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A comparison between 1-factor count and resonant pattern count in plane non-bipartite graphs

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The concept of resonant (or Clar) pattern is extended to a plane non-bipartite graph G in this paper: a set of disjoint interior faces of G is called a *resonant pattern* if such face boundaries are all M-conjugated cycles for some 1-factor (Kekulé structure or perfect matching) M of G. In particular, a resonant pattern of benzenoids and fullerenes coincides with a sextet pattern. By applying a novel approach, the principle of inclusion and exclusion in combinatorics, we show that for any plane graphs, 1-factor count is not less than the resonant pattern count, which generalize the corresponding results in benzenoid systems and plane bipartite graphs. Applications to fullerenes are also discussed.

KEY WORDS: plane graph, fullerene, benzenoid, Kekulé structure, resonant pattern

AMS subject classification: 05C70, 05C90, 92E10

1. Introduction

During the last three decades some important graph-theoretical approaches were established for general resonance theory of polycyclic hydrocarbons, such as Herndon's work [10] and Randić conjugated circuit model [16,17]. The sextet patterns of benzenoid systems reflect the combinatorial background of Clar's concept of the aromatic sextet [5,15], and can be used for the calculation of the resonance energy of benzenoid hydrocarbons [1,9]. Some nice mathematical properties ever were revealed: for cata-condensed benzenoid systems [11,15] there exists a one-to-one correspondence between the sextet patterns and Kekulé structures, the latter is called 1-factor or perfect matching in graph theory; For general benzenoid system the sextet pattern count is no larger than Kekulé structure count. Gutman [8] and John [12] independently defined the cell polynomial for counting resonant patterns of plane bipartite graphs that extends naturally Hosoya and Yamaguchi's sextet polynomial [11]. John et al. [13] showed that the 1-factor count is larger than or equal to the resonant pattern count. Further Shiu et al. [19] gave a simple criterion for these two quantities being identical.

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It is natural to ask whether such a relation exists for fullerene graphs [7] (the molecular graphs of fullerenes, planar three-connected cubic graphs 12 of whose faces are pentagons and any remaining faces are hexagons). In fact the famous member buckministerfullerene [14] of fullerenes has 5828 sextet patterns [20] and 12500 Kekulé structures [18]. In this paper we extend naturally the concept of sextet pattern or resonant pattern to general plane graphs and show that the corresponding relation still holds by applying a new approach, i.e. the principle of inclusion and exclusion in combinatorics. Since benzenoid systems, coronoid systems, and planar alternant systems, and planar non-alternant systems (for example, fullerene graphs) as well, are special types of plane graphs (see a recently detailed survey [17]), we not only extend greatly the previous result but also give a positive answer to the above problem.

2. Concepts and main results

A plane graph G is an embedding of a planar graph in the Euclidean plane. An interior face of G is said to be a *cell* if its boundary is a cycle. An even-cell means a cell that is bounded by a cycle with even sides. For convenience, a cell may be simply referred to its boundary. Without loss of generality we confine our consideration to plane graphs without loops and multiple edges and such that each edge is drawn as a straight segment and each cell as a polygon.

Let G be a plane graph with vertex-set $V(G)$ and edge-set $E(G)$. A 1-factor (or perfect matching, Kekulé structure) of G is a set of pairwise disjoint edges of G that cover all of its vertices. For a 1-factor M of G, a cycle C of G is called M-alternating (or conjugated) if the edges of C appear alternately on and off the M. Such an alternating cycle is called a resonant cycle. A face is called *resonant* if its boundary is a resonant cycle. For example, the plane bipartite graph in figure 1 represents a derivative of biphenylene, cells $C_1, \ldots, C_6$ are alternating, and together with C_7 are all resonant.

Definition 1. A set S of pairwise disjoint cells of a plane graph G is called *resonant pattern* (or Clar pattern), if G has a 1-factor M such that all cells in S are simultaneously M-alternating cycles.

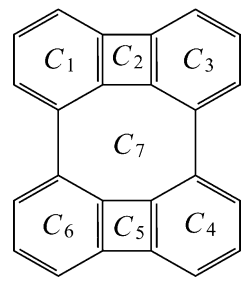

Figure 1. A plane bipartite graph with a Kekule structure.

Equivalently, a resonant pattern of G means a set S of pairwise disjoint even cells of G such that $G - S$ has a 1-factor, where $G - S$ denotes the subgraph obtained from G by deleting all vertices in cells of S together with their incident edges. Note that the empty set is a resonant pattern of a plane graph with a 1-factor, and a plane graph without a 1-factor has no resonant patterns.

Throughout this paper, let $\mathcal{K}(G)$ and $\mathcal{R}(G)$ denote the sets of 1-factors and resonant pattern of a plane graph G, respectively. Let $k(G) := |\mathcal{K}(G)|, r(G) := |\mathcal{R}(G)|$. Namely, $k(G)$ and $r(G)$ are the numbers of 1-factors and resonant patterns of a plane graph G, respectively.

In particular, resonant patterns of benzenoid systems and fullerenes are usual sextet patterns, which consists of only aromatic (π-electron) sextets (i.e. benzenoid hexagons). For example, $\{C_1, C_3, C_3\}$ in figure 2 (right) is a sextet pattern of coronene; $\{C_1, C_3\}$ in figure 3 (right) is a sextet pattern of corannulene ([3], a part of buckminsterfullerene), the central cell is not resonant since it is an odd cell and the other cells (hexagons) are all aromatic sextets: Dodecahedron has a unique resonant pattern $\emptyset$.

For a plane system G consisting of exclusively pentagonal and hexagonal cells, the sextet polynomial $B_G(x)$ is defined as

$$B_G(x) = \sum_{k=0}^{m} r(G, k)x^k, \tag{1}$$

where $r(G, k)$ denotes the number of sextet patterns with k resonant sextets of G and m is the Clar number, i.e. the maximum number of sextets in sextet patterns. Hence $r(G) = B_G(1)$. The sextet polynomial of coronene is [15] $B_{\text{coronene}}(x) = 1 + 7x + 9x^2 + 2x^3$. Hence $r(\text{coronene}) = B_{\text{coronene}}(l) = 19$ and $k(\text{coronene}) = 20$.

Let G be a plane bipartite graph (i.e., all cycles have even length). Then G is called *elementary* if G is connected and each edge is contained in a 1-factor, and *weakly elementary* [19] if each conjugated cycle with its interior form an elementary graph. A subgraph H of G is said to be *nice* if $G - V(H)$ has a 1-factor. So a resonant cycle of G is a nice cycle and a *pair* of resonant cycles mean two disjoint cycles that form a nice subgraph.

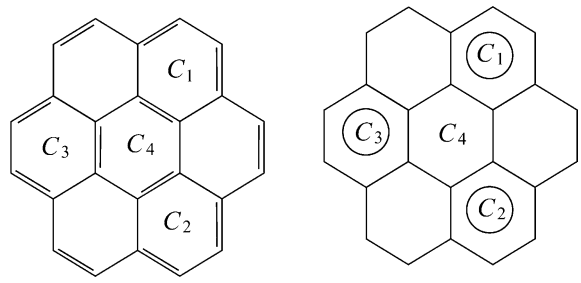

Figure 2. A Kekulé structure (left) and sextet pattern (right) of coronene.

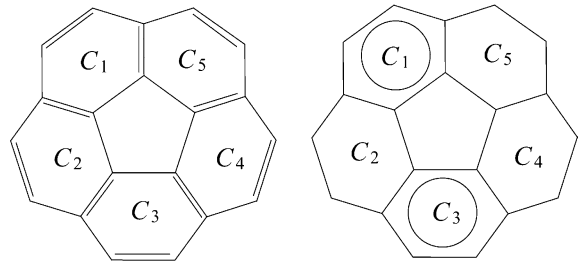

Figure 3. A Kekulé structure (left) and a resonant pattern (right) of corannulene.

For benzenoid systems and general plane bipartite graphs G the following theorems show that the 1-factor count $k(G)$ is no less than resonant pattern count $r(G)$.

Theorem 2.1. ([21]). For a benzenoid system $G, r(G) \leqslant k(G)$, and equality holds if and only if G contains no coronene (figure 2) as its nice subgraph.

Theorem 2.2. ([13,19]). Let G be a connected plane bipartite graph. Then $r(G) \leqslant k(G)$, and equality holds if and only if G is weakly elementary and for any pair of resonant cycles their interior regions are disjoint.

In this paper we mainly consider plane non-bipartite graphs. For example, the resonant patterns of corannulene (figure 3) are as follows: $\emptyset$, $\{C_1\}$, $\{C_2\}$, $\{C_3\}$, $\{C_4\}$, $\{C_5\}$, $\{C_1, C_3\}$, $\{C_1, C_4\}$, $\{C_2, C_4\}$, $\{C_2, C_5\}$, $\{C_3, C_5\}$. Hence $B_{\text{corannulene}}(x) = 1+5x+5x^2$. It is computed [4] that $k(\text{corannulene}) = 11$. That is, $r(\text{corannulene}) = k(\text{corannulene}) = 11$. For dodecahedron ($C_{20}$) and buckminsterfullerene (C_{60}) we have that $r(C_{20}) < k(C_{20})$ and $r(C_{60}) < k(C_{60})$. In general we have the following main result of this paper, whose proof will be given in next section.

Theorem 2.3. For any plane graphs $G, r(G) \leqslant k(G)$.

3. Proof of main theorem 2.3

The proofs of Theorems 2.1 and 2.2 completely rely on the bipartite property of graphs and the existence of a root Kekulé structure. In non-bipartite case such root Kekulé structure does not exist. So we must seek for a new approach.

To prove Theorem 2.3 we set up the following lemmas. For disconnected plane graphs G, we have the following relations concerning the parameters $k(G)$ and $r(G)$.

Lemma 3.1. Let $G_1, G_2, \ldots G_n (n \geqslant 1)$ be the components of a plane graph G with a 1-factor. Then

$$k(G) = \prod_{i=1}^{n} k(G_i) \tag{2}$$

and

$$r(G) \leqslant \prod_{i=1}^{n} r(G_i). \tag{3}$$

Second equality holds if and only if every resonant cell of each G_i is also a cell of G.

Proof. It is obvious that G has a 1-factor if and only if every $G_i, i = 1, 2, \ldots, n$, has a 1-factor and

$$\mathcal{K}(G) = \left\{ \bigcup_{i=1}^{n} M_i : M_i \in \mathcal{K}(G_i), i = 1, 2, \ldots, n \right\}, \tag{4}$$

which implies equation (2).

For any $S \in \mathcal{R}(G)$, let $S_i := \{C \in S : C \subseteq G\}, i = 1, 2, \ldots, n$. Since every resonant cell of G must be contained in some component, we have that $\bigcup_{i=1}^{n} S_i = S$ and $S_i \in \mathcal{R}(G), i = 1, 2, \ldots, n$. Hence $S \in \{\bigcup_{i=1}^{n} S_i' : S_i' \in \mathcal{R}(G_i), i = 1, 2, \ldots, n\}$ and

$$\mathcal{R}(G) \subseteq \left\{ \bigcup_{i=1}^{n} S_i' : S_i' \in \mathcal{R}(G_i), i = 1, 2, \ldots, n \right\}. \tag{5}$$

The inequality (3) follows from the above relation.

Finally $r(G) = \prod_{i=1}^{n} r(G_i)$ if and only if equality in relation (5) holds; equivalently, every resonant cell of each G_i forms a resonant pattern of G and is thus a cell of G. □

The reduction method for 1-factor count of a graph described in the following lemma is obvious and well-known (see figure 4).

Lemma 3.2. Let ux be any edge of a graph G. Then

$$k(G) = k(G - uv) + k(G - u - v). \tag{6}$$

Our reduction procedure for the resonant pattern count of a plane graph G always proceeds at a *boundary edge* of G, i.e. an edge lying on the boundary of the exterior face of G (for example, uv is a boundary edge of G in figure 4).

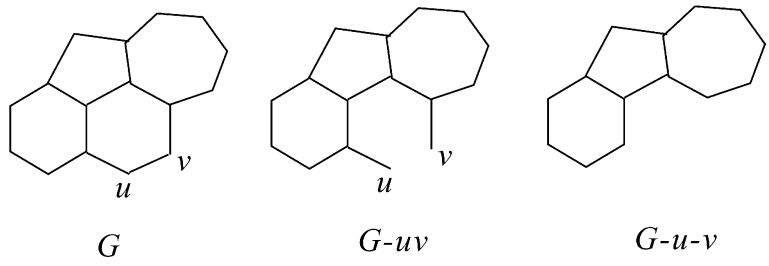

Figure 4. An example for edge-deletion and vertex-deletion of a plane graph.

Lemma 3.3. Let G be a connected plane graph with a 1-factor. If a boundary edge uv of G lies on the boundary C of some interior face, then

$$\mathcal{R}(G) \subseteq \mathcal{R}(G') \cup \mathcal{R}(G'') \cup \{S' \cup \{C\} : S' \in \mathcal{R}(G') \cap \mathcal{R}(G'')\}, \tag{7}$$

where $G' := G - uv$ and $G'' := G - u - v$.

Proof. For any $S \in \mathcal{R}(G)$, there is a 1-factor $M \in \mathcal{K}(G)$ such that all cells in S are simultaneously M-alternating. We distinguish the following two cases.

Case 1. $C \in S$. Since C is an M-alternating cell, then $M' := M \oplus C = (M \cup E(C)) \backslash (M \cap E(C)) \in \mathcal{K}(G)$. Without loss of generality we suppose $uv \notin M$. Then $uv \in M', M \in \mathcal{K}(G')$, and $M' \backslash \{uv\} \in \mathcal{K}(G'')$. Since M is a 1-factor of G' and all cells in $S \backslash \{C\}$ are disjoint M-alternating cells of G', then we have that $S \backslash \{C\} \in \mathcal{R}(G')$. By the same reason we have that $S \backslash \{C\} \in \mathcal{R}(G'')$. Hence $S \backslash \{C\} \in \mathcal{R}(G') \bigcap \mathcal{R}(G'')$ and

$$S \in \{S' \cup \{C\} : S' \in \mathcal{R}(G') \cap \mathcal{R}(G'')\}.$$

Case 2. $C \notin S$. If $uv \in M$, none of u and v lie on a cell in S since uv is a boundary edge of G and each cell in S contains no uv. Hence $M \backslash \{uv\}$ is a 1-factor of G'' and S consists of disjoint $(M \backslash \{uv\})$-alternating cells of G'', which imply that S is a resonant pattern of G''. If $uv \notin M$, we have that $S \in \mathcal{R}(G')$ in an analogous manner.

Summing up the above, we have

$$S \in \mathcal{R}(G') \cup \mathcal{R}(G'') \cup \{S' \cup \{C\} : S' \in \mathcal{R}(G') \cap \mathcal{R}(G'')\},$$

which implies the required relation (7). □

Lemma 3.4. Let G be a connected plane graph with a 1-factor. If $e = uv$ is a boundary edge of G, then

$$r(G) \leqslant r(G - uv) + r(G - u - v). \tag{8}$$

Proof. Let $G' := G-e$ and $G'' := G-u-v$. If e is a cut-edge of G, there are two cases: (1) e belongs to all 1-factors of G. Then $\mathcal{R}(G) = \mathcal{R}(G'')$, and $\mathcal{R}(G') = \emptyset$ since G' has no 1-factor; (2) e belongs to none of 1-factors of G. Then $\mathcal{R}(G'') = \emptyset$ and $\mathcal{R}(G) = \mathcal{R}(G')$. Hence equality in (8) holds, i.e. $r(G) = r(G') + r(G'')$.

So we now suppose that e is not a cut-edge of G. Then e must lie in the boundary (say C) of some interior face of G. By Lemma 3.3 we have

$$\mathcal{R}(G) \subseteq \mathcal{R}(G') \cup \mathcal{R}(G'') \cup \{S' \cup \{C\} : S' \in \mathcal{R}(G') \cap \mathcal{R}(G'')\}.$$

Then

$$\begin{aligned} r(G) &\leqslant |\mathcal{R}(G') \cup \mathcal{R}(G'')| + |\mathcal{R}(G') \cap \mathcal{R}(G'')| \\ &= |\mathcal{R}(G')| + |\mathcal{R}(G'')| \text{ (by Principle of Inculsion and Exclusion)} \\ &= r(G') + r(G''). \end{aligned}$$

Hence the lemma follows. □

Proof of Theorem 2.3. If the plane graph G in question has no 1-factor, then $r(G) = k(G) = 0$. Hence we suppose G has a 1-factor and we shall prove $r(G) \leqslant k(G)$ by induction on the number $|E(G)|$ of edges.

If $|E(G)| = 1, r(G) = k(G) = 1$. In what follows, suppose that $|E(G)| > 1$ and the assertion holds for plane graphs with smaller number of edges than $|E(G)|$. If G is disconnected, then by the induction hypothesis we have that $r(G_i) \leqslant k(G_i)$ for all component $G_i (1 \leqslant i \leqslant n)$ of G. Hence the result follows immediately from relations (2) and (3) in Lemma 3.1:

$$r(G) \overset{(3)}{\leqslant} \prod_{i=1}^{n} r(G_i) \leqslant \prod_{i=1}^{n} k(G_i) \overset{(2)}{=} k(G).$$

So we suppose G is connected. Let $e = uv$ be a boundary edge of G. Then we have

$$\begin{aligned} r(G) &\leqslant r(G-uv) + r(G-u-v) \text{ (by Lemma 3.4)} \\ &\leqslant k(G-uv) + k(G-u-v) \text{ (by induction hypothesis)} \\ &= k(G). \text{ (by Lemma 3.2)} \end{aligned}$$

Hence the theorem follows. □

4. Discussions

For benzenoid hydrocarbons there are several empirical equations relating Kekulé structure count and resonance energy [9,10]. However, Austin et al. [2] showed raw Kekulé count is a poor guide to π-electronic stability for fullerenes. In fact they exhibited Kekulé counts of all 1812 fullerene isomers of C_{60} and

found exactly 20 isomers surpassing the count of 12500 Kekulé structures for the icosahedral C_{60}. By using the Heisenberg model, Flocke et al. [6] found that a smaller set of 5828 Kekulé structures of buckminsterfullerene already gives 99.82% of the ground state energy of the full set of Kekulé structures. Each one of such chosen Kekué structures superposes the Fries Kekulé structure of buckminsterfullerene to produce a sextet pattern. In fact the chosen 5828 Kekulé structures have a one-to-one correspondence with all the sextet patterns. Shiu et al. [20] computed the sextet polynomial of buckminsterfullerene

$$B_{C_{60}}(x) = 5x^8 + 320x^7 + 1240x^6 + 1912x^5 + 1510x^4 + 660x^3 + 160x^2 + 20x + 1$$

and the sextet pattern count $B_{C_{60}}(1) = 5828$.

Hence it is useful to compute the number $B_F(1)$ of sextet patterns of fullerene graphs F. We can show this quantity of any fullerene graph is equal to or less than the number of Kekulé structures as the following proposition says.

Proposition 4.1. For any Fullerene graph F, $B_F \leqslant k(F)$.

Proof. When every fullerene graph F is drawn in the plane such that the outer face is bounded by a pentagon, each resonant pattern of this Schlegel-diagram corresponds uniquely a sextet pattern. Hence the result follows from Theorem 2.3. □

Proposition 4.2. Let G be a connected plane graph with a 1-factor. Let e be a boundary edge of G such that e lies on the boundary C of an interior face. If e is a non-fixed edge (those edge contained in some 1-factors of G and not in others) and C is not resonant, then $r(G) < k(G)$.

Proof. Since $e =: uv$ is a non-fixed edge, then both $G' := G - uv$ and $G'' := G - u - v$ have 1-factors. Hence $\emptyset \in \mathcal{R}(G') \cap \mathcal{R}(G'')$. Since C is not resonant, $S' \cup \{C\}$ is not a resonant pattern of G for any $S' \in \mathcal{R}(G') \cap \mathcal{R}(G'')$. Hence by Lemma 3.3 we have

$$\mathcal{R}(G) \subseteq \mathcal{R}(G') \cup \mathcal{R}(G'').$$

Then

$$\begin{aligned} r(G) &\leqslant |\mathcal{R}(G') \cup \mathcal{R}(G'')| \\ &= |\mathcal{R}(G')| + |\mathcal{R}(G'')| - |\mathcal{R}(G') \cap \mathcal{R}(G'')| \\ &\leqslant r(G') + r(G'') - 1 \\ &< r(G') + r(G''), \end{aligned}$$

which implies $r(G) < k(G)$ by Theorem 2.3 and Lemma 3.2. □

Since every fullerene graph is 2-extendable [22] (i.e. any pair of disjoint edges are contained in a 1-factor), all edges are non-fixed. Hence the above proposition implies the following corollary at once.

Corollary 4.3. For any Fullerene graph F with adjacent pentagons, $B_F(1) < k(F)$.

For all 1812 fullerene isomers of C_{60}, only icosahedronal C_{60} (or buckminsterfullerene) satisfies the isolated pentagon rule (IPR) [2]. Together with the previous discussions we always have $B_F(1) < k(F)$ for all fullerene graphs F with 60 vertices. In general we propose the following conjecture.

Conjecture 4.4. For any Fullerene graphs F, $B_F(1) < k(F)$.

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