

Resonance Delocalizabilities of Polyacenes

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Abstract This paper describes a derivation of a closed expression of resonance delocalizabilities in the Hückel model of polyacenes. The derivation stems from the decomposition of determinants corresponding to the resonance delocalizabilities into two elementary types of determinants, followed by obtaining closed expressions for the elementary types of determinants. The process of the derivation is greatly facilitated by using graphs as representing determinants of symmetric matrices. The resulting expression of the resonance delocalizabilities reproduces and generalizes the features of site reactivities known from the numerical evaluation of superdelocalizabilities for several smaller polyacenes.

1. Introduction

Resonance delocalizability is one of practical indices of reactivity in the Hückel model, essentially equivalent to “a simple reactivity index” proposed by Fukui *et al.* (Fukui, Kato, Nagata, and Yonezawa, 1961), closely related to Dewar’s localization energy (Dewar 1952; Dewar and Longuet-Higgins 1952; Fukui, Yonezawa, and Nagata, 1957), and regarded as a substitute for superdelocalizability (Fukui, Yonezawa, and Nagata, 1954), one of the most reliable indices of reactivity in the Hückel model. Besides being a better (qualitative) approximation to superdelocalizability than frontier electron density (Fukui, Yonezawa, and Singu 1952; Fukui, Yonezawa, Nagata, and Singu, 1954), resonance delocalizability requires no solution of the Hückel eigenvalue problem, directly related to the adjacency matrix (Isihara, 2001).

Though the numerical evaluation of resonance delocalizabilities is surely much simpler than that of superdelocalizabilities, this is not a real advantage any more nowadays, at least with regard to evaluations for individual systems, because of great developments of computational techniques and circumstances. An advantage of resonance delocalizability left significant is, if any, a possibility that a closed expression may be found out for a family of systems having a specific structure. Closed expressions of eigensolutions in the Hückel model are known for several families but the summation process involved in superdelocalizabilities strongly prevents us from reaching their closed expressions. This situation is true for linear chains, the simplest family (Isihara, 1997).

This paper derives a closed expression of resonance delocalizabilities for the polyacene family, for which, of course, no closed expression of superdelocalizabilities is known so far. The second section is preliminary, giving a general description on graphical treatment used here. The third section is principal, deriving the closed expression. The fourth section

concerns what follows from the expression.

2. Preliminaries

Suppose the Hückel model of a regular alternant having $2m$ sites colored black and white. Numbering the m black sites from 1 to m and the white from $m+1$ to $2m$, we can write the adjacency matrix A of the alternant in the form

$$A = \begin{pmatrix} 0 & \mathbf{B} \\ \mathbf{B}^T & 0 \end{pmatrix} \tag{1}$$

with an $m \times m$ invertible submatrix \mathbf{B} and its transepose \mathbf{B}^T . Let \mathbf{L}_B and \mathbf{L}_W denote the black-site submatrix $\mathbf{B}\mathbf{B}^T$ and the white-site one $\mathbf{B}^T\mathbf{B}$ in A^2 , respectively, and let $\mathbf{L}(r)$ stand for the matrix obtained by deleting the r -th row and the r -th column from a matrix \mathbf{L} . Then, the resonance delocalizability R_r on site r is defined by

$$R_r = \begin{cases} |\mathbf{L}_B(r)| & (1 \leq r \leq m) \\ |\mathbf{L}_W(r-m)| & (m+1 \leq r \leq 2m) \end{cases} \tag{2}$$

(Isihara 2001). If the alternant has dichromatic symmetry, proper numbering makes \mathbf{L}_B and \mathbf{L}_W identical and we may work with either black or white sites (Isihara, 2007).

Let $G(\mathbf{L})$ denote the graph corresponding to a symmetric matrix \mathbf{L} . We can easily draw $G(\mathbf{L}_B)$ and $G(\mathbf{L}_W)$ from $G(\mathbf{A})$, in particular, if $G(\mathbf{A})$ is a chemical graph, while $G(\mathbf{L}_B(r))$ and $G(\mathbf{L}_W(r))$ follow immediately by deleting the vertex r and all edges incident to r from $G(\mathbf{L}_B)$ and $G(\mathbf{L}_W)$. It is convenient for the present purpose to regard $G(\mathbf{L})$ as representing the determinant of a symmetric matrix \mathbf{L} and to call it the detgraph of \mathbf{L} distinctively. Detgraphs can be decomposed into or reduced to detgraphs according to properties of determinants. Graphical representation provides a lucid perspective, reflecting structural features of systems and visualizing the process of calculations. Though not necessarily intrinsic, it must be indispensable in practice.

The following three ways of decomposition or reduction of detgraphs suffice for the present purpose. The weight of any edge is assumed and kept to be unity there.

1) Partitioning. An edge connecting two parts of a detgraph can be removed with subtracting the detgraph obtained from the original one by deleting the two verticies connected by the edge and all edges incident to the verticies.



2) Shifting. The weight w of a vertex of a detgraph can be shifted to v with adding the detgraph obtained from the original one by deleting all edges incident to the vertex and

by replacing the weight of the isolated vertex with $w-v$.



3) Trimming. We can remove the end vertex of weight 1 together with the incident edge, decreasing the weight of the vertex losing the edge by 1. As well, we can remove the vertex of weight 1 bridging two vertices connected by an edge together with the edge and two bridging edges, decreasing each weight of the two vertices by 1.



More general trimming is, of course, possible but it hardly seems to be fruitful because of causing fractional weights in vertices and edges. What should be tried is not necessarily full reduction but rather relevant transformation into detgraphs calculable in some other way. No haphazard trimming will yield any tractable result.

The most powerful aid for chemical detgraph is Kekulé structure enumeration, on which so many results have been accumulated, in particular, for benzenoid hydrocarbons (Cyvin and Gutman, 1988). Let C be the adjacency matrix of an alternant having black and white sites of the same number and let a detgraph $G(F)$ correspond to the black- or white-site submatrix in C^2 . Then, denoting the algebraic structure count (Wilcox, Jr., 1968; 1969) of graph G by $ASC(G)$, we have

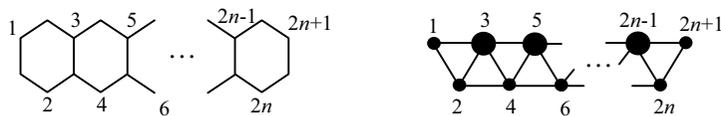
$$|F| = ASC(G(C))^2 \quad (3)$$

(Dewar and Longuet-Higgins, 1952). If any Kekulé structure of graph $G(C)$ has an identical parity, the right hand side can be replaced by $K(G(C))^2$ with $K(G)$ standing for the number of Kekulé structures of graph G .

Utilization of graphs for determinants is not novel at all in mathematical chemistry (Trinajstić, 1983; Dias, 1993) but has been oriented almost exclusively to fragmentation of characteristic polynomials of adjacency matrices. Hence, Aside from the partitioning mentioned above, no naïve decomposition or reduction prevails.

3. Derivation

Suppose the polyacene of n rings. Since this system is dicromatically symmetric, it is enough to work with its black sites. The following figure shows the graph of the adjacency matrix and that of the black-site submatrix in the squared adjacency matrix together with the numbering of sites used here.



From now on, the large black spot on a vertex indicates weight 3 and the small one weight 2. Aside from the graph of the adjacency matrix above, where all vertices are weightless, the vertex without a spot means the vertex of weight 1. Typical detgraphs for R_r and their decompositions by partitioning are exemplified by

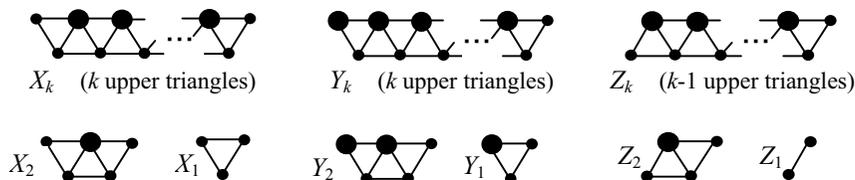


for odd r and by

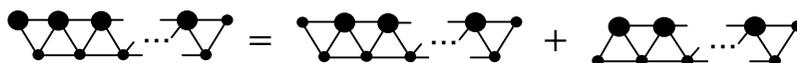


for even r . Note that all constituent detgraphs here fall into two types.

Now, define the three types of detgraphs X_k , Y_k , and Z_k for natural number k as shown in the following figure.



Since these three are related by shifting as



and X_k is given explicitly by

$$X_k = (k + 1)^2 \tag{4}$$

from the number of Kekulé structures of the k -ring polyacene, the relationship

$$Y_k = Z_k + (k + 1)^2 \tag{5}$$

immediately follows. On the other hand, decomposing Z_k by shifting as



and reducing the first detgraph in the right hand side by the successive trimming



we obtain the relationship

$$Z_k = Y_{k-1} + 1. \quad (6)$$

Relevant elimination in these two relationships leads us to the recurrence formula

$$Z_k = Z_{k-1} + k^2 + 1, \quad (7)$$

which is solved in an ordinary way to provide

$$Z_k = (k+1)(2k^2 + k + 6)/6 \quad (8)$$

and

$$Y_k = (k+1)(2k^2 + 7k + 12)/6 \quad (9)$$

as well. The resulting expressions of X_k , Y_k , and Z_k allow us to extend the range of k to all integers with the relationships between them kept unchanged, so that it is appropriate to add $X_0=1$, $Y_0=2$, $Z_0=1$, and $X_{-1}=Y_{-1}=Z_{-1}=0$ to the definition.

It is readily found that the decompositions of R_r exemplified above can be written in the general form

$$\begin{cases} R_{2t+1} = Z_t Z_{n-t} - Y_{t-1} Y_{n-t-1} & (0 \leq t \leq n) \\ R_{2t} = Y_{t-1} Y_{n-t} - Z_{t-1} Z_{n-t} & (1 \leq t \leq n) \end{cases} \quad (10)$$

including the case of the end ring sites. This can be still simplified by the relationships between Y_{k-1} and Z_k and between Y_k and Z_k as

$$\begin{cases} R_{2t+1} = Z_t + Z_{n-t} - 1 & (0 \leq t \leq n) \\ R_{2t} = (n-t+1)^2 Z_{t-1} + t^2 Z_{n-t} + t^2 (n-t+1)^2 & (1 \leq t \leq n) \end{cases} \quad (11)$$

into which we have only to substitute the expression of Z_k . Thus, we attain

$$R_r = n_+ \begin{cases} (3r^2 - 6n_+ r + 4n_+^2 + 11)/12 & (\text{odd } r) \\ (r^4 - 4n_+ r^3 + 2(2n_+^2 - 7)r^2 + 28n_+ r)/48 & (\text{even } r) \end{cases} \quad (12)$$

with the abbreviation

$$n_+ \equiv n+1. \quad (13)$$

To see the nature of R_r , it will be relevant to make use of the auxiliary site index

$$s \equiv r - (n+1) \quad (14)$$

varying from $-n$ to n . Then, R_r can be rewritten in the “symmetric” form

$$R_{s+n+1} = n_+ \begin{cases} (3s^2 + n_+^2 + 11)/12 & (s + n + 1 \text{ odd}) \\ ((s^2 - n_+^2 - 7)^2 - 49)/48 & (s + n + 1 \text{ even}). \end{cases} \quad (15)$$

Note that the lower of the right hand side decreases as $|s|$ increases in the prescribed range, quite opposite to the upper.

4. Remarks

The closed expression of R_r obtained in the preceding section suffices to analyze site reactivities of the polyacene system fully generally. The symmetry of the system allows us to confine the range of sites to $1 \leq r \leq n+1$. It is obvious from

$$R_{r+2} - R_r = -n_+(n-r) < 0 \quad (1 \leq \text{odd } r \leq n-1) \quad (16)$$

that R_r on odd-numbered site r decreases as r increases. On the other hand, we have

$$R_{r+2} - R_r = n_+(v-n+r)(n-r)(v+n-r) > 0 \quad (2 \leq \text{even } r \leq n-1) \quad (17)$$

with

$$v \equiv \sqrt{n_+^2 + 6} \quad (18)$$

because of $v > n$. Namely, R_r on even-numbered site r increases as r does. Moreover, since it holds that

$$R_2 - R_1 = n^2 - 1 < 0 \quad (n \geq 2), \quad (19)$$

there follows the sequence

$$R_{2\lfloor n/2 \rfloor + 1} < \cdots < R_3 < R_1 < R_2 < R_4 < \cdots < R_{2\lfloor (n+1)/2 \rfloor} \quad (20)$$

a general result on site reactivities of polyacenes.

Resonance delocalizability is a relative index of reactivity, only valid for intrasystem comparison, and it is suitable to “normalize” it for intersystem comparison or for comparison with superdelocalizability as

$$\rho_r \equiv \lambda |B^2|^{-1} R_r \quad (21)$$

with the smallest positive eigenvalue λ of the adjacency matrix (Isihara, 2001). As for polyacenes, fortunately, it is known that

$$\lambda = (\sqrt{9 - 8 \cos(\pi/n_+)} - 1)/2 \quad (22)$$

(Coulson, 1948) and $|B^2|$ is merely X_n , that is, $(n+1)^2$. Comparison between ρ_r and S_r for

several smaller polyacenes is shown in Table 1, where we can see complete qualitative agreement between them.

In the next place, let us examine intersystem behaviors. The intrasystem maximum $\rho_{\max}(n)$ of ρ_r is calculated to be

$$\rho_{\max}(n) = \frac{\lambda(n)}{48} \begin{cases} n_+(n_+^2 + 14) & (\text{odd } n) \\ n(n+2)(n_+^2 + 13)/n_+ & (\text{even } n) \end{cases} \quad (23)$$

and it is readily found that

$$\rho_{\max}(n+1) > \rho_{\max}(n) \quad (24)$$

by applying power series expansion to $\lambda(n)$. Forming a sharp contrast with this, the minimum

$$\rho_{\min}(n) = \frac{\lambda(n)}{12n_+} \begin{cases} (n_+^2 + 14) & (\text{odd } n) \\ (n_+^2 + 11) & (\text{even } n) \end{cases} \quad (25)$$

fulfills

$$\rho_{\min}(n+1) < \rho_{\min}(n). \quad (26)$$

This tendency of $\rho_{\max}(n)$ and $\rho_{\min}(n)$ agrees with the tendency of $S_{\max}(n)$ and $S_{\min}(n)$ for smaller polyacenes seen in Table 1.

Lastly, let us touch the asymptotic behavior of ρ_r in long ($n \gg 1$) polyacenes. By virtue of the principal term approximation

$$\lambda(n) \cong \pi^2 n^{-2} \quad (27)$$

Table 1
Resonance delocalizabilities and superdelocalizabilities of smaller polyacenes

System \ Site	6	4	2	1	3	5	7
Naphthalene	ρ_r			0.755	0.549	0.344	
	S_r			0.994	0.873	0.703	
Anthracene	ρ_r		1.036	0.673	0.466	0.259	
	S_r		1.314	1.073	0.922	0.720	
Tetracene	ρ_r		1.121	0.590	0.413	0.236	0.177
	S_r		1.505	1.122	0.961	0.750	0.717
Pentacene	ρ_r	1.373	1.123	0.519	0.372	0.226	0.153
	S_r	1.917	1.634	1.154	0.991	0.778	0.734
Hexacene	ρ_r	1.500	1.089	0.460	0.339	0.218	0.145
	S_r	2.005	1.730	1.178	1.014	0.800	0.753

S_r : Fukui, Yonezawa, and Nagata, 1957.

the characteristic n -dependence

$$\begin{cases} \rho_{\max}(n) \cong (\pi^2 / 48)n \\ \rho_{\min}(n) \cong (\pi^2 / 12)n^{-1} \end{cases} \quad (28)$$

immediately follows. In the end ring, $\rho_2(n)$ as well as $\rho_1(n)$ still behaves as

$$\rho_2(n) \cong \rho_1(n) \cong (\pi^2 / 3)n^{-1} \quad (29)$$

while it is observed that

$$\rho_{2[\sqrt{n}/2]}(n) \cong \pi^2 / 3 \quad (30)$$

for sufficiently large n . Namely, in long polyacenes, high reactivity concentrates on even-numbered sites in the central region but not acutely.

Accepted May, 31, 2008

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