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Counting Conjugated Circuits in Benzenoid Chains

Tomislav Došlić

Faculty of Civil Engineering, University of Zagreb,
Kačićeva 26, 10000 Zagreb, CROATIA

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Abstract

We present explicit formulas for the total number of conjugated circuits of a given length in polyacene and fibonacene chains and analyze asymptotic behavior of the expected number of conjugated circuits in long chains of the considered types.

1 Introduction

The conjugated-circuit model has been successfully applied to many conjugated systems, in particular to benzenoids and fullerenes. The basic postulate of the model is that the stability of a conjugated molecule is determined mostly by its conjugated circuits, i.e., by circuits within Kekulé structures in which single and double bonds come in the alternating order. We refer reader to [3] for a brief description of the model and also for references explaining it in more detail. Besides providing a neat introduction to the model, the cited reference is concerned with enumerating short conjugated circuits in unbranched benzenoid chains, in particular in polyacenes and fibonacenes, by recursively constructing families of single- and multivariate counting polynomials. Our goal in the present paper is to give explicit formulas for the results of reference [3] and then to use them to analyze the asymptotic behavior of the expected number of conjugated circuits of given lengths in the considered benzenoid classes.

2 Definitions and preliminaries

The literature on benzenoid systems is vast; we recommend [1] for a thorough exposition. For any graph-theoretic terms not defined here we refer the reader to any of standard monographs on graph theory, such as, e.g., [2].

A **benzenoid system** is a 1-connected collection of congruent regular hexagons arranged in the plane in such a way that any two hexagons having a common point intersect in a whole edge. From the conditions of regularity and congruence it follows that benzenoid systems are subsets (with 1-connected interior) of a regular tiling of the plane by hexagonal tiles. To each benzenoid system we assign a graph, taking the vertices of hexagons as the vertices of the graph, and the sides of hexagons as the edges of the graph. The resulting **benzenoid graph** is simple, plane, and bipartite. In the rest of the paper, when referring to benzenoids, we will be referring to the corresponding benzenoid graphs.

The vertices lying on the border of the unbounded face of a benzenoid graph are called **external**; other vertices, if present, are called **internal**. A benzenoid graph without internal vertices is called **catacondensed**. If no hexagon in a catacondensed benzenoid is adjacent to three other hexagons, we say that the benzenoid is a **chain**. It is clear that in a benzenoid chain there are exactly two hexagons adjacent to one other hexagon; those two hexagons are called **terminal**, while any other hexagons (if present) are called **interior**. An interior hexagon is called **straight** if the two edges it shares with other hexagons are opposite to each other. If the two shared edges are not opposite, the hexagon is called **kinky**. (Note that the shared edges cannot be adjacent, since this would result in an internal vertex. Hence the above definitions cover all possible cases.)

Let us consider a benzenoid chain with n hexagons. If all its $n-2$ interior hexagons are straight, we call the chain a **polyacene** and denote it by A_n. If all interior hexagons are kinky, the chain is called a **polyphenacene** and denoted by Z_n. However, for reasons that will become clear soon, we will call such chain a **fibonacene**.

A **Kekulé structure** in a benzenoid graph G is a collection M of edges of G such that each vertex of G is incident to exactly one edge from M. It is implicit in the definition that no edges of M share a vertex; hence M is a matching, and even more, it is a **perfect matching** in G. The number of Kekulé structures of a benzenoid graph G is denoted by $K(G)$. In chemical parlance the edges of a Kekulé structure are called double bonds, while the remaining edges are called single bonds.

It is an easy exercise to show that $K(A_n) = n + 1$ and $K(Z_n) = F_{n+2}$, where F_{n+2} denotes the $(n + 2)$-nd Fibonacci number. Furthermore, $K(A_n) \leq K(B_n) \leq K(Z_n)$ for any benzenoid chain B_n with n hexagons. Those two facts justify our choice of name for Z_n and also the notational choice of A_n and Z_n for the extremal chains.

Let M be a Kekulé structure in a graph G. Any closed path consisting of edges that alternate with respect to M is called a **conjugated circuit**. A conjugated circuit is necessarily of even length; in benzenoid graphs that length cannot be divisible by 4. Hence, conjugated circuits in a benzenoid chain on n hexagons can be of length $4k + 2$ for $1 \leq k \leq n$.

3 Main results

3.1 Polyacenes

It is easy to see that in A_n there are exactly $2n$ conjugated circuits of length 6, $2(n-1)$ conjugated circuits of length 10, $2(n-2)$ conjugated circuits of length 14, etc. This follows from the fact that exactly one of the vertical edges of A_n participates in any perfect matching of A_n. Each of $n-1$ interior vertical edges gives rise to exactly two conjugated circuits of length 6, and each of two peripheral vertical edges gives rise to one such circuit. The situation is similar for longer conjugated circuits, whose numbers decrease by one for each interior vertical edge that is too close to one end of the chain. The case $n=3$ is shown in Fig. 1. As the length of the longest possible conjugated circuit cannot exceed $4n+2$, we have the following result.

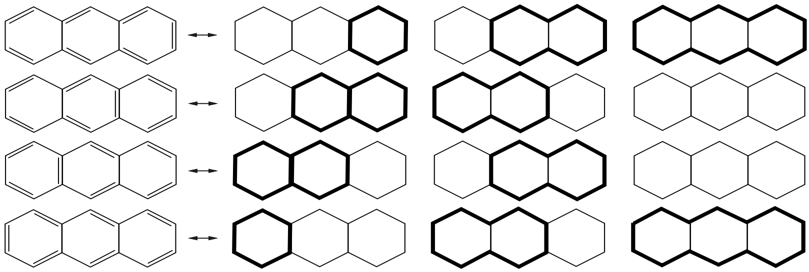

Figure 1: All possible conjugated circuits in A_3.

Theorem 1

The number of conjugated circuits of length $4k+2$ in A_n is equal to $2(n+1-k)$. The total number of all conjugated circuits in A_n is equal to $n(n+1)$. ■

It is obvious that the expected number of conjugated circuits of length $4k+2$ in A_n is equal to $\frac{2(n+1-k)}{n+1}$, and that the expected number of all conjugated circuits in A_n is equal to n. That completely settles the case of polyacenes.

3.2 Fibonacenes

We have already mentioned that the Kekulé structures in Z_n are counted by Fibonacci numbers F_{n+2}. The same sequence counts the number of perfect matchings in ladder graphs $L_n = P_{n+1} \Box P_2$. (Here P_m denotes a path on m vertices, and $\Box$ denotes the Cartesian product of two graphs.) Hence there should be a correspondence between Kekulé structures of Z_n and perfect matchings of L_n. Indeed, if one looks at the portion of Z_6 between two dashed horizontal lines in Fig. 2, it is easy to see that that strip contains a half of each hexagon. By replacing the three edges not in the strip by a single horizontal edge we obtain a ladder graph, and there is only one way of extending the part of perfect matching of Z_n in the strip to a perfect matching in the ladder graph.

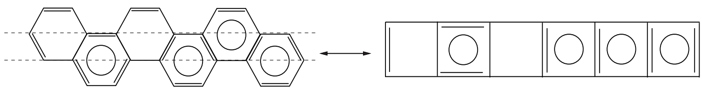

Figure 2: The correspondence between Z_n and L_n.

Conjugated circuits of length 6 in the particular Kekulé structure of Z_6 shown in Fig. 2 are indicated by small circles in the corresponding hexagons. From the right hand side of the same figure we see that to each conjugated 6-circuit in Z_6 corresponds a square in L_6 whose four vertices are covered by two parallel edges. Hence the number of conjugated 6-circuits in Z_n is equal to the number of squares in L_n whose four vertices are paired by two parallel edges. We note that such squares are also conjugated. Hence the number of conjugated 6-circuits in Z_n is equal to the number of conjugated squares in L_n. We find the L_n interpretation more suitable for the combinatorial reasoning that follows.

Among better known combinatorial interpretations of Fibonacci numbers are binary strings without adjacent ones; it is well-known that the number of binary strings of length n without adjacent ones is equal to F_{n+2} [4]. This is exactly the number of perfect matchings in L_n, and if we look more closely at them, we see that the squares whose vertices are paired by horizontal edges cannot be adjacent. By writing 1 for each such square and 0 otherwise, we obtain F_{n+2} binary strings without adjacent ones. The correspondence for the case $n = 4$ is shown in Fig. 3.

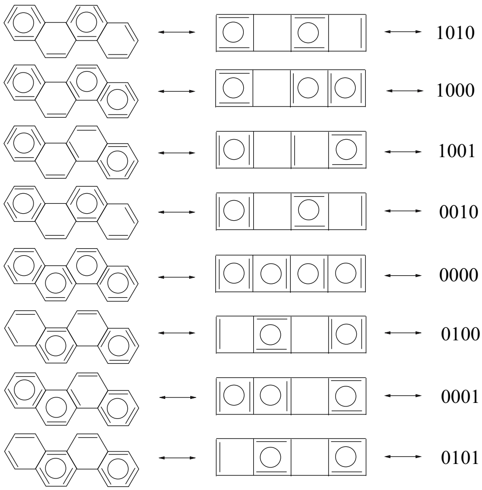

Figure 3: Conjugated circuits in Z_n, in L_n and the corresponding binary strings.

Now the total number of ones in all binary strings of length n is equal to the total number of conjugated squares in L_n whose vertices are paired by horizontal edges. A closer look at Fig. 3. reveals that the ones in binary strings account for exactly half of the conjugated squares. This suggests that there is a correspondence between the conjugated squares with horizontal edges and the ones with vertical edges. Each conjugated square with vertical edges corresponds to a zero in binary string representation, but the opposite is not true, since a zero corresponding to a conjugated square cannot be adjacent to one. Hence, the conjugated squares with vertical edges correspond to insulated zeroes, i.e., to zeroes not adjacent to ones. We now prove by induction on n that in all binary strings of length n without adjacent ones the number of insulated zeroes is equal to the number of ones.

Lemma 2

Let $\mathcal{S}_n$ be the set of all binary strings of length n without adjacent ones. Then the total number of ones in $\mathcal{S}_n$ is equal to the number of insulated zeroes in $\mathcal{S}_n$.

Proof

We proceed by induction on n. For $n = 2$ we have the strings 00, 01 and 10. Both zeroes in the first string are insulated, there are exactly two ones, and the claim is valid. Let us now assume that the claim is valid for some $n \geq 2$. Write all strings from $\mathcal{S}_{n+1}$ in the lexicographic order one below the other so that their digits form a rectangular array. The array has F_{n+3} rows and $n+1$ columns. Label the columns from right to left by the consecutive numbers from 1 to $n+1$. We claim that for each 1 in column k there is an insulated 0 in the same column F_{k+1} places above it, and that the correspondence is bijective. By looking at the case $n = 2$ we see that the claim is valid. The case $n = 3$ is shown in Fig. 4., with insulated zeroes encased in rectangles. Let us look more closely at the array $\mathcal{S}_{n+1}$. It can be divided in three

$$\begin{array}{c|ccc}
\boxed{0} & \boxed{0} & \boxed{0} & \boxed{0} \\
\boxed{0} & \boxed{0} & 0 & 1 \\
\boxed{0} & 0 & 1 & 0 \\
0 & 1 & 0 & \boxed{0} \\
0 & 1 & 0 & 1 \\
\cline{2-4}
1 & 0 & \boxed{0} & \boxed{0} \\
1 & 0 & 0 & 1 \\
1 & 0 & 1 & 0
\end{array}$$

Figure 4: With proof of Lemma 2.

sub-arrays by separating its leftmost column and dividing the rest by a line below its F_{n+2}-nd row, as indicated in Fig. 4. The most important is the leftmost column. Its first F_{n+2} rows contain insulated zeroes, next F_{n+1} rows contain leading zeroes that are not insulated, and the lower-most F_{n+2} rows contain ones. Clearly, to each one in the leftmost column corresponds unique zero in the same column F_{n+2} places above it, and *vice versa*. The remaining two sub-arrays satisfy the claim by the inductive hypothesis, and this completes the step of induction. ∎

Hence the total number of conjugated 6-circuits in Z_n is twice the number of ones in $\mathcal{S}_n$. It remains to count ones in $\mathcal{S}_n$. Let us denote this number by a_n. The sequence starts with $a_1 = 1$, $a_2 = 2$, $a_3 = 5$. We note that a string from $\mathcal{S}_n$ has 1 in place k if and only if it does not have 1 in places $k-1$ and $k+1$. The remaining substrings are of length $k-2$ and $n-k-1$, and the number of such substrings is equal to $F_k F_{n+1-k}$. By summing over all k we obtain that a_n is equal to the convolution of the Fibonacci numbers with themselves, $a_n = \sum_{k=1}^{n} F_k F_{n+1-k}$.

The sequence of Fibonacci numbers convolved with themselves is well-known and well researched. It appears as sequence $A001629$ in [5], and we refer the reader to this reference for a number of formulas and further results. The most informative for our purposes is the representation in terms of Fibonacci numbers given by $a_n = (nF_{n+1} + 2(n+1)F_n)/5$.

Theorem 3

The total number of conjugated 6-circuits in Z_n is equal to $\frac{2}{5}(nF_{n+1} + 2(n+1)F_n)$.

■

Now we can compute the average number of conjugated 6-circuits in a Kekulé structure of a fibonacene on n hexagons. The exact formula is obtained by dividing $\frac{2}{5}(nF_{n+1} + 2(n+1)F_n)$ by F_{n+2}, but more interesting is the behavior of this quantity for large n. Since the quotient $\frac{F_n}{F_{n+1}}$ tends to the Golden Section ratio $\varphi = \frac{\sqrt{5}-1}{2} \approx 0.618034$ for $n \longrightarrow \infty$, we have the following asymptotic behavior of the expected number of conjugated 6-circuits in fibonacenes.

Corollary 4

An average Kekulé structure in Z_n contains approximately $\frac{2}{5}\varphi(2\varphi + 1)n$ conjugated 6-circuits. ■

Numerically, $\frac{2}{5}\varphi(2\varphi + 1) \approx 0.55279$.

By a similar reasoning we may also find the number of longer conjugated circuits in a fibonacene on n hexagons. Let $c_{n,k}$ denotes the number of conjugated circuits of length $4k+2$ in Z_n. Obviously, $c_{n,k} = 0$ for $k > n$. From Theorem 3 we have $c_{n,1} = \frac{2}{5}(nF_{n+1} + 2(n+1)F_n)$, and for larger k the number is given by following formula.

Theorem 5

$$c_{n,k} = c_{n+1-k,1}.$$

■

The total number of conjugated circuits in Z_n is now readily obtained by computing the sequence of partial sums of $c_{n,1}$. We denote this quantity by t_n. It can be neatly expressed in terms of Fibonacci numbers; the following result can be obtained by straightforward manipulation of generating function of $c_{n,1}$.

Theorem 6

The total number of conjugated circuits in a fibonacene on n hexagons is given by

$$t_n = 1 + \frac{1}{5}\left((n-3)F_{n+1} + (3n-2)F_{n+2}\right).$$

■

By dividing the above formula by F_{n+2} we obtain the following asymptotics of the expected number of conjugated circuits in a Kekulé structure in Z_n.

Corollary 7

The expected number of all conjugated circuits in Z_n behaves asymptotically as $\frac{3+\varphi}{5}n$ for large values of n. ■

4 Concluding remarks

At the end of the paper we would like once more to revisit reference [3]. Although we have presented neat explicit formulas for the number of conjugated circuits of any given length in fibonacene chains, the above reference still contains some interesting challenges. For example, the coefficients of the conjugated 6-circuit polynomials in Table II on p. 374 can be arranged in a triangular array whose row sums give Fibonacci numbers. (The coefficients count the Kekulé structures containing a given number of conjugated 6-circuits.) That triangular array does not appear in [5], and it is quite likely that determining the explicit formulas for its elements could lead to a new family of identities for Fibonacci numbers.

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