Resonance Polynomials of Cata-condensed Hexagonal Systems

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Joint work with Dong Ye & Xiaoya Zha

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A *hexagonal system* is a finite 2-connected plane bipartite graph in which each interior face is bounded by a regular hexagon of side length one.
Benzenoid hydrocarbon:

Graphene:
Question: Is there some connections between structures of these molecules and their chemical stability?

- Homo-Lumo Gap ($\Delta = \lambda_H - \lambda_L$, difference between two middle eigenvalues)
- Kekulé count (# of perfect matchings)
- Clar number (the maximum # of disjoint hexagons)
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F. J. Rispoli gave a method to compute Kekulé count (\# of perfect matchings) in hexagonal systems.

- Let $A(a_{ij})$ be the biadjacency matrix of a hexagonal system $G$.

- \[ \Phi(G) = |\det(A)|. \]

Note: $\Phi(G)$ is the number of perfect matchings of $G$. 

```
\begin{align*}
\text{b}_1 & \quad \text{b}_2 \\
\text{b}_3 & \quad \text{b}_4 \\
\text{b}_5 & \quad \text{b}_6 \\
\text{b}_7 & \quad \text{b}_8
\end{align*}
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\begin{align*}
\text{w}_1 & \quad \text{w}_2 \\
\text{w}_3 & \quad \text{w}_4 \\
\text{w}_5 & \quad \text{w}_6 \\
\text{w}_7 & \quad \text{w}_8
\end{align*}
```
A hexagonal system is *cata-condensed* if all vertices appear on its boundary.
• A set of disjoint hexagons $\mathcal{H}$ of a hexagonal system $G$ is a **resonant set** if a subgraph $G'$ consisting of deleting all vertices covered by $\mathcal{H}$ from $G$ has a perfect matching.

• A resonant set is a **forcing resonant set** if $G'$ has a unique perfect matching.

Disjoint hexagonal set: $\{1,4\}$
- A set of disjoint hexagons $\mathcal{H}$ of a hexagonal system $G$ is a *resonant set* if a subgraph $G'$ consisting of deleting all vertices covered by $\mathcal{H}$ from $G$ has a perfect matching.

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Disjoint hexagonal set: $\{1, 4\}$
• (Zheng & Hanse, 1993) The Clar number problem of hexagonal system can be solved by an integer program.

• (Abeledo & Atkinson, 2006) The Clar number problem of hexagonal system can be solved by an linear programming which was conjectured by Zheng & Hanse.
(Zheng & Chen, 1985)
A maximum resonant set of a hexagonal system is a forcing resonant set.

The spectrum of forcing resonant set can be defined as: $\text{spec}_{\text{FRS}}(G) = \{|H| : H \text{ is a forcing resonant set of } G\}$. 
• (Zheng & Chen, 1985) A maximum resonant set of a hexagonal system is a forcing resonant set.

• The *spectrum* of forcing resonant set can be defined as: 
\[ \text{spec}_{FRS}(G) = \{ |\mathcal{H}| : \mathcal{H} \text{ is a forcing resonant set of } G \}. \]
Definition 1

Let $G$ be a cata-condensed hexagonal system. The forcing resonant polynomial $P_G(x)$ can be defined as

$$P_G(x) = \sum_{i=0}^{cl(G)} a_i x^i \quad (1)$$

where $a_i$ is the number of forcing resonant sets of size $i$. 
- (Zhang, Chen, Guo & Gutman, 1991)
  A hexagonal system $H$ has $cl(H) = 1$ if and only if $H$ is a linear chain.
- $spec_{FRS}(L_k) = \{1\}$
The coefficient vector of $G$:

$$a = \begin{bmatrix} a_{cl}(G) \\ a_{cl}(G)-1 \\ \vdots \\ a_1 \end{bmatrix}$$

where $a_i$ is the coefficient of $x^i$ in $P_G(x)$, then $a$ is called the the coefficient vector of $G$. 
Proposition 1

Let $G$ be a graph of disjoint union of cata-condensed hexagonal systems $G_1, G_2, \ldots G_k$. Then

$$P_G(x) = \prod_{i=1}^{k} P_{G_i}(x).$$

(2)
A pendant chain L:
Lemma 2

Let $G$ be a cata-condensed hexagonal system. Every forcing resonant set of $G$ contains exactly one hexagon of $L$ if $L$ is not a non-pendant chain with two hexagons.
Corollary 3

Every forcing resonant set $\mathcal{H}$ hits every maximal linear hexagonal chain.
Lemma 4
Let $G$ be a cata-condensed hexagonal system. Let $A$ be a hexagon of $G$. Then,

$$P_G(x) = P_G(x, A^C) + P_G(x, A)$$
Theoretical part
Theorem 5

Let $G$ be a cata-condensed hexagonal system and $L$ be a pendant chain with $r$ hexagons. Let $H$ be the subgraph consisting of all hexagons of $G$ except these in $L$, and $H'$ be the subgraph of $H$ consisting of all hexagons except these contained in the maximal linear chains of $G$ with a common hexagon with $L$. Then,

$$P_G(x) = (r - 1)xP_H(x) + xP_{H'}(x)$$

(3)
How to construct the weighted tree:
Steps:

- Start with a pendant chain $L$. $L$ corresponds with the fist vertex in $(T, w)$.
- The children of a vertex $v$ in $(T, w)$ are defined to be the maximal linear hexagonal chains which share a common hexagon with the corresponding chain of the vertex $v$.
- Continue to do step 2 until the number of vertices equals the number of maximal linear hexagon chains.

Note that the vertex which corresponds with the initial pendant hexagonal chain $L$ is the root of $(T, w)$. 
function cal_poly

if Tree is empty then
    \[ P_{tree}(x) = 1; \]
else
    Find left subtree and right subtree of the tree \( T \);
    Find left subtree and right subtree of the left subtree;
    Find left subtree and right subtree of the right subtree;
    Recursive formula;
end
end
G. Brinkmann, G. Caporppssi and P. Hansen proposed a method to construct enumerate fusenes and bezenoids in 2002.

<p>| | | | | | | | |</p>
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Figure 1: Cata-condensed benzenzoind systems with six hexagons
### Table III

**CATA-condensed Benzenoid System with 6 Hexagons**

<table>
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<tr>
<th>Graph number</th>
<th>Polynomial</th>
<th>Clar number</th>
<th>Coefficient vector</th>
<th>x coordinate</th>
<th>HOMO-LUMO gap</th>
<th>( \Phi(G) )</th>
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Figure 2: Using least square method to fit the data points from tab 3
We obtain the following conclusions by comparing the experiment results:

- The coefficient vector we proposed increases as the HOMO-LUOM gap increases.
- The stability of $G$ is relative with the coefficient vector. The one that has larger coefficient vector has better stability.
- The coefficient vector we proposed is a refined indicator than the existing method, Clar number, to predict the stability of $G$. 
Thanks!