CROATICA CHEMICA ACTA CCACAA **49** (1) 89—100 (1977)

CCA-979

YU ISSN 0011—1643
539.19:516
Note

On the Topological Spectra of Composite Molecular Systems*

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Received April 8, 1976

It has been shown that topological spectrum of some large molecules comprises the complete set of eigenvalues of the topological matrix of some of their constituting fragments. Several relationships between the coefficients of the fragmental eigenvectors and those of the composite system have been derived. Some sufficient conditions that a system comprise a spectrum of its parts have been found and their use illustrated.

In the early applications of semiempirical MO methods the problem of the fragmentation of a large secular determinant received a considerable attention[1-4]. Heilbronner[3] presented a formula** which connects the characteristic polynomial of a composite molecule C obtained by joining the two components A and B at positions a and b with a bond h (see Figure 1), C≡A—B, and the characteristic polynomials of components A and B, respectively,

$$C\,(x) \equiv [A\,(x) + q_a\, A^a\,(x)]\,[B\,(x) + q_b\, B^b\,(x)] - h^2\, A^a\,(x)\, B^b\,(x) \qquad (1)$$

where C(x), A(x), and B(x) are the characteristic polynomials of molecules C, A, and B, respectively. Similarly, $A^a(x)$ and $B^b(x)$ are the characteristic polynomials of the fragments of the initial molecules which are obtained after the removal of atoms a and b from molecules A and B. q and h represent parameters which characterize the nature of the atoms and bonds, respectively. We use in eq. (1) the symbol ≡ (identically equal) to emphasize that the equality is valid for every value of the variable x.

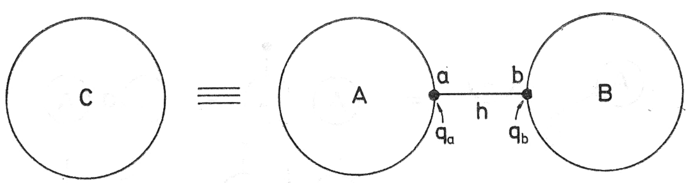


Figure 1. Schematic representation of a composite molecule.

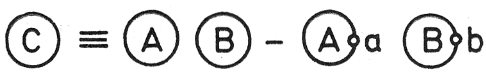
* Reported in part at the Quantum Chemistry School, Repino near Leningrad, U.S.S.R., December 1973, Contribution No. 191 of the Laboratory of Physical Chemistry.

** Recently Schwenk[5] has somewhat generalized this particular result of Heibronner.

Since the graph-theoretical formalism[6] is much more convenient for the generalization of this rather specific result of Heilbronner, eq. (1) can be symbolically rewritten as follows*,

(2)

where symbol ○ represents the characteristic polynomials of the corresponding graphs, whilst ○ represents the characteristic polynomials of the subgraphs obtained after the vertex and all incident edges joining it to other vertices have been removed. However, for graph-theoretical considerations the above relationship of Heilbronner is too general and may be further simplified by taking $q_a = q_b = 0$ and $h = 1$, which acknowledge the fact that in graphs one does not ordinarily recognize the different character of individual vertices or edges[7]. Then:



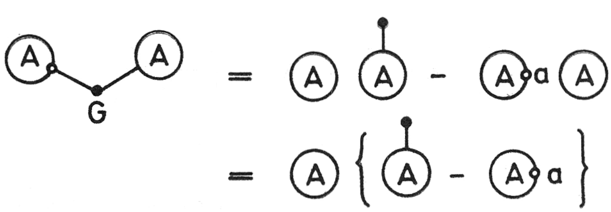
(3)

On the basis of relation (3) one can derive a theorem relating a part of the spectrum of the composite molecule to the spectrum of one of its component molecules.

Theorem

*Graphs having two or more identical fragments linked via a single vertex (of degree not higher than 3)**, or through a bridge*** in which the fragment itself makes the linkage, contain the complete spectrum of their fragments.*

Instead of presenting a detailed proof of the theorem (this proof is analogous to the proof of the theorem concerning the construction of isospectral molecules and graphs[10,11]) we will illustrate it on a simple system. A generalization to the more complicated systems is straightforward. Let us consider a system consisting of two identical fragments Ⓐ linked *via* a single vertex. Using relation (3) we can write symbolically,



(4)

* In order to avoid confusion in notation the graph vertices will be denoted with full dots throughout this paper.

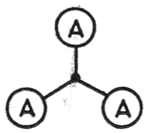
** This side condition is not a necessary but a sufficient one.

*** Note, the bridge consists of vertices and incident edges only (see text below).

where A and A represent the characteristic polynomials of the subgraphs of graph G, whereas Aa is the characteristic polynomial of the fragment obtained by excising vertex a which connects A with the rest of the system. It is precisely the property of G that forms the basis for other more general situations. We will show several interesting special cases of graphs satisfying the Theorem.

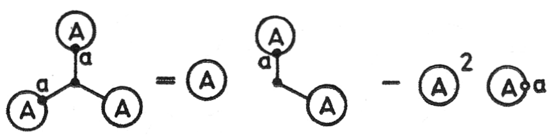
Examples

(*i*) A molecule of the type



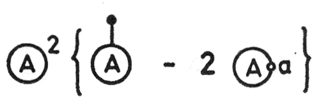
(5)

contains in its spectrum the spectrum of part A twice. Namely, by applying the fragmentation relationship once we obtain:



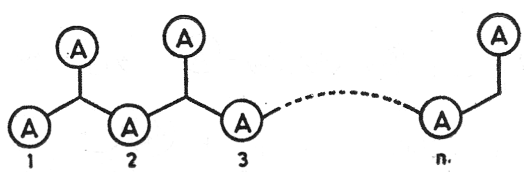
(6)

Since A^{a}—A also contains A, as stated in the above illustrative proof, eq. (6) reduces to



(7)

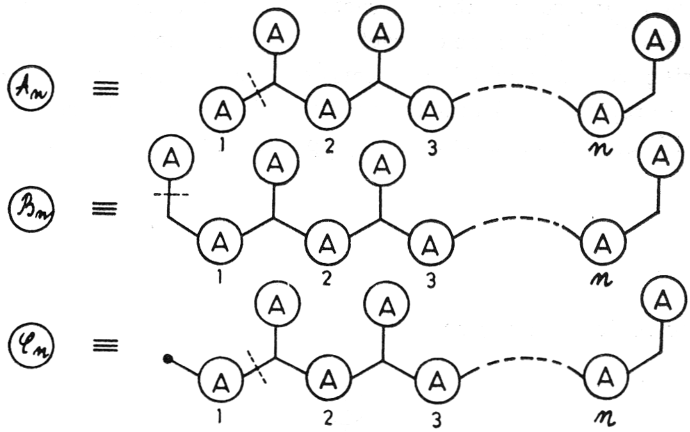
(*ii*) The above example may be generalized. A polymeric molecule contains



(8)

in its spectrum the spectrum of fragment A n times. The proof is given below.

Let us represent symbolically the following polymeric molecules



(9)

(10)

(11)

$\mathcal{A}_n$ and $\mathcal{C}_n$ may be considered to be subgraphs of graph $\mathcal{B}_n$. Using fragmentation relation (3) the following recurrence formulae are obtained:

$$\mathcal{A}_n = A\left\{ \mathcal{B}_{n-1} - A\; \mathcal{A}_{n-1} \right\} \;;\; n \geqslant 1 \qquad (12)$$

$$\mathcal{B}_n = A\; \mathcal{C}_n - A\; \mathcal{A}_n \qquad (13)$$

$$\mathcal{C}_n = A\; \mathcal{B}_{n-1} - A\; A\; \mathcal{A}_{n-1} \qquad (14)$$

Hence, by introducing (12) into (13) one obtains the following expression:

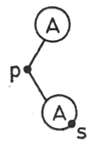
$$\mathcal{B}_n = A\left\{ \mathcal{C}_n - A\left[\mathcal{B}_{n-1} - A\; \mathcal{A}_{n-1} \right] \right\} ;\; n \geqslant 1 \qquad (15)$$

Similarly, the substitution of (15) into (14) yield the relation:

$$\mathcal{C}_n = A\left\{ A\left[\mathcal{C}_{n-1} - A\left| \mathcal{B}_{n-2} - A\; \mathcal{A}_{n-2} \right| \right] - A\; \mathcal{A}_{n-1} \right\} ; n \geqslant 2 \qquad (16)$$

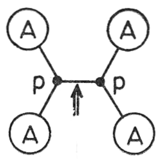
According to eqs. (12), (15), and (16) graphs $\mathcal{A}_n$, $\mathcal{B}_n$ and $\mathcal{C}_n$ contain in their spectrum the complete spectrum of fragment A. This procedure can be recurrently repeated, leading finally to the result that $\mathcal{A}_n$ and $\mathcal{B}_n$ contain n times in their spectra the spectrum of the fragment A, and that $\mathcal{C}_n$ contains (n-1) times in its spectrum the spectrum of the same fragment.

(*iii*) Molecules obtained by a link of two representative fragments of the type

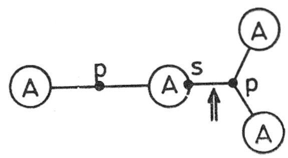


(17)

through a bridge connecting directly vertices p or by a link of the same two fragments through a bridge connecting vertex p of one fragment with a vertex s of the other, will also contain the spectrum of fragment A twice. Thus graphs



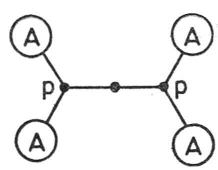
and



(18)

contain A^2 The edge linking two terminal parts is indicated by an arrow. To confirm that these graphs comprise the spectrum of A twice, fragmentation relationship (3) should be applied to the vertices of the edge indicated.

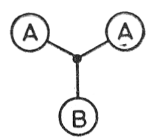
(*iv*) The molecular systems obtained by linking the fragments of type (17) *via* a residual (which can in a special case be a single vertex) will also contain the spectrum of the fragment A twice. Thus graph (19) comprises



(19)

the spectrum of A^2. Futhermore, the above graph also contains the complete spectrum of the constitutive fragment (17).

(*v*) A molecule of the type



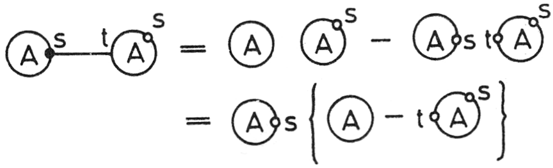
(20)

contains in its spectrum the spectrum of fragment A.

In addition, we wish to mention that a supplement to the theorem may be proposed, such as,

A molecule of the type A^s—A^s *contains in its spectrum the complete spectrum of its fragment* A$_s$

The proof may be carried out following the fragmentation procedure:



(21)

Examples of this case are given in Figure 2.

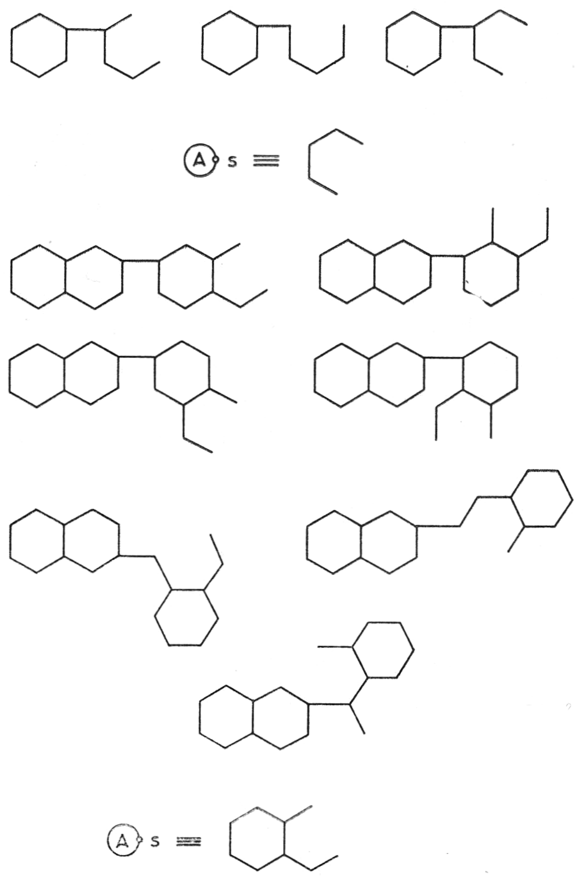


Figure 2. Examples of graphs (A)—(A)s comprising the complete spectrum of fragment (A)s.

One can derive many analogous relations for cases in which a compound is contained once, twice or several times in a composite systems. In the next section the approach is extended to the consideration of eigenvectors of a fragment and those of a system which comprise the spectrum of the fragment.

EIGENVECTORS OF A COMPOSITE SYSTEM AND OF FRAGMENTS

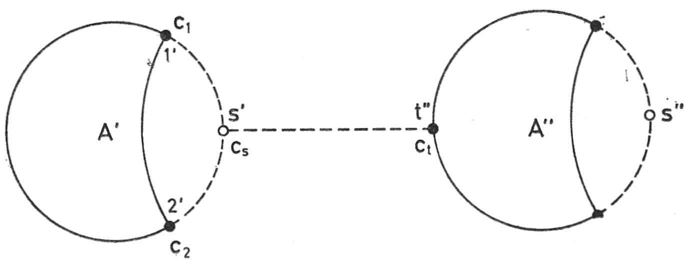
Again we will consider a special case as an example, as this suffices to indicate all the relevant properties of the system built from more general constituting parts.

Let ψ_{A^s} be an eigenfunction* of the adjacency matrix[6] of a subgraph A s (obtained after the removal of a vertex s from the constitutive graph A) and let the corresponding eigenvalue be x_i. The eigenfunction ψ_{A^s} is a linear combination of the atomic orbitals associated with individual vertices completely defined by a set of n-1 numbers (where n is the number of vertices in a graph A) and representing topological orbital, TO. The analogy with the molecular orbital is apparent in situations where one atomic orbital per atom is employed. Each vertex (atom) μ of a system (molecule) gives rise to one condition of the type:

$$x_i \, c_\mu + \sum_{\nu \neq \mu} c_\nu = 0 \tag{22}$$

where c_ν is the TO-coefficient at vertex ν and the summation is extended over all vertices connected to vertex μ**.

We shall now consider two such systems A' s and A'' s and their respective TO's: ψ''_{A^s} and ψ'_{A^s} (see Figure 3).



Ψ'_{A^s} Ψ''_{A^s}

Figure 3. Schematic representation of fragments leading to a composite system.

* For the sake of brevity in the following text we will refer to an eigenfunction of the adjacency matrix simply as a topological orbital (TO).

** This is, in fact, equivalent to an identical relationship valid in the Hückel MO theory[12].

Any linear combination of ψ'_{A^s} and ψ''_{A^s} is also an eigenfunction of the system composed of these two units, as long as the two parts are independent of each other, *i. e.*, if there is no edge, signifying interaction, between them. The coefficients of TO ψ'_{A^s} at positions $1'$ and $2'$ are c_1 and c_2, respectively, while the coefficient of TO ψ''_{A^s} at position t'' (where fragment (A') is connected to fragment (A'')) is c_t. If we now introduce edges $(1', s')$, $(2', s')$, and (s', t''), then TO

$$\psi = a\,\psi'_{A^s} + b\,\psi''_{A^s} \tag{23}$$

where

$$a\,(c_1 + c_2) = -\,b\,c_t \tag{24}$$

satisfies condition (22) and hence it is, up to the normalization factor, a TO of the composite system (Figure 4).

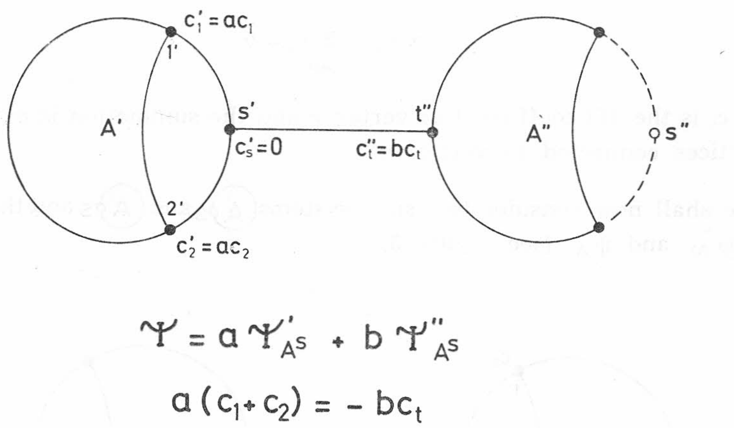


Figure 4. Schematic representation of a composite system connected by a single edge (s, t).

The conditions imposed by vertices $1'$, $2'$, and t'' are automatically fulfilled, since the TO coefficient at position s' vanishes. The condition imposed by vertex s', *i. e.*:

$$x\,c_s' + c_1' + c_2' + c_t'' = 0 \tag{25}$$

is satisfied by virtue of relation (24). In the special case of $c_1 = -\,c_2$, ψ reduces to ψ''_{A^s}, whereas when $c_t = 0$ it reduces to ψ'_{A^s}.

Using the above approach one can, in a similar way, obtain the corresponding relations among the coefficients of the other examples given previously. Some examples of actual molecules having the property of comprising the spectrum of their fragments are illustrated in Figure 5. when fragment (A) is benzene or naphthalene.

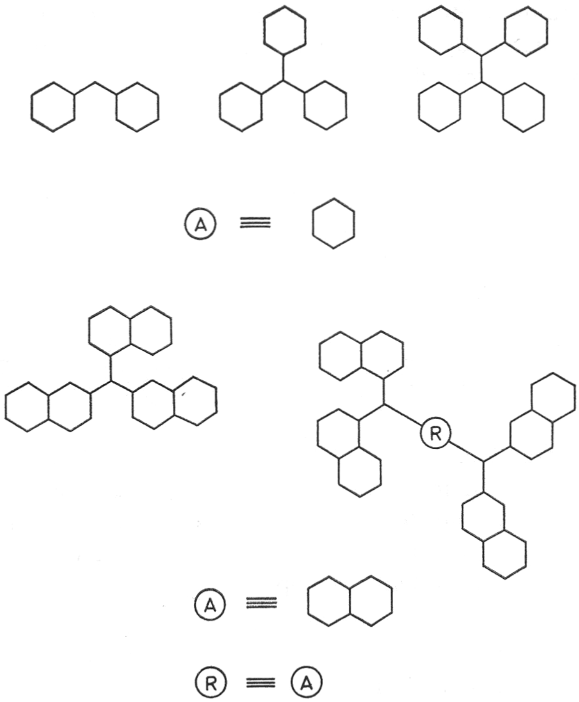
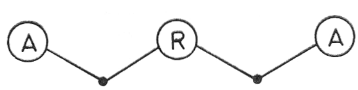


Figure 5. Examples of graphs comprising the spectrum of their fragments.

Note that in the case of naphthalene derivatives it is irrelevant whether the substituent is attached at an alpha- or beta-position.

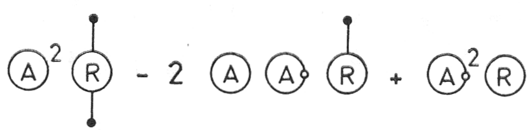
SOME SUFFICIENT CONDITIONS THAT A SYSTEM COMPRISE THE TOTAL SPECTRUM OF ITS FRAGMENTS

We shall proceed by examining systems which have several identical fragments and have not been incorporated in the previous procedure for the construction of composite systems comprising eigenvalues of their fragments as they show such a property only under special conditions. Let us consider a composite system of the form:*



(26)

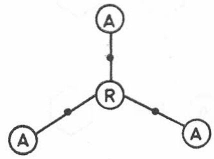
By applying fragmentation relationship (3) in succession one obtains that the characteristic polynomial of such a system can be written in the form:



(27)

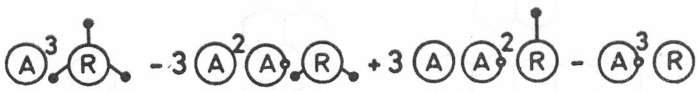
* Note, that this case is similar to case (18).

There is no common factor in the above decomposition, hence no fragment that will be comprised by the spectrum of the whole. However, if R = A such a factor exists. Similarly from:



(28)

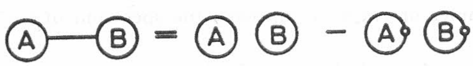
one obtains the expresion:



(29)

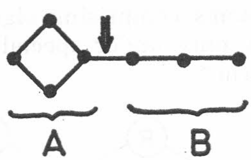
Again, in the special case when R = A, the common factor assures that the system contain the spectrum of its fragment A. Note, however, the binomial character of the above two decompositions. The very procedure of derivation of these expressions reveals their combinatorial origin. Thus, the generalization to other similar systems is apparent.

The above approach illustrates the way of formulating some sufficient conditions on a system that contains the eigenvalues of its fragment. Let us consider once again fragmentation relation (3):



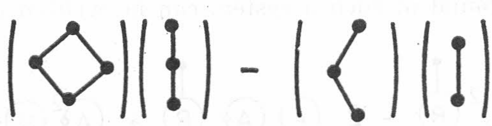
(30)

The sufficient conditions that the composite system comprise the spectrum of its fragment are that either B = A or B = A.
In both cases one of the two factors in the binomial expression on the right hand side of eq. (30) is identical. The situation is illustrated below. Consider a graph



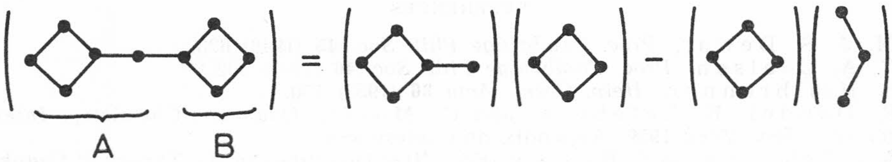
(31)

By applying relationship (30) one obtains for the form of the characteristic polynomial



(32)

The common factor is the characteristic polynomial of subgraphs B. Another example, in which B is now the monocyclic four-vertices ring system, gives

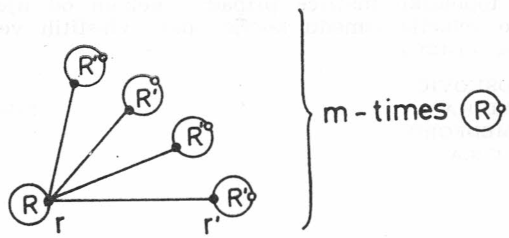


(33)

The brackets symbolize the characteristic polynomial of the fragment embraced. Such graphs may be constructed with any residual R. They will have the following form:

(34)

They consist of R and R', where the prime denotes an excise of a single vertex. Many graphs will satisfy the above general condition, however, they nevertheless represent a special class of graphs characterized by the unique property that their spectrum comprises the spectrum of fragment R'. Thus, the spectrum of R' is at the same time partially the spectrum of the system R—R', and one can refer to such graphs as *subspectral graphs,* and to R' as *subspectral component.* One should recognize the fact that the edge r—r' defines uniquely the subdivision of the composite graph. Moreover, vertex r, but not r', can be the site used for the construction of even larger systems obtained by attaching additional residuals to it, *i. e.* (35),



(35)

is the most general subspectral system. This becomes apparent by the application of fragmentation relation (3). The endformula for this case is given by

$$R'^{\,m}\left[R - m\,R'\right] \tag{36}$$

All the previously considered examples are special cases of the above general subspectral graph. In addition, we can see that the origin of the excessive degeneracy often occurring in the Hückel approach, and which has been traced back to a higher symmetry of molecular graphs as compared to the symmetry of molecular skeletons[13], does in fact depend on the nature of R' and its occurence and not on the symmetry properties of R in the cases of subspectral graphs.

Acknowledgements. We would like to thank the referees for their valuable and extensive comments.

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SAŽETAK

O topološkim spektrima složenih molekularnih sustava

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Pokazano je da topološki spektar nekih velikih molekula sadrži potpuni skup vlastitih vrijednosti topološke matrice pripadne nekom od njegovih fragmenata. Izvedeno je nekoliko relacija između koeficijenata vlastitih vektora fragmenta i cijeloga molekularnog sustava.

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Prispjelo 8. travnja 1976.