

SOME ASPECTS OF GRAPH SPECTRAL THEORY OF CONJUGATED  
MOLECULES

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1. Introduction

In this work we will consider molecular graphs, named Hückel graphs<sup>1</sup>, which are used to depict conjugated molecules. These graphs are connected and planar with the even number of vertices ( $N$ ). The maximal valency of a vertex ( $D_{\max}$ ) in Hückel graphs is 3. We will use the basic definitions and concepts of graph theory detailed in our earlier work<sup>2</sup>.

Let us first briefly discuss the equivalence between the Hückel theory and the graph spectral theory of conjugated molecules<sup>3-5</sup>. Hamiltonian matrix in Hückel theory ( $\mathbf{H}$ ) is given by<sup>3</sup>

$$\mathbf{H} = \alpha \mathbf{1} + \beta \mathbf{A} \quad (1)$$

where  $\mathbf{1}$  is a unity matrix,  $\mathbf{A}$  is an adjacency (topological) matrix of a Hückel graph,  $\alpha$  and  $\beta$  are the Coulomb and resonance integrals, respectively, of Hückel theory. Hückel determinant may be written as follows

$$\det | \mathbf{H} - E_i \mathbf{S} | = 0 \quad (2)$$

Introducing Hückel approximations and Eq. (1) into (2), one obtains

$$\det \left| \left( \frac{E_i - \alpha}{\beta} \right) \mathbb{1} - \mathbf{A} \right| = 0 \quad (3)$$

The adjacency matrix of a graph is defined as

$$A_{rs} = \begin{cases} 1 & \text{if } \underline{r} \text{ and } \underline{s} \text{ are adjacent vertices} \\ 0 & \text{otherwise} \end{cases} \quad (4)$$

The set of eigenvalues  $\{x_1, x_2, \dots, x_N\}$  belonging to the adjacency matrix  $\mathbf{A}$  of the graph G is called the spectrum of the graph (sometimes the graph spectrum). The graph spectrum is the set of roots of the secular equation:

$$\det |x \mathbb{1} - \mathbf{A}| = 0 \quad (5)$$

If Eqs. (3) and (5) are compared it appears that the numbers  $\frac{E_i - \alpha}{\beta}$  are actually making up the spectrum of a Hückel graph:

$$E_i = \alpha + x_i \beta \quad ; i=1, 2, \dots, N \quad (6)$$

Using  $\beta$  as an energy unit and  $\alpha$  as the zero-point, we have

$$E_i = x_i \quad (7)$$

and hence, the eigenvalues of the adjacency matrix are identical with Hückel molecular orbital energy levels. From Eq. (1) it is seen that  $\mathbf{H}$  and  $\mathbf{A}$  commute and have, therefore, the same eigenvectors. Thus, the eigenvectors of the adjacency matrix are identical with the Hückel molecular orbitals.

Hückel molecular orbitals corresponding to  $x > 0$ ,  $x=0$ , and  $x < 0$  are called bonding, non-bonding, and antibonding, respectively. The number of bonding, non-bonding, and antibonding MO's is denoted as  $N_+$ ,  $N_0$ , and  $N_-$ , respectively. They are related to the total number of atoms in a conjugated molecule (N) as follows:

$$N_+ + N_0 + N_- = N \quad (8)$$

Note, that the polynomial

$$P(G; x) = \det |x \mathbf{1} - \mathbf{A}| \quad (9)$$

is called the characteristic polynomial of the graph G and it contains important information about the conjugated molecule. Characteristic polynomial has the following form:

$$P(G; x) = \sum_{n=0}^N a_n x^{N-n} \quad (10)$$

where  $a_n$  are the coefficients of the  $P(G; x)$ .  $P(G; x)$  is of degree N. We wish to show in the sections which follow the relations between the  $a_n$  and  $N_+$ ,  $N_0$ , and  $N_-$ .

## 2. Number of bonding molecular orbitals ( $N_+$ )

The following relations between  $N_+$ ,  $N_0$ , and  $P(G; x)$  exist<sup>6</sup>:

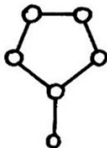
$$a_N = a_{N-1} = \dots = a_{N-N_0+1} = 0 \quad (11)$$

$$a_{N-N_0} \neq 0 \quad (12)$$

$$\text{Ch} (a_N, a_{N-1}, \dots, a_1, a_0) = N_+ \quad (13)$$

where ch denotes the number of changes of sign in the sequence of numbers.

### Example



fulvene graph ( $N=6$ )

$$P(G; x) = x^6 - 6x^4 + 8x^2 - 2x - 1$$

$$a_N \neq 0; \quad N_0 = 0$$

$$\text{Ch}(-1, -2, 8, -6, 1) = N_+ = 3$$

$$N_- = N - N_+ - N_0 = 3$$

Characteristic polynomial of fulvene graph is constructed using the Coulson-Sachs method as described by Graovac et al.<sup>7</sup> Unfortunately, the evaluation of  $P(G; x)$  for larger graphs by the Coulson-Sachs graphical method becomes unwieldy. Therefore, another graph-theoretical approach may be more convenient (see Section 4).

### 3. Non-bonding molecular orbitals (NBMO $\equiv$ $N_0$ )

It is of importance to establish the presence of non-bonding molecular orbitals (NBMO) in conjugated structures because their existence leads to prediction<sup>8</sup> that such molecules should have open-shell ground state and should be very reactive. Here we will outline a simple method for determination of  $N_0$ . Since we know that the number of NBMO's is identical with the number of zeros in the graph spectrum, and since

$$\det \mathbf{A} = \prod_{i=1}^N x_i \quad (14)$$

The determinant of  $\mathbf{A}$  will be zero if, and only if, there exists at least one zero in the graph spectrum. Therefore, the problem of determining  $N_0$  is closely related to the problem of evaluation  $\det \mathbf{A}$  of the graph in question. We have derived the following expression for the evaluation of the determinant of adjacency matrix:

$$\det \mathbf{A} = (-)^{N/2} (K^+ - K^-)^2 + (-)^N \sum_{\mathbf{s} \in S_n^{\text{oo}}} (-)^{c(\mathbf{s})} 2^{r(\mathbf{s})} \quad (15)$$

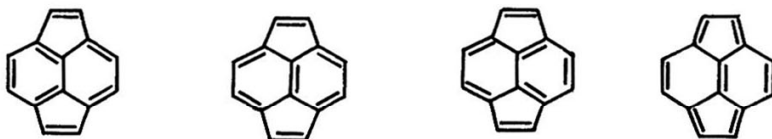
where  $K^+$  and  $K^-$  are Kekulé structures of even and odd parity<sup>9</sup>,  $S_n^{\text{oo}}$  is a Sachs graph with odd-membered rings<sup>7,10</sup>,  $c(\mathbf{s})$  and  $r(\mathbf{s})$  are the number of components and the number of cyclic components of the Sachs graph  $\mathbf{s}$ , respectively. The following rule may be used

for determining the parity of two Kekulé structures<sup>11</sup>: if the structure obtained by superposition of two Kekulé graphs contains an even (odd) number of  $[4m]$ -membered rings, the Kekulé structures in question have the same (opposite) parity. For more details about Sachs and Kekulé graphs see communication in these Proceedings by Graovac and Trinajstić<sup>12</sup>.

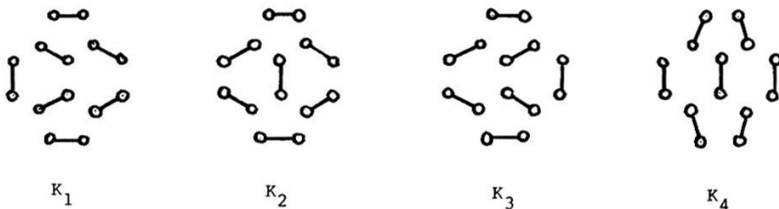
The use of formula (15) will be illustrated on pyracyclene.

(1) We first write down Kekulé structures and the corresponding Kekulé graphs of pyracyclene.

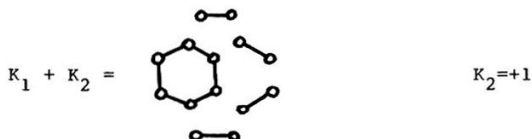
Kekulé structures

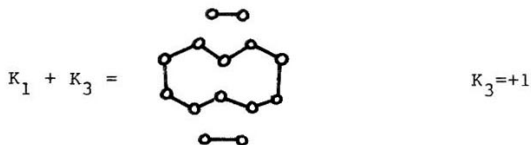


Kekulé graphs



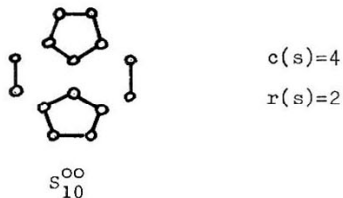
(2) Now, we determine their parities.  $K_1$  structure is arbitrarily selected to be even (+1). Then,





Therefore,  $K^+ = 3$  and  $K^- = 1$ .

(3) Pyracyclene has only one Sachs graph containing the odd-membered rings:



Thus, it follows

$$\det \mathbf{A} = (-)^7 (3 - 1)^2 + (-)^{14} (-)^4 2^2 = 0 \quad (16)$$

Therefore, pyracyclene must have at least one NBMO.

The actual number of zeros in the graph spectrum may be obtained following the Longuet-Higgins-Živković algorithm<sup>8,13</sup> for enumeration of  $N_0$ . Let us first consider the eigenvalue equation:

$$\mathbf{C}_i \mathbf{A} = x_i \mathbf{C} \quad (17)$$

In the case of  $N_0 \neq 0$ ,  $x_i = 0$  and  $\mathbf{C}_i = \mathbf{C}_0 \equiv \text{NBMO}$ :

$$\mathbf{C}_0 \mathbf{A} = 0 \quad (18)$$

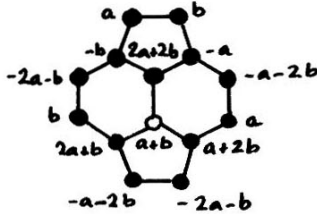
or in scalar form:

$$\sum_{j \rightarrow k}^N c_{0j} = 0; \quad k=1, 2, \dots, N \quad (19)$$

The summation is over all vertices  $j$  joined to the vertex  $k$ .

It should be also noted<sup>13</sup> that a number of independent parameters in unnormalized NBMO is equal to  $N_0$ .

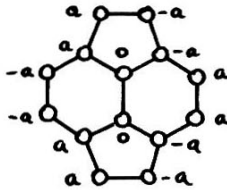
The use of this approach will be also illustrated for pyracyclene.



Each vertex for which Eq. (19) is fulfilled is denoted by ●. In order that Eq. (19) is fulfilled for the last (unmarked) vertex of pyracyclene the following relation must hold:

$$a + b = 0 \quad (20)$$

Thus, only one parameter ( $\underline{b} = -a$ ) is independent, and consequently,  $N_0 = 1$ .



The chemistry of pyracyclene<sup>14</sup> is in accord with this prediction.

#### 4. Number of antibonding orbitals ( $N_-$ )

The following relations which are formally analogous to Eqs. (11) - (13):

$$D_N = D_{N-1} = \dots = D_{N-N_0+1} = 0 \quad (21)$$

$$D_{N-N_0} \neq 0 \quad (22)$$

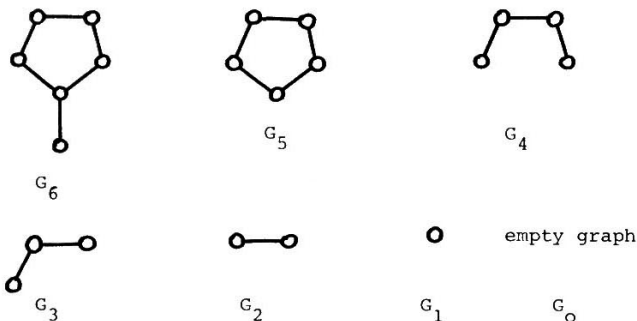
$$\text{Ch} (D_N, D_{N-1}, \dots, D_1, D_0) = N_- \quad (23)$$

can be used for enumeration of antibonding orbitals<sup>15</sup>. They may be also used for enumerating  $N_0$  and  $N_+$ , and thus, this method may replace that one described in Section 2. Note, that  $D_N$  can be determined from the relation:

$$\det \mathbf{A}_n = D_n \quad (n=1,2,\dots,N) \quad (24)$$

It should be also noted that  $\mathbf{A}_{n-1}$  is the submatrix of  $\mathbf{A}_n$ , obtained by deletion of the  $n$ -th row and the  $n$ -th column of  $\mathbf{A}_n$ . Thus,  $D_{n-1}$  is a minor of  $D_n$ . Besides, by definition  $D_0=1$ . The sequence of numbers  $(D_N, D_{N-1}, \dots, D_1, D_0)$  may be denoted as  $[\mathbf{D}_n]$  and it is called "decomposition" of the graph  $G$ . The sequence  $\mathbf{D} = (G_n, G_{n-1}, \dots, G_1, G_0)$  is the decomposition of  $G_n$  ( $n=1,2,\dots,n$ ). The application of the above approach is illustrated for fulvene.

(1) First we consider the decomposition of the fulvene graph:





(2) Secondly, the D numbers are evaluated:  $D_6 = \det \mathbf{A}_6 = -1$ ,  $D_5 = \det \mathbf{A}_5 = 2$ ,  $D_4 = \det \mathbf{A}_4 = 1$ ,  $D_3 = \det \mathbf{A}_3 = 0$ ,  $D_2 = \det \mathbf{A}_2 = -1$ ,  $D_1 = \det \mathbf{A}_1 = 0$ , and  $D_0 = 1$ .

$$(3) \text{Ch}(-1, 2, 1, 0, -1, 0, 1) = N_- = 3$$

$$D_N \neq 0; N_O = 0$$

$$N_+ = N - (N_- + N_O) = 3$$

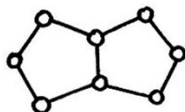
However, the whole procedure may be simplified even more because of identity:

$$\text{Ch}(D_N, \dots, D_n, \dots, D_0) = \text{Ch}(D_N, \dots, D_n) + \text{Ch}(D_n, \dots, D_0) \quad (25)$$

$$N_- = \text{Ch}(D_N, \dots, D_n) + N_-(n) \quad (26)$$

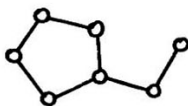
Thus, if we know  $N_-(n)$  it is sufficient to calculate  $(D_N, \dots, D_n)$ .

The application of these considerations will be demonstrated for pentalene.



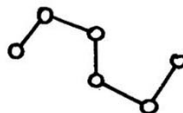
$G_8$

$$D_8 = 0$$



$G_7$

$$D_7 = -2$$



$G_6$

$$D_6 = -1$$

$$N_- = \text{Ch}(0, -2, -1) + N_-(6) = 0 + 6/2 = 3$$

$$D_N = 0; N_O = 1$$

$$N_+ = N - (N_- + N_O) = 4; N_+ > N_-$$

Pentalene should be a highly reactive electron-deficient molecule. The experimental findings<sup>16</sup> support this theoretical result.

##### 5. Classification of conjugated hydrocarbons based on

their graph spectral characteristics

We define a vector  $\vec{n}$  as

$$\vec{n} \equiv \vec{n}(G) = (N_+ - N_-, N_0) \quad (27)$$

which determines a point with integer coordinates in the upper half-plane of a two-dimensional coordinate system. Note, that

$$\vec{n} = 0 \quad (28)$$

is necessary condition for  $\pi$ -electron system to be stable. There are also other reasons for chemical stability, hence Eq. (28) alone is not a sufficient condition for a conjugated system to be stable.

If Eq. (28) holds, it is  $N_+ = N_- = N/2$  and all bonding MO's are doubly occupied in the ground state. In the case  $N_+ > N_-$  there are unoccupied bonding MO's, while for  $N_+ < N_-$  there are occupied antibonding MO's, both causing the high reactivity and/or instability of the  $\pi$ -electron system. Besides, systems with  $N_+ > N_-$  may be classified as electron-deficient molecules because they tend to accept electrons from a suitable donor in their empty bonding MO levels. Systems with  $N_+ < N_-$  are electron-excessive molecules and show tendency to generate cations. Finally, if  $N_+ = N_-$  and  $N_0 > 0$  a polyradical ground state is expected and such structures are extremely reactive.

7. Conclusions

We suppose that after going through this work a question could be asked immediately: Why to develop and use the graph spectral theory when it does give hardly any information not available from Hückel calculations? We, however, feel that there are several good points in favour of developing the graph spectral theory of conjugated molecules. These may be summarised as below:

(i) A number of results may be obtained without any use of computers by just a pencil and a paper. This is of importance for experimental chemists who are sometimes kept away from using current computational theories because of necessity to carry them out on computers using the specialized programs.

(ii) Sometimes a purely numerical computerized examination hides away the importance of a particular feature of a molecule which may encounter for some properties of the molecule.

(iii) The obtained graph theoretical results have a general validity and may be formulated as theorems and/or rules which may be then applied to any similar group of molecules without any further numerical or conceptual work.

(iv) Finally, it is not our intention to compete with standard HMO calculations, but rather to develop a symbolism that permits chemists to think graphically, i.e. to learn as much as possible about the chemical behaviour of the molecule by examining the properties of its molecular graph.

Full account about various aspects of the graph spectral theory of conjugated molecules would appear in our Authors Review in Croatica Chemica Acta<sup>17</sup>.

#### Acknowledgements

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## 8. Literature

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