Journal of Informatics and Mathematical Sciences
Vol. 10, No. 3, pp. 391–398, 2018
ISSN 0975-5748 (online); 0974-875X (print)
Published by RGN Publications
DOI: 10.26713/jims.v10i3.807

http://www.rgnpublications.com

Research Article

Bounds of HOMO-LUMO Gap for Certain Nanotubes and Nanotori

Uzma Ahmad* and Saira Hameed

Department of Mathematics, University of the Punjab, Lahore, Pakistan
***Corresponding author:** uzma.math@pu.edu.pk

Abstract. The eigenspectrum $\mu_1 \geq \mu_2 \geq \cdots \geq \mu_m$ with the middle eigenvalues μ_h and μ_l, where $h = \lfloor (m+1)/2 \rfloor$ and $l = \lceil (m+1)/2 \rceil$ of simple connected graph G' with m number of vertices contribute significantly in the Hückel Molecular Theory. The HOMO-LUMO gap $\Delta_{G'}$ is defined as $\Delta_{G'} = \mu_h - \mu_l$ subject to the condition that the number of electrons are in one to one correspondence with the number of vertices. In this article, the upper bounds for the HOMO-LUMO gap corresponding to the connected graphs of nanotube $TUC_4C_8(S)$ and C_4C_8 nanotorus by using matrix theory are estimated.

Keywords. Molecular graph; Eigenspectrum; HOMO-LUMO gap; Bipartite graphs; Hermitian matrix

MSC. 15A18; 05C50; 15A45; 05C35

Received: February 4, 2018 **Accepted:** August 23, 2018

1. Introduction

The eigenvalues and eigenvectors of chemical graph have a direct relation with molecular orbital energies in the Hückel model. While dealing with interaction of molecules, the two molecular orbitals that strongly interact are HOMO (*Highest Occupied Molecular Orbital*) and LUMO (*Lowest Unoccupied Molecular Orbital*). The study of HOMO-LUMO gap is particularly useful in the prediction or estimation of stability and strength of complexes. In theoretical chemistry, HOMO-LUMO separation ([6], [7], [16]), HOMO-LUMO gap ([4],[12]), HOMO-LUMO map ([2],[3]) and HOMO-LUMO index ([11], [13],[14]) are widely studied.

Consider a simple connected graph G' with m number of vertices and eigenspectrum $\mu_1 \geq \mu_2 \geq \cdots \geq \mu_m$. The HOMO-LUMO gap is defined as $\Delta_{G'} = \mu_h - \mu_l$, where $h = \lfloor (m+1)/2 \rfloor$, $l = \lceil (m+1)/2 \rceil$ and μ_h and μ_l are the middle eigenvalues.

The *carbon nanotubes* (CNTs) were first discovered by Iijima in 1991 as multi walled structures. These nanostructures are allotropes of carbon in a cylindrical shape. CNTs exhibit remarkable mechanical characteristics and are found to be one of the stiffest and most elastic known materials. Nanotubes are studied extensively in solid-state physics due to their immense applications in nanotechnology, electronics, optics, materials science, and architecture. These are useful for metal-free catalysis of organic/inorganic reactions. In metrology and chemical study, nanoprobes (*Nanotube-based field emitters*) have wide range of applications.

The lattice C_4C_8 is a regular graph of degree 3 and is formed by arranging squares C_4 and octagons C_8 alternatively. The cylinder made by rolling this lattice is a nanotube TUC_4C_8 (Figure 1) and when this nanotube is bent into a torus it forms a C_4C_8 nanotorus (Figure 2). For details on C_4C_8 nanotubes and nanotori (see [9], [1], [10]).

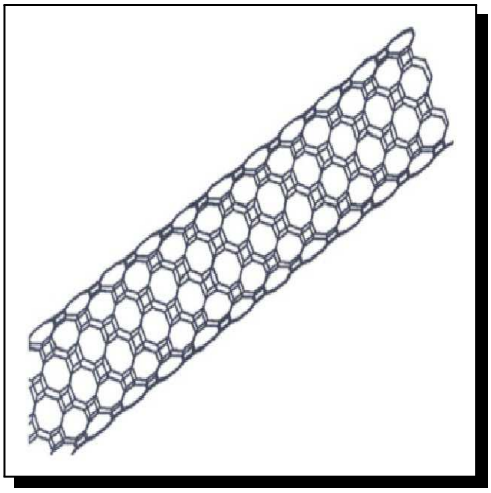

Figure 1. Nanotube $TUC_4C_8(S)$

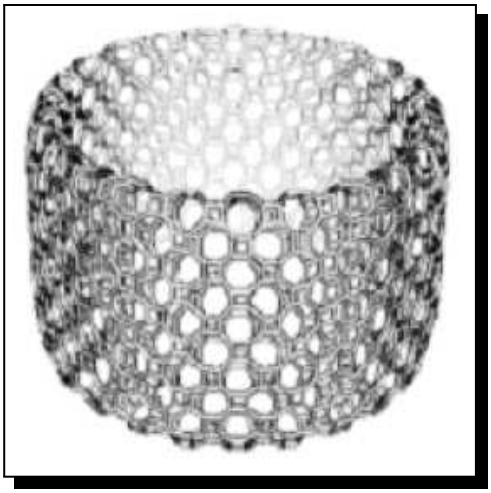

Figure 2. C_4C_8 nanotorus

The calculation of HOMO-LUMO gap of different nanotubes by using *density function theory* (DFT) is carried out by various authors in [15], [5], [8]. In all these methods the numerical value of HOMO-LUMO gap is obtained using different programming based data. So far little effort has been made to get theoretical/mathematical expressions for determination of HOMO-LUMO gap. Klein *et al*. [12] deduced elegant but simple upper bound for the HOMO-LUMO gap of molecular pi network of connected subgraphs of graphene sheets and corresponding nanotubes. In this paper, we continue the work of Klein *et al*. [12] and estimate the bounds on the HOMO-LUMO gap for C_4C_8 network and corresponding open ended nanotube and nanotorous by using linear algebra and decompositions method. The proposed bound is totally dependent on the length of nanotube which is helpful to determine the behavior of HOMO-LUMO gap with respect to its length, whereas the bound proposed by Klein *et al*. [12] is in terms of degrees of vertices. Moreover, as compared to DFT methods where only the numerical approximations are made,

our method provides an explicit bound in terms of length of nanotube (without any hypothesis). This can be helpful in theoretical study of nanotubes.

For any bipartite graph G, the set of vertices can be split into disjoint subsets of starred and circled vertices that is $V^*(G) = \{v_1, v_2, \cdots, v_r\}$ and $V^\circ(G) = \{v_{r+1}, v_{r+2}, \cdots, v_n\}$, respectively. Let $B(G) = (b_{ij})$ be the $r \times (n-r)$ matrix defined as $b_{ij} = 1$, if $v_i v_j \in E(G)$, where $v_i \in V^*(G)$ and $v_j \in V^\circ(G)$ and otherwise $b_{ij} = 0$. The matrix $B(G)$ is called biadjacency matrix of G. Now we can write adjacency matrix of the graph G denoted by $A(G)$ as

$$A(G) = \begin{pmatrix} O & B \\ B^T & O \end{pmatrix}. \tag{1}$$

The eigenspectrum of the graph can be helpful in predicting certain properties of graph structure, for example, the graph G is bipartite if and only if for each eigenvalue μ of G, $-\mu$ is also an eigenvalue of G.

Theorem 1.1 (Rayleigh-Ritz quotient)**.** *If $B \in C^{n\times n}$ is a Hermitian matrix, then the minimum eigenvalue $\mu_{\min}(B)$ of B is*

$$\mu_{\min}(B) = \min_{w \in C^n, w \neq 0} w^\dagger B w / w^\dagger w,$$

where $w^\dagger$ denote the conjugate transpose of the vector w.

2. Main Results

Let G be the molecular graph of C_4C_8 lattice. Since this graph is bipartite, its set of vertices $V(G)$ can be split into two disjoint subsets $V^*(G)$ and $V^\circ(G)$ consisting of starred and circled vertices.

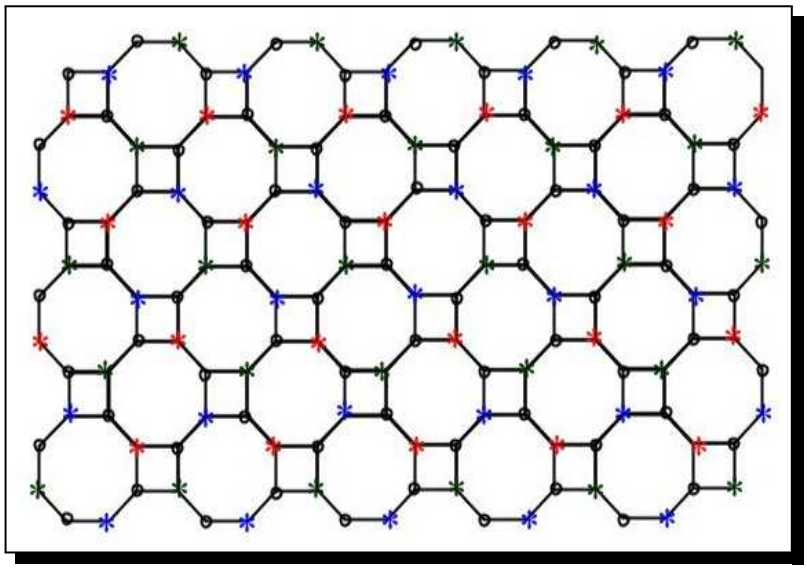

Figure 3. C_4C_8 lattice illustrating bipartition of vertices as starred $*$ and circled $\circ$ vertices

Two graphs, starred graph G^* and circled graph G° are constructed. The graph G^* (respectively G°) is formed by drawing an edge corresponding to each path of length 2 between

any two starred (respectively circled) vertices of G. Clearly the graph G^* (respectively G°) is tripartite. Hence, the set of vertices $V(G^*) = V^*$ splits into three disjoint subsets V_X^*, V_Y^* and V_Z^*, in which the vertices of one class are adjacent to the vertices of remaining two classes only. The vertices of V_X^*, V_Y^* and V_Z^* are colored red, blue and green, respectively. In Figure 4, the graph G^* is shown, where yellow lines are the edges of G^*. The graph G^* is in fact $C_2C_3C_4$ net. Similarly $V(G^\circ) = V^\circ$ splits into three disjoint subsets V_X°, V_Y° and V_Z°.

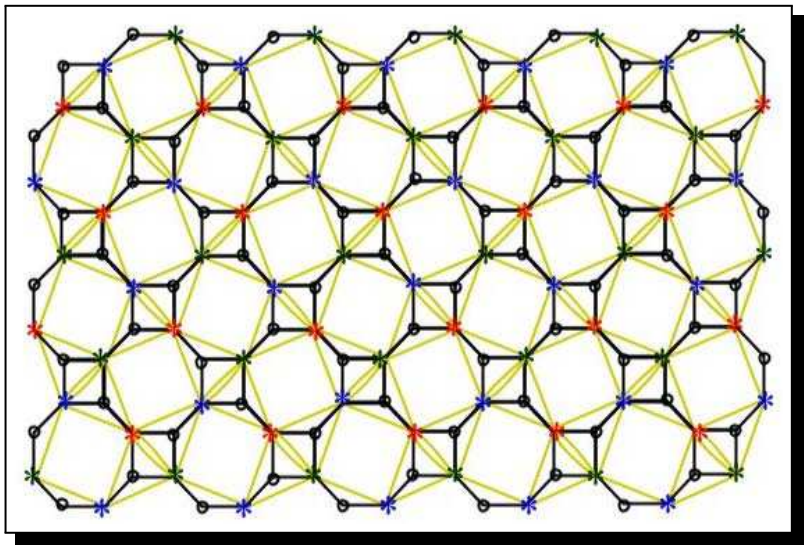

Figure 4. The graph G^*

Lemma 2.1. *Let G be the molecular graph of C_4C_8 lattice. Then*

$$A(G^*) = \begin{bmatrix} O & A_{XY} & A_{XZ} \\ A_{XY}^T & O & A_{YZ} \\ A_{XZ}^T & A_{YZ}^T & O \end{bmatrix}, \tag{2}$$

where $A_{\omega\eta}$ is a matrix with $(A_{\omega\eta})_{ij}$ is the number of edges between $V_i \epsilon V_\omega^*$ and $V_j \epsilon V_\eta^*$.

Now consider the adjacency matrix of any bipartite graph G,

$$A = A(G) = \begin{bmatrix} O & B \\ B^T & O \end{bmatrix}.$$

We note that

$$A^2 = \begin{bmatrix} O & BB^T \\ B^TB & O \end{bmatrix} = \begin{bmatrix} O & C^* \\ C^\circ & O \end{bmatrix},$$

where $C^* = BB^T$ and $C^\circ = B^TB$. This further shows that the eigenvalues of A^2 are the eigenvalues of C^* and C°.

Lemma 2.2 ([12]). *For a connected bipartite graph G with $\mu_{\min}C^*$ and $\mu_{\min}C^\circ$ as the least positive eigenvalues of C^* and C°, respectively, then*

$$\Delta(G) = 2\min\left\{\sqrt{\mu_{\min}C^*}, \sqrt{\mu_{\min}C^\circ}\right\},$$

where C^* and C° are defined as above.

Lemma 2.3. *The matrix C^* corresponding to the C_4C_8 lattice is given by*

$$C^* = \begin{bmatrix} D_X & A_{XY} & A_{XZ} \\ A_{XY}^T & D_Y & A_{YZ} \\ A_{XZ}^T & A_{YZ}^T & D_Z \end{bmatrix},$$

where D_X, D_Y and D_Z are diagonal matrices with diagonal entries as vertex degrees and $A_{\omega\eta}$ is a matrix with $(A_{\omega\eta})_{ij}$ is the number of edges between $V_i \epsilon V_\omega^*$ and $V_j \epsilon V_\eta^*$.

Theorem 2.1. *For the matrix C^* of the C_4C_8 lattice, the minimum eigenvalue of C^* satisfies,*

$$\mu_{\min}(C^*) \leq \frac{(|E(G)| - |E(G^*)|)}{|V^*|}.$$

Proof. Let V_J, where $J \in \{X, Y, Z\}$ has j elements and V_J be the column vectors of order $j \times 1$ all of whose entries are 1s. Now, we take a nonzero matrix $U \in C^n$ defined by

$$U = \begin{bmatrix} V_X \\ \alpha V_Y \\ \alpha^2 V_Z \end{bmatrix},$$

where 1, α, α^2 be the cube roots of unity.

Then we have

$$\begin{aligned} U^\dagger U &= \begin{bmatrix} V_X^T & \alpha^2 V_Y^T & \alpha V_Z^T \end{bmatrix} \begin{bmatrix} V_X \\ \alpha V_Y \\ \alpha^2 V_Z \end{bmatrix} \\ &= V_X^T V_X + V_Y^T V_Y + V_Z^T V_Z \\ &= x + y + z = |V^*| \end{aligned} \tag{3}$$

and

$$\begin{aligned} U^\dagger C^* U &= \begin{bmatrix} V_X^T & \alpha^2 V_Y^T & \alpha V_Z^T \end{bmatrix} \begin{bmatrix} D_X & A_{XY} & A_{XZ} \\ A_{XY}^T & D_Y & A_{YZ} \\ A_{XZ}^T & A_{YZ}^T & D_Z \end{bmatrix} \begin{bmatrix} V_X \\ \alpha V_Y \\ \alpha^2 V_Z \end{bmatrix} \\ &= (V_X^T D_X V_X + \alpha V_X^T A_{XY} V_Y + \alpha^2 V_X^T A_{XZ} V_Z) \\ &\quad + (\alpha^2 V_Y^T A_{XY}^T V_X + V_Y^T D_Y V_Y + \alpha V_Y^T A_{YZ} V_Z) \\ &\quad + (\alpha V_Z^T A_{XZ}^T V_X + \alpha^2 V_Z^T A_{YZ}^T V_Y + V_Z^T D_Z V_Z) \\ &= (V_X^T D_X V_X + V_Y^T D_Y V_Y + V_Z^T D_Z V_Z) + (\alpha V_X^T A_{XY} V_Y + \alpha^2 V_Y^T A_{XY}^T V_X) \\ &\quad + (\alpha^2 V_X^T A_{XZ} V_Z + \alpha V_Z^T A_{XZ}^T V_X) + (\alpha V_Y^T A_{YZ} V_Z + \alpha^2 V_Z^T A_{YZ}^T V_Y) \\ &= \left(\sum_{v_i \in V_X^*} d_{v_i}(G) \right) + \left(\sum_{v_j \in V_Y^*} d_{v_j}(G) \right) + \left(\sum_{v_k \in V_Z^*} d_{v_k}(G) \right) + (\alpha M_{XY}^* + \alpha^2 M_{XY}^*) \\ &\quad + (\alpha M_{XZ}^* + \alpha^2 M_{XZ}^*) + (\alpha M_{YZ}^* + \alpha^2 M_{YZ}^*), \end{aligned}$$

where (M_{IJ}^*) denotes the number of edges between V_I^* and V_J^* with $(I, J) \in \{X, Y, Z\}$.

Thus we can write

$$U^{\dagger}C^{*}U = \left(\sum_{v_i \in V^*} d_{v_i}(G)) - (M^*_{XY} + M^*_{XZ} + M^*_{YZ}\right)$$
$$= |E(G)| - |E(G^*)|. \tag{4}$$

By using (3) and (4),

$$\frac{U^{\dagger}C^{*}U}{U^{\dagger}U} = \frac{|E(G)| - |E(G^*)|}{|V^*|}.$$

Now, by Rayleigh-Ritz quotient,

$$\mu_{\min}(C^*) = \min_{V \in C^n, V \neq 0} \frac{V^{\dagger}C^{*}V}{V^{\dagger}V}$$
$$\leq \frac{U^{\dagger}C^{*}U}{U^{\dagger}U}$$
$$= \frac{|E(G)| - |E(G^*)|}{|V^*|}.$$

So, $\mu_{\min}(C^*) \leq \dfrac{|E(G)| - |E(G^*)|}{|V^*|}$. □

Now consider $2D$ lattice of open ended $TUC_4C_8(S)$ nanotube which consists of n rows of alternating squares and octagons, i.e., the length of the tube is n. Now if we label the octagons in first row by $1,2,3,\cdots,m$ then the total number of octagons in $2D$ lattice of $TUC_4C_8(S)$ is mn. We simply denote this graph by $TUC_4C_8(m,n)$, where $m,n > 1$.

Lemma 2.4. *The number of elements in the set of edges and vertices of the graph* $TUC_4C_8(S)$ (m,n) *is given by*

$$|E(TUC_4C_8(S)(m,n))| = 6mn + 4m$$

and

$$|V(TUC_4C_8(S)(m,n))| = 4mn + 4m.$$

Lemma 2.5. *For the starred graph* G^* *(Respectively circled graph* G°*) constructed from the graph* $TUC_4C_8(S)(m,n)$ *as illustrated in Figure* 4*,*

$$|E(G^*)| = |E(G^{\circ})| = 6mn + 2m$$

and

$$V^*(G)| = |V^{\circ}(G)| = 2mn + 2m\,.$$

Theorem 2.2. *For the graph* $TUC_4C_8(S)(m,n)$*, where* $m,n \in N - \{1\}$ *of nanotube,*

$$\Delta(TUC_4C_8(S)(m,n)) \leq 2/\sqrt{(n+1)}.$$

Proof. It is easy to see that the graph $TUC_4C_8(S)(m,n)$ is also bipartite and its corresponding starred and circled graphs are tripartite. By using Theorem 2.1,

$$\mu_{\min}(C^*) \leq (|E(TUC_4C_8(S)(m,n))| - |E(G^*)|)/|V^*|.$$

Now by applying Lemma 2.4 and Lemma 2.5,

$$\mu_{\min}(C^*) \leq 1/(n+1)$$

and the result immediately follows from Lemma 2.2. □

Theorem 2.3. *For the molecular graph T of $C_4C_8(m,n)$ nanotorus, where $n \equiv 0 (\mathrm{mod}\, 6)$, $\Delta(T) \leq 0$.*

Proof. Let m be the number of octagons in each row of two dimensional lattice of C_4C_8 nanotorus. Since there are n such rows,

$$|E(T)| = |E(T^*)| = 6mn, \tag{5}$$

where T^* is corresponding starred graph of T. As T is bipartite and T^* is tripartite for $n \equiv 0 (\mathrm{mod}\, 6)$, the result immediately follows from Theorem 2.1 and (5). □

3. Conclusion

The upper bounds of HOMO-LUMO gap for C_4C_8 lattice, nanotube and nanotorus are estimated. Theorems 2.1, 2.2 and 2.3 constitute the main results. The estimated upper bound for the HOMO-LUMO gap of C_4C_8 nanotube is $2/\sqrt{(n+1)}$, which depends only on the parameter n, length of the nanotube. The behavior of this bound is shown in the Figure 5.

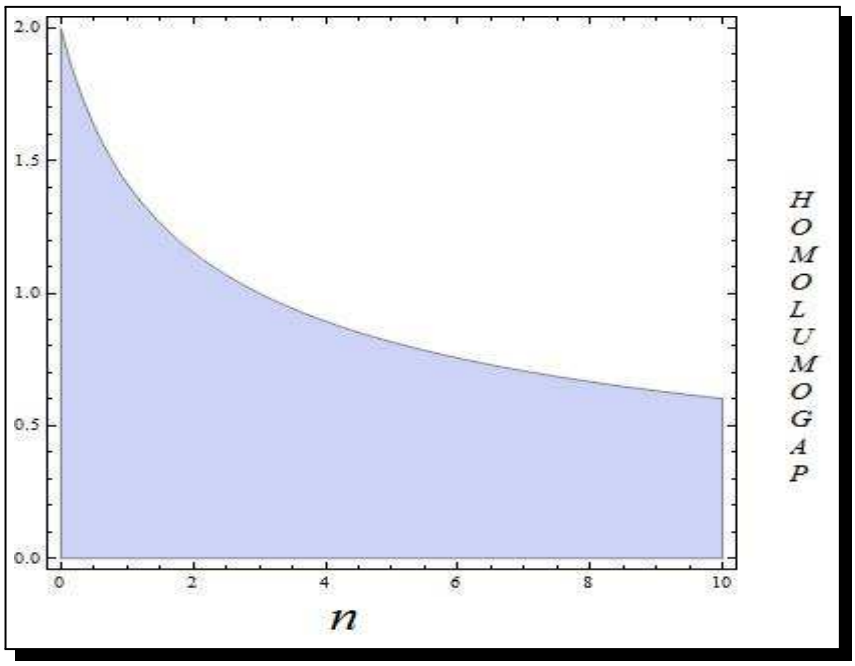

Figure 5. Behavior of HOMO-LUMO bound of TUC_4C_8 with the length of nanotube n

This might be more convenient and helpful in theoretical study of molecular orbital theory of nanotubes as compared to *Density functional Theory* (DFT) which only gives programming based numerical approximations of HOMO-LUMO gap using certain hypothesis.

Competing Interests

The authors declare that they have no competing interests.

Authors' Contributions

All the authors contributed significantly in writing this article. The authors read and approved the final manuscript.

References

[1] S. Ahmad, U. Ahmad, M. Imran and N. Farah, The Omega and Sadhana polynomials of nanotube $TUC4[p,q]$, *Can. J. Chem.* **94** (2016), 490.

[2] P.W. Fowler and T. Pisanski, HOMO-LUMO map for fullerenes, *Acta Chim. Slov.* **57** (2010), 513.

[3] P.W. Fowler and T. Pisanski, HOMO-LUMO map for chemical graphs, *MATCH Commun. Math. Comput. Chem.* **64** (2010), 373.

[4] P.W. Fowler, P. Hansen, G. Capoross and A. Soncini, Polyenes with maximum HOMO-LUMO gap, *Chem. Phys. Lett.* **342** (2001), 105. DOI: 10.1016/S0009-2614(01)00570-X.

[5] M. Gallo, A. Favila and D. Glossman-Mitnik, DFT studies of functionalized carbon nanotubes and fullerenes as nanovectors for drug delivery of antitubercular compounds, *Chemical Physics Letters* **447** (2007), 105–109.

[6] I. Gutman, Note on a topological property of the HOMO-LUMO separation, *Z. Naturforsch.* **35** (1980), 458, DOI: 10.1515/zna-1980-0419.

[7] I. Gutman, J.V. Knop and N. Trinajsti, A graph-theoretical analysis of the HOMO LUMO separation in conjugated hydrocarbons, *Z. Naturforsch.* **29B** (1974), 80, DOI: 10.1515/znb-1974-1-225.

[8] M. Hesabi and M. Hesabi, The interaction between carbon nanotube and skin anti-cancer drugs: a DFT and NBO approach, *Journal of Nanostructure in Chemistry* **3** (2013), 22.

[9] A. Heydari, On the modified Schultz index of $C_4C_8(S)$ nanotori and nanotube, *Digest. J. Nanomater. Bios.* **5**(1) (2010), 51.

[10] Y. Huo, J. Liu, S. Ahmad, N. Farah, U. Ahmad, M.R. Farahani and M. Imran, On certain topological indices of TUC_5C_8 nanotubes, *Journal of Computational and Theoretical Nanoscience* **13** (2016), 9158.

[11] G. Jakli, P.W. Fowler and T. Pisanski, HL-index of a graph, *Ars Math. Contemp.* **5** (2012), 99.

[12] D.J. Klein, Y. Yang and D. Ye, HOMO-LUMO gap for sub-graphenic and sub-buckytubic species, *Proc. R. Soc. A* **471**: 20150183 (2015).

[13] X. Li, Y. Li, Y. Shi and I. Gutman, Note on the HOMO-LUMO index of graphs, *MATCH Commun. Math. Comput. Chem.* **70**(2013), 85.

[14] B. Mohar, Median eigenvalues and the HOMO-LUMO index of graphs, *J. Comb. Theory B*. **112** (2015), 78, DOI: 10.1016/j.jctb.2014.12.001.

[15] A. Rochefort, D.R. Salahub and P. Avouris, Effects of finite length on the electronic structure of carbon nanotubes, *J. Phys. Chem. B* **103** (1999), 641 – 646.

[16] F.J. Zhang and A. Chang, Acyclic molecules with greatest HOMO LUMO separation, *Discrete Appl. Math.* **98** (1999), 165, DOI: 10.1016/S0166-218X(99)00119-5.