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On molecular graphs and digraphs of annulenes and their spectra

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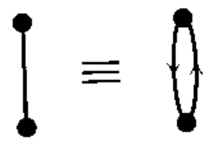
A molecular graph, consisting of undirected edges, can be represented as a sum of two digraphs, consisting of oppositely oriented directed edges. In the case of annulenes, the eigenvalue spectrum of the molecular graph is equal to the sum of the eigenvalue spectra of the respective two molecular digraphs.

Keywords: molecular graph, molecular digraph, annulene, spectrum (of graph).

INTRODUCTION

In the standard graph representation of organic molecules[1,2] edges represent covalent chemical bonds (usually between two carbon atoms). These edges are assumed to be undirected, as is the entire molecular graph. On the other hand, an undirected edge can always be viewed as being equivalent to a pair of oppositely oriented directed edges:



Bearing in mind that a covalent bond is formed by a pair of electrons of oppositely oriented spins, the right-hand side of the above diagram (as well as the entire concept of molecular graph) gets a new interpretation. Such a view of molecular graphs was elaborated in some details by one of the present authors.[3]

An unidrected graph G can be decomposed into a pair of digraphs, G and G^*, containing oppositely oriented directed edges.[4] It may be said that G is the sum of the diagraphs G and G^*, and write $G = G + G^*$.

For instance, the azulene graph can be decomposed as follows:

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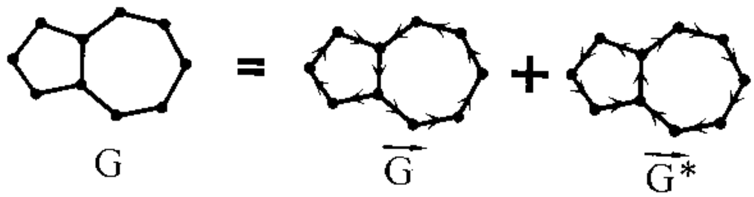
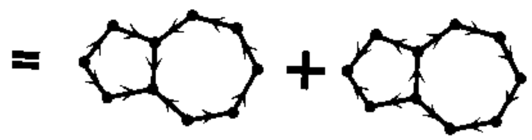


(A)

Clearly, this is not the only possible digraph decomposition of the azulene graph, as the examples (B) and (C) show:

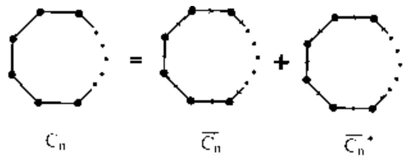
(B)



(C)

Of particular importance are the digraph decompositions of molecular graphs of conjugated -electron systems, in which there are directed cycles, such as (A) and (B). The directed cycles in such molecular digraphs provide a model for the behavior of the -electrons in an external magnetic field and are thus relevant for the theory of ring currents and aromaticity.[3,5–8]

The molecular graphs representing annulenes are the (undirected) cycles C_n, n = 3,4,... . They have a unique decomposition into directed cycles C_n and $C^*{}_n$:



In what follows, it will be demonstrated that the directed cycles have another unique property: the sum of their eigenvalues is equal to the eigenvalue of the undirected cycle. In order to do this a few general properties of the spectra of (molecular) digraphs have to be established.

SOME PROPERTIES OF THE SPECTRA OF DIGRAPHS

The spectrum of a digraph G is the collection of the eigenvalues of its adjacency matrix $A(G)$. The adjacency matrix $A(G^*)$ is the transpose of $A(G)$. Therefore one has:

Theorem 1. The digraphs G and G^* have equal spectra.

Because $A(G)$ is not symmetric, the eigenvalues of a digraph may be complex numbers. However, if a complex number z belongs to the spectrum of G, then also its complex conjugate z^* belongs to the spectrum. This has the following cosequence.

Let the digraph G possess n vertices and let its eigenvalues be denoted by $_1(G)$, $_2(G), \ldots, \ _n(G)$.

Theorem 2. The eigenvalues of the digraphs G and G^* can always be labeled so that for all $k = 1,2, \ldots, n$, $\ _k(G) + \ _k(G^*)$ has a real-value.

Proof. If $\ _k(G)$ is real-valued, then choose $\ _k(G)^*$ to be equal to $\ _k(G)$. Then, of course, $\ _k(G) + \ _k(G^*)$ is also real-valued and Theorem 2 holds.

If $\ _k(G)$ is complex-valued, then choose $\ _k(G^*)$ to be equal to $\ _k(G^*)$, which also is an eigenvalue of G. Theorem 2 follows from the fact that the sum of a complex number and its conjugate is real-valued.

Theorem 3. (a) If G does not possess directed cycles, then all its eigenvalues are equal to zero. (b) If G does possess directed cycles, then at least one of its eigenvalues is positive and real, and at least three of its eigenvalues are non-zero.

Proof. The Sachs theorem[1,9,10] as formulated for digraphs has to be applied.[9] If the characteristic polynomial of G is written in the form

$$(G, \quad) = \ ^n + \sum_{K \quad 1}^{n} a_k \ ^{n-k} \tag{1}$$

then

$$a_k = \sum_{S} (-1)^{p(S)} \tag{2}$$

with the summation going over all k-vertex subgraphs S of G that consist entirely of directed cycles; the number of directed cycles in S is p(S).

Note that the digraphs considered in this paper possess no directed 1- and 2-cycles, and therefore from (2) follows $a_1 = a_2 = 0$.

If directed cycles are absent from G, then $a_k = 0$ for all $k = 1,2, \ldots, n$ and the characteristic polynomial (1) assumes the form $(G, \quad) = \ ^n$. From this, part (a) of Theorem 3 follows immediately.

If G has at least one directed cycle, then by (2) at least one a_k is non-zero, implying that not all eigenvalues are equal to zero. Then, from the Perron-Frobenius theorem,[10] one eigenvalue of G must be positive. As $a_1 = 0$, the sum of the eigenvalues is equal to zero. As $a_2 = 0$, the sum of the squares of the eigenvalues is equal to zero. Therefore, at least one pair of eigenvalues must be complex-valued. This implies part (b) of Theorem 3.

Part (b) of Theorem 3 cannot be improved since digraphs with exactly one positive and two complex-valued eigenvalues (*e.g.,* the directed triangle: $_1 = 1$, $_2 = -1/2 + i\sqrt{3}/2$, $_3 = -1/2 - i\sqrt{3}/2$) exist.

A RELATION BETWEEN THE SPECTRA OF THE ANNULENE GRAPHS AND DIGRAPHS

In this section, it is assumed that the eigenvalues of G and G^* are labeled as described in the Proof of Theorem 2, namely so that the sum $_k(G) + \ _k(G^*)$ is real-valued.

As is well known,[1,10] the eigenvalues of any (undirected) graph G are real-valued.

In the general case, the eigenvalues $_k(G)$ are not related either to the eigenvalues of G or to the sum $_k(G) + \ _k(G^*)$. At least, the present authors cannot envisage such a relation. The annulene graphs C_n seem to provide a noteworthy exception. Namely, the eigenvalues of C_n and C_n are related.

Theorem 4. If $C_n = C_n + C_n{}^*$, such that C_n is a directed cycle, then $_k(C_n) = \ _k(C_n) + \ _k(C_n{}^*)$ hold for all $k = 1,2, \ldots , n$ and for all $n = 3,4, \ldots$.

Proof. The fact that

$$_k(C_n) = 2 \cos \frac{2 \ k}{n} \quad ; \quad k = 1,2, \ldots, n \tag{3}$$

is well known.[1,10]

It will now be shown that

$$(C_n, \ ) = \ ^n - 1$$

To do this formula (2) is applied, noting that the only directed cycle contained in C_n is C_n itself. Consequently, $a_1 = a_2 = \ldots = a_{n-1} = 0$ and $a_n = -1$, because $p(C_n) = 1$.

Now, the eigenvalues of C_n are the solutions of the equation $(C_n, \ ) = 0$, *i.e.,* of $^n - 1 = 0$. These are just the n-th roots of unity:

$$_k(C_n) \quad \exp \frac{2i \ k}{n} \quad \cos \frac{2 \ k}{n} \quad i \sin \frac{2 \ k}{n}; \quad k = 1,2,\ldots, n. \tag{4}$$

Consequently, the eigenvalues of $C_n{}^*$ are:

$$_k(C_n) \quad \exp \quad \frac{2i \ k}{n} \quad \cos \frac{2 \ k}{n} - i \sin \frac{2 \ k}{n}; \quad k = 1,2,\ldots, n. \tag{5}$$

Theorem 4 follows by combining Eqs. (3) – (5).

The chemical implications of Theorem 4 are based on the fact that the eigenvalues of a molecular graph of a -electron system pertain to the -molecular orbital energy levels. In case of annulenes, these orbital energies may be decomposed into two (complex-valued) contributions, each associated with a kind of circular motion of the

-electrons (in two opposite directions). This clearly has a relation to the cyclic conjugation in these molecules.

To the authors' best knowledge, no graphs, other than the annulene graphs (and edgeless graphs), possess the distinguished property

$$ {}_k(G) = \quad {}_k(G) + \quad {}_k(G^*) \tag{6}$$

fol all $k = 1,2, \dots , n$. The proof of the nonexistence of such graphs would be of some value. The discovery of more graphs satisfying Eq. (6) would, however, be of much greater importance.

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И З В О Д

О МОЛЕКУЛСКИМ ГРАФОВИМА И ДИГРАФОВИМА АНУЛЕНА И ЊИХОВИМ СПЕКТРИМА

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Молекулски граф, који садржи неоријентисане гране, може се приказати као збир двају диграфова, који садрже оријентисане гране супротног усмерења. У случају анулена спектар сопствених вредности молекулског графа једнак је збиру спектара одговарајућа два молекулска диграфа.

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