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The Clar Structure of Fullerenes

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ABSTRACT

A *fullerene* is a 3-regular plane graph $\Gamma = (V, E, F)$ consisting only of pentagonal and hexagonal faces. Fullerenes are designed to model carbon molecules. The *Clar number* and *Fries number* are two parameters that are related to the stability of carbon molecules. We introduce *chain decompositions*, a new method to find lower bounds for the Clar and Fries numbers. In Chapter 3, we define the *Clar structure* for a fullerene, a less general decomposition designed to compute the Clar number for classes of fullerenes. We use these new decompositions to understand the structure of fullerenes and achieve several results. In Chapter 4, we classify and give a construction for all fullerenes on $|V|$ vertices that attain the maximum Clar number $\frac{|V|}{6} - 2$. In Chapter 5, we settle an open question with a counterexample: we construct an infinite family of fullerenes for which a set of faces attaining the Clar number cannot be a subset of a set of faces that attains the Fries number. We develop a method to calculate the Clar number directly for many infinite families of fullerenes.

THE CLAR STRUCTURE OF FULLERENES

by

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Introduction

1.1 Background and Definitions

A *Fullerene* is a 3-regular plane graph $\Gamma = (V, E, F)$ consisting only of pentagonal and hexagonal faces. Fullerenes are designed to model carbon molecules. The vertices of the graph represent carbon atoms and edges represent chemical bonds between them. The term "fullerene" is also used to denote the actual carbon molecule. A specific fullerene with 60 atoms, C_{60}, was the first pure carbon molecule discovered and is the most common naturally occurring carbon molecule. C_{60} was first synthesized by Kroto, Heath, O'Brien, Curl and Smalley in 1985, and the discovery earned Kroto, Curl, and Smalley a Nobel prize in 1996. In 1991, C_{60} was named *Science Magazine*'s "Molecule of the Year." Nanotubes are also examples of fullerenes. The smallest fullerene is the dodecahedron.

Carbon atoms form four chemical bonds. Three of these are strong bonds, and one is weak. In the graphical representation of a fullerene, we represent the three strong bonds by the edges in the graph. The fourth bond is represented chemically as a double bond.

A *perfect matching* of a graph is a set of edges of Γ such that each vertex is incident with exactly one edge. Over a fullerene, the edges of a perfect matching correspond to double bonds, and chemists call this matching a *Kekulé structure*. We refer to edges in a given Kekulé structure as *Kekulé edges*. Petersen's Theorem states that in a bridgeless 3-regular graph, there is always a perfect matching [10]. We therefore know that a fullerene always has at least one Kekulé structure. Propositions 1.1, 1.2, and 1.4 are standard in the literature on fullerenes and are presented here for future reference.

Proposition 1.1. *Let K be a Kekulé structure on a fullerene $\Gamma = (V, E, F)$. Let P be the set of pentagons and H be the set of hexagons in Γ. Then*

1. $|K| = \frac{|V|}{2}$
2. $|E| = \frac{3|V|}{2}$
3. $|P| = 12$
4. $|H| = \frac{|V|}{2} - 10$

Proof.

1. Each vertex is incident with exactly one edge in the Kekulé structure, and every edge in K is incident with two vertices. Thus $|V| = 2|K|$.

2. Every vertex is of degree 3, so $3|V| = 2|E|$.

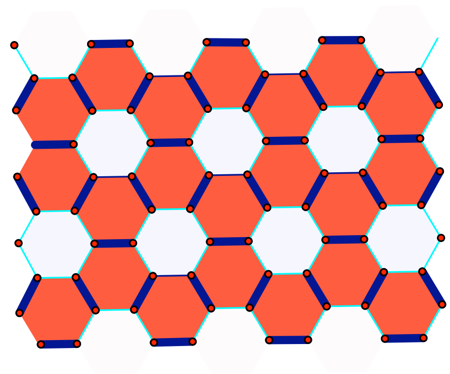
3. Summing together the number of vertices around each face gives $6|H| + 5|P|$ vertices. Each vertex is incident with three faces, so $6|H|+5|P| = 3|V|$. Substituting $3|V| = 2|E|$ gives $2|E| = 6|H| + 5|P|$ and we know that $|F| = |H| + |P|$. By Euler's formula, $|V| - |E| + |F| = 2$, so $6|V| - 6|E| + 6|F| = 12$, and by substitution, $2(6|H| + 5|P|) - 3(6|H| + 5|P|) + 6(|H| + |P|) = 12$. Simplifying shows that $|P| = 12$.

4. $6|H|+5|P| = 3|V|$ and $|P| = 12$, so $6|H|+60 = 3|V|$. Solving for $|H|$ gives the result.

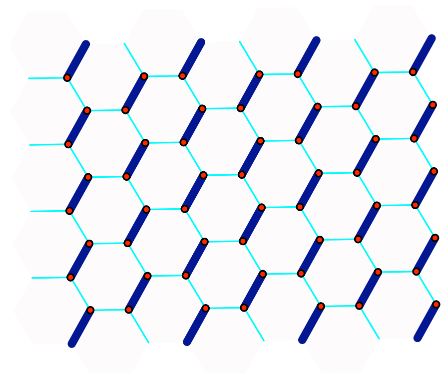
□

1.2 The Clar, Fries, and Face-Independence Numbers

Given a Kekulé Structure on a fullerene Γ, a face of Γ may have 0, 1, 2 or 3 of its bounding edges in K. The set of faces that have exactly i of their edges in K is denoted by $B_i(K)$. The faces in the set $B_0(K)$ are called the *void* faces of K, and the faces in the set $B_3(K)$ are called the *benzene* faces of K. The number of benzene



(a) The red faces are benzene faces.



(b) In this Kekulé structure, none of the faces is a benzene face.

Figure 1.1: Two Different Kekulé Structures. The thick blue edges represent edges in the Kekulé structure.

faces over a fullerene is dependent upon which Kekulé structure is chosen. A patch of a fullerene is pictured in Figure 1.1 with two different Kekulé structures. The thick blue edges represent edges in each Kekulé structure. In Figure 1.1(a), the red faces are all benzene faces; in Figure 1.1(b), none of the faces is a benzene face.

The *Fries number* of a fullerene Γ is the maximum number of benzene faces over all possible Kekulé structures for Γ. We define a *Fries set* to be a set of benzene faces that attains the Fries number for a Γ. The *Clar number* of a fullerene Γ is the cardinality of a maximum independent set of benzene faces over all Kekulé structures for Γ. We define a *Clar set* to be an independent set of benzene faces that attains the Clar number for Γ. It has been found experimentally that the Clar and Fries numbers for organic structures are related to the stability of the molecules. Clar and Gutman

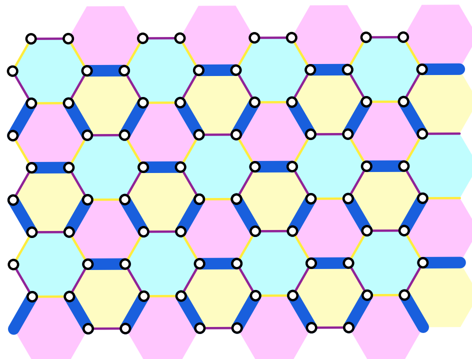


Figure 1.2: Kekulé structure with face 3-coloring. The void faces are in the blue color class. Thick blue edges represent edges in the Kekulé structure.

each theorized that this correlation would hold for carbon molecules [1].

It is natural to ask whether a Clar set is always a subset of some Fries set, or equivalently, if there is a Kekulé structure that simultaneously gives a Fries set and a Clar set. It was generally assumed that this was true. Settling this open question was the initial research problem for this dissertation, and in Chapter 5 we show that this assumption is false by constructing an infinite family of fullerenes for which a Clar set is never a subset of a Fries set.

To motivate the next result we consider a *hexagonal patch*: a plane graph in which all faces are hexagons except for possibly one *outside face*, all vertices are of degree 2 or 3 and all vertices of degree 2 are incident with the outside face. A hexagonal patch may be thought of as either a region of the hexagonal tessellation of the plane or a region of a fullerene that includes no pentagons. As a region of the hexagonal tessellation, a hexagonal patch inherits a face 3-coloring that is unique up to interchanging the color classes. In a face 3-coloring of a hexagonal patch, each color class is a maximal face-independent set. We construct a partial Kekulé structure over such a patch in the following way: choose one color class to be the set of void faces. Let all of the edges not bounding a void face be in the Kekuké structure. On the interior of this patch, all of the faces in the other two color classes are benzene faces. Figure 1.2 shows a patch with a face 3-coloring and associated Kekulé structure. The blue faces are the void faces, the pink and yellow faces are all benzene faces and this set is part of a potential Fries set. Furthermore, either the pink faces or the yellow faces can be chosen as part of a potential Clar set. On the interior of this patch, two-thirds of the faces are benzene faces and one-third of the faces form an independent set of benzene faces. By Proposition 1.1 (3, 4), the number of faces in a fullerene is approximately half the number of vertices. Thus we might expect the Fries number of a fullerene $\Gamma = (V, E, F)$ to be bounded above by $\frac{|V|}{3}$ and the Clar number to be bounded above by $\frac{|V|}{6}$. We see in the proposition below that this is indeed the case.

Proposition 1.2. *Let K be a Kekulé structure for a fullerene $\Gamma = (V, E, F)$.*

1. $|B_3(K)| = \dfrac{|V|}{3} - \delta_F(K)$, *where* $\delta_F(K) = \dfrac{|B_1(K)| + 2|B_2(K)|}{3}$.

2. *For an independent set X of faces in Γ, let $V^*(X)$ be the set of vertices not incident with a face in X and let $P^*(X)$ be the set of pentagons not in the set X. Then* $|X| = \dfrac{|V|}{6} + 2 - \dfrac{|P^*(X)| + |V^*(X)|}{6}$.

3. *For an independent set of faces X in $B_3(K)$, $|X| = \dfrac{|V|}{6} - \delta_C(K,X)$ where $\delta_C(K,X) = \dfrac{|V^*(X)|}{6}$.*

Proof.

1. Summing the number of edges from K bounding each face gives $|B_1(K)| + 2|B_2(K)| + 3|B_3(K)|$ and counts each of the edges in K twice. Thus $2|K| = |B_1(K)| + 2|B_2(K)| + 3|B_3(K)|$, and by Proposition 1.1, $|2K| = |V|$. Solving for $|B_3(K)|$ gives $|B_3(K)| = \dfrac{|V|}{3} - \dfrac{|B_1(K)| + 2|B_2(K)|}{3}$.

2. Since X is an independent set of faces, each vertex of Γ is incident with at most one face in X. The total number of vertices incident with a face in X is 6 times the number of hexagons in X plus 5 times the number of pentagons in X: $6(|X| - (12 - |P^*(X)|)) + 5(12 - |P^*(X)|) = 6|X| - 12 + |P^*(X)| = |V| - |V^*(X)|$. Solving for $|X|$ gives $|X| = \frac{|V|}{6} + 2 - \frac{|P^*(X)| + |V^*(X)|}{6}$.

3. Let X be an independent set of faces in $B_3(K)$. Every benzene face must be a hexagon, so $P^*(X) = 12$. Thus $|X| = \frac{|V|}{6} - \frac{|V^*(X)|}{6}$.

□

We call $\delta_F(K)$ the *Fries deficit* of K and $\delta_C(K,X)$ the *Clar deficit* of K with respect to the set X. Fowler [3] and Graver [9] characterized fullerenes that attain the maximum of $\frac{|V|}{3}$ for the Fries number and gave a method for constructing all fullerenes that attain this maximum. We show that the maximum possible Clar number is $\frac{|V|}{6} - 2$ and in Chapter 4 we give a characterization and construction for the fullerenes that achieve this maximum.

Over a region of a fullerene that includes a pentagon, a face 3-coloring is not possible and the Kekulé structure described above is disrupted. To compute or estimate the Clar and Fries numbers, we isolate patches of the fullerene containing the pentagons so that the remainder of the fullerene consists solely of hexagons and admits a face 3-coloring. One can then construct a partial Kekulé structure by selecting one color class to be the void set as described above. The problem is then to extend the partial Kekulé structure over the patches containing pentagons while minimizing the Clar and Fries deficits. One such decomposition was introduced by Graver in [7], in which pentagons were connected by a "spanning tree" of polygonal paths of hexagons.

In [7] and [8], Graver introduced *clear fields* and *Coxeter coordinates*, two concepts that are used to describe the structure of fullerenes. Let $\Gamma = (V, E, F)$ be a fullerene and let $\Gamma^* = (F, E, V)$ be its dual. Two faces f_1 and f_2 are contained in a *clear field* if all shortest dual paths between the corresponding vertices f_1^* and f_2^* consist only of degree-6 vertices. We say that two faces of Γ are *nearby* if they are contained in a clear field. A clear field between two pentagons is pictured in Figure 1.3 and we often depict a patch of a fullerene containing pentagons in this way. We draw the patch in the hexagonal tessellation of the plane. At each pentagon, we insert a $60°$ wedge and identify the two rays bounding the wedge.

For a pair of nearby faces, the position of the two faces in relation to one another

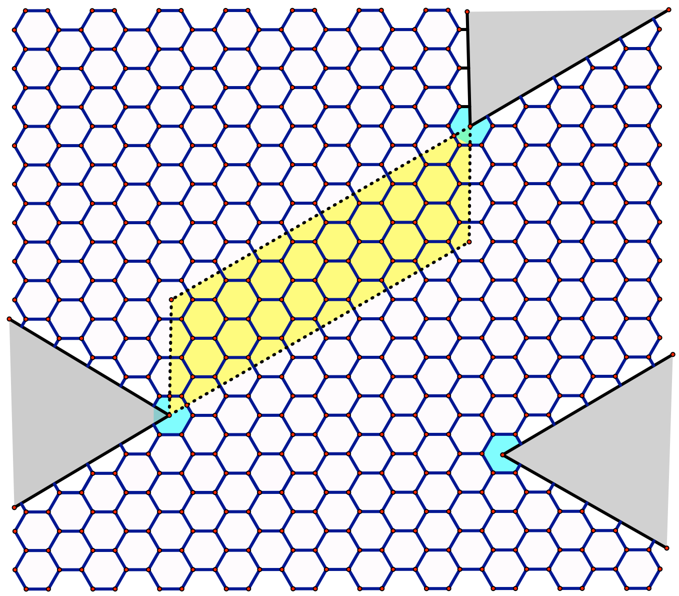


Figure 1.3: A clear field between two pentagons drawn in the hexagonal tessellation. The pentagonal faces are blue. At each pentagon, a 60° wedge is cut out and the two rays bounding the wedge are identified.

is given by their *Coxeter coordinates*. Two faces are joined by edges running through centers of hexagonal faces (corresponding to paths in the dual graph). A shortest dual path between nearby faces can be oriented as two straight line segments with a 120° left turn between them, or in some cases, as one straight line segment. Examples of these two cases are pictured in Figure 1.4. In the case with a 120° left turn, the Coxeter coordinates are given as the ordered pair (m, n): a straight line segment containing m faces before a 120° left turn, and another with n faces after the turn. In the case with one straight line segment of length m, the coordinate is given just

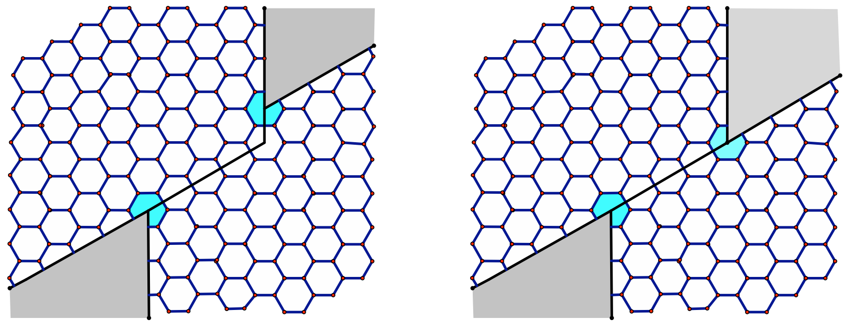


Figure 1.4: Pairs of pentagons with Coxeter coordinates (4,1) and Coxeter coordinate (4). The pentagons are shown in blue.

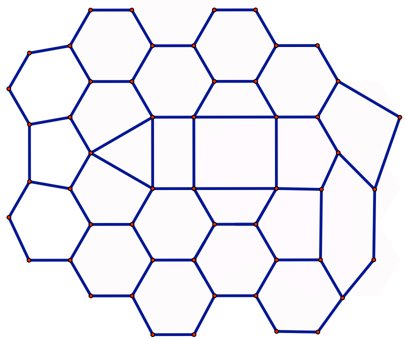
as (m).

One important family of fullerenes is the class of *leapfrog fullerenes* and their construction is given in [4]. We define the leapfrog construction more generally for an arbitrary plane graph. Given a plane graph $\Omega = (V, E, F)$, the *leapfrog construction* produces Ω^ℓ, a new 3-regular plane graph called the *leapfrog graph* of Ω. To construct Ω^ℓ, first take the dual $\Omega^* = (F, E, V)$ and then take the snub of Ω^*. For each vertex f^* of degree j in Ω^*, the snub construction replaces f^* with j new vertices, one for each edge incident to f^*, and connects these j vertices in a j-cycle bounding a new face f^ℓ. (See Figure 1.5.) A *face-only vertex covering* of a plane graph is a set of faces X such that each vertex is incident with exactly one face of X.

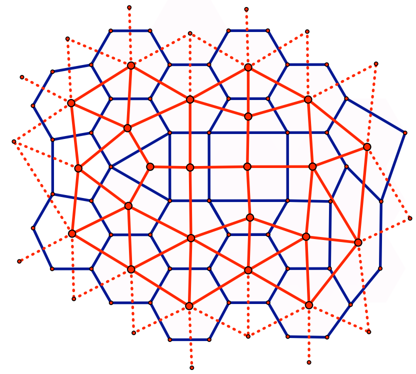
Lemma 1.3. *Let Ω^ℓ be the leapfrog of the plane graph $\Omega = (V, E, F)$. Ω^ℓ is 3-regular and has a face corresponding to each face of Ω and a face corresponding to each vertex of Ω. A face of Ω^ℓ corresponding to a face of degree j from Ω has degree j. A face* *of Ω^ℓ corresponding to a vertex of degree k from Ω has degree $2k$. The faces F^ℓ of Ω^ℓ corresponding to faces of Ω form a face-only vertex covering of Ω^ℓ.*

Proof. A face $f \in F$ of degree j becomes a vertex f^* of degree j in the dual Ω^*. The vertex f^* becomes a face of degree j when we take the snub of Ω^*. A vertex $v \in V$ of degree k becomes a face v^* of degree of degree k in Ω^*. When we take the snub of Ω^*, each vertex bounding the face v^* becomes an edge, and the corresponding face f_v in Ω^ℓ is of degree $2k$. The snub operation replaces all vertices of Ω^* by faces and introduces new vertices only of degree 3: a vertex w of Ω^ℓ is incident with two edges bounding a new face f^ℓ (corresponding to a vertex f^* in Ω^*), and one edge that had been incident to f^* in Ω^*. We see that the vertex w is incident with f^ℓ and that f^ℓ is adjacent to only faces that correspond to vertices in Ω. Thus the faces in F^ℓ form a face-only vertex covering of Ω^ℓ. □

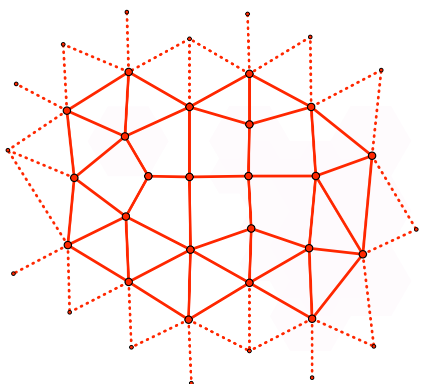
Note that if Γ is a fullerene, then the leapfrog graph Γ^ℓ is also a fullerene: since all vertices of Γ have degree 3, the faces of Γ^ℓ corresponding to these vertices are all hexagons. All faces of Γ^ℓ corresponding to faces of Γ are hexagons and pentagons. Fowler showed in [3] that a leapfrog fullerene on $|V|$ vertices attains the Fries number $\frac{|V|}{3}$. Graver proved in [9] that leapfrog fullerenes are the only fullerenes to satisfy this upper bound. The *face-independence number* of a plane graph is the maximum cardinality of a set of faces such that no two share an edge. By Proposition 1.2 the face-independence number of a fullerene on $|V|$ vertices is bounded above by $\frac{|V|}{6} + 2$. Combining the results from [3] and [9], we have the following proposition.



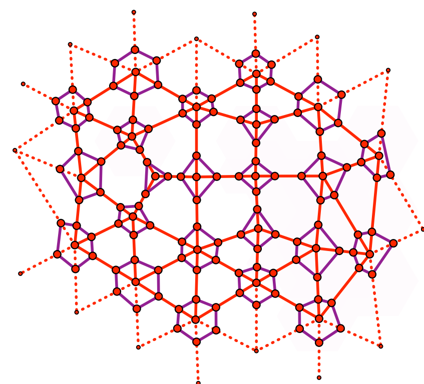
(a) A patch of a plane graph Ω.



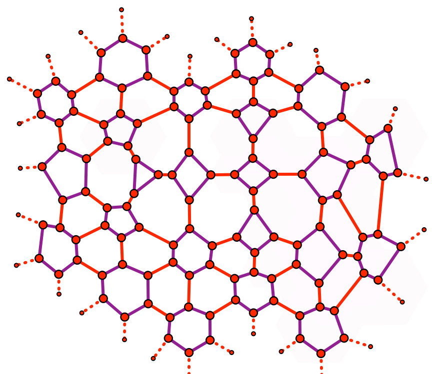
(b) We first take the dual of Ω



(c) The dual of Ω, Ω^*



(d) We take the snub of Ω^*.



(e) We now have the leapfrog graph Ω^ℓ.

Figure 1.5: The leapfrog construction on a patch of a plane graph, Ω.

Proposition 1.4. *The following are equivalent for a fullerene* $\Gamma = (V, E, F)$*:*

1. *The Fries number of* Γ *is* $\frac{|V|}{3}$*;*

2. *The face-independence number of* Γ *is* $\frac{|V|}{6} + 2$*;*

3. Γ *is a leapfrog fullerene;*

4. *For each pair of nearby pentagons with Coxeter coordinates* (m, n)*,* $m \equiv n$ *(mod 3) and for each pair of nearby pentagons with Coxeter coordinate* (m)*,* $m \equiv 0$ *(mod 3).*

The equivalence of (4) to the first three statements is not obvious; for a proof, see Graver [9]. One may view Proposition 1.4 as a constructive characterization of those fullerenes that achieve the maximum possible Fries number of $\frac{|V|}{3}$. These leapfrog fullerenes also achieve the maximum possible face independence number of $\frac{|V|}{6} + 2$ by including all pentagons in the independent set of faces. We show that the maximum possible Clar number for a fullerene on $|V|$ vertices is $\frac{|V|}{6} - 2$ and prove a theorem parallel to Proposition 1.4 that constructively characterizes all fullerenes that achieve the Clar number $\frac{|V|}{6} - 2$. The Clar number of a fullerene is less understood than the Fries number, and the former parameter is the primary focus of this dissertation. For small fullerenes, the Clar number has been calculated through computer searches. We develop a theory to directly compute the Clar number for many infinite classes of fullerenes.

In Chapter 2 we introduce a new decomposition designed to find lower bounds for the Clar and Fries numbers. In Chapter 3, we create a less general decomposition specifically conceived to compute the Clar number. Each of these decompositions is based on *chains*, a new concept we introduce to describe the structure of fullerenes. We define chains formally in the next chapter, but essentially chains are alternating sequences of faces and edges that connect pairs of pentagons over a fullerene.

Consider a pentagon f_0 and an edge e_1 such that exactly one vertex of e_1 is incident with f_0 and exactly one vertex of e_1 is incident with a face f_1. If f_1 is also a pentagon, then f_0, e_1, f_1 is the entire chain. If not, choose an edge e_2 connecting f_1 to a third face f_2, and so on. In Chapter 2, we show that the twelve pentagons can be paired by six chains such that the six chains have no edges in common. The structure of these chains can be complicated. Chains can twist around one another, making computations for calculation the Clar number difficult. Furthermore, there may be many different chain decompositions and it is not clear which one(s) actually give the Clar number. For our applications we consider a less general case. To avoid chains twisting around one another, we introduce the concept of *non-interfering* chains, permitting us to connect paired pentagons by chains of minimum length. To eliminate the possibility of still better chain decompositions, we introduce the concept of *widely separated* pairs of pentagons to ensure that all alternate chain decompositions have larger Clar deficits. These conditions restrict the classes of fullerenes for which we can compute the Clar number. However, this restriction allows us to achieve several major results: we construct an infinite family of fullerenes for which no Clar set is contained in a Fries set; we classify and give a construction for all fullerenes on $|V|$ vertices that attain the maximum Clar number $\frac{|V|}{6} - 2$; we develop a method to calculate the Clar number directly for many infinite families of fullerenes.

Chapter 2

Chains and Improper Face 3-Colorings

2.1 Improper Face 3-Colorings

As noted in Chapter 1, the faces of a hexagonal patch of a fullerene may be 3-colored. The following general theorem was proven by Saaty and Kainen. We state it here for future reference.

Theorem 2.1 (Saaty and Kainen [11]). *A 3-regular plane graph is face 3-colorable if and only if each face has even degree.*

Over a patch of faces that includes a pentagon, a proper face 3-coloring is clearly not possible: the five faces adjacent to a pentagon cannot alternate in color. Thus any face coloring of a fullerene using three colors is an *improper face 3-coloring*. If two faces that share an edge have the same color, we call them *incompatible* faces. Let Γ be a fullerene with a Kekulé structure K. We construct an improper face 3-coloring based on this Kekulé structure. Given a face f of Γ, we say that an edge e *exits* f if e shares exactly one vertex with f. We say that e *lies on* f if both vertices of e are incident with f.

Lemma 2.2. *Let Γ be a fullerene with Kekulé structure K.*

1. *An odd number of edges in K exit any pentagonal face of Γ. An even number of edges (possibly 0) in K exit any hexagonal face.*

2. *Either all edges in K exiting f exit from consecutive vertices around f or f is a hexagon with exactly two edges in K exiting f from opposite vertices.*

Proof.

1. Let f be a face of Γ. If an edge in K lies on f, it is incident with two adjacent vertices on f. Thus an even number of vertices (possibly 0) of f are covered by edges in K that lie on f. If f is a hexagon, an even number of vertices remain to be covered by edges from K that exit f. A pentagon always has an odd number of vertices remaining from which edges in K exit.

2. Suppose exactly two edges e_1 and e_2 exit f. Then f is a hexagon, and either e_1 and e_2 exit from vertices of f that are adjacent to one another or they are separated by edges in K that lie on f, each of which covers two adjacent vertices.

Thus e_1 and e_2 exit from adjacent vertices or opposite vertices (of distance 3) around f.

Suppose more than two edges in K exit a face f. We know that an odd number of edges in K exit a pentagon and an even number of edges in K exit a hexagon. If exactly three edges exit a pentagon or four edges exit a hexagon, then there are two vertices on the face remaining to be covered by an edge in K that lies on f, so these two vertices must be adjacent. Therefore, the edges from K that exit f exit from consecutive vertices around f. If all vertices incident with f are covered by edges that exit f, then these vertices clearly exit from consecutive vertices around f.

□

For each face f with edges from K exiting f, we construct a *coupling* of these exit edges. If an even number of edges in K exit f, we group the exit edges into pairs. If an odd number of edges in K exit f, all but one of the exit edges are coupled over f. For each pentagon, call the uncoupled exit edge the *initial* edge for that pentagon. We say that the coupling of edges in K exiting f is *non-crossing* if we can connect the exit edges through lines over f that do not cross one another (see Figure 2.1).

Lemma 2.3. *For each face f of Γ, the edges in K that exit f admit a non-crossing coupling. All possible couplings around a face are pictured in Figure 2.1.*

Proof. Let h be a hexagon in Γ. By Lemma 2.2, an even number of edges in K exit h. If there are exactly two exit edges, couple these edges. If more than two edges in

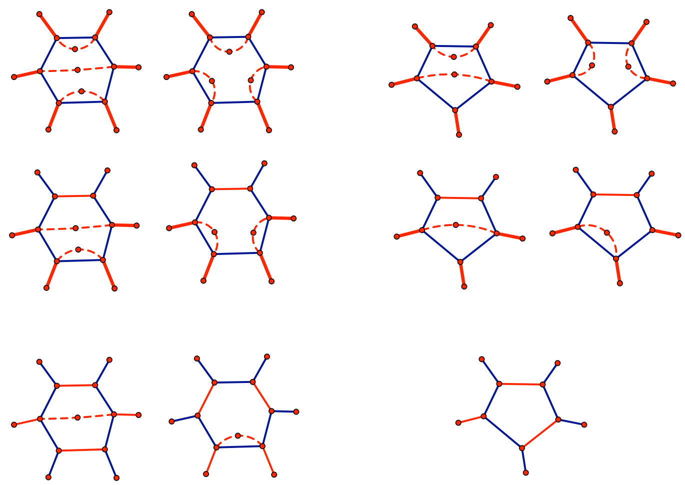


Figure 2.1: All possible non-crossing couplings over a face of Γ. The edges in K are shown in red.

K exit h, these edges must be incident with consecutive vertices around h by Lemma 2.2. Couple these edges in the following way: Choose two edges in K that exit h from adjacent vertices to form a couple. If there are two remaining edges in K that exit h, couple these together. If there are four edges remaining to be coupled, couple together two edges that exit from adjacent vertices of h. The remaining two edges are then coupled and either exit from adjacent vertices of h or vertices on opposite sides of h.

An odd number of edges in K exit each pentagon. If a single vertex of a pentagon p is covered by an exit edge in K, this is the initial edge and is not coupled over p. If more than one edge in K exits a pentagon, p, we know these edges exit from consecutive vertices on p. Couple the edges in the following way: Choose one edge to be the initial edge. If exactly two exit edges remain, couple them together. If four remain, couple two consecutive exit edges, and let the remaining two be a couple.

In all cases, this is a non-crossing coupling. At most one pair of edges from K exits from non-adjacent vertices around f. Two pairs of exit edges coupled over a face f cross only if both pairs exit from vertices that are not adjacent. $\square$

Each edge in K that is not an initial edge from a pentagon has two couplings, one over each face that it exits. The twelve initial edges have at most one coupling. Given a coupling for a fullerene Γ, define a *chain* in Γ to be an alternating sequence $f_0, e_1, f_1, e_2, ..., e_k, f_k$ of faces f_i of Γ and edges e_i in K such that e_i and e_{i+1} are coupled edges exiting f_i for $1 \leq i \leq k-1$, e_1 exits f_0 and e_k exits f_k. We require further that if e_1 (or e_k) is not an initial edge, $f_0 = f_k$ and that e_1 is coupled with e_k over f_0. If $f_0 = f_k$, we say that the chain is *closed.* A closed chain contains no initial edges and creates a circuit. If the chain $f_0, e_1, f_1, e_2, ..., e_k, f_k$ contains initial edges, we say that the chain is *open.* In this case, e_1 and e_k are initial edges, so f_0 and f_k are pentagons. A chain $f_0, e_1, f_1, e_2, ..., e_k, f_k$ makes a *sharp turn* at f_i if e_i and e_{i+1} exit from adjacent vertices of f_i.

The assigned coupling of exit edges over each face determines six open chains between pairs of pentagons and ensures that each edge in K is included in exactly one chain. By the construction of the coupling in Lemma 2.3, the chains may share faces but do not cross one another. For the remainder of the chapter, we assume that the couplings constructed are non-crossing.

Lemma 2.4. *Let Γ be a fullerene with Kekulé structure K and a coupling assignment. The set of edges in K decomposes into*

1. *Six open chains connecting pairs of pentagons;*
2. *Closed chains.*

Proof. From the fullerene $\Gamma = (V, E, F)$ with a coupling, construct a new graph with vertex set V and edge set K together with edges between coupled pairs. In this graph, the twelve initial vertices exiting pentagons have degree 1 and the remaining vertices have degree 2 (one edge from K and one from the coupling). Such a graph decomposes into paths and circuits. The six paths that terminate at initial vertices of pentagons correspond to the six open chains, and the remaining circuits correspond to closed chains. $\square$

Let the set T denote the edges in K within the six open chains and S denote the set of faces exited by edges from T. Ignoring the closed chains, we call the resulting set of six open chains between pairs of pentagons a *chain decomposition* (S, T) of Γ. For a fullerene Γ with a chain decomposition (S, T), we define an *expansion* $\mathcal{E}(S, T)$ of Γ as follows: "widen" each edge in T into a quadrilateral face by splitting its incident vertices and joining each split pair by a new edge. Each vertex incident with an edge in T becomes an edge of $\mathcal{E}(S, T)$, each edge in T splits lengthwise into two edges of $\mathcal{E}(S, T)$.

Lemma 2.5. *Let Γ be a fullerene with a chain decomposition (S, T). The expansion $\mathcal{E}(S, T)$ of Γ is face 3-colorable.*

Proof. The coupling determines the continuation of the chain, so either both edges of a coupled pair are in T or neither edge is in T. Thus an even number of edges from T exit a hexagon, and an odd number exit a pentagon. Each edge e in T that exits a face f in S becomes a quadrilateral face of $\mathcal{E}(S, T)$, and the vertex of e incident with f becomes an edge. If a face f in S is exited by n edges from T, then its degree in the expansion $\mathcal{E}(S, T)$ is increased by n. Therefore, every face in the expansion $\mathcal{E}(S, T)$ has even degree. $\mathcal{E}(S, T)$ is now a 3-regular graph with all faces of even degree. Thus by Theorem 2.1, $\mathcal{E}(S, T)$ has a face 3-coloring. □

Theorem 2.6. *Let Γ be a fullerene with a chain decomposition (S, T). Then there is an improper face 3-coloring over which the incompatibilities occur exactly at faces that share an edge in T. Up to a permutation of colors, this improper face 3-coloring is unique.*

Proof. Give the expansion $\mathcal{E}(S, T)$ a proper face 3-coloring. We can return to the fullerene Γ by collapsing each of the quadrilateral faces back into edges in T while retaining the coloring of the remaining faces. Two faces of Γ that share an edge in T correspond to opposite faces around a quadrilateral of $\mathcal{E}(S, T)$, and accordingly have the same color. Two faces of Γ that share an edge not in T share the same edge of $\mathcal{E}(S, T)$, hence they are assigned different colors. □

Lemma 2.7. *Let Γ be a fullerene with a chain decomposition (S, T) and let $f_0, t_1, f_1, ...t_k, f_k$ be an open chain. In the associated improper face 3-coloring of Γ,*

1. *All faces $f_0, f_1, ..., f_k$ are in the same color class.*
2. *All faces incident with one of the edges $t_1, t_2, ..., t_k$ are in a second color class.*

Proof. Consider the face f_{i-1} in the open chain and assume the color assigned to the corresponding face f'_{i-1} in the expansion $\mathcal{E}(S, T)$ is yellow. Thus the color assigned to the face t'_i of the expansion corresponding to the edge t_i of Γ must be a different color, say blue. Let g_i and d_i denote the two faces that share the edge t_i of Γ. In the expansion the corresponding faces g'_i and d'_i are adjacent to f'_{i-1} and t'_i, so g_i and d_i must be in the remaining color class, red. The edge t_i also exits the face f_i, and so t'_i, g'_i and d'_i are adjacent to f'_i. Thus f'_i must be in the yellow color class. If the chain makes a sharp turn when entering the next edge t_{i+1}, then t'_{i+1} is adjacent to f'_i and either g'_i or d'_i, and thus must be in the blue color class. If there is not a sharp turn, then by Lemma 2.3, t_{i+1} exits f_i from a vertex on the opposite side of f_i, a distance of three vertices. The faces incident with f'_i alternate in color, so t'_i and t'_{i+1} must be in the same color class. □

2.2 Chains

Let Γ be a fullerene with a chain decomposition (S,T). Let $f_0, t_1, f_1, t_2, f_2, ...t_k, f_k$ be an open chain of this decomposition. Each face f_i is exited by the edges t_i and t_{i+1}

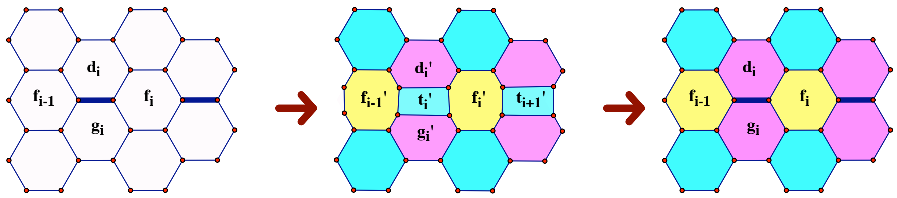


Figure 2.2: Expansion of edges of distance 3 around f with face 3-coloring

in the chain. The initial faces f_0 and f_k must be pentagons and the remaining f_i can be hexagons or pentagons. We define the *augmented chain* to be the open chain together with the faces incident with edges in T over the chain. For each edge t_i in the open chain, we denote the two faces incident with it as d_i and g_i, where d_i is the face on the left if we are traversing the chain in increasing order over the indices (see Figure 2.3). If a chain makes a sharp turn to the left when entering edge t_{i+1}, then $d_i = d_{i+1}$; if the chain makes a sharp turn to the right, then $g_i = g_{i+1}$. We say that two augmented chains are *separated* if they do not share any vertices. We say that an augmented chain is *detached* if it is separated from every other augmented chain in this decomposition.

Let Γ be a fullerene with a chain decomposition and an improper face 3-coloring. We now use the chain decomposition and the improper face 3-coloring to form a new Kekulé structure for Γ that gives a lower bound for the Clar number and Fries number over the fullerene.

Choose one of the three color classes and let C be the set of faces in this color class outside of the augmented chains. We call this set of faces a *Clar scheme* for Γ.

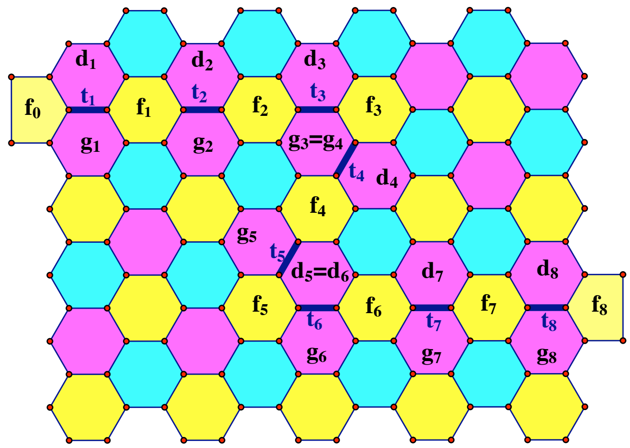


Figure 2.3: An augmented chain $f_0, t_1, f_2, ..., t_8, f_8$ between pentagons f_0 and f_8. Dark blue edges represent edges in T.

By Theorem 2.6, all improperly colored faces are contained in the augmented chains, as are all of the pentagons. Therfore C is an independent set of hexagonal faces, and every vertex outside of the augmented chains is incident with exactly one face in C. Given a Clar scheme C, we construct a partial Kekulé structure for Γ in the following way: For each face in C, choose three alternating bounding edges to be in the matching. The Clar scheme includes all faces in the chosen color class outside of the augmented chains, so each vertex outside of the augmented chains is covered by the matching. We call this matching the *Kekulé scheme* derived from C.

In the theorem below, we show that given a Clar scheme C with detached chains, it is possible to extend the Kekulé scheme derived from C over these augmented chains, possibly adding additional independent benzene faces to the set containing C. Let

C' be a maximal independent set of benzene faces containing C over the extension. The cardinality of C' is a lower bound for the Clar number of the fullerene, and by Proposition 1.2, $|C'| = \frac{|V|}{6} - \frac{|V^*(C')|}{6}$ where $V^*(C')$ is the set of vertices not incident with a face in C'. The contribution to $|V^*(C')|$ over a chain depends on the position of the faces in C relative to the chain. For each case, we find the contribution to $|V^*(C')|$ over the chain. Within an augmented chain $f_0, t_1, f_1, ..., t_k, f_k$, we define *non-consecutive sharp turns* to be those that do not share a common edge in the chain.

Theorem 2.8. *Let Γ be a fullerene with a chain decomposition (S, T) into detached augmented chains. Let C be a Clar scheme and K_C the derived Kekulé scheme. Then it is possible to complete K_C to a Kekulé structure K, possibly adding additional independent benzene faces. Let C' denote this enlarged set of independent benzene faces containing C. Let $f_0, t_1, f_1, ..., t_k, f_k$ be a detached augmented chain and let d_i and g_i denote the faces incident with t_i in the chain.*

1. *If the set C is contained in the same color class as the quadrilateral faces $\{t_i'\}$ in the expansion $\mathcal{E}(S, T)$, then the contribution to $|V^*(C')|$ over the chain is $2k$.*

2. *If the set C is contained in the color class that includes the set of faces $\{d_i, g_i\}$ and l is the number of non-consecutive sharp turns over the chain, then the contribution to $|V^*(C')|$ is $4k - 6l$.*

3. *If the set C is contained in the color class that includes the faces $\{f_i\}$, then the*

contribution to $|V^*(C')|$ *is* $6k + 4$.

Proof. The Kekulé scheme K_C contains three alternating edges bounding each face in C, so the only vertices not incident with a face in C are over the six augmented chains. By Lemma 2.7 (1), the improperly colored faces $\{d_i, g_i : 1 \le i \le k\}$ over the augmented chain are all in one color class and the faces f_i in the open chain are all in a second color class over the improper face 3-coloring of Γ. The type of repair necessary to this chain depends only upon which of the color classes includes the set C.

Case 1: The set C is contained in the same color class as the quadrilateral faces $\{t'_i\}$ in the expansion $\mathcal{E}(S, T)$ over the augmented chain. In this case, the only vertices along the chain not covered by faces in C are the vertices incident with the edges t_i. Adding these k edges to K_C extends the Kekulé scheme to cover the vertices of the chain and contributes $2k$ vertices to $|V^*(C')|$.

Case 2: The set C is contained in the color class that includes the (improperly colored) set of faces $\{d_i, g_i\}$ incident with edges in T along the chain. For each pair of faces incident with an edge in T, exactly one of the two faces is added to C', the enlargement of C.

We know from the construction of the coupling in Lemma 2.3 that coupled edges over a hexagon h exit either from opposite vertices on h (continue without a turn) or through adjacent vertices (sharp turns). The chain $f_0, t_1, f_1, t_2, f_2, ...t_k, f_k$ has k edges; let l be the number of non-consecutive sharp turns. Over segments of the open chain with no turns, there are two improperly colored faces for each edge in T and which of these faces is included in C' is inconsequential. The unchosen face has one edge incident with a face in C' and four remaining vertices that are not incident with a face in C'. These vertices are consecutive on the face and can be covered by adding two Kekulé edges incident with the face. Each non-consecutive sharp turn contains two edges in T. Therefore, there are $k - 2l$ edges in T that each contribute four vertices to $|V^*(C')|$.

If the chain makes a sharp turn, there are three improperly colored faces pairwise incident with two edges in T. Without loss of generality, if the chain makes a sharp right turn from t_i to t_{i+1}, then the edge t_i is incident with the faces d_i and $g_i = g_{i+1}$ and t_{i+1} is incident with $g_i = g_{i+1}$ and d_{i+1}. We choose the two faces d_i and d_{i+1} outside of the turn to be in C'. The single interior face $g_i = g_{i+1}$ is chosen not to be in C'. Two edges t_i and t_{i+1} of $g_i = g_{i+1}$ are incident with faces in C', so there are only two consecutive vertices on this interior face that must be covered by a new Kekulé edge (see Figure 2.4).

If the chain makes consecutive sharp turns, the interiors of the turns alternate between faces in C' and faces not in C' with two uncovered vertices. Each non-consecutive sharp turn contributes two adjacent vertices to $V^*(C')$ that can be covered by a single edge in K. On the other hand, in a consecutive pair of sharp turns, the interior is covered by a face in C' and does not contribute any vertices to $V^*(C')$. The total number of vertices in $V^*(C')$ over the chain is $4(k - 2l) + 2l = 4k - 6l$. An

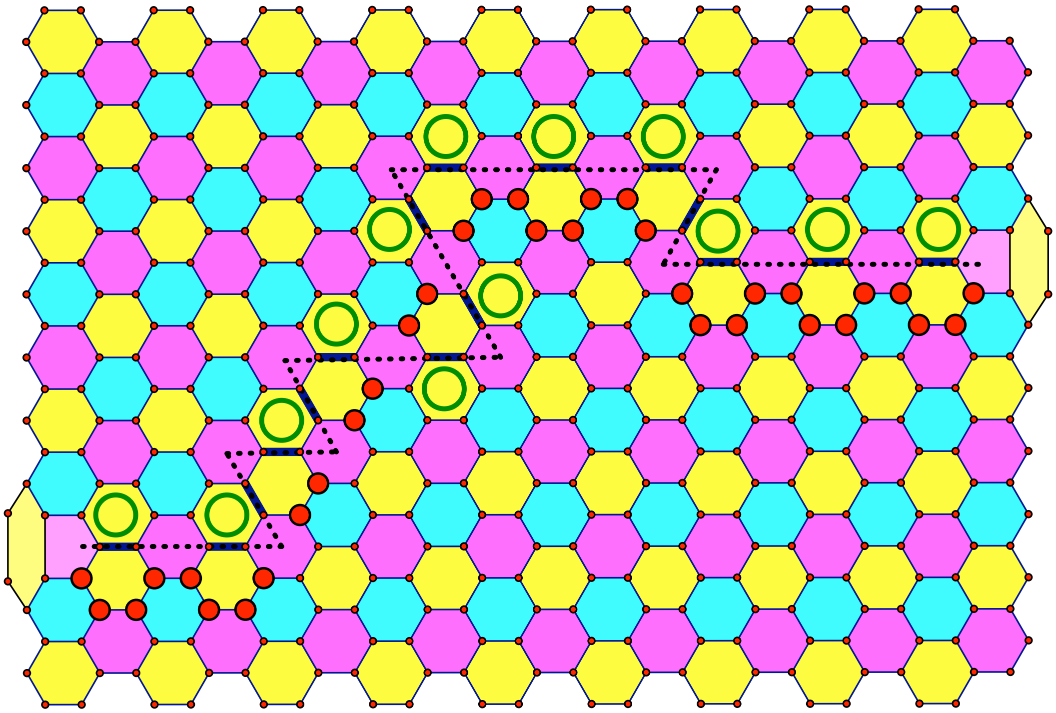


Figure 2.4: Case 2: The edges in T are dark blue; the faces in C are the yellow faces not incident with edges in T. The yellow faces with green circles are added to C to get C'. The large red vertices belong to $V^*(C')$. Over this chain, there are $k = 16$ edges in T and $l = 5$ non-consecutive sharp turns. Thus the contribution to $|V^*(C')|$ is $4 \times 16 - 6 \times 5 = 34$.

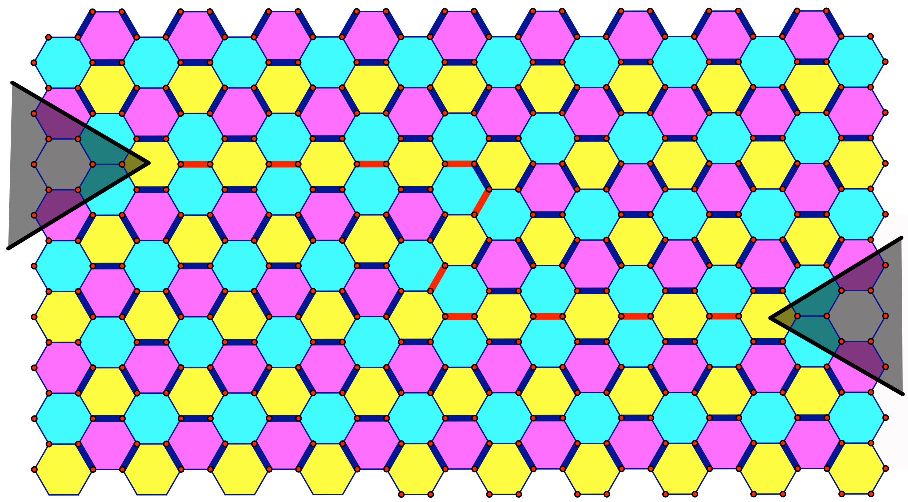
example is worked out in Figure 2.4.

Case 3: The set C is contained in the color class that includes the set of faces $\{f_i\}$. By Lemma 2.2, at least one edge of K exits the pentagon f_0 and begins an open chain that ends with the pentagon f_k. First extend K_C by adding the edges $t_0, t_1, ...t_k$ to K. Since t_i exits f_i, f_i cannot be a benzene face and thus cannot belong to C' for $1 \leq i \leq k$; since f_0 is a pentagon, f_0 cannot belong to C'. Hence each vertex incident with f_i belongs to $V^*(C')$. The faces f_i are in the color class that includes the set C, so no vertex incident with a face f_i is covered by a face in C'. For each face f_i, the vertices that are not incident with t_i or t_{i-1} are either consecutive or two adjacent pairs of vertices. In either case, pairs of these vertices can be covered by edges of K. The vertices in $V^*(C')$ are exactly those incident with the faces f_i. There are $k-1$ hexagons and two pentagons in the chain, so the contribution to $|V^*(C')|$ is $6(k-1)+10 = 6k+4$. □

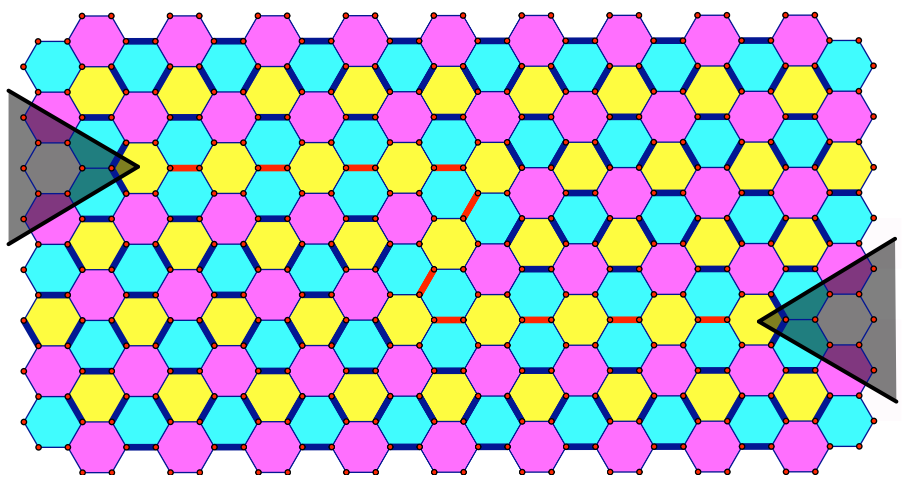
Let Γ be a fullerene with a given chain decomposition and associated improper face 3-coloring. A *Fries scheme* D consists of the faces in one of the three color classes. In contrast with a Clar scheme, the set D includes the faces of that color class within the augmented chains. We then construct the *Kekulé scheme derived from* D, a partial Kekulé structure consisting of the edges that join two faces from D. (See Figure 2.5.) Outside of the augmented chains, every vertex is on an edge joining two faces in D, so all vertices outside of the augmented chains are incident with exactly one edge in the Kekulé scheme derived from the Fries scheme.

Corollary 2.9. *Let Γ be a fullerene with a chain decomposition in which the augmented chains are detached. Let D be a Fries scheme and K_D the Kekulé scheme derived from D. Then there is a Kekulé structure K such that the symmetric difference $K_D \triangle K$ is contained in the augmented chains.*

Proof. Consider a fullerene Γ with a chain decomposition in which the augmented chains are detached. Given a Fries scheme D and the Kekulé scheme K_D derived



(a) Here the Fries scheme, D, consists of the faces in the blue color class.



(b) Here the Fries scheme, D, consists of the faces in the pink color class.

Figure 2.5: The Kekulé scheme derived from D consists of edges joining two faces in D. Dark blue edges represent Kekulé edges, red edges represent edges in T. In each case, all vertices outside of the augmented chain are covered by exactly one edge in the Kekulé scheme.

from D, choose a second color class to contain a Clar scheme C, the set of hexagons within the second color class and outside of the augmented chains. Construct a Kekulé scheme K_C derived from C consisting of three alternating edges on each face of C, choosing the edges that join two faces in D. Outside of the augmented chains, this K_C is identical to K_D: each of the edges in K_C connects two faces in the color class containing D. Since every face in the second color class is included in C outside of the augmented chains, each of the vertices outside of the chains are covered by edges from K_C. By Theorem 2.8, we can extend K_C to a Kekulé structure K while only changing edges inside of the augmented chains. Thus K and K_D differ only within the augmented chains. $\square$

In summary, Corollary 2.9 shows that we can choose a set of faces D to be the Fries scheme, we can create a Kekulé scheme K_C based on C with the Fries scheme in mind: for each face in C, we have two choices for the set of alternating bounding edges to include in K_C. We always choose faces that connect two faces in D. Since outside of the chains, K_C is equivalent to the Fries scheme we would derive directly from D, extending K_C to a Kekulé structure using the method of Theorem 2.8 forms a Kekulé structure that differs from a Kekulé scheme derived directly from D only within the augmented chains. We can then calculate a lower bound for the Fries number from this Kekulé structure. This is not necessarily the best Kekulé structure based on a Fries scheme; the corollary is showing only that one can be completed by only repairing edges within the augmented chains.

Theorem 2.8 and Corollary 2.9 show that when a fullerene admits a chain decomposition with detached chains, we can construct Kekulé structures where the only contributions to the Clar and Fries deficits come from the augmented chains.

Chapter 3

Clar Structures

3.1 Clar Structures

Chapter 2 describes a method for calculating lower bounds for the Clar number of a fullerene through a chain decomposition. In this chapter we construct a Kekulé structure that achieves the Clar number for a fullerene and see that this structure comes from a chain decomposition. We begin in a new general setting to describe this construction.

Define a *vertex covering* (C, A) of a 3-regular plane graph $\Omega = (V, E, F)$ to be a set of faces C and edges A such that all vertices of Ω are incident with exactly one element of $C \cup A$.

Lemma 3.1. *Let Ω be a plane graph with a vertex covering (C, A). On every face of even degree, there is an even number (possibly zero) of edges in A that exit the face.*

On every face of odd degree that does not belong to C, there is an odd number of edges in A that exit the face.

Proof. Let Ω be a plane graph with a vertex covering (C, A) and let f be a face of Ω that is not in C. Note that every edge in A that lies on f covers two adjacent vertices on f, as does every face in C adjacent to f. The proof proceeds exactly as in Lemma 2.2 of Chapter 2. □

The vertex covering (C, A) is a face-only vertex covering if the set A is empty.

Lemma 3.2. *If C is a face-only vertex covering of a plane graph Ω, then C must contain all of the faces of Ω with odd degree.*

Proof. We see in Lemma 3.1 that if p is a face of odd degree in Ω and p is not in a vertex covering (C, A), then at least one edge from A exits p, so $A \neq \emptyset$. □

Fowler and Pisanski referred to a face-only vertex covering in a fullerene Γ as a *perfect Clar structure* [5]. We define a *Clar structure* (C, A) of a fullerene Γ to be a vertex covering where C consists only of hexagonal faces and at most two edges in A lie on any face of Γ. Given a Clar structure (C, A), choose three alternating edges on each face in C. Together with the edges in A, these edges form a Kekulé structure K. We say that K is a *Kekulé structure associated with the Clar structure* (C, A). Note that the faces in C form a maximal independent set of benzene faces. Conversely, given a fullerene Γ with a Kekulé structure K, we can form a *Clar structure* (C, A) *associated with* K: take C to be a maximal independent set of benzene faces and A

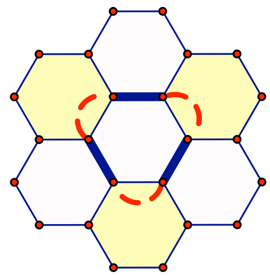


Figure 3.1: A benzene chain. Edges in A exit yellow faces from adjacent vertices to form a short closed chain.

to be the remaining edges in K. The Clar number of a fullerene is given by a Clar structure (C, A) with a maximum number of faces in C.

Lemma 3.3. *Let* Γ *be a fullerene with* $|V|$ *vertices and a Clar structure* (C, A)*. Then* $|C| = \dfrac{|V|}{6} - \dfrac{|A|}{3}$.

Proof. We see in Proposition 1.2 that for an independent set C of benzene faces in a Kekulé structure K, $|C| = \frac{|V|}{6} - \frac{|V^*(C)|}{6}$ where $V^*(C)$ is the set of vertices not incident with a face in C. In a Clar structure (C, A), $2|A| = |V^*(C)|$. □

We want to maximize the number of independent benzene faces, and we know that $|C| = \frac{|V|}{6} - \frac{|A|}{3}$, so our goal is to find a Clar structure (C, A) that minimizes $|A|$. Given a fullerene Γ with Clar structure (C, A), define a *Clar chain* to be an open or closed chain using only edges from A. Let K be a Kekulé structure associated with (C, A). For any face in C, we call the three edges in K bounding this face together with the three faces exited by these edges a *benzene chain* (see Figure 3.1).

Lemma 3.4. *Let (C, A) be a Clar structure for a fullerene Γ. Let K be a Kekulé structure associated with (C, A). Then there is a non-crossing coupling for K such that:*

1. *The chains are either Clar chains or benzene chains corresponding to the faces in C.*
2. *The coupling of edges in A can be chosen so that all edges coupled around pentagons exit from adjacent vertices on the pentagon.*
3. *There are six open Clar chains connecting pairs of pentagons.*

Proof. Let (C, A) be a Clar structure and let K be a Kekulé structure associated with (C, A). We want to show that there is a non-crossing coupling of the edges in K that has the properties above. We choose this coupling in accordance with Lemma 2.3 to ensure that the edges in A do not cross one another. In this lemma, the first step to couple the edges around a hexagon is to choose a pair of edges exiting the face from adjacent vertices. Around a pentagon, the first step is to choose the initial exit edge, and the second is to couple a pair of edges exiting from adjacent vertices.

Consider the three Kekulé edges bounding a face in C. These are not edges in A, and therefore none can be the initial edge of a pentagon. Any two of these edges exit a common face from adjacent vertices of that face. Thus for each face in C we can couple the edges together to form a benzene chain. Only the edges in A remain to be coupled. For each hexagon h of Γ, an even number of edges from A exit h by Lemma

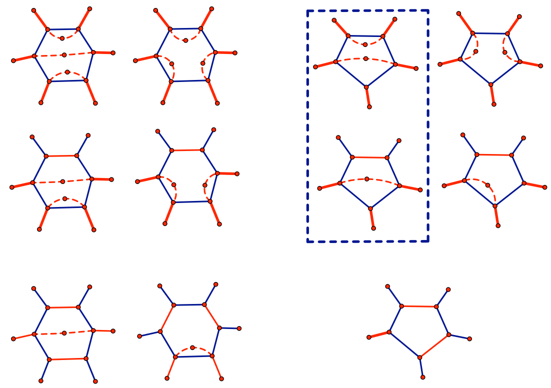


Figure 3.2: For Clar chains, edges in A coupled over pentagons must exit from adjacent vertices. The indicated couplings are avoided.

3.1. We can couple these edges around h in accordance with Lemma 2.3.

Consider a pentagon p of Γ. If a single edge from A exits p, this is the initial edge and is not coupled over p. If more than one edge in A exits p, we know that the edges from A exit from adjacent vertices on p. Couple the edges in the following way: Choose edges exiting from adjacent vertices on p to be coupled. If a single edge remains, it is the initial edge of the pentagon. If three remain, couple two edges exiting from adjacent vertices and let the remaining edge be the initial edge of the pentagon. From chapter 2, we see that there must be six open Clar chains connecting pairs of pentagons. □

This method is more restrictive than that of Lemma 2.3, because coupled edges over pentagons only exit from adjacent vertices, ensuring (2) (see Figure 3.2).

Let Γ be a fullerene with a Clar structure (C, A) with an associated Kekulé structure K and a coupling for K as in Lemma 3.4. We define the *expansion* $\mathcal{E}(C, A)$ to be the graph obtained by the following operation: widen the edges in A into quadrilateral faces as described in Section 2.1. Each vertex incident with an edge in A becomes an edge, and each edge in A splits lengthwise into two edges. Note that the expansion in Chapter 2 only expanded edges contained in open chains; here there may be additional edges in A contained in closed Clar chains. The advantage is that the set C of independent hexagons is preserved; the faces of C and the quadrilateral faces in $\mathcal{E}(C, A)$ corresponding to edges from A form a color class in $\mathcal{E}(C, A)$. Thus in the associated improper face 3-coloring for Γ, no faces in the set C are improperly colored.

Lemma 3.5. *Let Γ be a fullerene with a Clar structure (C, A). The expansion $\mathcal{E}(C, A)$ is face 3-colorable. All faces of $\mathcal{E}(C, A)$ corresponding to faces in C and edges in A in Γ are in one color class of $\mathcal{E}(C, A)$. Furthermore, Γ has an associated improper face 3-coloring for which the only improperly colored faces are those that share edges in A. For an open or closed Clar chain $f_0, a_1, f_1, a_2, f_2, ...a_k, f_k$ in this improper 3-coloring, the faces f_i are all in one of the remaining two color classes, and the faces incident with edges in A over the chain are all in the third color class.*

Proof. Let f be a face of degree d in the fullerene Γ. If j edges from A exit f, then the corresponding face in $\mathcal{E}(C, A)$ has degree $d + j$. By Lemma 3.1, pentagons in Γ are exited by an odd number of edges from A, hexagons by an even number of edges from A. Thus every face in $\mathcal{E}(C, A)$ is of even degree, and $\mathcal{E}(C, A)$ is face 3-colorable by Theorem 2.1. Since (C, A) is a vertex covering of Γ, the faces of $\mathcal{E}(C, A)$ corresponding to the faces in C and the edges in A comprise one color class. Suppose that these faces are blue. For any open or closed chain $f_0, a_1, f_1, a_2, f_2, ...a_k, f_k$ (where $f_k = f_0$ if the chain is closed), the argument given in Lemma 2.7 shows that the faces f_i are all in a second color class (red or yellow). Each face sharing an edge a_i over the chain is in the third color class (yellow or red). □

Let $f_0, a_1, f_1, a_2, f_2, ...a_k, f_k = f_0$ be a closed Clar chain. The fullerene is now partitioned into three parts: the chain $f_0, a_1, f_1, a_2, f_2, ...a_k, f_k = f_0$, and two regions. We say that the region containing the least number of pentagons is the *interior* of the chain and the region on the other side of the chain is the *exterior*. If both sides contain the same number of pentagons, we arbitrarily choose one region to be the interior. Define a *chain circuit* $\mathcal{C}$ around the interior to be an elementary circuit containing the edges a_i connected by paths on the boundaries of the f_i. There are many possible circuits for the closed chain $f_0, a_1, f_1, a_2, f_2, ...a_k, f_k = f_0$, depending on whether we connect each edge a_i to a_{i+1} by a path of vertices on f_i incident with the interior or the exterior of the Clar chain for each i. For a chain circuit $\mathcal{C}$ around a closed Clar chain $f_0, a_1, f_1, a_2, f_2, ...a_k, f_k = f_0$, we define the *interior of* $\mathcal{C}$ to be the interior of $f_0, a_1, f_1, a_2, f_2, ...a_k, f_k = f_0$ together with the faces f_i that do not share an edge of $\mathcal{C}$ with the interior of the chain $f_0, a_1, f_1, a_2, f_2, ...a_k, f_k = f_0$.

Lemma 3.6. *Let Γ be a fullerene with a Clar structure (C, A) and an associated cou-*

pling. If $|C|$ is the Clar number for Γ, then every closed Clar chain $f_0, a_1, f_1, a_2, f_2, ...a_k, f_k = f_0$ has a pentagon in its interior.

Proof. Consider a closed Clar chain with no pentagons in its interior. There may additionally be nested closed chains in the interior; let $f_0, a_1, f_1, a_2, f_2, ...a_k, f_k = f_0$ be the innermost closed Clar chain. For $i = 1, 2, ..., k$, let g_i and d_i be the faces incident with a_i on the interior and exterior of the chain, repectively. Give Γ the improper face 3-coloring associated with (C, A), and assume that C is contained in the blue color class. By Lemma 3.5, all faces f_i belong to a second color class, say yellow, and all g_i and d_i are in the remaining color class (red). By Lemma 3.4 Clar chains are non-crossing. Consequently, there are no edges from A in the interior of this innermost Clar chain. Thus by Lemma 3.5, all faces are in the interior of $f_0, a_1, f_1, a_2, f_2, ...a_k, f_k = f_0$ properly 3-colored.

Consider two faces g_i and d_i that share an edge a_i of the chain. The faces g_i and d_i are red, and each is adjacent to the yellow faces f_{i-1} and f_i. The interior face g_i conforms with the proper face 3-coloring of the interior of the chain. If the interior coloring is extended to the exterior face d_i, then d_i would be a blue face. We see that this is the case for all of the improperly colored faces d_j, g_j incident with edges a_j over the chain for $1 \leq j \leq k$. The faces $\{d_j\}$ together with the set of blue faces in the interior of the chain form an independent set. If we interchange the blue and red color classes within the interior of the chain, then the set of faces in the interior together with the faces $\{d_j\}$ are properly face 3-colored. All vertices on the chain circuit and its interior are then incident with exactly one blue face. Now let C'' be the collection of all blue faces and let $A'' = A \setminus \{a_1, a_2, ..., a_k\}$. Now (C'', A'') is a Clar structure, and $|C''| > |C|$ by Lemma 3.3. Therefore, if (C, A) is a Clar structure that attains the Clar number, then a closed chain containing only hexagons in its interior cannot exist. □

Lemma 3.7. *A chain circuit $\mathcal{C}$ is of even length if and only if its interior contains an even number of pentagons.*

Proof. Suppose that there are h hexagonal faces and p pentagonal faces in the interior of $\mathcal{C}$. If an edge of one of these faces is on the circuit, then the edge is incident with only one of these faces. If the edge is in the interior, it is incident with two of these faces. Let I be the number of edges in the interior. Then the number of edges on the circuit is $6h + 5p - 2I = 2(3h - I) + 5p$. So the number of edges on the circuit is even exactly when p is even. □

Lemma 3.8. *Let $f_0, a_1, f_1, a_2, f_2, ...a_k, f_k = f_0$ be a closed Clar chain such that each of the f_i's are hexagons. Then all of its chain circuits have even length.*

Proof. By the construction of the coupling for the Clar structure (C, A), the paired edges exiting a hexagon f_i exit from adjacent vertices of f_i (a sharp turn) or from vertices on opposite sides of f. The distance traveled by the chain circuit from the edge a_i to a_{i+1} is odd (distance 1, 5, or 3). As the chain circuit goes around a hexagon f_i from a_i to a_{i+1}, it passes through an even number of vertices not included in the coupled edges $a_1, a_2, ..., a_k$. Thus the chain circuit is of even length. □

Lemma 3.9. *For any closed Clar chain, there exists a chain circuit that includes an even number of pentagons on its interior.*

Proof. By Lemmas 3.7 and 3.8, if each of the faces f_i in the closed Clar chain $f_0, a_1, f_1, a_2, f_2, ...a_k, f_k = f_0$ is a hexagon, then there is an even number of pentagons on the interior regardless of how the chain circuit is chosen. Suppose that there is an odd number of pentagons in the interior of the chain. By Lemma 3.7, some face f_j must be a pentagon. We can choose the chain circuit to traverse the outside of this pentagon, and the inside of every other face f_i on the chain. We have chosen a chain circuit for $f_0, a_1, f_1, a_2, f_2, ...a_k, f_k = f_0$ that contains an even number of pentagons in its interior. □

In Chapter 2, to define an improper face 3-coloring, the closed chains are ignored, and we define a face 3-coloring for the graph $\mathcal{E}(\Gamma)$ obtained by expanding only the edges in open chains joining pentagons and then choosing a color class for the Clar faces. If we ignore the closed chains here, it may be the case that none of the resulting color classes contains C. Hence we cannot ignore closed chains in this chapter.

We have shown that in a coupling of a Clar structure (C, A), the Clar chains are a special case of the chains in Chapter 2, and thus the lemmas already proven about chains hold. Define a *straight chain segment* to be an alternating chain $f_0, a_1, f_1, a_2, ...a_k, f_k$ of edges in A and hexagons f_i such that the edges a_i and a_{i+1} exit from opposite vertices of f_i for each i. A straight chain segment with k edges in A connects a pair of faces with Coxeter coordinates (k, k). Any edge in A is part of a straight chain

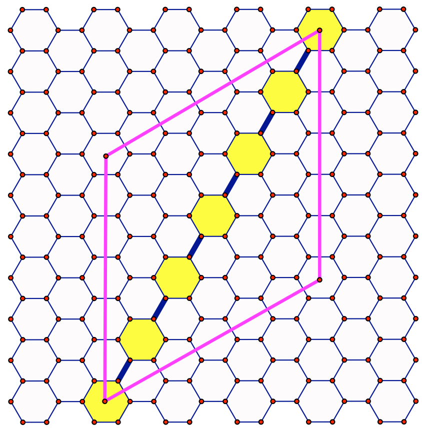


Figure 3.3: A straight chain segment with six edges in A joining a pair of faces with Coxeter coordinates $(6, 6)$. Dark blue edges represent edges in A.

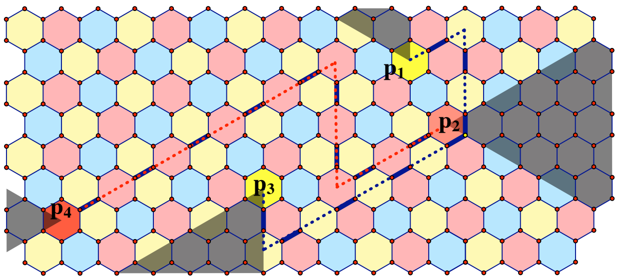
segment of length at least one. Thus any Clar chain between two faces is a sequence of straight chain segments. We can visualize a straight chain segment with k edges as the diagonal of a parallelogram with edges of length k through faces and with the straight chain along the diagonal of the parallelogram (see Figure 3.3).

Lemma 3.10. *Every open Clar chain in a fullerene* Γ *with Clar structure* (C, A) *is a sequence of straight chain segments with only sharp turns.*

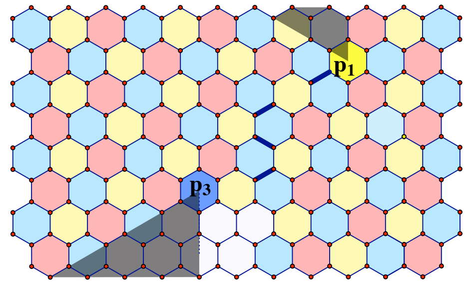
Proof. By Lemma 3.4, the coupling is chosen so that edges in A coupled over a pentagon exit from adjacent vertices. Thus Clar chains always make sharp turns as they pass through pentagons. Because the coupling is non-crossing, coupled edges through a hexagon exit from adjacent vertices (a sharp turn) or vertices on opposite sides of the hexagon (a continuation of a straight chain segment). □

We say that a Clar structure (C, A) has a coupling with *non-interfering* Clar chains if for every pair of pentagons p_1 and p_2 joined by a Clar chain there is no other pentagon that has a vertex in common with any shortest chain joining p_1 and p_2 in any coupling of (C, A). For the rest of this paper, we consider pairs of pentagons that can be joined by non-interfering Clar chains. When more than two pentagons interact, chains can become quite complicated; a small example is given in Figure 3.4(a) containing pentagons p_1, p_2, p_3, and p_4. In this example, nearby pentagons p_1 and p_2 are in different color classes and cannot be joined directly with Clar chains by Lemma 3.5. We must instead take a Clar chain between p_1 and p_3 that twists around the pentagon p_4. If we consider a similar patch that does not contain the pentagons p_2 and p_4 (see Figure 3.4(b)), then the pentagons p_1 and p_3 are in different color classes and cannot be connected by a Clar chain. The ability to connect a pair of pentagons by a Clar chain can depend upon the positions of other pentagons when we consider the more general case.

Restricting our attention to non-interfering Clar chains still permits us to solve two major open problems: to classify fullerenes that attain the theoretical maximum for the Clar number, as well as to find classes of fullerenes for which the Clar and Fries number cannot be attained with the same Kekuklé structure. We are also able to compute the Clar number for several classes of fullerenes. In future research, we aim to develop an understanding of Clar chains more generally, but for now, we focus on non-interfering chains.



(a) A Clar chain connecting pentagons p_1 and p_3, another connecting pentagons p_2 and p_4.



(b) When we remove the other two pentagons, p_1 and p_3 cannot be connected by a Clar chain. White faces represent faces that cannot be colored in our improper face 3-coloring.

Figure 3.4: Chains can become complicated when more than two pentagons interact.

Lemma 3.11. *Assume two pentagons are joined by a non-interfering Clar chain. Then any shortest Clar chain joining them is composed of alternating right and left turns.*

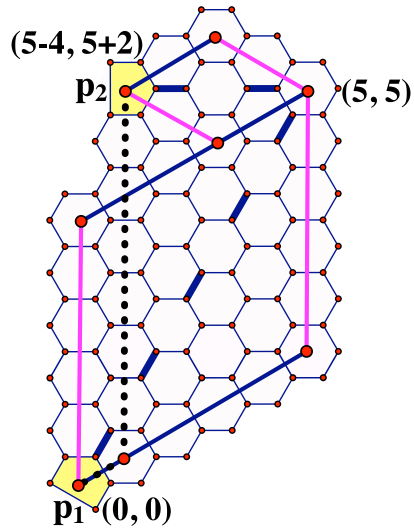
Proof. If a Clar chain takes two consecutive right turns, we have turned 120° and are traveling toward the first straight chain segment. Thus a face reached by two consecutive right turns could be reached by two shorter segments. □

Suppose the chain connecting pentagons p_1 and p_2 consists of a straight chain segment with k edges in A, then a sharp left turn followed by a straight chain segment with l edges in A. Begin with the pentagon p_1. The first straight chain segment goes to the face with Coxeter coordinates (k, k). The side of the second parallelogram goes backwards $2l$ faces along the side of the first parallelogram (in the first coordinate) and l faces in the positive direction in the second coordinate. If $2l \leq k$, the second parallelogram ends at p_2 with coordinates $(k-2l, k+l)$. (See Figure 3.5(a).) If we instead have a sharp right turn and $2l \leq k$, then the coordinates are reversed, and the segment has Coxeter coordinates $(k+l, k-2l)$.

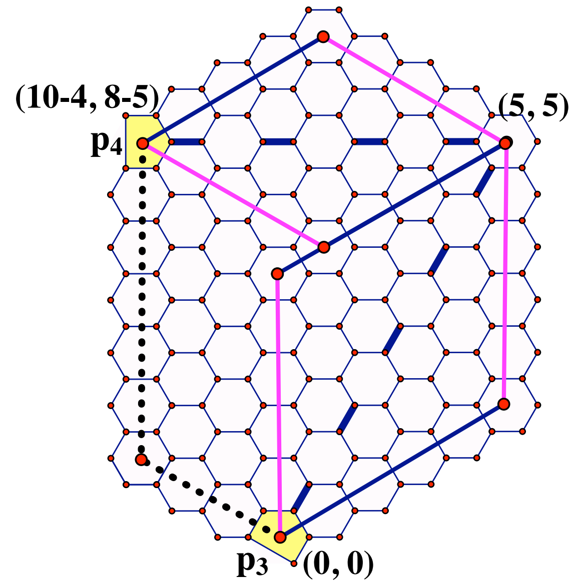
If $2l > k \geq l$, then going backwards $2l$ faces in the first coordinate after a sharp left turn takes us to $k-2l < 0$. Since this is negative, we re-orient the segment so that it is in the positive direction, and we have $2l-k$ as our second Coxeter coordinate. In the case of a sharp left turn, going backwards $2l$ faces takes us past the point (k); it takes us to the coordinate $(2k-2l, 2l-k)$. Going forwards l faces in the now-first coordinate takes us to $(2k-l, 2l-k)$. (See Figure 3.5(b).) For a sharp right turn, the Coxeter coordinates of the segment are $(2l-k, 2k-l)$.

Lemma 3.12. *Suppose two faces of a fullerene Γ can be connected by a Clar chain and the orientations of the parallelograms are given. If the segments alternate between right and left turns, the sum of the edges in A over any such Clar Chain is the same regardless of the number of turns.*

Proof. If a chain alternates between right and left turns, the jth parallelogram is in the same orientation as the first parallelogram for j odd, and in the same orientation as the second for j even since all turns are at $60°$ angles. Any parallelograms with the same orientation are adding edges to A in the same direction. Thus one parallelogram with k edges in $|A|$ reaches the same face as r parallelograms with $k_1, k_2, ...k_r$ parallelograms in the same orientation such that $k_1 + k_2 + ... + k_r = k$. So a parallelogram with k



(a) A straight chain segment of length $k = 5$ followed by a straight chain segment of length $l = 2$. The Coxeter coordinates between p_1 and p_2 are $(1, 7)$.



(b) A straight chain segment of length $k = 5$ followed by a straight chain segment of length $l = 4$. The Coxeter coordinates between p_3 and p_4 are $(6, 3)$.

Figure 3.5: Pairs of pentagons connected by two straight chain segments. The pentagonal faces are yellow.

edges in A followed by a parallelogram with l edges in A reaches the same point as any number of parallelograms with alternating turns such that diagonals of the odd-numbered parallelograms add up to k and the diagonals of the even-numbered parallelograms add up to l. $\square$

3.2 Calculating the Number of Edges in A over a Clar Chain

To find the Clar number for classes of fullerenes, we would like to calculate the number of edges in A over Clar structures (C, A) for these fullerenes, since $|C| = \frac{|V|}{6} - \frac{|A|}{3}$. In this section, we calculate $|A|$ over non-interfering Clar chains. We show that if two pentagons can be connected by a non-interfering Clar chain, then there is a Clar chain between them consisting of at most two straight chain segments. By Lemmas 3.11 and 3.12, any chain that alternates between right and left turns contributes a minimum number of edges to A. Thus a chain with a single turn contributes a minimum number of edges to A.

To describe Clar chains in the non-interfering case, consider two pentagons p_1 and p_2 that are joined by a Clar chain. Start with the hexagonal tessellation and at each pentagon, cut out a 60° wedge and identify the rays bounding the wedge. Assign the faces the improper face 3-coloring given by the chain. The chain and the two wedges split our region and the face 3-colorings above and below the split must match when the wedges are collapsed (see Figure 3.6). For any Clar structure (C, A), the edges in A in the Clar chain between p_1 and p_2 together with the faces in C must form a vertex covering over this patch.

Let p_1 and p_2 be pentagons connected by a Clar chain. Suppose that the Coxeter coordinates of the segment between p_1 and p_2 are (m, n). We can assume without loss

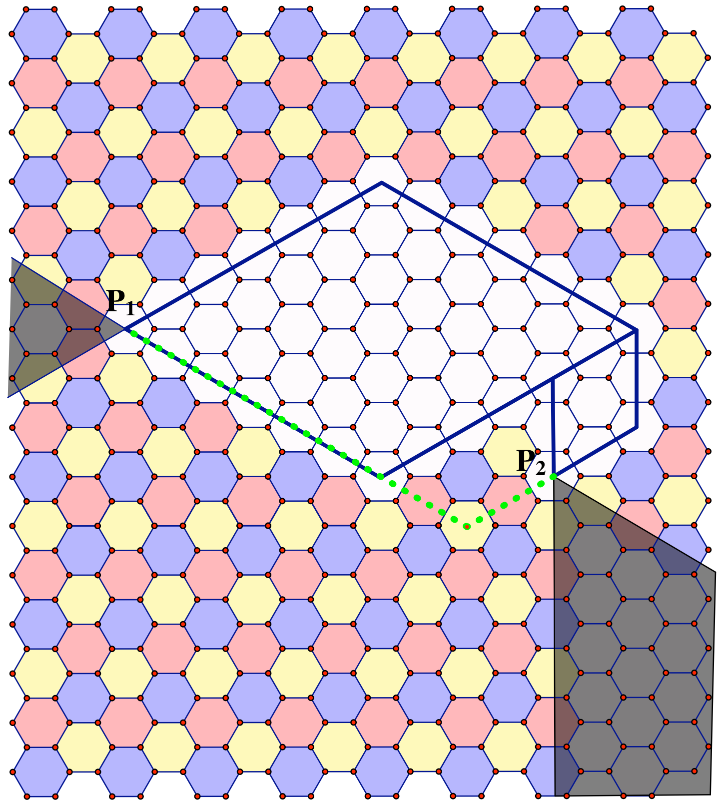


Figure 3.6: The Coxeter coordinates of the segment between pentagons p_1 and p_2 are $(8, 2)$. If the yellow faces contain the set C, this chain is of Type 1. If the red faces contain the set C, the chain is of Type 2. If the blue faces contain the set C, this chain is of Type 3.

of generality that $m \geq n$. Begin with p_1 at the origin and consider a parallelogram with sides parallel to the directions of the Coxeter coordinates (see Figure 3.6). The chain is of *Type 1* if all four of the vertices of p_1 outside of the parallelogram are covered by a face in C. The chain is of *Type 2* if exactly two of the vertices outside of the parallelogram are covered by a face in C. The chain is of *Type 3* if none of the vertices outside of the parallelogram is covered by a face in C.

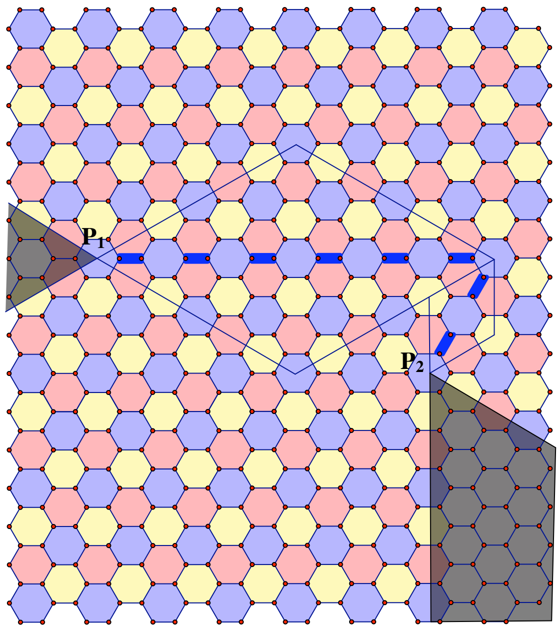
Lemma 3.13. *Let p_1 and p_2 be two pentagons joined by a chain of Type 1 and let (m, n) (or (m)) be Coxeter coordinates of the segment between them, where $m \geq n$. Then this chain contributes m edges to A and $m \equiv n \pmod 3$.*

Proof. Suppose the first straight segment has a edges in A and the second has b edges in A. The Coxeter Coordinates between p_1 and the face at the sharp turn are (a, a). The next straight segment has Coxeter Coordinates (b, b), and travels backwards b faces in the direction of the second coordinate, arriving at a face with coordinates $(a, a - b)$. Our final step goes b steps in the first coordinate and another b steps backwards in the second coordinate. The Coxeter coordinates of the segment between p_1 and p_2 are then $(a + b, a - 2b)$, which we know is equal to (m, n). Since $a + b$ and $a - 2b$ are congruent modulo 3, $m \equiv n \pmod 3$. Solving for a and b we find that $a = \frac{n+2m}{3}$ and $b = \frac{m-n}{3}$. The number of edges in the two straight chain segments is $a + b = m$. This argument works in the special case where the segment between p_1 and p_2 has Coxeter coordinate (m) since (m) is equivalent to the Coxeter coordinates $(m, 0)$. □

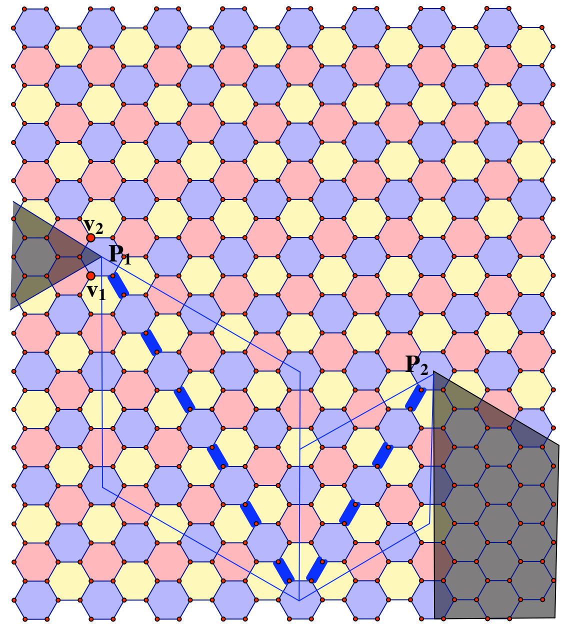
A completed chain of Type 1 is shown in Figure 3.7(a).

Lemma 3.14. *Let p_1 and p_2 be two pentagons joined by a chain of Type 2 and let (m, n) be Coxeter coordinates of the segment between p_1 and p_2, where $m \geq n$. This chain contributes $m + n$ edges to A and $m \equiv n \pmod 3$.*

Proof. By definition of Type 2, exactly two of the vertices of p_1 are covered by a face in C. Let v_1, v_2, v_3, v_4, v_5 be the vertices bounding p_1 in clockwise order, with



(a) A chain of Type 1 connecting pentagons p_1 and p_2. The blue faces contain the set C.



(b) A chain of Type 2 connecting pentagons p_1 and p_2. The red faces contain the set C. Vertices v_1 and v_2 are the vertices of p_1 incident with a face in C outside the parallelogram.

Figure 3.7: Chains of Type 1 and 2. Thick blue edges are edges in A.

v_1 and v_2 incident with a face in C. A chain of Type 1 is not possible: the first edge would exit from the vertex v_4, and the vertices v_3 and v_5 would not be covered by an element of $C \cup A$. The first edge in A must exit p_1 from v_3 or v_5, and we cover the remaining two adjacent vertices with another face in C. Thus there are two choices for the direction of the first parallelogram; by symmetry, the direction chosen is inconsequential.

Choosing to exit v_5, we use two straight chain segments to reach p_2 with the first

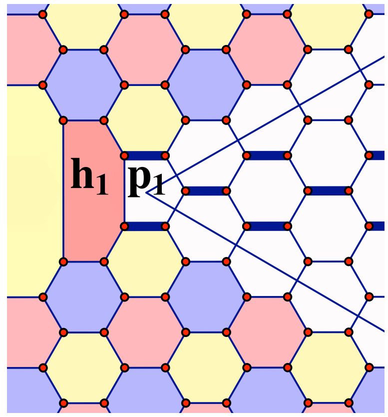


Figure 3.8: A chain of Type 3 begins with a pentagon p_1 and must also start a closed Clar chain through the hexagon h_1. Here the blue faces contain the set C, the thick edges represent edges in A.

containing a edges in A and the second containing b edges in A, where $a \geq b$. (See Figure 3.7(b).) If we begin with the coordinates $(0, 0)$, the coordinates at the end of the first parallelogram are (a, a), and we are at distance (b, b) from p_2. When traveling along the next parallelogram, we go backwards $2b$ faces along the first parallelogram (in the direction of the second coordinate) and b faces in the direction of the first coordinate. The difference from Type 1 is that here, $2b > a$. We end with the coordinates $(2a-b, 2b-a)$=(m, n). Solving for a and b gives $a = \frac{2m+n}{3}$ and $b = \frac{2n+m}{3}$ and hence $a + b = n + m$. Since $m - n = 3a - 3b$, $m \equiv n \pmod 3$. □

A completed chain of Type 2 is shown in Figure 3.7(b).

Lemma 3.15. *Let p_1 and p_2 be two pentagons joined by a chain of Type 3 and let (m, n) be Coxeter coordinates of the segment between them, where $m \geq n$. Then this* *chain contributes* $3m + 2$ *edges to* A *and* $m \equiv n$ *(mod 3).*

Proof. By definition of Type 3, none of the vertices of p_1 is covered by a face in C. This means that p_1 and p_2 are in the independent set of faces containing C. Thus all the vertices of the pentagon must be covered by edges in A. If exactly one edge in A exits the pentagon, then the other four vertices of the pentagon are covered by two edges in A lying on the pentagon. These two edges exit a hexagon h_1 and are coupled over h_1, then continue a Clar chain with two adjacent hexagons each adjacent to p_1 (see Figure 3.8). The Clar chains beginning with h_1 end with a hexagon h_2 adjacent to p_2. The union of the two chains connecting h_1 and h_2 form a closed chain around the interior chain connecting p_1 and p_2. Because p_1 is not adjacent to any face in C, we can choose the direction of the Clar paths to be in the direction of the first Coxeter coordinate. The coordinates between the h_1 and h_2 are also (m, n). The interior chain connecting the pentagons p_1 and p_2 is a chain of Type 1; the interior consists of two straight chain segments of lengths a and b, where $a + b = m$. By Lemma 3.13, $m \equiv n$ (mod 3), and the interior Clar chain joining p_1 and p_2 contributes m edges to $|A|$. The Clar chains between h_1 and h_2 are parallel to the open chain. One chain is of the same length, and the other travels around the parallelogram, so its length is $a+b+2$. The total number of edges in A is $3m + 2$. This proof works in the special case where the segment between p_1 and p_2 has Coxeter coordinate (m) since (m) is equivalent to the Coxeter coordinates $(m, 0)$.

To show that $3m + 2$ edges are needed, note that the shortest Clar chain between

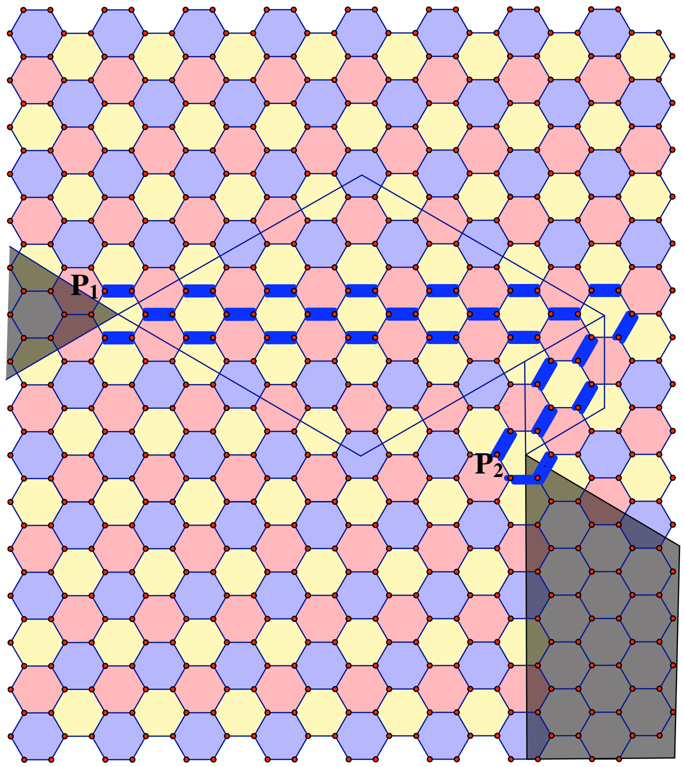


Figure 3.9: A chain of Type 3 connects pentagons p_1 and p_2. Thick blue edges represent edges in A.

pentagons with coordinates (m, n) is of length m. This chain contains $m-1$ hexagons and two pentagons. We know that none of the vertices on these faces is covered by a face in C, so each of these vertices must be covered by an edge from A. There are $6(m-1)$ vertices from the $m-1$ hexagons and ten vertices from the two pentagons. These $6m+4$ vertices need $3m+2$ edges in A to cover them. $\square$

Lemma 3.16. *Let Γ be a fullerene with a Clar structure (C, A) and a coupling. If $|C|$ is the Clar number for Γ, then any closed Clar chain with exactly two pentagons p_1 and p_2 in its interior together with the open Clar chain connecting the pentagons* *contributes the same number of edges to A as a Clar chain of Type 3 between p_1 and p_2.*

Proof. Let $f_0, a_1, f_1, a_2, f_2, ...a_k, f_k = f_0$ be a closed Clar chain with exactly two pentagons p_1 and p_2 in its interior. By Lemma 3.4, there are six open Clar chains connecting pairs of pentagons, and the Clar chains are non-crossing. Thus there must be some open Clar chain $p_1, e_1, h_1, e_2, h_2, ...e_l, p_2$ joining p_1 and p_2 that is contained completely inside the closed Clar chain $f_0, a_1, f_1, a_2, f_2, ...a_k, f_k = f_0$. Give Γ an improper face 3-coloring associated with the Clar structure (C, A). By Lemma 3.5, we can assume without loss of generality that the faces of C are blue in this face 3-coloring, and that the faces $f_0, f_1, f_2, ...f_k = f_0$ of the closed chain are red.

Consider the case in which the faces $p_1, h_1, h_2, ...p_2$ of the open chain are also in the red color class. We can remove the closed chain by interchanging the colors blue and yellow in the interior. After this change, the pentagons p_1 and p_2 are still red. Since they are not in the color class containing C, the chain between the pentagons is of Type 1 or Type 2. We know from Lemmas 3.13 and 3.14 that for a pair of pentagons with Coxeter coordinates (m, n), $m \geq n$, a chain of Type 1 contributes m edges to A and a chain of Type 2 contributes $m + n$ edges. A closed chain surrounding them has at least $2m$ edges in A, and there remain edges from A in the open chain. Therefore, deleting the closed chain and interchanging the interior face colors decreases A. Such a closed chain does not exist in a Clar structure that attains the Clar number.

Consider the case in which the faces of the open chain $p_1, h_1, h_2, ...p_2$ are in the yellow color class. Removing the closed chain interchanges the colors of the blue and yellow faces, so p_1 and p_2 would be in the blue color class. Since the pentagons cannot be in the set C, we no longer have a vertex covering (C, A). This results in a chain of Type 3: there are $3m + 2$ edges in A connecting the pentagons, and all vertices of the pentagons are covered by edges in A. The open chain $p_1, e_1, h_1, e_2, h_2, ...e_l, p_2$ is in the interior of $f_0, a_1, f_1, a_2, f_2, ...a_k, f_k = f_0$. Thus if the coordinates between p_1 and p_2 are (m, n) with $m \geq n$, then an open chain containing these pentagons must have length at least $2(m + 1)$. Therefore, the open chain $p_1, e_1, h_1, e_2, h_2, ...e_l, p_2$ together with the closed chain $f_0, a_1, f_1, a_2, f_2, ...a_k, f_k = f_0$ contributes at least $3m + 2$ edges to A. □

A chain of Type 3 occurs when the independent set containing C also contains the paired pentagonal faces of an open chain. To change the color class of the pentagons, we use a closed chain and then connect the pentagons with a chain of Type 1.

Let Γ be a fullerene that allows a coupling of a Clar structure with non-interfering Clar chains. Let (m_i, n_i) be the Coxeter coordinates of the segments between each pair of pentagons connected by a Clar chain in this coupling for $1 \leq i \leq 6$. For an arbitrary Clar structure of Γ, there are three choices for the set of faces containing C outside of the six clear fields containing the pairs of pentagons. These three choices give three distinct Clar structures. Given one of these Clar structures, the number of edges contributed to $|A|$ by the pair with Coxeter coordinates (m_i, n_i) is $\max\{m_i, n_i\}$ if the chain is of Type 1, $m_i + n_i$ if the chain is of Type 2, and $3\max\{m_i, n_i\} + 2$ if the chain is of Type 3. For each of the three choices, we determine the total number of edges in $|A|$ and let M be the minimum of these three sums. We define such a pairing of pentagons to be *widely separated* over the fullerene if for any two pentagons that are not paired together, one of the Coxeter coordinates of the segments joining them is at least $\frac{M}{2} - 2$.

Lemma 3.17. *Let Γ be a fullerene over which the pairs of pentagons are widely separated. If (C, A) is a Clar structure that attains the Clar number for Γ, then (C, A) includes no closed chain with more than two pentagons in its interior.*

Proof. Suppose (C, A) is a Clar structure that attains the Clar number for Γ, and that (C, A) includes a closed Clar chain $f_0, a_1, f_1, ..., a_k, f_k = f_0$ with three or more pentagons in its interior. By Lemma 3.9, there exists a chain circuit $\mathcal{C}$ for $f_0, a_1, f_1, ..., a_k, f_k = f_0$ that includes an even number of pentagons in its interior. Thus at least four pentagons are in the interior of $\mathcal{C}$. By definition of widely separated, the interior of $\mathcal{C}$ contains at least two pairs of pentagons for which one of the Coxeter coordinates of the segments joining them is at least $\frac{M}{2} - 2$. Therefore the length of $f_0, a_1, f_1, ..., a_k, f_k = f_0$ is at least $2(\frac{M}{2} - 2) + 2 = M - 2$. There are additional edges in A for each of the six chains between paired pentagons, so the total contribution to $|A|$ is greater than M. Thus, (C, A) does not attain the Clar number for Γ. $\square$

Theorem 3.18. *Let Γ be a fullerene over which the pairs of pentagons are widely separated. Let M be the minimum sum of the edges in A over the three possible choices for the face set containing C. Then $\frac{|V|}{6} - \frac{M}{3}$ is the Clar number for Γ.*

Proof. By Lemma 3.4, any Clar structure (C, A) over Γ contains six Clar chains connecting pairs of pentagons. Let M denote the minimum number of edges in A over the three possible choices for the set C outside of the six clear fields. If a different pairing is chosen for any pentagon, then there are at least two new pairs of pentagons. For each new pair, one of the Coxeter coordinates is at least $\frac{M}{2} - 2$ since the original chains were widely separated. Chains connecting the other four pairs each contribute at least one edge to A, giving a total of at least M edges in A. By Lemma 3.17, any closed Clar chain containing more than one pair of pentagons increases the size of A. Thus any other Clar structure contains at least M edges in A. The conclusion follows by Lemma 3.3. $\square$

Chapter 4

Fullerenes with Complete Clar Structure

In this chapter, we describe a class of fullerenes for which the Clar number is maximal with respect to the number of vertices in Γ. Let Γ be a fullerene with a Clar structure (C, A). By definition the cardinality of C is a lower bound for the Clar number of a fullerene, and we proved in Lemma 3.3 that $|C| = \dfrac{|V|}{6} - \dfrac{|A|}{3}$. To describe a class of fullerenes for which $|C|$ is maximal with respect to the number of vertices, we find fullerenes for which $|A|$ is minimal. By Lemma 3.1 at least one edge from A exits each of the twelve pentagons. There are additional edges in A if one of these edges exits a hexagon. Therefore $|A| \geq 6$, and equality holds exactly when all edges from A connect pairs of pentagons. We say that a Clar structure is *complete* if $|A| = 6$, in which case $|C| = \frac{|V|}{6} - 2$. We can summarize the above in the following lemma:

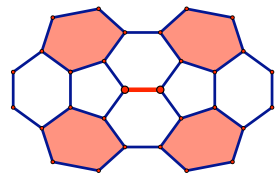


Figure 4.1: Two pentagons paired by a single edge in A

Lemma 4.1. *If a fullerene* Γ *has a complete Clar structure* (C, A)*, then there exists a pairing of the twelve pentagonal faces such that each pair is connected by a single edge. The only edges in* A *are the six edges between pairs of pentagonal faces.*

Ye and Zhang called fullerenes with complete Clar structure *extremal fullerenes* [12]. They went on to construct the 18 extremal fullerenes on 60 vertices.

4.1 The Leapfrog Construction

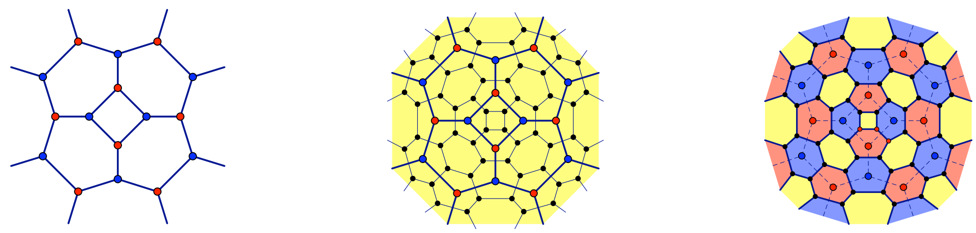
The leapfrog construction was described in Chapter 1. By Proposition 1.4, a fullerene $\Gamma = (V, E, F)$ attains the Fries number $\frac{|V|}{3}$ if and only if Γ has a face-only vertex covering. The Kekulé structure that attains the Fries number $\frac{|V|}{3}$ is constructed by taking the faces in the face-only vertex covering to be the void faces. By Lemma 3.1, all of the pentagons of Γ must be in this face-only vertex covering. We say that a fullerene with these properties has a *complete Fries structure*. We now use the leapfrog construction in a different way to construct the fullerenes that admit a complete Clar structure.

Let Ω^ℓ be the leapfrog of the plane graph $\Omega = (V, E, F)$. By Lemma 1.3, the faces F^ℓ of Ω^ℓ corresponding to the faces F of Ω form a face-only vertex covering of Ω^ℓ. The set of edges that do not bound a face in F^ℓ forms a perfect matching of Ω^ℓ, that is, a Kekulé structure if Ω^ℓ is a fullerene. Extending this notation, we write V^ℓ for the set of faces in Ω^ℓ corresponding to the vertex set V of Ω and U^ℓ to denote a set of faces of Ω^ℓ corresponding to a subset U of V.

Lemma 4.2. *Given a 3-regular plane graph Ψ with a face-only vertex covering Q, there is a unique plane graph $\Omega = (V, E, F)$ such that Ω^ℓ=Ψ and $F^\ell = Q$.*

Proof. Consider the planar dual Ψ^* of Ψ constructed by placing vertices in the centers of faces and connecting vertices if the corresponding faces of Ψ share an edge. Now construct a subgraph $\Omega = (V, E, F)$ of Ψ^* by deleting all the vertices corresponding to the faces in Q and all edges incident with those vertices. (See Figure 4.2(c) with the yellow faces as the vertex cover.) A face of degree j of Ψ that is not in Q corresponds to a vertex of degree $\frac{j}{2}$ in Ω; a face of Ψ that is in Q and has degree k corresponds in Ω to a face of degree k. Thus $\Omega = (V, E, F)$ is a plane graph such that $\Omega^\ell = \Psi$ and $F^\ell = Q$, and Ω is unique up to isomorphism. $\square$

Given a 3-regular plane graph Ψ with a face-only vertex covering Q, we call the graph obtained by the process in Lemma 4.2 the *reverse leapfrog* of (Ψ, Q) and denote the graph by $(\Psi, Q)^{-\ell}$, or simply $\Psi^{-\ell}$ if Q is understood. By Lemma 1.3, any leapfrog graph is 3-regular and has a face-only vertex covering. Combining Lemma 1.3 with Lemma 4.2 leads to the following characterization of leapfrog graphs:



(a) A bipartite plane graph $\Omega = (V, E, F)$

(b) The leapfrog graph Ω^ℓ is shown superimposed on Ω.

(c) The yellow faces F^ℓ are a face-only vertex covering of Ω^ℓ. The red and blue faces of Ω^ℓ correspond to the vertex bipartition of Ω.

Figure 4.2: The leapfrog transformation of a bipartite plane graph

Theorem 4.3. *A plane graph Ψ is a leapfrog graph if and only if Ψ is 3-regular and has a face-only vertex covering.*

Lemma 4.4. *Given a bipartite plane graph $\Omega = (V, E, F)$ with vertex partition $V = U \cup W$, the sets of faces U^ℓ, W^ℓ, F^ℓ form a face 3-coloring of Ω^ℓ.*

Proof. The set of faces F^ℓ is a face-only vertex covering for Ω^ℓ. The remaining faces in Ω^ℓ correspond to vertices in Ω. Since Ω is bipartite, each face in F^ℓ is bounded by alternating faces from U^ℓ and W^ℓ. By Lemma 1.3 any leapfrog graph is 3-regular. Thus each vertex in Ω^ℓ is incident with exactly one face from each of the sets U^ℓ, W^ℓ and F^ℓ. □

Theorem 4.5. *Suppose Ψ is a 3-regular plane graph. Then the following are equivalent:*

1. *Ψ is bipartite;*

2. *Ψ is face 3-colorable;*

3. *$\Psi = \Omega^\ell$ for some bipartite plane graph, Ω.*

Proof. ($1 \iff 2$) Ψ is bipartite if and only if all faces have even degree. Thus by Theorem 2.1, Ψ is face 3-colorable if and only if it is bipartite.

($2 \implies 3$) The graph Ψ is 3-regular, so if Ψ has a proper face 3-coloring, each vertex is incident with a face of each color and each color class Q_i is a face-only vertex covering. By Lemma 4.2, there is a unique graph Ω_i acquired by taking the reverse leapfrog of Ψ with respect to the vertex-covering Q_i for each i. In $\Omega_i = (\Psi, Q_i)^{-\ell}$, the faces of Q_i correspond to the faces of Ω_i. The remaining face-only vertex covers, Q_j, Q_k, correspond to the vertices of Ω_i. Since Q_j and Q_k are independent in Ψ, the corresponding vertices form a bipartition of the vertices in Ω_i.

($3 \implies 2$) Suppose that $\Psi = \Omega^\ell$ for some bipartite plane graph Ω with vertex bipartition $V = U \cup W$. By Lemma 4.5, the sets of faces U^ℓ, W^ℓ, F^ℓ form the color classes for a face 3-coloring of Ψ. □

4.2 Fullerenes with Complete Clar Structures

An $\{(a, b), k\}$-*sphere* is a k-regular plane graph with faces only of degrees a and b. Fullerenes are exactly the class of $\{(5, 6), 3\}$-spheres. Given a fullerene Γ with a complete Clar structure (C, A), we see that the six pairs of pentagons together with

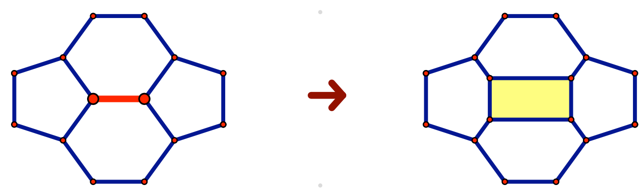


Figure 4.3: Expansion of Γ over an edge in A

the edges between them are equivalent to the open chains discussed in Chapter 2 and 3. As in Section 3.1, we define the *expansion* of the fullerene as follows: widen each of the six edges in A between pentagonal pairs into a quadrilateral faces. Each vertex covered by A becomes an edge, and each pentagon becomes a hexagon. We denote this new $\{(4,6),3\}$-sphere by $\mathcal{E}(C,A)$ and the set of quadrilateral faces by A'. If Γ has f faces, then $\mathcal{E}(C,A)$ has six quadrilateral faces and f hexagonal faces.

Lemma 4.6. *Let Γ be a fullerene with a complete Clar structure (C,A). Let $\mathcal{E}(C,A)$ be the expansion of Γ and let $C' = C \cup A'$. Then:*

1. *There is a face 3-coloring of $\mathcal{E}(C,A)$ such that the set C' forms one color class.*

2. *The reverse leapfrog $(\mathcal{E}(C,A),C')^{-\ell} = \Theta$ is a $\{(4,6),3\}$-sphere.*

3. *The two face color classes of $\mathcal{E}(C,A)$ other than C' correspond to the vertex color classes of the bipartite graph Θ.*

Proof.

1. By Lemma 3.5, the expansion $\mathcal{E}(C,A)$ is face 3-colorable with the faces in C' forming one color class.

2. Since $\mathcal{E}(C, A)$ is a 3-regular graph and C' is a face-only vertex covering of $\mathcal{E}(C, A)$, there is a unique graph Θ such that $\Theta^\ell = \mathcal{E}(C, A)$ and the faces of Θ correspond to C' by Lemma 4.2. The faces of $\mathcal{E}(C, A)$ in C' are of degree 4 and 6, so by Lemma 1.3, the faces of Θ are of degree 4 and 6. The remaining faces of $\mathcal{E}(C, A)$ are hexagons and correspond to the vertices of Θ. Thus by Lemma 1.3, Θ is 3-regular. So Θ is a $\{(4, 6), 3\}$-sphere.

3. By Theorem 4.5, the remaining two face color classes of $\mathcal{E}(C, A)$ correspond to a bipartition of the vertices in Θ.

□

We see that a fullerene with complete Clar structure corresponds to a $\{(4, 6), 3\}$-sphere Θ. We want to determine the conditions under which a $\{(4, 6), 3\}$-sphere corresponds to one or more fullerenes with complete Clar structure.

Consider an arbitrary $\{(4, 6), 3\}$-sphere Θ and let Θ^ℓ be the leapfrog graph of Θ. By Lemma 1.3, Θ^ℓ is also a $\{(4, 6), 3\}$-sphere; Θ^ℓ is 3-regular and has a face of degree j corresponding to each face of degree j from Θ and a face of degree 6 corresponding to each vertex of Θ. Also by Lemma 1.3, the faces of Θ^ℓ corresponding to the faces from Θ form a face-only vertex covering of Θ^ℓ. Thus the quadrilateral faces of Θ^ℓ are part of an independent set, and each quadrilateral face in Θ^ℓ is bounded by four hexagons.

For each quadrilateral face of Θ^ℓ, choose two opposite hexagons adjacent to the quadrilateral to form a pair. We denote this set of paired hexagons by $\mathcal{P}$. We define

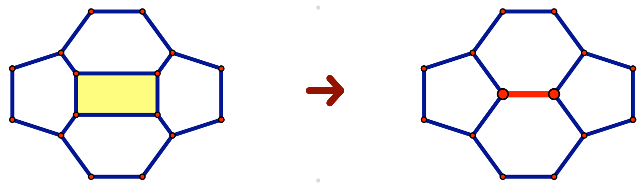


Figure 4.4: The reverse expansion around a quadrilateral face in $(\Theta^\ell, \mathcal{P})$.

the *reverse expansion procedure* on the pair $(\Theta^\ell, \mathcal{P})$ as follows: for each quadrilateral face of Θ^ℓ, contract each of the two opposite edges that the quadrilateral shares with paired hexagons into a vertex. We then obtain the graph $\mathcal{E}^{-1}(\Theta^\ell, \mathcal{P})$, the *reverse expansion* of Θ^ℓ with respect to $\mathcal{P}$. Now each quadrilateral of Θ^ℓ has become an edge in $\mathcal{E}^{-1}(\Theta^\ell, \mathcal{P})$ and the degree of each face in $\mathcal{P}$ is decreased by 1 for each quadrilateral that the face is paired over.

Lemma 4.7. *Let Θ^ℓ be the leapfrog of a $\{(4,6),3\}$-sphere Θ. Let $\mathcal{P}$ be the set of hexagons paired on opposite sides of the quadrilateral faces of Θ^ℓ. The reverse expansion of this pair, $\Gamma = \mathcal{E}^{-1}(\Theta^\ell, \mathcal{P})$ is a fullerene if and only if $\mathcal{P}$ is a set of twelve distinct hexagons. When Γ is a fullerene, Γ admits a complete Clar structure. Γ also admits a complete Fries structure if and only if the hexagons in $\mathcal{P}$ are part of a face-only vertex covering of Θ^ℓ.*

Proof. It follows from Euler's formula that any $\{(4,6),3\}$-sphere has exactly six quadrilateral faces. Thus in Θ^ℓ, there are six quadrilaterals across which we pair opposite hexagons to create the set $\mathcal{P}$. If $\mathcal{P}$ is a set of twelve distinct hexagons, then each hexagon belongs to exactly one pairing and is contracted into a pentagon. Hence

Γ is a fullerene. If $|\mathcal{P}| < 12$, then some hexagon in $\mathcal{P}$ is paired across two or more quadrilaterals. That hexagon is contracted into a face of degree less than 5 and thus Γ is not a fullerene.

The quadrilaterals of Θ^ℓ are part of a face-only vertex covering corresponding to the faces of Θ by Lemma 1.3. Denote this face-only vertex covering by C'. Let C denote the hexagons of $\Gamma = \mathcal{E}^{-1}(\Theta^\ell, \mathcal{P})$ corresponding to hexagons in C' of Θ^ℓ and let A denote the set of edges formed by collapsed quadrilaterals from Θ^ℓ. The set $C \cup A$ forms a vertex covering of Γ, and thus if Γ is a fullerene, then (C, A) is a complete Clar structure for Γ.

Every face of Θ^ℓ has even degree, and thus Θ^ℓ is face 3-colorable by Theorem 2.1. A face 3-coloring of Θ^ℓ corresponds to an improper face 3-coloring of Γ in which the only incompatible faces are those that share an edge in A. Hence the pentagons of Γ are in the same color class exactly when the faces of $\mathcal{P}$ are in the same color class of Θ^ℓ, that is, if and only if $\mathcal{P}$ is part of a face independent set since Θ^ℓ is 3-regular. The pentagons are all in one color class in the improper face 3-coloring if and only if they are part of of a face-only vertex covering, which is equivalent to the condition that the trivalent graph Γ be a leapfrog graph by Theorem 4.3. By Proposition 1.4, the fullerene Γ is a leapfrog graph if and only if Γ admits a complete Fries structure. $\square$

When is it not possible to find a disjoint set $\mathcal{P}$ of opposite hexagonal faces adjacent to each quadrilateral? Consider the $\{(4,6),3\}$-sphere Θ. Quadrilaterals in Θ correspond to quadrilaterals in Θ^ℓ. The four hexagons bounding a quadrilateral in Θ^ℓ

correspond to the vertices of the quadrilateral in Θ. Pairing disjoint hexagons with quadrilaterals in Θ^ℓ is equivalent to choosing diagonal vertices for each quadrilateral in Θ. These diagonal vertices become opposite hexagons in Θ^ℓ, and contract into pentagons in the fullerene. We indicate these vertices around a quadrilateral face in Θ by drawing a diagonal line connecting the vertices. (See Figure 4.5.) We define a *diagonalization* of a $\{(4,6),3\}$-sphere Θ to be a choice of pairs of diagonal vertices for each quadrilateral face so that no vertex is chosen twice. We can contract Θ^ℓ into a fullerene with a complete Clar structure exactly when a diagonalization of Θ is possible. A *perfect diagonalization* of a $\{(4,6),3\}$-sphere Θ, is a diagonalization in which all vertices chosen are in the same cell of the bipartition and hence correspond to faces in the same color class of a face 3-coloring of Θ^ℓ by Lemma 4.5. We have proven the following lemma:

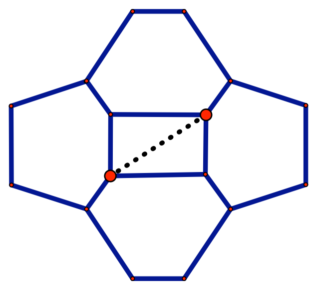
Lemma 4.8. *Let Θ be a $\{(4,6),3\}$-sphere. Then*

1. *Θ^ℓ admits a pairing of hexagons with $|\mathcal{P}| = 12$ if and only if Θ admits a diagonalization.*

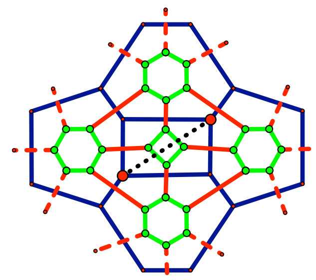
2. *Θ^ℓ admits a pairing of hexagons with $|\mathcal{P}| = 12$ where $\mathcal{P}$ is part of a face-only vertex covering of Θ^ℓ if and only if Θ admits a perfect diagonalization.*

Lemma 4.9. *Let Θ be a $\{(4,6),3\}$-sphere. Then*

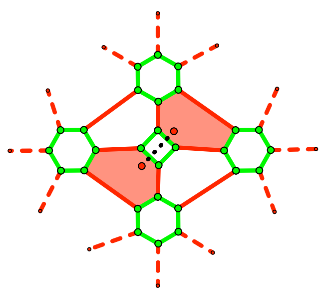
1. *Θ admits a diagonalization if and only if no vertex meets three quadrilaterals.*



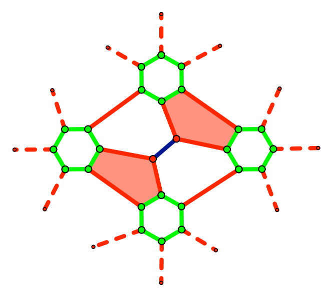
(a) A diagonal pair of vertices incident with a quadrilateral in Ω.



(b) Take the leapfrog, Ω^ℓ.



(c) The diagonal vertices in Ω correspond to hexagons in Ω^ℓ.



(d) The hexagons become pentagons in $\mathcal{E}^{-1}(\Theta^\ell, \mathcal{P})$.

Figure 4.5: Choose diagonal vertices for each quadrilateral in Θ. These vertices correspond to opposite hexagons bounding a quadrilateral face in Θ^ℓ. We collapse an edge of each of the paired hexagons to construct $\mathcal{E}^{-1}(\Theta^\ell, \mathcal{P})$.

2. *Θ admits a perfect diagonalization if and only if no vertex in Θ is incident with more than one quadrilateral.*

Proof. There are at most three quadrilateral faces at any vertex in Θ. Since Θ is 3-regular, any two faces that share a vertex share an edge containing that vertex. Suppose some vertex x is incident with three quadrilateral faces s_1, s_2, and s_3. One easily checks that any multiset of diagonal edges through these quadrilaterals includes some vertex twice. (See Figure 4.6.) If every vertex in Θ is incident with at most two quadrilaterals, then one easily checks that we may choose diagonal vertices incident with each quadrilateral such that no vertex is chosen twice.

If two quadrilaterals s and s' share an edge, then the vertices incident with s and s' must both be part of any diagonalization, and so the diagonalization cannot be perfect; the vertices chosen cannot be in the same cell of the bipartition. If the quadrilaterals are disjoint and U is one cell of the vertex bipartition, we may choose diagonal vertices in U for each quadrilateral. □

Theorem 4.10.

1. *The fullerenes on n vertices that admit a complete Clar structure are in one-to-one correspondence with the diagonalized $\{(4,6),3\}$-spheres on $\frac{n}{3}+4$ vertices.*

2. *The fullerenes on n vertices that admit a complete Clar structure and a complete Fries structure are in one-to-one correspondence with the perfectly diagonalized $\{(4,6),3\}$ spheres on $\frac{n}{3}+4$ vertices.*

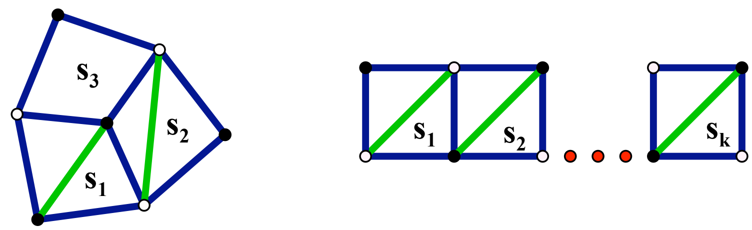


Figure 4.6: If three quadrilaterals in Θ share a vertex, then any choice of diagonal vertices for each quadrilateral includes some vertex twice. If at most two quadrilaterals share each vertex, we can choose diagonal vertices for each quadrilateral of Θ so that no vertex is chosen twice.

Proof. By Lemma 4.7, a leapfrog $\{(4,6),3\}$-sphere Θ^ℓ can be contracted into a fullerene Γ with complete Clar structure exactly when it is possible to find a set of pairings $\mathcal{P}$ of twelve distinct hexagons bounding opposite sides of the six quadrilateral faces and by Lemma 4.8 this is equivalent to a diagonalization of Θ. By Proposition 1.4 and Lemma 4.7, the contracted fullerene Γ is leapfrog exactly when the hexagons we choose to collapse are all in the same color class. By Lemmas 4.5 and 4.9, this occurs for each perfect diagonalization of a $\{(4,6),3\}$-sphere.

If the fullerene $\Gamma = \mathcal{E}^{-1}(\Theta^\ell, \mathcal{P})$ has n vertices, then Θ^ℓ has $n + 12$ vertices; the reverse expansion contracts the six quadrilateral faces into six edges. Thus Θ is one-third the order of Θ^ℓ and has $\frac{n}{3} + 4$ vertices. $\square$

For each $\{(4,6),3\}$-sphere in which no vertex lies on two quadrilaterals, two perfect diagonalizations are possible. We have two choices for the diagonal in a quadrilat-

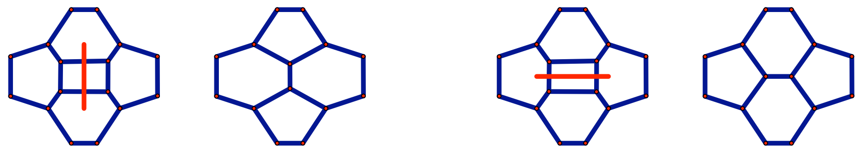


Figure 4.7: Two choices for contracting a quadrilateral face in Θ^{ℓ}. A different choice is equivalent to a Stone-Wales transformation of the fullerene.

eral face. For each of the other quadrilaterals, we must choose diagonal vertices in this same bipartition. Thus for each $\{(4,6),3\}$-sphere on which no two quadrilaterals share a vertex, there are two perfectly diagonalized $\{(4,6),3\}$-spheres and two corresponding fullerenes with a complete Fries structure and a complete Clar structure.

For each diagonalization of a $\{(4,6),3\}$-sphere Θ, Θ^{ℓ} can be contracted into a different fullerene with complete Clar structure. How many such diagonalizations are there for a $\{(4,6),3\}$-sphere? Given a quadrilateral face in Θ, we have two choices for the pair of diagonal vertices incident with that face. Suppose two quadrilaterals, s_1 and s_2, share a vertex in Θ. Then s_1 and s_2 share an edge, and a diagonal pair of vertices incident with s_1 includes one vertex on that edge. A diagonal pair of vertices incident with s_2 must also include a vertex on this edge, and there is only one choice remaining for the pair of diagonal vertices incident with s_2.

We call a set of quadrilaterals in Θ a *block* if each of the quadrilaterals in the set shares a vertex with another quadrilateral in the set. Once we choose a pair of diagonal vertices for one quadrilateral, the choice of diagonal vertices is forced for each of the other quadrilaterals in the block. (See Figure 4.6.) Thus if Θ has b blocks, there are 2^b diagonalized $\{(4,6),3\}$-spheres and 2^b corresponding fullerenes with complete Clar structure. Note that $1 \leq b \leq 6$, so a given $\{(4,6),3\}$-sphere could yield as many as 64 fullerenes with complete Clar structure. Choosing a different diagonal in Θ corresponds to choosing the other pair of hexagons around a quadrilateral in Θ^ℓ to be in $\mathcal{P}$. Choosing a different pair of hexagons around a quadrilateral in Θ^ℓ to contract is equivalent to a Stone-Wales transformation [4] of the four faces in the fullerene (see Figure 4.7). We can get from any one of these fullerenes to another through a series of Stone-Wales transformations. Thus each $\{(4,6),3\}$-sphere Θ in which no vertex lies on three quadrilaterals represents an equivalence class of fullerenes with complete Clar structure under the Stone-Wales equivalence.

Chapter 5

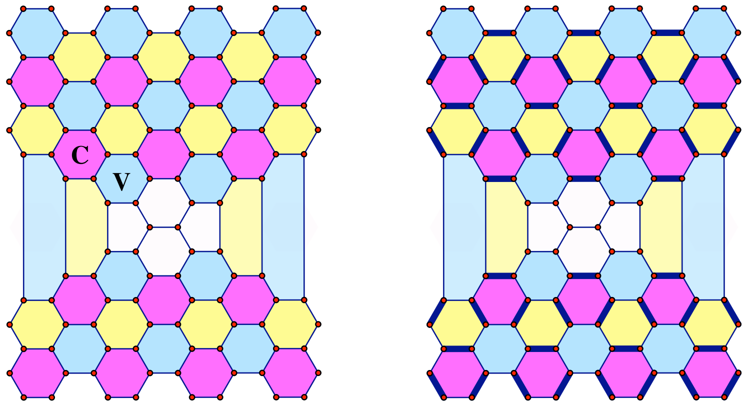
Class for which the Clar and Fries Number Cannot be Attained by the Same Kekulé Structure

5.1 Introduction

It is part of the folklore of fullerenes that a set of independent benzene faces that attains the Clar number for a fullerene is contained in the set of benzene faces that gives the Fries number. In this chapter, we describe a class of fullerenes for which this does not hold: for fullerenes in this class, any Kekulé structure that attains the Fries number cannot give the Clar number; any Kekulé structure that attains the Clar number cannot give the Fries number.

A face 3-coloring is not possible over a fullerene, but a partial 3-coloring can be constructed except over relatively small *excluded patches* containing the pentagonal faces. We can begin to construct a Kekulé structure consisting of edges connecting the faces in one color class as described previously. This structure must be extended inside each excluded patch to complete the Kekulé structure. To attain the Fries number, this extension must be chosen so that $|B_1(K)| + 2|B_2(K)|$ is minimized. To achieve the Clar number, this extension must be chosen so that $|A|$, the number of Kekulé edges not on a Clar face, is minimized. In the examples we construct here, pairs of nonadjacent pentagons are joined by a single edge, and we refer to such patches as *basic patches*. These basic patches are widely separated to ensure that no other pairing of pentagons could yield the Fries or Clar number.

To construct the partial Kekulé structure outside of the basic patches, we choose one color class of independent faces to be the void faces. We must then choose another color class to be the set C contributing to the Clar number. Thus there are six possible options for choosing the partial Kekulé structure and the partial Clar structure. In Section 5.2, we show that for exactly one of these six choices around a basic patch, no completion of the Kekulé structure simultaneously minimizes the contribution to $|A|$ and $|B_1(K)| + 2|B_2(K)|$ over the patch. In Section 5.3, we construct fullerenes with six basic patches so that for each of the six choices for void and Clar faces, exactly one of these basic patches requires different extensions of the Kekulé structure to minimize the Clar deficit and the Fries deficit. Thus for our class of fullerenes, no



(a) A partial face 3-coloring outside of a basic patch.

(b) A partial Kekulé structure given by the choice of void faces outside of the basic patch.

Figure 5.1: The white faces represent a basic patch. The void faces are contained in the set of blue faces, the Clar faces in the set of pink faces.

Kekulé structure attains both the Fries and the Clar number for the fullerene.

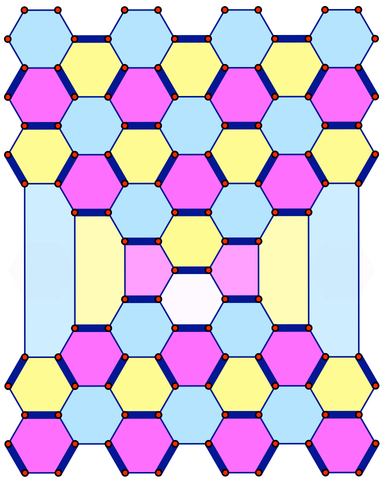
5.2 Basic Patches

5.2.1 A choice for the void and Clar faces that requires two Kekulé extensions.

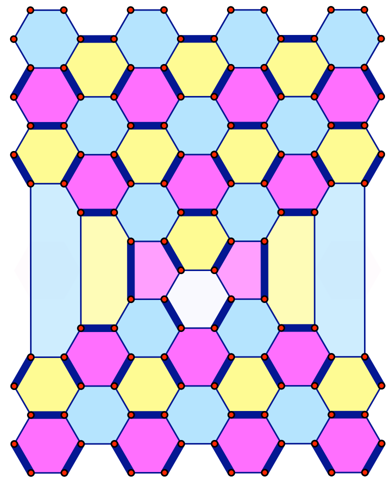
Figure 5.1(a) depicts a basic excluded patch. For the faces surrounding the basic patch, the set of blue faces is chosen to be the set of void faces and the pink faces are chosen to be Clar faces. Figure 5.1(b) shows the partial Kekulé structure given by this choice of void faces; all edges that join two blue faces are in the partial Kekulé structure. We need to extend this to a Kekulé structure. Figure 5.2(a) shows the extension of this choice that minimizes $|A|$ and 5.2(b) shows the extension that minimizes $|B_1(K)| + 2|B_2(K)|$. We prove that no single extension minimizes both deficits.

Extension 1: We first extend the Kekulé structure to minimize the Clar deficit. Outside the patch, we start with a partial Kekulé structure in which each pink hexagonal face is a benzene face (Figure 5.1(b)). None of the ten vertices incident with one of the two pentagons is covered by a face in C, so these vertices must be covered by edges from A in the vertex covering (C, A). In the partial Kekulé structure, every hexagon that is not in C is adjacent to a face in C. Thus no extension can increase $|C|$ over the patch. Any extension that does not reduce $|C|$ must cover only the ten vertices incident with the pentagons. There is only one perfect matching for these ten vertices, and it is shown as a completion of the Kekulé structure in Figure 5.2(a). Note that this is a Clar chain of Type 3 between the two pentagons. Over the patch in this extension, $|A| = 5$ and $|B_2(K)| = 6$, $|B_1(K)| = 4$, giving $|B_1(K)|+2|B_2(K)| = 16$

Extension 2: The Kekulé structure in Figure 5.2(b) has $|A| = 8$ and $|B_2(K)| = 4$, $|B_1(K)| = 2$, giving $|B_1(K)|+2|B_2(K)| = 10$. While $|A|$ is not minimized, $B_2(K)$ and $B_1(K)$ are both smaller than in Extension 1. Extension 1 is the only extension that minimizes the Clar deficit, and that extension does not minimize the Fries deficit. Thus for this choice of void and Clar faces over a basic patch, any structure that



(a) Extension 1 minimizes the Clar deficit. Here $|A| = 5$ and $|B_2(K)| = 6$, $|B_1(K)| = 4$.



(b) Extension 2 minimizes the Fries deficit. Here $|A| = 8$ and $|B_2(K)| = 4$, $|B_1(K)| = 2$.

Figure 5.2: Extension 1 and Extension 2 on a basic patch where the Clar faces are pink and the void faces are blue.

contributes the maximum number of faces toward the Clar number over this patch cannot achieve the maximum number of benzene faces.

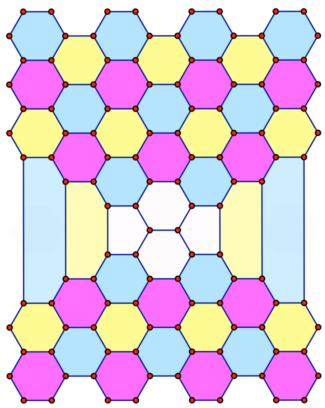
5.2.2 Extending Kekulé structures over basic patches with other choices for the void and Clar faces

We show that the choice for the void faces and faces in C described in Section 5.2.1 is the only case over such a patch for which $|A|$ and $|B_1(K)| + 2|B_2(K)|$ cannot be minimized simultaneously. There are five options remaining for the choice of void and Clar faces around the patch, and for each of these choices, only one extension is necessary to minimize both the Clar and Fries deficits.

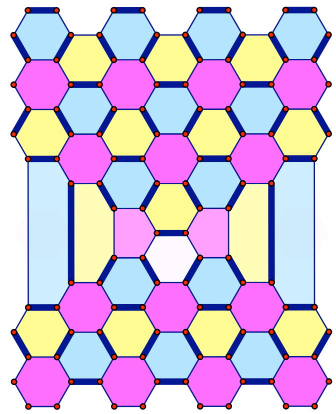
Suppose we let the blue faces be the void faces and the yellow faces be the Clar faces. Then the Kekulé structure in Figure 5.2(b) has a minimal Fries deficit of $|B_1(K)| + 2|B_2(K)| = 10$. Every yellow hexagon is a benzene face, so we also have a maximum number of faces contributing to the Clar count, with $|A| = 2$ (a Clar chain of Type 2).

Suppose that the void faces are in color class that includes the pentagons (here, the pink faces). Then the edges joining these faces complete a Kekulé structure over the patch, as seen in Figure 5.3(b). $|B_1| = |B_2| = 0$, so the number of benzene faces over the patch is clearly maximized. We must also choose a color class to be the Clar faces. Since all hexagons in the remaining two color classes are benzene faces, $|C|$ is also maximized over the patch for either choice. Thus the same Kekulé structure maximizes the number of Clar faces and the number of benzene faces over the patch.

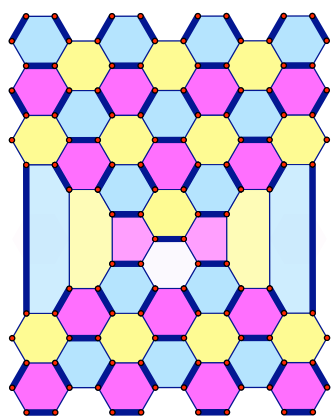
Suppose that the yellow faces are the void faces. Begin a partial Kekulé structure consisting of all edges that join two yellow faces. Extend this Kekulé structure so that all blue and pink hexagons are benzene faces as in Figure 5.3(c). For either choice of the Clar faces, $|C|$ is clearly maximized over this patch. $|B_1| = |B_2| = 2$, and any local change increases $|B_1(K)| + 2|B_2(K)|$ and decrease the number of benzene faces. Thus both the Clar and Fries deficits are minimized in this extension.



(a) A basic patch with a partial face 3-coloring.



(b) The pink faces represent the void faces.



(c) The Yellow faces are void.

Figure 5.3: Over a basic patch, we choose other color classes for the void and Clar faces and consider extensions of the resulting Kekulé structure.

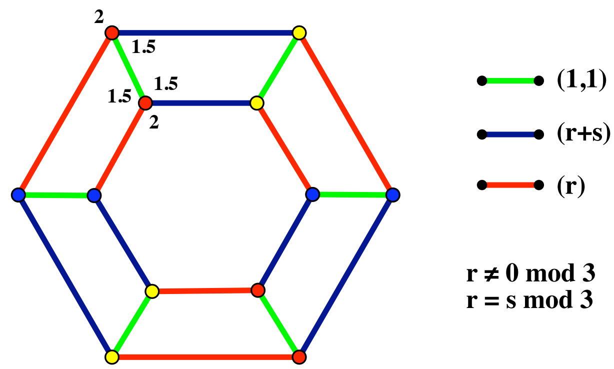


Figure 5.4: The vertices of this auxiliary graph represent the pentagons in a fullerene. The edges give the Coxeter coordinates of the segments between nearby pentagons.

We see that for every case except that described in section 5.2.1, the same Kekulé structure maximizes the number of faces contributing to the Clar number and the Fries number over the basic excluded patch.

5.3 Fullerenes over which the Clar and Fries numbers cannot be attained simultaneously

We saw in the previous section that there are six choices for the void faces and the Clar faces. We also saw that given an excluded patch, the Kekulé structure of all but one of these choices can be extended to the basic patch while simultaneously maximizing the number benzene faces and the number of Clar faces. To force the existence of a patch in which these parameters cannot be maximized by the same Kekulé structure, we need a fullerene with patches so that one of them is the exceptional patch for each the six choices. One infinite class of examples can be found in Graver's "Catalog of Highly Symmetric Fullerenes," pictured in Figure 5.4 with segment and angle types. The paper describes these parameters [6]. For our purpose, it is only necessary to understand that the vertices represent pentagonal faces and in our case the green edges represent the excluded patches which, in our example, are pairs of pentagons joined by a single edge. Furthermore, the partial face 3-coloring is different around each of the six excluded patches. Thus regardless of which of the six color choices for the color class of the void faces and the color class of the Clar faces is made, one of the six patches is such that one Kekulé structure maximizes the Clar number, while another Kekulé structure maximizes the Fries number, and the two parameters cannot be maximized simultaneously.

An example with $s = 1$, $r = 7$ is shown on the next page. In the next chapter, we show that a fullerene in this class with $r \geq 7$ is widely separated. Thus the Clar number is achieved by a Kekulé structure with Clar chains between pentagons together in basic patches. In this coloring, the red faces indicate the set containing C and the void set is contained in the blue color class. A pair of pentagons lies in a basic patch on each interior corner. The edges in A are represented by thick red edges and the remaining edges in the Kekulé structure are represented by thick blue edges. A blue arrow indicates the excluded patch over which the number of faces in

C and the number of benzene faces cannot be maximized simultaneously.

In the first figure, there are 272 benzene faces and there are 135 faces in C. In the second figure, there are 274 benzene faces and 134 faces in C. The first figure attains the Clar number but not the Fries number for the fullerene, and the reverse is true for the second. Hence the set of faces that attains the Clar number is not contained in a set of faces that attains the Fries number.

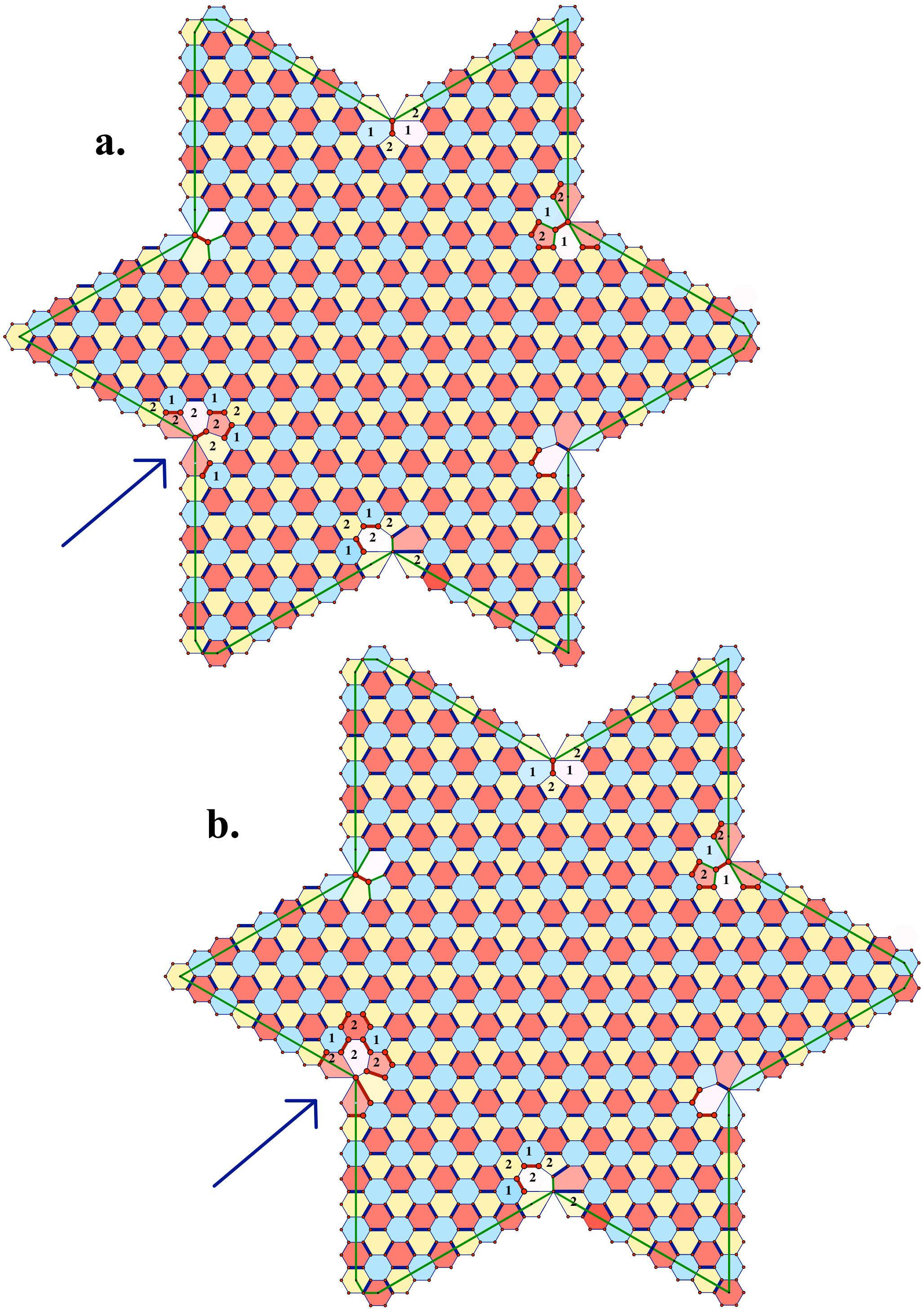
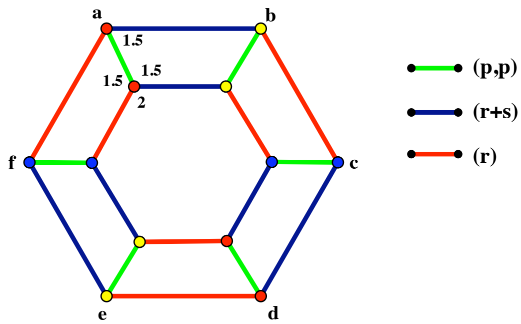


Figure 5.5: The Clar faces are red and the void faces are blue. An arrow indicates the patch over which the Fries and Clar deficits cannot be minimized simultaneously. Figure (a) minimizes the Clar deficit, Figure (b) minimizes the Fries deficit. The numerals represent faces in the sets B_1 and B_2.

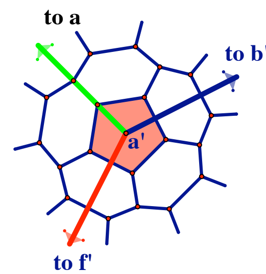
Chapter 6

Examples and Future Research

In this Chapter, we use the methods established in Chapters 2 and 3 to find the Clar number for several classes of fullerenes. The first two examples are taken from Graver's "A Catalog of All Fullerenes with Ten or More Symmetries" [6], and the Clar number is found when the parameters are such that we have pairs of pentagons that are widely separated. In the next section, we find the Clar number for Icosahedral Leapfrog fullerenes. Recall from Lemma 3.3 that for a fullerene with a Clar structure (C, A), the number of faces in C is $\frac{|V|}{6} - \frac{|A|}{3}$. We regularly use Lemmas 3.13, 3.14, and 3.15, which state that for a pair of pentagons joined by a segment with Coxeter coordinates (m, n) where $m \geq n$, a chain of Type 1 contributes m edges to A, a chain of Type 2 contributes $m + n$ edges to A, and a chain of Type 3 contributes $3m + 2$ edges to A.



(a) The vertices of this auxiliary graph represent the pentagons in a fullerene. The edges give the Coxeter coordinates of the segments between nearby pentagons.



(b) The pentagon a' in the fullerene Γ is represented by a red vertex of the auxiliary graph. Here we see the patch surrounding the pentagon a'.

Figure 6.1: Class of Fullerenes that generalizes the family described in Chapter 5. The pentagons are paired over green segments with Coxeter coordinates (p, p).

6.1 Two Classes of Widely Separated Fullerenes

We first find the Clar number for a family of fullerenes that generalizes the class given in Chapter 5. Figure 6.1(a) shows an auxiliary graph that represents a general fullerene in this class. The vertices of the auxiliary graph represent the twelve pentagons in the fullerene. The edges represent segments between nearby pentagons, and the colors code the Coxeter coordinates of these segments, defined by the parameters p, r and s. The numbers shown in Figure 6.1(a) represent angle types between two segments joined by a common pentagon, and the meaning of these numerals is shown in Figure 6.1(b). For a detailed description, see [6]. Different choices for parameters r, p, and s result in all fullerenes within this family. Graver showed in [6] that the number of vertices for a fullerene in this family is $12r^2 + 2s^2 + 12rs + 12p(2r + s)$. These fullerenes are widely separated when p is much smaller than r (an inequality is given shortly). In this case, the six open Clar chains must pair pentagons joined by segments with Coxeter coordinates (p, p), represented by green edges in Figure 6.1. There are several cases depending on the congruence classes of r and s modulo 3. We consider the congruence in Chapter 5 as well as the congruence resulting in a leapfrog fullerene.

Suppose that $r \not\equiv 0 \pmod 3$ and $r \equiv s \pmod 3$, giving $r + s \not\equiv 0 \pmod 3$. Let a, b, c, d, e, f be pentagonal faces on the fullerene in clockwise order as shown in Figure 6.1. In a partial face 3-coloring that avoids the Clar chains between segments with Coxeter coordinates (p, p), a and b are in different color classes since the segment between a and b has coordinate $(r + s)$, where $r + s \not\equiv 0 \pmod 3$. Similarly, the segment between b and c has Coxeter coordinate (r), and so b and c are in different color classes. Since $r \not\equiv 0$ but $r \equiv s \pmod 3$, $r + s \not\equiv r \pmod 3$. Thus a and c are in different color classes. We see that a and d are in one color class, b and e are in a second color class, and c and f are in a third color class. Each of these pentagons is paired over a segment with another pentagon and the Coxeter coordinates over these segments are (p, p), so each pair is in the same color class. We want to compare the segment types for faces in the same color class. Without loss of generality, say that a and d are red, b and e are yellow, and c and f are blue. Note that the Coxeter coordinates between a and the yellow face b are $(r + s)$, the coordinate between d and the yellow face e is (r). There are two possibilities for the position of the yellow color class around a red pentagon. The pentagon a and the pentagon d must each have a different position with respect to the yellow faces. Thus all six possible colorings around these segments are represented. The type of Clar chain only depends on the position of the faces in the color class containing C. This class is symmetric, and regardless of the color chosen, there are two chains of each of the three types. Thus the total contribution to A is $2p + 2(p + p) + 2(3p + 2) = 12p + 4$. The next closest pentagons that are unpaired have coordinates (r). This choice of Clar chains is widely separated when $r \geq \frac{12p+4}{2} - 2 = 6p$. For this class, the number of vertices is $|V| = 12r^2 + 2s^2 + 12rs + 12p(2r + s)$. Thus, when the chains are widely separated, the Clar number is

$$\frac{12r^2 + 2s^2 + 12rs + 12p(2r + s)}{6} - \frac{12p + 4}{3}$$

$$= 2r^2 + \frac{1}{3}(s^2 - 4) + 2rs + 4rp + 2p(s - 2)$$

Note that $s \not\equiv 0 \pmod 3$, and so $s^2 \equiv 1 \pmod 3$. Thus the above expression is always an integer.

Suppose that $r \equiv s \equiv 0 \pmod 3$. By Proposition 1.4, this is a leapfrog fullerene. All of the pentagons are in the same color class, say the set of red faces. We choose one of the remaining color classes to contain the set C in order to avoid having any chains of Type 3. Consider one pair of pentagons with Coxeter Coordinates (p, p) and choose C to be the color class that allows this chain to be of Type 1. This is possible because the chain type is defined by the position of the Clar faces with respect to the segment between the two pentagons. Once we choose the set C around the first segment, the types for the remaining segments are forced. As we go around this chain, the red color class remains the same (it is a perfect face-independent set) and the remaining two colors are transposed. Thus, at the next pair of pentagonal faces, the position of the remaining two color classes in relation to the pentagons has switched, and the segment is of Type 2. The segment types alternate between Type 1 and Type 2, so we have three chains of Type 1, each contributing p edges to A, and three chains of Type 2, each contributing $2p$ edges to A. The total number of edges in A is $9p$. Again, the Coxeter coordinates between the next closest unpaired pentagons is (r). The (p, p) Clar chains are widely separated when $r \geq \frac{9p}{2} - 2$. In this case, the Clar number is

$$\frac{12r^2 + 2s^2 + 12rs + 12p(2r + s)}{6} - \frac{9p}{3}$$
$$= 2r^2 + \frac{1}{3}s^2 + 2rs + 4rp + 2ps - 3p$$

Since $s \equiv 0 \pmod 3$, the expression is always an integer.

We compute the Clar number for another class of fullerenes with a different symmetry group, and the auxiliary graph for this class is pictured in Figure 6.2. Again, the vertices of the auxiliary graph represent pentagons. The five segments with arrows connect to a common pentagon. The fullerenes in this class are attained by choosing values for the parameters r and s. Graver showed in [6] that the number of vertices for a fullerene in this class is $24p^2 + 48pr + 20r^2$. The fullerenes are widely

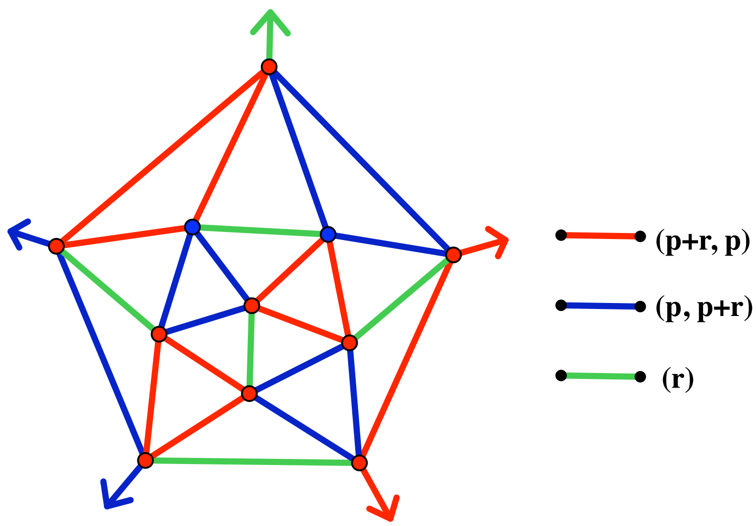


Figure 6.2: The auxiliary graph for a class of symmetric fullerenes. Vertices represent pentagons, edges show the Coxeter coordinates of segments between nearby pentagons. The pentagons paired over segments with coordinates (r).

separated when $r \equiv 0 \pmod 3$ and r is small in comparison with p (an inequality follows shortly). The paired pentagons are then connected by segments with Coxeter coordinates (r), and the six open Clar chains are between these pairs, represented by green edges in Figure 6.2. All coordinates between nearby pentagons are congruent modulo 3, so this is a leapfrog fullerene by Proposition 1.4. All of the pentagonal faces are in the same color class, so we choose the set C to be either of the two independent sets of faces that do not contain the pentagons. Then each of the Clar chains must be of Type 1 or Type 2. For segments with only coordinate (r), Type 1 and Type 2 each contribute r edges to A. Thus the total number of edges in A over the fullerene is $6r$. We see that these chains are widely separated if for any other pair of pentagons, one of the Coxeter coordinates is at least $\frac{6r}{2} - 2 = 3r - 2$. The next closest pairs have coordinates $(p + r, p)$ and $(p, p + r)$. Thus if $p \geq 2r - 2$, then chains with Coxeter coordinates (r) are widely separated. The number of vertices for fullerenes in this class is $|V| = 24p^2 + 48pr + 20r^2$, so the Clar number is

$$\frac{|V|}{6} - \frac{|A|}{3} = \frac{24p^2 + 48pr + 20r^2}{6} - \frac{6r}{3} = 4p^2 + \frac{10}{3}r^2 + 8pr - 2r.$$

The restriction that $r \equiv 0 \pmod 3$ ensures that this is always an integer.

These few examples were chosen to illustrate our computational approach to the Clar number. Using these techniques in conjunction with the Catalog [6], the Clar number can be easily computed for many infinite families of fullerenes. In the next section, we employ our theory to compute the Clar number for a family of fullerenes in which the pentagons are not widely separated.

6.2 Icosahedral Leapfrog Fullerenes

The natural generalization of C_{60} is the class of icosahedral leapfrog fullerenes. To construct an icosahedral fullerene, choose an equilateral triangle from the hexagonal tessellation with vertices at the centers of hexagons and copy this triangle onto each face of the icosahedron. The result is a fullerene with the twelve pentagonal faces at

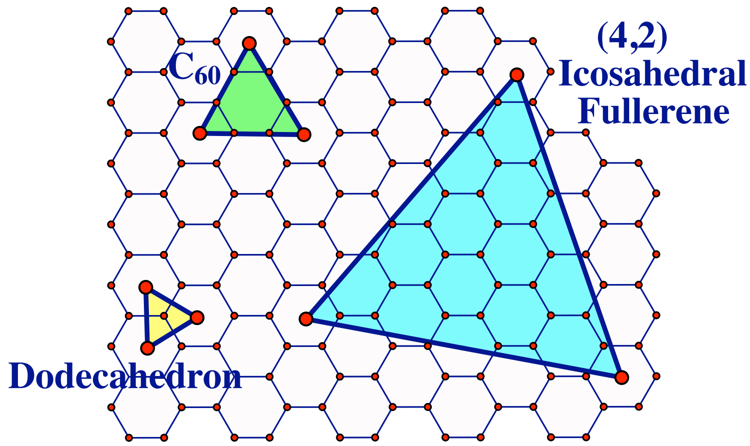


Figure 6.3: To form an icosahedral fullerene, replace each face of an icosahedron with an equilateral triangle from the hexagonal tessellation with vertices at the centers of faces.

the twelve vertices of the icosahedron. This construction was first given by Coxeter [2]. An icosahedral fullerene is uniquely determined by the Coxeter coordinates (m, n) of the sides of the triangle, and the icosahedral fullerene is a leapfrog fullerene exactly when m and n are congruent modulo 3.

Consider an icosahedral leapfrog fullerene with parameters (m, n) and assume without loss of generality that $m \geq n$. Since the fullerene is leapfrog, any pair of pentagons can be connected by a Clar Chain. The shortest segments between pentagons have Coxeter coordinates (m, n), and thus $6m$ is a lower bound for A, which would be achieved if we could pair pentagons with six Clar chains of Type 1. Attaining this lower bound for $|A|$ would show that the Clar number for Γ is $\frac{|V|}{6} - 2m$. We show that such a pairing is possible.

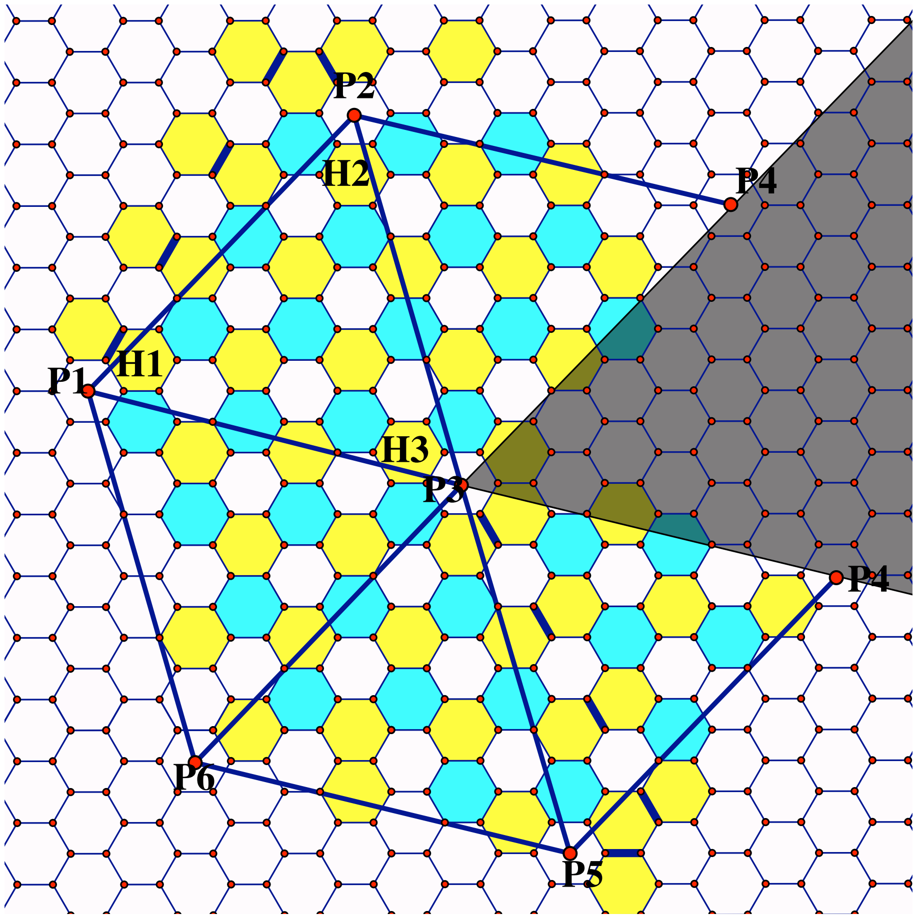


Figure 6.4: Five equilateral triangles that share P_3 as a vertex.

Theorem 6.1. *Suppose* Γ *is an icosahedral fullerene with parameters* (m, n) *where* $m \geq n$ *and* $m \equiv n$ *(mod 3). Then the Clar number for* Γ *is* $|C| = \frac{|V|}{6} - 2m$.

Proof. Since all of the segments between nearby pentagons are congruent modulo 3, the pentagons are all in one color class, say red, in any an improper face 3-coloring derived from a Clar structure. To attain the Clar number, we must choose the color class containing C to be one of the remaining two colors. Consequently, all chains are of Type 1 or Type 2. Choose a pair of pentagons P_1 and P_2 with Coxeter coordinates

(m, n), to connect with a Clar chain. We can then choose the color class for C so that the chain is of Type 1. We may assume that this is the blue color class, and begin a partial face 3-coloring. Now choose a pentagon P_3 that completes the equilateral triangle with P_1 and P_2. There are five equilateral triangles with a P_3 as a vertex, with edges $\{P_1, P_2\}$, $\{P_2, P_4\}$, $\{P_4, P_5\}$, $\{P_5, P_6\}$, $\{P_6, P_1\}$ in clockwise order (see Figure 6.4). The improper face 3-coloring in Figure 6.4 results when the Clar chain connecting P_1 and P_2 is of Type 1 and forces the chain connecting P_3 and P_5 to also be of Type 1. We now show that this holds in general.

Assume that $n \neq 0$. (If all the segments have coordinates (m), then Type 1 and Type 2 are the same, and any pairing will work). There is an (m, n) segment from P_3 to P_1; consider the $(m-1, n-1)$ segment contained in this segment between hexagons H_3 and H_1 adjacent to P_3 and P_1, respectively. The coordinates between these two faces are also congruent modulo 3, so these faces are in the remaining color class, say yellow. We have constructed a Clar chain of Type 1 between P_1 and P_2, and the face H_1 is incident with an edge of this Clar chain. The faces of the partial 3-coloring alternate yellow and blue around the red pentagon P_3. Thus as we reach the second face from H_3 on either side of the pentagon, both are in the yellow color class, and shares an edge of the Clar chain. This is a Clar chain of Type 1 between the pentagons P_3 and P_5.

If we choose Clar chains between adjacent pairs of pentagonal faces so that all nearby segments have this relationship, then each of the Clar chains can be of Type

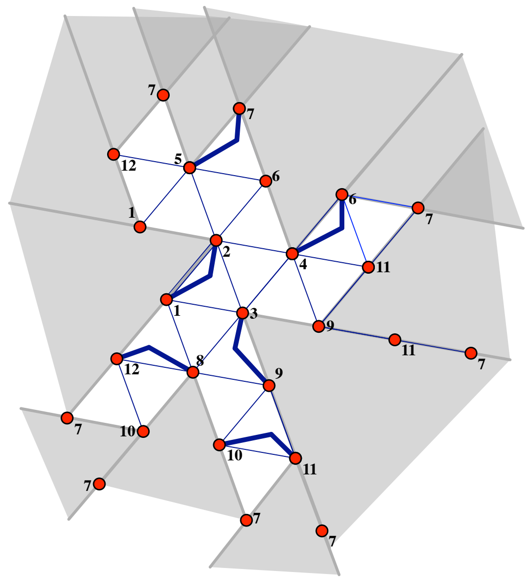


Figure 6.5: The Leapfrog Icosahedron with a pairing of pentagons, all of Type 1.

1 with length m. There are many such pairings, and one is shown for an arbitrary icosahedral fullerene in Figure 6.5. This set of chains meets the lower bound $|A| = 6m$ over the icosahedral fullerene, and so the Clar number is of Γ is $|C| = \frac{|V|}{6} - 2m$. $\square$

6.3 Future Research

A major area for future research is the general structure of chain decompositions. In particular, what is the Fries analog to Clar chains? We now understand non-interfering Clar chains, and can use them to find the Clar number for fullerenes with widely separated pairs of pentagons. The interaction between two or more chains is not understood; if chains share adjacent faces, the number of edges contributed to

A is often different from when the chains are non-interfering. As we saw in Figure 3.4, chains may also zigzag around pairs of pentagons, and the ability to connect two pentagons through a Clar chain may depend upon the relation of the chain to other pentagons.

As noted above, we can use Clar chains to find the Clar number for many classes of fullerenes with widely separated pairs of pentagons. This method could be applied to other classes of fullerenes to catalog the Clar number for large classes of fullerenes. We would like to have an analogous understanding of widely separated sets of four or six pentagons (we need only consider even groupings of pentagons, because we know that pairs must be connected by open Clar chains). Fullerenes with two widely separated sextets of pentagons would be a subset of the class of nanotubes. Nanotubes are fullerenes with two caps each containing six pentagons and separated by a cylinder of hexagons. We would like to distinguish between classes in which chains must connect pentagons in different caps and those for which each of the open chains can connect two pentagons within the same cap.

For fullerenes with widely separated pairs of pentagons, we have shown that any Clar structure that attains the Clar number does not include closed Clar chains other than those equivalent to chains of Type 3. It remains to be determined whether closed chains may exist more generally.

We know that there are fullerenes for which the Clar number and the Fries number cannot be attained by the same Kekulé structure; that is, there is no Kekulé structure K such that a set of faces $B_3(K)$ attaining the Fries number contains an independent subset attaining the Clar number. One open question would be to classify fullerenes that do satisfy this property. For example, it may be the case that in leapfrog fullerenes, the Fries and Clar number can always be attained from the same Kekulé structure.

In Chapter 2, we introduced chain decompositions and show that Clar and Fries schemes can be completed into Kekulé structures for decompositions with detached chains. We would like to show that these decompositions can be completed in general. The decomposition of a fullerene could also be used to find bounds for the Fries number. Under what restrictions does a chain decomposition result in the Fries number, and when does the same decomposition result in both the Clar number and Fries number?

Chain decompositions allowed us to find an improper face 3-coloring for fullerenes. This approach may lead to a similar result for planar graphs in general. A 3-regular plane graph contains open chains connecting pairs of faces of odd degree, and we can consider an improper face 3-coloring from the expansion of the edges of these chains as in Theorem 2.6.

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