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A graph-theoretical method for stepwise factorisation of symmetric graphs for simultaneous determination of eigenvectors and eigenvalues

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Abstract. A simple pictorial algorithm for factorisation of symmetric chemical graphs (weighted and unweighted) leading to simultaneous determination of their eigenvalues and eigenvectors has been devised. The method does not require group-theoretical techniques (viz. identification of the point group of the species under study, formation of symmetry-adopted linear combinations using character tables etc.). It requires consideration of only one symmetry element, e.g., a reflection plane and is based on elementary row and column operations which keep the secular determinant of the adjacency matrix unchanged (except possibly for a multiplicative constant).

Keywords. Symmetric graphs; adjacency operator; adjacency matrix; reflection plane; linear combination of bases; secular determinant.

1. Introduction

During the last two decades graph theory has received much attention for its applications in chemistry (Rouvray 1976; Graovac 1977; Gutman 1986). For studying the various chemically relevant features of a graph, the adjacency matrix $\mathbb{A}$ of the graph can be handled in mainly two ways: (a) by constructing the characteristic polynomial $|\mathbb{A} - E\mathbb{I}|$ and finding its zeros (E, the eigenvalues) and eigenvectors of the matrix; (b) by diagonalising the matrix $\mathbb{A}$ which is equivalent to factoring the secular determinant $|\mathbb{A} - E\mathbb{I}|$. There are well-established group-theoretical methods for the second purpose, but as graph-theoretic techniques are easier to apply, algorithms have been developed for block-diagonalisation of adjacency matrices of symmetric, unweighted graphs by splitting them into smaller disconnected graphs with weighted vertices and edges (McClelland 1974, 1982; King 1977; Hall 1977; D'Amato 1979). But these algorithms do not apply to general weighted graphs. McClelland's (1982b) algorithm for block-factorisation of graphs with local symmetry is very efficient but it uses a unitary transformation of $\mathbb{A}$ and the topological background for construction of this unitary transformation matrix is not clearly brought out in this work. Recently, Randic *et al* (1985) have developed a method, known as 'ultimate pruning method', for factoring the characteristic polynomial. This method results in factors containing polynomials of linear chains and is thus not very

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efficient – it requires computation of eigenvalues from each factor separately and does not give the eigenvectors directly.

In the present communication, we report a simple pictorial algorithm for construction of proper linear combinations of basis vectors (representing the vertices of a graph) such that operation of the operator $\hat{A}$, under which the elements of the adjacency matrix are defined, on these new linear combinations gives results that can be represented by a set of disconnected graphs and thus a graph-factorisation is possible. For graphs (weighted or unweighted) of sufficient symmetry repetition of the procedure leads to pictorial evaluation of eigenvalues and eigenfunctions simultaneously. The method uses only a reflection plane and does not require character tables, projection operators etc. as is used in group theory.

2. Outline of the approach

Let us define a linear operator $\hat{A}$ over a finite set $\{\phi_i\}$ such that

$$\langle \phi_i|\hat{A}|\phi_i\rangle = \alpha_i, \tag{1}$$

and

$$\begin{aligned}\langle \phi_i|\hat{A}|\phi_j\rangle &= \beta_{ij}, \quad \text{whenever } |i-j|=1,\\ &= 0, \quad \text{whenever } |i-j|\neq 1.\end{aligned} \tag{2}$$

We may call $\hat{A}$ an 'adjacency operator' whose matrix represents a graph G with vertices labelled by the finite set of natural numbers $\{i\}$. In G, the vertices carry weights $\alpha_1, \alpha_2, \ldots$ and the (i,j)-edge carries weight β_{ij}. The set $\{\phi_i\}$ constitutes the basis vectors describing the vertices of G.

Now if we construct a new normalised set $\{\psi_i\}$ by the linear combination

$$\psi_j = \sum_i C_{ij}\phi_i, \tag{3}$$

then

$$\langle \psi_l|\hat{A}|\psi_j\rangle = \alpha\langle \psi_l|\psi_j\rangle, \tag{4}$$

if for all ϕ_i having non-zero coefficient in ψ_j,

$$\alpha_i = \alpha. \tag{5}$$

Thus, $\langle \psi_l|\hat{A}|\psi_j\rangle = 0$, ensures orthogonality of ψ_l and ψ_j and vice versa, if condition (5) is fulfilled. So under condition (5) we can construct a new graph with vertices described by the vectors $\{\psi_i\}$ such that whenever two vertices l and j of this new graph are disconnected, the vectors ψ_l and ψ_j are orthogonal, and vice versa. If, in addition, the coefficients C_{ij} are so chosen that the secular determinant $|\mathbb{A} - E\mathbb{I}|$ of the new graph is the same as that of the old graph (or, one is a scalar multiple of the other) then three purposes are fulfilled: (a) the initial graph is factorised into two smaller, disjoint components, (b) the eigenvalues of the factor graphs are the same as those of the initial graph partitioned into two sets and (c) orthonormal basis vectors $\{\psi_i\}$ describing the vertices of the factorised new graph are obtained as linear combinations of the initial set $\{\phi_i\}$.

For factorisation of the initial graph as far as possible in order to simultaneously determine eigenvalues and eigenvectors, we require an algorithm which will produce

suitable linear combinations of the initial bases satisfying condition (5) and maintaining the secular determinant unchanged (to the extent of a scalar factor). The procedure should be repeated successively till we end up with a situation under which condition (5) is not obeyed.

3. The algorithm

Let there exist a symmetry plane (σ) in the graph G. There may be three possible cases.

3.1. *Case I, σ bisects some edges only*

In this case the vertices are divided into two sets such that the vertices in one set are mirror images of those in the other. We arbitrarily call one set 'object' and the other set 'image', the side of the σ-plane containing the object set being (+)ve and the other side (−)ve. Let the functions (ϕ) denoting these two sets of vertices be grouped as follows,

$$\begin{array}{ll} \text{object (+)ve side:} & \phi_i,\ \phi_j, \phi_k, \ldots\ldots \\ & \updownarrow\ \updownarrow\ \updownarrow \\ \text{image (−)ve side:} & \phi_m, \phi_n, \phi_p, \ldots\ldots \end{array}$$

Here the sign $\leftrightarrow$ has been used to indicate correspondence between an object and its image. We now form the following linear combinations,

$$\begin{aligned} \psi_i &= (\phi_i + \phi_m)/(2)^{\frac{1}{2}}, \quad \psi_m = (\phi_i - \phi_m)/(2)^{\frac{1}{2}}, \\ \psi_j &= (\phi_j + \phi_n)/(2)^{\frac{1}{2}}, \quad \psi_n = (\phi_j - \phi_n)/(2)^{\frac{1}{2}}, \end{aligned} \tag{6}$$

and so on. Next we draw a new graph G_1 by deleting those edges of G which were bisected by the σ-plane; increase the weights of the 'object' vertices which were linked to the deleted edges and decrease the weights of the corresponding 'image' vertices by an amount equal to the weights of the respective deleted edges. G_1 is now a factorised graph whose vertices are represented by the set $\{\psi_i\}$. The mathematical basis for this is as follows. As σ is a reflection plane, condition (5) is automatically satisfied, i.e. $\alpha_i = \alpha_m$, $\alpha_j = \alpha_n$ etc. and so according to (4), the orthonormal pairs (ψ_i, ψ_m), $(\psi_j, \psi_n), \ldots$. will represent disjoint pairs of vertices (i,m), $(j,n), \ldots$. if a new graph G_1 is drawn with $\{\psi_i\}$ as bases. The vertex and edge weights of this new graph can be obtained from actual calculation of the matrix elements $\langle\psi_i|\hat{A}|\psi_j\rangle$, and will turn out to abide by the rule just described. Thus, if the mirror image pairs of vertices i and m are joined in the initial graph G by an edge of weight β_{im}, then

$$\begin{aligned} \langle\psi_i|\hat{A}|\psi_i\rangle &= \tfrac{1}{2}[\alpha_i + 2\beta_{im} + \alpha_m] = \alpha_i + \beta_{im}, \\ \langle\psi_m|\hat{A}|\psi_m\rangle &= \tfrac{1}{2}[\alpha_i - 2\beta_{im} + \alpha_m] = \alpha - \beta_{im}, \\ \langle\psi_m|\hat{A}|\psi_i\rangle &= 0. \end{aligned} \tag{7}$$

which makes G_1 a factorised graph with new vertex weights. In the factors of G_1, we find symmetry planes wherever possible and repeat the above procedure.

At this stage it is convenient to demonstrate the procedure with some examples.

The adjacency operator $\hat{A}$ occurs in chemical graph theory for many purposes and here we use $\hat{A}$ to represent the Hamiltonian operator $\hat{H}$ in HMO formalism. In all the following examples we shall denote the initial graph by G, the graph after the first step factorisation by G_1 and so on.

Example 1 – Cyclobutadiene: The graph (G) of this system, and a mirror plane (σ) which divides the vertex basis functions as

$$\begin{array}{ll} \text{object } (+): & \phi_2 \quad \phi_3 \\ & \updownarrow \quad \updownarrow \\ \text{image } (-): & \phi_1 \quad \phi_4, \end{array}$$

have been shown in figure 1.

So according to (6) the normalised basis functions for the factorised graph G_1 are,

$$\psi_1 = \frac{1}{(2)^{\frac{1}{2}}}(\phi_2 - \phi_1), \quad \psi_2 = \frac{1}{(2)^{\frac{1}{2}}}(\phi_2 + \phi_1),$$

$$\psi_3 = \frac{1}{(2)^{\frac{1}{2}}}(\phi_3 + \phi_4), \quad \psi_2 = \frac{1}{(2)^{\frac{1}{2}}}(\phi_3 - \phi_4), \tag{8}$$

where the subscripts with ψ correspond to the initial vertex labels. As usual in HMO theory, we take $\langle \phi_i | \hat{H} | \phi_i \rangle = \alpha$ as the zero and $\langle \phi_i | \hat{H} | \phi_j \rangle = \beta$ (i, j adjacent) as the unit of energy, where the vertices i and j represent conjugated carbon atoms as in benzene. Now according to the algorithm as explained in (7) we find that the vertex weights of 1, 2, 3, and 4 are respectively -1, 1, 1, -1 (as $\alpha = 0$ and $\beta_{12} = \beta_{34} = 1$) and G_1 is graph with two disconnected fragments. Since each fragment is symmetrical we divide each by σ-planes (here, a common σ-plane) and repeating the procedure we finally get the completely factorised graph G_2 with weights 0, 2, 0, -2 for the vertices 1, 2, 3 and 4 respectively, which are described by the orthonormal functions,

$$\psi'_1 = [1/(2)^{\frac{1}{2}}](\psi_1 + \psi_4) = [1/(2)^{\frac{1}{2}}][[1/(2)^{\frac{1}{2}}](\phi_2 - \phi_1 + \phi_3 - \phi_4)]$$
$$= \tfrac{1}{2}(\phi_2 - \phi_1 + \phi_3 - \phi_4),$$
$$\psi'_2 = [1/(2)^{\frac{1}{2}}](\psi_2 + \psi_3) = [1/(2)^{\frac{1}{2}}][[1/(2)^{\frac{1}{2}}](\phi_2 + \phi_1 + \phi_3 + \phi_4)]$$
$$= \tfrac{1}{2}(\phi_1 + \phi_2 + \phi_3 + \phi_4),$$
$$\psi'_3 = [1/(2)^{\frac{1}{2}}](\psi_2 - \psi_3) = \tfrac{1}{2}(\phi_1 + \phi_2 - \phi_3 - \phi_4),$$
$$\psi'_4 = [1/(2)^{\frac{1}{2}}](\psi_1 - \psi_4) = \tfrac{1}{2}(\phi_2 - \phi_1 - \phi_3 + \phi_4),$$

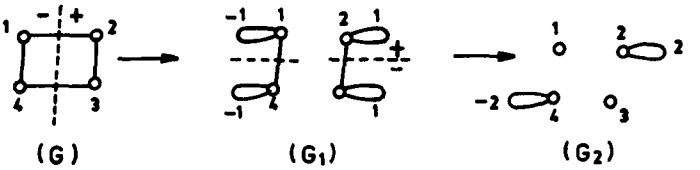

Figure 1. Factorisation of cyclobutadiene graph: case I of the algorithm.

The secular determinants $|\mathbb{A} - E\mathbb{I}|$ for G, G_1 and G_2 are respectively

$$\begin{array}{cccc} \phi_1 & \phi_2 & \phi_3 & \phi_4 \\ \hline \end{array}$$

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

(a)

$$\begin{array}{cccc} \psi_1 & \psi_2 & \psi_3 & \psi_4 \\ \hline \end{array}$$

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

(b)

$$\begin{array}{cccc} \psi'_1 & \psi'_2 & \psi'_3 & \psi'_4 \\ \hline \end{array}$$

$$\begin{vmatrix} -E & 0 & 0 & 0 \\ 0 & -E+2 & 0 & 0 \\ 0 & 0 & -E & 0 \\ 0 & 0 & 0 & -E-2 \end{vmatrix},$$

(c)

which can be easily constructed by looking at the respective graphs. The determinant (a) can be transformed into (b) by the following row and column operations carried out successively.

(i) $R_1 \to (R_1 - R_2)/(2)^{\frac{1}{2}}$, (ii) $C_1 \to (C_1 - C_2)/(2)^{\frac{1}{2}}$,

(iii) $R_2 \to [R_2 + R_1/(2)^{\frac{1}{2}}](2)^{\frac{1}{2}}$, (iv) $C_2 \to [C_2 + C_1/(2)^{\frac{1}{2}}](2)^{\frac{1}{2}}$,

(v) $C_3 \to (C_3 + C_4)/(2)^{\frac{1}{2}}$, (vi) $R_3 \to (R_3 + R_4)/(2)^{\frac{1}{2}}$,

(vii) $R_4 \to [(R_4 - R_3/(2)^{\frac{1}{2}}](2)^{\frac{1}{2}}$ and (viii) $C_4 \to (C_4 - C_3/(2)^{\frac{1}{2}})(2)^{\frac{1}{2}}$.

A hint about the required operations can be obtained from an inspection of transformations (8) necessary for the first step factorisation. The first of (8) hints at the successive row–column operations, $R_1 \to (R_1 - R_2)/(2)^{\frac{1}{2}}$, $C_1 \to (C_1 - C_2)/(2)^{\frac{1}{2}}$. The second of (8) can be written as $\psi_2 = (2)^{\frac{1}{2}}[(\phi_1 - \phi_2)/2 + \phi_2]$ which hints at the successive row–column changes, $R_2 \to (2)^{\frac{1}{2}}[R_1/(2)^{\frac{1}{2}} + R_2]$, $C_2 \to (2)^{\frac{1}{2}}[C_1/(2)^{\frac{1}{2}} + C_2]$.

Thus, (b) is identical with (a), and similarly, (c) is identical with (b) except for a multiplicative constant. So the values of E obtained by equating the determinant (c) to zero are the eigenvalues of the original graph. As (c) is completely diagonalised, we can say that the vertex weights of G_2 are eigenvalues of G. Moreover, the set $\{\psi'_i\}$ is orthonormal as the functions have been constructed satisfying conditions (4) and (5). Hence $\{\psi'_i\}$ is the set of eigenfunctions of G.

Example 2 – A cubic lattice: In this case the factorisation process following our algorithm is shown in figure 2. The eigenvalues are the vertex weights of the final factorised graph, e.g., ± 1, ± 1, ± 1, ± 3. The eigenfunctions can also be obtained very easily by following the factorisation steps shown in this figure. Thus, corresponding to the eigenvalue -1, which is the weight of the vertex 1, the eigenfunction is,

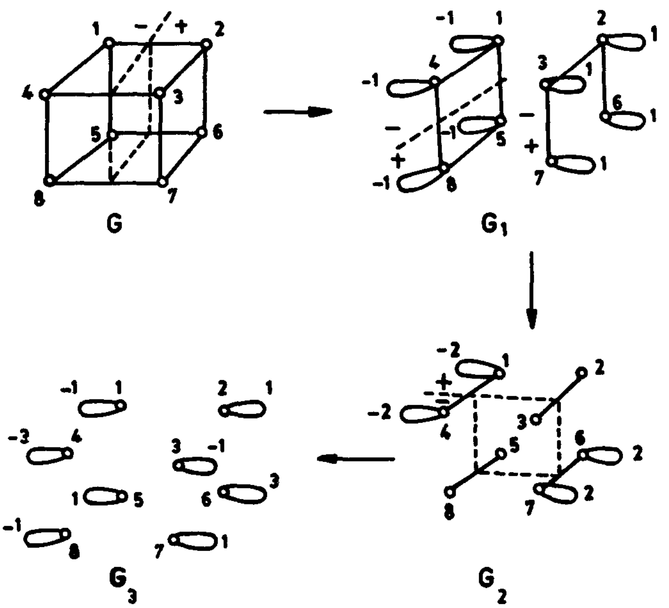

Figure 2. Factorisation of the graph for a cubic lattice: case I of the algorithm.

$$\psi_1^{(3)} = [1/(2)^{\frac{1}{2}}](\psi_1^{(2)} + \psi_4^{(2)}) = [1/(2)^{\frac{1}{2}}]\{[1/(2)^{\frac{1}{2}}][(\psi_5^{(1)} - \psi_1^{(1)}) + (\psi_8^{(1)} - \psi_4^{(1)})]\}$$
$$= [1/2(2)^{\frac{1}{2}}](\phi_1 - \phi_2 - \phi_3 + \phi_4 - \phi_5 + \phi_6 + \phi_7 - \phi_8).$$

Here and in subsequent discussions we have used the notation $\psi_k^{(i)}$ to denote the normalised function representing the kth vertex at the ith step of factorisation.

All the eigenfunctions and the corresponding eigenvalues of the cubic lattice are shown in table 1.

3.2 *Case II. σ passes through some vertices but does not bisect any edge*

Here the σ-plane divides the vertices into three sets:

Set lying on σ: $\phi_a, \phi_b, \phi_c \ldots\ldots$

object set (+): $\phi_i, \phi_j, \phi_k \ldots\ldots$

$\updownarrow \quad \updownarrow \quad \updownarrow$

image set (−): $\phi_m, \phi_n, \phi_p \ldots\ldots$

The algorithm for construction of the linear combination of ϕ's to represent the vertices of the factorised graph is,

$$\psi_x^{(1)} = \phi_x, \quad \text{for all } x \text{ lying on } \sigma,$$
$$\psi_i^{(1)} = [1/(2)^{\frac{1}{2}}](\phi_i + \phi_m), \quad \psi_m^{(1)} = [1/(2)^{\frac{1}{2}}](\phi_i - \phi_m), \tag{9}$$
$$\psi_j^{(1)} = [1/(2)^{\frac{1}{2}}](\phi_j + \phi_n), \quad \psi_n^{(1)} = [1/(2)^{\frac{1}{2}}](\phi_j - \phi_n).$$

The factorised graph with the above ϕ's as bases are obtained as follows. Delete

Table 1. Eigenvalues and eigenfunctions of a cubic lattice corresponding to figure 2.

Eigenvalue	Eigenfunction	Labels of the associated vertices
-1	$(\phi_6-\phi_5-\phi_2+\phi_1+\phi_7-\phi_8-\phi_3+\phi_4)/2(2)^{\frac{1}{2}}$	1
1	$(\phi_6+\phi_5-\phi_2-\phi_1+\phi_7+\phi_8-\phi_3-\phi_4)/2(2)^{\frac{1}{2}}$	2
-1	$(\phi_6+\phi_5-\phi_2-\phi_1-\phi_7-\phi_8+\phi_3+\phi_4)/2(2)^{\frac{1}{2}}$	3
-3	$(\phi_6-\phi_5-\phi_2+\phi_1-\phi_7+\phi_8+\phi_3-\phi_4)/2(2)^{\frac{1}{2}}$	4
1	$(\phi_6-\phi_5+\phi_2-\phi_1+\phi_7-\phi_8+\phi_3-\phi_4)/2(2)^{\frac{1}{2}}$	5
3	$(\phi_6+\phi_5+\phi_2+\phi_1+\phi_7+\phi_8+\phi_3+\phi_4)/2(2)^{\frac{1}{2}}$	6
1	$(\phi_6+\phi_5+\phi_2+\phi_1-\phi_7-\phi_8-\phi_3-\phi_4)/2(2)^{\frac{1}{2}}$	7
-1	$(\phi_6-\phi_5+\phi_2-\phi_1-\phi_7+\phi_8-\phi_3+\phi_4)/2(2)^{\frac{1}{2}}$	8

the edges connecting the vertices on the σ plane with those on the $(-)$ve side. For each deleted edge with weight β_d, multiply the weight of its mirror image by $(2)^{\frac{1}{2}}\beta_d$. Keep all the vertex weights unchanged. This algorithm also can be proved very easily. Thus, if the vertex a lies on the σ-plane and it is connected to the vertices i on the object side $(+)$ve and m on the image side $(-)$ve, then from the linear combinations shown in (8) we have

$$\begin{aligned}\langle\psi_i^{(1)}|\hat{A}|\psi_a^{(1)}\rangle &= \langle[1/(2)^{\frac{1}{2}}](\phi_i+\phi_m)|\hat{A}|\phi_a\rangle \\ &= [1/(2)^{\frac{1}{2}}](\beta_{ia}+\beta_{am}) = (2)^{\frac{1}{2}}\beta_{am} \text{ (as } \sigma \text{ is a symmetry plane)} \\ &= (2)^{\frac{1}{2}}\beta_d, \qquad (10)\\ \langle\psi_m^{(1)}|\hat{A}|\psi_a^{(1)}\rangle &= [1/(2)^{\frac{1}{2}}](\beta_{ia}-\beta_{im}) = 0, \\ \langle\psi_i^{(1)}|\hat{A}|\psi_i^{(1)}\rangle &= \langle\psi_m|\hat{A}|\psi_m\rangle = \alpha,\end{aligned}$$

and

$$\langle\psi_a^{(1)}|\hat{A}|\psi_a^{(1)}\rangle = \langle\phi_a|\hat{A}|\phi_a\rangle = 0.$$

In the last of the above set of equations it may be noted that in ψ_a the only ϕ having a non-zero coefficient is α_a and so if ϕ_a is different from the other α's, condition (5) is not violated. Thus, factorisation of pyridine by this procedure is possible.

We now demonstrate the algorithm for case II with some examples.

Example 3 – Cyclobutadiene: We have used the same system as in example 1 to verify that the algorithms for cases I and II lead to the same result. The graph (G) of this system and the derived graphs G_1, G_2 and G_3 obtained by algorithm II (the last one by algorithm I) are shown in figure 3. With ϕ_1, ϕ_2, ϕ_3 and ϕ_4 as bases, the functions describing the vertices are,

$$\begin{aligned}&\psi_1^{(1)} = \phi_1, \quad \psi_2^{(1)} = [1/(2)^{\frac{1}{2}}](\phi_2+\phi_4), \quad \psi_3^{(1)} = \phi_3, \\ &\psi_4^{(1)} = [1/(2)^{\frac{1}{2}}](\phi_2-\phi_4), \quad \text{for } G_1; \\ &\psi_1^{(2)} = [1/(2)^{\frac{1}{2}}](\psi_3^{(1)}-\psi_1^{(1)}), \quad \psi_2^{(2)} = \psi_2^{(1)}, \quad \psi_3^{(2)} = [1/(2)^{\frac{1}{2}}](\psi_3^{(1)}+\psi_1^{(1)}), \\ &\psi_4^{(2)} = \psi_4^{(1)}, \quad \text{for } G_2;\end{aligned}$$

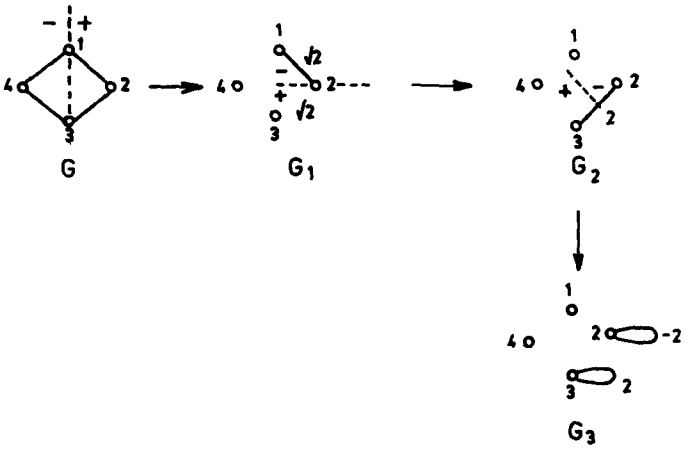

Figure 3. Factorisation of cyclobutadiene graph: case II of the algorithm.

Table 2. Eigenvalues and eigenfunctions of cyclobutadiene as obtained from figure 3.

Eigenvalue	Eigenfunction	Labels of the associated vertices
0	$(\phi_3 - \phi_1)/(2)^{\frac{1}{2}}$	1
−2	$(\phi_3 + \phi_1 - \phi_2 - \phi_4)/2$	2
2	$(\phi_3 + \phi_4 + \phi_1 + \phi_2)/2$	3
0	$(\phi_2 - \phi_4)/(2)^{\frac{1}{2}}$	4

$$\psi_1^{(3)} = \psi_1^{(2)}, \quad \psi_2^{(3)} = [1/(2)^{\frac{1}{2}}](\psi_3^{(2)} - \psi_2^{(2)}), \quad \psi_3^{(3)} = [1/(2)^{\frac{1}{2}}](\psi_3^{(2)} + \psi_2^{(2)}),$$
$$\psi_4^{(3)} = \psi_4^{(2)}, \quad \text{for } G_3.$$

The eigenvalues of cyclobutadiene are obtained from the vertex weights of G_3, and the corresponding eigenfunctions are $\psi_i^{(3)}$, $i = 1, 2, 3, 4$. These are given in terms of ϕ's in table 2. We note that the set of eigenvalues (0, 0, ± 2) is the same in both the algorithms. The eigenfunctions for the non-degenerate eigenvalues ± 2 are also found to be the same in the two algorithms. For the degenerate eigenvalues (0, 0) the eigenfunctions obtained by the two algorithms apparently differ, but any one set is acceptable because it is easy to verify that the eigenfunction set obtained by one algorithm can be converted into the other set by constructing suitable orthonormal linear combinations.

Example 4 – A tetrahedral graph: Although this graph does not represent any actual conjugated molecule in the HMO formalism we have included it to show how easily the eigenfunctions corresponding to its 3-fold degenerate eigenvalues can be computed by the present algorithm. One may obtain the eigenvalues by constructing the characteristic polynomial and equating it to zero but then difficulty arises if one attempts to obtain the 3-fold degenerate eigenfunctions by directly solving the secular equations or by recent graph-theoretical methods (Kassman 1985).

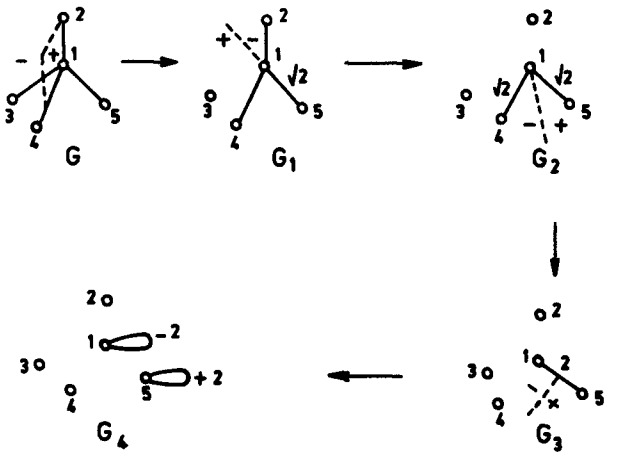

Figure 4. Factorisation of a tetrahedral graph: case II of the algorithm.

Table 3. Eigenvalues and eigenfunctions of a tetrahedral graph as obtained from figure 4.

Eigenvalue	Eigenfunction	Labels of the associated vertices
-2	$(\phi_5+\phi_4+\phi_3+\phi_2-2\phi_1)/2(2)^{\frac{1}{2}}$	1
0	$(\phi_4-\phi_2)/(2)^{\frac{1}{2}}$	2
0	$(\phi_5-\phi_3)/(2)^{\frac{1}{2}}$	3
0	$(\phi_5+\phi_3-\phi_4-\phi_2)/2$	4
$+2$	$(\phi_5+\phi_4+\phi_3+\phi_2+2\phi_1)/2(2)^{\frac{1}{2}}$	5

The tetahedral graph G and the stepwise factorised graphs G_1, G_2, G_3 and G_4 are shown in figure 4. From the completely factorised graph G_4 the eigenvalues are found to be 0, 0, 0, ± 2. The functions describing the vertices of G_1, G_2, G_3 and G_4 can be easily constructed by following the diagrams in figure 4 and are given in table 3. As G_4 is completely factorised the basis functions describing its vertices are also the eigenfunctions of G; the corresponding eigenvalues, as read off from the vertex weights of G_4, are also shown in table 3.

Example 5 – Naphthalene: The first-step factorisation of the graph (G) of this system is done by the algorithm described in case II and the second step by the algorithm of case I. The process is described in figure 5. As G_2 in this case consists of four asymmetric components, complete diagonalisation of the secular determinant of G is not possible – it can only be factorised into four blocks. This is also the case when we apply group-theoretic techniques on the HMO matrix of the naphthalene molecule (which belongs to D_{2h} point group). The eigenvalues and the basis vectors obtained from the four factor subgraphs of G_2 are shown in table 4 and when the final eigenfunctions are computed using these bases, the results agree completely with results obtained by applying group theory.

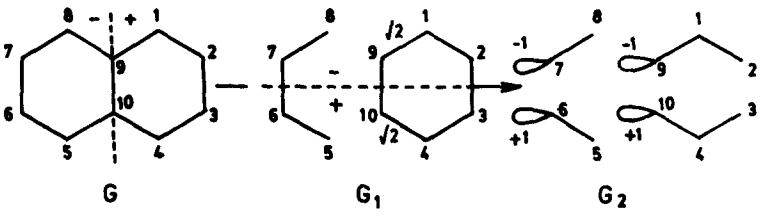

Figure 5. Factorisation of the graph of naphthalene: utilisation of cases I and II of the algorithm in separate steps.

Table 4. Eigenvalues and basis vectors describing the vertices of the final factor subgraphs of naphthalene obtained from figure 5.

Subgraphs	Eigenvalue	Basis vector
7, 8	$(-1\pm\sqrt{5})/2$	$\psi_7^{(2)}=(\phi_7-\phi_2-\phi_6+\phi_3)/2$ $\psi_8^{(2)}=(\phi_8-\phi_1-\phi_5+\phi_4)/2$
5, 6	$(1\pm\sqrt{5})/2$	$\psi_6^{(2)}=(\phi_6-\phi_3+\phi_7-\phi_2)/2$ $\psi_5^{(2)}=(\phi_5-\phi_4+\phi_8-\phi_1)/2$
1, 2, 9	$-1, (-1\pm\sqrt{13})/2$	$\psi_1^{(2)}=(\phi_1+\phi_8-\phi_4-\phi_5)/2$ $\psi_2^{(2)}=(\phi_2+\phi_7-\phi_3-\phi_6)/2$ $\psi_9^{(2)}=(\phi_9-\phi_{10})/(2)^{\frac{1}{2}}$
3, 4, 10	$1, (1\pm\sqrt{13})/2$	$\psi_3^{(2)}=(\phi_3+\phi_6+\phi_2+\phi_7)/2$ $\psi_4^{(2)}=(\phi_4+\phi_5+\phi_1+\phi_8)/2$ $\psi_{10}^{(2)}=(\phi_{10}-\phi_9)/(2)^{\frac{1}{2}}$

Example 6 – Benzene: We have chosen this example to enable one to perceive the ease with which the present algorithm can be used, as compared to the group-theoretic method of block-factorisation. Figure 6 demonstrates how the graph of benzene is factored into four components, two of which (associated with vertex-labels 5 and 6) directly give two benzene eigenvalues ± 1 and the corresponding eigenfunctions,

$$\psi_6^{(2)}=[1/(2)^{\frac{1}{2}}][\psi_5^{(1)}+\psi_6^{(1)}]=\tfrac{1}{2}(\phi_2+\phi_3-\phi_5-\phi_6), \quad \text{for } E=+1,$$

and

$$\psi_5^{(2)}=[1/(2)^{\frac{1}{2}}][\psi_5^{(1)}-\psi_6^{(1)}]=-\tfrac{1}{2}(\phi_2-\phi_3+\phi_5-\phi_6), \quad \text{for } E=-1.$$

For the component associated with vertex-labels 1 and 2, the basis vectors are,

$$\psi_1^{(2)}=[1/(2)^{\frac{1}{2}}][\psi_1^{(1)}+\psi_4^{(1)}]=[1/(2)^{\frac{1}{2}}](\phi_1+\phi_4),$$

and

$$\psi_2^{(2)}=[1/(2)^{\frac{1}{2}}][\psi_2^{(1)}+\psi_3^{(1)}]=\tfrac{1}{2}(\phi_2+\phi_3+\phi_5+\phi_6).$$

With these two as bases the secular determinant $|\mathbb{A}-E\mathbb{I}|$ for the subgraph under consideration is

$$\begin{vmatrix} -E & (2)^{\frac{1}{2}} \\ (2)^{\frac{1}{2}} & -E+1 \end{vmatrix},$$

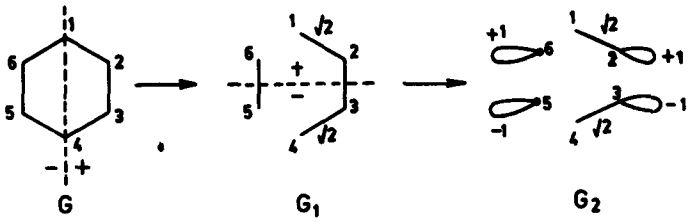

Figure 6. Factorisation of the graph of benzene: utilisation of cases I and II of the algorithm in separate steps.

which gives eigenvalues $E = -1, 2$ and the final eigenfunctions are,

$$[1/(3)^{\frac{1}{2}}]\psi_1^{(2)} + ((2)^{\frac{1}{2}}/3)\psi_2^{(2)} = [1/(6)^{\frac{1}{2}}](\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6), \quad \text{for } E = 2,$$

and

$$[(2)^{\frac{1}{2}}/3]\psi_1^{(2)} - [1/(3)^{\frac{1}{2}}]\psi_2^{(2)} = [1/2(3)^{\frac{1}{2}}](2\phi_1 - \phi_2 - \phi_3 + 2\phi_4 - \phi_5 - \phi_6), \quad \text{for } E = -1.$$

In the same way the last subgraph associated with the vertex labels 3 and 4 can be worked out.

3.3 *Case III. σ passes through a set of vertices and bisects some edge simultaneously*

In such a case we can apply the algorithms developed in cases I and II simultaneously. For example, a pyrrole-like graph can be factored into two blocks as shown in figure 7.

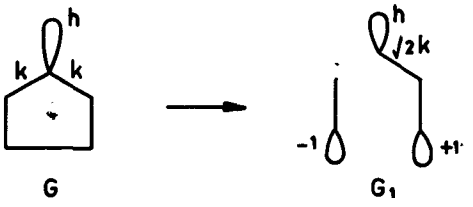

Figure 7. Factorisation of a pyrrole-like graph: illustration of case III of the algorithm.

4. Concluding remarks

The algorithms developed are, in the final form, almost the same as those used by McClelland (1982) for graphs with local symmetry. But our procedure differs in several important respects: (1) in McClelland's algorithm used for local symmetry, the symmetric components of G must be connected by a vertex (marked ● in his paper) but ours is a general procedure, applicable to symmetric components joined by vertices or edges; (2) McClelland's algorithm can be used only for unweighted graphs because the necessary unitary transformation matrix has been so designed. But our algorithm can be also used for weighted graphs and general formulas, (7) and (10), have been given for computation of the necessary vertex and edge weights required to construct the factor subgraphs.

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