CHAPTER-3

Two new graph-theoretical methods for generation of eigenvectors of chemical graphs.

3.1. Introduction: Although graph theory has developed very significantly in the last two decades for various purposes, graph-theoretical methods for generation of eigenvectors of chemical graphs are few in number. Expressions for eigenvectors in closed form for some limited class of compounds are known since the time of Hückel[1,2]; but in recert years only one paper, that of Kassman[3], has appeared which deals with gereration of eigenvectors of general chemical graphs. This method utilises Chebyshev polynomials and expresses the eigenvector components in terms of eigenvalues.
The object of the present investigation is to find new graph-theoretical methods for expressing eigenvectors as polynomials in eigenvalues. Two methods have been reported in this chapter. Method (A) invloves the use of Ulam's subgraphs which came into prominence with the famous Ulam's conjecture[4], one of the unresolved problems in mathematics. Such subgraphs have been utilised by Randic[5] for the generation of CP of graphs but they have not yet been used for construction of eigenvectors. Method (B) is based on a cofactor approach. In both the methods eigenvector components have been obtained as polynomials in terms of eigenvalues.

The organisation of the chapter is as follows. In Section 3.2 the principle of method (A) has been outlined; in Section 3.3 the method has been illustrated; in Section 3.4 two important results about degenerate eigenvalues have been proved and illustrated. In Sections 3.5 & 3.6, two important graph-spectral properties of complete graphs (K_n) and annulenes (C_n) which are consequences of the results derived in Section 3.4 have been proved. In Section 3.7 the principle of method (B) has been explained and in Section 3.8 method (B) has been illustrated.

3.2. Method(A): An Ulam subgraph of a graph G has been defined in Chapter 2. If v_1, v_2, v_3, ..., v_n are the vertices of G, we shall denote the collection of Ulam subgraphs of G by $\{(G-v_i)\}$, i = 1 to n. Let $x_1, x_2, \ldots, x_n$, be the eigenvalues of G. To begin with, we assume that all the eigenvalues are distinct. If we arbitrarily attach a self-loop of weight h to the r-th vertex and form a graph G', then[6]

$$P(G'; x) = P(G; x) - hP(G - v_r; x) \qquad \ldots (3.1)$$

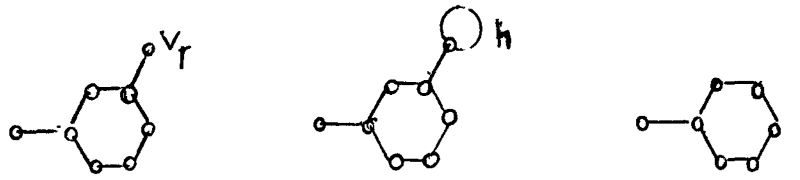
where $G - v_r$ is an Ulam subgraph of G, and the P's denote CP's of the graphs in parentheses (Fig. 3.1).

The secular determinant $\Delta(G')$ of G' can be expanded as

$$\Delta(G') = \begin{vmatrix} a_{11}-x & a_{12} & \cdots & a_{1r} & \cdots & a_{1n} \\ a_{21} & a_{22}-x & \cdots & a_{2r} & \cdots & a_{2n} \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ a_{r1} & a_{r2} & \cdots & a_{rr}-x & \cdots & a_{rn} \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ a_{n1} & a_{n2} & \cdots & \cdots & \cdots & a_{nn}-x \end{vmatrix}$$

$$= \Delta(G) - h[\delta\Delta(G)/\delta h]$$

$$= \Delta(G) - h[\delta(\Delta(G))/\delta x].[\delta x/\delta h]. \qquad \ldots. (3.2)$$



G G' $G-v_r$

Fig.3.1 A graph G, its derived graph G' and the rth Ulam subgraph $G-v_r$.

Thus

$$P(G';x) = P(G;x) - hP'(G;x)(\delta x/\delta h) \qquad \ldots. (3.3)$$

where $P'(G;x)$ is the first derivative of the CP of G. Comparing eqns.(3.1) & (3.3) we find

$$P(G-v_r;x) = P'(G;x)(\delta x/\delta h)$$

and puting $x=x_j$, the j-th eigenvalue,

$$P(G-v_r;x_j) = P'(G;x_j)C_{rj}^2 \qquad \ldots. (3.4)$$

where, by Coulson-Longuet-Higgins[7] perturbation technique,

$$(\delta x_j/\delta h) = C^2_{rj} \qquad \ldots. (3.5)$$

Here C_{rj} is the eigenvector coefficient of the r-th vertex corresponding to the j-th eigenvalue. Writing the derivative $P'(G;x)$ as the sum of the CP's of all the Ulam subgraphs[5,8] of G, we obtain from (3.4) the following working formula:

$$C^2_{rj} = [P(G-v_r;x_j)]/[P'(G;x_j)] = [P(G-v_r;x_j)]/[\sum_{r=1}^{n} P(G-v_r;x_j)] \quad \ldots(3.6)$$

The signs of C_{rj} can be ascertained by examining the secular equations as we show in the following section.

3.3. Illustrations of Method (A)

(i) Butadiene : The graph G and its Ulam subgraphs for this system are shown in fig.3.2a, and their respective CP's are,

$$P(G;x) = x^4 - 3x^2 + 1, \quad P(G-v_1;x) = x^3 - 2x = P(G-v_4;x),$$
$$P(G-v_2;x) = x^3 - x = P(G-v_3;x).$$

Eigenvalues of G are ± 0.618034, ± 1.618034. We denote these eigenvalues by x_1, x_2, x_3 and x_4 such that $x_1>x_2>x_3>x_4$. Then using eqn.(3.6) we obtain,

$$|C_{11}| = |C_{41}| = 0.3717480, \quad |C_{21}| = |C_{31}| = 0.6015009,$$
$$|C_{12}| = |C_{42}| = 0.6015009, \quad |C_{22}| = |C_{32}| = 0.3717480,$$
$$|C_{13}| = |C_{43}| = 0.6015009, \quad |C_{23}| = |C_{33}| = 0.3717480,$$
$$|C_{14}| = |C_{44}| = 0.3717480, \quad |C_{24}| = |C_{34}| = 0.6015009.$$

(a)

(b)

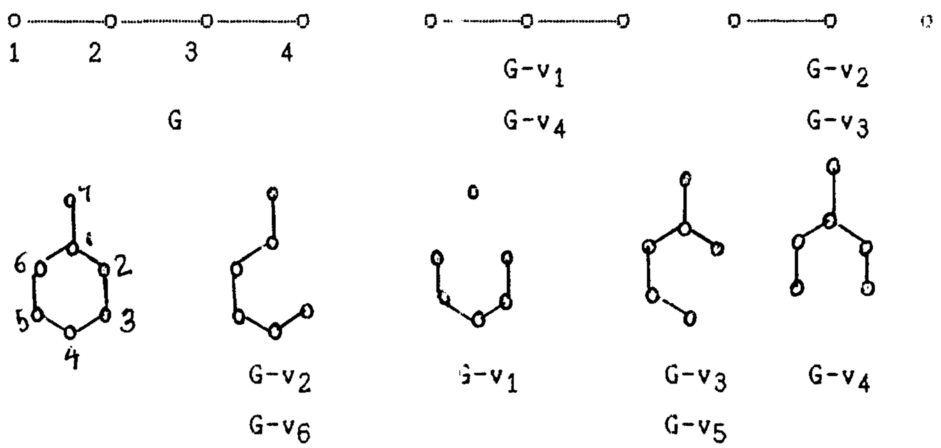


Fig.3.2 (a) Graph of butadiene and its Ulam subgraphs.
(b) Graph of benzyl radical and its Ulam subgraphs.

For assigning proper signs to these coeficients we note that

$$\det(A-xI) = \begin{vmatrix} -x & 1 & 0 & 0 \\ 1 & -x & 1 & 0 \\ 0 & 1 & -x & 1 \\ 0 & 0 & 1 & -x \end{vmatrix} = 0$$

which yields the secular equations,

$$-C_{1j}x_j + C_{2j} = 0 \qquad \text{.... (3.7a)}$$
$$C_{1j} - C_{2j}x_j + C_{3j} = 0 \qquad \text{.... (3.7b)}$$
$$C_{2j} - C_{3j}x_j + C_{4j} = 0 \qquad \text{.... (3.7c)}$$
$$C_{3j} - C_{4j}x_j = 0 \qquad \text{.... (3.7d)}$$

Equation (3.7a) shows that C_{1j} and C_{2j} are of same or opposite signs according to whether x_j is +ve or -ve. Similar is the sign relationship between C_{3j} and

C_{4j} as (3.7d) shows. We can determine all the eigenvector coefficients with their proper signs. These values have been found to be in agreement with those obtained from the general formula[2] for linear chains(L_n),

$$C_{rj} = \sqrt{[2/(n+1)]}\ \sin[rj\pi/(n+1)] \qquad .... (3.8).$$

(ii) <u>Benzyl radical</u> : The necessary graph and Ulam subgraphs for this system are shown in fig.2b. For this system,

$$\begin{aligned}
&P(G;x) = x^7 - 7x^5 + 13x^3 - 7x,\\
&P(G-v_1;x) = x^6 - 4x^4 + 3x^2,\\
&P(G-v_2;x) = x^6 - 5x^4 + 6x^2 - 1 = P(G-v_6;x), \qquad .... (3.9)\\
&P(G-v_3;x) = x^6 - 5x^4 + 5x^2 = P(G-v_5;x),\\
&P(G-v_4;x) = x^6 - 5x^4 + 5x^2 - 1.
\end{aligned}$$

The eigenvalues of G are 0, ±1, ±1.25928, ±2.101003, which as before, are denoted by x_i(i = 1 to 7) such that $x_1 > x_2 > .... > x_7$. Now using eqn. (3.6) the magnitudes of the eigenvector coefficients can be found. For their signs we consider the secular determinant,

$$\det(\mathbf{A}-x\mathbf{I}) = \begin{vmatrix} -x & 1 & 0 & 0 & 0 & 1 & 1 \\ 1 & -x & 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & -x & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & -x & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & -x & 1 & 0 \\ 1 & 0 & 0 & 0 & 1 & -x & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & -x \end{vmatrix} = 0$$

which yields

$$- C_{1j}x_j + C_{2j} + C_{6j} + C_{7j} = 0 \qquad .... (3.10a)$$
$$C_{1j} - C_{2j}x_j + C_{3j} = 0 \qquad .... (3.10b)$$
$$C_{2j} - C_{3j}x_j + C_{4j} = 0 \qquad .... (3.10c)$$
$$C_{3j} - C_{4j}x_j + C_{5j} = 0 \qquad .... (3.10d)$$
$$C_{4j} - C_{5j}x_j + C_{6j} = 0 \qquad .... (3.10e)$$
$$C_{1j} + C_{5j} - C_{6j}x_j = 0 \qquad .... (3.10f)$$
$$C_{1j} - C_{7j}x_j = 0 \qquad .... (3.10g)$$

We demonstrate here the determination of eigenvector corresponding to $x_3 = 1$. Eqn.(3.6) yields

$$\begin{aligned}
&|C_{13}| = |C_{43}| = |C_{73}| = 0,\\
&|C_{23}| = |C_{33}| = |C_{53}| = |C_{63}| = 0.5 \qquad .... (3.11)
\end{aligned}$$

Eqn.(3.10f) gives $C_{53} = C_{63}$;(3.10c) gives $C_{23} = C_{33}$; (3.10d) gives $C_{33} = -C_{53}$. Thus if we arbitrarily assign a + ve sign to C_{23}, we get the proper signs of all the remaining non-zero eigenvector coefficients.

$$C_{13} = 0,\ C_{23} = +0.5,\ C_{33} = +0.5,\ C_{43} = 0,$$
$$C_{53} = -0.5,\ C_{63} = -0.5,\ C_{73} = 0 \qquad \text{.... (3.12)}$$

3.4. Cases of degenerate eigenvalues: For degenerate eigenvalues we can prove the following two results:

(I) If x_j is a degenerate eigenvalue of G, then it is a root of all Ulam subgraphs of G. *

(II) If the factor $x-x_j$ occurs (p-1) times in the highest common factor (HCF) of $P(G-v_i;x)$ for all i, then x_j is an eigenvalue of G with p-fold degeneracy.

Proof of (I) : If x_j is a degenerate eigenvalue of G then $P'(G;x_j) = 0$ and since eigenvectors of G exist for all its eigenvalues, eqn.(3.6) gives,

$$P(G-x_i;x_j) = 0 \text{ for all i.} \qquad \text{.... (3.13)}$$

Thus x_j is a root of all Ulam subgraphs of G.

Proof of (II): Let x_j be an eigenvalue of G with p-fold degeneracy. Then,

$$P(G;x) = (x-x_j)^p f(x) \qquad \text{.... (3.14)}$$

where f(x) is a function of degree n-p,n being the number of vertices in G. Differentiation of eqn.(3.14) gives

$$P'(G;x) = (x-x_j)^{p-1}\, \phi(x) \qquad \text{.... (3.15)}$$

i.e. $P(G-v_1;x) + P(G-v_2;x) + \ldots + P(G-v_n;x) = (x-x_j)^{p-1}\phi(x)$ .... (3.16)

which shows that $(x-x_j)^{p-1}$ is the HCF of each term on the left hand side of eqn.(3.15). Eqn.(3.16) thus shows that every Ulam subgraph of G has a factor $(x-x_j)^{p-1}$ in its CP when x_j is some p-fold degenerate eigenvalue of G. Conversely, let $(x-x_j)^{p-1}$ be the HCF of $P(G-v_i;x)$, i= 1 to r. Then

$$P'(G;x) = \sum_{i=1}^{n} P(G-v_i;x) = (x-x_j)^{p-1}F_{(r)}(x) \qquad \text{.... (3.17)}$$

where $F_{(r)}(x)$ is a function of degree r such that r+p = n. Integrating (3.17) by parts, one finally obtains

$$P(G;x) = [(x-x_j)^p F_{(r)}(x)/p] - [(x-x_j)^{p+1}F_{(r-1)}(x)/(p+1)] - \ldots \ldots$$
$$\ldots - (x-x_j)^{p+r}F_{(o)}(x)/(p+r) + \text{const.}$$

The constant of integration is zero since $P(G;x_j) = 0$. Thus ,

$$P(G;x) = (x-x_j)^p f(x) \qquad \text{.... (3.18)}$$

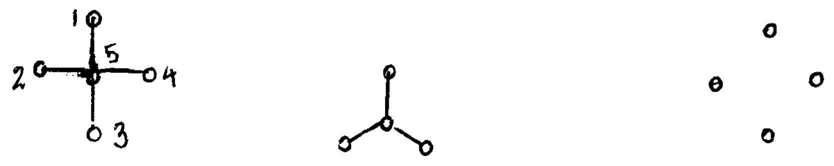
This completes the proof of (II).

* Dias in J. Mol. Struct. (Theochem), 165 (1988) 125, has shown that this forms the basis for a compact compendium of select eigenvalues of well over 2000 molecules.

Illustration of result (I) : It is well known that benzene (having a C_6 graph) has two degenerate roots +1 and -1, each with two-fold degeneracy. Every Ulam subgraph of C_6 is L_5, a linear chain with 5 vertices.

$P(L_5;x) = x^5 - 4x^3 + 3x$, for which +1 and -1 are roots.

Illustration of result (II) : Let us consider a tetrahedral graph with vertex enumeration as shown in fig.3, where its Ulam subgraphs are also shown. Here, $P(G;x) = x^3(x^2-4)$; $P(G-v_i;x) = x^2(x-3)$ for i=1,2,3,4 and $P(G-v_5;x) = x^4$.



G $\qquad$ $G-v_i$, i=1,2,3,4. $\qquad$ $G-v_5$

Fig.3.3. Graph of a tetrahedron and its Ulam subgraphs.

Thus the HCF of the CP's of the Ulam subgraphs is $(x-0)^2$ and we see that 0 is a root of G with 3-fold multiplicity.

3.5. A graph spectral property of annulenes : n-Annulenes have cycles (C_n) as their graph. Each Ulam subgraph of C_n is a linear chain L_{n-1}. We now show that L_{n-1} cannot have multiple roots. The eigenvalues of L_{n-1} are of the form

$$x_j = 2\cos(j\pi/n),\ j = 1 \text{ to } n-1. \qquad \ldots.(3.19)$$

So, if L_{n-1} has a degenerate root, one must have at least

$$(j\pi/n) = 2\pi - (j\pi/n),$$

which yields j = n and thus j exceeds the range specified in eqn.(3.19). So every root in each of the Ulam subgraphs of C_n occurs only once and so by (II) C_n cannot show more than two-fold degeneracy. This result has been obtained by many workers in a variety of ways[6,9,10]. The present proof is only an addition to them, but it is obviously very simple.

3.6. A graph spectral property of complete graphs (K_n): K_n is a graph with n vertices such that all possible pairs of vertices are connected. It is easy to recognise that every Ulam subgraph of K_n is a complete graph K_{n-1}. Now, K_3 has the CP,

$$P(K_3;x) = (x+1)^2(x-2).$$

So -1 is a root of K_3 with two-fold multiplicity. Hence according to (II), -1 is a root of K_4 with 3-fold multiplicity, and inductively, -1 is a root of K_n with (n-1)-fold multiplicity. This is a well known result in graph-spectral theory[8], proved here in a very simple way.

3.7. Method (B): In GT, the CP of a graph G is defined as

$$P(G;x) = (-1)^n \det(\mathbf{A}-x\mathbf{I}) = (-1)^n \Delta(x) \qquad \ldots. (3.20)$$

where **A** is the adjacency matrix of G, **I** is the unit matrix of the size of **A** and {x} is the set of eigenvalues obtained by equating P(G;x) to zero. In HMO formalism, this x is the energy of a π-molecular orbital with α (the coulomb integral of sp^2 carbon) equal to zero and β (the resonance integral between two adjacent sp^2 carbon atoms) the unit of energy.

If $(a_{i1}, a_{i2}, \ldots\ldots, a_{in})$ is the i-th row of $\Delta(x)$, then the eigenvectors C_j, j=1 to n, can be shown[11] to be given by

$$C_j = A_{ij}/\surd(\sum_{j=1}^{n} A_{ij}^2) \qquad \ldots. (3.21)$$

where A_{ij} is the cofactor of a_{ij} in $\Delta(x)$.

For A_{ii} the i-th row and the i-th column are struck off. The equivalent subgraph is thus one obtained by deleting the i-th vertex and all edges incident to it from G. The CP of the subgraph, Q(x), is thus $(-1)^{n-1}$ times the minor of a_{ii}. So

$$A_{ii} = (-1)^{i+i} \, (-1)^{n-1} \, Q(x) \qquad \ldots. (3.22)$$

For A_{ij} we first notice which elements in the i-th row are non-zero. If there are a number of self-avoiding paths from the i-th to the j-th vertex, say $L_1(i \to u \to s \to j)$, $L_2(i \to u' \to s' \to j)$ etc., then the elements $a_{iu}, a_{iu'}$ etc. are non-zero along the i-th row. If z is a vertex attached to i but not belonging to any path from i to j, then elements of the type a_{iz} are also non-zero in the i-th row. When, for determination of A_{ij}, the i-th row and the j-th column are struck off, the elements $a_{iu}, a_{iu'}$ are struck off together with elements of the type a_{iz}. But in the residual minor M the transpose elements $a_{ui}, a_{u'i}$, a_{zi} etc. still persist and are non-zero since $\Delta(x)$ is symmetric. The contribution of a_{ui} and $a_{u'i}$ can be obtained by tracing the paths L_1 and L_2 seperately. We first consider L_1. We can expand M along the column occupied by a_{ui} but in M this element now occupies the $(u-n_r)$-th row and $(i-n_c)$-th column and so the first factor in the minor M of a_{ij} for the path L_1 is

$$f_{i \to u} = (-1)^{u-n_r+i-n_c} . w_{(i,u)} \qquad \ldots. (3.23)$$

where n_r = number of rows above the u-th row of Δ which are already struck off, n_c = number of columns in the left of the i-th column of Δ which are already struck off, and $w_{(i,u)}$ = weight of the edge (i,u). Now, in the minor M there will be a column having $a_{uz} = a_{sz} = a_{jz} = 0$ since the vertex z does not belong to L_1 and is thus not connected to u,s and j ; so the contribution of a_{zi} to M will be zero. We now strike off the u-th row and the i-th column of Δ and get a minor M' reduced in size. Since in L_1 the vertex s is linked to u, we find , by the same type of argument as above, that only the term a_{su} of Δ makes a non-zero contribution to M' for the path L_1. But after striking off the i-th row and j-th column first and then the u-th row and s-th column of Δ, the element a_{su} occupies in M' the $(s-n'_r)$th and the $(u-n'_c)$th column where n'_r and n'_c have similar meanings as before. Thus the second factor of A_{ij} resulting from the path L_1 is,

$$f_{u\rightarrow s} = (-1)^{s-n'_r + u-n'_c} . w(u,s) \qquad .... (3.24)$$

On striking off the s-th row and u-th column of Δ, the element a_{sj} is cut off but a_{js} remains in the residual minor M". Position of a_{js} in M" is the intersection of the $(j-n''_r)$th row and $(s-n''_c)$th column, and so the third factor in A_{ij} for the path L_1 is

$$f_{u\rightarrow s} = (-1)^{j-n''_r + s-n''_c} . w(s,j) \qquad .... (3.25)$$

The successive striking off of rows and columns indicated above means deletion of the vertices i,u,s and j and all edges incident to them,resulting in the subgraph $G-L_1$. Hence the path L_1 contributes to the cofactor A_{ij}, a term

$$A_{ij}(L_1) = (-1)^{i+j} f_{i\rightarrow u}\, f_{u\rightarrow s}\, f_{s\rightarrow j} (-1)^v Q(G-L_1;x) \qquad .... (3.26)$$

where v is the number of vertices in $G-L_1$.

The same procedure is to be followed for the path L_2 and contributions from all such paths are to be added algebraically, i.e.,

$$A_{ij} = \sum_r A_{ij}(L_r) \qquad .... (3.27)$$

where r runs over all the self-avoiding paths from i to j. The CP, $Q(G-L_r;x)$, can be obtained by Aihara's[12] method for both weighted and unweighted subgraphs, with the additional requirement that

$$Q(\emptyset) = 1 \qquad .... (3.28)$$

where $\emptyset$ denotes null subgraph occuring at the time of computing the cofactors.(It is to be recalled that a null set of Sachs graphs contributes nothing to the corresponding coefficients in the CP of the whole graph). Using the eigenvalues (x) in eqns.(3.22) and (3.27) we get the cofactors and finally from (3.21) the eigenvectors are determined.

3.8. Illustrations of method (B): Although the above development seems a little belaboured, the actual procedure is quick and easy to apply. we illustrate the method for the graphs G_1 to G_6 (fig3.4) of which G_4 and G_5 will be required in our subsequent application of the method to charge-transfer complexes (chapter 7). The eigenvector polynomials obviously depend upon the starting vertex i (i.e. the row along which the cofactors are determined) and we have found that selecting the vertex of the lowest degree is convenient. If along some row all the C_j's are found to be 0, then some other row must be tried.

For the cofactor polynomials of G_1, we choose the 7-th row as this vertex is one of those with the lowest degree.

$$A_{77} = (-1)^{7+7}(-1)^{6}\, Q(G_1) = x^6 - 7x^4 + 10x^2 - 2 \qquad \text{.... (3.29)}$$

where G is the subgraph obtained by deleting the vertex 7 and the edge 4-7 from G_1.

From the vertex 7 to 1, there is one path, $7 \rightarrow 4 \rightarrow 3 \rightarrow 1$. So

$$A_{71} = (-1)^{7+1} f_{7\rightarrow 4}\, f_{4\rightarrow 3}\, f_{3\rightarrow 1} (-1)^{3}\, Q(\text{o}5,\ 2\text{o}\!-\!\!-\!\text{o}6),$$

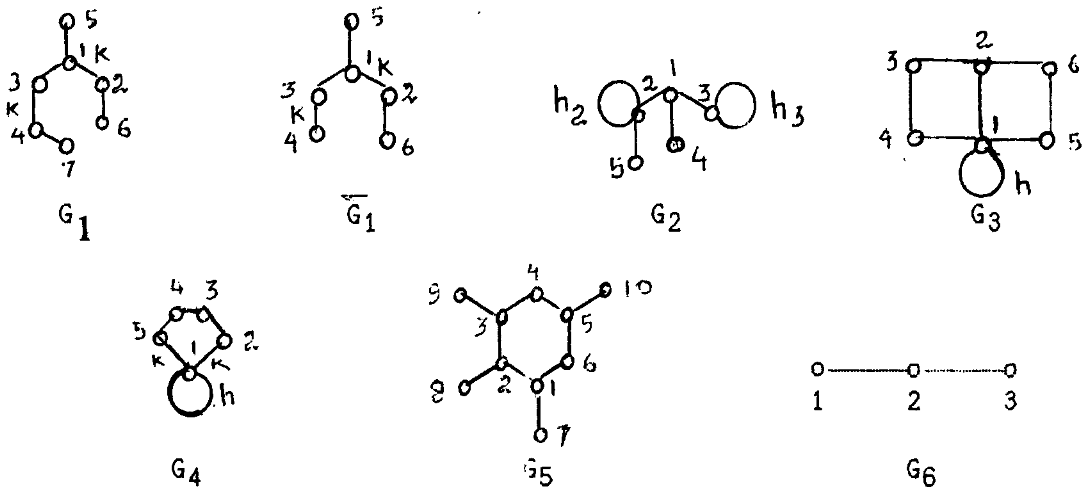


Fig.3.4. Some graphs treated by method (B)

where the figures in parentheses after Q mean that required subgraph consists of the isolated vertex 5 and the connected vertices 2 and 6. The translational factors are obtained by the following block diagrams, B_1, B_2 and B_3 which are to be drawn and read consecutively. The horizontal and the vertical lines intersecting at an encircled point correspond to the translation considered and other lines correspond to row and columns deleted previously.

Three blocks are drawn merely for the sake of clarity. With a little practice one can easily obtain the factors by a single diagram, as we have illustrated for G_3. Thus,

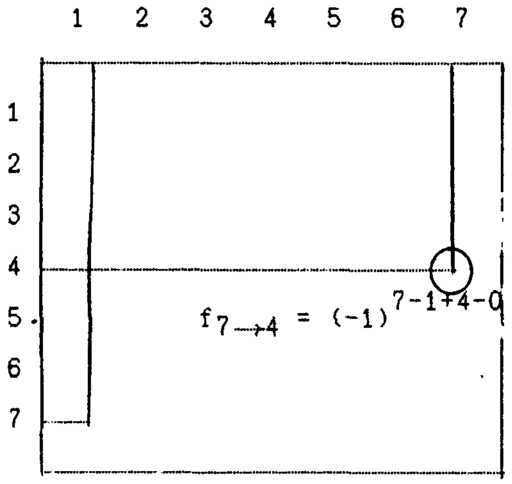
$$A_{71} = k.x(x^2-1). \qquad \text{.... (3.30)}$$

From 7 to 2 we have the path $7 \rightarrow 4 \rightarrow 3 \rightarrow 1 \rightarrow 2$. Hence

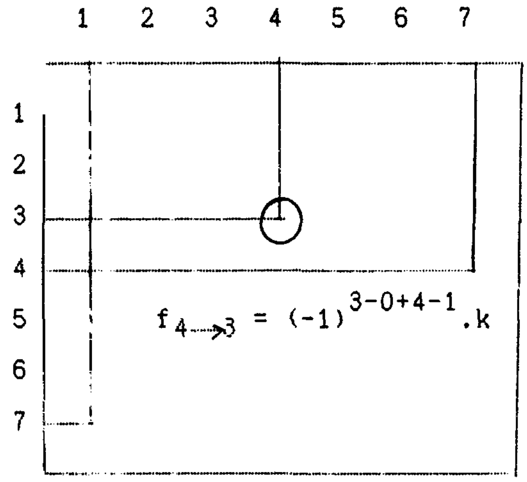
$$A_{72} = (-1)^{9} f_{7\rightarrow 4}\, f_{4\rightarrow 3}\, f_{3\rightarrow 1}\, f_{1\rightarrow 2} (-1)^{2}\, Q(\text{o}6,\ \text{o}5),$$

where (o6, o5) is the subgraph containing the isolated vertices o6 and o5. By drawing consecutive blocks as before one easily finds that

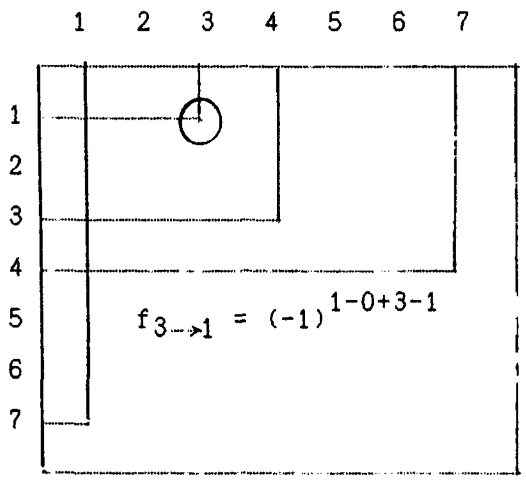
$$f_{7\to4} = (-1)^{4-0+7-1} \quad , \quad f_{4\to3} = (-1)^{3-0+4-1}.k$$
$$f_{3\to1} = (-1)^{1-0+3-1} \quad , \quad f_{1\to2} = (-1)^{2-1+1-0}.k$$



B_1



B_2



B_3

and finally,

$$A_{72} = k^2.x^2 \qquad \text{.... (3.31)}$$

From 7 to 3 we have the path $7\to4\to3$ and

$$A_{73} = (-1)^{10}\, f_{7\to4}\, f_{4\to3}(-1)^4 Q(\underset{5}{o}—\underset{1}{o}\overset{k}{—}\underset{2}{o}—\underset{6}{o}).$$

Counting as before one finds

$$f_{7\to4} = (-1)^{4-0+7-1}, \quad f_{4\to3} = (-1)^{3-0+4-1}.k$$

and $A_{73} = k[x^4 - (2+k^2)x^2 + 1]$ .... (3.32)

Similarly, $A_{74} = (-1)^{11}\, f_{7\to4}(-1)^5 Q(\underset{3}{o}—\underset{1}{\overset{o5}{o}}\overset{k}{—}\underset{2}{o}—\underset{6}{o}),$

where $f_{7\to 4} = (-1)^{4-0+7-1}$,

and thus $A_{74} = x^5 - (3+k^2)x^3 + 2x$ .... (3.33)

The other two cofactors are similarly found to be

$A_{75} = k(x^2-1)$, ... (3.34)

$A_{76} = k^2.x$ .... (3.35)

For the weighted graph G_2, we find cofactors along the fifth row.

$A_{51} = (-1)^6 f_{5\to 2}\, f_{2\to 1}(-1)^2 Q[o4,\ o3\ ]$,

where [o4, o3] means a subgraph having the isolated vertices 4 and 3 of which the latter is self-looped with weight h_3. Block diagrams for the consecutive translations $5\to 2$ and $2\to 1$ are B'_1 and B'_2 respectively as shown below. Thus,

$A_{51} = x(x-h_3)$ .... (3.36)

$A_{52} = (-1)^{5+2} f_{5\to 2}(-1)^3\ Q[\overset{4}{o}\text{—}o\text{—}\overset{3}{o}\ h_3]$

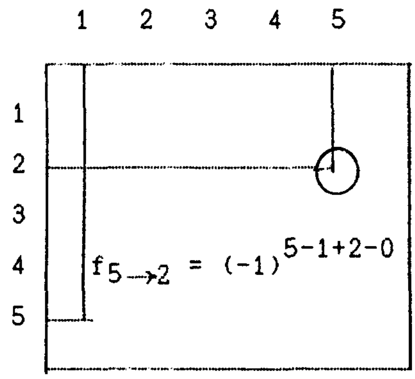
$= x^3 - h_3x^2 - 2x + h_3$ .... (3.37)

$A_{53} = (-1)^8 f_{5\to 2}\ f_{2\to 1}\ f_{1\to 3}(-1)\ Q(o4) = x$ .... (3.38)

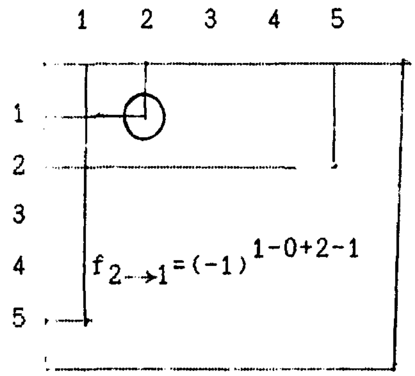
$A_{54} = x - h_3$ .... (3.39)

$A_{55} = x^4 - (h_2+h_3)x^3 + (h_2h_3-3)x^2 + 2(h_2+h_3)x - h_2h_3$ .... (3.40)

For G_3 we only demonstrate the construction of the cofactor A_{46} which requires



B'$_1$



B'$_2$

the following four paths to be considered separately:

Path I : $4\to 1\to 2\to 6$, Path II : $4\to 1\to 5\to 6$,

Path III : $4\to 3\to 2\to 6$, Path IV : $4\to 3\to 2\to 1\to 5\to 6$.

The contributions of these paths are respectively $-x^2$, $-(x^2-xh-1)$, $-(x^2-1)$ and -1, obtained by the methods just described. Noteworthy is the path IV where we are left with a null subgraph contributing $(-1)^0\ Q(\emptyset) = 1$. In a single diagram B, we illustrate the method of determination of the translational factors for path IV.

The points of intersection a,b,c,d and e correspond to the consecutive translations $4\to 3$, $3\to 2$, $2\to 1$, $1\to 5$ and $5\to 6$ respectively for path IV. Considering the point a first we find that no row above the third and no column to the left of the fourth are struck off; b and c are results of subsequent translations. Therefore,

$$f_{4\to3} = (-1)^{3-0+4-0} = -1.$$

Next considering b and c consecutively, we find as before,

$$f_{3\to2} = (-1)^{2-0+3-0} = -1,$$

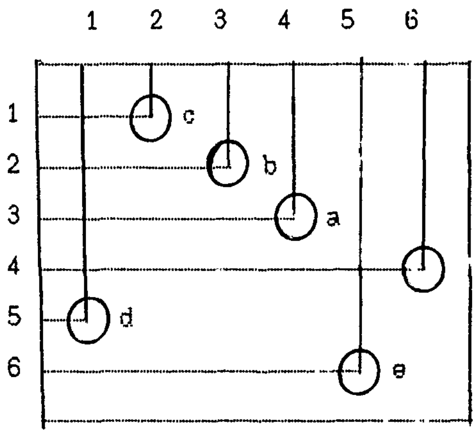
$$f_{2\to1} = (-1)^{1-0+2-0} = -1.$$

For d we see that above the fifth row, four rows have been already cut off and to the left of the first coloumn there is none. So

$$f_{1\to5} = (-1)^{5-4+1-0} = 1.$$

Thus,

$$A_{46}(\text{Path IV}) = (-1)^{4+6}.(-1)(-1)(-1)(1)(1)(-1)^{0}Q(\emptyset) = -1.$$



B

Table 1. Cofactor polynomials and eigenvectors of a pyrrole-like system with $h=0.5$, $k=0.5$ and $x = 1.7446442$

Cofactor polynomial (A_{2j})	$1/\sqrt{(\Sigma A^2_{2j})}$	Eigen coefficients
$A_{21} = k(x^3-2x-1)$		$C_1 = 0.321315$
$A_{22} = x^4-hx^3-(k^2+2)x^2+2hx+k^2$		$C_2 = 0.399229$
$A_{23} = x^3-hx^2-(k^2+1)x+(k^2+h)$	4.3898187	$C_3 = 0.537066$
$A_{24} = x^2+(k^2-h)x-k^2$		$C_4 = 0.537066$
$A_{25} = k^2x^2+x-(k^2+h)$		$C_5 = 0.399229$

In this way, determining the contributions from all the paths and using eqn.(3.27),we find that for G_3,

$$A_{46} = -3x^2 + xh + 1,$$

which we have verified by directly working out with

$(-1)^n \det(A-xI)$ for G_3.

For the pyrrole-like system with graph G_4, the procedure is exactly similar and we just state the cofactor polynomials in table 1.The eigenvectors for h = 0.5, k = 0.5, corresponding to the eigenvalue x = 1.7446442 have also been given in the same table and they are all in agreement with those recorded by Coulson[2]. The same cofactor polynomials have been found to hold good for the other eigenvalues and for other sets of values of h and k recorded by Coulson[2].

3.9.Concluding remarks : Method (A) gives the squares of eigenvector components using the not-so-widely used Ulam subgraphs.Such squares are useful in explaining many experimentally observed trends. For example, squares of such coefficients for the highest occupied molecular orbitals have been utilised in the calculation of various reactivity indices[13] and in the interpretation of trends in the CT bands of molecular complexes[14-16]. Although method (A) fails to give all the eigenvectors for degenerate eigenvalues, it leads to the determination of multiplicities of the latter; it also proves some important properties of K_n and C_n in a simple way.

Method (B) also is inapplicable to cases of real degeneracy, but in case of accidental degeneracy the problem can be got rid of by using SALC and then drawing the derived graphs corresponding to the block-factors of the secular determinant. *

This work, together with some applications in charge-transfer complexes (described in section B) appeared in Proc.Ind.Acad.Sci.(Chem.Sci.) 101 (1989) 499.

* Method (A) is ideally suited for electron density determinations and Method (B) is ideally suited for bond order determinations.

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