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Eigenspectral Analysis of Pendant Vertex- and Pendant Edge-Weighted Graphs of Linear Chains, Cycles, and Stars

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Three classes of pendent vertex- and pendant edge-weighted graphs of linear chains (class I), stars (class II), and cycles (class III) have been presented. These graphs (particularly class I and III) represent heteroconjugated π-systems. Sometimes such graphs appear as factored subgraphs of some complicated graphs. The eigenspectra of these graphs have been found out in analytical forms. These eigenspectra have been utilized i) to calculate the band (i.e., HOMO–LUMO) gaps of such graphs, ii) to find out three classes of inversely proportional graphs (with inversely proportional pairs of eigenvalues), and iii) to express eigenspectra of some complicated graphs in analytical forms along with some subspectral relationships. In the limit of n (number of vertices) to infinity, the band gap of the graph of class I has been shown to be the same with that calculated by considering its hypothetical "cyclic dimer." Reciprocal graphs have also been considered in this context. These graphs are not all hypothetical. A few of them have also been synthesized.

Spectra of graphs, which are the zeros of their corresponding characteristic polynomials, have many chemical applications; for instance, they have been used in chemical kinetics,[1] quantum chemistry, dynamics of oscillatory reactions, and in determining the stabilities of reaction networks[2] and estimating the stabilities of conjugated systems[3] and the electronic structure of organic polymers.[4]

Using a plane of symmetry, McClelland[5] developed graph fragmentation technique and described corresponding rules. D'Amato[6] showed the factorization of a graph with two- or three-fold rotational symmetry. The determination of the isospectrality and/or subspectrality of graphs were reviewed in detail by D'Amato and colleagues.[7] Davidson[8] presented a general graph factorization method with the use of rotational symmetry that was independently elaborated later by Shen.[9] Dias[10,11] has presented both symmetry plane and rotational factorization techniques with more complicated as well as interesting molecular graphs. Using the symmetry plane factorization Dias[10,12] calculated all the eigenvalues of C_{60} fullerene. Hosoya and Tsukano[13] developed an efficient technique for factorization of higher symmetry graphs by using topological symmetry rather than the geometrical symmetry of the molecular network, obtained the eigenvalues of C_{60} more efficiently than Dias[10,12] and recently applied the technique to more complicated hexabenzocoronene torus.[14] McClelland[5] showed the reduction procedure of graph having arbitrary edge weight but no vertex weight by alternating starring procedure analogous to that of Coulson and Rushbrooke.[15] Mukherjee and Das[16] developed a graph squaring technique for reduction of graphs of linear chains in which edge weights are arbitrary and vertex weights are equal in magnitude but opposite in sign. Recently, two procedures[17] have been developed to obtain analytical expressions of eigenspectra; one is for linear chains and cycles with alternant vertex weights and the same edge weight and the other is for linear chains having one or two terminal edge(s) of weight $\sqrt{2}$ times that of the remaining edges. In general vertex- and/or edge-weighted graphs are the graphical representations of heteroconjugated systems. Sometimes they may represent factored subgraphs. Extensive work on alternant conjugated systems having few heteroatoms was done by Gutman.[18,19]

The electronic states of an infinite conjugated network have been found to be well predicted by an important theoretical quantity called the "density of states." Hosoya and co-workers[20] showed the use of the eigenvalues of the "cyclic dimer (CD)," that represent the singular points to the "density of states," for governing the conducting behavior of the periodic polymer. The HMO model for π-electronic systems has been considered widely as the primary step to investigate novel conducting behavior of organic polymers as well as Peierl's distortions and solitonic excitations[21–24] that might occur under some circumstances.

In this communication, three classes of pendant vertex- and pendant edge-weighted graphs have been presented. Their eigenspectral analysis has been made and subsequently been used to calculate band gaps, to search for inversely proportional graphs, and to find out eigenspectra of some complicated graphs in analytical forms. Reciprocal graphs are one kind of inversely proportional graphs where the proportionality constant is unity. The discussion in detail is given in the following sections.

Results and Discussion

Three Classes of Pendant Vertex- and Pendant Edge-Weighted Graphs. Class I: G_1: A graph of this class is shown in Figure 1. It is a linear chain of n vertices each of which is joined to a pendant vertex by a pendant edge of weight k. Each pendant vertex has a self-loop of weight h. The unit R_1 shown in Figure 1 may be considered as the recurring or repeating unit of the graph G_1. The irreducible graph

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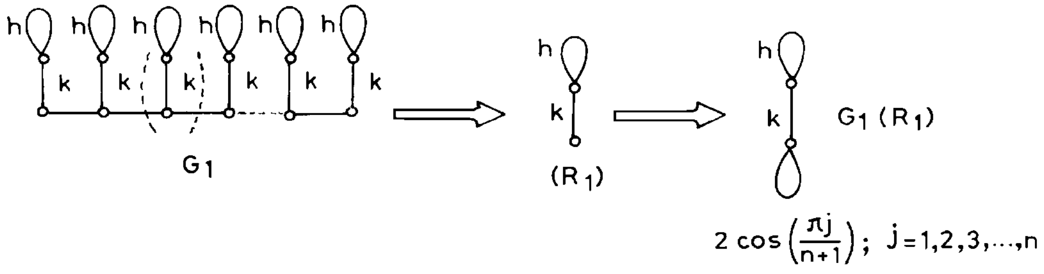


Figure 1. Graph of G_1 and a scheme for generation of its irreducible graph.

$G_1(R_1)$ of G_1 can be constructed by attaching a self-loop of weight $2\cos[\pi j/(n+1)]$ to the vertex that repeats in the main chain of G_1. In some recent works,[17] this procedure has been discussed in details. The adjacency matrix of $G_1(R_1)$ can be obtained by introducing i-th vertex weight as (i, i) element, i–j edge weight as (i, j) element of the said matrix and so on. Now it is usual to write down the secular determinant corresponding to this adjacency matrix for obtaining eigenspectra of $G_1(R_1)$ or G_1. The determinantal equation obtained for the irreducible graph, $G_1(R_1)$, is

$$\begin{vmatrix} \lambda - h & -k \\ -k & \lambda - 2\cos[\pi j/(n+1)] \end{vmatrix} = 0 \tag{1}$$

Equation 1 results in a quadratic equation

$$\lambda^2 - [h + 2\cos[\pi j/(n+1)]]\lambda + [2h\cos[\pi j/(n+1)] - k^2] = 0 \tag{2}$$

which ultimately gives the analytical expression of eigenspectra of G_1 as

$$\lambda(G_1) = \left[(h + 2\cos[\pi j/(n+1)]) \pm \sqrt{(h - 2\cos[\pi j/(n+1)])^2 + 4k^2}\right] \Big/ 2; \quad j = 1,2,3,\ldots,n \tag{3}$$

From eq 3 it is easy to find out that the energy eigenvalues corresponding to HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) for all values of h and k ($k \neq 0$ which, of course, is always the meaningful case)[25] as

$$\lambda(G_1)_{\text{HOMO}} = \left[(h + 2\cos[n\pi/(n+1)]) + \sqrt{(h - 2\cos[n\pi/(n+1)])^2 + 4k^2}\right] \Big/ 2 \tag{4}$$

and

$$\lambda(G_1)_{\text{LUMO}} = \left[(h + 2\cos[\pi/(n+1)]) - \sqrt{(h - 2\cos[\pi/(n+1)])^2 + 4k^2}\right] \Big/ 2 \tag{5}$$

Thus the band gap for G_1 will be

$$\Delta\lambda(G_1) = -2\cos[\pi/(n+1)] + \left[\sqrt{(h + 2\cos[\pi/(n+1)])^2 + 4k^2} + \sqrt{(h - 2\cos[\pi/(n+1)])^2 + 4k^2}\right] \Big/ 2 \tag{6}$$

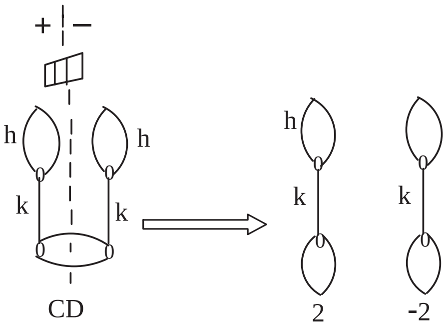


Figure 2. Cyclic dimer (CD) of G_1 and its factorization.

As $n \to \infty$, $\cos[\pi/(n+1)] \to 1$, thus in the case of infinite polymer (G_1) the band gap (ΔG_1) between the valence and the conduction band will be

$$\Delta(G_1) = -2 + \left[\sqrt{(h+2)^2 + 4k^2} + \sqrt{(h-2)^2 + 4k^2}\right] \Big/ 2 \tag{7}$$

This expression of band gap (eq 7) can easily be shown by considering the hypothetical "cyclic dimer" with the same recurring unit[20] as that of the infinite polymer (G_1). The "cyclic dimer" of G_1 and its factorization are shown in Figure 2. The eigenvalues of the "cyclic dimer" can be obtained by solving the quadratic equations resulting from the determinantal equation corresponding to the mirror fragments[5] of the CD. Thus, the band gap calculated from the eigenvalues of the CD has been found to be $-2 + [\sqrt{(h+2)^2 + 4k^2} + \sqrt{(h-2)^2 + 4k^2}]/2$ which is exactly equal to that given by eq 7. It is revealed from eq 7 that the band gap of the polymer of class I will be non-zero for all values of h and k (except $h = 0$ and $k = 0$) and the polymers corresponding to the graphs of class I should be non conducting polymers.

Class II: G_2: A graph (G_2) of this class represents a graph of a star in which each pendant vertex with self-loop of weight h is connected to one central and $(n-1)$ peripheral vertices by edges of equal edge weight k as shown in Figure 3. A $(n-1)$-fold rotational symmetry axis may be imagined which passes through the pendant edge connecting the central vertex of the graph. This graph can subsequently be factorized by using rotational symmetry[6] into one 4-vertex (G_{21}) and $(n-2)$ number of 2-vertex (G_{22}) subgraphs. The 4-vertex subgraph can further be factorized using symmetry plane factorization[5] into two 2-vertex graphs. The eigenspectra of these factored two-vertex subgraphs can easily be calculated from their determinantal equations followed by solving the quadratic equations. The entire scheme is shown in Figure 3. The eigenspectra of the subgraphs are

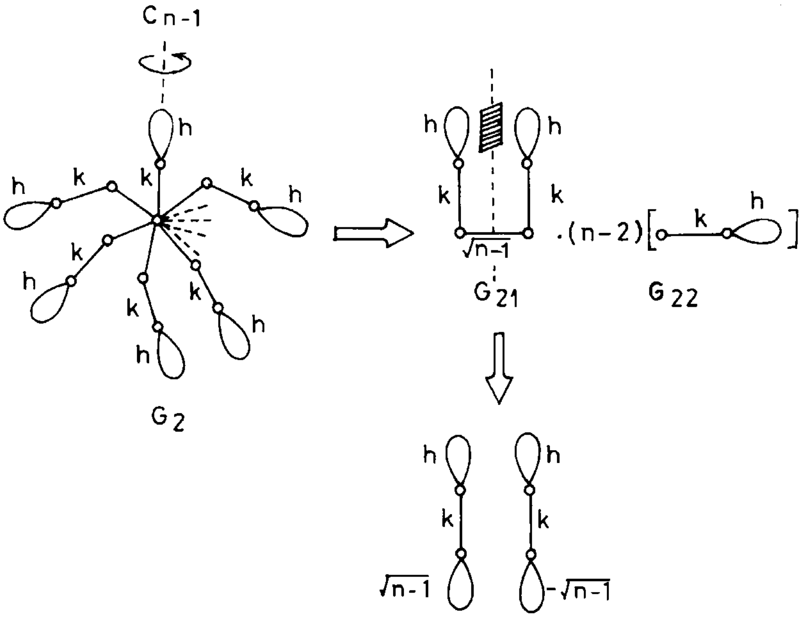


Figure 3. Graph of G_2 and a scheme for generation of its irreducible graph.

$$\lambda(G_{21}) = \left[h + \sqrt{n-1} \pm \sqrt{(h-\sqrt{n-1})^2 + 4k^2}\right]\Big/2;$$
$$\left[h - \sqrt{n-1} \pm \sqrt{(h+\sqrt{n-1})^2 + 4k^2}\right]\Big/2 \quad (8)$$

$$\lambda(G_{22}) = \left[h \pm \sqrt{h^2 + 4k^2}\right]\Big/2 \quad (9)$$

Thus, the expression of eigenspectra of G_2 will be

$$\lambda(G_2) = \left[h + \sqrt{n-1} \pm \sqrt{(h-\sqrt{n-1})^2 + 4k^2}\right]\Big/2;$$
$$\left[h - \sqrt{n-1} \pm \sqrt{(h+\sqrt{n-1})^2 + 4k^2}\right]\Big/2$$
$$\text{and} \quad \left[h \pm \sqrt{h^2 + 4k^2}\right]\Big/2; \left[h \pm \sqrt{h^2 + 4k^2}\right]\Big/2;$$
$$\left[h \pm \sqrt{h^2 + 4k^2}\right]\Big/2 \ldots \text{ up to } (n-2)\text{-th terms} \quad (10)$$

The energy eigenvalues corresponding to the HOMO and LUMO will be

$$\lambda(G_2)_{\mathrm{HOMO}} = \left[h - \sqrt{n-1} + \sqrt{(h+\sqrt{n-1})^2 + 4k^2}\right]\Big/2 \quad (11)$$

and

$$\lambda(G_2)_{\mathrm{LUMO}} = \left[h + \sqrt{n-1} - \sqrt{(h-\sqrt{n-1})^2 + 4k^2}\right]\Big/2 \quad (12)$$

Thus, corresponding band gap for the graph G_2 will be

$$\Delta\lambda(G_2) = -\sqrt{n-1} + \left[\sqrt{(h+\sqrt{n-1})^2 + 4k^2} + \sqrt{(h-\sqrt{n-1})^2 + 4k^2}\right]\Big/2 \quad (13)$$

From eq 13 it is clear that $\Delta\lambda(G_2) \to \infty$ as $n \to \infty$. Thus, the molecular species corresponding to this graph (if it exists) will have a large band gap.

Class III: G_3: A graph (G_3) in this class is a cycle of n vertices to each of which a pendant vertex is attached with a pendant edge-weight of k. The weight of each pendant vertex is represented by a self-loop of weight h. The irreducible graph ($G_3(R_1)$) of G_3 can be constructed[17] by considering a pendant edge with two vertices as repeating or recurring unit (R_1) as shown in Figure 4. The eigenvalue expression for this graph can be obtained by solving the quadratic equation generated from the determinantal equation of the said irreducible graph as follows.

$$\begin{vmatrix} \lambda - h & -k \\ -k & \lambda - 2\cos[2\pi j/n] \end{vmatrix} = 0 \quad (14)$$

Equation 14 results in the quadratic eq 15

$$\lambda^2 - [h + 2\cos[2\pi j/n]]\lambda + [2h\cos[2\pi j/n] - k^2] = 0 \quad (15)$$

whose solutions constitute the eigenspectra of G_3

$$\lambda(G_3) = \left[h + 2\cos[2\pi j/n] \pm \sqrt{(h - 2\cos[2\pi j/n])^2 + 4k^2}\right]\Big/2; \quad j = 0, 1, 2, \ldots, (n-1) \quad (16)$$

For all values of h and k

$$\frac{\mathrm{d}\lambda(G_3)}{\mathrm{d}\lambda_j} = \frac{\mathrm{d}\lambda_\pm}{\mathrm{d}\lambda_j}$$
$$= -\frac{2\pi}{n}\sin\frac{2\pi j}{n}\left[1 - \frac{1}{\sqrt{1 + (2k/[h - 2\cos(2\pi j/n)])^2}}\right]$$
$$= 0, -, -, -, \ldots \text{ up to } [(n/2) - 1]\text{-th terms,}$$
$$0, +, +, +, \ldots \text{ up to } [(n/2) - 1]\text{-th terms for even } n$$
$$= 0, -, -, -, \ldots \text{ up to } [(n-1)/2]\text{-th terms,}$$
$$+, +, +, \ldots \text{ up to } [(n-1)/2]\text{-th terms for odd } n \quad (17)$$

Equation 17 indicates the order that the energy levels follow

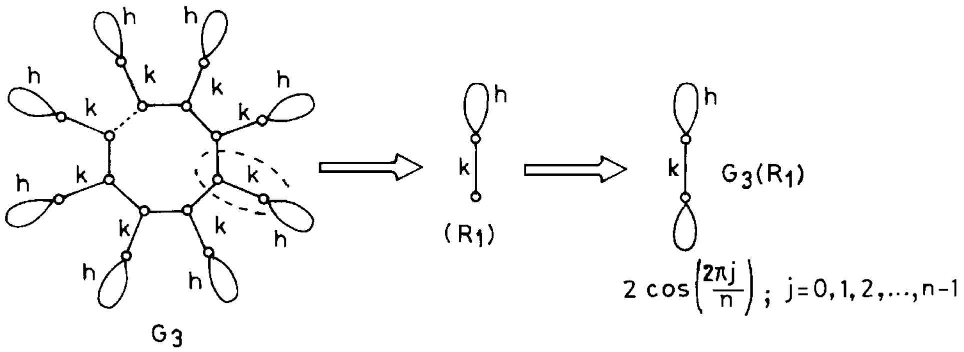


Figure 4. Graph of G_3 and a scheme for generation of its irreducible graph.

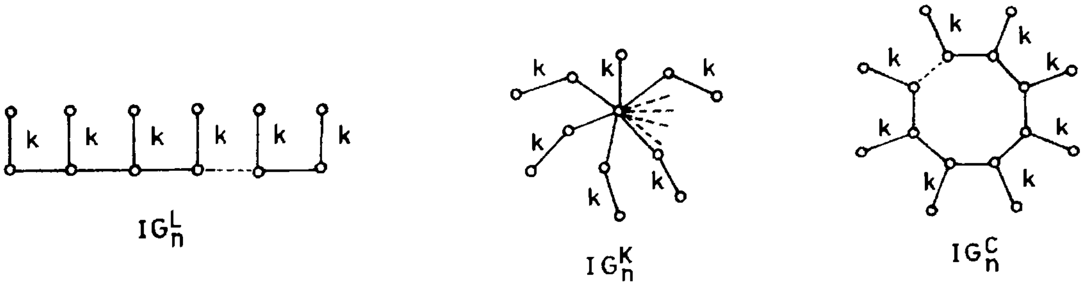


Figure 5. Graphs of IG_n^L, IG_n^K, and IG_n^C.

for even n:

$$\lambda_0^+ > \lambda_1^+, \lambda_{n-1}^+ > \lambda_2^+, \lambda_{n-2}^+ > \ldots > \lambda_{n/2}^+ \quad \text{and}$$
$$\lambda_0^- > \lambda_1^-, \lambda_{n-1}^- > \lambda_2^-, \lambda_{n-2}^- > \ldots > \lambda_{n/2}^-$$

and for odd n:

$$\begin{aligned} &\lambda_0^+ > \lambda_1^+, \lambda_{n-1}^+ > \lambda_2^+, \lambda_{n-2}^+ > \ldots > \lambda_{(n-1)/2}^+ \quad \text{and} \\ &\lambda_0^- > \lambda_1^-, \lambda_{n-1}^- > \lambda_2^-, \lambda_{n-2}^- > \ldots > \lambda_{(n-1)/2}^- \end{aligned} \tag{18}$$

The proof of $\lambda_{n/2}^+ > \lambda_0^-$ for even n and $\lambda_{(n-1)/2}^+ > \lambda_0^-$ for odd n is as follows: The difference (D) of energy between $\lambda_{n/2}^+$ and λ_0^- for even n is a function of h and k as

$$\begin{aligned} D &= \lambda_{n/2}^+ - \lambda_0^- \\ &= \frac{1}{2}\left[-4 + \sqrt{(h+2)^2 + 4k^2} + \sqrt{(h-2)^2 + 4k^2}\right]. \end{aligned} \tag{19}$$

For positive D the above statement follows: The variation of D with respect to k for all values of h can be obtained as

$$\frac{\mathrm{d}D}{\mathrm{d}k} = 2k\left[\frac{1}{\{(h+2) + 4k^2\}^{1/2}} + \frac{1}{\{(h-2) + 4k^2\}^{1/2}}\right] \tag{20}$$

The right hand side of eq 20 will be positive for $k > 0$, negative for $k < 0$ and zero for $k = 0$ which indicates that D should be positive. Similarly $\lambda_{(n-1)/2}^+ > \lambda_0^-$ follows for odd n. Thus the band gap depends on either n is even or odd. For even n:

$$\Delta\lambda(G_3) = \left[-4 + \sqrt{(h+2)^2 + 4k^2} + \sqrt{(h-2)^2 + 4k^2}\right] \Big/ 2 \tag{21a}$$

and for odd n:

$$\begin{aligned} \Delta\lambda(G_3) = \Big[&-2(1 + \cos(\pi/n)) + \sqrt{(h + 2\cos(\pi/n))^2 + 4k^2} \\ &+ \sqrt{(h-2)^2 + 4k^2}\Big] \Big/ 2 \end{aligned} \tag{21b}$$

From eq 21 it has been found that the band gap does not depend on n whereas for odd n this gap depends on n. When $n \to \infty$, the band gap for both the cases of odd and even n polymers of this class will be the same and is expressed as

$$\Delta(G_3) = -2 + \left[\sqrt{(h+2)^2 + 4k^2} + \sqrt{(h-2)^2 + 4k^2}\right] \Big/ 2 \tag{22}$$

It is to note here that the eq 22 is exactly equal to that for the linear polymer expressed by eq 7 as was expected too.

For $h = 0$ and $k \neq 0$ two important classes of graphs may arise that are discussed in the ongoing sections.

Inversely Proportional Graphs (for $h = 0$ and $k \neq 0$). For $h = 0$, the graphs G_1, G_2, and G_3 are converted into the graphs of IG_n^L, IG_n^K, and IG_n^C respectively as shown in Figure 5. The expressions of eigenspectra and the band gaps for these graphs can be derived easily and are discussed below classwise.

Class I: IG_n^L: The eigenspectra of this graph can easily be shown in analytical form with the help of eq 3 as

$$\begin{aligned} \lambda(IG_n^L) = \cos[\pi j/(n+1)] \pm \sqrt{\cos^2[\pi j/(n+1)] + k^2}; \\ j = 1, 2, 3, \ldots, n \end{aligned} \tag{23}$$

The graph IG_n^L represents a class of graphs, which have inversely proportional pairs of eigenvalues that can be revealed from the expression of eigenspectra (eq 23) of IG_n^L. For any graph in this class, j-th eigenvalue is $\lambda_j = \cos[\pi j/(n+1)] + \sqrt{\cos^2[\pi j/(n+1)] + k^2}$ and $[(n+1) - j]$-th eigenvalue can be written using eq 23 as

$$\begin{aligned} &\lambda_{[(n+1)-j]} \\ &\quad = \cos[[(n+1) - j]\pi/(n+1)] \\ &\qquad + \sqrt{\cos^2[[(n+1) - j]\pi/(n+1)] + k^2} \end{aligned}$$

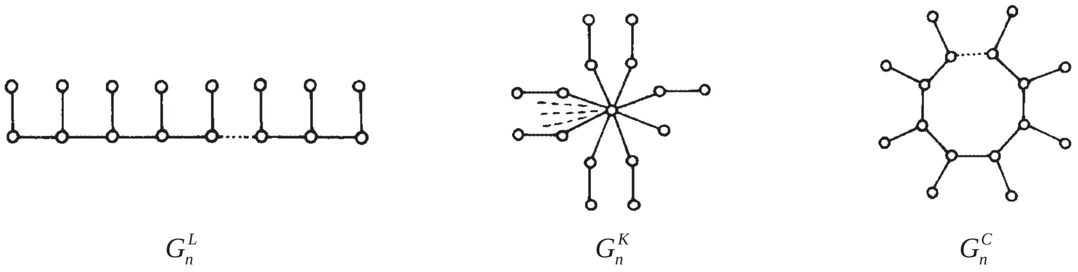

G_n^L G_n^K G_n^C

Figure 6. Graphs of G_n^L, G_n^K, and G_n^C.

$$\begin{aligned} &= \cos[\pi - \pi j/(n+1)] \\ &\quad + \sqrt{\cos^2[\pi - \pi j/(n+1)] + k^2} \\ &= -\cos[\pi j/(n+1)] + \sqrt{\cos^2[\pi j/(n+1)] + k^2} \end{aligned} \quad (24)$$

Now $\lambda_j \cdot \lambda_{[(n+1)-j]} = \cos^2[\pi j/(n+1)] + k^2 - \cos^2[\pi j/(n+1)] = k^2$. Therefore, $\lambda_j \cdot \lambda_{[(n+1)-j]} = k^2$ and hence the inversely proportionality relationship follows: From eq 6 the band gap for the molecules represented by this class of graphs can be expressed as

$$\begin{aligned} \Delta\lambda(IG_n^L) &= 2\Big[-\cos[\pi/(n+1)] + \sqrt{(\cos^2[\pi/(n+1)]) + k^2}\Big] \\ &= 2\lambda(IG_n^L)_{\mathrm{HOMO}} \end{aligned} \quad (25)$$

The band gap of infinite polymer of this class will be

$$\Delta(IG_n^L) = 2\Big[-1 + \sqrt{1+k^2}\Big] \quad (26)$$

which is not equals to zero for the above case. Thus the molecules represented by the graphs of this class should be non conductive.

Class II: IG_n^K: The eigenspectra of this graph, shown in Figure 5, is obtained by putting $h = 0$ directly in eq 10 as $\lambda(IG_n^K) = [\pm\sqrt{n-1} \pm \sqrt{n-1+4k^2}]/2$,

$$[\pm k, \pm k, \pm k, \pm k, \pm k \ldots \text{ up to } (n-2)\text{-th terms}] \quad (27)$$

It is easy to follow from eq 27 that all $(n-2)$ eigenvalues of magnitude $\pm k$ are in inversely proportional relationship with the proportionality constant, k^2. Now in the case of other eigenvalues expressed by eq 27: Let one eigenvalue (λ_1) be $\lambda_1 = [\sqrt{n-1} + \sqrt{n+4k^2-1}]/2$ and the other eigenvalue (λ_2) be $\lambda_2 = [-\sqrt{n-1} + \sqrt{n+4k^2-1}]/2$. So $\lambda_1\lambda_2 = k^2$. Thus, inversely proportional relationship among the eigenvalues of IG_n^K follows and the graphs are called inversely proportional graphs of class II.

The band gap for the graphs of this class should be expressed from eq 13

$$\Delta\lambda(IG_n^K) = -\sqrt{n-1} + \sqrt{n-1+4k^2} = 2\lambda(IG_n^K)_{\mathrm{HOMO}} \quad (28)$$

where $\lambda(IG_n^K)_{\mathrm{HOMO}}$ is the energy eigenvalue of the HOMO of IG_n^K. Thus it is found from eq 28 that the band gap for the molecules represented by this graph in the limit of $n \to \infty$ will be very high.

Class III: IG_n^C: The eigenvalue expression for this graph, shown in Figure 5, has been found to be in analytical form with the help of eq 16

$$\begin{aligned} \lambda(IG_n^C) &= \cos[2\pi j/n] \pm \sqrt{\cos^2[2\pi j/n] + k^2}; \\ & j = 0, 1, 2, \ldots, (n-1) \end{aligned} \quad (29)$$

The graphs in this class have inversely proportional pairs of eigenvalues that follow easily from eq 29. Let the j-th eigenvalue of IG_n^C be $\lambda_j = \cos[2\pi j/n] + \sqrt{\cos^2[2\pi j/n] + k^2}$ and $(n-j)$-th eigenvalue ($\lambda_{(n-j)}$) can be expressed using eq 29 as

$$\begin{aligned} \lambda_{(n-j)} &= \cos[2\pi(n-j)/n] \\ &\quad + \sqrt{\cos^2[2\pi(n-j)/n] + k^2} \\ &= -\cos[2\pi j/n] + \sqrt{\cos^2[2\pi j/n] + k^2}. \end{aligned} \quad (30)$$

Now $\lambda_j\lambda_{(n-j)} = k^2$ and hence the inversely proportionality relationship follows: The expressions of the band gap for molecules represented by the graphs of this class can be written using eq 21. For even n:

$$\Delta\lambda(IG_n^C) = 2\Big[-1 + \sqrt{1+k^2}\Big] = 2\lambda(IG_n^C)_{\mathrm{HOMO}} \quad (31a)$$

and for odd n:

$$\begin{aligned} \Delta\lambda(IG_n^C) &= \Big[-(1+\cos(\pi/n)) \\ &\quad + \sqrt{\cos^2(\pi/n) + k^2} + \sqrt{1+k^2}\Big] \\ &= 2\lambda(IG_n^C)_{\mathrm{HOMO}} \end{aligned} \quad (31b)$$

Thus for odd n the band gap of a molecule in this class depends on n, whereas for even n the band gap is independent of n. For the infinite cyclic polymer the band gap can be obtained with the limit $n \to \infty$. In the case of both odd and even n the band gaps for these cyclic polymers are the same and is equal to that for even n. From eq 31a it is clear that the band gap will not be zero and the corresponding molecules should be non conductive.

Reciprocal Graphs. In the case of $h = 0$ and $k = 1$, the graphs G_1, G_2, and G_3 represent three classes of reciprocal graphs e.g., G_n^L, G_n^K, and G_n^C respectively as shown in Figure 6. These graphs have reciprocal pairs of eigenvalues and recently have been found out.[26] The characteristic polynomial (CP) coefficients of these graphs have been determined by simple manipulation of Pascal's triangle.[27] Recently, CP coefficients of such graphs have been expressed directly in terms of the number of pendant vertices.[28] Topological indices[29] of such graphs e.g., Cardinalities, Wiener, and Hosoya indices have been studied more recently. Cardinalities of these graphs have subsequently been used to find out topological bond orders of the molecules represented by such graphs. It should be mentioned at this point that "comb-like" graphs (G_n^L) had been analyzed much earlier by Gutman et al.[30] in connection with the study of the effect of branching on molecular properties of acyclic polyenes. Very recently Dias[31] has presented new

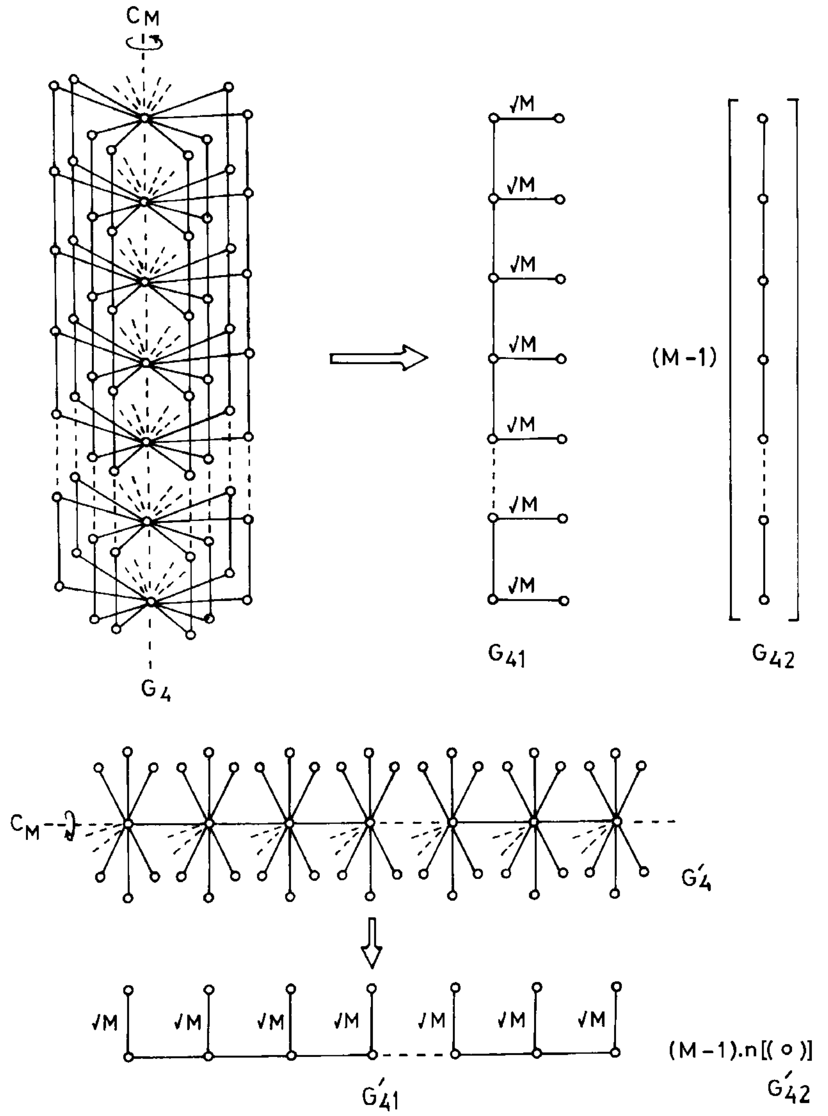


Figure 7. Graphs of G_4 and G'_4 along with their factorization schemes.

examples of reciprocal graphs while reviewing molecules corresponding to reciprocal graphs and discussed some essential features of cross conjugation with its importance in the design of conducting and ferromagnetic polymers. Klein and Misra[32] have studied minimally Kekulenoid π-networks and reactivity for acyclics and found that the inverses of the adjacency matrix of such minimally Kekulenoid graphs can be represented by the adjacency matrix of the Kekulenoid transform graphs. They have used two classes of reciprocal graphs in this context e.g., dendralenes and radialenes.

The eigenspectra of reciprocal graphs (G_n^L, G_n^K, and G_n^C) can easily be expressed using eqs 3, 10, and 16 respectively by putting $h = 0$ and $k = 1$. Similarly the expressions of the band gaps of these graphs can also be obtained with the use of eqs 6, 13, and 21 respectively. The band gap of the infinite polymers (G_n^L and G_n^C) from eqs 7 and 22 is found to be equal to 0.84842. So the dendralenes and radialenes are expected to be non-conductive.[30] The band gap for the molecules of infinite n corresponding to the reciprocal graph (G_n^K) can be obtained from eq 13 and found to be very high.

Eigenspectra of Some Complicated Graphs. The eigenspectra of some complicated graphs, such as G_4 and G'_4 as shown in Figure 7, G_5 shown in Figure 8, and G_6 shown in Figure 9 can be expressed in analytical forms with the help of the expression of eigenspectra of inversely proportional graphs that are obtained by putting $h = 0$ in the eigenspectra of graphs shown in Figure 1.

Graph G_4 contains M number of n-vertex linear chains. Each vertex of these linear chains is attached to one of n vertices lying along the M-fold symmetry axis as shown in Figure 7. Using the rotational symmetry factorization technique[6] the graph may be factorized into two types of graphs. One is G_{41} and other is G_{42} of $(M - 1)$ number; G_{41} is a graph of the type IG_n^L and G_{42} is a simple chain of n vertices. Graph G'_4 is a linear chain of n vertices each of which is joined to the number of pendant vertices (M). This graph can be factorized by considering a rotational symmetry[6] axis of M-fold that passes through the linear chain into G'_{41} and $(M - 1)n$, the number of isolated vertices (G'_{42}) of zero eigenvalue each. Schemes for the factorizations of graphs G_4

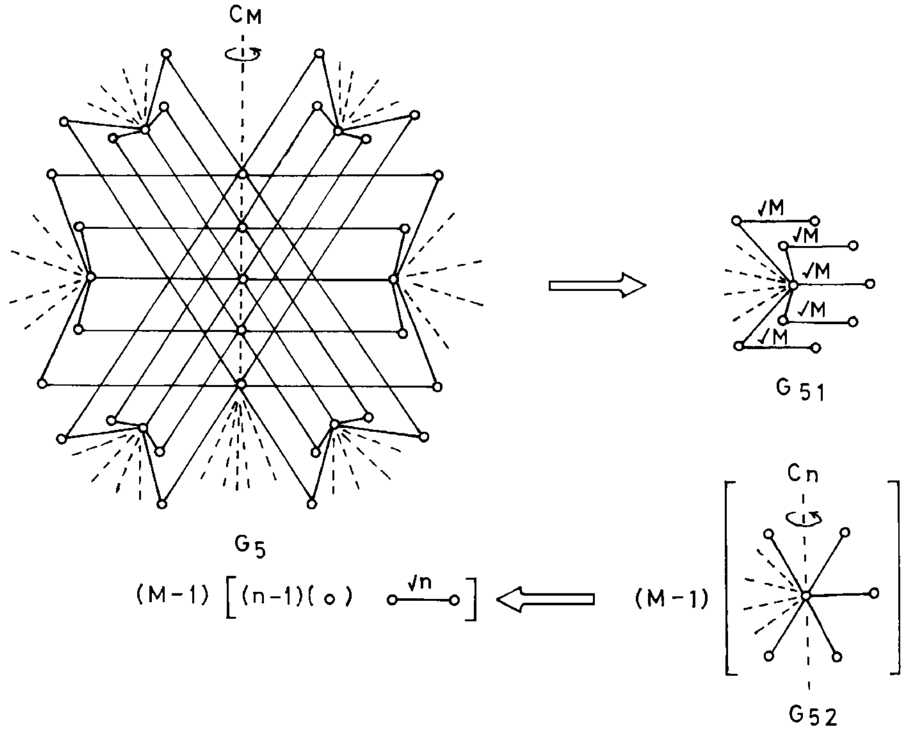


Figure 8. Graph of G_5 along with its factorization scheme.

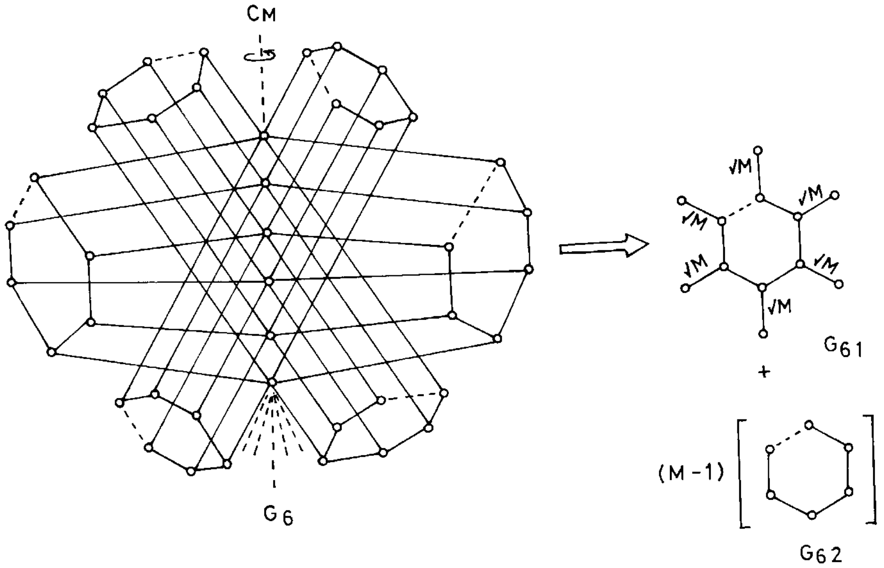


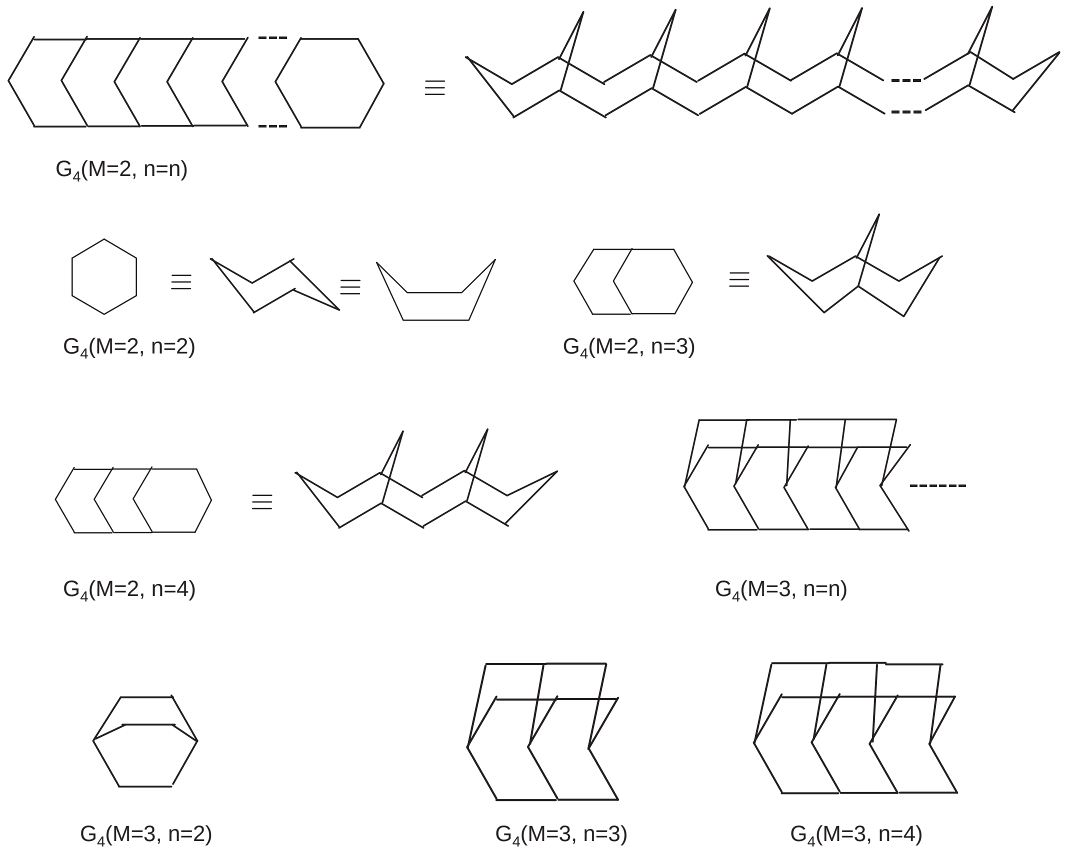
Figure 9. Graph of G_6 along with its factorization scheme.

and G'_4 are shown in Figure 7 and the respective eigenvalue expressions are given in Table 1. From the factorization scheme shown in Figure 7 it is evident that eigenspectra of the graph G_4 contains the eigenspectra of *n*-polyenes (G_{42}) (i.e., polyacetylene) and that of G_{41} (i.e., IG_n^L for $k = \sqrt{M}$), thus the latter graphs are subspectral[7] to the former graph. Similarly the graphs G'_{41} (i.e., IG_n^L for $k = \sqrt{M}$) and isolated vertices (G'_{42}) are subspectral[7] to G'_4. Both the graphs (G_4 and G'_4) may represent hypothetical molecules whose central vertices may be carbon atoms (for $M \leq 3$) or other higher valent atoms (for $M \geq 3$). The hypothetical infinite polymer corresponding to G_4 may be a conducting polymer since it contains the eigenspectra of infinite polyacetylenes.[20,24] The hypothetical molecules corresponding to G'_4 should be metallic, since it contains non-bonding molecular orbitals (NBMOs).[20,24]

The graph G_5, shown in Figure 8, is a star-like complicated graph in which *n*, the number of central vertices act as pendant vertices of *M* number of G_{52} (a graph with one central and $(n-1)$ peripheral vertices). A rotational axis of *M*-fold passing through the number of central vertices (*n*) can be considered to decompose[6] G_5 into G_{51} and G_{52}. The eigenvalue of G_{51} can be calculated using eq 16 and that of the graph G_{52} can be obtained by $(n-1)$-fold rotational symmetry passing

Table 1. Analytical Expressions of Eigenspectra of G_4, G_4', G_5, and G_6

Graph	Eigenvalue expression
G_4	$\cos[\pi j/(n+1)] \pm \sqrt{\cos^2[\pi j/(n+1)] + M}$; $j = 1, 2, 3, \ldots, n$ and $(M-1)$ fold of $\{2\cos[\pi j/(n+1)];\ j = 1, 2, 3, \ldots, n\}$
G_4'	$\cos[\pi j/(n+1)] \pm \sqrt{\cos^2[\pi j/(n+1)] + M}$; $j = 1, 2, 3, \ldots, n$ and $(M-1)n$ zeros.
G_5	$[\pm\sqrt{n-1} \pm \sqrt{n+4M-1}]/2$; $[\pm\sqrt{M}, \pm\sqrt{M}, \pm\sqrt{M}, \pm\sqrt{M}, \pm\sqrt{M} \ldots$ up to $(n-2)$-th terms]; $\pm\sqrt{n}$; $(M-1)(n-1)$ zeros.
G_6	$\cos[2\pi j/n] \pm \sqrt{\cos^2[2\pi j/n] + M}$; $j = 0, 1, 2, \ldots, (n-1)$ and $(M-1)$ fold of $\{2\cos[2\pi j/n];\ j = 0, 1, 2, \ldots, (n-1)\}$



G_4(M=2, n=n)

G_4(M=2, n=2)

G_4(M=2, n=3)

G_4(M=2, n=4)

G_4(M=3, n=n)

G_4(M=3, n=2)

G_4(M=3, n=3)

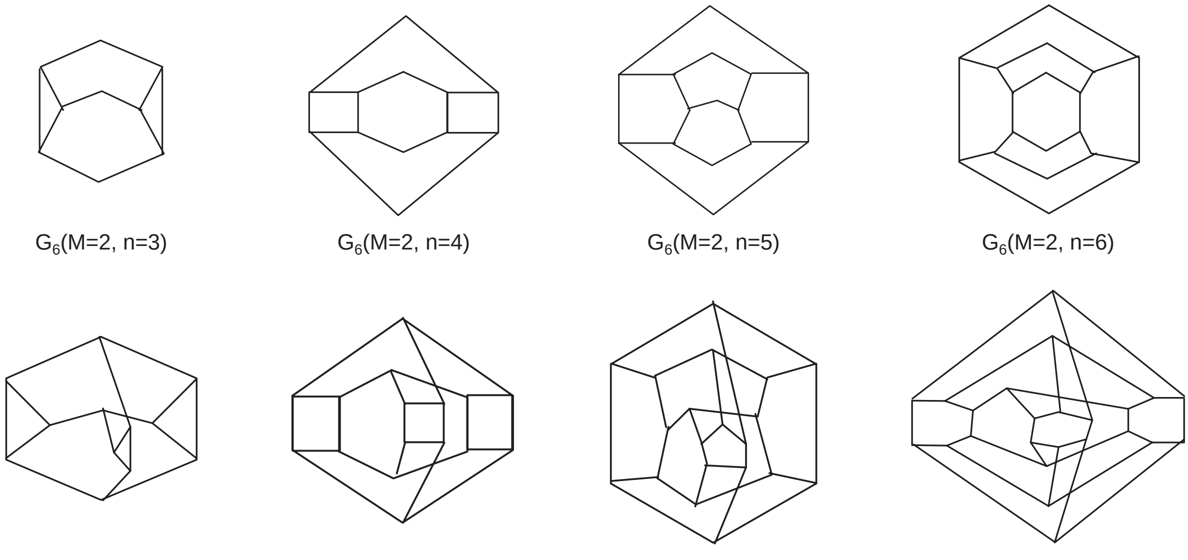
G_4(M=3, n=4)

Figure 10. A few hydrocarbons corresponding to the graph G_4.

through the central vertex of the star. The factorization is illustrated in Figure 8 and eigenvalue expression is given in Table 1. From the factorization scheme as well as from the expressions of eigenspectra of G_5 it is revealed that both the graphs, G_{51} (i.e., IG_n^K for $k = \sqrt{M}$) and G_{52}, are subspectral[7] to the original graph, G_5.

The expression of eigenspectra of IG_n^C can be used to obtain the expression of eigenspectra of other complicated graphs in analytical forms. For example, the graph G_6 is one such graph, shown in Figure 9, whose eigenvalue has to be calculated. The graph G_6 has the number of central vertices (n), which act as pendant vertices of the number of n-polygons (M) as shown in Figure 9. This graph can be decomposed into graph G_{61} and $(M-1)$, the number of n-polygons (G_{62}) with the help of M-fold rotational symmetry.[6] The axis of the rotation is assumed to pass through the central vertices of G_6. The scheme with illustration is shown in Figure 9 and the eigenvalue of G_6 is given in Table 1. On the basis of this scheme as well the eigenvalue expression the subspectral[7] relation between G_6 and the fragmented graphs G_{61} (i.e., IG_n^C for $k = \sqrt{M}$) and G_{62} is clear.

Graphs as shown in Figures 10 and 11 respectively have been obtained by assigning some specific values of M and n for the graphs G_4 and G_6. These graphs have vertex-degree ≤ 3 and thus they may represent of conjugated hydrocarbon molecules or radicals. A few of them are well known. For examples G_4 ($M = 2$, $n = 2$) is benzene. G_4 ($M = 2$, $n = n$) represents $(n-1)$-cyclic conjugated radical (for odd n) or molecules (for even n). G_4 ($M = 3$, $n = n$) represent bridged cyclic conjugated molecules or radicals. Similarly the graphs corresponding to G_6 are the molecules or radicals of fused ring systems. The eigenvalues of these systems have been calculated by putting the values of M and n in the respective analytical expressions given in Table 1 and are displayed in Table 2.



G_6(M=2, n=3) G_6(M=2, n=4) G_6(M=2, n=5) G_6(M=2, n=6)

G_6(M=3, n=3) G_6(M=3, n=4) G_6(M=3, n=5) G_6(M=3, n=6)

Figure 11. A few hydrocarbons corresponding to the graph G_6.

Table 2. Eigenvalues and Total π-Electron Energies of the Graphs G_4 ($M = 2$ and 3 and $n = 2$, 3, and 4) and G_6 ($M = 2$ and 3 and $n = 3$, 4, 5, and 6)

Graphs	Eigenvalues	π-Electron energy in β unit
G_4 ($M = 2$, $n = 2$)	2.0, 1.0, 1.0, −1.0, −1.0, −2.0	8.0
G_4 ($M = 2$, $n = 3$)	2.2882, 1.4142, 1.4142, 0.8740, 0.0, −0.8740, −1.4142, −1.4142, −2.2882	11.9812
G_4 ($M = 2$, $n = 4$)	2.4383, 1.7566, 1.6180, 1.1386, 0.8202, 0.6180, −0.6180, −0.8202, −1.1386, −1.6180, −1.7566, −2.4383	16.7794
G_4 ($M = 3$, $n = 2$)	2.3028, 1.3028, 1.0, 1.0, −1.0, −1.0, −1.3028, −2.3028	11.2112
G_4 ($M = 3$, $n = 3$)	2.5779, 1.7320, 1.4142, 1.4142, 1.1637, 0.0, 0.0, −1.1637, −1.4142, −1.4142, −1.7320, −2.5779	16.604
G_4 ($M = 3$, $n = 4$)	2.7207, 2.0684, 1.6180, 1.6180, 1.4504, 1.1027, 0.6180, 0.6180, −0.6180, −0.6180, −1.1027, −1.4504, −1.6180, −1.6180, −2.0684, −2.7207	23.6284
G_6 ($M = 2$, $n = 3$)	2.7320, 2.0, 1.0, 1.0, −0.7320, −1.0, −1.0, −2.0, −2.0	13.464
G_6 ($M = 2$, $n = 4$)	2.7320, 2.0, 1.4142, 1.4142, 0.7320, 0.0, 0.0, −1.4142, −1.4142, −0.7320, −2.0, −2.7320	16.5848
G_6 ($M = 2$, $n = 5$)	2.7320, 2.0, 1.7566, 1.7566, 0.8202, 0.8202, 0.6180, 0.6180, −0.7320, −1.1386, −1.1386, −1.6180, −1.6180, −2.4383, −2.4383	22.2434
G_6 ($M = 2$, $n = 6$)	2.7320, 2.0, 2.0, 2.0, 1.0, 1.0, 1.0, 1.0, 0.7320, −0.7320, −1.0, −1.0, −1.0, −1.0, −1.0, −2.0, −2.0, −2.0, −2.7320	26.928
G_6 ($M = 3$, $n = 3$)	3.0, 2.0, 2.0, 1.3028, 1.3028, −1.0, −1.0, −1.0, −1.0, −1.0, −2.3028, −2.3028	19.2112
G_6 ($M = 3$, $n = 4$)	3.0, 2.0, 2.0, 1.7320, 1.7320, 1.0, 0.0, 0.0, 0.0, 0.0, −1.0, −1.7320, −1.7320, −2.0, −2.0, −3.0	22.928
G_6 ($M = 3$, $n = 5$)	3.0, 2.0684, 2.0684, 2.0, 2.0, 1.1027, 1.1027, 0.6180, 0.6180, 0.6180, 0.6180, −1.0, −1.4504, −1.4504, −1.6180, −1.6180, −1.6180, −1.6180, −2.7207, −2.7207	31.6286
G_6 ($M = 3$, $n = 6$)	3.0, 2.3028, 2.3028, 2.0, 2.0, 1.3028, 1.3028, 1.0, 1.0, 1.0, 1.0, 1.0, −1.0, −1.0, −1.0, −1.0, −1.0, −1.3028, −1.3028, −2.0, −2.0, −2.3028, −2.3028, −3.0	38.4224

Total π-electron energy, which is a useful parameter[3] to study physicochemical properties of conjugated systems, has been calculated for such graphs from their respective eigenvalues and is shown in Table 2.

Conclusion

The eigenspectra of G_1, G_2, and G_3 have been obtained in analytical forms (eqs 3, 10, and 16) that are used to find the band gaps of the corresponding graphs. These expressions are utilized to find the eigenspectra of (i) inversely proportional graphs, (ii) reciprocal graphs, and (iii) other complicated graphs of higher symmetry. The graphs (G_1, G_2, and G_3 as well as IG_n^L, IG_n^K, and IG_n^C) discussed here represent heteroconjugated systems. Each pendant vertex of these graphs is occupied by heteroatoms (O, S, NR, etc.). The molecules corresponding to the graphs of class I (G_1) are heteroanologous polyvinylidene compounds and those of type III are heteroanologous cyclic polyvinylidene compounds. Heteroanologous polyvinylidene[25] compounds were conjectured to be high conducting materials,[33] although the band gaps corresponding to these molecules are non-zero. The conducting properties exhibited by these molecules may be due to the solitonic excitations[21,24] in the presence of lone pair electrons on the heteroatoms (O, S, or NR). Reciprocal graphs are not all hypothetical; some of them have been synthesized.[34,35]

Graphs G_4, G_6 (for $M \leq 3$), and G_4' (for $M \leq 2$) represent conjugated hydrocarbon molecules. The eigenspectra of such molecules can easily be obtained by putting the values of M and n in the corresponding equations given in Table 1. The values of band gaps of these graphs can be calculated from the knowledge of their respective eigenspectra.

Graphs G_4 and G_6 may also represent hypothetical (complex) molecules whose central vertices (through which rotational axis passes) are higher valent atoms (for $M \geq 3$). Similarly G_5 may represent a hypothetical molecule whose central vertices are either carbon or higher valent atoms (for $n > 3$).

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References

1 L. Glass, *J. Chem. Phys.* **1975**, *63*, 1325.

2 R. B. King, *Theor. Chim. Acta* **1980**, *56*, 269.

3 I. Gutman, O. E. Polansky, *Mathematical Concepts in Organic Chemistry*, Springer-Verlag, Berlin, **1986**; *Theor. Chim. Acta* **1981**, *60*, 203.

4 K. Balasubramanian, *J. Comput. Chem.* **1985**, *6*, 656.

5 B. J. McClelland, *J. Chem. Soc., Faraday Trans. 2* **1974**, *70*, 1453; **1982**, *78*, 911; *Mol. Phys.* **1982**, *45*, 189.

6 S. S. D'Amato, *Mol. Phys.* **1979**, *37*, 1363; *Theor. Chim. Acta* **1979**, *53*, 319.

7 S. S. D'Amato, B. M. Gimarc, N. Trinajstić, *Croat. Chem. Acta* **1979**, *54*, 1.

8 R. A. Davidson, *Theor. Chim. Acta* **1981**, *58*, 193.

9 M. Shen, *Int. J. Quantum Chem.* **1990**, *38*, 551.

10 J. R. Dias, *Molecular Orbital Calculations Using Chemical Graph Theory*, Springer-Verlag, New York, **1993**.

11 J. R. Dias, *THEOCHEM* **1988**, *165*, 125; **1997**, *417*, 49; *Mol. Phys.* **1995**, *85*, 1043; **1996**, *88*, 407.

12 J. R. Dias, *J. Chem. Educ.* **1989**, *66*, 1012.

13 H. Hosoya, Y. Tsukano, *Fullerene Sci. Technol.* **1994**, *2*, 381.

14 H. Hosoya, T. Tsukano, K. Nakada, S. Iwata, U. Nagashima, *Croat. Chem. Acta* **2004**, *77*, 89.

15 C. A. Coulson, G. S. Rushbrooke, *Proc. Cambridge Philos. Soc.* **1940**, *36*, 193.

16 A. K. Mukherjee, D. K. Das, *Int. J. Quantum Chem.* **1993**, *46*, 519.

17 B. Mandal, *Int. J. Quantum Chem.* **2005**, *103*, 140; *THEOCHEM* **2005**, *757*, 99.

18 I. Gutman, *Z. Naturforsch., A: Phys. Sci.* **1981**, *36a*, 1112.

19 I. Gutman, *Z. Naturforsch., A: Phys. Sci.* **1983**, *39a*, 152.

20 H. Hosoya, H. Kumazaki, K. Chida, M. Ohuchi, Y.-D. Gao, *Pure Appl. Chem.* **1990**, *62*, 445.

21 W. P. Su, J. R. Schrieffer, A. J. Heeger, *Phys. Rev. Lett.* **1979**, *42*, 1698; *Phys. Rev. B* **1980**, *22*, 2099.

22 S. Kivelson, O. L. Chapman, *Phys. Rev. B* **1983**, *28*, 7236.

23 M.-H. Whangbo, *Acc. Chem. Res.* **1983**, *16*, 95.

24 L. M. Tolbert, *Acc. Chem. Res.* **1992**, *25*, 561.

25 I. Gutman, H. Hartmann, *Bull. Soc. Chim. Beograd* **1983**, *48*, 127.

26 J. Sarkar, *Mol. Phys.* **1997**, *90*, 903.

27 B. Mandal, K. Datta, A. K. Mukherjee, M. Banerjee, *Mol. Phys.* **1999**, *96*, 1609.

28 B. Mandal, M. Banerjee, A. K. Mukherjee, *Int. J. Quantum Chem.* **2005**, *101*, 119.

29 B. Mandal, M. Banerjee, A. K. Mukherjee, *Int. J. Quantum. Chem.* **2004**, *99*, 119; *Mol. Phys.* **2005**, *103*, 2665.

30 I. Gutman, B. Ruščić, N. Trinajstić, C. F. Wilcox, Jr., *J. Chem. Phys.* **1975**, *62*, 3399.

31 J. R. Dias, *Croat. Chem. Acta* **2004**, *77*, 325.

32 D. J. Klein, A. Misra, *Croat. Chem. Acta* **2004**, *77*, 179.

33 G. Wegner, *Angew. Chem.* **1981**, *93*, 352; J. H. Perlstein, *Angew. Chem.* **1977**, *89*, 534.

34 G. W. Griffin, L. I. Peterson, *J. Am. Chem. Soc.* **1962**, *84*, 3398.

35 H. Hopf, G. Mass, *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 931.