

## RECURRENCE RELATIONSHIPS FOR THE COMPUTATION OF THE NUMBER OF KEKULÉ STRUCTURES

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### Abstract

On the basis of expansions of the characteristic and acyclic polynomials of conjugated hydrocarbons, five recurrence relationships enabling the computation of the number of Kekulé structures are presented.

### 1. Introduction

Molecular topology determines a large number of physico-chemical properties of chemical compounds [1–10]. Among them, the determination of the number of Kekulé structures of benzenoid hydrocarbons has attracted the attention of theoretical chemists over a relatively long period of time. Explicit combinatorial expressions enabling the calculation of the Kekulé structure count have been derived for a large number of classes of benzenoid hydrocarbons [9–14].

A Kekulé structure of an unsaturated conjugated hydrocarbon is a structural formula including hydrogens in which every carbon atom is tetravalent,  $sp^2$ -hybridized, and incident to exactly one double bond.

Some of the most important theorems concerning the computation of the number of Kekulé structures of benzenoids are summarized. Based on expansions of the characteristic and acyclic polynomials of the molecular graphs of conjugated hydrocarbons, in terms of the corresponding polynomials of certain subgraphs of the molecular graph, five recurrence relations enabling the computation of the number of Kekulé structures will be presented.

### 2. Notation and definitions

We shall use the standard graph notation and terminology [15];  $G$  will denote a graph with  $N$  vertices:  $v_1, v_2, \dots, v_N$ ; the degree of the vertex  $v_i$  will be denoted by  $d_i$ . The edge connecting vertices  $v_i$  and  $v_j$  is denoted by  $e_{ij}$ . The subgraph  $G - v_i$  is obtained from the graph  $G$  by deletion of the vertex  $v_i$  and its incident edges. The subgraph  $G - e_{ij}$  is obtained from the graph  $G$  by deletion of the edge  $e_{ij}$ . The subgraph  $G - C_i$  is obtained from the graph  $G$  by deleting all the vertices of the cycle  $C_i$  and their incident edges.

The adjacency matrix of a graph  $G$  with  $N$  vertices,  $A = A(G)$ , is the square  $N \times N$  symmetric matrix which contains information about the connectivity of the vertices in  $G$ . Its entries are defined as

$$a_{ij} = \begin{cases} 1, & \text{for vertices } i, j \text{ adjacent,} \\ 0, & \text{otherwise.} \end{cases} \quad (1)$$

The characteristic polynomial of the graph  $G$  may be expressed as follows [15]:

$$\text{Ch}(G, x) = \det(x\mathbf{I} - \mathbf{A}) = \sum_{n=0}^N a_n x^{N-n}, \quad (2)$$

where  $\mathbf{I}$  is the unit matrix.

The acyclic (matching) polynomial was defined as [16]

$$\text{Ac}(G, x) = \sum_{k=0}^N (-1)^k P(G, k) x^{N-2k}, \quad (3)$$

where  $P(G, k)$  is the number of ways of choosing  $k$  disjoint edges from  $G$ .

It is known that the number  $K(G)$  of Kekulé structures is related in a simple manner to the adjacency matrix  $A$  of the aromatic hydrocarbon, namely [17]

$$\det A(G) = (-1)^{N/2} K(G)^2. \quad (4)$$

$K(G)$  obeys the following known recurrence relationship [18]:

$$K(G) = K(G - e_{ij}) + K(G - v_i - v_j). \quad (5)$$

If the vertex  $v_i$  is of degree one, we obtain

$$K(G) = K(G - v_i - v_j). \quad (6)$$

If the conjugated system  $G$  is an essentially disconnected benzenoid composed of two non-interacting fragments  $G_1$  and  $G_2$ , then

$$K(G) = K(G_1)K(G_2). \quad (7)$$

If  $G$  is a benzenoid graph with  $N$  vertices, then [19]

$$\text{Ch}(G, 0) = (-1)^{N/2} K(G)^2. \quad (8)$$

If  $G$  is a graph with  $N$  vertices, then [20]

$$\text{Ac}(G, 0) = (-1)^{N/2} K(G). \quad (9)$$

The free terms, i.e. the coefficients of  $x^0$ , of the characteristic and acyclic polynomials, are denoted by  $\text{Ch}(G, 0)$  and  $\text{Ac}(G, 0)$ , respectively.

LEMMA 1 [14]

If  $B$  is a benzenoid graph and  $C_i$  is its cycle with  $nc$  vertices, then in the interior of  $C_i$  there is an odd number of vertices, whenever  $nc \equiv 0 \pmod{4}$ .

### 3. Graph polynomials recurrence relationships

The characteristic polynomial of a graph  $G$ ,  $\text{Ch}(G)$ , can be expressed as a linear function of the characteristic polynomials of its subgraphs obtained after the removal of an edge  $e_{ij}$ , the vertices  $v_i$  and  $v_j$ , and all  $r$  cycles  $C_k$  containing the edge  $e_{ij}$  [17]:

$$\text{Ch}(G) = \text{Ch}(G - e_{ij}) - \text{Ch}(G - v_i - v_j) - 2 \sum_{k=1}^r \text{Ch}(G - C_k). \tag{10}$$

The decomposition of the graph  $G$  at its edge  $e_{ij}$  gives the following equality in terms of acyclic polynomials of the graph  $G$ ,  $\text{Ac}(G)$ , and its subgraphs [21]:

$$\text{Ac}(G) = \text{Ac}(G - e_{ij}) - \text{Ac}(G - v_i - v_j). \tag{11}$$

The expansion of the characteristic polynomial is given in the following equation in terms of the characteristic polynomials of its subgraphs, corresponding to the decomposition of the graph  $G$  at its vertex  $v_i$  [22]:

$$\text{Ch}(G) = x \text{Ch}(G - v_i) - \sum_{j=1}^{d_i} \text{Ch}(G - v_i - v_j) - 2 \sum_{k=1}^r \text{Ch}(G - C_k), \tag{12}$$

where the second summation goes over all  $r$  cycles which contain vertex  $v_i$ .

In a similar way, we obtain the expression of the acyclic polynomial of the graph  $G$  decomposed at its vertex  $v_i$  [22]:

$$\text{Ac}(G) = x \text{Ac}(G - v_i) - \sum_{j=1}^{d_i} \text{Ac}(G - v_i - v_j). \tag{13}$$

Let  $G$  be a graph with  $g_1$  and  $g_2$  as two distinct vertices, and let  $H$  be another graph with  $h_1$  and  $h_2$  as two distinct vertices. We construct the composed graph  $G:H$  by identifying  $g_1$  with  $h_1$  and  $g_2$  with  $h_2$ .

The characteristic polynomial of the composed graph  $G:H$  is expressed by the following equality [23]:

$$\begin{aligned}
\text{Ch}(G:H) &= \text{Ch}(G)\text{Ch}(H - h_1 - h_2) + \text{Ch}(G - g_1)\text{Ch}(H - h_2) \\
&+ \text{Ch}(G - g_2)\text{Ch}(H - h_1) + \text{Ch}(G - g_1 - g_2)\text{Ch}(H) \\
&- x[\text{Ch}(G - g_1)\text{Ch}(H - h_1 - h_2) + \text{Ch}(G - g_2)\text{Ch}(H - h_1 - h_2) \\
&+ \text{Ch}(G - g_1 - g_2)\text{Ch}(H - h_1) + \text{Ch}(G - g_1 - g_2)\text{Ch}(H - h_2)] \\
&+ x^2\text{Ch}(G - g_1 - g_2)\text{Ch}(H - h_1 - h_2) - 2 \sum_g \sum_h \text{Ch}(G - P_g)\text{Ch}(H - P_h),
\end{aligned} \tag{14}$$

where the summations are over all paths  $P_g$  and  $P_h$  from  $G$  and  $H$ , respectively, connecting vertices  $g_1$  and  $g_2$  with  $h_1$  and  $h_2$ , respectively.

In a similar way, we express the acyclic polynomial of graph  $G:H$ , namely [23]

$$\begin{aligned}
\text{Ac}(G:H) &= \text{Ac}(G)\text{Ac}(H - h_1 - h_2) + \text{Ac}(G - g_1)\text{Ac}(H - h_2) \\
&+ \text{Ac}(G - g_2)\text{Ac}(H - h_1) + \text{Ac}(G - g_1 - g_2)\text{Ac}(H) \\
&- x[\text{Ac}(G - g_1)\text{Ac}(H - h_1 - h_2) + \text{Ac}(G - g_2)\text{Ac}(H - h_1 - h_2) \\
&+ \text{Ac}(G - g_1 - g_2)\text{Ac}(H - h_1) + \text{Ac}(G - g_1 - g_2)\text{Ac}(H - h_2)] \\
&+ x^2\text{Ac}(G - g_1 - g_2)\text{Ac}(H - h_1 - h_2).
\end{aligned} \tag{15}$$

#### 4. Kekulé structures recurrence relationships

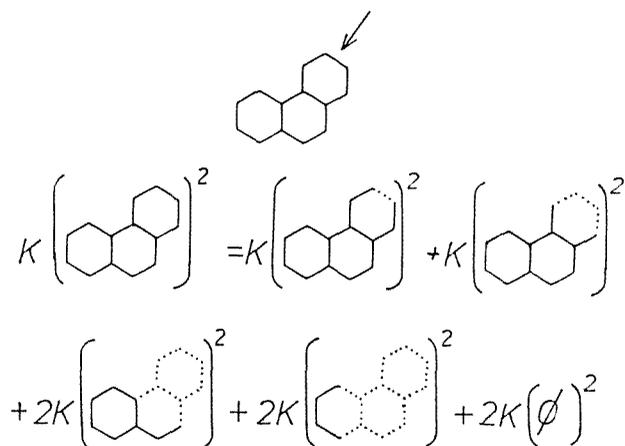
Based on the recurrence relationships (10)–(15) in terms of the characteristic and acyclic polynomials of conjugated hydrocarbons, we will derive five recurrence relationships enabling the computation of the number of Kekulé structures.

##### THEOREM 1

Let  $G$  be a benzenoid graph. Then  $K(G)$  can be expressed as a function of the number of Kekulé structures of the subgraphs of  $G$  which do not contain the edge  $e_{ij}$ :

$$K(G)^2 = K(G - e_{ij})^2 + K(G - v_i - v_j)^2 + 2 \sum_{k=1}^r K(G - C_k)^2, \tag{16}$$

where the summation goes over all  $r$  cycles in  $G$  which contain the edge  $e_{ij}$ .



Scheme 1.

The proof is straightforward by applying equality (8) to the recurrence relationship (10). An illustrative example (phenanthrene) is shown in scheme 1. On this and the following examples, the place of application of the theorems is indicated by an arrow pointing to the corresponding edge or vertex.

The graphical equation shown in scheme 1 gives the following equality expressed by the corresponding number of Kekulé structures:

$$5^2 = 3^2 + 2^2 + 2 \cdot 2^2 + 2 \cdot 1^2 + 2 \cdot 1^2.$$

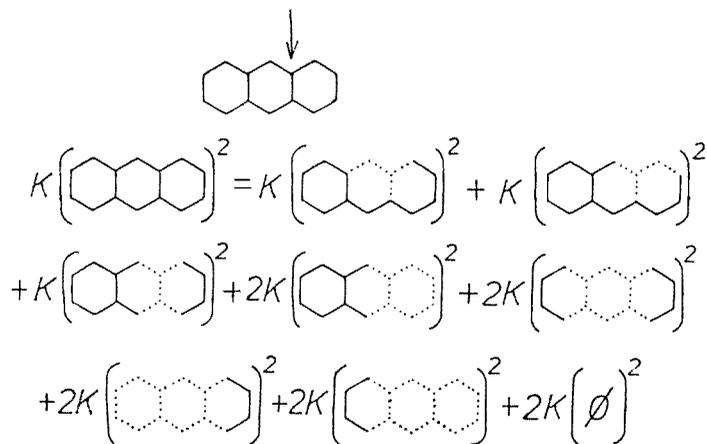
Using equality (9) in the corresponding decomposition in terms of acyclic polynomials (eq. (10)), we obtain the well-known equation (5).

**THEOREM 2**

The number of Kekulé structures of a benzenoid graph  $G$  is related to the number of Kekulé structures of the subgraphs of  $G$  obtained after the removal of the vertex  $v_i$  with each of its  $d_i$  neighbours and of each of the  $r$  cycles  $C_k$  containing vertex  $v_i$ :

$$K(G)^2 = \sum_{j=1}^{d_i} K(G - v_i - v_j)^2 + 2 \sum_{k=1}^r K(G - C_k)^2. \tag{17}$$

This can be easily shown using eqs. (8) and (12). In scheme 2, we give another example, anthracene.



Scheme 2.

From the graphical example of theorem 2, we obtain the following equality for the number of Kekulé structures of the corresponding graphs:

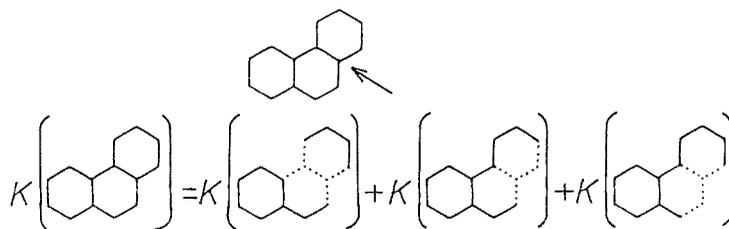
$$4^2 = 2^2 + 1^2 + 1^2 + 2 \cdot 1^2.$$

**THEOREM 3**

The number of Kekulé structures of a graph  $G$  can be expressed in terms of the number of Kekulé structures of the subgraphs of  $G$ , corresponding to the deletion of the vertex  $v_i$  and each of its  $d_i$  neighbours in turn:

$$K(G) = \sum_{j=1}^{d_i} K(G - v_i - v_j). \tag{18}$$

The proof comes from eqs. (9) and (13). The theorem is illustrated for the same benzenoid hydrocarbon as above, phenanthrene.



Scheme 3.

The graphical example for theorem 3 gives the following expression for the number of Kekulé structures of the corresponding graphs:

$$5 = 2 \cdot 1 + 2 + 1.$$

For theorems 2 and 3 one must note that if  $G$  has an even number of vertices, then  $G - v_i$  has an odd number of vertices and  $K(G - v_i) = 0$ . Obviously, the term corresponding to the subgraph  $G - v_i$  was omitted.

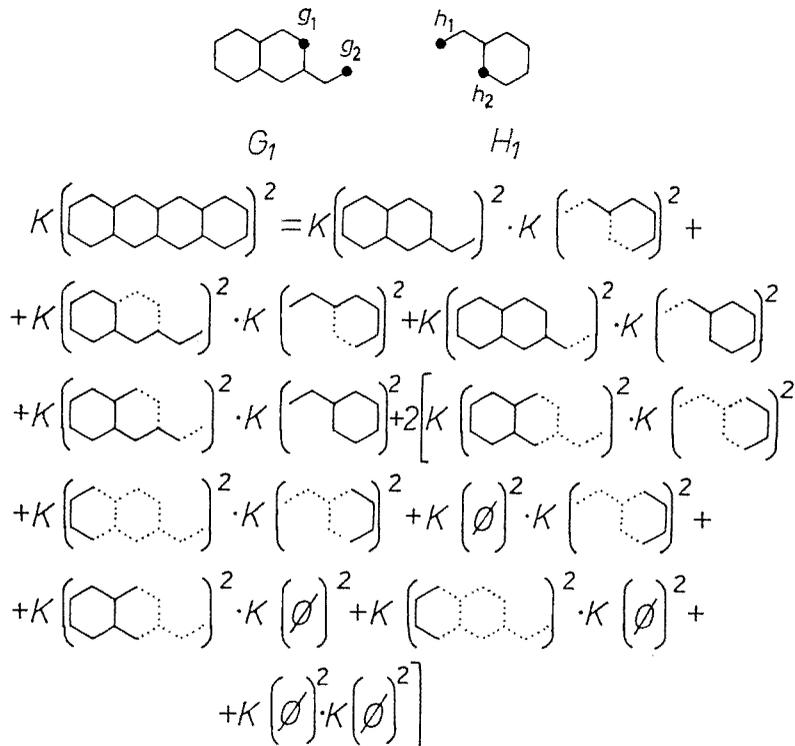
**THEOREM 4**

The number of Kekulé structures of the composed benzenoid graphs  $G:H$  is equal to

$$\begin{aligned} K(G:H)^2 &= K(G)^2 K(H - h_1 - h_2)^2 + K(G - g_1)^2 K(H - h_2)^2 \\ &\quad + K(G - g_2)^2 K(H - h_1)^2 + K(G - g_1 - g_2)^2 K(H)^2 \\ &\quad + 2 \sum_g \sum_h K(G - P_g)^2 K(H - P_h)^2, \end{aligned} \tag{19}$$

where the summations are over all paths  $P_g$  connecting vertices  $g_1$  and  $g_2$ , and paths  $P_h$  connecting vertices  $h_1$  and  $h_2$ , from  $G$  and  $H$ , respectively.

We prove this equality using eqs. (8) and (14) and lemma 1. An application of the theorem is illustrated in scheme 4 for the graphs  $G_1$  and  $H_1$ , and  $G_1:H_1$  is tetracene.



Scheme 4.

The graphical relation illustrated in scheme 4 can be translated in terms of the number of Kekulé structures of the graph  $G:H$  and its subgraphs from eq. (19):

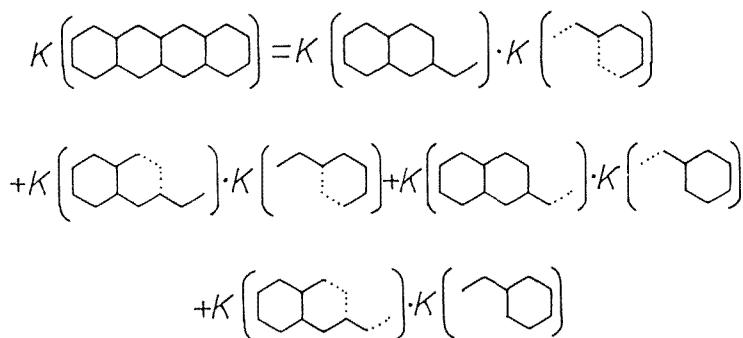
$$5^2 = 3^2 \cdot 1^2 + 0 \cdot 0 + 0 \cdot 0 + 1^2 \cdot 2^2 + 2 \cdot [1^2 \cdot 1^2 + 1^2 \cdot 1^2].$$

**THEOREM 5**

The number of Kekulé structures of the composed graph  $G:H$  is equal to

$$K(G:H) = K(G)K(H - h_1 - h_2) + K(G - g_1)K(H - h_2) \\ + K(G - g_2)K(H - h_1) + K(G - g_1 - g_2)K(H). \quad (20)$$

The proof comes from eqs. (9) and (15). The theorem is illustrated by the same graphs  $G_1$ ,  $H_1$  and  $G_1:H_1$  as in the preceding case.



Scheme 5.

From the graphical expression of theorem 5, we obtain the following equality for the number of Kekulé structures of the graphs depicted in scheme 5:

$$5 = 3 \cdot 1 + 0 \cdot 0 + 0 \cdot 0 + 1 \cdot 2.$$

Obviously, if  $G$  and  $H$  contain even numbers of vertices, eq. (19) reduces to

$$K(G:H)^2 = K(G)^2 K(H - h_1 - h_2)^2 + K(G - g_1 - g_2)^2 K(H)^2 \\ + 2 \sum_g \sum_h K(G - P_g)^2 K(H - P_h)^2, \quad (21)$$

while eq. (20) becomes

$$K(G:H) = K(G)K(H - h_1 - h_2) + K(G - g_1 - g_2)K(H). \quad (22)$$

If  $G$  and  $H$  contain odd numbers of vertices, eq. (19) reduces to

$$K(G:H)^2 = K(G - g_1)^2 K(H - h_2)^2 + K(G - g_2)^2 K(H - h_1)^2 + 2 \sum_g \sum_h K(G - P_g)^2 K(H - P_h)^2 \quad (23)$$

and eq. (20) gives

$$K(G:H) = K(G - g_1)K(H - h_2) + K(G - g_2)K(H - h_1). \quad (24)$$

If  $G$  has an even and  $H$  has an odd number of vertices, we have

$$K(G:H) = 0. \quad (25)$$

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