

By first principle DFT (B3LYP) approximation-the geometrical stability of H-graphene cluster in the basis 3-21G

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Available online at: www.isca.in, www.isca.me

Received 30th September 2018, revised 25th March 2019, accepted 20th April 2019

Abstract

First-principle DFT(B3LYP) levels of calculations is studied for the geometric stability and electronic properties of H-graphene clusters(C_N) (where $N = 6, 10, 13, 16, 22, 24, 27, 30, 35, 37, 40, 42, 45, 47, 48, 50, 52, 54, 70$ and 96) and perform the DOS spectrum on selective graphene clusters $C_{16}H_{10}$, $C_{24}H_{12}$, $C_{30}H_{14}$, $C_{48}H_{18}$, $C_{70}H_{22}$ and $C_{96}H_{24}$ using Mulliken population analysis by the program Gaussian 03W. It is found that the ground state energy is depended on the nature of shape and sizes, and carbon atoms' number contained on H-graphene. The binding energy per unit number of carbon atoms increase until less than 30 and saturated at 30 or more carbon atoms numbers. For pure H-graphene C_{32} , its value is about 8.03 eV/atom, which is acceptable with previous reported data 7.91 eV/atom under the study of DFT (B3LYP) on the basis set 3-21G. The HOMO-LUMO gap in NBO is also observed for selective H-graphene clusters $C_{16}H_{10}$, $C_{24}H_{12}$, $C_{30}H_{14}$, $C_{48}H_{18}$, $C_{70}H_{22}$ and $C_{96}H_{24}$.

Keywords: H-graphene, density functional theory (DFT), HOMO-LUMO energy, DOS spectrum, natural bond Orbitals (NBOs).

Introduction

Carbon atom is tetrahedral and tightly bounded covalently to neighboring four atoms in single or multiple layers and found in nature in different states as a back bone of organic molecules. Both diamond (sp^3) and graphite (sp^2) are the pure state of carbon. Due to the different arrangement of carbon atoms, diamond and graphite have different properties especially electrical. Such as diamond is bad conductor and very hard, while graphite is good conductor and lubricant¹. Carbon should be stable to observe their various properties in nature and artificial, geometrically².

The earliest artificial pure carbon material, spherical molecule was fullerene³, found in 1985. Again, the carbon structure was reshaped as quasi one-dimensional nano-tubes in 1991. After few years later, a 2D flat monolayer sheet of sp^2 - tightly bonded atoms of carbon into honeycomb lattice was experimentally discovered, named graphene⁴.

Graphene exhibits extraordinary electronic properties and having unique configuration on its pie and pie asterisk bands collapsed to each other at one point on Fermi energy level, known as Dirac point. Also it exhibits a linear dispersion between E versus k. The exceptional properties of graphene including high current per unit area and thermal conductivity, ballistic transport, field emitter, optically active, chemical dullness components of integrated circuits, conducting electrodes (transparence), sensors and super hydrophobicity at

nanometer scale and anomalous quantum Hall effect⁵, has provoked the scholars for its research field⁶. More, recently, graphene based electronics devices have become realistic, indicative of that the initial thought purposed for graphene can be realized⁷. Both high electrical conductivity and optical transparence of graphene possess the features of transparent conducting electrodes which is necessary for a variety of applications similar to in touch-screen, LCD, OLED and photovoltaic cells. Therefore, graphene based materials have enormous significant uses in data storage, nanotechnology, surface catalysis, electronic and magnetic memory appliances⁸⁻¹¹.

The first-principles method is used for studying and predicts the properties of atomic and molecular system¹². The various mathematical transformations and hypothetical techniques are considered to solve the equations on the basis of fundamental quantum mechanics' laws¹³. It mainly calculates the energy in ground state and wave function of many electrons system, which further allows the calculation of various properties like dipole moment, vibrational frequency, optimization energy, nuclear quadrupole moment etc.

The first-principles approaches can be classified into three main categories: the Hartree-Fock, the quantum Monte-Carlo and the density functional approaches. Among these approaches, DFT is discussed as the electron density rather than wave function of atomic, molecular and solid system¹⁴. This approach is in principle exact, but the exact form of the exchange correlation

potential is unrecognized. So as to perform the *ab initio* calculations, the Gaussian 03W set of programs is operated in lab¹⁵. The structural stability of H-graphene consisting of 6 to 96 atoms of carbon is observed by DFT approach. Details of calculation method Beck-3-parameters-Lee-Yang-Parr hybrid (B3LYP) functional together with the set 3-21G^{16,17} is described on Section II. The result of this analysis would help to fit H-L gap on metal-semiconductor properties of graphene and study binding energy (B.E.), binding energy per carbon (B.E./N_C), density of state (DOS) and HOMO-LUMO energy gap are deliberated in Section III.

Methodology

One of the most useful and fundamental approach to take into account of electron correlation is the density functional theory. Many electrons system in Schrodinger equation solves the electronic orbital in DFT depends upon electron density, while one-electron spin orbital in the Hartree-Fock approach. The basic approach of the DFT is to approximate the electron correlation by means of general functional of electron density. The first and second Hohenberg-Kohn theorems¹⁸ are discussed at first and then Kohn-Sham approach for the calculation of exchange correlation potential¹⁹.

Consider electronic Hamiltonian of many-electron system obtained within the approximation, Born-Oppenheimer, which can be expressed as

$$H=T+V_{ne}+V_{ee} \quad (1)$$

Where, kinetic energy is denoted by 'T' of electrons, the Coulomb electrostatics attraction of electrons and nuclei by V_{ne} and V_{ee} for the Coulomb repulsion among the electrons. The middle term of equation (1) is, for M nuclei and N electrons system

$$V_{ne}=\sum_{i=1}^N V_{ext}(r_i) \quad (2)$$

Where,

$$V_{ext}(r_i)=\sum_{i=1}^N \frac{Z_n}{|r_i-R_n|} \quad (3)$$

is called the external potential on the ith electron due to M nuclei present in the system. With this Hamiltonian, the ground state energy can be written as

$$E_0=\langle\Psi_0|T|\Psi_0\rangle+\langle\Psi_0|V_{ne}|\Psi_0\rangle+\langle\Psi_0|V_{ee}|\Psi_0\rangle$$

Or,

$$E_0=T+V_{ne}+V_{ee} \quad (4)$$

Since the ground state wave function is represented by $|\Psi_0\rangle$ for N no. of electron system.

This work performs DFT calculations to study the ground state geometry and stability of H-graphene, using the first-principles

calculations by Gaussian 03W set of programs with B3LYP exchange correlation functional on the basis 3-21G.

The graphene cluster containing the number of carbon atoms 6, 10, 13, 16, 19, 22, 24, 27, 30, 32, 35, 37, 40, 42, 45, 47, 48, 50, 52, 54, 70, 96 is used to study its stability under the DFT (B3LYP) approach. In literature a systematic study of ground state energy of graphene sheets is the function of C_N on a first principle method, but it was not found. Moreover this study also discusses the population analysis with the charge distribution NBO and HOMO-LUMO gap. HOMO-LUMO is the difference in energy on highest occupied and lowest unoccupied energy level molecular orbitals.

H-graphene cluster was optimized at first without any symmetric restriction and optimize geometry was used to calculate the frequency for each cluster to study of the geometrical stability of H-graphene. With global minima, these frequencies for each cluster were real, ensuring each optimize structure. The B.E. can be calculated of H-graphene by using the relation;

$$E_{B.E.}=E_{H-graphene}-N_C E_{Carbon} \quad (5)$$

Where, E_{Carbon} and E_{H-graphene} is the ground state energies of isolated N_C and corresponding H-graphene cluster respectively.

Also, the B.E./N_C is the binding energy divided by total no. of carbon atoms in corresponding graphene cluster:

$$E_{B.E. \text{ per carbon atom}}=\frac{E_{Binding \ Energy}}{N_C} \quad (6)$$

Results and discussion

The B.E. and Structural equilibrium of grapheme: The optimization for H-graphene having C_N = 6, 10, 13, 16, 19, 22, 24, 27, 30, 32, 35, 37, 40, 42, 45, 47, 50, 52, 54, 70, 96 and corresponding ground state energies are acquired by the calculation of B.E. on the DFT. The variation of B.E. of graphene by using equation '5' with N_C is shown in Figure-2, as the B.E. increases with increasing in N_C.

On studying the stability of H-graphene, B.E./N_C is estimated on using the equation '6'. By the DFT (B3LYP) levels of approximation, the B.E./N_C of the graphene clusters (C_N) with 3-21G increases in increasing the number of carbon atom on cluster size and tending toward saturation. So, the larger size of clusters is relatively more stable than smaller sized as shown below in Figure-3.

The zero principal state energy linearly decreases with the increasing N_C in DFT(B3LYP) approximation as shown in figure '2'. So, It is a function of carbon atom that is related by the best fitted straight line equation $E(C_N) = 0.33753 - 37.87809 N_C$. The energy (E) is measured in units of Hartree.

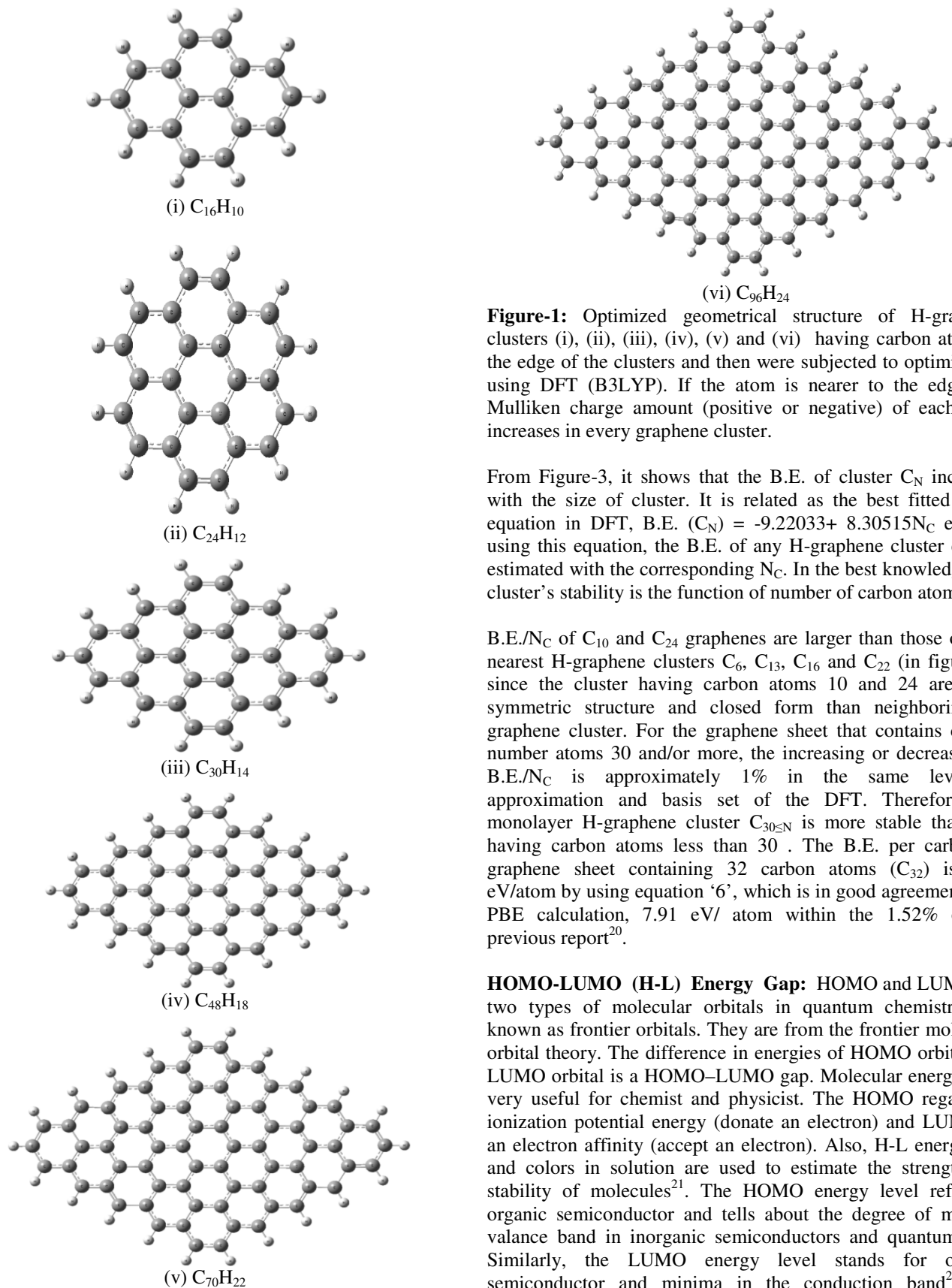


Figure-1: Optimized geometrical structure of H-graphene clusters (i), (ii), (iii), (iv), (v) and (vi) having carbon atom on the edge of the clusters and then were subjected to optimization using DFT (B3LYP). If the atom is nearer to the edge, the Mulliken charge amount (positive or negative) of each atom increases in every graphene cluster.

From Figure-3, it shows that the B.E. of cluster C_N increases with the size of cluster. It is related as the best fitted linear equation in DFT, B.E. (C_N) = $-9.22033 + 8.30515N_C$ eV. By using this equation, the B.E. of any H-graphene cluster can be estimated with the corresponding N_C . In the best knowledge, the cluster's stability is the function of number of carbon atom.

B.E./ N_C of C_{10} and C_{24} graphenes are larger than those of the nearest H-graphene clusters C_6 , C_{13} , C_{16} and C_{22} (in figure 4), since the cluster having carbon atoms 10 and 24 are more symmetric structure and closed form than neighboring H-graphene cluster. For the graphene sheet that contains carbon number atoms 30 and/or more, the increasing or decreasing in B.E./ N_C is approximately 1% in the same level of approximation and basis set of the DFT. Therefore, the monolayer H-graphene cluster $C_{30 \leq N}$ is more stable than that having carbon atoms less than 30. The B.E. per carbon of graphene sheet containing 32 carbon atoms (C_{32}) is 8.03 eV/atom by using equation '6', which is in good agreement with PBE calculation, 7.91 eV/atom within the 1.52% of the previous report²⁰.

HOMO-LUMO (H-L) Energy Gap: HOMO and LUMO are two types of molecular orbitals in quantum chemistry, are known as frontier orbitals. They are from the frontier molecular orbital theory. The difference in energies of HOMO orbital and LUMO orbital is a HOMO-LUMO gap. Molecular energies are very useful for chemist and physicist. The HOMO regards to ionization potential energy (donate an electron) and LUMO as an electron affinity (accept an electron). Also, H-L energy gap and colors in solution are used to estimate the strength and stability of molecules²¹. The HOMO energy level refers an organic semiconductor and tells about the degree of maxima valance band in inorganic semiconductors and quantum dots. Similarly, the LUMO energy level stands for organic semiconductor and minima in the conduction band²². For

estimating most reactive position H-L energy gap is used by the frontier electron density in π -electron systems and explain some type of reaction in conjugated (π^*) systems too²³.

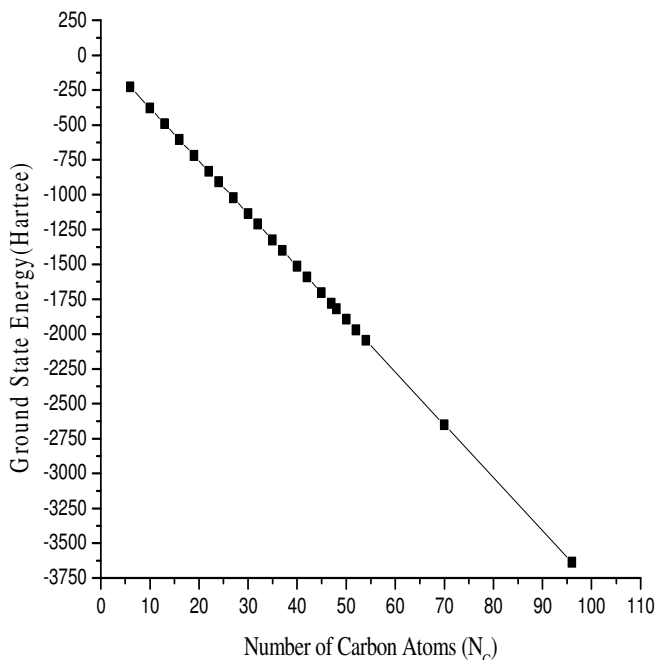


Figure-2: The linear dependency of ground state energy of C_N with N_C in the first principle of DFT (B3LYP) level of approximation. The linear equation is obtained as: $E(C_N) = 0.33752 - 37.87809N_C$.

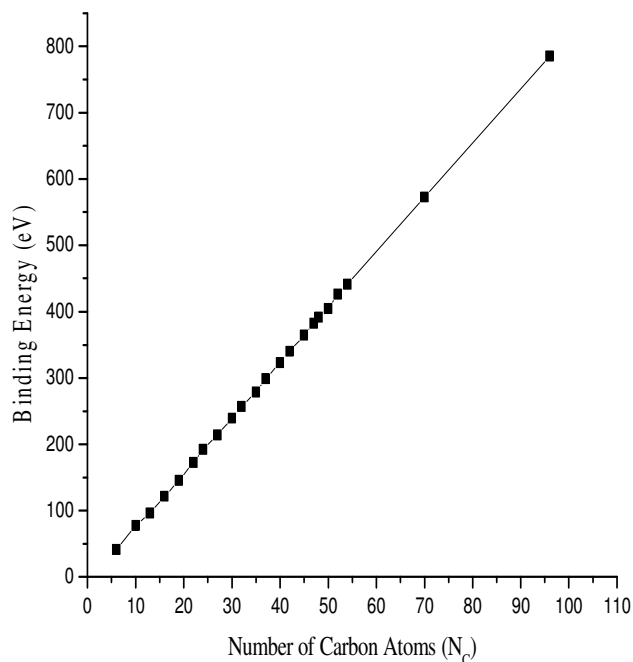


Figure-3: The B.E. of graphene clusters (C_N) is directly depended on the carbon atoms (N_C). Best fitted line is B.E. (C_N) = $(-9.22033 + 8.30515 N_C)$ eV.

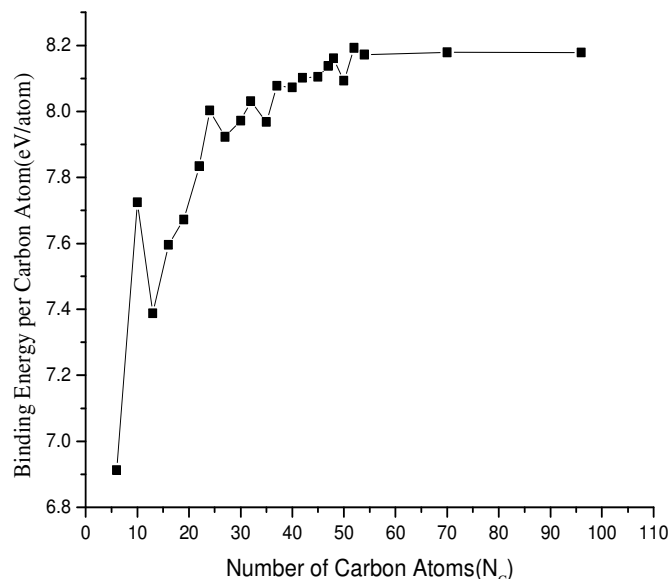


Figure-4: The relation of B.E./ N_C in eV/atom with N_C in the first principle DFT(B3LYP)/3-21G level of approximation.

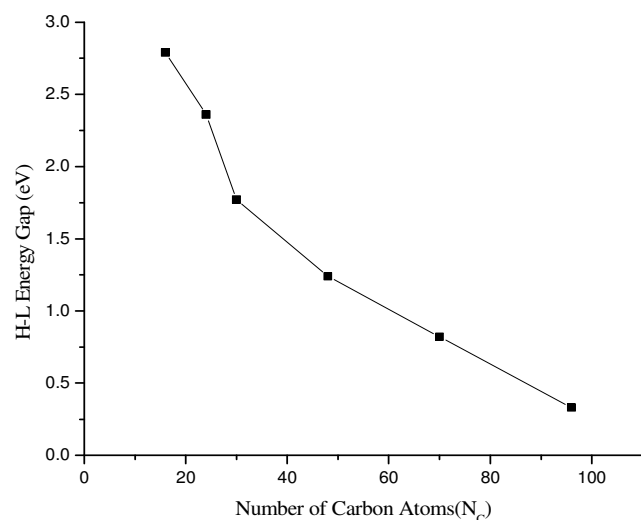


Figure-5: HOMO-LUMO (H-L) energy gap among H-graphene with number of carbon atoms.

In this work, the structural dependence of H-L energy gap of some H- graphene clusters is studied by using NBOs (Natural Bond Orbital) analysis. H-L energy gap decreases with increase in number of atom of corresponding H- graphene cluster²⁴ i.e. H-L energy gap is a negative function of cluster size as shown in figure 5. It is acceptable with the previous calculations²⁵. From this figure, it is seen that large energy gap is appeared for small size cluster, because of the significance of quantum effect in small size H-graphene clusters. For large size of H-graphene cluster, H-L energy gap is very small and so the quantum effect becomes insignificant. In general, the H-L energy gap would be zero for too large size of H-graphene clusters and it concludes that its electronic properties would be same as that of pure graphene.

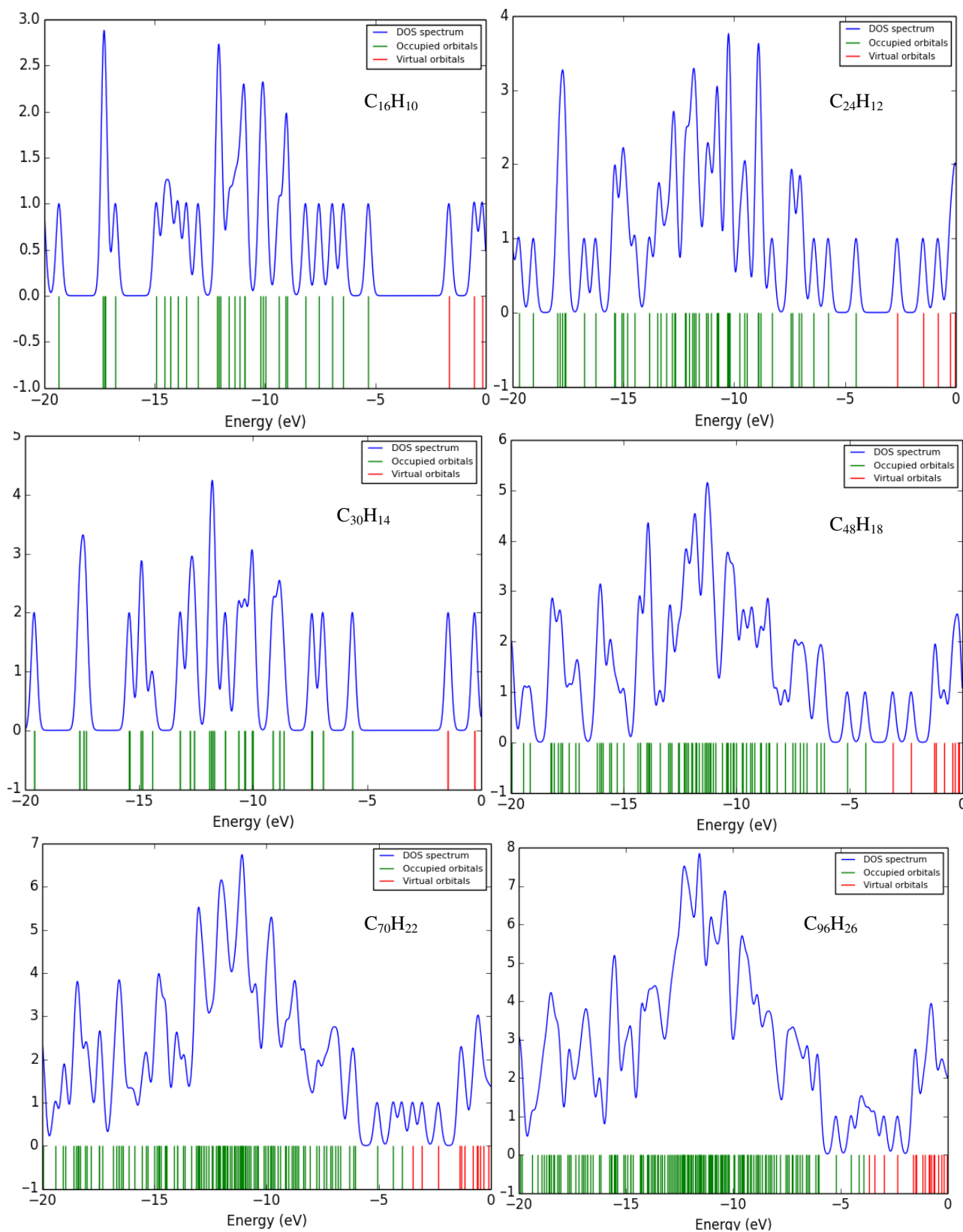


Figure-6: DOS spectrum for H-graphene clusters (C₁₆H₁₀, C₂₄H₁₂, C₃₀H₁₄, C₄₈H₁₈, C₇₀H₂₂ and C₉₆H₂₆) using Mulliken population analysis with DFT(B3LYP) in 3-21G of calculation.

DOS spectrum for each H-graphene cluster is plotted by using Gauss Sum 3.0 software²⁶ under the basis of Mulliken Population analysis and the occupied and unoccupied molecular orbitals can be seen of corresponding H-graphene clusters in Figure-6. From this figure, the electron levels becomes closer and at the same time fermi level energy increases with increase in cluster size.

Conclusion

The geometrical stability and energy of passivated graphene cluster having the carbon $N_C = 6, 10, 13, 16, 22, 24, 27, 30, 32, 35, 37, 40, 42, 45, 48, 50, 52, 54, 70, 96$ are studied on DFT(B3LYP) approximation of level 3-21 by using the Gaussian 2003W set. It is found that the ground state energy decreases with increase in number of carbon atoms in graphene sheet and its stability can be estimated with increase in carbon atoms. The ground state energy is linearly depended on the number of carbon atoms as the best fitted equation, $E(C_N) = 0.33752 - 37.87809N_C$. In the present work, it is observed that the B.E. increases linearly on the increased in size of graphene cluster or N_C .

The linear equation of the variation of B.E. with number of carbon atoms in DFT approximation is B.E. (C_N) = $-9.22033 + 8.30515N_C$ eV as shown in figure 3 having positive slope. The variation of B.E./ N_C (eV/atom) of graphene and carbon atoms' number (N_C) figure 4 shows that the 2D single layer graphene sheet containing the carbon atoms 30 and/or more is more steady than that containing less carbon clusters. So that a larger sized H-graphene cluster is relatively saturated than small sized.

From the calculations, we have also analyzed the population analysis performed by using the Gaussview 4.1W set of Programs under the Natural Bond Orbitals (NBOs) analysis i.e. the charge division and HOMO-LUMO gap for the $C_{16}H_{10}$, $C_{24}H_{12}$, $C_{30}H_{14}$, $C_{48}H_{18}$ and $C_{70}H_{22}$ system using the study of first principle DFT (B3LYP) with the choice 3-21G level of set. The NBOs explain a transfer of charge to the H-graphene sheet. It is important for the adsorption of metal in graphene sheet. The HOMO-LUMO gap in NBO study for the $C_{16}H_{10}$, $C_{24}H_{12}$, $C_{30}H_{14}$, $C_{48}H_{18}$, $C_{70}H_{22}$ and $C_{96}H_{24}$ clusters are 2.79, 2.36, 1.77, 1.24, 0.82 and 0.33eV respectively.

Also, the B.E./ N_C for C_{32} is 8.03 eV/ atom, which is acceptable with previous reported data 7.91 eV/atom and $C_{70}H_{22}$ and/or more carbon atom graphene clusters are more stable. The results will be studied on the structural stability of H-graphene with large number of carbon atom and adsorption of halogens and active metals on the choice of different basis sets of the work.

Acknowledgements

This research was supported by Central Department of Physics, Tribhuvan University and Kathford International College of Engineering and Management, Balkumari, Nepal.

References

1. Kasper M., Siegmann K. and Sattler K. (1997). Evaluation of an in situ sampling probe for its accuracy in determining particle size distributions from flames. *Journal of aerosol science*, 28(8), 1569-1578.
2. Kasper M., Sattler K., Siegmann K., Matter U. and Siegmann H.C. (1999). The influence of fuel additives on the formation of carbon during combustion. *Journal of Aerosol Science*, 30(2), 217-225.
3. Slanina Z. (2000). Andreas Hirsch, Ed.: Fullerenes and Related Structures Springer-Verlag, Berlin — Heidelberg, 1999. *Fullerene Science and Technology*, 8(1-2), 125-126.
4. Novoselov K.S., Geim A.K., Morozov S.V., Jiang D., Zhang Y., Dubonos S.V. and Firsov A.A. (2004). Electric field effect in atomically thin carbon films. *Science*, 306(5696), 666-669.
5. Zhang Y., Tan Y.W., Stormer H.L. and Kim P. (2005). Experimental observation of the quantum Hall effect and Berry's phase in grapheme. *Nature*, 438(7065), 201-204.
6. Geim A. and Novoselov K. (2007). The rise of grapheme *Nature Materials*, 6(3), 183-191.
7. Leenaerts O., Partoens B. and Peeters F.M. (2008). Paramagnetic adsorbates on graphene: A charge transfer analysis. *Applied Physics Letters*, 92(24), 243125.
8. Ferrari A.C., Meyer J.C., Scardaci V., Casiraghi C., Lazzeri M., Mauri F., Piscanec S., Jiang D., Novoselov K.S., Roth S. and Geim A.K. (2006). Raman spectrum of graphene and graphene layers. *Physical review letters*, 97(18), 187401.
9. Choe D.H., Bang J. and Chang K.J. (2010). Electronic structure and transport properties of hydrogenated graphene and graphene nanoribbons. *New Journal of Physics*, 12(12), 125005.
10. Seneor P., Dlubak B., Martin M.B., Anane A., Jaffres H. and Fert A. (2012). Spintronics with graphene. *MRS bulletin*, 37(12), 1245-1254.
11. Sarma S.D., Adam S., Hwang E.H. and Rossi E. (2011). Electronic transport in two-dimensional graphene. *Reviews of modern physics*, 83(2), 407.
12. Blinder S.M. (1965). Basic concepts of self-consistent-field theory. *American Journal of Physics*, 33(6), 431-443.
13. Geerlings P., Van Alsenoy C. and Van Doren V. (2001). Density functional theory and its application to materials. Melville, NY: American Institute of Physics.
14. Prasad R. (2010). Quantum chemistry. Tunbridge Wells: New age Science.
15. Frisch A.E., Frisch M. and Trucks G. (2005). Gaussian '03. Wallingford: Gaussian.

16. Becke A.D. (1993). Density-functional thermochemistry. III. The role of exact exchange. *The Journal of chemical physics*, 98(7), 5648-5652.
17. Lee C., Yang W. and Parr R.G. (1988). Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Physical review B*, 37(2), 785-789.
18. Hohenberg P. and Kohn W. (1964). Inhomogeneous electron gas. *Physical review*, 136(3B), B864-B871.
19. Kohn W. and Sham L. (1965). Self-Consistent Equations Including Exchange and Correlation Effects. *Physical Review*, 140(4), A1133-A1138.
20. Bhattacharya A., Bhattacharya S., Majumder C. and Das G.P. (2010). Transition-metal decoration enhanced room-temperature hydrogen storage in a defect-modulated graphene sheet. *The Journal of Physical Chemistry C*, 114(22), 10297-10301.
21. ORGEL L. (1963). Ligand-field theory. *Endeavour*, 22(85), 42-47.
22. Bredas J.L. (2014). Mind the gap!. *Materials Horizons*, 1(1), 17-19.
23. Choi C. and Kertesz M. (1997). Conformational Information from Vibrational Spectra of Styrene, trans-Stilbene, and cis-Stilbene. *The Journal of Physical Chemistry A*, 101(20), 3823-3831.
24. Karki D.B. and Adhikari N.P. (2014). First-principles study of the stability of graphene and adsorption of halogen atoms (F, Cl and Br) on hydrogen passivated graphene. *International Journal of Modern Physics B*, 28(21), 1450141.
25. Lonfat M., Marsen B. and Sattler K. (1999). The energy gap of carbon clusters studied by scanning tunneling spectroscopy. *Chemical physics letters*, 313(3-4), 539-543.
26. O'boyle N.M., Tenderholt A.L. and Langner K.M. (2008). CcLib: a library for package-independent computational chemistry algorithms. *Journal of computational chemistry*, 29(5), 839-845.