Isospectral and Subspectral Molecules

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Isospectral molecules are non-identical structures which possess the same spectrum of eigenvalues. Methods for recognizing isospectrality, procedures of Heilbronner, Herndon and Živković for constructing new isospectral mates, and the specification of the relationship among the eigenvectors of the adjacency matrix of isospectral pairs are discussed here.

Instances of isospectral graphs are relatively rare. There are many cases, however, in which the spectrum of one molecular graph contains the spectrum of a second, smaller graph. In such cases, the larger, composite, graph and the smaller, component graph are said to be subspectral. Methods of McClelland, Hall and D'Amato for determining subspectrality of graphs are reviewed in detail. It appears that all known cases of subspectral molecules, but one, can be explained by various decomposition or factorization schemes.

No chemical evidence is found so far that shows a relationship among the measured properties of isospectral or subspectral molecules. However, the existence of isospectral and subspectral molecules prevented the use of characteristic polynomial for the unique characterization of molecules in various classification schemes and in computerized chemical documentation.

1. INTRODUCTION

A chemical structural (constitutional) formula is a mathematical graph. The former shows how bonds connect the different atoms in a molecule; the latter describes abstract vertices linked by edges. Throughout this article we will be concerned only with hydrogen-suppressed molecular graphs. Several reviews discuss the applications of graph theory to a wide variety of chemical properties that depend on the internal connectivity of a molecule. The connectivity of a graph is contained in its adjacency matrix. If an edge links vertices i and j then the number one appears at the intersection of the i-th row and j-th column of the adjacency matrix. If no edge connects the two vertices then the ij-th matrix element is zero. For a graph of N vertices the adjacency matrix is an \( N \times N \) symmetric array. The determinant of the adjacency matrix can be expanded to produce the characteristic polynomial of the graph which can be solved for N roots called the eigenvalues or, collectively, the spectrum of the graph. At one time it was supposed that its spectrum and characteristic polynomial might be a unique property of a graph and there-
fore graphs with identical spectra would be identical or isomorphic, but demonstrated counterexamples have shown otherwise.\textsuperscript{17-20} For some years now, examples have been known for which two or even more non-isomorphic graphs have identical characteristic polynomials and therefore identical spectra.\textsuperscript{21} Non-identical graphs with identical spectra are called isospectral\textsuperscript{2} or cospectral\textsuperscript{1} graphs.

The eigenvalues of the adjacency matrix of a graph are related to the Hückel molecular orbital energy levels of planar conjugated hydrocarbons\textsuperscript{8,8,11,22-26}. Therefore there must exist non-identical isomeric molecules which are isospectral. A classical example is provided by molecular graphs 1 and 2 corresponding to 1,4-divinylbenzene and 2-phenylbutadiene.

Their spectra are identical: Spectrum of 1 = spectrum of 2 = \((\pm 2.214, \pm 1.675, \pm 1.000, \pm 1.000, \pm 0.539)\). Such coincidences are at least very curious and they might be chemically significant.\textsuperscript{27} However, there are strong opposing views based on the photoelectron spectra of isospectral molecules, depicted by 1 and 2 above, denying any relevance of this concept for chemistry.\textsuperscript{28} On the other hand, isospectrality has found use in physics\textsuperscript{29}, not to mention applied mathematics.\textsuperscript{30-33} We feel that it is important to investigate properties of isospectral molecules and to see how their occurrence is related to properties of molecules in order to trace those which might be strongly dependent on the isospectrality of molecular skeletons.

A much larger number of instances occur in which all of the eigenvalues of one graph appear among those of another, larger graph, and the two graphs are then said to be subspectral. The smaller graph can usually be recognized as a structural fragment or component of the larger, composite graph. There are still other examples in which two or more graphs share some, but not all, eigenvalues. These are examples of partially isospectral graphs. In many cases the partial isospectrality of two graphs occurs because they share a common subspectral component.

Although a large number of papers in the mathematical literature have been concerned with isospectral graphs,\textsuperscript{12,13,20,21,30-34} only a few chemical papers have so far studied the properties of isospectral molecules.\textsuperscript{27,35-42} In this review we will summarize the work previously reported on isospectral molecules and offer comments on the much larger group of subspectral molecules. We will not pursue the problem of partially isospectral molecules nor the interesting related question of why certain eigenvalues occur much more often than others.

2. ISOSPECTRAL MOLECULES

There are three problems we wish to address concerning isospectral molecules: (1) Given two non-identical molecules, how can one tell if they are
Isospectral? (2) What are the available methods for generating isospectral molecules? (3) Given a particular molecule, is it possible to determine whether one or more isospectral mates exist and if so can one derive the isospectral partners?

2.1. Determination of Isospectrality

The first problem is the easiest to solve. Several methods exist for determining isospectrality of a pair of molecules. The obvious brute-force way is to calculate the eigenvalues of the adjacency matrix of each molecule and compare eigenvalues. If the two sets of eigenvalues match exactly, then the two molecules are isospectral. Another way is to work out the characteristic polynomial of the adjacency matrix of each molecule. If the coefficients of comparable terms in the characteristic polynomials are identical term by term then the molecules are isospectral.

The coefficients of the characteristic polynomial can be determined individually by the Coulson-Sachs procedure. A graph $G$ has the characteristic polynomial,

$$P(G; x) = \sum_{n=0}^{N} a_n x^{N-n}$$

The expressions for the first few coefficients are particularly simple. For all graphs $a_0 = 1$ and $a_1 = 0$. Then,

$$a_2 = -e$$

where $e$ is the number of edges in the graph or bonds in the molecule.

$$a_3 = -2n_3$$

where $n_3$ is the number of three-membered rings in the graph or molecule. Expressions for the coefficients of higher terms are more complicated, but there is one important generalization: every term in the expressions for the odd-numbered coefficients $a_{2k+1}$ contains a factor related to the number of odd-membered rings of size $2k + 1$ or less in the graph. Thus, for graphs containing no odd-membered rings all the odd-numbered coefficients are zero. This result shows that systems containing only even rings, such as 1 and 2, will have necessarily the graph spectrum symmetric with respect to $x = 0$. This is, possibly, the simplest proof of the pairing theorem introduced by Coulson and Rushbrooke.

The existence of Coulson-Sachs expressions for constructing the individual coefficients suggests that one could make a term-by-term calculation and comparison of characteristic polynomial coefficients for a pair of graphs; the first non-identical pair of comparable coefficients that arises would demonstrate non-isospectrality and further comparisons could be discontinued. The simplicity of the expressions for the coefficients $a_2$ and $a_3$ leads to the following simple counting rules that can quickly reveal basic differences between two graphs that prevent them being isospectral. These conditions are necessary but not sufficient for isospectrality.

1. Isospectral graphs must have the same number of vertices. The number of vertices determines the numbers of eigenvalues in the spectrum and graphs with different numbers of eigenvalues cannot be isospectral.
2. Isospectral graphs must have the same number of edges. Since $a_2 = -e$, graphs with different number of edges will have different values of $a_2$ and therefore cannot be isospectral.

3. An acyclic graph and a graph containing rings cannot be isospectral. To form a ring requires an additional edge beyond those present in the acyclic graph. Therefore, cyclic graphs necessarily have more edges and different coefficients $a_2$ than acyclic graphs.

4. Isospectral graphs without fused rings must have the same number of rings. The same number of non-fused rings assures that the graphs will have the same number of edges and the same $a_2$. For graphs with fused rings the situation is more complicated because the number of fused rings is not related to the number of edges in a linear way.

5. Isospectral graphs must have the same number of three-membered rings. Since $a_3 = -2n_3$, graph with different numbers of three-membered rings will have different values of $a_3$ and therefore cannot be isospectral.

6. Graphs containing only even-membered rings cannot be isospectral with those containing any odd-membered rings. The Coulson-Sachs expressions for all the odd coefficients $a_{2k+1}$ are zero for graphs containing no odd-membered rings. For a graph containing odd-membered rings at least one $a_{2k+1}$ must be non-zero. Another justification for this rule is based on the fact that the alternant systems contain no odd-membered rings and for every eigenvalue there is another eigenvalue of equal magnitude but opposite sign (the pairing theorem). Non-alternant systems must contain at least one odd-membered ring and their energy levels are not paired. Therefore, alternant and non-alternant systems cannot be isospectral.

Rules 1 and 2 are specific statements of the fact that isospectral molecules must be isomers. Analysis of the Coulson-Sachs expressions for higher coefficients of the characteristic polynomial might lead to further conditions for isospectrality.

Heilbronner has shown how to factor the secular determinant or characteristic polynomial of a composite molecule $C$ composed of two fragments $A$ and $B$ linked by a bond between atom $a$ in $A$ and atom $b$ in $B$. For normal homo-atomic molecules the characteristic polynomial of the composite molecule $C$ can be expressed as

$$P(C; x) = P(A; x)P(B; x) - P(A(-a); x)P(B(-b); x)$$

where $\begin{array}{c} \text{A} \\ \text{B} \end{array}$ and $\begin{array}{c} \text{A}_a \\ \text{B}_b \end{array}$ represent the characteristic polynomials of fragments $A$ and $B$, and $\begin{array}{c} \text{A}_a \\ \text{B}_b \end{array}$ are the characteristic polynomials of fragments $A$ and $B$ with atoms $a$ and $b$ removed, respectively. Equation (4) is restated below in different notation.

Factorization of this type can reduce the characteristic polynomial to smaller pieces which either can be immediately seen to be identical or else the polynomials of the fragments can be easily worked out, perhaps by the Coulson-
-Sachs procedure, and then compared for isospectrality. As an example, break up the acyclic graphs 3 and 4 across the bonds as indicated.

![Graphs 3 and 4](image)

Applying the Heilbronner factorization formula for the characteristic polynomials we obtain,

\[
\begin{align*}
\mathcal{C}_3 &= [L_5] \cdot \left[ \begin{array}{c} 1 \\ 1 \\ 1 \\
\end{array} \right] - [L_4] \cdot [L_3] \\
\mathcal{C}_4 &= [L_5] \cdot \left[ \begin{array}{c} 1 \\ 1 \\ 1 \\
\end{array} \right] - [L_3] \cdot [L_4]
\end{align*}
\]

where \([L_N]\) is the characteristic polynomial of the linear graph (chain) with \(N\) vertices and \((>)\) is the polynomial for the structure enclosed in brackets. The expressions \(\mathcal{C}_3\) and \(\mathcal{C}_4\) are identical hence the graphs 3 and 4 are isospectral mates.\(^{20}\)

Randić\(^{45}\) has proposed an interesting criterion for investigating whether two graphs are isospectral or not. He uses the fact that the characteristic polynomial is related to random walks\(^{49}\). (A random walk in a graph is a sequence of edges which can be continuously traversed, starting from any vertex and ending on any vertex, also permitting the use of the same edge several times.)\(^{18,49}\) This relationship is reflected in the identity of the information given by the characteristic polynomial and spectral moments of a graph.\(^{29}\) The random walks considered here are self-returning walks, i.e. random walks starting and ending at the same vertex. Self-returning walks starting at a vertex \(q\) are given by the \(q\)th diagonal elements of the adjacency matrix \(A\) raised to the powers \(n\): \((A^n)_{qq} n = 1, 2, \ldots, N\). For each \(n\), the spectral moment of a graph is the trace of the matrix \(A^n\). Two graphs are isospectral if they have identical sequences of spectral moments, \(n = 1, 2, \ldots, N\).

As an example, we consider the Harary-Balaban isospectral pair.\(^{17}\)

![Graphs 5 and 6](image)
Graphs 5 and 6 have identical spectral moments and thus represent isospectral mates.

Another point of view is that of deciding whether identical spectra originate from identical graphs or non-identical graphs. Randić has proposed a procedure that he claims can establish the identity of two apparently different graphs. It is based on a direct comparison of the adjacency matrices and hence he has developed a procedure for setting up these matrices uniquely.

Here we wish to mention that the procedure developed by Hall for recognizing isospectral systems is really a method for tracing the subspectral systems.

### 2.2. Construction of Isospectral Systems

The generation of isospectral molecules is a more complex problem, but several methods are available and will be reviewed here.

#### 2.2.1. Isospectral Graphs Derived from a Common Frame

Consider a graph which contains one or more pairs of vertices which have the property that the removal of each vertex in turn produces two identical or isospectral graphs. Vertices having this property may be called isospectral points or active sites. A graph containing isospectral points may serve as the common frame in a newly-constructed isospectral pair of graphs, derived from the common frame by attaching two different graphical fragments to the isospectral points in a reciprocal relationship.

The isospectral points in the styrene graph 7, for example, are the vertices labeled $a_1$ and $a_2$ in the drawing below.
Randić has produced a valuable criterion for detecting the isospectral points. The isospectral points always have identical sequences of atom self-returning walks. For the graph 7 the following list of self-returning walks for different atoms is derived from the powers of the adjacency matrix.

<table>
<thead>
<tr>
<th>Atom label</th>
<th>Self-Returning Walks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n=1</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>2 (a₁)</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>4,8</td>
<td>0</td>
</tr>
<tr>
<td>5,7</td>
<td>0</td>
</tr>
<tr>
<td>6 (a₂)</td>
<td>0</td>
</tr>
</tbody>
</table>

As expected, the positions 2 (a₁) and 6 (a₂) have identical sequences of self-returning walks.

An examination of their tabulated eigenvalues confirms the fact that the graph resulting from the removal of a₁, denoted by 7 (−a₁), and the graph resulting from the removal of a₂, denoted by 7 (−a₂), are isospectral.

(The symbol "=" is used here to signify an isospectral relationship.) Since a₁ and a₂ are isospectral points, two arbitrary graphical fragments A and B may be attached to a₁ and a₂ in a reciprocal manner (i.e., by an ordered replacement) to generate a new pair of isospectral graphs 8 and 9.
The graph 10, shown below, contains a pair of vertices whose successive removal generates a pair of identical, rather than isospectral, graphs.

Since the vertices $a_1$ and $a_2$ are isospectral points in 10, two isospectral graphs 11 and 12 may be constructed from 10 by the reciprocal attachment of two arbitrary fragments C and D at $a_1$ and $a_2$.

In many cases, the original graphical frame contains more than one pair of isospectral points. The graph 10, for example, has as a second pair of isospectral points the vertices labeled $\beta_1$ and $\beta_2$ in the illustration below.

The successive deletion of $\beta_1$ and $\beta_2$ from 10 produces the two isospectral graphs $10(-\beta_1)$ and $10(-\beta_2)$. 
It is thus possible to construct an isospectral quartet 13, 14, 15, and 16 by first attaching two fragments A and B to 10 at sites $\beta_1$ and $\beta_2$ then attaching two additional fragments C and D at sites $a_1$ and $a_2$.

Frequently, one (or both) of the isospectral graphs derived from a common frame contain its own isospectral points at which additional fragments may be substituted in a reciprocal fashion to generate a new common-frame isospectral points, denoted here by $\beta_1$ and $\beta_2$.

The vertices $\beta_1$ and $\beta_2$ are isospectral points by virtue of the fact that $2(-\beta_1)$ and $2(-\beta_2)$ are isospectral.
It should be noted at this point that, although $\beta_1$ in 2 is the same vertex as $a_2$ in the styrene frame, it is not generally true that isospectral points retain their unique properties in common-frame derivatives; here, for example, removal of $a_1$ from 2 does not produce a graph which is isospectral with or identical to the graphs $2(-\beta_1)$ and $2(\beta_2)$.

The isospectrality of common-frame graphs can be accounted for by an application of Heilbronner's decomposition theorem, as stated in Eq. (4). Consider two graphs $D_1$ and $D_2$, derived by the reciprocal attachment of two fragments (A and B) to the isospectral points ($a_1$ and $a_2$) of a common frame D, as illustrated below.

The characteristic polynomial of $D_1$ may be obtained by successive applications of Heilbronner's theorem:

$$D_1 = A^a a_1^D B - A^a a_1^D a_2^B b B$$

$$= B (A^a D - A^a a_1^D)$$

$$- B^b (A^a D^a_2 - A^a a_1^D)$$

$$= B A^a D - B A^a a_1^D - A B^b D^a_2$$

$$+ A^a b a_1^D a_2^D.$$

The characteristic polynomial of $D_2$ may be obtained in the same manner:

$$D_2 = A B D - A B^a a_1^D$$

$$- B A^a D^a_2$$

$$+ B^b a_1^D a_2^D.$$
Since the graphs \( D(-a_1) \) and \( D(-a_2) \) are either isospectral or identical, the characteristic polynomials of the graphs \( D_1 \) and \( D_2 \) are identical term-by-term; therefore \( D_1 \) and \( D_2 \) are isospectral.

2.2.2. Isospectral Graphs Derived from an Isospectral Pair

Consider a pair of graphs \( G_1 \) and \( G_2 \) which are known to be isospectral. (These graphs may be derived from a common frame, or they may be structurally unrelated). Suppose that it is possible to identify a vertex \( a_1 \) in \( G_1 \) and a vertex \( a_2 \) in \( G_2 \) such that the deletion of these vertices and their adjoining edges produces two identical or isospectral graphs. In such a case, \( a_1 \) and \( a_2 \) constitute a pair of substitution partners in the sense that a new pair of isospectral graphs may be generated by the substitution of an arbitrary graphical fragment \( R \) into \( G_1 \) at vertex \( a_1 \) and into \( G_2 \) at vertex \( a_2 \).

The isospectral graphs 17 and 18 have been studied extensively by Randić and co-workers. The vertices labeled \( a_1 \) and \( a_2 \) serve as substitution partners for these graphs, since the graphs \( 17(-a_1) \) and \( 18(-a_2) \) are identical.

From the twofold symmetry of 17 and 18, it is evident that these particular graphs contain a second pair of substitution partners equivalent to \( a_1 \) and \( a_2 \); these may be denoted by \( a_3 \) (in 17) and \( a_4 \) (in 18).
It is therefore possible to attach two arbitrary fragments $R$ and $S$ to 17 at vertices $a_1$ and $a_3$ and to 18 at vertices $a_2$ and $a_4$ to obtain two families of graphs which are isospectral for any given fragments $R$ and $S$.

Further inspection of 17 and 18 reveals yet another pair of substitution partners, for deletion of the vertices labeled $b_1$ and $b_2$ produces the graph shown below.

The most general form of the isospectral families derivable by substitution from the graphs 17 and 18 is thus:

The common-frame graphs 19 and 20 contain vertices which are substitution partners by virtue of the fact that the removal of these vertices produces two isospectral graphs, rather than two identical graphs.
Attachment of a fragment $R$ to the substitution partners of 19 and 20 leads to isospectral graphs of the form:

The generic styrene derivatives 8 and 9 have been studied at length both by Herndon and Ellzey\textsuperscript{27} and by Živković et al.\textsuperscript{36} These graphs contain two pairs of symmetry-equivalent substitution partners which may be used to construct isospectral families of the form:
(Recall that $A$ and $B$ represent arbitrary graphical fragments in 8 and 9.) It should be noted that vertices comprising substitution partners are called unrestricted substitution points by Herndon and Ellzey,\textsuperscript{27} whereas they are called active sites by Živković et al.\textsuperscript{36} in the case of 17 and 18\textsuperscript{37} and inactive sites in the case of 8 and 9.\textsuperscript{36}

The isospectrality of a pair of graphs derived by substitution from isospectral parents can be accounted for by an application of the simplified form of Heilbronner's decomposition theorem\textsuperscript{47} given in Equations (4) and (5).

Let $G_1(a_1)-R(r)$ and $G_2(a_2)-R(r)$ denote the graphs constructed by substitution of the fragment $R$ at vertices $a_1$ and $a_2$ in the isospectral graphs $G_1$ and $G_2$. Heilbronner's formula gives as the characteristic polynomial of the substituted graphs:

\begin{align}
G_1(a_1)-R(r) & = G_1 - G_1(a_1) \tag{11} \\
G_2(a_2)-R(r) & = G_2 - G_2(a_2) \tag{12}
\end{align}

Since the parent graphs $G_1$ and $G_2$ are known to be isospectral, and since $G_1(-a_1)$ and $G_2(-a_2)$ are either isospectral or identical, the characteristic polynomials of the substituted graphs are identical, and thus the substituted graphs are isospectral.

2.2.3. Properties of $L_s$ and $L_o$

Heilbronner\textsuperscript{34} has developed an elegant procedure which is useful both for accounting for observed instances of isospectrality between and among bipartite graphs and for constructing isospectral partners for certain bipartite graphs.

Suppose that the vertices of a bipartite graph (which may be considered the molecular graph of an alternant hydrocarbon)\textsuperscript{2} are numbered in such a way that the »starred« vertices are numbered 1, 2, ..., $n_s$ and the »unstarred« vertices are numbered $(n_s + 1), \ldots (n_s + n_o)$, where $n_s$ and $n_o$ represent the number of starred and unstarred vertices and, for convenience, $n_s$ is less than or equal to $n_o$. The adjacency matrix of a bipartite graph numbered in this manner has the form,\textsuperscript{25,54,55}

$$A = \begin{pmatrix} O & B \\ B^T & O \end{pmatrix},$$

since vertices in the starred set are adjacent only to vertices in the unstarred set, and vice-versa. The eigenvector of $A$ also assumes a partitioned form $(u \, v)^T$, where $u$ and $v$ represent, respectively, the coefficients of the starred and unstarred vertices.

Suppose next that $A$ is applied twice to its eigenvector. The equation may be written as

$$A^2 \begin{pmatrix} u \\ v \end{pmatrix} = \lambda^2 \begin{pmatrix} u \\ v \end{pmatrix}$$

\textsuperscript{(14)}
or as

\[
\begin{pmatrix}
BB^T & O \\
0 & B^T B
\end{pmatrix}
\begin{pmatrix}
u \\
v
\end{pmatrix} = \varepsilon^2
\begin{pmatrix}
u \\
v
\end{pmatrix}.
\]

Notice that the submatrix \(BB^T\) of the block-diagonal matrix \(A^2\) pertains only to the starred vertices and that the submatrix \(B^TB\) pertains only to the unstarred vertices. Performance of the matrix multiplication produces two equations, the first of which refers to the starred vertices alone and the second of which refers to the unstarred vertices alone.

\[
BB^T u = \varepsilon^2 u
\]

\[
B^TB v = \varepsilon^2 v.
\]

Consider now a graph \(L_s\) constructed in such a way that its adjacency matrix is given by \(BB^T\). Such a graph must contain \(n_s\) vertices and must have \(n_s\) positive eigenvalues \(\lambda\) which are related to the eigenvalues of the original graph by \(\lambda = \varepsilon^2\). Consider a graph \(L_o\) constructed in a similar fashion, so that its adjacency matrix is given by \(B^TB\). \(L_o\) must contain \(n_o\) vertices, and its spectrum must be identical to that of \(L_s\) except that the spectrum of the former contains zero as an eigenvalue \((n_o - n_s)\) times. It follows that the spectrum of the original graph may be obtained from the spectrum of \(L_s\) or from the spectrum of \(L_o\) by first listing the \(2n_s\) positive and negative square roots of \(\lambda\), them listing zero \((n_o - n_s)\) times.\(^8\)

Heilbronner has described a straightforward method for drawing the \(L_s\) and \(L_o\) graphs without actually writing out \(A\) and performing the matrix multiplication to obtain the matrices \(BB^T\) and \(B^TB\). His procedure is based on the graph theoretical theorem which states that the elements of the matrix \(A^2\) identify all walks of length 2 in the graph described\(^2\) by \(A\). When \(A^2\) is written in the partitioned form shown in equation (15), it is clear that the elements of \(BB^T\) describe the walks of length 2 from each starred vertex to each of the other starred vertices and that the elements of \(B^TB\) list the walks of length 2 from each unstarred vertex to each of the other unstarred vertices. Thus, the \(i, j\)th element of \(BB^T\) is equal to the number of different ways in which one may reach the \(j\)th starred vertex from the \(i\)th starred vertex in two steps (this can be done in only one way unless vertices \(i\) and \(j\) belong to a 4-membered cycle). The \(i, i\)th element of \(BB^T\) corresponds to the degree of the \(i\)th starred vertex, since one may describe a walk of length 2 by starting at vertex \(i\), stepping out to each neighbor of \(i\), then stepping back to \(i\). The elements of \(B^TB\) are defined in an analogous manner.

These considerations give rise to a three-step procedure for constructing \(L_s\) and/or \(L_o\) for any bipartite graph \(G\) which contains no 4-membered cycles:

1) The vertices belonging to the starred and unstarred sets are re-written separately.

2) Those vertices which are connected by a walk of length 2 in \(G\) are linked by a single edge.

3) A weight equal to its degree in \(G\) is assigned to each vertex in the new graphs.

Heilbronner's construction process is applied to the styrene graph in the illustration below.
By constructing \( L_* \) and \( L_0 \), one may rapidly verify the existence of an isospectral relationship between two bipartite graphs having the same total number of vertices. If at least one of the two graphs \( L_* \), \( L_0 \) of a graph \( G \) is identical to or isospectral with at least one of the graphs \( L'_* \), \( L'_0 \) of \( G' \), then \( G \) and \( G' \) are isospectral. A comparison of the \( L_* \) and \( L_0 \) graphs of the styrene derivatives 1 and 2, for example, shows immediately that 1 and 2 are isospectral.

It is slightly more difficult to confirm the isospectrality of the graphs 21 and 22, since neither of the graphs \( L_* (21) \), \( L_0 (21) \) is identical to \( L_* (22) \) or \( L_0 (22) \).
In this case, the spectra of the constructed graphs must actually be computed; nonetheless, the calculation involved is much simpler than that required to obtain the spectrum of 21 and 22, since the determinants which must be expanded are of order 2 × 2 and 4 × 4, rather than 8 × 8 and 8 × 8 (recall that it is only necessary to compute the $2n_\ast$ positive and negative square roots of the $n_\ast$ eigenvalues of $L_\ast$, then to list zero as an eigenvalue $n_\ast - n_\ast \times$ times).

Constructed starred and unstarred graphs (as $L_\ast$ and $L_0$ may be called) may also be used, in many cases, to construct an isospectral partner for a given bipartite graph by a wrapping procedure. Given a bipartite graph $G$ containing $n_\ast$ starred vertices and $n_0$ unstarrered vertices, it may be possible to wrap the $L_\ast$ graph of $G$ with $n_0$ vertices in such a way that a new bipartite graph $G'$ is produced, for which $L'_{\ast} = L_\ast$. In cases for which this procedure is possible, $G'$ is necessarily isospectral with $G$.

The wrapping process may be illustrated by its application to the molecular graph of 1,1-diphenylethylene 23.

As a first step, the $L_\ast$ and $L_0$ graphs are constructed by inspection of 23.

Next, seven unstarrered vertices are placed among the vertices of $L_\ast$ (23) in such a way that their edge pattern differs from that of $L_0(23)$. 
A new graph 24 is now constructed by joining the starred and unstarred vertices in the wrapped form of $L_*$ (23).

Since the $L_*$ graph of 24 is identical to the $L_*$ graph of 23, 24 must be an isospectral partner of 23. An examination of compilations of pi electron eigenvalues reveals that the common-frame molecular graphs representing 1,1-diphenylethylene and vinylbiphenyl are, in fact, isospectral. 51-53

### 2.2.4. Coefficient Regularities in Isospectral Graphs

Investigations of isospectral graphs have revealed many interesting regularities among the eigenvectors of the adjacency matrices of such graphs. Since the topological eigenvectors are identical to the molecular orbitals obtained by a simple Hückel LCAO treatment, 22 their observed regularities may be related to molecular properties, such as bond order, charge density, and free valence, which can be calculated from the Hückel MO's.

The eigenvectors of the 1,4-divinylbenzene (1) and 2-phenylbutadiene (2) graphs have been studied in detail by Živković et al. 36

These authors have pointed out that the coefficients of the vertices ($a_1$, $a_2$, $a_3$, $a_4$) which serve as substitution partners for these common frame isospectral graphs are identical (to within a sign) for a given eigenvalue. Furthermore, they note that the coefficients of the isospectral point of the common frame to which the ethylene fragment has been attached ($a_2$ in 1 and $a_1$ in 2) are
equal, as are the coefficients of the unsubstituted isospectral points of the common styrene frame ($a_1$ in 1 and $a_2$ in 2). Finally, the coefficients of the vertices within the ethylene fragment are identical in the two graphs. These relationships may be seen more clearly by examining the coefficients associated with the lowest common eingenvalue of 1 and 2 ($\varepsilon = 2.214$), as shown in the diagram below.

The relationships among the coefficients of the vertices in a generalized pair of isospectral styrene derivatives may be diagrammed, with arrows linking vertices whose coefficients are equal.

The alternation properties of the styrene frame (indicated in the diagram above by enlarged vertices) provide an explanation for the observed coefficient regularities. By applying Heilbronner's construction procedure to 8 and 9, it is immediately evident that these graphs have the same $L_*$ graph.
Clearly, the vertex $a_1$ (or $a_3$) in $L_8$ (8) is equivalent to $a_2$ ($a_4$) in $L_9$ (9), just as $a_1$ and $a_2$ in $L_8$ (8) are respectively equivalent to $a_3$ and $a_4$ in $L_9$ (9); thus these pairs of equivalent vertices necessarily have the same coefficient in $\mu$, the eigenvector of the adjacency matrix of the $L_9$ graph. Coefficient regularities in bipartite isospectral graphs sharing a frame other than styrene may be explained by a similar analysis.

Coefficient regularities among structurally unrelated isospectral graphs have not previously been described. Several regularities appear among the coefficients of the vertices of the graphs 17 and 18 (see Table I).

First, it may be noted that the coefficients of the vertices $a_1$ and $a_3$ in 17 are related by symmetry, as are the coefficients of $a_2$ and $a_4$ in 18. Secondly, as in the case of the isospectral styrene derivatives, the coefficients of the vertices which function as substitution partners in 17 and 18 are equal; that is, the coefficient of $a_1$ (or $a_3$) equals the coefficient of $a_2$ (or $a_4$), and the coefficient of $b_1$ equals the coefficient of $b_2$. The explanation for the regularities observed in this case is not readily apparent, since Heilbronner's construction procedure is not applicable to 17 and 18.

Another interesting feature of the coefficients of the two graphs may be noted. It has been observed by D'Amato\(^{40}\) that several additivity relationships exist among the coefficients of vertices in 17 and 18 and that such relationships may be predicted from certain features of the graphs $17(-a_1) = = 18(-a_2)$ and $17(-b_1) = 18(-b_2)$. These relationships and features will now be described in some detail.

Additivity relationships among coefficients in a single graph. In the graph $17(-a_1)$, it is observed that the sum of the coefficients of vertices 2 and 6 is equal to the sum of the coefficients of vertices 1 and 4 for the first, third and last eigenvalues. (The coefficients of all vertices in this graph are listed in Table II.)
<table>
<thead>
<tr>
<th>Vertex in 17</th>
<th>$\varepsilon = 2.473$</th>
<th>$\varepsilon = 1.463$</th>
<th>$\varepsilon = 0.618$</th>
<th>$\varepsilon = 0.000$</th>
<th>$\varepsilon = -1.000$</th>
<th>$\varepsilon = -1.618$</th>
<th>$\varepsilon = -1.935$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_1$</td>
<td>0.331</td>
<td>0.247</td>
<td>0.602</td>
<td>0.378</td>
<td>0.000</td>
<td>-0.372</td>
<td>0.432</td>
</tr>
<tr>
<td>$a_2$</td>
<td>0.331</td>
<td>0.247</td>
<td>-0.602</td>
<td>0.378</td>
<td>0.000</td>
<td>0.372</td>
<td>0.432</td>
</tr>
<tr>
<td>$b_1$</td>
<td>0.404</td>
<td>-0.373</td>
<td>0.000</td>
<td>-0.378</td>
<td>0.707</td>
<td>0.000</td>
<td>0.235</td>
</tr>
<tr>
<td>$c_1$</td>
<td>0.499</td>
<td>-0.273</td>
<td>0.372</td>
<td>0.000</td>
<td>-0.354</td>
<td>0.602</td>
<td>-0.227</td>
</tr>
<tr>
<td>$c_2$</td>
<td>0.499</td>
<td>-0.273</td>
<td>-0.372</td>
<td>0.000</td>
<td>-0.354</td>
<td>-0.602</td>
<td>-0.227</td>
</tr>
<tr>
<td>$c_3$</td>
<td>0.130</td>
<td>0.433</td>
<td>0.000</td>
<td>-0.756</td>
<td>-0.354</td>
<td>0.000</td>
<td>0.314</td>
</tr>
<tr>
<td>$c_4$</td>
<td>0.320</td>
<td>0.643</td>
<td>0.000</td>
<td>-0.000</td>
<td>0.354</td>
<td>0.000</td>
<td>-0.609</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Vertex in 18</th>
<th>$\varepsilon = 2.473$</th>
<th>$\varepsilon = 1.463$</th>
<th>$\varepsilon = 0.618$</th>
<th>$\varepsilon = 0.000$</th>
<th>$\varepsilon = -1.000$</th>
<th>$\varepsilon = -1.618$</th>
<th>$\varepsilon = -1.935$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_2$</td>
<td>0.331</td>
<td>0.247</td>
<td>0.602</td>
<td>-0.378</td>
<td>0.000</td>
<td>-0.372</td>
<td>-0.432</td>
</tr>
<tr>
<td>$a_4$</td>
<td>0.331</td>
<td>0.247</td>
<td>-0.602</td>
<td>-0.378</td>
<td>0.000</td>
<td>0.372</td>
<td>-0.432</td>
</tr>
<tr>
<td>$b_2$</td>
<td>0.404</td>
<td>-0.373</td>
<td>0.000</td>
<td>0.378</td>
<td>0.707</td>
<td>0.000</td>
<td>-0.235</td>
</tr>
<tr>
<td>$d_1$</td>
<td>0.225</td>
<td>0.534</td>
<td>0.372</td>
<td>0.378</td>
<td>0.000</td>
<td>0.602</td>
<td>0.147</td>
</tr>
<tr>
<td>$d_2$</td>
<td>0.225</td>
<td>0.534</td>
<td>-0.372</td>
<td>0.378</td>
<td>0.000</td>
<td>-0.602</td>
<td>0.147</td>
</tr>
<tr>
<td>$d_3$</td>
<td>0.594</td>
<td>-0.173</td>
<td>0.000</td>
<td>-0.378</td>
<td>0.000</td>
<td>0.000</td>
<td>0.683</td>
</tr>
<tr>
<td>$d_4$</td>
<td>0.404</td>
<td>-0.373</td>
<td>0.000</td>
<td>0.378</td>
<td>-0.707</td>
<td>0.000</td>
<td>-0.235</td>
</tr>
</tbody>
</table>
The vertices whose coefficients are to be added together have been labeled with $x$'s and $o$'s for ready identification; the sum of the $x$-marked vertices equals the sum of the $o$-marked vertices.

In the graph $17(-a_1)$, a similar relationship is found to exist between the sum of the coefficients of vertices 1 and 2 and the sum of the coefficients of vertices 4 and 5 for all but the second eigenvalue (see Table III).

The additivity relationships in both cases may be explained by an analysis of the matrix equation

$$A C = C \lambda,$$

where $A$ represents the adjacency matrix of a given graph, $C$ represents the matrix of its eigenvectors, and $\lambda$ represents the diagonal matrix of its eigenvalues. Examining a particular element of the matrix product on each side of equation (23), one obtains:

$$(A C)_{ij} = \sum_m A_{im} C_{mj}.$$
equations (24) and (25) may be combined to give
\[ \Sigma_{m} A_{im} C_{mj} = C_{ij} \lambda_{jj}. \]  
(26)

For a given value of \( j \), equation (26) reduces to
\[ \Sigma_{m} A_{im} c_{m} = c_{i} \lambda, \]  
(27)

where \( c_{i} \) is the coefficient of vertex \( i \) in the \( j \)th eigenvector \( c_{j} \). A particular term in the summation of the left-hand side of equation (27) is zero if no edge exists between vertices \( i \) and \( m \), whereas it has the value \( 1 \cdot c_{m} \) if an edge does exist between vertices \( i \) and \( m \). For every vertex in the graph of interest, then, there is an equation that relates the product of \( \lambda \) and the coefficient of that vertex to the sum of the coefficients of all the vertices adjacent to that vertex. (This sum rule has been exploited in previous cases.)

When the sum rule defined by equation (27) is applied to the graph \( 17 (- a_{i}) \), the following set of equations is obtained:

\[
\begin{align*}
c_2 &= c_1 \lambda \\
c_1 + c_3 &= c_2 \lambda \\
c_2 + c_4 &= c_3 \lambda \\
c_3 + c_5 + c_6 &= c_4 \lambda \\
c_4 + c_6 &= c_5 \lambda \\
c_5 + c_0 &= c_6 \lambda
\end{align*}
\]  
(28) - (33)

A comparison of the sum of equations (28) and (31) with the sum of equations (29) and (33)-or, equivalently, (29) and (32)-leads immediately to the conclusion that \( c_{1} + c_{4} = c_{2} + c_{5} \) (or \( c_{2} + c_{3} \)).

\[
\begin{align*}
(c_2 + c_5) + (c_3 + c_6) &= \lambda (c_1 + c_4) \\
(c_1 + c_4) + (c_2 + c_3) &= \lambda (c_2 + c_6)
\end{align*}
\]  
(28) + (31)  
(29) + (33)

The additivity relationships observed in the graph \( 17 (- b_{i}) \) may also be explained by, first, applying the sum rule to each vertex to generate six equations:

\[
\begin{align*}
d_2 &= d_1 \varepsilon \\
d_1 + d_3 + d_6 &= d_2 \varepsilon \\
d_2 + d_4 &= d_3 \varepsilon \\
d_3 + d_5 &= d_4 \varepsilon \\
d_4 + d_6 &= d_5 \varepsilon \\
d_2 + d_5 &= d_6 \varepsilon
\end{align*}
\]  
(34) - (39)

then comparing the sum of equations (34) and (35) with the sum of equations (37) and (38).

\[
\begin{align*}
(d_1 + d_3) + (d_2 + d_5) &= \varepsilon (d_1 + d_4) \\
(d_1 + d_3) + (d_4 + d_6) &= \varepsilon (d_2 + d_5)
\end{align*}
\]  
(34) + (35)  
(37) + (38)

Clearly, \( d_1 + d_2 = d_4 + d_5 \).
Predicting additivity relationships within a graph. The question arises as to how the additivity relationships observed in the graphs 17 (—a₁) and 17 (—b₁) might be predicted on the basis of structural features alone. Several guidelines for making such a prediction may be stated.

Examine again the graph 17 (—b₁). Notice that the x-marked vertices are connected to vertices 3 and 6, as are the o-marked vertices. Furthermore, the sum of the degrees of the x-marked vertex (four) is equal to the sum of the degrees of the o-marked vertices. These two conditions guarantee that the sum-rule equations (34) and (35) for vertices 1 and 2 together contain the same number of terms as the sum-rule equations (37) and (38) for vertices 4 and 5 and that, moreover, both sets of equations contain the terms \( d₃ \) and \( d₆ \).

In the case of 17 (—a₁), the o-marked vertices are connected to vertices 2, 3, 5, and 6, and the x-marked vertices are connected to vertices 1, 3, 4, and 5. Again, the sums of the degrees of the x-marked and o-marked vertices are equal. In this instance, however, the x and o vertices are not only connected to a common pair of vertices, as was the case in 17 (—b₁), but also connected in a reciprocal fashion to one another. The sum-rule equations for vertices 1 and 4 and the equations for vertices 2 and 6 thus contain \( c₃ \) and \( c₄ \) as common terms, and they contain the terms \((c₁ + c₄)\) and \((c₂ + c₃)\) in a reciprocal relationship.

Unfortunately, the process of searching a graph for the existence of vertices fulfilling these conditions is very tedious. The guidelines stated here may be more useful in explaining observed additivity relationships among coefficients than in predicting new ones.

Coefficient regularities in 17 and 18. The additivity relationships in the graphs 17 (—a₁) and 17 (—b₁) may now be related to certain coefficient regularities in 17 and 18.

Suppose that the x-marked vertices in 17 (—a₁) are bridged through a single vertex to produce the graph 17 and that the o-marked vertices are bridged through a single vertex to produce the graph 18.

The values of the coefficients at the marked positions have been indicated. Notice that the sum of the coefficients of the x-marked vertices in 17 is identical to the sum of the coefficients of the o-marked vertices in 18 and that the reverse is also true.
The graphs 17 and 18 may also be generated by bridging, through a single vertex, the $\times$-marked and $\circ$-marked vertices (respectively) of 17 ($= b_1$).

Again, the sum of the coefficients of the $\times$-marked vertices in 17 equals the sum of the coefficients of the $\circ$-marked vertices in 18, and vice versa.

These regularities observed here and in other cases have led D'Amato to make the following conjecture:

> Given the existence of additivity relationships such as those described for the graphs 17 ($= a_1$) and 17 ($= b_1$), it is possible to bridge the $\times$-marked vertices through a single vertex to form a new graph $G_x$ and to bridge the $\circ$-marked vertices in a similar fashion to form a new graph $G_\circ$. When this occurs, (1) $G_x$ and $G_\circ$ are either isospectral or identical; (2) the coefficient of the bridging vertex in $G_x$ is equal to the coefficient of the bridging vertex in $G_\circ$; (3) the sum of the coefficients of the $\times$-marked vertices in $G_x$ is equal to the sum of the coefficients of the $\circ$-marked vertices in $G_\circ$, and vice-versa; (4) the bridging vertices serve as substitution partners for the graphs $G_x$ and $G_\circ$.

It is hoped that one or more of these conclusions may soon be verified.

2.2.5. *Chemical Behavior of Isospectral Molecules*

No survey of current research involving isospectral graphs would be complete without addressing the question of experimentally measured chemical similarities among isospectral molecules, that is, among molecules represented by isospectral graphs. One might expect to find that the topologically dependent properties (ionization potential, oxidation or reduction potential, and so on) of isospectral molecules are closely related. This is apparently not the case, however. Heilbronner and Jones have measured the $\pi$ ionization potentials of the isospectral molecules 1,4-divinylbenzene and 2-phenylbutadiene (see Table IV) and have reported that the measured values “differ at least as much as those of any other 'nonisospectral' pair having $\pi$ systems of comparable size.” Unfortunately, no other experimental evidence is available to support or refute the findings of Heilbronner and Jones, since instances of isospectrality among molecular graphs are fairly rare. Perhaps some relationship among the
measured properties of isospectral molecules will be discovered in the future. Research in this direction is in progress. 56

**TABLE IV**

<table>
<thead>
<tr>
<th>Ionization Potentials of 1,4-Divinylbenzene and 2-Phenylbutadiene</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1,4-Divinylbenzene</td>
<td>2-Phenylbutadiene</td>
</tr>
<tr>
<td>5α\textsuperscript{+} \pi</td>
<td>3β\textsuperscript{+} \pi</td>
</tr>
<tr>
<td>4α\textsuperscript{+} \pi</td>
<td>2β\textsuperscript{+} \pi</td>
</tr>
<tr>
<td>3α\textsuperscript{-} \pi</td>
<td>2α\textsuperscript{-} \pi</td>
</tr>
<tr>
<td>20α\textsuperscript{-} σ</td>
<td>1 \beta\textsuperscript{-} \pi</td>
</tr>
<tr>
<td>2α\textsuperscript{-} \pi</td>
<td>10α\textsuperscript{-} σ</td>
</tr>
<tr>
<td></td>
<td>9α\textsuperscript{-} σ</td>
</tr>
</tbody>
</table>

* Ionization potentials are in electron volts. All values were obtained from reference 28.

An intriguing side result has come from the search for isospectral molecules. Schmidt 57 has found polycyclic conjugated molecules that have remarkably similar experimental spectra. As an example, consider the pair shown below with their first and second ionization potentials.

![Image of molecules]

These molecules have different Hückel spectra i.e., are not isospectral. In order to avoid confusion with the term isospectral, Clar and Schmidt refer to these molecules as isotopic.

### 3. SUBSPECTRAL MOLECULES

An examination of tabulated graph spectra 51-53 reveals that the occurrences of isospectral molecular graphs are rare. A much more common situation is that in which the spectra of two different molecules have one or more common eigenvalues. In some cases, the spectrum of one molecular graph contains the complete spectrum of a second, smaller (component) graph. The two graphs are then said to be subspectral. 39 Such a relationship does not require that the two molecules have the same number of vertices or edges or the same number of rings. The most important examples for chemistry would be those in which the highest occupied molecular orbitals (HOMO’s) are the same in two molecules and the lowest unoccupied molecular orbitals (LUMO’s) also match each other. Because of the pairing of bonding and antibonding energy levels in alternant hydrocarbons, 6 the coincidence of the LUMO is guaranteed if the HOMO levels match. A survey of the compilation of Hückel MO calculations reveals many examples. 54-55
Consider the eigenvalues of the bonding orbitals of butadiene, metadivinylbenzene, naphthalene, and cyclodecapentaene (25–28).

\[
\begin{array}{cccc}
0.61803 & 0.61803 & 0.61803 & 0.61803, 0.61803 \\
0.72806 & 1.0 & 1.30278 & 1.61803, 1.61803 \\
1.23992 & 1.30278 & 2.30278 & 2.0 \\
1.61803 & 1.61803 & 2.0 & \end{array}
\]

Structures 26–28 have an equal number of vertices and an equal number of eigenvalues, but they are not isospectral. They are, however, partially isospectral because their spectra contain the eigenvalues of butadiene, with which each is subspectral. In many, but not all, cases, we can identify the smaller molecule as a fragment of the larger one, just as 25 is a fragment in 26–28, with all the eigenvalues of the fragment appearing in the spectrum of the larger molecule. The trivial example of partially isospectral molecules whose spectra share only the zero eigenvalues of the non-bonding molecular orbitals will not be discussed here. Methods for enumerating the number of zeros in the graph spectrum have been reported elsewhere.

Chemically interesting cases of subspectrality are those in which both the fragment and the larger composite molecule are non-radicals and in which neither has non-bonding MO's. Therefore, we will consider only those examples in which both fragment and composite molecule have an even number of vertices.

There are several general schemes by which the spectrum of the fragment can be shown to be a part of that of the larger molecule.

3.1. Linear and Cyclic Polyenes

The energy levels of the linear system of \(N\) vertices appear in the spectrum of the cyclic system containing \(2N + 2\) vertices. Compare, for example, structures 25 and 28. The energy levels of linear and cyclic polyenes are known in analytical form.

i. Linear polyenes

\[
m_j = 2 \cos \left( \frac{j \pi}{N + 1} \right) \quad ; \quad j = 1, 2, \ldots, N
\]

ii. Cyclic polyenes

\[
m_j = 2 \cos \left( \frac{2j \pi}{K} \right) \quad ; \quad j = 1, 2, \ldots, K
\]
The energy levels of this cyclic system are

\[ m_j = 2 \cos \left( \frac{2j\pi}{2N+2} \right) = 2 \cos \left( \frac{j\pi}{N+1} \right) ; \quad j = 1, 2, \ldots, 2N+2 \]  

(42)

Thus, the spectrum of the \(2N+2\) cyclic system will contain all the eigenvalues of the \(N\) linear system.

### 3.2. Symmetric Singly Bridged Fragments

Živković and co-workers\(^{39}\) have used the Heilbronner factorization procedure\(^{47}\) to show why the eigenvalues of a fragment in some cases appear in the spectrum of the larger composite molecule. Consider the composite molecule \(G\) formed from two identical fragments \(A\) linked through a single vertex,

Using equation (4), the characteristic polynomial of \(G\) can be written as,

\[ G = A \begin{array}{c} \text{A} \end{array} \begin{array}{c} \text{A} \end{array} - \begin{array}{c} \text{A} \end{array} \begin{array}{c} \text{A} \end{array} a \begin{array}{c} \text{A} \end{array} = A \begin{array}{c} \text{A} \end{array} \begin{array}{c} \text{A} - \text{A} \end{array} \]

(43)

The characteristic polynomial of fragment \(A\) factors out of that for \(G\) and therefore the eigenvalues of \(A\) will appear in the spectrum of \(G\). This example is not very interesting because \(G\) has an odd number of vertices and therefore a non-bonding MO or a zero in its spectrum. The situation can be remedied by introducing the modification \(G'\) in which the substituent \(B\) contains an odd number of vertices and \(A\) has an even number,

Then, the characteristic polynomial of \(G'\) is given by,
The polynomial of $A$ factors out of that for $G'$, and, therefore, the spectrum of $A$ will be contained by the spectrum of $G'$. An example is structure 23, in which the fragment $A$ is benzene and $B$ is a single vertex.

Although the benzene spectrum is a component of that of 23, the HOMO's of the two molecules do not match.

### 3.3. Fragments Linked by Multiple Bridges

Using the same reasoning as that employed in the earlier work of Heilbronner, McClelland has developed the following simple rules for the decomposition of a molecule with a plane of symmetry into simpler fragments for the purpose of simplifying the characteristic polynomial or secular determinant. McClelland's approach allows one to draw two component graphs by fragmenting the composite graph along its plane of symmetry. The rules for the fragmentation process may be stated as follows:

1) The symmetry plane perpendicular to the plane of the graph divides the composite graph into two fragments or component graphs, $A$ and $B$.

2) Vertices lying on the plane of symmetry are included in the $A$ fragment.

3) The weight of the edge between a vertex lying on the plane of symmetry and a vertex not on the plane is $\sqrt{2}$.

4) If the symmetry plane bisects an edge between vertices $\mu$ and $\mu'$, then vertex $\mu$ (in $A$) is weighted $+1$ and vertex $\mu'$ (in $B$) is weighted $-1$. All other edge and vertex weights remain unchanged.
5) The eigenvalues of the composite graph may be obtained by finding the eigenvalues of the component graphs $A$ and $B$, which, should symmetry allow, might also be factorable by the application of rules 1 through 4.

McClelland's procedure may be illustrated by the application of these rules to the naphthalene (27) and cyclopentadienyl (29) graphs, as shown below.

In the diagram above, $X$ indicates an atom of weight +1 (or Coulomb integral of $a + \beta$) while 0 denotes an atom of weight $-1$ (or Coulomb integral of $a - \beta$). The quantity $\sqrt{2}$ written next to a bond indicates that the bond has a weight of $\sqrt{2}$ (the resonance integral for the bond is $\sqrt{2} \beta$). The factorization scheme described above is derived from a standard group theoretical approach to the HMO theory. McClelland demonstrated that the character table for the $C_2$ point group may be used to generate, from the $N \, 2p$, atomic orbitals $\Theta_1, \Theta_2, \ldots, \Theta_N$ comprising the molecular skeleton, $N$ symmetry-adapted orbitals $\Phi_1, \Phi_2, \ldots, \Phi_N$, which belong to either the $A$ or $B$ representation.

Let atomic orbitals paired by the symmetry operation be denoted by $\Theta_{\mu}$ and $\Theta_{\nu}$, and let the orbitals self-equivalent under the operation (that is, the orbitals lying on the symmetry plane) be denoted by $\Theta_k$. The symmetry orbitals belonging to the $A$-representation then have the form $\Theta_k$ or $\sqrt{2} (\Theta_k + \Theta_{\mu})$; the symmetry orbitals belonging to the $B$-representation have the form $\sqrt{2} (\Theta_k - \Theta_{\mu})$. Notice that, if atoms $\mu$ and $\nu$ are adjacent, then so are $\mu'$ and $\nu'$; furthermore, $\langle \Theta_{\mu} | H | \Theta_{\nu} \rangle = 0$ unless $\mu$ and $\nu$ represent the same atom or adjacent atoms. From these facts it follows that the matrix components of the Hamiltonian on the symmetry-adapted basis are given by: $\langle \Phi_{\mu} | H | \Phi_{\nu} \rangle = (\Theta_k | H | \Theta_{\mu}) = \beta$ if both or neither of the adjacent atoms $\mu$ and $\nu$ lie on the plane of symmetry; $\langle \Phi_{\mu} | H | \Phi_{\nu} \rangle = (\Theta_k | H | \sqrt{2} (\Theta_{\mu} + \Theta_{\nu})) = \sqrt{2} \beta$ if one of a pair of adjacent atoms lies on the plane of symmetry; and
Given the relationship between the Hückel parameters and the elements of the adjacency matrix of an edge- and vertex-weighted graph, the origin of McClelland's factorization rules is apparent.

Let us now consider fragments linked by multiple bridges. Consider the molecule formed from a pair of identical fragments linked across a plane of symmetry by vertices.

The bridging vertices may be bonded pairwise or they may have attached substituents which, if present, must be symmetrical with respect to the symmetry plane. Now divide into two fragments subject to the rules (2) and (3) above.

The eigenvalues of fragments , assuming is properly divided, will, therefore, appear in the spectrum of the composite molecule . Structures and serve as an example.
Two different composites may share eigenvalues because they share the same fragments. Simple examples are 26, 27, and 28, but the situation in the pair 32 and 33 is less obvious.

Structures 32 and 33 are not isospectral because of the repeated ethylene roots in 33.
The B fragments of 32 and 33 are, respectively, one and two ethylenes. Therefore, one set of \( \pm 1.0 \) eigenvalues appears in the spectrum of 32 and two sets in 33. The A fragments of 32 and 33 are identical. They are related to hexatriene, but with resonance integrals for 2–3 and 4–5 connections increased by the factor \( \sqrt{2} \).

The preceding examples all involve molecules in which vertices lie on the symmetry plane and no bonds cross the symmetry plane. These requirements ensure that at least the smaller B fragment will be obtained from the division with Coulomb and resonance integrals unchanged from those of the parent molecule.

If the symmetry plane cuts through bonds, then Coulomb integrals on both sides of the plane are changed (Rule 4) and the resulting pieces are no longer simple fragments of the composite. Consider 31 and 34.

Structure 31 is clearly a fragment of 34 but decomposition of 34 with the horizontal symmetry plane according to Rule 4 does not yield a simple hexatriene fragment.

In the diagram X signifies an atom with weight +1 (for atoms 1, 3, 4, and 6 of A (34)) while 0 denotes —1 weight (as in 1', 3', 4' and 6' of B (34)). Neither A (34) nor B (34) is identical to 31.

To see the relationship between the spectra of 31 and 34, divide 31, A (34) and B (34) vertically, cutting the 3–4 bond. Use the symbols \( Y \) and \( P \) to denote atoms with Coulomb integrals \( \alpha + 2 \beta \) (weight +2) and \( \alpha - 2 \beta \) (weight —2), respectively.
Fragments A (31) and AB (34) are identical, while B (31) matches BA (34). Since each member of the two pairs has three vertices, there should be six eigenvalues that coincide between the spectra of 31 and 34, and exactly that many matchings actually occur.

3.4. Hall’s Method for Determining Subspectral Graphs

Hall\textsuperscript{38} has demonstrated that, in the case of a bipartite graph for which a twofold symmetry operation exchanges starred and unstarred vertices, one may construct a component graph which is a contraction of the composite graph in the sense that its eigenvalues, together with their negatives, constitute the complete spectrum of the composite graph.

The mathematical basis for the construction of such a contraction graph lies in the twofold symmetry properties of the adjacency matrix of the composite graph. Suppose that the 2N vertices of the composite graph are numbered in such a way that the starred vertices are numbered 1 through N and the unstarred vertices are numbered N + 1 through 2N. The adjacency matrix of the composite graph then has the form

\[ A = \begin{pmatrix} 0 & B \\ B^T & 0 \end{pmatrix}. \]  

(46)

In order for the twofold symmetry operation, represented by

\[ S = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \]  

(47)

to commute with \( A \), the submatrix \( B \) must be symmetrical, that is, \( B = B^T \).
Consider the eigenvalue equation for $A$:
\[
\begin{pmatrix}
0 & B \\
B & 0
\end{pmatrix}
\begin{pmatrix}
u \\
v
\end{pmatrix}
= \varepsilon
\begin{pmatrix}
u \\
v
\end{pmatrix}.
\]
(48)

The subvectors $u$ and $v$ represent the coefficients of the starred and unstarred vertices, respectively. Performance of the matrix multiplication gives two equations:
\[
Bu = \varepsilon v
\]
(49)
\[
Bv = \varepsilon u
\]
(50)

Since $S$ commutes with $A$, $(u \ v)^T$ must also be an eigenvector of $S$; furthermore, the eigenvalues of $S$ are $+1$, and $-1$, since $S^2 = 1$. Thus the eigenvalue equation for $S$:
\[
\begin{pmatrix}
0 & 1 \\
1 & 0
\end{pmatrix}
\begin{pmatrix}
u \\
v
\end{pmatrix}
= \pm
\begin{pmatrix}
u \\
v
\end{pmatrix}
\]
(51)

implies that $u = \pm v$. Substitution of this relation into equations (49) and (50) produces a new eigenvalue equation:
\[
Bu = \pm \varepsilon u.
\]
(52)

It is clear from equation (52) that $u = \pm v$ is an eigenvector of $B$ with eigenvalue $+\varepsilon$ and that $u = -v$ is an eigenvector of $B$ with eigenvalue $-\varepsilon$. Hall concludes from this result that the graph containing $N$ vertices whose adjacency matrix is given by $B$ has eigenvectors identical to the $u$ eigenvectors of the original graph (to within a normalization constant) and eigenvalues which, together with their negatives, give the spectrum of the original graph. This smaller graph Hall designates as the contraction of the original graph.

Although Hall has not explicitly described the procedure by which a contraction graph may be constructed by mere inspection of a twofold symmetric composite graph, construction rules may easily be derived upon consideration of the form of the submatrix $B$.

Suppose that a twofold symmetry operation exchanges starred and unstarred vertices in a given composite graph. Let the set $m$ of starred vertices be numbered 1 through $N$, and let the set $n$ of unstarred vertices be numbered in such a way that the number assigned to each vertex in $n$ is $N$ greater than the number assigned to its symmetry partner in $m$, that is, let the vertex $n_i$ which is the symmetry partner of $m_i$ be numbered $N + i$. As a consequence of this numbering procedure, the elements of $B$ will be given by:
\[
B_{ii} = \begin{cases}
1 & \text{if } m_i \text{ and } n_i \text{ are adjacent in the composite graph,} \\
0 & \text{otherwise;} 
\end{cases}
\]
(53)
\[
B_{ij} = B_{ji} = \begin{cases}
1 & \text{if } m_i \text{ and } n_j \text{ (and therefore } n_i \text{ and } m_j \text{) are adjacent} \\
0 & \text{in the composite graph,} 
\end{cases}
\]
(54)

The rules for constructing a contraction graph may therefore be stated as follows:
1) Distinguish between the starred and unstarred vertices of the composite graph by some means, then sketch the twofold symmetry operation (reflection in a plane of symmetry, rotation about a C_2 axis, or inversion through a center of symmetry) which divides the composite graph into two symmetry-equivalent sets of vertices.

2) Number the starred and unstarred vertices by the procedure outlined above.

3) To draw the contraction graph, first draw the N vertices belonging to one of the symmetry-equivalent sets, preserving the adjacency relationships among the vertices in the set.

4) If a vertex m_i (or n_i) is adjacent to its symmetry partner n_i (m_i) in the original graph, then m_i (n_i) is weighted +1 in the contraction graph.

5) If a vertex m_i (n_i) is adjacent to a vertex n_i (m_i) in the original graph, then m_i and n_i (n_i and m_i) are joined by an edge of unit weight in the contraction graph.

These rules can be illustrated by the construction of two different contraction graphs for the naphthalene graph, as shown in Figure 1. In Figure 1 (a), the symmetry operation which exchanges starred and unstarred vertices is a twofold rotation around an axis perpendicular to the plane of the molecule.
whereas in Figure 1 (b), the twofold operation is reflection through a plane of symmetry perpendicular to the plane of the molecule. Notice that the contraction graph in (b) is identical to the A-fragment of naphthalene as derived by McClelland's procedure. It is clear that Hall's contraction process reduces to McClelland's fragmentation scheme in the case of composite graphs for which the twofold symmetry operation is a plane passing through one or more edges of the graph.

3.5. Factorization of Graphs with n-fold Symmetry

A third factorization procedure has been developed by D'Amato⁴⁰-⁴² which incorporates both McClelland's and Hall's procedures as special instances of a more general scheme for constructing the subspectral components of composite graphs possessing n-fold symmetry. The mathematical origin of this scheme is a unitary transformation upon the eigenvalue equation of the adjacency matrix of the composite graph by the matrix which represents the operation of n-fold rotation. King has reported a similar factorization procedure for graphs corresponding to polyhedra.⁷⁴ The factorization of twofold- and threefold-symmetric planar composite graphs by this procedure will now be described in detail.

3.5.1. Factorization of Graphs with Twofold Symmetry

Consider a bipartite or nonbipartite graph G characterized by a twofold symmetry operation which defines two equivalent sets of vertices r and s and, possibly, a set of vertices q which are self-equivalent under the twofold operation. The operation, which may be rotation about a twofold axis, inversion through a center of symmetry, or reflection through a plane perpendicular to the plane of the graph, need not exchange starred and unstarr ed vertices if G is a bipartite graph. The following rules may be used to construct the two graphs G⁺ and G⁻, which are the factors of G.

1) Draw the r set of vertices and all the edges connecting the members of the set. Then examine in G the vertices through which r and s are connected; for convenience, these may be called the bridging vertices.

2) If a bridging vertex r₁ is connected to its symmetry-equivalent partner s₁, then r₁ is weighted +1 in G⁺ and -1 in G⁻.

3) If r₁ is connected to a vertex s₂ which is symmetry-equivalent to a second bridging vertex r₂ in r, then the weight of the edge between r₁ and r₂ in G ( +1 if they are adjacent, zero if they are not) is increased by one unit in G⁺ and decreased by one unit in G⁻.

4) If any bridging vertex in r is connected to a q vertex in G, then the weight of the edge between the adjacent r and q vertices is \( \sqrt{2} \) in G⁺. The q vertices and their adjacent edges are omitted entirely in G⁻.

This factorization procedure is applied to the graphs corresponding to 1,2,5,6-dibenzanthracene (35), 1,2,5,6-dibenzopentalene (36), and 1,2,4,5-dibenzopentalene (37) in Figure 2. As used earlier, the symbols X and Y refer to atoms with weights +1 and +2, respectively, while 0 and P refer to atom weights -1 and -2, respectively.
The rules for constructing the component graphs by inspection of the composite graph originate in the symmetry properties of the adjacency matrix of the composite graph.

Consider first a twofold-symmetric composite graph which contains $2N$ vertices, $N$ vertices in each of the equivalent sets $r$ and $s$. (Exclude, for the present, any graph containing a set of vertices $q$ which are self equivalent under the twofold operation.) Let such a graph be denoted by $G_1$. The vertices of $G_1$ may be numbered in such a way that the number assigned to each vertex in $s$ is $N$ greater than the number assigned to its symmetry-equivalent partner in $r$. As a consequence of this numbering procedure, the adjacency matrix of $G_1$ takes the form:
\[ A(G_1) = \begin{pmatrix} B_1 & B_2 \\ B_2 & B_1 \end{pmatrix}. \] (55)

The elements of the \( N \times N \) submatrix \( B_1 \) correspond to adjacency relationships within the \( r \) set and within the \( s \) set; the elements of the \( N \times N \) symmetric submatrix \( B_2 \) represents the adjacency relationship between sets \( r \) and \( s \).

A unitary transformation on \( A(G_1) \) and its eigenvector \((u \ v)^T\) (where the subvectors \( u \) and \( v \) contain the coefficients of the \( r \) and \( s \) vertices, respectively) may be performed by the \( 2N \times 2N \) matrix representing twofold rotation:

\[ C_2 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = C_2^\dagger. \] (56)

The transformed eigenvalue equation is

\[ C_2^\dagger A(G_1) C_2 C_2^\dagger \begin{pmatrix} u \\ v \end{pmatrix} = \varepsilon C_2^\dagger \begin{pmatrix} u \\ v \end{pmatrix}. \] (57)

From the facts that (1) \( C_2 \) commutes with \( A(G_1) \); (2) \( C_2^2 = 1 \); and (3) the eigenvalues of \( C_2 \) are +1 and −1, equation (57) can be written as

\[ A(G_1) C_2^\dagger \begin{pmatrix} u \\ v \end{pmatrix} = \varepsilon C_2^\dagger \begin{pmatrix} u \\ v \end{pmatrix} = \pm \varepsilon \begin{pmatrix} u \\ v \end{pmatrix} \] (58)
or

\[ \begin{pmatrix} B_1 & B_2 \\ B_2 & B_1 \end{pmatrix} \begin{pmatrix} u \\ v \end{pmatrix} = \varepsilon \begin{pmatrix} v \\ u \end{pmatrix} = \pm \varepsilon \begin{pmatrix} u \\ v \end{pmatrix} \] (59)

Performance of the matrix multiplication in equation (59) gives

\[ B_1 v + B_2 u = \varepsilon v = \pm \varepsilon u \] (60)
\[ B_2 v + B_1 u = \varepsilon u = \pm \varepsilon v \] (61)

Clearly, \( u = \pm v \), and therefore equation (60) and (61) reduce to a single equation

\[ (B_1 \pm B_2) u = \varepsilon u \] (62)
or its equivalent

\[ (B_1 \pm B_2) v = \varepsilon v \] (63)

Thus it can be seen that \( u = +v \) is an eigenvector of \( B_1 + B_2 \), and \( u = -v \) is an eigenvector of \( B_1 - B_2 \); furthermore, the \( N \) eigenvalues of \( B_1 + B_2 \) and the \( N \) eigenvalues of \( B_1 - B_2 \) together comprise the spectrum of \( G_1 \). The graph \( G_1 \) may be factored, then, by constructing the two graphs \( G_+ \) and \( G_- \) each containing \( N \) vertices, which have as their respective adjacency matrices \( B_1 + B_2 \) and \( B_1 - B_2 \).

The relationship between the forms of \( B_1 \) and \( B_2 \) and the rules given earlier for constructing the component graphs may best be clarified by means of an example. Consider the 1,2,4,5-dibenzopentalene graph (37) shown in Figure 2.
The nonzero elements of $B_1$ (37) correspond to the adjacency relationships between and among the eight vertices within the $r$ set (or within the $s$ set); the nonzero elements of $B_2$ (37) represent the adjacency of vertices $r_1$ and $s_1$, $r_1$ and $s_2$, and $r_2$ and $s_1$.

$$B_1(VII) = \begin{pmatrix}
0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\
0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\
0 & 1 & 0 & 1 & 0 & 0 & 0 & 1 \\
0 & 0 & 1 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 0 & 1 & 0 & 1 & 0 \\
1 & 0 & 1 & 0 & 0 & 0 & 1 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0
\end{pmatrix}$$

$$B_2(VII) = \begin{pmatrix}
1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 1
\end{pmatrix}$$

It can be seen that the only nonzero diagonal element of $B_1 \pm B_2$ will be that corresponding to $r_1$:

$$(B_1 \pm B_2)_{11} = \pm 1.$$  \hfill (66)

Thus $r_1$ will be weighted $+1$ in $G_+$ and $-1$ in $G_-$; all other vertices will remain unweighted. All off-diagonal elements of $B_1 \pm B_2$ will be identical to the corresponding elements of $B_1$ except for those elements which represent the edge between $r_1$ and $r_2$:

$$(B_1 \pm B_2)_{12} = (B_1)_{12} \pm 1$$ \hfill (67)

$$(B_1 \pm B_2)_{21} = (B_1)_{21} \pm 1.$$ \hfill (68)

Therefore, the weight of the edge between $r_1$ and $r_2$ in $G_1$ (zero in this case) will increase by one unit in $G_+$ and decrease by one unit in $G_-$; the weights of all other edges will be unchanged. The origin of rules 1 through 3 (given at the beginning of this section) for constructing the subspectral components of a graph of the form of $G_1$ should now be apparent.

Suppose the composite graph of interest is identical to a graph of the form of $G_1$ except that it contains, in addition to the $r$ and $s$ vertices, a set of $n$ vertices (denoted by $q$) which are self-equivalent under the twofold operation. Let this graph be denoted by $G_1'$. The adjacency matrix of $G_1'$ can be written in the form

$$A(G_1') = \begin{pmatrix}
0 & D & D \\
D^T & B_1 & B_2 \\
D^T & B_2 & B_1
\end{pmatrix}$$

The nonzero elements of the $n \times N$ submatrices $D$ represent the edges between the $q$ vertices and the $r$ and $s$ vertices; the elements of the $N \times N$ submatrices

$$A(G_1') = \begin{pmatrix}
0 & D & D \\
D^T & B_1 & B_2 \\
D^T & B_2 & B_1
\end{pmatrix}$$
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$B_1$ and $B_2$ represent the adjacency relationships within and between sets $r$ and $s$, as previously described. (In the case of molecular graphs, $B_2$ is generally the zero matrix, since $r$ and $s$ vertices are adjacent only to $q$ vertices and not to each other.)

The matrix representing twofold rotation must now be written as

$$C_2' = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} = (C_2)^\dagger \quad (70)$$

since rotation about a twofold axis leaves the $q$ vertices unaffected. The eigenvalue equation for $A(G_1')$ becomes, under unitary transformation,

$$[(C_2)^\dagger A(G_1') C_2'] (C_2)^\dagger \begin{pmatrix} p \\ u \\ v \end{pmatrix} = \varepsilon (C_2)^\dagger \begin{pmatrix} p \\ u \\ v \end{pmatrix}, \quad (71)$$

where the subvector $p$ represents the coefficients of the $q$ vertices. Equation (71) may be written as

$$\begin{pmatrix} 0 & D & D^T \\ D^T & B_1 & B_2 \\ D^T & B_2 & B_1 \end{pmatrix} \begin{pmatrix} p \\ u \\ v \end{pmatrix} = \varepsilon \begin{pmatrix} p \\ u \\ v \end{pmatrix}, \quad (72)$$

since $C_2'$ commutes with $A(G_1')$ and since $(C_2')^2 = I$. By performing the matrix multiplication in (72), one obtains equations (73) through (75):

$$D v + D^T u = \varepsilon p \quad (73)$$

$$D^T p + B_1 v + B_2 u = \varepsilon v \quad (74)$$

$$D^T p + B_2 v + B_1 u = \varepsilon u. \quad (75)$$

The behavior of the eigenvector under transformation by $(C_2)^\dagger$ implies that, once again, $u = \pm v$. Therefore, equations (73) through (75) may be simplified in one of two ways, according to whether $u$ is equal to $+v$ or $-v$.

If $u = +v$, then equations (73) and (74) reduce to

$$2D u = \varepsilon p \quad (76)$$

$$D^T p + (B_1 + B_2) u = \varepsilon u. \quad (76)$$

From equations (76) and (77), one may reconstruct the matrix equation

$$\begin{pmatrix} 0 & 2D \\ D^T & B_1 + B_2 \end{pmatrix} \begin{pmatrix} p \\ u \end{pmatrix} = \varepsilon \begin{pmatrix} p \\ u \end{pmatrix}, \quad (78)$$

which implies that $(N + n)$ of the $(2N + n)$ eigenvalues of $G_1'$ are also eigenvalues of a graph $G_2'$, which has as its adjacency matrix

$$\begin{pmatrix} 0 & 2D \\ D^T & B_1 + B_2 \end{pmatrix}. \quad (79)$$
It is evident from the form of this matrix that $G_+'$ is identical to the $G_+$ factor of a graph of the form of $G_1$ except that the former contains a directed edge of weight 2 from each $q$ vertex to its adjacent vertex in $r$ and a directed edge of unit weight from the $r$ vertices to their neighboring $q$ vertices. Since these directed edges between $r$ and $q$ vertices do not belong to a cycle in $G_+'$, only the product of their weights is of interest, and therefore they can be replaced by two directed edges weighted $\sqrt{2}$ each, or, equivalently, by a single undirected edge weighted $\sqrt{2}$.

Referring again to equations (73) through (75), consider the second alternative, that is, that $u = -v$. In this case, the left-hand side of equation (73) reduces to zero, and the difference between equations (74) and (75) becomes

$$(B_1 - B_2)u = \varepsilon u.$$  

The second factor of $G_1'$ is the graph whose adjacency matrix is given by $B_1 - B_2$; it is therefore identical to the $G_-$ factor of $G_1$. Rules 1 through 4 for constructing the subspectral components of a graph of the form of $G_1'$ follow immediately from this analysis.

It should be noted that, in the case of a bipartite graph for which a twofold symmetry operation exchanges starred and unstarred vertices, the $G_+$ component constructed by the rules exposed earlier in this section is identical to Hall's contraction graph; compare, for example, the graph $G_+$ (35), shown in Figure 2, to the contraction graph for 1,2,5,6-dibenzanthracene drawn according to Hall's rules. In the case of graphs for which the symmetry element is a plane perpendicular to the plane of the graph, $G_+$ and $G$ are identical to McClelland's $A$-fragment and $B$-fragment, respectively; see, for example, $G_+$ (36) and $G_-$ (36) in Figure 2. The present method is thus the most general method yet developed for factoring an arbitrary twofold-symmetric composite graph into its subspectral components.

### 3.5.2. Factorization of Graphs with Threefold Symmetry

A procedure for factoring an arbitrary threefold-symmetric composite graph into its subspectral components has been developed by means of mathematical manipulations which are exactly analogous to those employed in the case of twofold-symmetric composite graphs, that is, by performance of a unitary transformation on the eigenvalue equation of the adjacency matrix of the composite graph after numbering the vertices of the composite graph in a manner consistent with its threefold symmetry. The factorization procedure and its derivation will now be described.

Consider a graph $G$ characterized by a threefold rotational operation which defines three equivalent sets of vertices $r$, $s$, and $t$ and, possibly, a self-equivalent vertex $q$ lying on the axis of rotation. The following rules may be used to construct two graphs, $G_a$ and $G_o$, such that the eigenvalues of $G_a$ and the eigenvalues of $G_o$ taken twice comprise the complete spectrum of $G$.

1) First, draw the vertices in set $r$, together with all the edges connecting members of the set. Then examine in $G$ the vertices through which $r$ is connected to $s$, $t$, and possibly $q$ (the bridging vertices of $r$).

2) If a bridging vertex $r_1$ is connected to a vertex $t_z$ which is symmetry-equivalent to a second bridging vertex $r_2$, then the weight of the undirected edge between $r_1$ and $r_2$ in $G$ (+1 if they are adjacent, zero if
they are not) is increased by one unit in $G_a$. In $G_a$, the weight of the directed edge from $r_2$ to $r_1$ is increased by $\omega = \exp(2\pi i/3)$, and the weight of the directed edge from $r_2$ to $r_1$ is increased by $\omega^* = \exp(-2\pi i/3)$. Furthermore, if these directed edges do not belong to a cycle in $G_a$, they may be replaced by an undirected edge whose weight is equal to the square root of the product of the weights of the directed edges, i.e., either $\sqrt{\omega \omega^*} = 1$ or $\sqrt{(1 + \omega)}(1 + \omega^*) = 1$.

3) If a bridging vertex $r_1$ is connected to its own symmetry partners $s_1$ and $s_2$ in $G$, then $r_1$ is weighted $+2$ in $G_a$ and $(\omega + \omega^*) = -1$ in $G_e$.

4) If $r_1$ is connected to $q$ in $G$, then the weight of the undirected edge between $r_1$ and $q$ in $G_a$ is $\sqrt{3}$; in $G_e$, this edge and the vertex $q$ are omitted.

The application of these rules may be illustrated by the examples given in Figure 3.

---

**Figure 3.** Factorization of the graphs representing acenaphthenyl (38), trimethylene-cyclopropenyl (39), and benzene (40) by the procedure of D’Amato.\(^{\text{49-51}}\)
The derivation of these rules will first be given for the type of threefold-
symmetric graph which contains \(3N\) vertices, \(N\) vertices in each of the equi-

valent sets \(r, s,\) and \(t\) (graphs containing a vertex lying on the threefold
rotational axis will be discussed in a later section). Let a graph of this type
be denoted by \(G_2\). If the vertices of \(G_2\) are numbered in such a way that the
number assigned to each vertex in \(s\) is \(N\) greater than the number assigned to
its symmetry partner in \(r\) and \(N\) less than the number assigned to its symmetry
partner in \(t\), then the adjacency matrix of \(G_1\) has the form:

\[
A (G_2) = \begin{pmatrix} B_1 & B_2 & B_3 \\ B_2 & B_3 & B_1 \\ B_3 & B_1 & B_2 \end{pmatrix}.
\] (80)

The elements of the symmetric submatrix \(B_1\) represent the adjacency relation-
ships within a single set, \(r, s,\) or \(t\); the elements of \(B_2\) and \(B_3 = (B_2)^T\) represent
the adjacency relationships between \(r\) and \(s, r\) and \(t,\) and \(s\) and \(t\).

The eigenvalue equation for \(A (G_2)\) is

\[
A (G_2) \begin{pmatrix} u \\ v \\ w \end{pmatrix} = \varepsilon \begin{pmatrix} u \\ v \\ w \end{pmatrix},
\] (81)

where the subvectors \(u, v,\) and \(w\) contain the coefficients of the \(r, s,\) and \(t\)
vertices, respectively. A unitary transformation on \(A (G_2)\) and its eigenvector
may be performed by the matrix which represents the operation of threefold
rotation:

\[
C_3 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & \omega \end{pmatrix} = C_3^\dagger
\] (82)

where \(\omega = \exp (2\pi i/3)\).

The transformed eigenvalue equation is

\[
[C_3^\dagger A (G_2) C_3] \begin{pmatrix} u \\ v \\ w \end{pmatrix} = \varepsilon \begin{pmatrix} u \\ v \\ w \end{pmatrix}
\] (83)

or

\[
\begin{pmatrix} B_1 & \omega^* B_2 & \omega B_3 \\ \omega B_2 & B_1 & \omega^* B_3 \\ \omega^* B_3 & \omega B_2 & B_1 \end{pmatrix} \begin{pmatrix} u \\ \omega w \\ \omega^* v \end{pmatrix} = \varepsilon \begin{pmatrix} u \\ \omega w \\ \omega^* v \end{pmatrix},
\] (84)

where the identities \(\omega^2 = \omega^*\), \((\omega^*)^2 = \omega\), and \(\omega \omega^* = 1\) have been employed.

Performance of the matrix multiplication gives three equations:

\[
B_1 u + (\omega^* B_2) (\omega w) + (\omega B_3) (\omega^* v) = \varepsilon u
\] (85)

\[
(\omega B_2) u + (\omega B_3) u + (\omega^* B_1) (\omega^* v) = \varepsilon \omega w
\] (86)

\[
(\omega^* B_3) u + (\omega B_1) (\omega w) + B_1 (\omega^* v) = \varepsilon \omega^* v.
\] (87)
These equations may be combined in several ways. The linearly independent combinations \((85) + \omega^* (86) + \omega (87), (85) + \omega (86) + \omega^* (87),\) and \((85) + (86) + (87)\) lead respectively to equations (88), (89), and (90):

\[
(B_1 + B_2 + B_3)(u + v + w) = \varepsilon (u + v + w) \quad (88)
\]

\[
(B_1 + \omega^* B_2 + \omega B_3)(u + \omega^* w + \omega v) = \varepsilon (u + \omega^* w + \omega v) \quad (89)
\]

\[
(B_1 + \omega B_2 + \omega^* B_3)(u + \omega w + \omega^* v) = \varepsilon (u + \omega w + \omega^* v) \quad (90)
\]

Clearly, the \(N\) eigenvalues of the matrix \((B_1 + B_2 + B_3)\), the \(N\) eigenvalues of \((B_1 + \omega^* B_2 + \omega B_3)\), and the \(N\) eigenvalues of \((B_1 + \omega B_2 + \omega^* B_3)\) together constitute the complete spectrum of \(A(G_2)\). Furthermore, since equation (90) is the complex conjugate of equation (89) and \(\varepsilon\) is real, the eigenvalues of the matrices \((B_1 + \omega^* B_2 + \omega B_3)\) and \((B + \omega B_2 + \omega^* B_3)\) are identical. Thus the graphs which have as their respective adjacency matrices \((B_1 + B_2 + B_3) = B_a\) and \((B_1 + \omega B_2 + \omega^* B_3) = B_e\) are the subspectral components of \(G_2\).

The relationship between the forms of \(B_a\) and \(B_e\) and the rules for constructing the component graphs \(G_{a,2}\) and \(G_{e,2}\) may be clarified by means of the following examples. Consider first the benzene graph (40), shown in Figure 3 and its adjacency matrix,

\[
A(40) = \begin{pmatrix}
0 & 1 & 0 & 0 & 0 & 1 \\
1 & 0 & 1 & 0 & 0 & 0 \\
0 & 1 & 0 & 1 & 0 & 0 \\
0 & 0 & 1 & 0 & 1 & 0 \\
0 & 0 & 1 & 0 & 1 & 0 \\
1 & 0 & 0 & 0 & 1 & 0
\end{pmatrix}
\]

Notice that \((B_a)_{12} = (B_e)_{21} = 1\), since \(r_1\) is adjacent to \(r_2\), and that \((B_a)_{21} = (B_e)_{12} = 1\), since \(r_1\) is adjacent to \(t_2\) and \(r_2\) to \(s_1\). \(B_a\) and \(B_e\) thus have the form,

\[
B_a = (B_1 + B_2 + B_3) = \begin{pmatrix}
0 & 2 \\
2 & 0
\end{pmatrix}
\]

\[
B_e = (B_1 + \omega B_2 + \omega^* B_3) = \begin{pmatrix}
0 & 1 + \omega^* \\
1 + \omega & 0
\end{pmatrix}
\]

These matrices can be considered the adjacency matrices of the edge-weighted graphs \(G_a (40)\) and \(G_e (40)\), shown in Figure 3.

As a second example, the graph 39 in Figure 3 has the adjacency matrix,

\[
A(39) = \begin{pmatrix}
0 & 1 & 1 & 0 & 1 & 0 \\
1 & 0 & 0 & 0 & 0 & 0 \\
1 & 0 & 0 & 1 & 0 & 1 \\
0 & 1 & 0 & 0 & 0 & 0 \\
1 & 0 & 1 & 0 & 0 & 1 \\
0 & 0 & 0 & 0 & 1 & 0
\end{pmatrix}
\]
The nonzero elements of $B_1$ are $(B_1)_{11} = 1$, since $r_1$ is connected to $r_2$; the nonzero elements of $B_2$ and $B_3$ are $(B_2)_{11} = (B_3)_{11} = 1$, because $r_1$ is connected to both $s_1$ and $t_1$. $B_a$ and $B_e$ are therefore given by

$$B_a = (B_1 + B_2 + B_3) = \begin{pmatrix} 2 & 1 \\ 1 & 0 \end{pmatrix}$$  \hspace{1cm} \text{(95)}$$

$$B_e = (B_1 + \omega B_2 + \omega^* B_3) = \begin{pmatrix} \omega + \omega^* & 1 \\ 1 & 0 \end{pmatrix} = \begin{pmatrix} -1 & 1 \\ 1 & 0 \end{pmatrix}$$  \hspace{1cm} \text{(96)}$$

Again, these may be considered the adjacency matrices of the vertex-weighted graphs $G_a$ (30) and $G_e$ (39), also shown in Figure 3. The origin of rules 1 through 3 for constructing the component graphs of composite graphs of the form of $G_2$ should now be apparent.

Suppose that the composite graph of interest is identical to a graph of the form of $G_2$ except that it contains an additional vertex $q$ which lies on the axis of rotation. Let this graph be denoted by $G_2'$. The adjacency matrix of $G_2'$ can then be written in the form

$$A(G_2') = \begin{pmatrix} 0 & D & D & D \\ D^\tau B_1 & B_2 & B_3 \\ D^\tau B_3 & B_1 & B_2 \\ D^\tau B_2 & B_3 & B_1 \end{pmatrix}.$$  \hspace{1cm} \text{(97)}$$

The nonzero element of the $1 \times N$ vector $D$ represents the edge between $q$ and each of the sets $r$, $s$, and $t$; the $N \times N$ submatrices $B_1$, $B_2$, and $B_3$ represent the adjacency relationships within and among the sets $r$, $s$, and $t$, as previously described.

The matrix representing threefold rotation must now be written as

$$C_3' = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & \omega \end{pmatrix} = (C_3')^t,$$  \hspace{1cm} \text{(98)}$$

since rotation about the threefold axis leaves $q$ unaffected. The eigenvalue equation for $A(G_2')$,

$$A(G_2') \begin{pmatrix} p \\ u \\ v \\ w \end{pmatrix} = \varepsilon \begin{pmatrix} p \\ u \\ v \\ w \end{pmatrix}$$  \hspace{1cm} \text{(99)}$$

(where $p$ is the coefficient of the vertex $q$), becomes under unitary transformation:

$$\begin{pmatrix} 0 & D & \omega^* D & \omega D \\ D^\tau & B_1 & \omega^* B_3 & \omega B_2 \\ \omega D^\tau & \omega B_2 & B_1 & \omega^* B_3 \\ \omega^* D^\tau & \omega^* B_3 & \omega B_2 & B_1 \end{pmatrix} \begin{pmatrix} p \\ u \\ w \end{pmatrix} = \varepsilon \begin{pmatrix} p \\ u \\ w \end{pmatrix}.$$  \hspace{1cm} \text{(100)}$$
Performance of the multiplication gives

\[ D u + (\omega^* D) (\omega w) + (\omega D) (\omega^* v) = \varepsilon p \]  
\[ D^T p + B_1 u + (\omega^* B_2) (\omega w) + (\omega B_2) (\omega^* v) = \varepsilon u \]  
\[ \omega D^T p + (\omega B_2) u + B_1 (\omega w) + (\omega^* B_3) (\omega^* v) = \varepsilon \omega w \]  
\[ \omega^* D^T p + (\omega^* B_2) u + (\omega B_3) (\omega w) + B_1 (\omega^* v) = \varepsilon \omega^* v. \]

Once again, equations (101) through (104) may be combined in several ways. Consider first a simplified form of equation (101) and the linear combination (102) + $\omega^*$ (103) + $\omega$ (104):

\[ D (u + v + w) = \varepsilon p \]  
\[ 3 D^T p + (B_1 + B_2 + B_3) (u + v + w) = \varepsilon (u + v + w). \]

From (105) and (106) can be reconstructed the matrix equation:

\[
\begin{pmatrix}
0 & D \\
3 D^T & B_1 + B_2 + B_3
\end{pmatrix}
\begin{pmatrix}
p \\
u + v + w
\end{pmatrix} = \varepsilon
\begin{pmatrix}
p \\
u + v + w
\end{pmatrix}
\]  

which implies that $(N + 1)$ of the $(3N + 1)$ eigenvalues of $G_2'$ are also eigenvalues of a graph $G_2$ which has as its adjacency matrix the first matrix on the left-hand side of equation (107). It is evident from the form of this matrix that $G_2'$ is identical to $G_2$ except that the former contains a directed edge of unit weight from an $r$ vertex to $q$ and a directed edge of weight 3 from $q$ to the $r$ vertex. Since these directed edges between $r$ and $q$ do not belong to a cycle in $G_2'$, only the product of their weights is of interest, and therefore they may be replaced by a single undirected edge weighted $\sqrt{3}$.

Consider next a second, linearly independent combination of equations (102) through (104), (102) + (103) + (104):

\[ (1 + \omega + \omega^*) D^T p + (B_1 + \omega B_2 + \omega^* B_3) (u + \omega w + \omega^* v) = \varepsilon (u + \omega w + \omega^* v). \]

Since $(\omega + \omega^*) = -1$, equation (108) reduces to equation (90); the second subspectral component of $G_2'$ has as its adjacency matrix $(B_1 + \omega B_2 + + \omega^* B_3) = B_e$ and is therefore identical to $G_e$. Rules 1 through 4 for constructing the subspectral components of a composite graph of the form of $G_2'$ follow immediately from this analysis.

It should be noted that the mathematical manipulations employed here for the case of graphs with twofold and threefold symmetry can be applied to the treatment of planar graphs with higher-fold rotational symmetry. By numbering the vertices of such graphs in a manner consistent with their symmetry properties, and by choosing an appropriate matrix by which to perform the unitary transformation, rules may easily be developed for factoring symmetric composite graphs into their subspectral components. The general treatment presented here should prove useful for future investigations of graph spectral regularities.

3.6. Other Cases

Although most examples of subspectral coincidences can be explained by the various decomposition or factorization schemes described here, a few
others cannot. For instance, the eigenvalues of $31$ are contained in the spectrum of $41$. 

But decomposition of $41$ along its plane of symmetry produces neither fragments directly related to $31$ nor pieces that can be further reduced by the symmetry rules. Randić\textsuperscript{7,8} has recently shown that a molecular orbital coefficient sum rule, based on nodal properties of the molecular orbitals, can explain the subspectral coincidences of $31$ and $41$. Furthermore, the sum rule scheme can be used to construct other cases of subspectrality for which the methods described earlier do not apply.

3.7. Chemical Behavior of Subspectral Molecules

As in the case of isospectral molecules, the topologically-dependent properties of subspectral molecules seem to bear little relationship to one another. As shown in Table V, the ionization potentials of the subspectral molecules pentacene, naphthalene, and butadiene are quite dissimilar, as are the ionization potentials of ethylene, benzene, anthracene, and 1,1-diphenylethylene. Even those molecules which share HOMO/LUMO eigenvalues differ widely in their

<table>
<thead>
<tr>
<th>Common HMO Eigenvalue</th>
<th>Pentacene</th>
<th>Naphthalene</th>
<th>Butadiene</th>
<th>Ethylene</th>
<th>Benzene</th>
<th>Anthracene</th>
<th>1,1-diphenylethylene</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon = 0.6180$</td>
<td>$A_{1u}$ 7.93</td>
<td>$A_{1u}$ 8.12</td>
<td>$B_g$ 8.12</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\varepsilon = 1.0000$</td>
<td>$B_{2u}$ 8.35</td>
<td>$B_{3u}$ 8.91</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$B_{1g}$ 9.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\varepsilon = 1.3028$</td>
<td>$A_{1u}$ 9.80</td>
<td>$B_{1g}$ 10.08</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\varepsilon = 1.6180$</td>
<td>$B_{2g}$ 10.85</td>
<td>$A_u$ 11.25</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\varepsilon = 2.0000$</td>
<td>$B_{3g}$ 13.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\varepsilon = 2.3028$</td>
<td>$B_{2u}$ 10.26</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
UV-visible absorption characteristics and in their oxidation and reduction potentials, as shown in Table VI.

**TABLE VI**

*Physicochemical Properties of Molecules Sharing HOMO/LUMO Eigenvalues*

<table>
<thead>
<tr>
<th>Subspectral Pair</th>
<th>Common Eigenvale <em>a</em></th>
<th>Reduction Half-Cell <em>b</em> Potential (volts)</th>
<th>Oxidation Half-Cell <em>b</em> Potential (volts)</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzene</td>
<td>ε = 1.0000</td>
<td>λ₁ = 261</td>
<td>&lt; -2.5</td>
</tr>
<tr>
<td>ethylene</td>
<td></td>
<td>λ₂ = 174</td>
<td>≤ -2.5</td>
</tr>
<tr>
<td>naphthalene</td>
<td>ε = 0.6180</td>
<td>λ₁ = 311</td>
<td>-2.50</td>
</tr>
<tr>
<td>1,3-butadiene</td>
<td></td>
<td>λ₁ = 217</td>
<td>-2.64</td>
</tr>
<tr>
<td>pyrene</td>
<td>ε = 0.4450</td>
<td>λ₃ = 335</td>
<td>-2.11</td>
</tr>
<tr>
<td>1,3,5-hexatriene</td>
<td></td>
<td>λ₃ = 266</td>
<td>-2.65</td>
</tr>
</tbody>
</table>

*a* Values were obtained from reference 76.  
*b* Values were obtained from reference 77.

**A. Concluding Remarks**

The fact that the characteristic polynomial does not uniquely represent the topology of a molecule ended attempts to produce a sorting device, based on either the characteristic polynomial or the connectivity (adjacency) matrix for coding and retrieving chemical structures in computer oriented systems. One can see clearly how a notation system based on the adjacency matrix would have had excellent storage characteristics. However, the failure of this approach triggered attempts to find other graph-theoretical polynomials or topological indexes which could perhaps distinguish isospectral molecules.

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IZOSPEKTRALNE I SUBSPEKTRALNE MOLEKULE

S. S. D'Amato, B. M. Gimarc i N. Trinajstić

Izospektralne molekule su strukture, koje posjeduju identične Hückelove spektre. Opisane su različite graf-teorijske metode za prepoznavanje izospektralnosti i za konstrukciju novih izospektralnih struktura.

Subspektralne molekule su različite strukture, kod kojih Hückelov spektar veće strukture sadrži cijeli ili dio spektra manje strukture. Prikazani su vrlo detaljno graf-teorijski pristupi za studiranje subspektralnosti. Pokazalo se da se svi poznati slučajevi subspektralnih molekula, osim jednoga, mogu objasniti pomoću metoda dekompozicije odgovarajućih grafova.

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