Graph Theory and Molecular Orbitals. VIII. Kekule Structures and Permutations

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The relation between Kekule structures and permutations is discussed. It is shown that Kekule structures are permutations and that their number in alternant hydrocarbons is equal to the square root of the total number of permutations contained in the molecular graph.

As simple special cases of this result the Dewar-Longuet-Higgins equation 2 and the relation between the permanent of the adjacency matrix and the number of Kekule structures 3 are obtained.

Generalizations for nonalternant hydrocarbons are also given.

INTRODUCTION

It has been shown in the preceding papers of this series 1–4 that graph theory is a suitable mathematical technique for the study of electronic properties of conjugated systems.

The relation between the molecular orbital theory and the valence bond theory was established some 25 years ago 5 and thereafter numerous other results in this direction have been obtained 2,6. In recent years a new impetus is given to these investigations due to an increased interest for both simple molecular-orbital theory and valence-bond theory 7. Namely, the Hückel and resonance theory are in fact both topological approximations where the application of graph theory can be justified 8.

A directed graph can be related to a conjugated molecule 4 when carbon atoms are represented as small circles (vertices) and a pair of opposite oriented lines (edges) are drawn between two circles if and only if the corresponding atoms are connected. For example, the following directed graphs I, II, and III are the representations of butadiene, fulvene, and benzene, respectively:

\[ A_{pq} = \begin{cases} 1 & \text{if there is a direct edge from } p \text{ towards } q \\ 0 & \text{if there is not} \end{cases} \] (1)
According to the above definition the adjacency matrix of the molecular graph is necessarily symmetric, \( i.e. \)
\[
A = A^T
\] (2)

However, subgraphs of \( G \) do not need to possess both opposite directed edges at the same time. Thus, for example, IV and V are the subgraphs of the fulvene graph II:

![IV and V](image)

We are interested here only in subgraphs which contain all the vertices of the graph. The number of vertices in the graph \( G \) (and in all considered subgraphs) is \( N \). We suppose that \( N \) is even since this is a necessary condition for the existence of at least one Kekulé structure in the corresponding molecule.

If the conjugated molecule is alternant, the related graph is bipartite\(^{6,9} \). The starred vertices will be numbered with \( 1, 2, \ldots, u \) and the unstarred with \( u + 1, u + 2, \ldots, u + v \) \( (u + v = N) \). Then the adjacency matrix is of the form

\[
A = \begin{pmatrix} O & B \\ B^T & O \end{pmatrix}
\] (3)

We define a starred Kekulé graph as a subgraph of \( G \) with the property that only one edge starts from every starred vertex and only one ends at every unstarred one. The unstarred Kekulé graph is defined similarly, however, the edges start from unstarred and end at starred vertices.

For example, the benzene graph III has the following Kekulé graphs:

![Benzene Kekulé graphs](image)

Let \( K \) be the number of Kekulé structures of the molecule. It is evident that there are exactly \( K \) starred and \( K \) unstarred Kekulé graphs of the molecular graph; they will be denoted by \( k_j^* \) and \( k_j^0 \) \( (j = 1, 2, \ldots, K) \). \( k_j^* \) and \( k_j^0 \) are directed graphs and correspond to an undirected graph \( k_j \).

The adjacency matrices of Kekulé graphs (which are obviously not symmetric) are of the form

\[
A(k^*) = \begin{pmatrix} O & B(k) \\ O & O \end{pmatrix} \quad A(k^0) = \begin{pmatrix} O & O \\ B(k)^T & O \end{pmatrix}
\] (4)
Since there is just one unit in every row and every column of $B(k)$ it is a permutation matrix. Therefore, every Kekulé graph can be considered as a permutation of $N/2$ elements.

However, there exists one less trivial relation between Kekulé graphs and permutations. We define a (directed) Sachs graph as a subgraph of $G$ with the property that one edge starts from and one edge ends at every vertex of $G$. For example, the graph III has the following four Sachs graphs:

![Four Sachs graphs of graph III]

We will use the following notation. A Sachs graph is denoted as $s$. The set of Sachs graphs of the graph $G$ is $S(G) = S$. The number of elements in $S(G)$, or the number of Sachs graphs for a given graph $G$, is $|S|$. The number of components, or disconnected islands, of $s$ is $c(s)$ and among them there are $r_{4m}(s)$ $(4m)$-membered cycles. The subset of $S$ containing Sachs graphs with at least one odd-membered cycle is $S_{\text{odd}}$. Evidently, $S_{\text{odd}} = \emptyset$ for bipartite graphs.

Note that in Ref. 4, where undirected graphs have been considered, the definition of Sachs graph is different. Sachs graphs are the graphical representation of permutations. In order to realize this one should remember that a permutation is defined as a one-to-one mapping of a set into itself. In the Sachs graph vertices represent the elements of the set and edges indicate the mapping. Thus if $s \in S(G)$ we say that the permutation $s$ is contained in the graph $G$.

**BASIC THEOREMS**

For bipartite graphs there is a relation between the permutations and the Kekulé structures.

**Theorem 1**

The number of permutations contained in a (bipartite) graph is equal to the square of the number of Kekulé structures of the corresponding molecule, i.e.

$$|S| = K^2$$

In order to show this we will prove a more general statement.

It is obvious from (4) that the matrix $M = A(k^*) + A(k^0)$ is an adjacency matrix, say of the graph $h$, because $M_{pq} = 1$ or 0. Therefore, let be $h = k^* + k^0$ if and only if $A(h) = A(k^*) + A(k^0)$.

**Theorem 2**

Every $k^* + k^0$ is a Sachs graph. For a given $s$ of a bipartite graph there are exactly one $k^*$ and one $k^0$, and *vice versa*. I. e. there is a unique correspondence as

$$s_{ij} = k^*_i + k^0_j$$

Besides, $s_{ij} \neq s_{ji}$ for $i \neq j$. 
Note that this implies *Theorem 1*. There are $K^2$ different graphs of the form $k_i^* + k_j^0$. Hence, eq. (5) follows from *Theorem 2*.

**Proof**

From eq. (4)

$$A(h) = \begin{pmatrix} 0 & B(k^*) \\ B(k^0) & 0 \end{pmatrix}$$

(7)

Since $B(k)'s$ are permutation matrices $A(h)$ is a permutation matrix too. Thus $h$ is a Sachs graph.

Since $G$ is bipartite graph every graph from $S(G)$ is bipartite also. Therefore from (3)

$$A(s) = \begin{pmatrix} 0 & C(s) \\ D(s) & 0 \end{pmatrix}$$

(8)

$C$ and $D$ are necessarily permutation matrices. The »starring process« in bipartite graphs is unique (except that the symbols * and 0 can be interchanged) hence (8) is unique and the two Kekulé graphs are uniquely defined by $B(k^*) = C(s)$ and $B(k^0) = D(s)$. This completes the proof of the *Theorem 2*.

**APPLICATIONS**

It can be demonstrated\(^1\) that *Theorem 1* is the basis for every case of congruity between simple valence bond and molecular-orbital theory. Here we would like to show that the Dewar-Longuet-Higgins formula\(^2\)

$$\text{det } A = (-)^{N/2} (K^+ - K^-)^2$$

(9)

is a simple corrolary of eq. (5). To do this one should remember that Sachs established\(^{10}\) that

$$\text{det } A = \sum_{s \in S} (-)^{c(s)}$$

(10)

According to *Theorem 2* and eq. (10)

$$\text{det } A = \sum_{i=1}^{K} \sum_{j=1}^{K} (-)^{c(k_i^* + k_j^0)}$$

(11)

and if a »parity« $P_j$ is attributed to every Kekulé structure $k_j$ such that $P_j = +1$ or $-1$ and $(-)^{c(k_i^* + k_j^0)} = (-)^{N/2} P_j P_j$ eq. (9) follows, where $K^+$ and $K^-$ are the numbers of »even« ($P_j = +1$) and »odd« ($P_j = -1$) Kekulé structures ($K^+ + K^- = K$). Thus

$$\left| \sum_{i=1}^{K} P_j \right| = |K^+ - K^-|$$

(12)

It is, however, rather difficult to determine the parity of a Kekulé structure using the method of Dewar and Longuet-Higgins\(^2\). In order to overcome this difficulty a set of rules has been given by Wilcox\(^{12}\) covering several special types of molecules of interest in chemistry. We show here that there exists a very simple procedure for obtaining the $P_j$-values. The idea of this algorithm has been first given in Ref. 4a.
KEKULE STRUCTURES

Theorem 3

If the Kekulé structures $k_i$ and $k_j$ are of the same parity the Sachs graph $s_{ij} = k_i^* + k_j^0$ contains even number of $(4m)$-membered cycles, i.e.

$$p_i p_j = (-)^{r_{4m}} ( k_i^* + k_j^0 ) \quad (13)$$

Proof

Let $\sigma$ be a $N$-membered (directed) cycle.

Decompose $\sigma$ by deleting edges in such a way that the remaining subgraph is a Kekulé graph. If $N$ is even the obtained Kekulé graph possesses $N/2$ components. Thus, the decomposition of a $(4m + 2)$-membered cycle will not alter the parity of the number of components while the decomposition of a $(4m)$-cycle will. Since every Sachs graph (of a bipartite graph) can be in the above manner decomposed to Kekulé graphs, it follows

$$(-)^{c(\sigma)} = (-)^{N/2} (-)^{r_{4m}(\sigma)} \quad (14)$$

Applying Theorem 2 and using the definition of $P_j$ the Theorem 3 follows.

Theorem 3 is the basis of the following simple algorithm: if the figure obtained by superposition of the double bonds in two Kekulé structures contains an even (odd) number of $(4m)$-membered rings the Kekulé structures have the same (opposite) parity.

Example

The superposition figure $s$ $k_1$ and $k_2$ are of the same parity since $r_{4m}(s) = 2$.

The application of eq. (9) for predicting chemical behaviour is discussed in details elsewhere$^{4b,12}$.

A corollary of Theorem 3 is that in the following formula:

$$(-)^{N/2} \det A < K^2 \quad (15)$$

* If $N$ is odd it is, of course, not possible to obtain a Kekulé graph. This is the reason why Theorem 1 holds for bipartite graphs only.
the equality holds if and only if it is \( r_{mn}(s) = 0 \) for all \( s \in S \). In Ref. 1 it has been shown that the latter is fulfilled for a rather wide class of graphs including graphs of benzenoid hydrocarbons.

The relation between the permanent of the adjacency matrix and the number \( K \) can be obtained quite easily from (5). A reasoning similar to that which has been used in Ref. 10 in order to obtain eq. (10) leads to

\[
\text{per} \ A = \sum_{s \in S} (+)^{c(s)} = |S| \tag{16}
\]

Hence, from (5)

\[
\text{per} \ A = K^2 \tag{17}
\]

This equation was proved without the knowledge of eq. (5) in Ref. 3. Recently a novel proof of (17) was presented in a paper of Lee, Herndon and Phan.

A procedure which is similar to one given in the present paper leads to the generalization of eq. (5) for nonalternant hydrocarbons:

\[
|S| - |S_{\text{odd}}| = K^2 \tag{18}
\]

Then, a completely analogous consideration gives

\[
\det A = (-)^{N/2} (K^2 + K) + \sum_{s \in S_{\text{odd}}} (-)^{c(s)} \tag{19}
\]

\[
\text{per} \ A = K^2 + |S_{\text{odd}}| \tag{20}
\]

REFERENCES

11. e. g. J. Riordan; *An Introduction to Combinatorial Analysis*, Wiley, New York 1958.
IZVOD

Teorija grafova i molekularne orbitale. VIII. Kekuléove strukture i permutacije

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