

## Approach to zero band gap graphene sheets: A graph theoretical analysis

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A method of construction of graphs for extended graphene sheets of the formula  $C_{6n^2}H_{6n}$ ,  $n = 1, 2, 3, \dots$ , maintaining six-fold symmetry has been developed. It has been shown that their adjacency matrices, which are of size  $6n^2 \times 6n^2$ , can be reduced to  $n^2 \times n^2$  matrices by exploring rotational symmetry and the reduced matrix can be easily written down as the adjacency matrix of a directed graph with  $n^2$  vertices (called 'reduced graph' in this article). A scheme for drawing the reduced graph is devised and from this the graph eigenvalues can be easily determined. It has been shown that the HOMO-LUMO energy gap of the  $\pi$ -MOs decreases as  $n$  increases, and an almost gapless graphene sheet ( $\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}} = 4.5 \times 10^{-10} \beta$ , where  $\beta$  = resonance integral between two adjacent  $sp^2$ -C atoms) begins to form at  $6 \times 20^2$  carbon atoms arranged in a 2-dimensional hexagonal lattice.

Keywords: Graph theory, graphene, reduced graph, zero band gap.

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### 1. Introduction

Graphenes are electronically important materials of the present age. Single-layer hexagonal carbon lattices are called nanographenes (NGs) and theoretical study of such materials is of current interest<sup>1-3</sup>. Although all electron Green's function calculations together with the density functional theory are theoretically more rigorous for such materials<sup>4-8</sup>, simple Hückel level calculations considering only the  $\pi$ -electrons of the  $sp^2$ -hybridized carbon atoms of NGs with finite number of carbon atoms have recently been shown<sup>9</sup> to yield reliable results comparable to the sophisticated methods. On the other hand, molecular (hydrogen suppressed) graphs of polynuclear aromatic hydrocarbons (PAH) represent the network of  $\pi$ -orbitals and the graph eigenvalues, i.e. the eigenvalues of the adjacency matrices are known to be equivalent to the  $\pi$ -MO energies with the scaling  $\alpha = 0$  (Coulomb integral) and  $\beta = 1$  (Resonance integral)<sup>10-12</sup>. In the present paper graphene sheets with carbon atom skeleton represented by the PAH of formula  $C_{6n^2}H_{6n}$ ,  $n = 1, 2, 3, \dots$  has been studied by utilizing 6-fold rotational symmetry and their graph eigenvalues ( $\pi$ -MO energies) have been calculated graph theoretically in order to estimate the practicable minimum number of carbon atoms needed for the NG sheet to achieve zero band gap without overlap of conduction and valence bands.

### 2. Method for construction of graphs for extended graphene sheets maintaining 6-fold rotational symmetry

Two methods have been developed for this purpose as discussed below.

#### Method A:

Step 1: Start with a central hexagon and draw three dotted lines bisecting the three pairs of opposite edges.

Step 2: Along each line place two hexagons on opposite sides of the central hexagon. This will complete  $C_{24}$ ; all hexagons are fused and no extra vertex is needed (Fig. 1(a)).

Step 3: Along the dotted lines fuse one hexagon on each side. This will give three linear pentacenes intersecting at the central hexagon (Fig. 1(b)).

Step 4: Place one vertex at the centre of each gap between the linear polyacenes and join it to the nearest vertices to completely fuse the corresponding hexagons. This gives  $C_{54}$  (Fig. 1(c)).

Step 5: Again add one hexagon on opposite sides of each dotted line so that there are three linear heptacenes intersecting at the central hexagon (Fig. 1(d)).

Step 6: Each gap generated between the linear polyacenes now requires three vertices to be joined to the

nearest vertices for complete fusion of rings. This completes the construction of  $C_{96}$  (Fig. 1(e)).

In this way by progressively increasing the number of intersecting linear polyacenes along the dotted lines and filling up the gaps by 5, 7, ... vertices and completing the fusion processes, graphs for  $C_{150}$ ,  $C_{216}$ , ... can be drawn.

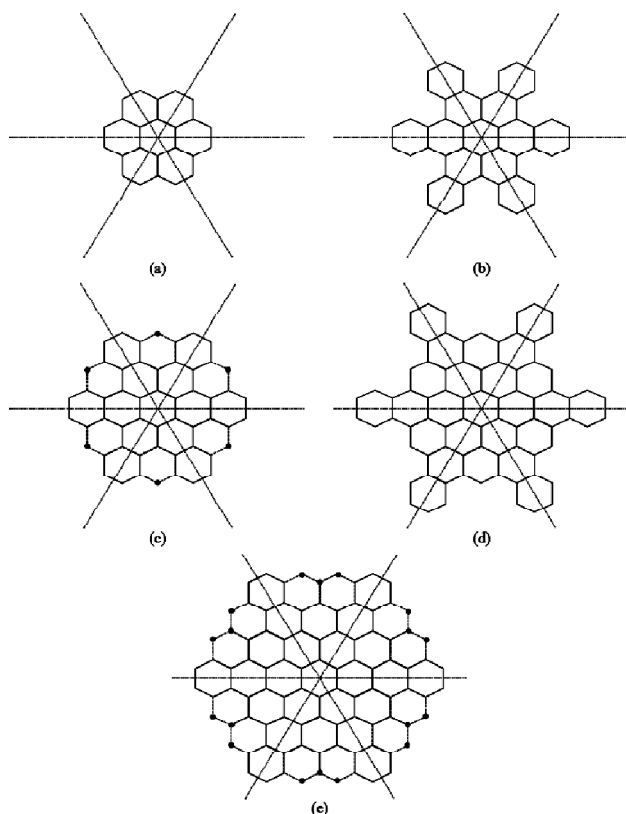


Fig. 1. Illustration of Method A for construction of graphene sheets maintaining 6-fold rotational symmetry.

*Method B:*

Step 1: Start with a linear polyacene containing  $(2n - 1)$  fused rings.

Step 2: Fuse  $(2n - 2)$  rings symmetrically above and below of the central polyacene.

Step 3: Fuse  $(2n - 3)$  rings symmetrically above and below the system obtained above.

Step 4: In this way proceed up to fusion of  $(2n - n) = n$  rings symmetrically above and below. This will complete the

construction of a graphene sheet with 6-fold symmetry having  $6n^2$  number of carbon atoms and  $3n^2 - 3n + 1$  number of fused rings.

This procedure is fairly simple and is illustrated in Fig. 2 for the  $C_{150}$  graphene sheet. Here  $150 = 6 \times 5^2$ , the central polyacene has 9 rings and the successive layers (above and below) have 8, 7, 6 and 5 rings respectively.

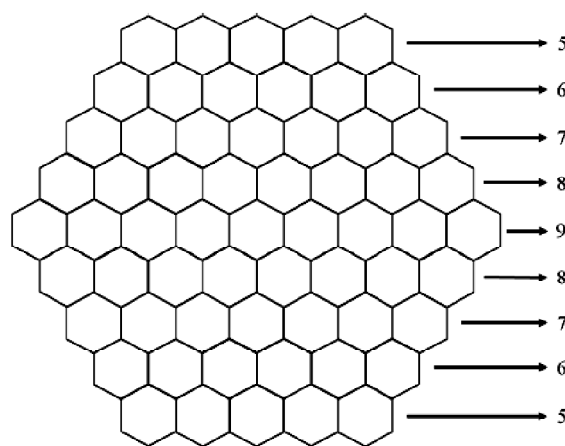


Fig. 2. Construction of  $C_{150}$  graphene sheet by Method B.

### 3. Reduction of the adjacency matrix using 6-fold rotational symmetry

The algorithm for utilizing  $r$ -fold rotational symmetry ( $r \geq 2$ ) to factorize the characteristic polynomial of a graph was developed by Davidson and independently by Shen<sup>13,14</sup>. According to this algorithm, the vertices of a graph with 6-fold rotational symmetry can be grouped in orbits such that any vertex in a given orbit can be transformed into another of the same orbit by a 6-fold rotation and no two vertices belonging to different orbits are rotationally equivalent. If the graph has  $N$  vertices, one can label the vertices in a given orbit with increment of  $N/6$ ; the procedure is as follows:

For the first orbit the vertex labels are 1,  $(1 + N/6)$ ,  $(1 + 2N/6)$ , ...,  $(1 + 5N/6)$ ; for the second orbit the vertex labels are 2,  $(2 + N/6)$ ,  $(2 + 2N/6)$ , ...,  $(2 + 5N/6)$  and so on.

The labeling scheme is illustrated for the  $C_{24}$  and  $C_{54}$  systems in Fig. 3.





### 5. Characteristic polynomials and eigenvalues of the graphene graphs

The characteristic polynomials of the reduced graphs in terms of  $b$  ( $= a + a^*$ ) for the systems  $C_6$ ,  $C_{24}$ ,  $C_{54}$  and  $C_{96}$  found from their corresponding adjacency matrices (**A**) are given in Table 1. These polynomials were constructed by the usual Laplacian expansion of the determinant  $|xI - \mathbf{A}|$  where

**Table 1.** Characteristic polynomials of the reduced graphs for graphene systems up to  $C_{96}$

System	Characteristics polynomial of the reduced graph
$C_6$	$x - b$
$C_{24}$	$x^4 - bx^3 - 4x^2 + 2bx + (b^2 + 1)$
$C_{54}$	$x^9 - bx^8 - 11x^7 + 9bx^6 + (b^2 + 37)x^5 - 26bx^4 - (3b^2 + 45)x^3 + 28bx^2 + (3b^2 + 14)x - (b^3 + 6b)$
$C_{96}$	$x^{16} - bx^{15} - 21x^{14} + 19bx^{13} + (b^2 + 173)x^{12} - 143bx^{11} - (13b^2 + 723)x^{10} + 536bx^9 + (67b^2 + 1652)x^8 - (b^3 + 1090b)x^7 - (169b^2 + 2070)x^6 + (3b^3 + 1184b)x^5 + (218b^2 + 1328)x^4 - (6b^3 + 622b)x^3 - (133b^2 + 352)x^2 + (5b^3 + 114b)x + (b^4 + 25b^2 + 16)$

$I$  is the unit matrix of the size of **A**. The graph eigenvalues are the zeros of the polynomials obtained by using the permitted values of  $b$ . These are given in Table 2 for systems up to  $C_{96}$ . It is found that the eigenvalues corresponding to  $b =$

2 are the negatives of those corresponding to  $b = -2$  and similarly the eigenvalues corresponding to  $b = 1$  and  $-1$  are equal in magnitude but opposite in sign. This is consistent with the fact that the graphenes are even alternant  $\pi$ -systems and their Hückel molecular orbital eigenvalues occur in  $\pm$ pairs<sup>15</sup>.

### 6. Variation of HOMO-LUMO energy gap with size of the graphene sheet

The graph eigenvalues, which are also the  $\pi$ -MO energies of the graphenes in  $\beta$  unit, are given in Table 2. When the energy of the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) are plotted against the number of carbon atoms ( $m$ ) of the  $C_{6n^2}$  systems ( $n = 1, 2, 3, 4$ ), the energy gap decreases asymptotically (Fig. 5); the two curves fit into the bi-exponential form

$$E_{LUMO} = 0.8177e^{-0.0872m} + 0.5440e^{-0.0090m} = -E_{HOMO}$$

with a correlation,  $r^2 = 1.0$ . The two curves practically touch each other ( $\Delta E = E_{LUMO} - E_{HOMO} = 4.5 \times 10^{-10} \beta$ ) at  $m = 6 \times 20^2 = 2400$  carbon atoms. Thus a graphene sheet with moderately large number of rings is expected to behave like a material between semiconductors (finite non-zero band gap) and metals (with overlapping valence and conduction bands).

**Table 2.** Eigenvalues of the  $\pi$ -MOs of graphenes obtained as zeros of the reduced graph characteristic polynomials for systems up to  $C_{96}$

System	Graph eigenvalues			
	$b = 2$	$b = 1$	$b = -1$	$b = -2$
$C_6$	2.0	1.0	-1.0	-2.0
$C_{24}$	-1.2143, -1.0, 1.5392, 2.6751	(2-fold degenerate) -1.6751, -0.5392, 1.0, 2.2143	(2-fold degenerate) 1.6751, 0.5392, -1.0, -2.2143	1.2143, 1.0, -1.5392, -2.6751
$C_{54}$	-2.0, -1.9406, -1.0464, -1.0, 0.5786, 1.0, 1.3526, 2.2155, 2.8401	-2.3095, -1.6057, -1.3915, -0.6818, 0.3420, 1.0, 1.2375, 1.8053, 2.6039	2.3095, 1.6057, 1.3915, 0.6818, -0.3420, -1.0, -1.2375, -1.8053, -2.6039	2.0, 1.9406, 1.0464, 1.0, -0.5786, -1.0, -1.3526, -2.2155, -2.8401
$C_{96}$	-2.3928, -2.3414, -1.6978, -1.6175, -1.0760, -1.0, -0.8392, -0.3595, 0.6930, 0.8631, 1.2520, 1.5774, 1.5869, 1.9252, 2.5213, 2.9052	-2.5820, -2.1310, -1.9544, -1.3633, -1.2799, -1.0451, -0.7424, -0.2295, 0.4972, 1.0, 1.0673, 1.2989, 1.5895, 1.8638, 2.2536, 2.7628	2.5820, 2.1310, 1.9544, 1.3633, 1.2799, 1.0451, 0.7424, 0.2295, -0.4972, -1.0, -1.0673, -1.2989, -1.5895, -1.8638, -2.2536, -2.7628	2.3928, 2.3414, 1.6978, 1.6175, 1.0760, 1.0, 0.8392, 0.3595, -0.6930, -0.8631, -1.2520, -1.5774, -1.5869, -1.9252, -2.5213, -2.9052

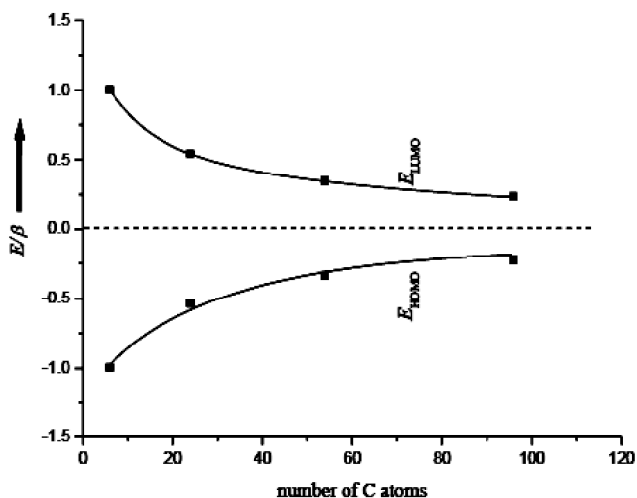


Fig. 5. Variation of HOMO-LUMO energy gap with increase in size of the graphene sheet.

## 7. Conclusion

It has been shown that 6-fold rotational symmetry can be utilized in conjunction with graph theoretical methods to obtain the  $\pi$ -MO energies of extended graphene sheets and their HOMO and LUMO energy levels approach each other asymptotically as the number of fused hexagonal rings increases. The experimental observation of graphene as a novel electronic material with zero band gap is thus explained by a simple graph theoretical approach.

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