Aromaticities and reactivities based on energy partitioning

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Abstract - A scheme based on energy partitioning via moments is proposed to deal with aromaticities and reactivities of conjugated systems. The REPE is computed through the enumeration of cyclic fragments, thus either the finite or infinite systems can be treated with facility. Point-energy, edge-energy, and ring resonance energy have been introduced for rationalizing the site reactivity, bond lengths and local aromaticity. This approach is graphical in essence without consulting to the solution of secular equation, i.e., the energy sequence, MO(molecular orbital)'s and related quantities defined.

INTRODUCTION

In recent years, moments have attracted a considerable attention of theoreticians with particular interests in Hückel MO theory (ref. 1-5). The importance and advantage of utilizing moments rest upon their topological meaning in relationship to the connectivity of a molecule. Let us review their definition

\[ u_1 = \sum_{j=1}^{N} x_j = \text{Tr}(A^2) = \sum_{j=1}^{N} A^2_{jj} \]

where \( u_1 \) denotes the 1-th moment, \( A \) is the adjacency matrix with its elements being 1 when the row vertices and column vertices are connected by edges and zero otherwise, \( x_j \) represents the j-th-member of energy sequence. Due to each term in the right-hand summation of Eq.(1) represents a self-adjoint walk of length 1 starting from vertex \( j \), one can derive moment formulae in terms of molecular fragments one by one (ref.1,5). In the following, lower members are given with symbols and diagrams of fragments in Fig.1 for benzenoid hydrocarbons.


Moreover, one can classify molecular fragments into acyclic and cyclic species according to whether they involve at least one ring or not. Accordingly, \( u_1 \) can be partitioned into \( u_1^a \) and \( u_1^c \), the acyclic and cyclic components, fulfilling

\[ u_1 = u_1^a + u_1^c \]

In table 1, the fragment counts together with acyclic, cyclic and total values of moments (1≤8) for naphthalene are tabulated for illustration.

Within the Hückel MO approximation, the total \( \pi \)-electron energy of the ground state of alternants and parts of non-alternants can be written as

\[ E = 2 \sum_{i=1}^{N} x_i = \sum_{i=1}^{N} |x_i| \]
Table 1. Moments (u₁, u₂ and u₄) and fragment counts of naphthalene with 1/8

<table>
<thead>
<tr>
<th>l=0</th>
<th>l=2</th>
<th>l=4</th>
<th>l=6</th>
<th>l=8</th>
</tr>
</thead>
<tbody>
<tr>
<td>u₁</td>
<td>10</td>
<td>22</td>
<td>78</td>
<td>322</td>
</tr>
<tr>
<td>u₂</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>24</td>
</tr>
<tr>
<td>u₄</td>
<td>10</td>
<td>22</td>
<td>78</td>
<td>346</td>
</tr>
</tbody>
</table>


The absolute value |x| can be expanded in terms of even powers of x (ref.1)

\[ |x| = \alpha_0 + \alpha_2 x^2 + \alpha_4 x^4 + \ldots + \alpha_{2L} x^{2L} \ldots \]

(5)

provided the point x=0 is excluded. In practice, Eq.(5) is truncated and coefficients \( \alpha_0, \alpha_2, \ldots, \alpha_{2L} \) can be determined numerically by least-squares fits in the interval, \( -3.00 \leq x \leq 3.00 \), or by expansion in terms of Chebyshev polynomials (ref.6). In Table 2, three numerical sets of \( \alpha_{2L} \) for \( L = 2, 4 \) and 6 obtained by least square fits (ref.5) are tabulated.

Table 2. Numerical values of \( \alpha_{2L} \) for \( L = 2, 4 \) and 6

<table>
<thead>
<tr>
<th>L</th>
<th>( \alpha_0 )</th>
<th>( \alpha_2 )</th>
<th>( \alpha_4 )</th>
<th>( \alpha_6 )</th>
<th>( \alpha_8 )</th>
<th>( \alpha_{10} )</th>
<th>( \alpha_{12} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.3904</td>
<td>0.5262</td>
<td>-0.0283</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.2393</td>
<td>0.9253</td>
<td>-0.2105</td>
<td>0.02733</td>
<td>-0.00130</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>0.1783</td>
<td>1.2955</td>
<td>-0.6277</td>
<td>0.2042</td>
<td>-0.03565</td>
<td>0.00310</td>
<td>-0.000105</td>
</tr>
</tbody>
</table>

Accordingly, Eq.(4) can be transformed into

\[ E = \alpha_0 u_0 + \alpha_2 u_2 + \ldots + \alpha_{2L} u_{2L} \]

(6)

which is fundamental for dealing with aromaticities and reactivities.

AROMATICITY

The aromaticity of finite molecules has been investigated systematically on the idea expressed by Brelow and Dewar (ref.7-11). Among them, benzene is the most aromatic with largest REPE and has equal C-C bond lengths. On the other hand, graphite is an infinite hexagon lattice with equal C-C bond lengths approaching to benzene. Recently, Klein, Seitz and Schmalz (ref.12-14) studied a series of icosahedral carbon cages with graphite as a limit. They calculated REPE's by Hess-Schaad method (ref.9) which increase monotonously from \( C_{60} \) to \( C_{240} \) and approach to 0.053 for graphite. We intend to investigate the variation of aromaticity along with three imagined paths in detail when benzene is growing up to graphite. The general formula of REPE obtained for each homologous series exhibits a trend dependent on the dimensionality that the species is growing up. Let us discuss them below.

Spherical carbon cage \( C_N \) with \( l_h \) symmetry

Because moments can be divided into acyclic and cyclic components fulfilling Eq.(3), the total \( \pi \)-electron energy splits up too, i.e.,

\[ E = E' + E'' \]

(7)

where \( E' \), the acyclic energy is used to be the reference and the cyclic component \( E'' \) equals the resonance energy. Therefore,

\[ \text{REPE} = \frac{E''}{N} = \frac{1}{N} \sum_{l=0}^{L} \alpha_{2L} u_{2L} = \frac{1}{N} \sum_{G'} \beta_{G'} [G'] \]

where \( \beta_{G'} \) represents the energy contribution per fragment \( G' \) which involves one ring at least. The numerical values of \( \beta_{G'} \) have also been tabulated elsewhere (ref.5).
It can be proved that the only icosahedral cage structures that can be constructed form an infinite sequence with the number of vertices given by (ref. 12,14)

$$N = 20(h^2 + hk + k^2)$$  \hspace{1cm} (04k<h) \hspace{1cm} (9)

with h and k integers. These cage structures are conveniently viewed by showing a single face of the master icosahedron on which each structure is based (ref. 15). Fig.2 illustrates such diagrams up to $N=540$.

![Fig.2. Repeat units for the icosahedral carbon cages](image)

For these icosahedral cage structures, $C_N$'s, it is not difficult to carry out the cyclic components $u_{21}^i$ one by one in terms of $N$. The formulae for $l=3, 4, 5$ and 6 are given as follows

$$u_6^i = 6N - 120$$
$$u_8^i = 96N - 1920$$
$$u_{10}^i = 1110N - 22080$$
$$u_{12}^i = 11382N - 227160 + 3600\delta_{N,60} + 720\delta_{N,80}$$  \hspace{1cm} (10)

On substituting them into Eq.(8) and utilizing the coefficients for $L=6$ in Table 1, we obtain the general formula for REPE for $C_N$

$$\text{REPE}(C_N) = 0.0489 - 0.657/N - (0.378\delta_{N,60} + 0.0756\delta_{N,80})/N$$  \hspace{1cm} (11)

which gives a limit value of 0.0489 for graphite as $N \to \infty$. On the other hand, the ascending trend of REPE($C_N$) with respect to $N$ is easily inspected from the differential below

$$d\text{REPE}(C_N)/dN = 0.657/N^2 > 0 \hspace{1cm} (N=60,80)$$  \hspace{1cm} (12)

In Table 3, REPE's for closed shell carbon cages calculated according to Eq.(11) are tabulated up to $N=1980$, where values given by Klein, Seitz and Schmalz (KKS) are also listed for comparison.

<table>
<thead>
<tr>
<th>$C_N$</th>
<th>Eq.(11)</th>
<th>KSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{60}$</td>
<td>0.032</td>
<td>0.031</td>
</tr>
<tr>
<td>$C_{80}$</td>
<td>0.040</td>
<td></td>
</tr>
<tr>
<td>$C_{140}$</td>
<td>0.044</td>
<td></td>
</tr>
<tr>
<td>$C_{180}$</td>
<td>0.045</td>
<td>0.045</td>
</tr>
<tr>
<td>$C_{240}$</td>
<td>0.046</td>
<td>0.047</td>
</tr>
<tr>
<td>$C_{320}$</td>
<td>0.047</td>
<td></td>
</tr>
<tr>
<td>$C_{420}$</td>
<td>0.047</td>
<td></td>
</tr>
<tr>
<td>$C_{540}$</td>
<td>0.048</td>
<td></td>
</tr>
<tr>
<td>Graphite</td>
<td>0.049</td>
<td>0.053</td>
</tr>
</tbody>
</table>
Polyacene and parallelogram-like hexagon lattice

Polyacene is a linearly fused benzenoid system with an arbitrary number of hexagons, \( n \), and total vertices (the number of carbon atoms), \( N=4n+2 \). With the same procedure, one can derive the formulae for cyclic components \( u_{23}^l \) of \( L=6 \) at first, and substituting them into Eq. (8) with \( \alpha_{21}^l \)'s of \( L=6 \), the formula of REPE is

\[
REPE(n) = \frac{(0.0837n+0.256+0.0766)}{(4n+2)} \quad (13)
\]

Its differential with respect to \( n \) is as follows

\[
dREPE(n)/dn = -0.857/N^2 \quad (14)
\]

This means that aromaticity of polyacene decreases monotonously with its chain lengths.

Let us consider the parallelogram-like species with \( n \) and \( m \) hexagons along the intersections of the parallelogram shown in Fig.3.

It represents a large number of benzenoid systems because \( n \) and \( m \) are arbitrary positive integers. For example, it reduces to polyacene when \( m=1 \). In the same way, the general formula of REPE for the parallelogram-like species displayed in Fig.3 can be also derived as follows

\[
REPE(m,n) = \frac{[0.0489mn+0.00222(m+n)+0.0966]}{(mn+m+n)} \quad (m,n>1) \quad (15)
\]

It repeatedly gives the limit value, 0.0489, for graphite when \( m \) and \( n \) approach to infinite simultaneously. The partial differential of \( REPE(m,n) \) with respect to \( n \) is equal to

\[
dREPE(m,n)/dn = \frac{[0.0467m^2-0.0966(m+1)]}{(mn+m+n)^2} \quad (16)
\]

which induces the following conditions

\[
dREPE(m,n)/dn \begin{cases} <0 & \text{when } m<3 \\ =0 & \text{when } m=2.8 \approx 3 \\ >0 & \text{when } m>3 \\ \end{cases} \quad (17)
\]

Eq. (17) means \( m=3 \) is a transition point below which \((m=1 \text{ or } 2) \) REPE decreases in proportion to the chain lengths of the polymer, on the contrary, the aromaticity of parallelogram-like benzenoid species increases with its length, \( n \), if \( m>3 \). These are better indicated in Fig.4.

Kertesz and Hoffmann have examined the \( \pi \)-electron bands of the three members \((n=\infty; m=1,2,3) \) of the lattice displayed in Fig.3 by extended Hückel calculations. They concluded that the energy gaps due to distortion sharply decreases
with the value of $m$ in accordance with a power law for the energy gap openings (ref.6), i.e.,

$$E_g = c_m |\delta/B|^m$$

with $|\delta/B| << 1$ (18)

This seems to agree with the behavior of $REPE(m,n)$ that the partial differential $\partial REPE(m,n)/\partial n$ increases with the number of coupled polyacenic chains, $m$.

**Benzenoid lattice with $D_{6h}$ symmetry**

For this species, let us enumerate the number of hexagons, $n$, from the center horizontally shown in Fig.5

![Fig.5. Benzenoid lattice with $D_{6h}$ symmetry](image)

Accordingly, we can derive the following formula

$$REPE(n) = 0.0489(1 - 1.5007/n + 2.0409/n^2)$$

(19)

and find a transition point occurring at $n=3$, namely

$$\frac{dREPE(n)}{dn} = 0, \text{ if } n=2.73$$

(20)

The existence of transition points for aromaticity in the cases of lattices shown in Figs.3 & 5 comes from the competition between the di- and tri-valent vertices. As a result, one can think reasonably that in large benzenoid systems, the di-valent vertices play the role of anti-aromaticity, diminishing the value of $REPE$; on the other hand, tri-valent vertices behave aromatically, increasing the value of $REPE$. When the transition points are exceeded in the both cases, the tri-valent vertices increase sharply with chain lengths, leading to an ascending trend of $REPE$'s.

**SITE REACTIVITY AND BOND LENGTHS**

As moment $u_1$ is defined in terms of self-adjoint walks, $W^j_1$ ($j=1,2,...,N$), for each vertex (atom) which individualizes the vertex numerically, therefore, point-energy (ref.5) can be introduced for each carbon atom in accordance with

$$E = \sum_{j=1}^{N} E_j,$$

where $E_j$ is the point-energy of atom $j$, an well-behaved index in relation to site reactivity. As consequences, the following statements can be deduced.

1. Site reactivity decreases as the vertex degree increases, namely, the mono-valent vertices are most active and tri-valent vertices are most inert.

2. The site reactivities of atoms with equal valency are proportional to the valency of their adjacent atoms. This can be illustrated diagrammatically in Fig.6.

![Fig.6. Sequences of site reactivities](image)

Similarly, moments can be classified into edge components, $w^e_{l1}$,and edge-energy (ref.5) can be defined accordingly,

$$E = N \sum_{e} E_e, \quad E_e = \sum_{l=1}^{L} \alpha_{e2l} w^e_{2l}$$

(22)

where $e$ is a current index for degrees (C-C). We have the following statements in addition.

3. The bond length of an edge varies in proportion to its degree (Fig.7).
(4). For edges with equal degree, bond lengths vary in inverse proportion to degrees of their adjacent vertices (fig. 7).

Fig. 7. Ascending sequences of bond lengths in conjugated systems

LOCAL AROMATICITY

There have been considerable works (ref. 17-19) on this topic. Here, we discuss local aromaticity by defining the resonance energy for a particular hexagon, \( h \),

\[
(\text{RE})_h = \sum_{r} \beta_{G^r}[G^r]_r / n_r
\]

where \( \tau \) runs through all rings enveloping the hexagon considered, \( n_r \) is the number of hexagons that the \( \tau \)th ring accommodates, and \( [G^r]_r \) enumerates cyclic fragment, \( G^r \), covering the \( \tau \)th ring. An insight into the role of fragments can be inspected from Eq. (23). For example, there are four different types of hexagons in catafusenes (ref. 18) shown in Fig. 8. We can tabulate the counts of \( [G^r]_r \) of them in Table 4.

Table 4. \([G^r]_r\) for various hexagons in catafusenes

<table>
<thead>
<tr>
<th>( [G^r] )</th>
<th>( \beta_{G^r} )</th>
<th>P</th>
<th>L</th>
<th>K</th>
<th>T</th>
</tr>
</thead>
<tbody>
<tr>
<td>[61]</td>
<td>-0.1535</td>
<td>2</td>
<td>4</td>
<td>4</td>
<td>6</td>
</tr>
<tr>
<td>[511]</td>
<td>0.02924</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>6</td>
</tr>
<tr>
<td>[6101]</td>
<td>0.03176</td>
<td>0</td>
<td>2</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>[61001]</td>
<td>0.03176</td>
<td>0</td>
<td>2</td>
<td>1</td>
<td>3</td>
</tr>
</tbody>
</table>

On comparing [61], we have \( (\text{RE})_P > (\text{RE})_L > (\text{RE})_K > (\text{RE})_T \). Furthermore, due to \( \beta_{511} \beta_{61001} < 0 \), we have \( (\text{RE})_P > (\text{RE})_L \). Therefore, we have a trend of local aromaticity for hexagons of catafusenes (ref. 18): \( P > L > K > T \).

REFERENCES