Note on a Topological Property of the HOMO-LUMO Separation

Ivan Gutman

Faculty of Science, University of Kragujevac, 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 π-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 π-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

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

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 $\mathbf{S}$ of all Sachs graphs of the graph G.

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

$$\alpha(G) = \alpha(G, x) = \sum_{s \in \mathbf{S}^0} (-1)^{c(s)} \, x^{n-n(s)} \tag{2}$$

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

Let $C_1, C_2, \ldots, C_r$ be the cycles of the graph G and let $\mathbf{t} = (t_1, t_2, \ldots, t_r)$ 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 $\mu(G, \mathbf{t})$

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

is a generalization of both the characteristic and the matching polynomials. Namely, for $\mathbf{t} = (1, 1, \ldots, 1)$, Eq. (3) reduces to Eq. (1) since the $T(s) = 1$ for all $s \in \mathbf{S}$. For $\mathbf{t} = (0, 0, \ldots, 0)$, Eq. (3) coincides with Eq. (2) because then $T(s) = 1$ for $s \in \mathbf{S}^0$ and $T(s) = 0$ for $s \in \mathbf{S} \setminus \mathbf{S}^0$. 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 $\mathbf{t} = (0, 1, \ldots, 1)$. This leeds to

$$\mu(G) = \varphi(G) + 2\varphi(G - C_1)$$

as it was demonstrated elsewhere [8].

Requests for reprints should be sent to Doc. Dr. Ivan Gutman, Faculty of Science, P.O.Box 60, 34000 Kragujevac, Yugoslavia.

0340-4811 / 80 / 0400-0458 $ 01.00/0. — Please order a reprint rather than making your own copy.

The μ polynomial can be expanded as

$$\mu(G, \mathbf{t}) = \alpha(G) - 2\sum_i t_i\, \alpha(G - C_i) + 4\sum_{i,j} t_i t_j\, \alpha(G - C_i - C_j) - 8\sum_{i,j,k} t_i t_j t_k\, \alpha(G - C_i - C_j - C_k) + \cdots .$$

Therefrom,

$$\frac{\partial \mu(G, \mathbf{t})}{\partial t_a} = -2\alpha(G - C_a) + 4\sum_j t_j\, \alpha(G - C_a - C_j) - 8\sum_{j,k} t_j t_k\, \alpha(G - C_a - C_j - C_k) + \cdots$$

and we obtain the following important conclusion:

$$\frac{\partial \mu(G, \mathbf{t})}{\partial t_a} = -2\mu(G - C_a, \mathbf{t}) .$$

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 β units) of the pertinent π-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 π-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 $\mu(G, \mathbf{t})$ and which has the properties $h(\mathbf{t}) = h$ for $\mathbf{t} = (1, 1, \ldots, 1)$ and $h(\mathbf{t}) = h^0$ for $\mathbf{t} = (0, 0, \ldots, 0)$. In general $h(\mathbf{t})$ is a complex number.

In the following we will restrict our considerations to the case when $h(\mathbf{t}) \neq 0$. Then also $\mu'(G, \mathbf{t}, h(\mathbf{t})) \neq 0$. Series expansion of $h(\mathbf{t})$ gives

$$h(\mathbf{t}) = h^0 + \sum_{a=1}^{r} t_a \frac{\partial h(\mathbf{t})}{\partial t_a} + \cdots . \tag{4}$$

Since $\mu(G, \mathbf{t}, h(t)) = 0$, one concludes that

$$\frac{\partial h(\mathbf{t})}{\partial t_a} = -\frac{\partial \mu(G, \mathbf{t}, h(\mathbf{t}))}{\partial t_a} \Big/ \frac{\partial \mu(G, \mathbf{t}, h(\mathbf{t}))}{\partial h(\mathbf{t})} = 2\,\frac{\mu(G - C_a, \mathbf{t}, h(\mathbf{t}))}{\mu'(G, \mathbf{t}, h(\mathbf{t}))} .$$

If we neglect the higher order terms in the expansion (4), then for $\mathbf{t} = (1, 1, \ldots, 1)$ we obtain

$$h \approx h^0 + 2\sum_{a=1}^{r} \frac{\varphi(G - C_a, h)}{\varphi'(G, h)}$$

i.e.

$$2(h - h^0) \approx \sum_a R(G, C_a) \tag{5}$$

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 $R(G, C)$. 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

$$\operatorname{sign} \varphi'(G, h) = -(-1)^{n/2} .$$

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 $\varphi(G - C) \neq 0$ or $\varphi(G - C, 0) = 0$. The former will happen if C is a conjugated circuit in G [9]. Then

$$\operatorname{sign} \varphi(G - C, h) = (-1)^{(n-|C|)/2} .$$

Therefrom,

$$\operatorname{sign} R(G, C) = -(-1)^{|C|/2}$$

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).

[1] For review see: A. Graovac, I. Gutman and N. Trinajstić, Topological Approach to the Chemistry of Conjugated Molecules, Springer-Verlag, Berlin 1977.
[2] I. Gutman, J. V. Knop, and N. Trinajstić, Z. Naturforsch. **29b**, 80 (1974).
[3] G. G. Hall, Mol. Phys. **33**, 551 (1977).
[4] I. Gutman and D. H. Rouvray, Chem. Phys. Letters **62**, 384 (1979).
[5] D. Cvetković, M. Doob, and H. Sachs, Spectra of Graphs. Theory and Application, Academic Press, New York 1980.
[6] I. Gutman and H. Hosoya, Theor. Chim. Acta **48**, 279 (1978); C. D. Godsil and I. Gutman, Z. Naturforsch. **34a**, 776 (1979).
[7] For details on Möbius graphs and explanation of the present notation see: I. Gutman, preceeding paper.
[8] S. Bosanac and I. Gutman, Z. Naturforsch. **32a**, 10 (1977).
[9] For the definition of conjugated circuits and details about their role in the theoretical chemistry of conjugated molecules see: M. Randić, Chem. Phys. Letters **38**, 68 (1976); J. Amer. Chem. Soc. **99**, 444 (1977).