Note on a Topological Property of the HOMO-LUMO Separation

Ivan Gutman
Faculty of Science, University of Kragujcvac, Yugoslavia

Z. Naturforsch. 35a, 458—460 (1980); received September 13, 1979

The effect of cycles on the HOMO-LUMO separation of alternant conjugated hydrocarbons is examined. A general topological regularity is established, namely that (4m + 2)-membered conjugated circuits increase and (4m)-membered conjugated circuits decrease the HOMO-LUMO separation. Möbius cycles exhibit an opposite effect.

In recent years a graph theoretical technique was developed, which enabled one to analyse and partially understand the dependence of the \( \pi \)-electron properties of conjugated molecules on molecular topology [1]. The HOMO-LUMO separation (i.e. the difference between the energy of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO)) belongs among those \( \pi \)-electron characteristics of a conjugated system, for which the graph theoretical approach was not very successful. The previously obtained results about the topological properties of the HOMO-LUMO separation are rather limited [2—4]. In the present paper we offer a general topological rule which elucidates the effect of cycles on the HOMO-LUMO separation of alternant conjugated hydrocarbons.

An auxiliary graph theoretical polynomial

According to the Sachs theorem [1, 5] the characteristic polynomial of a graph \( G \) (with \( n \) vertices) is calculated as

\[
\varphi(G) = \varphi(G, x) = \sum_{s \in S} (-1)^{c(s)} 2^{r(s)} x^{n - n(s)} \tag{1}
\]

where \( c(s) \), \( r(s) \) and \( n(s) \) is the number of components, cyclic components and vertices, respectively, of the Sachs graph \( s \). The summation goes over the set \( S \) of all Sachs graphs of the graph \( G \).

The matching polynomial \( \chi(G) \) of the graph \( G \) can be presented as [6]

\[
\chi(G) = \chi(G, x) = \sum_{s \in S^0} (-1)^{c(s)} x^{n - n(s)} \tag{2}
\]

with the summation going over the set \( S^0 \) of all acyclic Sachs graphs of \( G \) (i.e. those elements of \( S \) which have the property \( r(s) = 0 \)).

Let \( C_1, C_2, \ldots, C_r \) be the cycles of the graph \( G \) and let \( t = (t_1, t_2, \ldots, t_r) \) be an \( r \)-dimensional vector, the components of which are arbitrary numbers. We shall associate the weight \( t_i \) with the cycle \( C_i \) \( (i = 1, 2, \ldots, r) \).

Let \( T(s) \) be the product of the weights of all those cycles which belong to the Sachs graph \( s \). If \( r(s) = 0 \), then by definition \( T(s) = 1 \). The polynomial \( \mu(G, t) \)

\[
\mu(G) = \mu(G, t) = \mu(G, t, x) = \sum_{s \in S} (-1)^{c(s)} 2^{r(s)} x^{n - n(s)} T(s) \tag{3}
\]

is a generalization of both the characteristic and the matching polynomials. Namely, for \( t = (1, 1, \ldots, 1) \), Eq. (3) reduces to Eq. (1) since the \( T(s) = 1 \) for all \( s \in S \). For \( t = (0, 0, \ldots, 0) \), Eq. (3) coincides with Eq. (2) because then \( T(s) = 1 \) for \( s \in S^0 \) and \( T(s) = 0 \) for \( s \in S \setminus S^0 \). Further, if \( G^* \) is the Möbius graph derived from the Hückel graph \( G \) [7], then the polynomial \( \varphi(G^*) \) is obtained from Eq. (3) by setting \( t_i = -1 \) if the edge with negative weight belongs to the cycle \( C_i \) and \( t_i = +1 \) if the edge with negative weight does not belong to \( C_i \).

The parameter \( t_i \) can be understood as the extent to which the cycle \( C_i \) contributes to the characteristic polynomial. When \( t_i = +1 \), then the contribution of \( C_i \) is "normal". When \( t_i = 0 \), the contribution of \( C_i \) is neglected. The choice \( t_i = -1 \) corresponds to Möbius cycles.

Thus, for example, if we wish to neglect the contribution of a single cycle, say \( C_1 \), to \( \varphi(G) \), then we must set \( t = (0, 1, \ldots, 1) \). This leads to

\[
\mu(G) = \varphi(G) + 2 \varphi(G - C_1)
\]

as it was demonstrated elsewhere [8].
The \( \mu \) polynomial can be expanded as
\[
\mu(G, t) = \alpha(G) - 2 \sum_i t_i \alpha(G - C_i) + 4 \sum_{i,j} t_i t_j \alpha(G - C_i - C_j) - 8 \sum_{i,j,k} t_i t_j t_k \alpha(G - C_i - C_j - C_k) + \cdots.
\]

Therefrom,
\[
\frac{\partial \mu(G, t)}{\partial t_a} = -2 \alpha(G - C_a) + 4 \sum_j t_j \alpha(G - C_a - C_j) - 8 \sum_{j,k} t_j t_k \alpha(G - C_a - C_j - C_k) + \cdots
\]
and we obtain the following important conclusion:
\[
\frac{\partial \mu(G, t)}{\partial t_a} = -2 \mu(G - C_a, t).
\]

**The method**

In this paper we will be interested in the smallest non-negative zero of \( \varphi(G, x) \), which will be denoted by \( h \). If \( G \) is a bipartite graph (i.e. the molecular graph of an alternant hydrocarbon [1]), then \( 2h \) is just the HOMO-LUMO separation (in \( \beta \) units) of the pertinent \( \pi \)-electron system [3, 4].

Let \( h^0 \) be the smallest non-negative zero of the matching polynomial of \( G \). Then \( 2h^0 \) is the HOMO-LUMO separation of the reference structure of the conjugated \( \pi \)-electron system under consideration. Since in the matching polynomial the effect of all cycles is neglected, the quantity \( 2(h - h^0) \) can be interpreted as the joint effect of all cycles on the HOMO-LUMO separation.

The generalization (3) enables the introduction of a function \( h(t) \) with \( r \) variables \( t_1, t_2, \ldots, t_r \), which is a zero of the polynomial \( \mu(G, t) \) and which has the properties \( h(t) = h \) for \( t = (1, 1, \ldots, 1) \) and \( h(t) = h^0 \) for \( t = (0, 0, \ldots, 0) \). In general \( h(t) \) is a complex number.

In the following we will restrict our considerations to the case when \( h(t) \neq 0 \). Then also \( \mu'(G, t, h(t)) \neq 0 \).

Series expansion of \( h(t) \) gives
\[
h(t) = h^0 + \sum_{a=1}^r t_a \frac{\partial h(t)}{\partial t_a} + \cdots. \tag{4}
\]

Since \( \mu(G, t, h(t)) = 0 \), one concludes that
\[
\frac{\partial \mu(G, t, h(t))}{\partial t_a} = -\frac{\partial \mu(G, t, h(t))}{\partial t_a} \quad \text{and} \quad \frac{\partial \mu(G, t, h(t))}{\partial h(t)} = \frac{\partial \mu(G, t, h(t))}{\partial h(t)}.
\]

If we neglect the higher order terms in the expansion (4), then for \( t = (1, 1, \ldots, 1) \) we obtain
\[
h \approx h^0 + 2 \sum_{a=1}^r \frac{\varphi(G - C_a, h)}{\varphi(G, h)}
\]
i.e.
\[
2(h - h^0) \approx \sum_a R(G, C_a)
\]
where
\[
R(G, C) = 4 \frac{\varphi(G - C, h)}{\varphi(G, h)}.
\]
Equation (5) has a natural interpretation, namely that the quantity \( R(G, C) \) represents (approximately) the effect of the cycle \( C \) on the HOMO-LUMO separation of the alternant conjugated hydrocarbon, whose molecular graph is \( G \). Furthermore, the joint effect of all cycles on the HOMO-LUMO separation is (approximately) additive.

**Discussion**

Whether a cycle \( C \) has an increasing or decreasing effect on the HOMO-LUMO separation depends mainly on the sign of \( \varphi(G-C) \). We show now that (provided some acceptable assumptions are fulfilled) the sign of \( R(G, C) \) depends solely on the size \( |C| \) of the cycle \( C \).

Let the number of vertices of the graph \( G \) be \( n \). Then \( G - C \) possesses \( n - |C| \) vertices. It is easy to verify that
\[
\text{sign } \varphi'(G, h) = -(-1)^{n/2}.
\]

In order to determine the sign of \( \varphi(G - C, h) \) we will assume that \( h \) is smaller than the smallest positive zero of \( \varphi(G - C) \). Despite a few exceptions, this assumption is true for the great majority of bipartite molecular graphs.

Two possibilities exist: either \( \varphi(G - C) = 0 \) or \( \varphi(G - C, 0) = 0 \). The former will happen if \( C \) is a conjugated circuit in \( G \) [9]. Then
\[
\text{sign } \varphi(G - C, h) = (-1)^{n-|C|}.
\]

Therefore,
\[
\text{sign } R(G, C) = (-1)^{|C|/2}
\]
and one deduces the following result.
**Rule 1.** 
(4m + 2)-membered conjugated circuits in an alternant hydrocarbon have an increasing effect on the HOMO-LUMO separation; (4m)-membered conjugated circuits have a decreasing effect on the HOMO-LUMO separation.

If $C^* = C_a$ is a Möbius-type cycle, then one has to set $t_a = -1$ in Equation (4). Consequently, Eq. (5) is to be slightly modified for Möbius graphs. The effect of a Möbius cycle on the HOMO-LUMO separation is equal to $R(G^*, C^*) = -R(G, C) = -4\varphi(G - C, h)/\varphi'(G, h)$.

**Rule 2.** 
(4m + 2)-membered conjugated Möbius circuits in an alternant Möbius system have a decreasing effect on the HOMO-LUMO separation; (4m)-membered conjugated Möbius circuits have an increasing effect on the HOMO-LUMO separation.

If $C$ is not a conjugated circuit in $G$ [9], then $\varphi(G - C, 0) = 0$ and therefore also $\varphi(G - C, h) \approx 0$.

**Rule 3.** 
If a cycle in an alternant hydrocarbon or Möbius system is not a conjugated circuit, then its effect on the HOMO-LUMO separation is small and is of no chemical significance. The sign of the effect of such cycles cannot be reliably deduced on the basis of the $R(G, C)$ index, since it (the sign) depends on the higher order terms of Equation (4).

---