Journal of Discrete Mathematics and Its Applications 7 (4) (2022) 209–221

Journal of Discrete Mathematics and Its Applications

Available Online at: http://jdma.sru.ac.ir

Shahid Rajaee Teacher Training University

Computing the Clar number of nanotubes and other fullerenes

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Academic Editor: Alireza Ashrafi

Abstract. We exhibit a polynomial time algorithm that computes the Clar number of any nanotube. This algorithm can be easily extended to one that computes the Clar number of fullerenes whose pentagon-clusters are all of even size. Computing the Clar number of planar graphs is NP-hard. However, it is not known if computing the Clar number of fullerenes is a tractable problem. We show that the latter problem can be suitably approximated in polynomial time. We also discuss the existence of *fpt-algorithms* for this important problem of cheminformatics.

Keywords: Clar number, fullerene, nanotube
Mathematics Subject Classification (2010): 05C76.

1 Introduction

Fullerene graphs are the graphical representation of fullerene molecules, an important class of carbon molecules that has became very important in material science and technology. Therefore, fullerene graphs have attracted the attention of many researchers in the last decade and, as a consequence, nowadays we know many things about fullerenes. However, there are also many questions that remain unanswered. We study one of those questions, the question about the existence of efficient algorithms computing the *Clar number* of fullerenes. The Clar number is a topological index of planar graphs, an index that seems to be related to molecular stability [10]. It is known that computing the Clar number of general planar graphs is NP-hard (see [3]), and it is also known that the same problem can be solved in polynomial time for bipartite planar graphs (see [1]). Fullerene graphs are *almost bipartite*, any fullerene

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Received 23 October 2022; Revised 10 November 2022; Accepted 22 November 2022
First Publish Date: 1 December 2022

has exactly 12 odd faces, and it means that fullerene are only 12 faces apart from bipartiteness and proved tractability, however it is not known if the Clar number of fullerene can be computed in polynomial time.

Organization of the work and contributions. This work is organized into five sections including the introduction. In section 2 we introduce the Clar number of fullerene. In section 3 we extend the latter notion to general planar graphs, and we discuss some results that are related to the computation of the Clar number for several different classes of planar graphs. In section 4 we exhibit a polynomial time algorithm that can be used to compute the Clar number of nanotubes and fullerenes of even signatures. In section 5 we discuss the case of odd signatures. We study the existence of approximation algorithms, as well as the existence of *fpt-algorithms,* for this demanding problem (see [7]).

2 The Clar number of fullerenes

Fullerene graphs are *3-connected planar cubic* graphs, whose faces are either hexagons or pentagons. Fullerene graphs are of special interest in chemical graph theory. It happens that those graphs are the *molecular graphs* of the carbon molecules called fullerene. In this work we study an algorithmic problem related to fullerene graphs. First, we declare some definitions.

Definition 1. Given a graph G, a *perfect matching* of G is a set of pairwise node-disjoint edges which covers the whole graph.

Thus, given graph G and given a perfect matching M, it must happen that:

1. Given $e \neq s$ two edges in M, those two edges do not have a common node.
2. Given v, a node of G, there exists $e \in M$ such that e covers v (v is incident with e).

Recall that G is a cubic graph, if and only if, all the nodes of G have degree three. Notice that if G is a cubic graph representing a carbon molecule, then the perfect matchings of G correspond to the *Kekule structures* of the molecule. The number of different Kekule structures (the number of perfect matchings) is a structural index that encodes important information about the physico-chemical properties of the molecule. Sometimes it is necessary to compute the exact number of Kekule structures (a task that can be efficiently solved for planar molecules using Kasteleyn's algorithm [13]), other times it is sufficient to ensure that the number of Kekule structures is large.

It was conjectured for long time that fullerene graphs have exponential many perfect matchings. Observe that the later conjecture is a special case of *The Lovasz-Plummer Conjecture* stating that *cubic bridgeless graphs* have exponential many perfect matchings (see [6] and the references therein). The conjecture was proved for fullerene graphs by Kardoš, Kral and co-workers [11], and very recently for general cubic bridgeless graphs by Kral et al [6]. It is worth to remark that some of the key ideas introduced in [11] were instrumental in the constructions that were used in [6] to settle the Lovasz-Plummer conjecture. This suggests

that fullerene graphs could play the important role of a *drosophila* that could be used to test conjectures about cubic (planar) graphs. Important evidence concerning the later claim is provided by the recent attack to *Barnette Conjecture* [12]. In the aforementioned reference F. Kardoš proved the conjecture for fullerene, and then he extended his proof to planar graphs with faces of size at most six.

Kardoš, Kral et al proved that there exists $C > 0$, such that any fullerene graph with n nodes has at least 2^{Cn} perfect matchings. To this end, they proved that any fullerene graph admits a matching with a large number of *resonant hexagons*. Given a fullerene graph G and given a perfect matching M, a resonant hexagon for M is a hexagonal face C such that $C \cap M$ is constituted by exactly three edges. Notice that given a perfect matching M and a resonant hexagon for M, say C, one can define a new matching $M_{\{C\}}$ by excluding the three edges in $M \cap C$, and replacing them by the three edges in $M^c \cap C$ (here M^c denotes the complement of M). Now suppose that there are K resonant hexagons for M, say $C_1, ..., C_K$, which are node-disjoint (pairwise node-disjoint). Given $J \subset \{1, ..., K\}$, one can construct a new perfect matching $M_{\{C_i : i \in J\}}$ by simply switching the edges for each one of the hexagons in the set $\{C_i : i \in J\}$, that is: For all $i \in J$, one excludes the three edges in $M \cap C_i$, and he replaces them by the three edges in $M^c \cap C_i$. It is clear that given $J \neq I$, the matchings $M_{\{C_i : i \in J\}}$ and $M_{\{C_i : i \in I\}}$ are different. Thus, if there exist K node-disjoint resonant hexagons for the perfect matching M, then there exist at least 2^K different perfect matchings of G, which can be constructed from M using the K resonant hexagons. We say that such a set of node-disjoint resonant hexagons is a *Clar set* for M. The *Clar number* of M, denoted by $\mathcal{C}(M, G)$, is equal to

$$\max\{|A| : A \text{ is a Clar set for } M\}.$$

The *Clar number* of G, denoted by $Clar(G)$, is equal to

$$\max\{\mathcal{C}(M, G) : M \text{ is a perfect matching of } G\}.$$

Notice that if $Clar(G) = K$, the graph G has at least 2^K perfect matchings. Then, if G has a large Clar number, it must have a large number of perfect matchings (Kekule structures). Kardoš, Kral et al proved that the Clar number of fullerene G is bounded below by $\frac{n-380}{61}$, provided that G is a non-nanotube with n nodes [11]. This implies that the latter type of fullerene have exponential many matchings. It is easy to prove that nanotubes also have exponential many matchings. Thus, we have that The Lovasz-Plummer Conjecture holds true for the class of fullerene graphs.

Remark 1. The above purely theoretical fact seems to imply that all the fullerene molecules are stable (see [10]). The Clar number was introduced by Clar (see [4]), and it was proposed as a numerical index that could be useful in the study of benzenoids. If G is a molecular graph, the quantity $Clar(G)$ carries important information about the structural and physicochemical properties of the corresponding molecule. It has been observed that a combination of Clar and Kekule numbers can be used as an indicator of the relative stability of fullerenes and other planar molecules (see [15]). We can efficiently compute the Kekule number of planar (carbon) molecules using Kasteleyn algorithm [13], can we efficiently compute the Clar

number of those molecules? It seems that computing the Clar number of planar molecules is an important task of cheminformatics.

3 On computing the Clar number of fullerene graphs and general planar graphs

We can straightforwardly extend the notion of Clar number to planar graphs. Let G be a planar graph, and let c be a planar representation of G. Suppose that M is a perfect matching of G. The quantity $Clar(G,c,M)$ takes into account all the even faces that are resonant for M and not only the number of resonant hexagons. Let us introduce an algorithmic problem related to those notions.

Open Problem 3.1. #*Clar* : ***Computing the Clar Number of Planar Graphs***

- *Input:* (G,c)*, where* G *is a planar graph and* c *is a planar representation of* c*.*
- *Problem: Compute* $Clar(G,c)$*.*

We have the following important result [3].

Theorem 3.2. *The problem #Clar is NP-hard.*

The above result seems to be discouraging. However, we are not interested in solving the problem #*Clar* in its full generality, we are interested in its restriction to the class of fullerene graphs.

Notation 3.3. *Let* $\mathcal{C}$ *be a class of planar graphs, we use the symbol* #*Clar* $[\mathcal{C}]$ *to denote the restriction of the problem #Clar to the set of instances constituted by the elements of* $\mathcal{C}$*. We use the symbol* $\mathcal{F}$ *to denote the class of fullerene graphs, and the symbol* $2\mathcal{B}$ *to denote the class of 2-connected planar bipartite graphs.*

It is natural to ask: What is known about restrictions of #*Clar*? We have an important result that was proved by Abeledo and Atkinson [1]

Theorem 3.4. *The problem #Clar* $[2\mathcal{B}]$ *can be solved in polynomial time.*

A 2-connected planar graph is bipartite, if and only if, all its faces have even size. Thus, we have that hexagonal systems are bipartite, and it implies that one can efficiently compute the Clar number of benzenoids and other hexagonal carbon molecules. On the other hand we have that fullerene graphs are not bipartite because of their pentagonal faces. If one checks the NP-hardness proof provided by Berczi-Kovacs and Bernath [3], he will observe that the hard instances constructed in the proof are planar graphs containing a large number of odd faces. One can use *Euler's formula* to prove that any fullerene has exactly 12 pentagons. This is *The 12-pentagon Theorem* [8]. We observe that those 12 pentagonal faces are the only remaining obstacles: The problem #*Clar* $[\mathcal{F}]$ is only 12 faces apart from proved tractability (bipartiteness). Thus, we think that it is a good idea to classify fullerene according to the type of clusters that are formed by those pentagons.

3.1 Signatures of fullerene graphs

Let G be a fullerene. A *pentagonal-cluster* is a group of pentagonal faces whose union gives place to a connected subgraph of G and such that any other pentagonal face is node-disjoint from the faces in the cluster. The size of a cluster is the number of its faces.

Definition 2. A fullerene *signature* is a tuple of positive integers $(n_1,...,n_k)$, such that $n_1 \geq \cdots \geq n_k \geq 1$ and such that the equality $n_i = 12$ holds.

If $(n_1,...,n_k)$ is the signature of G, we have that the pentagonal faces of G are organized into k pentagonal-clusters, which are pairwise node-disjoint, and such that the size of the ith cluster is equal to n_i. Observe that the notion of signature corresponds to a classification of fullerenes. Given a signature η it defines the class

$$\mathcal{F}_\eta = \{F \in \mathcal{F} : \text{the signature of } F \text{ is equal to } \eta\}.$$

We have for instance that the signature of the *Buckminsterfullerene* C_{60} (see [14]) is equal to

$$(1,1,1,1,1,1,1,1,1,1,1,1).$$

We can use signatures to define important subclasses of $\mathcal{F}$.

Definition 3. A fullerene N is a nanotube, if and only if, its signature is equal to $(6,6)$. We use the symbol $\mathcal{N}$ to denote the class of all nanotubes. We say that a fullerene F is even, if and only if, all the entries of its signature are even integers. We use the symbol $\mathcal{E}$ to denote the class of even fullerenes.

It is important to remark that the class $\mathcal{N}$ is constituted by molecular graphs of *carbon nanotubes*. Carbon nanotubes are cylindrical carbon molecules with unusual properties which are valuable for nanotechnology, electronics, optics and other fields of materials science and technology [5]. The stability properties of carbon nanotubes are important in the technological applications of those molecules. Thus, it seems that the restriction $\#Clar[\mathcal{N}]$ is an important algorithmic problem related to mathematical nanosciences. We prove that the problems $\#Clar[\mathcal{N}]$ and $\#Clar[\mathcal{E}]$ can be solved in polynomial time (see below). We also show that $\#Clar[\mathcal{F}]$is fpt-tractable (see [7]).

Remark 2. Some other authors define nanotubes (nanocones) in a different way. Ghorbani and Naserpour computed closed formulae for the Clar number of two special classes of fullerenes that are different to the class $\mathcal{N}$ introduced above [9]. We use the notion of nanotube introduced in [11], and which is related to the notion of 5-cyclic edge cut: The class $\mathcal{N}$ is the set constituted by all the fullerenes admitting a 5-cyclic edge cut. It is important to remark that all those different classes of nanotubes are constituted by fullerenes of even signatures (see below).

3.2 Computing the Clar number of bipartite graphs

Suppose that we are given a planar graph G together with a planar representation (embedding) of it. We use the symbol c to denote the planar embedding. Let $\mathcal{E}$ be the set of edges of G, let $\mathcal{V}$ be the set of nodes and let $\mathcal{F}$ be the set of even faces determined by c. The problem of computing the Clar number of G can be formulated as a node set partitioning problem, where each node of G must be covered exactly once by either an edge or by the cycle boundary of one of the faces in $\mathcal{F}$. The key observation is that each proper partition of $\mathcal{V}$, say the partition $P = (\mathcal{V}(E), \mathcal{V}(F))$, gives place to a family of perfect matchings that we denote with the symbol $\mathcal{M}_P$. The family $\mathcal{M}_P$ can be obtained in the following way:

1. Identify the faces of (G,c) used to cover the nodes in $\mathcal{V}(F)$ with a Clar set for the perfect matchings in $\mathcal{M}_P$. The later set of faces, that we denote with the symbol F_P, is fully described by the following condition: $f \in F_P$, if and only if, exactly a half of the nodes of f belong to $\mathcal{V}(F)$.

2. Identify the edges that are used to cover the nodes in $\mathcal{V}(E)$ with the remaining edges included in those perfect matchings. We use the symbol E_P to denote the later set, the set E_P is fully described by the condition: $e \in E_P$, if and only if, the end-nodes of e belong to $\mathcal{V}(E)$.

The objective is to maximize the number of faces in the partition. This approach is represented by the following integer program

$$\textbf{IP-}Clar(G,c) = \max\left\{\left\langle \mathbf{1}^{|\mathcal{F}|}, y\right\rangle : y \in \mathbb{Z}_+^{|\mathcal{F}|},\, x \in \mathbf{Z}_+^{|\mathcal{E}|} \text{ and } (K_G)\,x + (R_{G,c})\,y = \mathbf{1}^{|\mathcal{V}|}\right\},$$

where the symbol K_G denotes the node-edge incidence matrix of G, the symbol $R_{G,c}$ denotes the node-face incidence matrix determined by the pair (G,c) and the symbol $\mathbf{1}^{|\mathcal{F}|}$ denotes the all ones vector of dimension $|\mathcal{F}|$ (the vector $\mathbf{1}^{|\mathcal{V}|}$ is defined accordingly).

The above representation of #*Clar* as an integer programming problem has been used before to study this hard optimization problem [1], other integer programming representations have been studied as well (see [2]). However, those representations does not yield an efficient solution of #*Clar*, recall that integer programming is NP-hard.

It is important to recall, at this point, that some integer programs are equivalent to their linear relaxations. We use the term *easy programs* to designate the latter type of integer programs. Notice that easy programs can be efficiently solved using linear programming. It means that we can use linear programming to compute the Clar number of any planar graph whose corresponding integer program **IP**-$Clar(G,c)$ is an easy program. We have to ask: Which are the linear programs that are easy? It is known that an integer program $(f, A \cdot X \geq b)$ is easy, if and only if, the constraint matrix A is *unimodular* [1]. Recall that a rectangular matrix A is unimodular, if and only if, the determinants of all its maximal order submatrices are equal to ± 1. Abeledo and Atkinson proved that given a planar bipartite and 2-connected graph G the matrix $[K_G R_{G,c}]$ is unimodular [1], here the symbol $[K_G R_{G,c}]$ stands

for the concatenation of the matrices K_G and $R_{G,c}$. It follows from the later result that given a planar bipartite and 2-connected graph G, the integer program **IP**-$Clar\,(G,c)$ is easy. It follows that problem $\#Clar\,[2\mathcal{B}]$ can be solved in polynomial time. We will try to extend the Theorem 3.4 (and the underlying approach) as much as possible.

Let (G,c) be a pair constituted by a planar graph and a planar representation of it, let V_0 be a set of nodes, let E_0 be a set of edges, and let F_0 be a set of faces. A matching of G satisfies the triple $[V_0,E_0,F_0]$, if and only if, the following three conditions are satisfied:

1. All the nodes in $\mathcal{V}(G)\setminus V_0$ are covered by M, and the nodes in V_0 are not incident with M.

2. For all $e\in E_0$, the edge e does not belong to M.

3. For all $f\in F_0$, the face f is not a resonant face for M.

Given a matching M satisfying the triple $[V_0,E_0,F_0]$, we define

$$Clar^*\left((G,c),[V_0,E_0,F_0],M\right)=\max\{|A|:A \text{ is a set of resonant faces for } M\}.$$

The $[V_0,E_0,F_0]$-Clar number of (G,c) is equal to

$$\max\{Clar^*\left((G,c),[V_0,E_0,F_0],M\right): M \text{ satisfies the triple } [V_0,E_0,F_0]\}.$$

We consider a variation of the problem $\#Clar$, that we call *Clar number with prescribed triples.* We use the symbol $\#ClarPT$ to denote the latter problem, which is the problem defined by:

- *Input:* $((G,c),[V_0,E_0,F_0])$, *where* G *is a planar 2-connected and bipartite graph,* c *is a planar representation of* G *and* $[V_0,E_0,F_0]$ *is a triple.*

- *Problem: Compute the* $[V_0,E_0,F_0]$*-Clar number of* (G,c).

First at all we prove that $\#ClarPT$ can be solved in polynomial time, then we use this result to design a polynomial time algorithm computing the Clar number of any fullerene whose signature is an even signature.

Proposition 3.5. *The problem* $\#ClarPT\,[2\mathcal{B}]$ *can be solved in polynomial time.*

Proof. Let $((G,c),[E_0,F_0])$ be an input of $\#ClarPT\,[2\mathcal{B}]$, and let $[KR]$ be the concatenation of the node-edge incidence matrix of G (the matrix K) and the node-face incidence matrix of (G,c) (the matrix R). The key observation is that the $[V_0,E_0,F_0]$-Clar number of (G,c) is equal to

$$\max\left\{\left\langle \mathbf{1}^{|\mathcal{F}|-|F_0|},y\right\rangle : y\in\mathbb{Z}_+^{|\mathcal{F}|-|F_0|},\, x\in\mathbf{Z}_+^{|\mathcal{E}|-|E_0|} \text{ and } K^{[E_0]}x+R^{[F_0]}y=\mathbf{\emptyset}_{V_0}\right\},$$

where $K^{[E_0]}$ is the matrix that is obtained from K by deleting all the columns corresponding to edges in E_0, $R^{[F_0]}$ is the matrix that is obtained from R by deleting all the columns corresponding to faces in F_0 and $\boldsymbol{\emptyset}_{V_0}$ is the characteristic vector of the set $\mathcal{V}(G) \setminus V_0$, that is:

$$\boldsymbol{\emptyset}_{V_0}[v] = \begin{cases} 1, \text{ if } v \notin V_0 \\ 0, \text{ otherwise} \end{cases}.$$

We observe that the constraint matrix $\left[K^{[E_0]} R^{[F_0]}\right]$ is obtained from the unimodular matrix $[KR]$ by deleting some columns. It follows that $\left[K^{[E_0]} R^{[F_0]}\right]$ is unimodular, and it implies that the problem $\#ClarFP$ can be solved in polynomial time using linear programming methods. Then, there exists some positive integer d such that the $[V_0, E_0, F_0]$-Clar number of (G, c) can be computed in time $O\left(|G|^d\right)$. □

4 Computing the Clar number of nanotubes and fullerenes of even signatures

We want to use Proposition 3.5 to compute the Clar number of some planar graphs that are not bipartite. We begin considering the class $\mathcal{N}$ constituted by all the nanotubes.

Recall that $\mathcal{N}$ is the class of fullerene graphs whose signature is equal to $(6,6)$. This means that the twelve pentagonal faces of a nanotube are grouped together into two pentagon-clusters of size 6 that are called *pentacaps*. The graphic below corresponds to a planar representation of a nanotube that we denote with the symbol N_4.

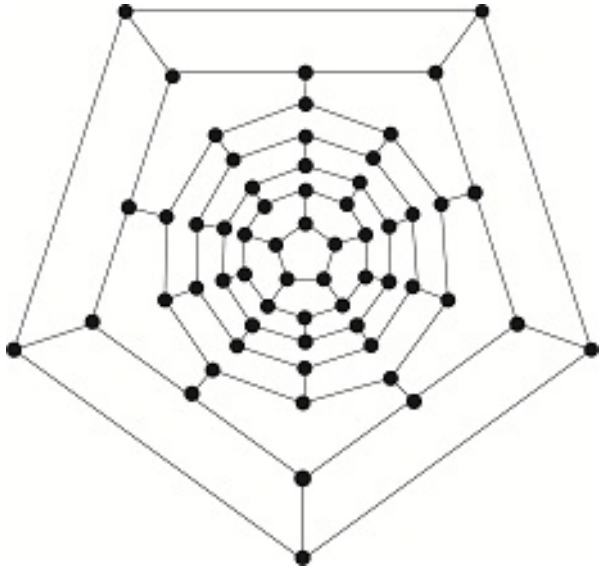

Figure 1. The nanotube N_4.

All nanotubes are similar. Given a nanotube N, it contains only two pentagonal clusters, and each one of those two clusters is constituted by six pentagons that are grouped together in the same way. Moreover, the two pentacaps of nanotube N are connected by a layered

graph constituted by a finite number of *bracelets*, each one constituted by five hexagons (see the Figure above). We have that the class of all nanotubes is equal to the set $\{N_i : i \geq 0\}$, where for all $i \geq 0$ the symbol N_i denotes the nanotube that contains exactly i bracelets.

Let $i \geq 0$, notice that the boundaries of the two pentacaps of N_i are cycles of length 10. Suppose that we delete the edges and the nodes that are enclosed by any one of those two cycles. Notice that we get a 2-coonected planar graph $\widehat{N_i}$ such that all its faces are even faces. Thus, we have that $\widehat{N_i}$ is a 2-connected planar and bipartite graph. The graphic below is a planar representation of $\widehat{N_4}$.

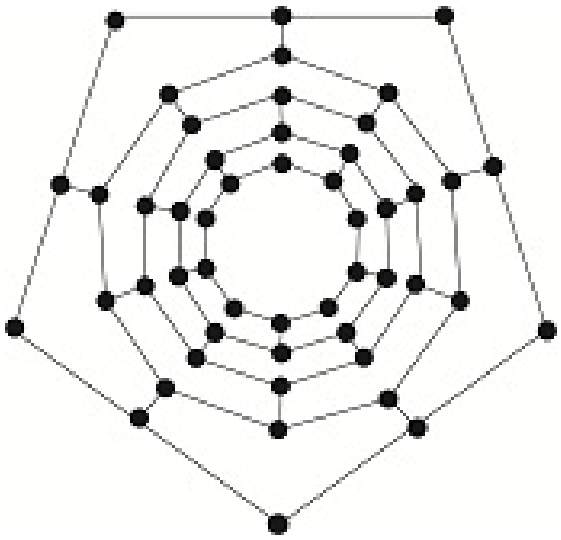

Figure 2. The graph $\widehat{N_4}$ obtained from N_4.

We can compute the Clar number of $\widehat{N_i}$ in polynomial time in i. Can we use this fact to efficiently compute the Clar number of N_i?

Notation 4.1. *Let us use the symbol $E_{CG}(i)$ to denote the set of edges of N_i that were deleted in the construction of $\widehat{N_i}$, that is: The symbol $E_{CG}(i)$ denote the set constituted by the twenty edges of N_i that are enclosed by the boundary of one of the two pentacaps. Let us use the symbol $V_{CG}(i)$ to denote the set of nodes the were deleted in the construction of $\widehat{N_i}$.*

Suppose that we are given a set $A \subset E_{CG}(i)$, and suppose that we want to compute the quantity

$$Clar(N_i, A) = \max\{Clar(N_i, M) : M \text{ is a perfect matching and } A \subset M\}.$$

Let $e \in A$, and suppose that e is incident with a node v that belongs to $\widehat{N_i}$. The two edges of $\widehat{N_i}$ that are incident with v become forbidden edges for all the matchings extending the set A. Observe that the face of $\widehat{N_i}$ that contains the node v becomes a forbidden face as well. Set

$$\mathcal{V}(A) = \left\{v \in \mathcal{V}\left(\widehat{N_i}\right) : v \text{ is incident with } A\right\},$$

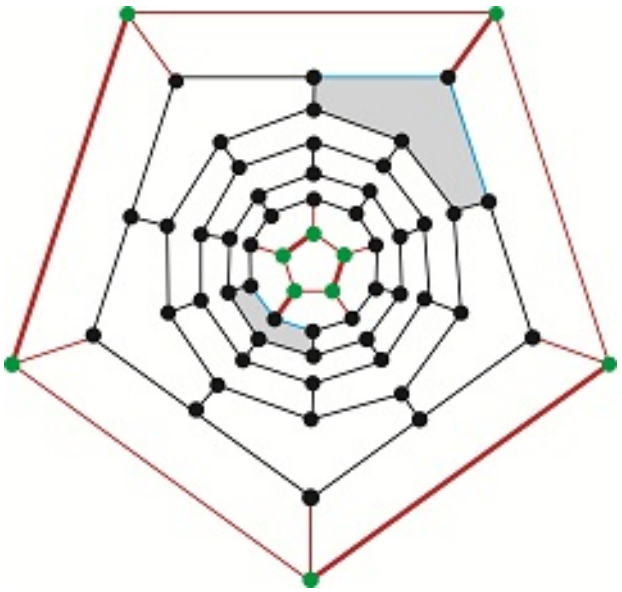

Figure 3. Green nodes are the nodes deleted from N_4 to build $\widehat{N_4}$. Red edges are the edges deleted from N_4 to built $\widehat{N_4}$. Red bold edges are the edges chosen to cover the green nodes. Blue edges are the forbidden edges determined by the bold edges, while bold faces are the forbidden faces determined by the bold edges.

the set $\mathcal{V}(A)$ determines a forbidden pair $[E_A, F_A]$ (see the Figure 3 below).

We observe that $Clar(N_i, A)$ is equal to

$$\max\left\{\left\langle \mathbf{1}^{|\mathcal{F}|-|F_A|}, y\right\rangle : y \in \mathbb{Z}_+^{|\mathcal{F}|-|F_A|},\ x \in \mathbf{Z}_+^{|\mathcal{E}|-|E_A|} \text{ and } K^{[E_0]}x + R^{[F_0]}y = \boldsymbol{\emptyset}_{\mathcal{V}(A)}\right\},$$

where $\boldsymbol{\emptyset}_{\mathcal{V}(A)}$ is the characteristic vector of the set $\mathcal{V}\left(\widehat{N_i}\right) \setminus \mathcal{V}(A)$. Thus, we get that $Clar(N_i, A)$ is equal to the $[\mathcal{V}(A), E_A, F_A]$-Clar number of the bipartite graph $\widehat{N_i}$. Recall that we can efficiently compute the later quantity. We use this fact to design a polynomial time algorithm computing the Clar number of nanotubes. We use the symbol $\mathcal{A}_1$ to denote this algorithm.

Remark 3. Recall that all the fullerene graphs are 3-connected, and recall that all the planar representations of a 3-connected planar graph are equivalent. Thus, the input of algorithm $\mathcal{A}_1$ can be a positive integer i encoding the nanotube N_i. Observe that N_i has exactly $10i + 20$ nodes.

Definition 4. We have that a matching M belongs to $\mathcal{M}(N_i)$, if and only if, the following two conditions are satisfied:

1. $M \subset E_{CG}(i)$.
2. The matching M covers the set $V_{CG}(i)$.

Notice that for all i the size of $\mathcal{M}(N_i)$ is bounded above by 2^{20}.

algorithm 4.2. *Procedure A_1 works, on input i, as follows:*

1. *List the subsets of $\mathcal{M}(N_i)$.*
2. *Let $A_1, ..., A_{K_i}$ be the list computed in step 1. For all $j \leq K_i \leq 2^{20}$ do:*
   (a) *Compute the triple $\left[\mathcal{V}(A_j), E_{A_j}, F_{A_j}\right]$.*
   (b) *Run, on input $\left(\left(\widehat{N_i}\right), \left[\mathcal{V}(A_j), E_{A_j}, F_{A_j}\right]\right)$, the algorithm in the proof of proposition 3.5. Use the variable X_j to store this value.*
3. *Compute $X = \max\{X_j : j \leq K_i\}$. Print X.*

The execution of steps 1 and 3 require time $O(1)$. Then, the running time of $\mathcal{A}_1$ is essentially equal to the running time employed in the second step. The later running time is $O\left((10i+20)^{20}\right)$. Therefore, we can conclude that $\mathcal{A}_1$ is a polynomial time algorithm computing the Clar number of nanotubes.

To finish with this section we only have to observe that the boundary of any even cluster is a cycle of even length. We get that the above algorithm can be straightforwardly extended to deal with fullerenes of even signatures. Thus, we have two polynomial time algorithms denoted $\mathcal{A}_1$ and $\mathcal{A}_2$, the first one solves the problem $\#Clar[\mathcal{N}]$ while the second one solves the problem $\#Clar[\mathcal{E}]$.

5 The Clar number for odd signatures

We begin this section by observing that there exists a naive polynomial time algorithm that approximates the Clar number of any fullerene within the ratio 11.

Lemma 5.1. *There exists a polynomial time algorithm that approximates the Clar number of any fullerene graph within the ratio* 11.

Proof. The approximation algorithm, denoted by approx-CF, is the following one:

Algorithm approx-CF works, on input F, as follows:

1. *Check if the signature of F is odd, in given case print $\left\lceil \frac{n-380}{61} \right\rceil$, (here n stands for the size of F). Otherwise go to step 3.*
2. *Run, on input F, the algorithm $\mathcal{A}_2$.*

We observe that if the signature of F is even the algorithm approx-CF computes the exact value of $Clar(F)$. Now suppose that the signature of F is odd, in this case the algorithm prints the value $\lceil \frac{n-380}{61} \rceil$. We claim that $\lceil \frac{n-380}{61} \rceil$ approximates the quantity $Clar(F)$ within the ratio 11. First we observe that F cannot be a nanotube. Then, we have that $Clar(F)$ is lowerbounded by $\frac{n-380}{61}$ (see [11]). If we suppose that n is large, we get that $Clar(F) \geq \frac{n-380}{61} \geq \frac{n}{62}$. On the other hand we have that $Clar(F) \leq \frac{n-12}{6}$ (see [16]). Notice that

$$11 \left\lceil \frac{n-380}{61} \right\rceil \geq 11 \left(\frac{n}{62} \right) \geq \frac{n}{6} \geq Clar(F) \geq \left\lceil \frac{n-380}{61} \right\rceil.$$

Thus, we have that $\lceil \frac{n-380}{61} \rceil$ approximates the quantity $Clar(F)$ within the ratio 11. □

We get from the above result the following conclusion: The real challenge, when coping with fullerenes of odd signatures, is to compute the Clar number exactly.

We wont exhibit a polynomial time algorithm computing the Clar number of general fullerene graphs. Actually, we do not know is such an algorithm exists. We will only observe that algorithm $\mathcal{A}_2$ can be turned into a *fixed parameter tractable algorithm* $\mathcal{A}_3$ solving the problem $\#Clar[\mathcal{F}]$ (see [7] for a pedagogical introduction to the basics of fixed parameter algorithms). Algorithm $\mathcal{A}_3$ is based on an easy observation and a naive idea:

- The observation is that given a fullerene G, the number of its odd clusters is an even integer.
- The naive idea is the following one: Given G, the odd clusters of G can be grouped in pairs. Then, given one of those pairs, one can merge the corresponding two clusters and some of the faces in between to define a large face whose boundary is an even cycle. If one does the same for all the pairs of clusters, he gets a bipartite graph $\widehat{G}$ that can be used to compute the Clar number of G. Graph $\widehat{G}$ plays the role of the graph $\widehat{N}$ that is used to compute the Clar number of a nanotube N.

Let F be a fullerene with n nodes. There exist positive constants C and d such that the running time of $\mathcal{A}_3$, on input F, is bounded above by the function $2^{C \cdot k(F)} n^d$. Here, the symbol $k(F)$ denotes a parameter related to F and which measures the distance between its odd clusters (see [3]). If F is an even fullerene the parameter $k(F)$ takes the value 0, and we get that the running time of $\mathcal{A}_3$, on input F, is bounded above by n^c. If the odd clusters of F are close to each other the parameter $k(F)$ gets a small value and the computation of $\mathcal{A}_3$, on input F, is still a feasible computation. However, the same cannot be said if the odd clusters of F are far away from each other (see [3] for more details related to this issue). Algorithm $\mathcal{A}_3$ does not work well for fullerene graphs containing an odd cluster that is far away from the remaining odd clusters. We have to conclude that there are some remaining problems related to the computation of Clar numbers of fullerenes.

Acknowledgements

The second author would like to thank the financial support provided by Universidad Nacional de Colombia through the project Hermes 32083.

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Citation: J. A. Montoya, L. V. Cadavid, Computing the Clar number of nanotubes and other fullerenes, J. Disc. Math. Appl. 7(4) (2022) 209–221.
https://doi.org/10.22061/jdma.2022.843