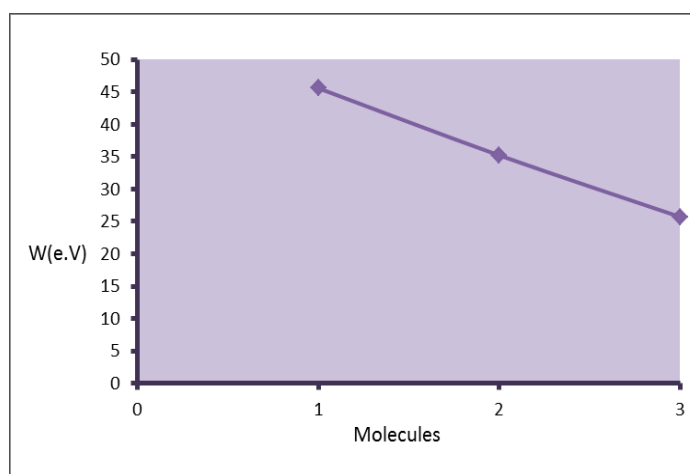
**Figure (7): The EA of the studied nanoribbons molecules .**



**Figure (8): The H of the studied nanoribbons molecules .**



**Figure (9): The S of the studied nanoribbons molecules .**



**Figure (10): The W of the studied nanoribbons molecules .**

## Conclusions

From the above results, one can conclude that:

The hybrid functional used for the calculations of geometrical optimization of the structures is a suitable function, as it satisfies the virial theorem and it gives values of bond C-C and C=C that lie in the same range of aromatic rings. The total energy decreases linearly with increasing the length of the ribbons. The ionization energy of the ribbons is independent of the increase of the length of the ribbons. All the studied carbon nanoribbons molecules have low electrochemical hardness, these structures have high softness. Increasing the length of the ribbons leads to change both the HOMO and LUMO energies, the effect on LUMO energy is more than it is on HOMO energy. The mode of variation of the energy gap reflects that the energy gap of the ribbon increases with increasing the length of the ribbon. the constructing nonoribbons have high reactivity to interact with the surrounding media.



## References

- Becke A.D., (1988), Phys. Rev. A 38, 3098.
- Becke A.D., (1993), J. Chem. Phys. 98, 5648.
- Bronner, C.; S. Stremlau, M. Gille, F. Brau, A. Haase, S. Hecht and P. Tegeder, Aligning the Band Gap of Graphene Nanoribbons by Monomer Doping, *Angew. Chem. Int. Ed.*, 52, 4422-4425, 2013.
- Buhl, M.; Hirsch, A., Spherical aromaticity of fullerenes. *Chemical Reviews* 2001, 101, (5), 1153-1183.
- Died Erich, F.; Etta, R.; Rubin, Y.; Whitten, R. L.; Beck, R.; Alvarez, M.; An, S.; Sentara, D.; Would, F.; Khamenei, K. C.; Koch, A., The higher fullerenes - Isolation and characterization of C76, C84, C90, C94, and C70O, an oxide of D5H-C70. *Science* 1991, 252, (5005), 548-551.
- Frisch, M. J.; G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, and E. S. Replogle *Gaussian 09*, Gaussian, Inc., Pittsburgh PA, 2009.
- Hirsch, A. The era of carbon allotropes nature materials, 9, 86-8871, 2010.
- Hirsch, A.; Brett Reich, M., *Fullerenes: Chemistry and Reactions*. Wiley-VCH Verlag GmbH&Co.: Weinheim, 2005.
- Howard, J. B.; McKinnon, J. T.; Makarov sky, Y.; LA fleur, A. L.; Johnson, M. E., Fullerenes C60 and C70 in flames. *Nature* 1991, 352, (6331), 139-141.
- Kratchmer, W.; Fotinopoulos, K.; Huffman, D. R., The infrared and ultraviolet absorption spectra of laboratory-produced carbon dust - evidence for the presence of the C-60 molecule. *Chemical Physics Letters* 1990, 170, (2-3), 167-170 .
- Kroto, H. W.; Heath, J. R.; Obrien, S. C.; Curl, R. F.; Smalley, R. E., C-60 - Buckminster fullerene. *Nature* 1985, 318, (6042), 162-163.
- Lee C.; W. Yang; R.G. Parr (1988), Phys. Rev. B 37, 785.
- Peter Atkins and Ronald Friedman, *MOLECULAR QUANTUM MECHANICS*, 4<sup>th</sup> edition, Oxford university press, 2006.
- Pope, C. J.; Marr, J. A.; Howard, J. B., Chemistry of fullerenes C-60 and C-70 formation in flames. *Journal of Physical Chemistry* 1993, 97, (42), 11001-11013.
- Richter, H.; Labrocca, A. J.; Greco, W. J.; Taghizadeh, K.; LA fleur, A. L.; Howard, J. B., Generation of higher fullerenes in flames. *Journal of Physical Chemistry B* 1997, 101, (9), 1556-1560.
- Schlegel H.B., (1982), J. Comput. Chem. 3, 214.

- Taylor, R.; Langley, G. J.; Kroto, H. W.; Walton, D. R. M., Formation of C<sub>60</sub> by pyrolysis of naphthalene. *Nature* 1993, 366, (6457), 728-731.
- Tremblay, J. F., Mitsubishi chemical aims at breakthrough. *Chemical & Engineering News* 2002, 80, (49), 16-17.
- Vamathevan, V.; Amal, R.; Beydouna, D.; Low, G. McEvoy, S. Photocatalytic Oxidation of Organics in Water using Pure and Silver-Modified Titanium Dioxide Particles. *Journal of Photochemistry and Photobiology A: Chemistry*. 2002, 148, 233-245.
- Zheng X. H. and Z. Zeng, Band Gap Engineering in Armchair-edged Graphene Nanoribbons by Edged Hydrogenation, *Computational Materials Science*, 62, 93-98, 2012.