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Packing resonant hexagons in fullerenes

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ABSTRACT

A fullerene graph G is a plane cubic graph such that every face is bounded by either a hexagon or a pentagon. A set $\mathcal{H}$ of disjoint hexagons of G is a resonant set (or sextet pattern) if $G - V(\mathcal{H})$ has a perfect matching. A resonant set is a forcing set if $G - V(\mathcal{H})$ has a unique perfect matching. The size of a maximum resonant set is called the Clar number of G. In this paper, we show the Clar number of fullerene graphs with a non-trivial cyclic 5-edge-cut is $(n-20)/10$. Combining a previous result obtained in Kardoš et al. (2009), it is proved in this paper that a fullerene has the Clar number at least $(n-380)/61$. For leapfrog fullerenes, we show that the Clar number is at least $n/6 - \sqrt{n/5}$. Further, it is shown that the minimum forcing resonant set has at least two hexagons and the bound is tight.

1. Introduction

A fullerene is a hollow carbon cage consisting only of carbon atoms that are arranged on pentagonal rings or hexagonal rings. Fullerenes are typical nano-materials, including closed-end single-walled carbon nanotubes. The molecule graph of a fullerene is called a fullerene graph, which is a cubic plane graph with only pentagonal faces and hexagonal faces. The vertex set and edge set of G are denoted by $E(G)$ and $V(G)$, respectively. A *matching* is a set of disjoint edges, i.e., any two edges in this set do not share a common end-vertex. A matching M is *perfect* (or a Kekulé structure) if every vertex of G is incident with exactly one edge in M. A cycle C is M-alternating if the edges of C alternate between M and $E(G) \setminus M$. A *resonant set* (or sextet pattern) of G is a set of disjoint M-alternating hexagons for some perfect matching M, i.e., $G - V(\mathcal{H})$ has a perfect matching where $V(\mathcal{H})$ is the set of vertices contained by hexagons in $\mathcal{H}$. The *Clar number* of a fullerene graph is the size of a maximum resonant set [1]. It is evident that resonant sets are important to energetic stability of fullerene molecules [2], and experimentally observed fullerenes have the largest Clar number over all fullerene isomers [3]. The Clar number of fullerene graphs can be used to estimate the number of perfect matchings. The number of perfect matchings of fullerene graphs has been well-studied (see [4–8]).

The Clar number of a fullerene graph can be formulated to a binary integer linear programming

$$\max\{\mathbf{1}^{\intercal}\mathbf{y} | \mathbf{Q}\mathbf{x} + \mathbf{R}\mathbf{y} = \mathbf{1}\}$$

where $\mathbf{Q}$ is the incident matrix, $\mathbf{R}$ is the vertex-hexagon incident matrix, and $\mathbf{x}$ and $\mathbf{y}$ are binary vectors. For benzenoid hydrocarbons, the Clar number problem can be relaxed to a linear programming problem and hence can be solved in polynomial time [9,10]. However, this relaxation does not work for the Clar number problem of fullerene graphs, so that the computation complexity of the Clar number problem of fullerene graphs remains open.

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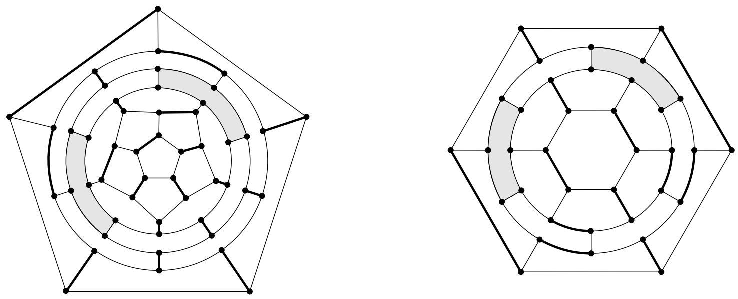

Fig. 1. Fullerene graphs with a forcing resonant set of size two (bold edges form a perfect matching in the remaining graphs by deleting resonant sets).

A sharp upper bound has been obtained in [11] as the following theorem. The fullerene graphs whose Clar numbers attain this bound have been characterized in [12,13].

Theorem 1.1 (*[11]*). *Let G be a fullerene graph with n vertices. Then* $\mathrm{cl}(G) \le \lfloor n/6 \rfloor - 2$.

A fullerene graph with n vertices exists for all even integers $n \ge 20$ except $n = 22$. A *cyclic k-edge-cut S* of a graph G is an edge cut such that $G - S$ has two components, each of which contains a cycle. A cyclic k-edge-cut S is trivial if one component of $G - S$ is a k-cycle. The *cyclic edge-connectivity* of a graph G is the size of the smallest cyclic edge-cut. The cyclic edge-connectivity of a fullerene graph is five [14,15]. The fullerene graphs with a non-trivial cyclic 5-edge-cut have been characterized in [8]. Kardoš et al. [7] show that a fullerene graph has exponentially many perfect matchings by proving that a fullerene graph without a non-trivial cyclic 5-edge-cut has a resonant set with at least $(n - 380)/61$ hexagons. In this paper, we show that if a fullerene graph G with n vertices has a non-trivial cyclic 5-edge-cut, then $\mathrm{cl}(G) = (n - 20)/10$. Combining the result from [7], the following lower bound on the Clar number of fullerene graphs follows.

Theorem 1.2. *Let G be a fullerene graph with n vertices. Then* $\mathrm{cl}(G) \ge (n - 380)/61$.

The class of leapfrog fullerenes is an important family of fullerenes due to their chemistry properties (a detailed definition of leapfrog fullerenes will be given in Section 2). In [5], Došlić show that a leapfrog fullerene with n vertices has a resonant set of size at least $n/8$. Hence the Clar number of a leapfrog fullerene is at least $n/8$, which can also be deduced from the structure properties obtained by Marušič in [16]. For leapfrog fullerenes with icosahedral symmetry, Graver [17] obtained a better lower bound.

Theorem 1.3 (*[17]*). *Let G be an icosahedral leapfrog fullerene with n vertices. Then* $\mathrm{cl}(G) \ge n/6 - 2(p + r)$ *where* $(p + r, p)$ *is the Coxeter coordinates of G.*

The Coxeter coordinates (x, y) are defined for a pair pentagons that can be joined by two straight hexagon-chains consisting of x hexagons and y hexagons, respectively. An icosahedral leapfrog fullerene has Coxeter coordinates $(p + r, p)$ for each pair of pentagons (see [18]). An icosahedral fullerene with Coxeter coordinates $(r, 0)$, it can be easily computed that $2(p + r) \le \sqrt{n/5}$ and equality holds if and only if $p = 0$ (see [17]), where n is the number of vertices. For more details of Coxeter coordinates of fullerenes, refer to [18,17]. In this paper, we obtain a general lower bound for all leapfrog fullerene graphs as follows, which improves the bound obtained in [5].

Theorem 1.4. *Let G be a leapfrog fullerene with n vertices. Then* $\mathrm{cl}(G) \ge n/6 - \sqrt{n/5}$.

A resonant set $\mathcal{H}$ of a fullerene graph G is a *forcing resonant set* if $G - V(\mathcal{H})$ has a unique perfect matching. A hexagonal system is a 2-connected plane graph such that every inner face is a hexagon. It has been shown that every maximum resonant set of a hexagonal system is a forcing set [19]. However, it is not true for fullerene graphs. For example, a maximum resonant set of a fullerene graph with a non-trivial cyclic 5-edge-cut is not a forcing set (see Remark in Section 3). Some fullerene graphs, such as C_{24}, even do not have a forcing resonant set. The *forcing hexagon-number* of a fullerene graph G is the minimum size of its forcing resonant sets, denoted by $f_{\mathrm{Hex}}(G)$. If a fullerene graph does not have a resonant set, then its forcing hexagon number is infinity. Che and Chen [20] characterized hexagonal systems with a forcing hexagon, i.e., the forcing hexagon-number is 1. For fullerene graphs, we have the following result.

Theorem 1.5. *Let G be a fullerene graph. Then* $f_{\mathrm{Hex}}(G) \ge 2$.

The bound in Theorem 1.5 is tight. The two fullerene graphs in Fig. 1 have forcing hexagon-number 2.