Topological Studies on Heteroconjugated Molecules. A New Pairing Theorem

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It is shown that the pairing property of Hückel molecular orbital energy levels holds also in the case of certain conjugated molecules containing heteroatoms.

1. Introduction

According to a well-known result of Coulson and Rushbrooke [1], the Hückel molecular energy levels of alternant hydrocarbons occur in pairs that are symmetrically arranged with respect to the energy of an isolated (carbon atom) *p*-orbital. Using the graph-theoretical reformulation of the Hückel molecular orbital model [2], the Coulson-Rushbrooke pairing theorem can be stated as

$$x_j + x_{n+1-j} = 0 \quad \text{for} \quad j = 1, 2, \ldots, n\,, \tag{1}$$

where $x_1, x_2, \ldots, x_n$ denote the eigenvalues of the molecular graph of an alternant hydrocarbon. Such graphs (called in graph theory bipartite) possess no self-loops. In the general case, (1) does not hold for graphs with self-loops. Hence, the pairing theorem cannot be applied to heteroconjugated molecules even if they have alternant topologies.

The aim of the present paper is to point out that there exists an exceptional class of heteroconjugated molecules whose Hückel molecular orbital energy levels are paired in the very same manner as are the energy levels of alternant hydrocarbons. In particular, we shall construct a class of molecular graphs with weighted self-loops whose eigenvalues satisfy (1).

In order to do this we need some preparations.

2. Preliminaries

Whereas conjugated hydrocarbons are represented by simple graphs [2], the molecular graphs of heteroconjugated molecules necessarily contain weighted self-loops and weighted edges [3–5]. Since the validity of the pairing theorem is not affected by the presence of weights on the edges [6], we shall focus our attention to molecular graphs containing self-loops only.

Let G be a graph without self-loops and let $v_1, v_2, \ldots, v_n$ be its vertices. Let G_h be the graph obtained from G by attaching weighted self-loops to some of its vertices. The weight of the self-loop on the vertex v_r is h_r, $r = 1, 2, \ldots, n$. (Of course, if $h_r = 0$ then there is no self-loop on the vertex v_r.)

Methods for the calculation of the characteristic polynomial of a graph possessing weighted self-loops have been elaborated elsewhere [3–5]. Using the results of [3–5] it is not difficult to see that the characteristic polynomials of G_h and G are related as

$$\begin{aligned}\Phi(G_h) = \Phi(G) &- \sum_r h_r \Phi(G - v_r) \\ &+ \sum_{r<s} h_r h_s \Phi(G - v_r - v_s) \\ &- \sum_{r<s<t} h_r h_s h_t \Phi(G - v_r - v_s - v_t) \\ &+ \ldots + (-1)^k h_1 h_2 \ldots h_k \\ &\cdot \Phi(G - v_1 - v_2 - \ldots - v_k)\,,\end{aligned} \tag{2}$$

provided self-loops (with non-zero weights) have been attached to the vertices $v_1, v_2, \ldots, v_k$.

In the case of one self-loop (*i.e.*, $k = 1$), (2) reduces to the well-known expression [7, 8]

$$\Phi(G_h) = \Phi(G) - h_1 \Phi(G - v_1)\,. \tag{3}$$

In the case of two self-loops (*i.e.*, $k = 2$), we have another special case of (2), namely

$$\begin{aligned}\Phi(G_h) = \Phi(G) &- h_1 \Phi(G - v_1) - h_2 \Phi(G - v_2) \\ &+ h_1 h_2 \Phi(G - v_1 - v_2)\,.\end{aligned} \tag{4}$$

The pairing theorem (1) is a consequence of the fact that the characteristic polynomial of bipartite graphs is either an even or an odd function. As a

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matter of fact, the characteristic polynomial of a bipartite graph G conforms to the following relation

$$\Phi(G, -x) = (-1)^n \Phi(G, x) ,$$

where n is the number of vertices of G. Hence, $\Phi(G, x)$ is an even function if n is even and $\Phi(G, x)$ is an odd function if n is odd.

If G is bipartite, then all its subgraphs are bipartite too. Hence, the subgraphs $G - v_r$, $G - v_r - v_s$ etc. are bipartite and their characteristic polynomials are either even or odd functions. However, if $\Phi(G, x)$ is even, then $\Phi(G - v_r, x)$ is odd (or vice versa). Consequently, the polynomial (3) is neither an even nor an odd function, which means that the pairing theorem cannot hold for heteroconjugated molecules with one heteroatom [8].

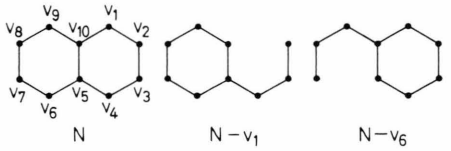
The right-hand side of (2) is also a polynomial without parity. Therefore, in the general case, the pairing theorem does not hold for heteroconjugated molecules irrespective of the number of heteroatoms they contain. However, there are some special cases where the pairing theorem holds, which will be examined in the subsequent section.

3. The Main Result

Let v_1 and v_2 be two vertices of a graph G. We say that v_1 and v_2 are equivalent if there is a symmetry operation (or more precisely: an element of the automorphism group of G [9]) which maps v_1 into v_2 and vice versa.

If v_1 and v_2 are equivalent, then the subgraphs $G - v_1$ and $G - v_2$ are isomorphic. In that case, of course, also the characteristic polynomials of $G - v_1$ and $G - v_2$ coincide.

For example, in the case of the naphthalene graph N the pairs of vertices v_1 and v_6 are equivalent. The subgraphs $N - v_1$ and $N - v_6$ are isomorphic.

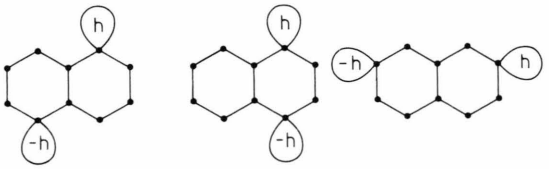


Other pairs of equivalent vertices of N are v_1 and v_4 or v_2 and v_8, etc.

Let F be the molecular graph of an alternant hydrocarbon and let v and w be its two equivalent vertices. Then we have the following extension of the Coulson-Rushbrooke theorem.

Pairing Theorem for Heteroconjugated Molecules. (a) If the molecular graph F_h of a heteroconjugated molecule has a self-loop of weight h on the vertex v and a self-loop of weight $-h$ on the vertex w, then its eigenvalues conform to (1).

For example, the pairing theorem holds for the following three molecular graphs derived from the naphthalene graph. The parameter h may be chosen to be any real-valued number.



Roughly speaking, the above theorem means that if we substitute two equivalent carbon atoms of an alternant hydrocarbon by heteroatoms having opposite electronegativity (relative to carbon), then the Hückel molecular orbital energy levels remain symmetric with respect to the energy of a carbon-atom p-orbital.

Having in mind the results given in the previous section, the proof of our pairing theorem is straightforward. Namely, if $h_1 = -h_2 = h$ and $\Phi(G - v_1) = \Phi(G - v_2)$, then (4) reduces to

$$\Phi(G_h) = \Phi(G) + h_1 h_2 \Phi(G - v_1 - v_2)$$

i.e.,

$$\Phi(F_h) = \Phi(F) - h^2 \Phi(F - v - w) . \qquad (5)$$

Since $F - v - w$ has $n - 2$ vertices, either both $\Phi(F)$ and $\Phi(F - v - w)$ are even functions (if n is even) or both are odd functions (if n is odd). Consequently, $\Phi(F_h)$ is either an even or an odd function, and, therefore, its zeros satisfy (1).

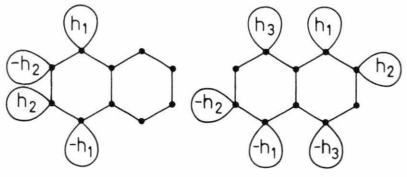
Using the same argument we can further extend our pairing theorem as follows.

Let $v_1, v_2, \ldots, v_{2k}$ be some vertices of a graph G. We say that the vertices $v_1, v_3, \ldots, v_{2k-1}$ are equivalent to the vertices $v_2, v_4, \ldots, v_{2k}$ if there is a symmetry operation (*i.e.*, an element of the automorphism group of G) which maps v_{2j-1} into v_{2j} and v_{2j} into v_{2j-1}, $j = 1, 2, \ldots, k$.

Let H be the molecular graph of an alternant hydrocarbon and let $v_1, v_2, \ldots, v_k$ and $w_1, w_2, \ldots, w_k$ be its equivalent vertices.

Pairing Theorem for Heteroconjugated Molecules. (b) If the molecular graph H_h of a heteroconjugated molecule has self-loops of weight h_r on the vertices v_r and self-loops of weight $-h_r$ on the vertices w_r, $r = 1, 2, \ldots, k$, then its eigenvalues conform to (1).

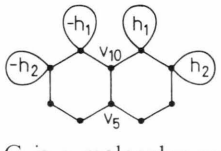
For example, the pairing theorem holds for the following two molecular graphs derived from the naphthalene graph. The parameters h_1, h_2 and h_3 may be any real-valued numbers.



4. Discussion

The validity of the pairing theorem for the above described heteroconjugated molecules does not imply that their charge distribution is uniform. For the uniformity of charge distribution some additional conditions must be fulfilled [6]. Nevertheless, if u is a vertex of F, such that the vertices v and w are equivalent in both F and $F - u$, then one can show that the HMO π-electron charge on the carbon atom corresponding to u in the heteroconjugated molecule represented by F_h is equal to zero.

For example, zero HMO π-electron charge will be calculated on the atoms corresponding to the vertices v_5 and v_{10} of the following molecular graph, irrespective of the value of the parameters h_1 and h_2.



If G is a molecular graph of an alternant hydrocarbon, then its characteristic polynomial can be written in the form [10]

$$\Phi(G) = \sum_j (-1)^j b_j(G)\, x^{n-2j}. \qquad (10)$$

It can be shown [10, 11] that $b_j(G)$ is non-negative for all values of j and that the total π-electron energy (in β units) is given by

$$E(G) = (1/\pi) \cdot \int_{-\infty}^{+\infty} \left[\log \sum_j b_j(G)\, x^{2j}\right] x^{-2}\, dx .$$

Consequently, the total π-electron energy is a monotonically increasing function of the coefficients b_j [11].

From (5) is seen that an expression of the form (6) can be written also for the characteristic polynomial of F_h. In particular, we have

$$b_j(F_h) = b_j(F) + h^2 b_{j-1}(F - v - w)$$

and $E(F_h)$ is a monotonically increasing function of the coefficients $b_j(F_h)$. It follows that $E(F_h)$ depends on h^2 and monotonically increases with increasing h^2. A chemical consequence of this result would be that the increase of the difference in the electronegativity of the two heteroatoms will cause a thermodynamic stabilization of the molecule.

We note in passing that one can find a graph F_h^* without self-loops, such that $\Phi(F_h) = \Phi(F_h^*)$. The graph F_h^* has a pair of directed edges between the vertices v and w, which are weighted by ih in one direction and by $-ih$ in the other direction ($i = \sqrt{-1}$).

As a final remark we would like to note that a number of fully analogous results can be obtained also for the matching polynomial $\alpha(G_h)$ of the graph G_h. (For details on matching polynomials see refs. [12, 13].) In particular, (2)–(5) remain valid if the symbols Φ are interchanged by α. Hence, the zeros of the matching polynomial of F_h conform to a pairing theorem analogous to (1). In this case the graph F needs not be bipartite.

Similarly, as in the case of the characteristic polynomial, one can find a graph F_h^* without self-loops, such that $\alpha(F_h) = \alpha(F_h^*)$. The graph F_h^* may have the structure as described above or may possess an undircted edge between the vertices v and w, weighted by h.

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