Bounds of HOMO-LUMO Gap for Certain Nanotubes and Nanotori

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Abstract. The eigenspectrum $\mu_1 \geq \mu_2 \geq \cdots \geq \mu_m$ with the middle eigenvalues $\mu_h$ and $\mu_l$, 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

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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 $\mu_h$ and $\mu_l$ 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, nanoprobe (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]).

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 \( V^*(G) = \{v_1, v_2, \ldots, v_r\} \) and \( V^o(G) = \{v_{r+1}, v_{r+2}, \ldots, v_n\} \), 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 \( v_j \in V^o(G) \) 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

\[
A(G) = \begin{pmatrix}
O & B \\
B^T & O
\end{pmatrix}.
\]

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 \( \mu \) 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 \( \mu_{\text{min}}(B) \) of \( B \) is

\[
\mu_{\text{min}}(B) = \min_{w \in C^n, w \neq 0} \frac{w^\dagger Bw}{w^\dagger w},
\]

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 \( V^o(G) \) consisting of starred and circled vertices.

![Figure 3. C_4C_8 lattice illustrating bipartition of vertices as starred * and circled o vertices](image)

Two graphs, starred graph \( G^* \) and circled graph \( G^o \) are constructed. The graph \( G^* \) (respectively \( G^o \)) 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 \( G^\circ \)) 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 \( V^\circ_X, V^\circ_Y \) and \( V^\circ_Z \).

![Figure 4. The graph \( G^* \)](image)

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

\[
A(G^*) = \begin{bmatrix}
O & A_{XY} & A_{XZ} \\
A_{TY}^T & O & A_{YZ} \\
A_{TZ}^T & A_{YZ}^T & O
\end{bmatrix},
\]

(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 \( C^\circ \).

**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 \( C^\circ \), respectively, then

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

where \( C^* \) and \( C^\circ \) 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 $V_i \omega V_{\omega}$ and $V_j \eta V_{\eta}$.

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

$$U = \begin{bmatrix} V_X \\ aV_Y \\ a^2V_Z \end{bmatrix},$$

where $1$, $\alpha$, $\alpha^2$ be the cube roots of unity.

Then we have

$$U^\dagger U = [V_X^T \quad \alpha^2V_Y^T \quad \alpha V_Z^T] \begin{bmatrix} V_X \\ \alpha V_Y \\ a^2V_Z \end{bmatrix} = V_X^TV_X + V_Y^TV_Y + V_Z^TV_Z = x + y + z = |V^*|$$

(3)

and

$$U^\dagger C^*U = [V_X^T \quad \alpha^2V_Y^T \quad \alpha V_Z^T] \begin{bmatrix} D_X & A_{XY} & A_{XZ} \\ A_{XY}^T & D_Y & A_{YZ} \\ A_{XZ}^T & A_{YZ}^T & D_Z \end{bmatrix} \begin{bmatrix} V_X \\ \alpha V_Y \\ a^2V_Z \end{bmatrix}$$

$$= (V_X^TD_XV_X + aV_Y^TA_{XY}V_Y + a^2V_Z^TA_{XZ}V_Z)$$

$$+ (\alpha^2V_Y^TA_{XY}^TV_X + V_Y^TD_YV_Y + \alpha V_Z^TA_{YZ}V_Z)$$

$$+ (\alpha V_Y^TA_{XZ}V_X + a^2V_Z^TA_{YZ}^TV_Y + V_Z^TD_ZV_Z)$$

$$= (V_X^TD_XV_X + V_Y^TD_YV_Y + V_Z^TD_ZV_Z) + (aV_Y^TA_{XY}V_Y + a^2V_Z^TA_{XZ}V_Z)$$

$$+ (\alpha V_Y^TA_{XY}^TV_X + \alpha^2V_Z^TA_{YZ}V_Z + aV_Y^TA_{YX}V_Z + a^2V_Z^TA_{YX}^TV_Y)$$

$$= \left( \sum_{v_i \in V_X^*} d_{v_i}(G) \right) + \left( \sum_{v_j \in V_Y^*} d_{v_j}(G) \right) + \left( \sum_{v_k \in V_Z^*} d_{v_k}(G) \right) + (aM_{XY}^* + a^2M_{XY}^*)$$

$$+ (aM_{XZ}^* + a^2M_{XZ}^*) + (aM_{YZ}^* + a^2M_{YZ}^*),$$

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

By using (3) and (4),
\[
U^\dagger C^* U U^\dagger U = \left( |E(G)| - |E(G^*)| \right) |V^*|.
\]

Now, by Rayleigh-Ritz quotient,
\[
\mu_{\text{min}}(C^*) = \min_{V \in C_n, V \neq 0} \frac{V^\dagger C^* V}{V^\dagger V} \leq \frac{U^\dagger C^* U}{U^\dagger U} = \frac{|E(G)| - |E(G^*)|}{|V^*|}.
\]

So, \( \mu_{\text{min}}(C^*) \leq \frac{|E(G)| - |E(G^*)|}{|V^*|} \). \qed

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 \( G^\circ \)) 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
\[
\mu_{\text{min}}(C^*) \leq \left( |E(TUC_4C_8(S)(m, n))| - |E(G^*)| \right) |V^*|.
\]
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 \( n \equiv 0(\mod 6) \), \( \Delta(T) \leq 0 \).

**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,
\[ |E(T)| = |E(T^*)| = 6mn, \quad (5) \]
where \( T^* \) is corresponding starred graph of \( T \). As \( T \) is bipartite and \( T^* \) is tripartite for \( n \equiv 0(\mod 6) \), 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.

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