Graph Theory and Molecular Orbitals. IV.* Further Application of Sachs Formula

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In the present note we would like to report a further application¹ of the Sachs formula² to conjugated hydrocarbons.

A survey of the HMO energy level diagrams of a number of conjugated hydrocarbons³⁻¹⁰ exhibits three characteristic energy level patterns as shown in Fig. 1. The HMO energy level distribution as indicated in case A is observed for the majority of conjugated molecules, but a number of examples is also found with either unoccupied bonding levels (case B; e.g. fulvalene)

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Fig. 1. Characteristic HMO energy level patterns of conjugated hydrocarbons.

or occupied antibonding levels (case C; e.g. heptafulvalene). The cases with NBMO's are omitted for the sake of simplicity. A discussion about the role of the NBMO's can be found, for example, in our earlier work\textsuperscript{17}.

Here, we would like to present several theorems in order to show how one can construct an arbitrary large number of structures of the same energy level distribution.

Conjugated molecules will be represented by graphs in the manner described earlier\textsuperscript{1,17}. Hence, HMO energies (in $\beta$ units) are identical with the roots $x_i$ ($i = 1, 2, \ldots, N$) of the characteristic polynomial:

$$P_G(x) = \sum_{n=0}^{N} a_n x^{N-n}$$

of the graph $G$ with $N$ vertices. The coefficients $a_n$ of the polynomial (1) can be calculated using the Sachs formula\textsuperscript{2}:

$$a_n = \sum_{s} (-)^{c(s)} 2^{r(s)}$$

where $s$ are the Sachs graphs (with $n$ vertices) of the graph $G$ having $c(s)$ total components and $r(s)$ ring components, respectively.

Let the function $\mu$ of the molecular graph $G$ be defined as follows

$$\mu(G) = \begin{cases} 
  k_a & \text{case A} \\
  k_b & \text{case B} \\
  k_c & \text{case C}
\end{cases}$$

where $k_a$, $k_b$, and $k_c$ are different numbers.

Additionally, it will be assumed that the graph transformations used in the following theorems cannot cause a change of sign for more than one energy level\textsuperscript{*}. Since, $a_N = x_1 x_2 \ldots x_N$ and $x_i$ is greater than zero for bonding MO's, the conservation of the sign of $(-)^{N/2} a_N$ is a sufficient condition for the function $\mu$ to remain unchanged after a transformation is performed on the graph.

**Theorem 1**

The introduction of a 4-membered chain in the graph does not alter the value of $\mu$. Let the graphs $G$ and $G_1$ be of the form:

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  \begin{figure}[h]
  \centering
  \includegraphics[width=0.5\textwidth]{figure}
  \caption{Graphs $G$ and $G_1$.}
  \end{figure}
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then

$$\mu(G_1) = \mu(G)$$

**Proof**

There is a one-to-one correspondence between the Sachs graph $s$ of the graph $G$ and $s_1$ of $G_1$. The four vertices of the introduced chain either belong

\textsuperscript{*} For more detailed discussion see Ref. 18.
to a ring \([c(s_1) = c(s); \tau(s_1) = \tau(s)]\) or to graphs \(\Gamma^*\) \([c(s_1) = c(s) + 2; \tau(s_1) = \tau(s)]\). Because

\[
(-c(s)) \cdot 2^{\tau(s)} = (-c(s)) \cdot 2^{\tau(s)}
\]

it follows that

\[
a_{N_1}(G_1) = a_N(G)
\]

and

\[
sign[(--)^{N_1}a_{N_1}(G_1)] = sign[(-)^N a_N(G)]
\]

where \(N_1 = N + 4\).

**Example**

\[
\mathcal{h}(\text{Diagram 1}) = \mathcal{h}(\text{Diagram 2}) = \mathcal{h}(\text{Diagram 3}) = \text{etc.} = k_C
\]

HMO energy level diagrams for these molecules are given in Fig. 2. Only several highest occupied and lowest empty levels are shown in this and in the following figures.

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**Theorem 2**

If the graph \(G_1\) is obtained by joining one vertex of the graph \(\Gamma\) to arbitrary position(s) of the graph \(G\), then

\[
\mu(G_1) = \mu(G)
\]

**Proof**

This proof is similar to that of theorem 1. The two introduced vertices in all Sachs graphs belong to a graph \(\Gamma\), therefore \(c(s_1) = c(s) + 1; \tau(s_1) = \tau(s)\). Hence,

\[
a_{N_1}(G_1) = -a_N(G)
\]

and

\[
sign[(-)^{N_1}a_{N_1}(G_1)] = sign[(-)^N a_N(G)]
\]

where \(N_1 = N + 2\).

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* graph \(\Gamma\) denotes the graph with two vertices and one edge: o—o.
Example

\[ \mu\left(\begin{array}{c}
\text{\includegraphics[width=0.2\textwidth]{example1.png}}
\end{array}\right) = \mu\left(\begin{array}{c}
\text{\includegraphics[width=0.2\textwidth]{example2.png}}
\end{array}\right) = \mu\left(\begin{array}{c}
\text{\includegraphics[width=0.2\textwidth]{example3.png}}
\end{array}\right) = \text{etc.} = k_\alpha \]

HMO energy level diagrams for the above molecules are given in Fig. 3.

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**Theorem 3**

If the graph \( G_1 \) is obtained by joining an arbitrary* bipartite graph \( B \) (with even number \( b \) of vertices) to the graph \( G \) by one edge, then

\[ \mu(G_1) = \mu(G) \]

**Proof**

Since no Sachs graph contains the edge which connects \( B \) to \( G \), it follows that

\[ a_{\mu_1}(G_1) = a_{\mu}(G) a_{\mu}(B) \]

and

\[ \text{sign } \left[ (-)^{\mu_1} a_{\mu_1}(G_1) \right] = \text{sign } \left[ (-)^{\mu} a_{\mu}(G) \right] \]

because \( \mu_1 = \mu + b \) and \( (-)^{\frac{b}{2}} a_{\mu}(B) > 0 \).

**Example**

\[ \mu\left(\begin{array}{c}
\text{\includegraphics[width=0.2\textwidth]{example4.png}}
\end{array}\right) = \mu\left(\begin{array}{c}
\text{\includegraphics[width=0.2\textwidth]{example5.png}}
\end{array}\right) = \mu\left(\begin{array}{c}
\text{\includegraphics[width=0.2\textwidth]{example6.png}}
\end{array}\right) = \text{etc.} = k_\beta \]

HMO energy level diagrams for these molecules are given in Fig. 4.

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* Bochvar and Stankevich have recently published a special case of this theorem, \( B \) being a \( b \)-membered chain.
**Theorem 4**

If the graph $G_1$ is obtained by joining the ends of a $(4m + 2)$-membered chain to nonadjacent vertices of the graph $G$ which are also joined together in the graph $G_1$, then

$$
\mu(G_1) = \mu(G)
$$

**Proof**

We will prove this theorem only for a 2-membered chain ($m = 0$), because the generalization for $m > 0$ is evident from theorem 1.

Sachs graphs $s_i$ containing all the $N_i$ vertices of the graph $G_i$ can be divided in six classes:

and hence

$$
\Sigma = \Sigma + \Sigma + \Sigma + \Sigma + \Sigma + \Sigma
$$

It can be easily verified using the Sachs formula (2) that

$$
\Sigma + \Sigma = 0
$$

$$
\Sigma_{s_1} = 1^2 2^3 3^4 4^5 5^6
$$
and
\[
\Sigma + \Sigma + \Sigma = 0
\]
Therefore,
\[
a_{N_1}(G_1) = \Sigma = \Sigma = -\Sigma = -a_N(G)
\]
and
\[
\text{sign} \left[ (-)^{N_x^2} a_{N_1}(G_1) \right] = \text{sign} \left[ (-)^{N_x^2} a_N(G) \right]
\]
where \( N_x = N + 2 \).

Example
\[
\kappa \left( \begin{array}{c}
\begin{array}{c}
\hline
\hline
\end{array}
\end{array} \right) = \kappa \left( \begin{array}{c}
\begin{array}{c}
\hline
\hline
\end{array}
\end{array} \right) = \kappa \left( \begin{array}{c}
\begin{array}{c}
\hline
\hline
\end{array}
\end{array} \right) = \text{etc} = k_a
\]
HMO energy level diagrams for these molecules are given in Fig. 5.

Fig. 5.

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REFERENCES
IZVOD

Teorija grafova i molekularne orbitale. IV. Daljnja primjena Sachsove formule

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Sachsova formula korištena je u nekoliko teorema koji pokazuju kako se može po volji konstruirati veliki broj policikličkih konjugiranih ugljikovodika iste raspodjele energetskih nivoa.