

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

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Abstract. Two new graph-theoretical methods, (A) and (B), have been devised for generation of eigenvectors of weighted and unweighted chemical graphs. Both the methods show that not only eigenvalues but also eigenvectors have full combinatorial (graph-theoretical) content. Method (A) expresses eigenvector components in terms of Ulam's subgraphs of the graph. For degenerate eigenvalues this method fails, but still the expressions developed yield a method for predicting the multiplicities of degenerate eigenvalues in the graph-spectrum. Some well-known results about complete graphs (K_n) and annulenes (C_n), viz. (i) K_n has an eigenvalue -1 with $(n-1)$ -fold degeneracy and (ii) C_n cannot show more than two-fold degeneracy, can be proved very easily by employing the eigenvector expressions developed in method (A). Method (B) expresses the eigenvectors as analytic functions of the eigenvalues using the cofactor approach. This method also fails in the case of degenerate eigenvalues but can be utilised successfully in case of accidental degeneracies by using symmetry-adapted linear combinations. Method (B) has been applied to analyse the trend in charge-transfer absorption maxima of the some molecular complexes and the hyperconjugative HMO parameters of the methyl group have been obtained from this trend.

Keywords. Graph-theory; Ulam's subgraphs; characteristic polynomials; eigenvectors; multiplicity of degenerate eigenvalues; complete graphs; cofactor polynomials.

1. Introduction

Methods of applying graph theory (GT) in physico-chemical problems have been developed significantly in the last two decades (for a detailed review see Harary 1967, Graovac *et al* 1977, Gutman and Polansky 1986). But so far graph-theoretical methods for generation of eigenvectors of adjacency matrices of graphs are few in number. Topological expressions for eigenvectors in closed forms for some limited class of compounds are known since the time of Hückel (Hückel 1932; Coulson and Streitwieser 1965) but in recent years only one paper, that of Kassman (1985), has appeared which deals with generation of eigenvectors of general chemical graphs. This method utilises Chebyshev polynomials and expresses the eigenvector components in terms of eigenvalues.

In the present work we report two new graph-theoretical methods for generation of eigenvectors. Method (A) involves the use of Ulam's subgraphs which came into prominence with the famous Ulam's conjecture (Ulam 1960), one of the unresolved

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problems in mathematics. Such subgraphs have been utilised by Randić (1982) for the generation of characteristic polynomials (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 paper is as follows. In §2, the principle of method (A) has been outlined; in §3, this method has been illustrated; in §4, two important results about degenerate eigenvalues have been proved and illustrated; in §§5 and 6, two important graph-spectral properties of complete graphs (K_n) and annulenes (C_n), which are consequences of the results derived in §4, have been proved; in §7, the principle of method (B) has been explained; in §8, method (B) has been illustrated, and in §9, it has been applied to the study of charge-transfer absorption maxima of a series of molecular complexes of polymethyl benzenes with ICl in CCl_4 .

2. Method (A)

An Ulam subgraph of a graph G is defined as a subgraph obtained by deleting a vertex and all the edges incident to this vertex from G . If $v_1, v_2, v_3, \dots, v_n$ 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, \dots, x_n be the eigenvalues of G . To begin with, we assume that all these eigenvalues are distinct. If we arbitrarily attach a self-loop of weight h to the r th vertex and form a graph G' , then (Gutman and Polansky 1986),

$$P(G'; x) = P(G; x) - hP(G - v_r; x), \quad (1)$$

where $G - v_r$ is an Ulam subgraph of G , and the P 's denote characteristic polynomials of the graphs in parentheses (figure 1).

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

$$\begin{aligned} \Delta(G') = & \begin{vmatrix} a_{11} - x & a_{12} & \cdots & a_{1r} & \cdots & a_{1n} \\ a_{21} & a_{22} - x & \cdots & a_{2r} & \cdots & a_{2n} \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ a_{r1} & a_{r2} & \cdots & a'_{rr} - x & \cdots & a_{rn} \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ a_{n1} & a_{n2} & \cdots & \cdots & \cdots & a_{nn} - x \end{vmatrix} \\ = & \Delta(G) - h[\partial\Delta(G)/\partial h] \text{ (upto a first order approximation)} \\ = & \Delta(G) - h[\partial(\Delta(G))/\partial x] \cdot [\partial x/\partial h]. \end{aligned} \quad (2)$$

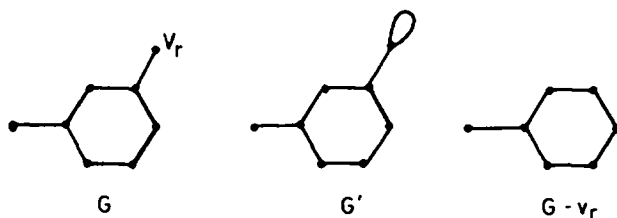


Figure 1. A graph G , its derived graph G' and the r th Ulam subgraph $G - v_r$.

Thus

$$P(G'; x) = P(G; x) - hP'(G; x)(\partial x/\partial h), \quad (3)$$

where $P'(G; x)$ is the first derivative of the characteristic polynomial of G . Comparing (1) and (3) we find

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

and putting $x = x_j$, the j th eigenvalue,

$$P(G - v_r; x_j) = P'(G; x_j)C_{rj}^2, \quad (4)$$

where, by the Coulson–Longuet-Higgins (1947) perturbation technique,

$$(\partial x_j/\partial h) = C_{rj}^2. \quad (5)$$

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 characteristic polynomials of all the Ulam subgraphs (Randić 1982; Beineke and Wilson 1978) of G , we obtain from (4) the following working formula:

$$C_{rj}^2 = \frac{P(G - v_r; x_j)}{P'(G; x_j)} = \frac{P(G - v_r; x_j)}{\sum_{r=1}^n P(G - v_r; x_j)}. \quad (6)$$

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

3. Illustrations of method (A)

3.1 Butadiene

The graph G and its Ulam subgraphs for this system are shown in figure 2a, and their respective characteristic polynomials are,

$$P(G; x) = x^4 - 3x^2 + 1,$$

$$P(G - v_1; x) = x^3 - 2x = P(G - v_4; x),$$

$$P(G - v_2; x) = x^3 - x = P(G - v_3; x).$$

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 (6), we obtain,

$$|C_{11}| = |C_{41}| = 0.3717480, \quad |C_{21}| = |C_{31}| = 0.6015009,$$

$$|C_{12}| = |C_{42}| = 0.6015009, \quad |C_{22}| = |C_{32}| = 0.3717480,$$

$$|C_{13}| = |C_{43}| = 0.6015009, \quad |C_{23}| = |C_{33}| = 0.3717480,$$

$$|C_{14}| = |C_{44}| = 0.3717480, \quad |C_{24}| = |C_{34}| = 0.6015009.$$

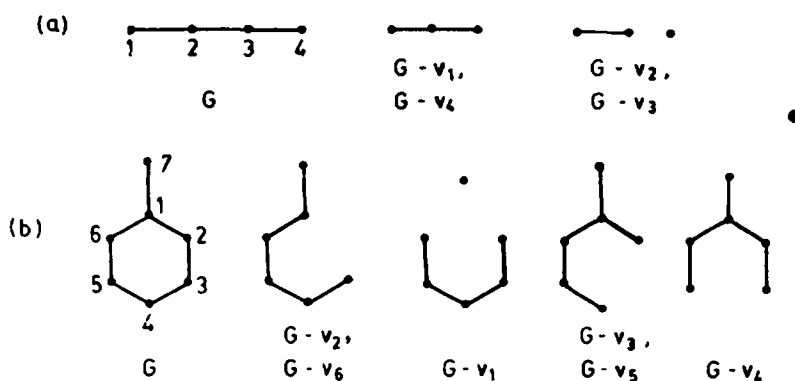


Figure 2. (a) Graph of butadiene and its Ulam subgraphs. (b) Graph of benzyl radical and its Ulam subgraphs.

For assigning proper signs to these coefficients we note that

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

which yields the secular equations,

$$-C_{1j}x_j + C_{2j} = 0, \quad (7a)$$

$$C_{1j} - C_{2j}x_j + C_{3j} = 0, \quad (7b)$$

$$C_{2j} - C_{3j}x_j + C_{4j} = 0, \quad (7c)$$

$$C_{3j}x_j - C_{4j} = 0. \quad (7d)$$

Equation (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 (7d) shows. We can arbitrarily assign a +ve sign to C_{1j} . Then using (7a-d) and the magnitudes $|C_{rj}|$, one 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 (Coulson and Streitwieser 1965) for linear chains (L_n),

$$C_{rj} = [2/(n+1)]^{1/2} \sin [rj\pi/(n+1)] \quad (8)$$

3.2 Benzyl radical

The necessary graph and Ulam subgraphs for this system are shown in figure 2b. For this system,

$$\begin{aligned} P(G; x) &= x^7 - 7x^5 + 13x^3 - 7x, \\ P(G - v_1; x) &= x^6 - 4x^4 + 3x^2, \\ P(G - v_2; x) &= x^6 - 5x^4 + 6x^2 - 1 = P(G - v_6; x), \\ P(G - v_3; x) &= x^6 - 5x^4 + 5x^2 = P(G - v_5; x), \\ P(G - v_4; x) &= x^6 - 5x^4 + 5x^2 - 1. \end{aligned} \quad (9)$$

The eigenvalues of G are $0, \pm 1, \pm 1.25928, \pm 2.101003$, which, as before, are denoted by x_i ($i = 1$ to 7) such that $x_1 > x_2 > \dots > x_7$. Now using (6) the magnitudes of the eigenvector coefficients can be found. For their signs we consider the secular determinant,

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

which yields

$$-C_{1j}x_j + C_{2j} + C_{6j} + C_{7j} = 0, \tag{10a}$$

$$C_{1j} - C_{2j}x_j + C_{3j} = 0, \tag{10b}$$

$$C_{2j} - C_{3j}x_j + C_{4j} = 0, \tag{10c}$$

$$C_{3j} - C_{4j}x_j + C_{5j} = 0, \tag{10d}$$

$$C_{4j} - C_{5j}x_j + C_{6j} = 0, \tag{10e}$$

$$C_{1j} + C_{5j} - C_{6j}x_j = 0, \tag{10f}$$

$$C_{1j} - C_{7j}x_j = 0. \tag{10g}$$

We demonstrate here the determination of eigenvectors corresponding to $x_3 = 1$. Equation (6) yields

$$\begin{aligned} |C_{13}| &= |C_{43}| = |C_{73}| = 0, \\ |C_{23}| &= |C_{33}| = |C_{53}| = |C_{63}| = 0.5. \end{aligned} \tag{11}$$

Equation (10f) gives $C_{53} = C_{63}$; (10c) gives $C_{23} = C_{33}$; (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.

$$\begin{aligned} C_{13} &= 0; & C_{23} &= +0.5; \\ C_{33} &= +0.5; & C_{43} &= 0; \\ C_{53} &= -0.5; & C_{63} &= -0.5; & C_{73} &= 0. \end{aligned} \tag{12}$$

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, (6) gives,

$$P(G - x_i; x_j) = 0, \text{ for all } i. \tag{13}$$

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,

$$P(G; x) = (x - x_j)^p f(x), \tag{14}$$

where $f(x)$ is a function of degree $n - p$, n being the number of vertices in G . Differentiation of (14) gives

$$P'(G; x) = (x - x_j)^{p-1} \phi(x), \tag{15}$$

i.e.

$$P(G - v_1; x) + P(G - v_2; x) + \dots + P(G - v_n; x) = (x - x_j)^{p-1} \phi(x), \tag{16}$$

which shows that $(x - x_j)^{p-1}$ is the HCF of each term on the left hand side of (15). Equation (16) thus shows that every Ulam subgraph of G has a factor $(x - x_j)^{p-1}$ in its characteristic polynomial 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

$$P'(G; x) = \sum_{i=1}^n P(G - v_i; x) = (x - x_j)^{p-1} F_{(r)}(x), \tag{17}$$

where $F_{(r)}(x)$ is a function of degree r such that $r + p = n$. Integrating (17) by parts, one finally obtains

$$P(G; x) = (x - x_j)^p F_{(r)}(x)/p - (x - x_j)^{p+1} F_{(r-1)}(x)/(p + 1) - \dots \\ \dots - (x - x_j)^{p+r} F_{(0)}(x)/(p + r) + \text{const.}$$

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

$$P(G; x) = (x - x_j)^p f(x). \tag{18}$$

This completes the proof of (II).

Illustration of the 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 the roots.

Illustration of the result (II): Let us consider a tetrahedral graph with vertex enumeration as shown in figure 3, where its Ulam subgraphs are also shown. Here

$$P(G; x) = x^3(x^2 - 4),$$

$$P(G - v_i; x) = x^2(x - 3), \text{ for } i = 1, 2, 3, 4,$$

and

$$P(G - v_5; x) = x^4.$$

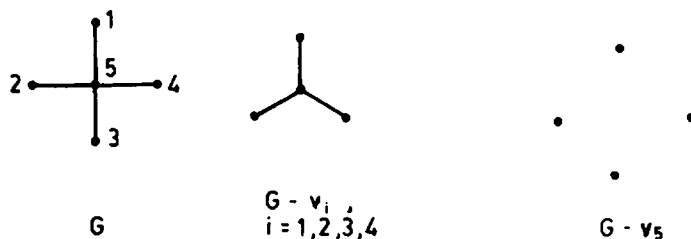


Figure 3. Graph of a tetrahedron and its Ulam subgraph.

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

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

$$x_j = 2 \cos(j\pi/n), \quad j = 1 \text{ to } n - 1. \tag{19}$$

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 (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 (Gutman and Polansky 1986; Graovac *et al* 1977; Mukherjee 1988). The present proof is only an addition to them, but it is obviously very simple.

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 characteristic polynomial,

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

So -1 is a root of K_3 with 2-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 (Beineke and Wilson 1978), proved here in a very simple way.

7. Method (B)

In GT, the CP of a graph G is defined as

$$P(G; x) = (-1)^n \det(A - xI) = (-1)^n \Delta(x), \tag{20}$$

where \mathbb{A} is the adjacency matrix of G , \mathbb{I} is the unit matrix of the size of \mathbb{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 sp^2 carbon atoms) the unit of energy.

If $(a_{i1}, a_{i2}, \dots, a_{in})$ is the i th row of $\Delta(x)$, then the eigenvectors $C_j, j = 1$ to n , can be shown to be given by (Streitwieser 1961)

$$C_j = A_{ij} \left(\sum_{j=1}^n A_{ij}^2 \right)^{-1/2}, \quad (21)$$

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

$$A_{ii} = (-1)^{i+i} (-1)^{n-1} Q(x). \quad (22)$$

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 $L_1(i \rightarrow u \rightarrow s \rightarrow j)$, $L_2(i \rightarrow u' \rightarrow s' \rightarrow j)$ 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 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 contributions of a_{ui} and $a_{u'i}$ can be obtained by tracing the paths L_1 and L_2 separately. 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

$$f_{i \rightarrow u} = (-1)^{u - n_r + i - n_c} w_{(i,u)}, \quad (23)$$

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 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 row and $(u - n'_c)$ 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,

$$f_{u \rightarrow s} = (-1)^{s - n'_r + u - n'_c} w_{(u,s)}. \quad (24)$$

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

$$f_{u \rightarrow s} = (-1)^{j - n_r'' + s - n_c''} w_{(s,j)}. \quad (25)$$

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

$$A_{ij}(L_1) = (-1)^{i+j} f_{i \rightarrow u} f_{u \rightarrow s} f_{s \rightarrow j} (-1)^v Q(G - L_1; x), \quad (26)$$

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.,

$$A_{ij} = \sum_r A_{ij}(L_r), \quad (27)$$

where r runs over all the self-avoiding path from i to j . The CP $Q(G - L_r; x)$, can be obtained by Aihara's (1976) method for both weighted and non-weighted subgraphs, with the additional requirement that

$$Q(\phi) = 1, \quad (28)$$

where ϕ denotes a null subgraph occurring 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 (22) and (27) we get the cofactors and finally from (21) the eigenvectors are determined.

8. Illustrations of method (B)

Although the above development seems a little belaboured, the actual procedure is quick and very easy to apply. We illustrate the method for the graphs $G_1 - G_6$ (figure 4) of which G_1 and G_2 will be required in our subsequent application of the method to charge-transfer complexes. 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 7th row as this vertex is one of these with the lowest degree.

$$\begin{aligned} A_{77} &= (-1)^{7+7} (-1)^6 Q(\bar{G}_1) \\ &= x^6 - 7x^4 + 10x^2 - 2, \end{aligned} \quad (29)$$

where \bar{G}_1 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

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

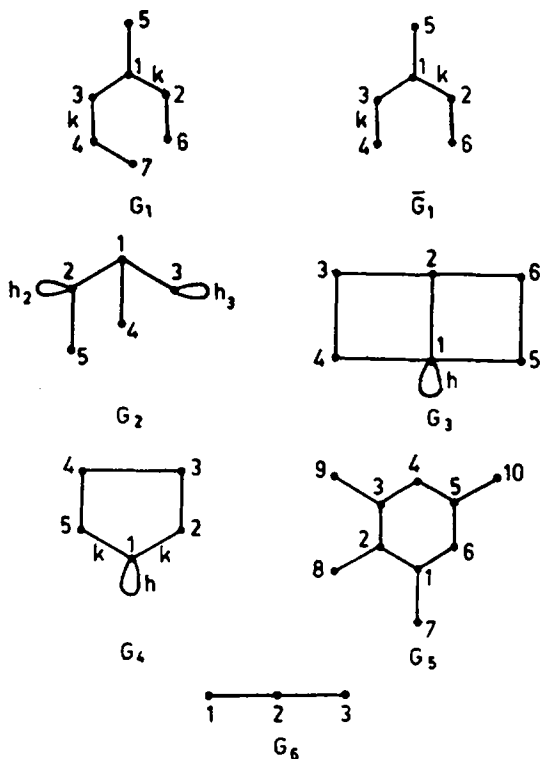


Figure 4. Some graphs treated by method (B).

where the figures in parentheses after Q mean that the 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 vertical lines intersecting at an encircled point correspond to the translation considered and the other lines correspond to rows 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,

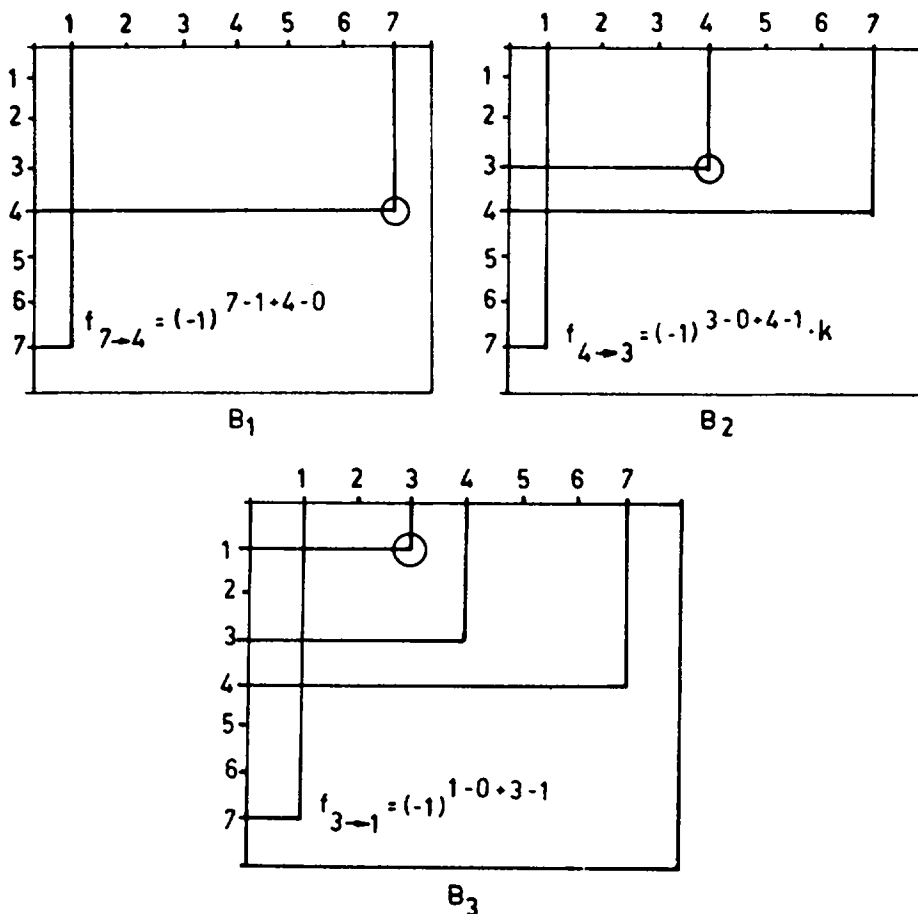
$$A_{71} = k \cdot x \cdot (x^2 - 1). \tag{30}$$

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

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

where $(6, 5)$ is the subgraph containing the isolated vertices 6 and 5. By drawing consecutive blocks as before one easily finds that

$$\begin{aligned} f_{7-4} &= (-1)^{4-0+7-1} \\ f_{4-3} &= (-1)^{3-0+4-1} \cdot k \\ f_{3-1} &= (-1)^{1-0+3-1} \\ f_{1-2} &= (-1)^{2-1+1-0} \cdot k \end{aligned}$$



and finally,

$$A_{72} = k^2 \cdot x^2. \tag{31}$$

From 7 to 3 we have the path $7 \rightarrow 4 \rightarrow 3$ and

$$A_{73} = (-1)^{1 \cdot 0} f_{7 \rightarrow 4} f_{4 \rightarrow 3} (-1)^4 Q(5 - 1^k - 2 - 6).$$

Counting as before one finds

$$f_{7 \rightarrow 4} = (-1)^{4-0+7-1}$$

$$f_{4 \rightarrow 3} = (-1)^{3-0+4-1} \cdot k$$

and

$$A_{73} = k[x^4 - (2 + k^2)x^2 + 1]. \tag{32}$$

Similarly,

$$A_{74} = (-1)^{11} f_{7 \rightarrow 4} (-1)^5 Q(3 - 1^k - 2 - 6),$$

5

where

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

and thus

$$A_{74} = x^5 - (3 + k^2)x^3 + 2x. \tag{33}$$

The other two cofactors are similarly found to be

$$A_{75} = k(x^2 - 1), \tag{34}$$

$$A_{76} = k^2x. \tag{35}$$

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

$$A_{51} = (-1)^6 f_{5 \rightarrow 2} f_{2 \rightarrow 1} (-1)^2 Q[4, 3(h_3)],$$

where $[4, 3(h_3)]$ 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 $5 \rightarrow 2$ and $2 \rightarrow 1$ are B_1' and B_2' respectively as shown below. Thus,

$$A_{51} = x(x - h_3) \tag{36}$$

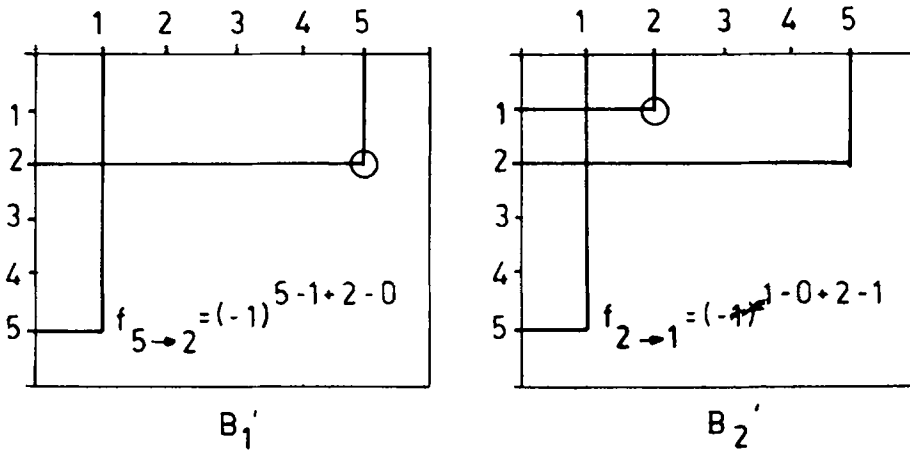
$$\begin{aligned} A_{52} &= (-1)^{5+2} f_{5 \rightarrow 2} (-1)^3 Q[4-1-3(h_3)] \\ &= x^3 - h_3x^2 - 2x + h_3, \end{aligned} \tag{37}$$

$$\begin{aligned} A_{53} &= (-1)^8 f_{5 \rightarrow 2} f_{2 \rightarrow 1} f_{1 \rightarrow 3} (-1)^1 Q(4) \\ &= x, \end{aligned} \tag{38}$$

$$A_{54} = x - h_3, \tag{39}$$

$$A_{55} = x^4 - (h_2 + h_3)x^3 + (h_2h_3 - 3)x^2 + 2(h_2 + h_3)x - h_2h_3. \tag{40}$$

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



the following four paths to be considered separately:

- Path I : 4 → 1 → 2 → 6,
- Path II : 4 → 1 → 5 → 6,
- Path III : 4 → 3 → 2 → 6,
- Path IV : 4 → 3 → 2 → 1 → 5 → 6.

The contributions of these paths are respectively $-x^2$, $-(x^2 - xh - 1)$, $-(x^2 - 1)$ and -1 , obtained by methods just described. Noteworthy is path IV where we are left with a null subgraph contributing $(-1)^0 Q(\phi) = 1$. In a single diagram \bar{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 $4 \rightarrow 3, 3 \rightarrow 2, 2 \rightarrow 1, 1 \rightarrow 5$ and $5 \rightarrow 6$ respectively for path IV. Considering a first we find that no row above the third and no column to the left of the fourth are struck off; the points b and c are results of subsequent translations. Therefore,

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

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

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

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

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

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

Thus,

$$\begin{aligned} A_{46}(\text{path IV}) &= (-1)^{4+6} \cdot (-1) \cdot (-1) \cdot (-1) \cdot (1) \cdot (1) \cdot (-1)^0 Q(\phi) \\ &= -1. \end{aligned}$$

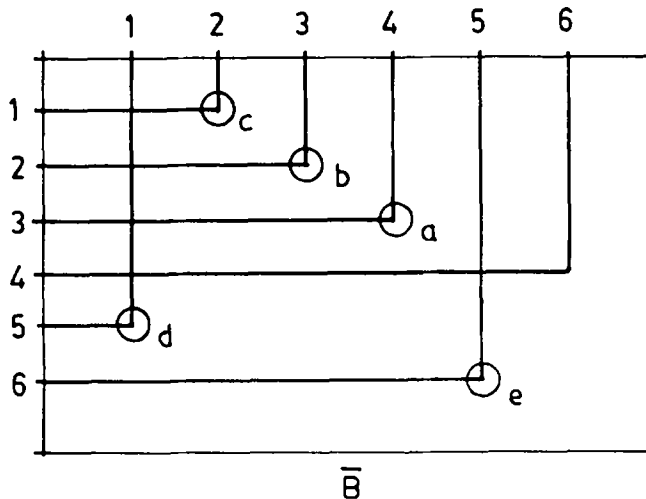


Table 1. Cofactor polynomials and eigenvectors of a pyrrole-like system with $h = 0.5$, $k = 0.5$ and $x = 1.7446442$.

Cofactor polynomial (A_{2j})	$(\sum A_{2j}^2)^{-1/2}$	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 (27), we find that for G_3 ,

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

which we have verified by directly working out with $(-1)^n \det(\mathbf{A} - x\mathbf{I})$ for G_3 .

For the pyrrole-like system with graph G_4 , the procedure being exactly similar 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 (Coulson and Streitwieser 1965). The same cofactor polynomials have been found to hold good for all the other eigenvalues and for other sets of values of h and k recorded by Coulson (Coulson and Streitwieser 1965).

9. Application of method (B) to the study of charge-transfer (CT) absorption maxima

The energy ($h\nu_{CT}$) of electronic CT transition observed in molecular complexes is expressed by the well-known equation (McConnell *et al* 1953; Mulliken and Person 1961),

$$h\nu_{CT} = I_D - E_A - C, \quad (41)$$

where I_D is the vertical ionisation potential of the donor, E_A is the vertical electron affinity of the acceptor and C is a term which sums the contributions from non-bonding species, polarisation and solvation. The main part of C comes from the electrostatic attraction between the negatively charged acceptor and positively charged donor in the excited state (Mulliken and Person 1969). Working with a common acceptor and a series of structurally similar donors in a given solvent one may use (41) in the form

$$h\nu_{CT} = -E_D + \text{const}, \quad (42)$$

where E_D is the energy of the highest occupied molecular orbital (HOMO) of the donor. If the donors form a series of progressively alkyl-substituted aromatic hydrocarbons, E_D can be expressed in terms of the Hückel parameters (Streitwieser 1961) of the alkyl groups using the Coulson-Longuet-Higgins perturbation technique (1947) and correlating such expressions with $h\nu_{CT}$ from (42) one may estimate the Hückel parameters for the alkyl group. However, the alkyl group (R) attached to the sp^2 -carbon atom may be treated in two models. In one, R exerts an inductive effect and changes the Coulomb integral of the conjugated C atom to which it is attached.

Using such a model, trends in CT absorption bands have been interpreted and the inductive effect HMO parameter estimated by a number of workers (Lepley 1964; Keyser 1974; Seal and Mukherjee 1984; Mukherjee and Seal 1986). In the second model, the hyperconjugative effect (Mulliken *et al* 1941) of the alkyl group is to be considered. Among several methods adopted for taking into consideration the hyperconjugation of R, we use here the one suggested by Matsen (1950) – R is regarded as a heteroatom contributing two π -electrons to the 'extended' conjugated system. Now if we apply the Coulson–Longuet-Higgins method to an alkylbenzene having many R-substituents we replace each R by $-\text{CH}_2$ (where C is sp^2 hybridised) and consider the resulting species as the unperturbed system. If E^0 is the energy of the HOMO of this unperturbed system, then for the alkylbenzene under consideration,

$$E_D = E^0 + h_R \beta \sum_r C_r^2 + 2(k_{C R} - 1) \beta \sum_{r>s} C_r C_s, \quad (43)$$

where r is the location of $-\text{CH}_2$ (i.e. of R), s is the location of the conjugated C-atom to which R is attached and C_r, C_s etc. are the atomic orbital coefficients of the atoms r, s etc. respectively in the LCAO wavefunction of the HOMO of the unperturbed system. Using (41) and (42) one obtains

$$(h\nu_{CT} + E^0) = -h_R \beta \sum_r C_r^2 - 2(k_{C R} - 1) \beta \sum_{r>s} C_r C_s + \text{const.} \quad (44)$$

Now, if experimental $h\nu_{CT}$ values are known for molecular complexes of a given acceptor with a series of alkylbenzenes and the required perturbational coefficients are calculated from the eigenvectors of the parent unperturbed systems, then by a linear regression of (44) one can estimate the hyperconjugative HMO parameters h_R and $k_{C R}$. A complete calculation of the eigenvectors by method (B) is shown here for the unperturbed system corresponding to 1,2,3,5-tetraalkylbenzene whose molecular graph is G_5 . To get rid of difficulties arising out of accidental degeneracy, we first use the usual group theoretic technique. The system belongs to the C_{2v} point group and has three A_2 -type and seven B_2 -type irreducible representations. The symmetry-adapted linear combinations (SALC) of A_2 symmetry are,

$$\begin{aligned} \Psi_1 &= 1/\sqrt{2}(\phi_1 - \phi_3), \\ \Psi_2 &= 1/\sqrt{2}(\phi_6 - \phi_4), \\ \Psi_3 &= 1/\sqrt{2}(\phi_7 - \phi_9), \end{aligned} \quad (45)$$

where $\{\phi_i\}$ is the set of π -type atomic orbitals of the sp^2 -carbon. The secular determinantal equation (with $\alpha = 0, \beta = 1$) for A_2 symmetry is,

$$\begin{vmatrix} -E & 1 & 1 \\ 1 & -E & 0 \\ 1 & 0 & -E \end{vmatrix} = 0.$$

From this determinant we can imagine an adjacency matrix,

$$\begin{vmatrix} 0 & 1 & 1 \\ 1 & 0 & 0 \\ 1 & 0 & 0 \end{vmatrix},$$

to which corresponds the graph G_6 .

The cofactors along the second row are,

$$A_{21} = x, \quad A_{22} = x^2 - 1 \quad \text{and} \quad A_{23} = 1. \quad (46)$$

The CP of G_6 gives eigenvalues $x = 0, \pm \sqrt{2}$, which in conjunction with (45) and (21) give eigenvectors of A_2 symmetry as shown in table 2A.

The SALC of B_2 symmetry are,

$$\begin{aligned} \Psi_1 &= 1/\sqrt{2}(\phi_1 + \phi_3), & \Psi_2 &= \phi_2, \\ \Psi_3 &= 1/\sqrt{2}(\phi_4 + \phi_6), & \Psi_4 &= \phi_5, \\ \Psi_5 &= 1/\sqrt{2}(\phi_7 + \phi_9), & \Psi_6 &= \phi_8, \end{aligned} \quad (47)$$

and

$$\Psi_7 = \phi_{10}.$$

The secular determinantal equation is,

$$\begin{vmatrix} -E & \sqrt{2} & 1 & 0 & 1 & 0 & 0 \\ \sqrt{2} & -E & 0 & 0 & 0 & 1 & 0 \\ 1 & 0 & -E & \sqrt{2} & 0 & 0 & 0 \\ 0 & 0 & \sqrt{2} & -E & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 & -E & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & -E & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & -E \end{vmatrix} = 0,$$

from which we can imagine an adjacency matrix (by putting $E = 0$) which corresponds to the graph G_1 with $k = \sqrt{2}$. Equations (29)–(35) give the cofactor polynomials. The CP of G_1 , obtained by Aihara's (1976) method is

$$P(G_1; x) = x^7 - (4 + 2k^2)x^5 + (5 + 3k^2 + k^4)x^3 - (2 + k^2)x. \quad (48)$$

With $k = \sqrt{2}$ the eigenvalues are obtained from $P(G_1; x) = 0$ by the Newton–Raphson method. These, in conjunction with (29)–(35) and (21) give the eigenvectors of B_2 symmetry as shown in table 2B. Similar symmetry-factorisation gives the graph G_2 for the parent system 1,2,3,4-tetraalkylbenzene. We note that for G_5 , the eigenvalue $x = 0$ occurs twice in two different irreducible representations. Had we applied the present cofactor method directly on G_5 , a problem would arise. Symmetry-factorisation not only helps us to get rid of this accidental degeneracy but also factorises rings into weighted trees and thus reduces the number of paths to be traced for determination of cofactors.

In table 3 are given the energies of the HOMO and the perturbational coefficients $\sum_r C_r^2$ and $\sum_{r>s} C_r C_s$ for the unperturbed systems corresponding to a series of polymethylbenzenes (PMB). The CT transition energies of the molecular complexes of these PMB's with ICl in CCl_4 are also given in table 3. The graphs of the unperturbed systems corresponding to the PMB's are shown in figure 5. The experimental CT transition energies are taken from the works of Farrell and Newton (1965) and the perturbational coefficients have been calculated by method (B). A linear regression according to (44) gives $h_{\text{Me}} = 1.35$ and $k_{\text{C Me}} = 0.98$ which are close to the previously reported values, $h_{\text{Me}} = 1.4\text{--}3.3$, and $k_{\text{C Me}} = 0.8$, obtained from other types of experimental data (Matsen 1950; Streitwieser and Nair 1959).

Table 2A. Eigenvalues and eigenvectors for the graph G_6 (i.e. of G_5 in A_2 symmetry).

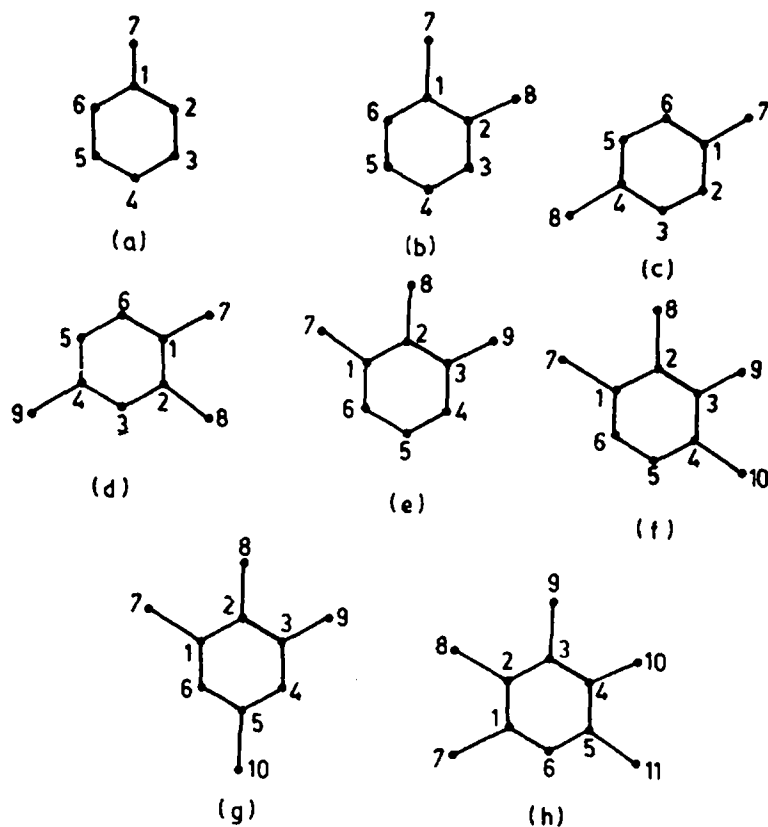
Eigenvalue (β)	Eigenvector		
	C_1	C_2	C_3
0	0	$-1/\sqrt{2}$	$1/\sqrt{2}$
$-\sqrt{2}$	$-1/\sqrt{2}$	$1/2$	$1/2$
$\sqrt{2}$	$1/\sqrt{2}$	$1/2$	$1/2$

Table 2B. Eigenvalues and eigenvectors of the graph G_1 (i.e. of G_2 in B_2 symmetry).

Eigenvalue	Eigenvector						
	C_1	C_2	C_3	C_4	C_5	C_6	C_7
0	0	0	$1/2$	0	$-1/2$	0	$-1/\sqrt{2}$
+0.564508	-0.2991662	0.3505417	-0.1346633	0.1577982	-0.5299593	0.6209687	0.2795160
-0.564508	0.2991662	0.3505417	-0.1346634	-0.1577982	-0.5299593	-0.6209687	0.2795160
+1.535554	0.2684925	0.4293743	-0.3697928	-0.5913742	0.1748505	0.2796217	-0.3851210
-1.535554	-0.2684925	0.4293743	-0.3697928	0.5913742	0.1748505	-0.2796217	-0.3851210
+2.307250	0.5817314	0.4390423	0.4691685	0.3540892	0.2521319	0.1902881	0.1534682
-2.307250	-0.5817314	0.4390423	0.4691685	-0.3540892	0.2521319	-0.1902881	0.1534682

Table 3. CT transition energies and calculated perturbational coefficients of PMB-ICI complexes in CCl_4 .

Donor	$h\nu_{\text{CT}}(\text{eV})$	Energy of HOMO (β)	$\sum C_r^2$	$\sum_{r>s} C_r C_s$
Toluene	4.3090	0	0.5714301	0
<i>p</i> -Xylene	4.2500	-0.3111078	0.6645892	-0.206761
<i>o</i> -Xylene	4.1645	-0.2949629	0.550935	-0.1680779
1,2,4-Trimethylbenzene	4.1505	-0.4194626	0.6305286	-0.2644832
1,2,3-Trimethylbenzene	4.0556	-0.488306	0.7502814	-0.3663668
1,2,3,4-Tetramethylbenzene	3.9776	-0.5062872	0.7832763	-0.3965627
1,2,3,5-Tetramethylbenzene	3.9776	-0.564508	0.7445881	-0.4203259
Pentamethylbenzene	3.8540	-0.6180339	0.7236066	-0.4472134

**Figure 5.** Graphs of the unperturbed systems corresponding to the PMB under consideration. (a) toluene, (b) *o*-xylene, (c) *p*-xylene, (d) 1,2,4-trimethyl benzene, (e) 1,2,3-trimethyl benzene, (f) 1,2,3,4-tetramethyl benzene, (g) 1,2,3,5-tetramethyl benzene, and (h) pentamethyl benzene.

10 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 (Fukui *et al* 1954) and in the interpretation of trends in the CT bands of molecular complexes (Lepley 1964; Keyser 1974; Mukherjee and Seal 1986). 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.

The hyperconjugative model used by Matsen (1950) can be justified only by an appeal to experiment. We have calculated the hyperconjugative HMO parameters of the methyl group by applying method (B) on the experimentally observed trends in CT bands of molecular complexes of ICl with methylbenzenes. The excellent agreement between the HMO parameters thus obtained and the previously reported values is additional support for Matsen's model.

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