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Internal Kekulé Structures for Graphene and General Patches

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Abstract

A *patch* is a plane graph whose boundary is an elementary circuit with only vertices of degree 2 or 3, with all degree-2 vertices restricted to the boundary. A *Kekulé structure* for a patch is a perfect matching. Not all patches admit a perfect matching; in this paper, we define *internal Kekulé structures*, which match all degree-3 vertices but not necessarily all degree-2 vertices. We consider internal Kekulé structures for general patches to determine what properties of Kekulé structures on hexagonal or graphene patches can be generalized to arbitrary patches, and when a graphene patch with a few *defective* (non-hexagonal) faces in the interior still "behaves like graphene" away from the defects.

1 Introduction

By a *patch* $\Pi = (V, E, F \cup \{f_O\})$ we mean a plane graph with one face f_O designated as the *outside face* such that all vertices have degree 2 or 3, with all degree-2 vertices restricted to the boundary of f_O; furthermore the boundary of f_O must be an elementary circuit which we call the *rim* of the patch. It is convenient to use the term *faces of* Π to mean the faces in F - excluding the outside face. A patch is said to be *even* if all of its faces have even degree. Since a plane graph cannot have just one face of odd degree, the outside face of an even patch is also even and so, for patches, being even and being bipartite are equivalent.

A *Kekulé structure* for a patch is a perfect matching. Some patches, including some even patches, may not admit a Kekulé structure. Specifically, it may be difficult, or not even possible, to include all degree-2 vertices on the rim in the matching. We avoid dealing with this problem on the rim and concentrate on *internal Kekulé structures*, that is, matchings that match all degree-3 vertices and some but not necessarily all degree-2 vertices. We say that a face f is *conjugated* by the internal Kekulé structure K if alternate edges of the boundary of f belong to K; clearly, only faces of even degree can be conjugated. We say that a face f is *void*, relative to internal Kekulé structure K, if no edge bounding f is in K.

At the recent conference, Computers in Scientific Discovery 7 (Computational Methods for Carbon Nanostructure Research), two interesting ideas concerning patches were raised. The first, discussed by Tomaž Pisanski, was: just how much of what we now know about Kekulé structures on hexagonal or graphene patches can be generalized to arbitrary patches? The second, discussed by Douglas Klein, was: when does a graphene patch with a few *defective* or *disordered* (non-hexagonal) faces in the interior still "behave like graphene" away from these defective faces? We will consider these questions in terms of internal Kekulé structures and the density of conjugated faces.

Lemma 1 *Let $\Pi = (V, E, F \cup \{f_O\})$ be a patch and K an internal Kekulé structure. Given a degree-3 vertex x, at most two of the faces at x can be conjugated and at most one of the faces at x can be void. Furthermore, if every face of Π is either conjugated or void then every degree-3 vertex of Π has exactly two of its faces conjugated and its third face void.*

Proof. Let f_1, f_2 and f_3 be the faces at the degree-3 vertex x; let e_i be the edge at x that does not bound f_i. Since exactly one of these edges is in K, we may assume that $e_3 \in K$ while $e_1, e_2 \notin K$. Hence e_1 and e_3 are consecutive edges bounding f_2, one of which is in K while the other is not. Hence f_2 could be conjugated but could not be void; similarly, f_1 could be conjugated but could not be void. But e_1 and e_2 are consecutive edges bounding f_3 neither of which is in K. Hence f_3 could not be conjugated but could be void. Furthermore if every face is either conjugated or void, then f_1 and f_2 must be conjugated and f_3 must be void. ■

We say that an internal Kekulé structure K is *perfect* if every face is either conjugated by K or void. We see by the lemma that an internal Kekulé structure is perfect when the conjugated faces (benzene faces in the case of benzenoids or graphene patches) are packed as densely as is possible - two meeting at each degree-3 vertex.

Lemma 2 *Let the patch* $\Pi = (V, E, F \cup \{f_O\})$ *be given.*

i. If K *and* K' *are perfect internal Kekulé structures for* Π*, then either* $K = K'$ *or* $K \cap K' = \emptyset$*. In the latter case the set of void faces of* K *and the set of void faces of* K' *are also disjoint.*

ii. If Π *has one or more odd faces, then* Π *admits at most one perfect internal Kekulé structure and, if it does, all odd faces are void in that Kekulé structure.*

iii. If Π *is even then* Π *admits at most three perfect internal Kekulé structures.*

Proof. (i) Let K and K' be perfect internal Kekulé structures for Π, let $e \in K \cap K'$ and let f be a face with e on its boundary. The face f must then be conjugated with respect to both K and K' and since the edges of K and K' must then alternate around f, K and K' must agree on the boundary of f. Now let f' be adjacent to f. If their common boundary edge e' is in $K \cap K'$ then f' is also conjugated in both K and K' and so K and K' also agree on the boundary of f'. If e' is not in $K \cap K'$ then the edges in K matching the endpoints of e' both bound f and therefore both are in K' also. It follows that the edges that bound f' and share an endpoint with e' do not belong to either K or K'. Hence in this case f' is void in both K and K' and K and K' agree on the boundary of f'. Since Π is the connected union of faces, once K and K' agree on one edge, they agree on the boundaries of the face or faces containing that edge and then on the boundaries of all adjacent faces and inductively they agree on the boundaries of all faces, i.e. $K = K'$. Finally, note that if f is a face of Π that is void for both K and K', then all edges with one endpoint on the boundary of f belong to both K and K' and, hence $K = K'$.

(ii) No odd face can be conjugated. Hence, if Π admits perfect internal Kekulé structures K and K', they both include the odd faces among their void faces and by (i), $K = K'$.

(iii) This result is easily checked if Π has just one face and so we assume that Π has at least one degree-3 vertex x. Since by (i) distinct perfect internal Kekulé structures are disjoint and each must include an edge at x, there can be at most three of them. ■

In fact, as we will prove in the next section, each even patch admits three distinct perfect internal Kekulé structures. This is clearly true for a graphene patch - a simply connected finite union of hexagons in the hexagonal tessellation of the plane. Such a patch inherits a unique (up to a permutation of colors) edge 3-coloring from the unique edge 3-coloring of the the hexagonal tessellation. One easily checks that each of these is a perfect internal Kekulé structure for the patch.

The problem of when a graphene patch or benzenoid is Kekuléan (admits a Kekulé structure) has been studied by H. Sachs [7], [4], Cyvin and Gutman [1], and later by the authors of this paper [2], [3]. In [2], we showed that if a graphene patch is Kekuléan then each of the three perfect internal Kekulé structures can be extended to a Kekulé structure for the entire patch; furthermore the adjustments necessary occur on, or very near, the rim - leaving the perfect internal Kekulé structure intact away from the rim. Since the problems with matching the rim vertices have already been thoroughly investigated, we will ignore the problem of extending perfect internal Kekulé structures to the entire rim. We should note that given a perfect internal Kekulé structure for a patch, only the degree-2 vertices on the boundaries of the void faces and the rim remain unmatched. In some cases, they may be easily paired up; in other cases this is not so easily done or simply impossible.

2 Perfect internal Kekulé structures for even patches

Lemma 3 *The faces of an even patch admit a proper face 3-coloring.*

Proof. Let $\Pi = (V, E, F, f_O)$ be an even patch. As we have already noted, Π is bipartite and we will assume that the vertices of Π have been colored black and white to identify the bipartition. A proof that every trivalent, bipartite plane graph is face 3-colorable appears in Saaty and Kainen [6]. Hence, if Π has only degree-3 vertices, then the entire plane graph, including the outside face, is face 3-colorable.

Now assume that Π has some degree-2 vertices. We cannot apply the Saaty and Kainen theorem directly, but we may alter Π to get a trivalent patch that leads to a face 3-coloring of Π. The first step is to replace paths of degree-2 vertices. Let $v_0, e_1, v_1, \ldots, v_k$, $k > 1$, be a path on the rim where v_0 and v_k have degree 3 while $v_1, \ldots, v_{k-1}$ have degree 2. If k is odd then one of v_0 and v_k is white and the other is black so we may replace this path by a single edge; if k is even then v_0 and v_k are assigned the same color: when $k = 2$, we leave this path unaltered; when $k \geq 4$, we replace this path by a path of length 2, coloring the new center vertex different from v_0 and v_k. See the leftmost graph in Figure 1.

This modified graph now has only "isolated" degree-2 vertices. If there are both white and black isolated degree-2 vertices, there must be a black-white pair contiguous to one

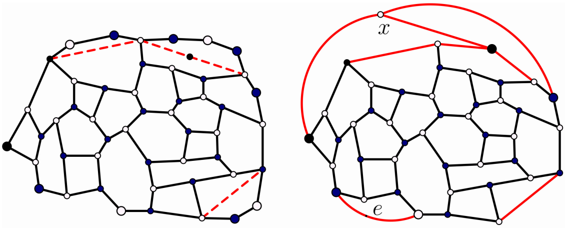

Figure 1: Even Patch modified to be trivalent

another along the rim - join them by an edge through the outside face. See edge e in the rightmost graph in Figure 1. Apply this modification to the resulting graph and repeat until all remaining isolated degree-2 vertices are assigned the same color - say black. Now all white vertices have degree 3 and so the number of edges is a multiple of 3. It follows that the number of isolated degree-2 black vertices is a multiple of 3. Partition these isolated degree-2 black vertices into contiguous sets of 3 and attach a new degree-3 white vertex in the outside face to each set - vertex x in the figure.

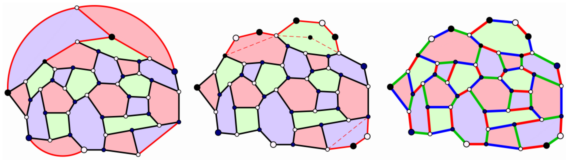

Figure 2: Edge/Face 3-coloring of an Even Patch

We now have a trivalent, bipartite patch which is therefore face 3-colorable. Furthermore, each face of Π can be identified with a face in this new graph, giving the face 3-coloring for Π that we seek. See Figure 2. ■

In general, such face 3-colorings of even patches are unique up to a permutation of colors; in these colorings the faces bounding say a green face alternate red - blue. Ambiguity arises when the face around such a green face are not adjacent to one another: consider three squares in a row colored red, green and red or blue for the third face. The easiest way to remove the ambiguity is to extend the face 3-coloring to the edges. By an *face-edge 3-coloring*, we mean a coloring of the faces and edges with 3 colors so that the following *coloring rules* are satisfied.

i. If a face is assigned color c_1, the edges bounding it are alternately assigned colors c_2 and c_3.
ii. Each edge and its bounding face or faces are all assigned different colors.

With this definition, one can easily verify that the face/edge 3-coloring of an even patch is unique up to a permutation of the colors. In the example of the three squares, the third face must be red since the edges around the green face alternate red and blue. Another very useful *coloring rule* involving vertex coloring of an even patches, easily proved from the first two rules, is:

iii. If at a white vertex the face or edge colors appear in clockwise order, then the face and edge colors appear in clockwise order around all white vertices and in counterclockwise order around all black vertices.

With these coloring rules we may now prove:

Theorem 1 *Let* Π *be an even patch. Then*

i. Π *admits an edge-face 3-coloring that is unique up to a permutation of the colors.*

ii. The edge color classes of this edge-face 3-coloring are three distinct perfect internal Kekulé structures for Π *and these are the only perfect internal Kekulé structure for* Π*.*

Proof. (i) We start by assuming that the intersection of any face with the rim is empty or a simple path. By Lemma 3, Π admits a face 3-coloring. Each internal edge of Π bounds two faces and they are assigned different colors. Hence we must color this edge with the third color. One easily sees that the coloring rules (i) and (ii) hold for these internal edges. Now consider any face with one or more edges on the rim. Since the rim edges of this face form a single path and since the face is even, the alternate coloring of its internal edges extends uniquely to the edges on this path.

Assume that Π admits a face f whose boundary has a disconnected intersection with the rim. We proceed by induction assuming that the theorem holds for all patches with fewer faces. We easily see that we can decompose Π into two smaller patches Π_1 and Π_2 that intersect in f and its boundary, see Figure 3. By the induction hypothesis each of these patches admits an edge-face 3-coloring. By permuting the colors, we can assume that f is assigned the same color in both patches (green in the figure). It may be possible that the edge colors on the boundary of f do not match. In this case, interchanging the other two colors (red and blue in the figure) in one of the patches (Π_2 in the figure) gives a perfect color match on the intersection of Π_1 and Π_2 and the required edge-face 3-coloring for Π.

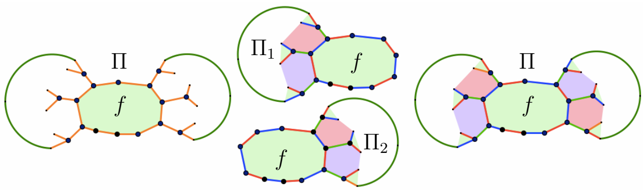

Figure 3: Building a Kekulé structure from one odd face

(ii) Since each degree-3 vertex is the endpoint of an edge from each color class, the edge set of each color class is an internal Kekulé structure and it follows directly from the coloring rules that these are perfect internal Kekulé structures. That there are no other perfect internal Kekulé structures follows from Lemma 2. ■

Corollary 1 *If Γ is a graphene patch with disordered faces only of even degree, then away from these disordered faces, the perfect internal Kekulé structures for Γ are the same as if it were pure graphene.*

Next we investigate graphene patches with a few disordered faces in their interiors, some of which are of odd degree. To study such patches we choose a simply connected subpatch in the interior containing all disordered faces and delete it. To be specific, a subpatch must be a patch, that is, its rim must be an elementary circuit and to be in the interior, its rim must be disjoint from the rim of the initial patch. By deleting it, we mean deleting all vertices, edges and faces in its interior leaving a single face f_I whose boundary is the rim of the subpatch. In the next two sections, we investigate the perfect internal Kekulé structures of the remaining annular patch and then consider extending perfect internal Kekulé structures of the annular patch to the entire patch.

3 Annular patches

By an *annular patch* $\Theta = (V, E, F \cup \{f_O, f_I\})$ we mean a plane graph with two non-adjacent faces f_O, designated as the *outside face*, and f_I, designated as the *inside face*, such that all vertices have degree 2 or 3, with all degree-2 vertices restricted to the boundaries of f_O and f_I. Again, a matching that matches all degree-3 vertices and some but not necessarily all degree-2 vertices is called an *internal Kekulé structure* for the annular patch and a *perfect internal Kekulé structure* of the annular patch is one in which all faces are either conjugated or void. We restrict our attention to annular patches that only contain faces (excluding f_O and f_I) of even degree. If one, and hence both, of f_O and f_I have even degree, Θ is bipartite; otherwise both f_O and f_I have odd degree and Θ is not bipartite. Identify a simple path joining a vertex on the *inner rim* (the boundary of f_I) to a vertex on the *outer rim* (the boundary of f_O). Duplicating and separating the copies of this path yields a new even patch - see Figures 4, 5 and 6. By Theorem 3, this new patch admits three perfect internal Kekulé structures. the natural questions is: do any or all of these internal Kekulé structures match up when the patch is glued back together to reform the annular patch?

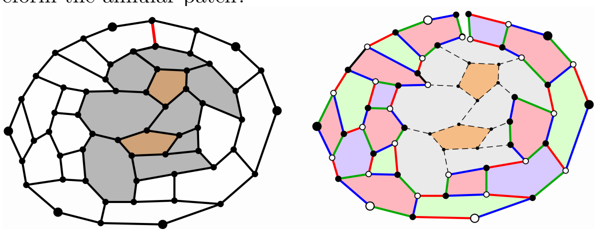

Figure 4: Annular patch obtained by deleting a subpatch containing two odd faces and an edge/face 3-coloring of the split annular patch.

If the number of faces of odd degree in the subpatch is even, then the inner, and hence the outer, rim is even and the annulus is bipartite. If we start at one copy of the splitting path and color the faces and edges around the split annulus using the coloring rules, this gives a face/edge 3-coloring of the even patch. Because the patch is bipartite, the vertex colors match on the split path. By coloring rule (iii), the face and edge color classes rotate in the same order around vertices of the same color. Starting at x_0 on the outer rim, if the right and left coloring of the edge joining x_0 to x_1 are the same then the orientations must agree at x_1 and the colorings will match on the edge (x_1, x_2) and inductively they will match along the entire splitting path. Similarly, if the right and left coloring of the edge joining x_0 to x_1 are the different then the orientations must disagree at x_1 and the colorings will differ on the edge (x_1, x_2) and inductively they will differ along the entire splitting path. Hence there are just two possibilities: either the colorings on either side of the splitting patch match and the annulus admits all three perfect internal Kekulé structures (Figure 4) or the colorings do not match and the annulus admits no perfect internal Kekulé structure (Figure 5).

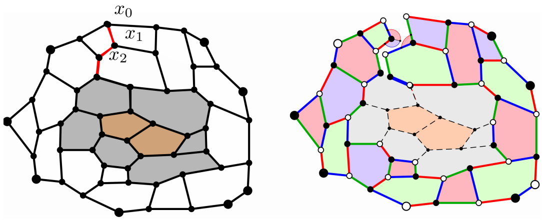

Figure 5: Odd faces: colors around the annulus not matching.

If the number of faces of odd degree in the subpatch is odd, then both rims are odd and the annulus is not bipartite. Specifically, if we color the vertices of the split annulus black and white, the vertices along the splitting path will be assigned opposite colors from each side (Figure 6). If we start at one copy of the splitting path and color the faces and

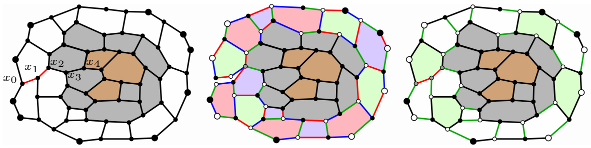

Figure 6: Odd faces: 1 color around the annulus matching.

edges around the split annulus using the coloring rules, we have that orientations of the face and edge colors are opposite when we get back to the splitting path. Starting at x_0 on the outer rim, if the assigned colors are different on the edge (x_0, x_1) (red and blue in Figure 6), then the two orientations will assign the same two colors, in reverse order, to another edge at x_1 and the third color from both orientations to the remaining edge. In the example in the figure, (x_0, x_1) is assigned blue from the right and red from the left; (x_1, x_2) is assigned red from the right and blue from the left; (x_2, x_3) is assigned green from both the right and left; and (x_3, x_4) is assigned blue from the right and red from the left. Moving from edge to edge along the splitting path, the same two colors are reversed from left to right while the third color is preserved. Hence exactly one of the color classes of faces and edges will match giving exactly one perfect internal Kekulé structure (Figure 6) for the annulus. We have proved:

Theorem 2 *Let* $\Theta = (V, E, F \cup \{f_O, f_I\})$ *be an annular patch.*

i. If Θ is bipartite then either Θ admits three distinct perfect internal Kekulé structures or no perfect internal Kekulé structures.

ii. If Θ is not bipartite then Θ admits exactly one perfect internal Kekulé structure.

4 Extension to the interior

The final question is: Given an annular patch obtained by deleting a subpatch containing some odd faces, can a perfect internal Kekulé structure for an annulus be extended to the deleted subpatch? The answer is yes; it follows from the Extension Theorem which we are about to prove. Assume that the annulus admits a perfect internal Kekulé structure, K. Our first step is to enlarge the central subpatch by moving any non-void faces of the annular patch that bound the subpatch into the subpatch. For example, the face f_3 in Figure 7 could have been included in the annular patch and is now transferred to the subpatch. The inner rim of the adjusted annular patch now consists of an alternating sequence of boundary segments of void faces and edges from K.

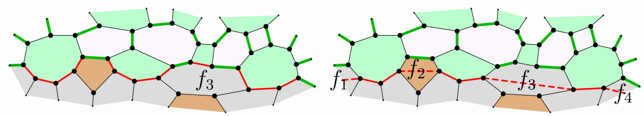

Figure 7: Extension of a perfect Kekulé structure for the annulus to the interior.

We have pictured a section of the new rim on the left in Figure 7, coloring the non-Kekulé edges of the new rim red. The degree-2 vertices of the new subpatch lie in paths of alternating red and green edges. On the right in the figure, we have replaced such paths by new edges, the red dashed edges, splitting some faces of the subpatch (faces $f_1, \ldots, f_4$). We now split the patch along this new boundary consisting of the solid and dashed red edges. The new annulus has all of its internal vertices matched by $\mathcal{K}$ and none of the vertices on its inner rim matched. The new inner subpatch is now trivalent. So by Petersen's theorem [5], this new inner subpatch admits a perfect matching. Combining this perfect matching with $\mathcal{K}$ gives a perfect matching for the entire patch with the dashed red edges included. See Figure 8.

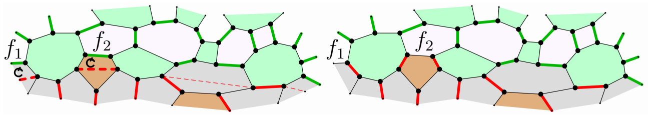

Figure 8: Extension of a perfect Kekulé structure for the annulus to the interior.

Our final step is to alter this matching to eliminate the dashed red edges. Those dashed red edges that do not occur in the matching are simply discarded. But some may occur in this matching. As we noted above, each dotted edge splits one of the original faces into two faces. We note that when a dashed edge is included in the matching, the part of the split face in the annulus is conjugated. Hence we may replace the edges of the matching that bound that face by the other edge bounding that face resulting in a matching that now does not include the dashed edge. Hence we may remove all dashed edges and have a matching that is internally perfect on the annulus, except for a few faces bounding central patch. In Figure 8, faces f_1 and f_2 that bound split faces were conjugated until the splitting edges were deleted. We have proved:

Theorem 3 *Let* Π *be a patch with a central patch containing all faces of odd degree, let* $\mathcal{K}$ *be a perfect internal Kekulé structure for the annular patch surrounding this central patch. Then* $\mathcal{K}$ *with a few possible alterations on faces bounding the central patch may be extended to an internal Kekulé structure for* Π.

In Figure 9 we illustrate this method by extending the perfect internal Kekulé structure for the annular patch in the example from Figure 6 to the interior - including the three odd faces.

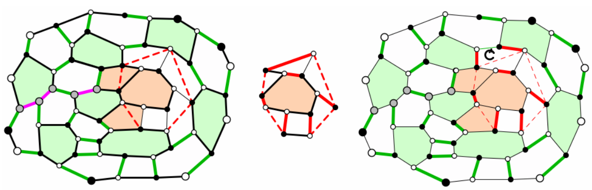

Figure 9: An extension for the example in Figure 6.

5 Conclusions and comments

Our first conclusion mentioned earlier is that all even patches behave like graphene in that they admit three perfect internal Kekulé structures. In particular, a graphene patch with a few defective even faces admits three perfect internal Kekulé structures that are identical to those of pure graphene away from the defective faces, see Figure 10.

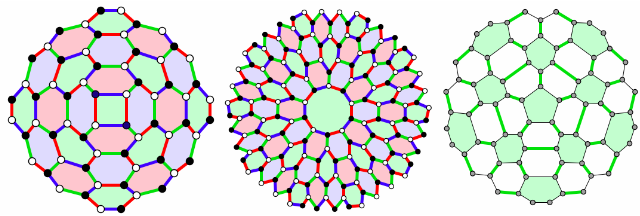

Figure 10: Graphene with one defective face.

Our second conclusion is that a graphene patch with a few defective faces, an odd number of which are of odd degree, admits exactly one internal Kekulé structure (for the entire patch) that is a perfect internal Kekulé structure for the annular patch away from the defective faces. See Figure 9. Our third conclusion is that a graphene patch with a few defective faces, an even number of which are of odd degree, either admits three internal Kekulé structures (for the entire patch) that are perfect internal Kekulé structures for the annular patch away from the defective faces or admits no internal Kekulé structures (for the entire patch) that are perfect internal Kekulé structure for the annular patch away from the defective faces.

It is actually rather easy to deduce which case holds by examining the boundary. Given a patch, add a pendant vertex in the outer face to every degree-2 vertex on the rim. Now select vertex on its rim, color that vertex white and color its edges red, blue and green in clockwise order. Moving clockwise around the rim, color the next vertex black and complete the coloring of the edges at that vertex using the counterclockwise orientation; the next vertex on the rim will be colored white and its edges colored using the clockwise orientation. We continue in this way until we return to the initial vertex.

i. If the vertex colors match and the edge colors match, then the number of odd faces in the patch is even (perhaps 0) and, if they can be isolated in a subpatch in the interior, the resulting annular patch admits three perfect internal Kekulé structures each of which extends to an internal Kekulé structure for the entire patch.

ii. If the vertex colors match but the edge do not colors match, then the number of odd faces in the patch is even, but not 0, and there will be no perfect internal Kekulé structures for the annular patch obtained by deleting any internal subpatch.

iii. If the vertex colors do not match then one of the edge colors must match, the number of odd faces in the patch is odd and, if they can be isolated in a subpatch in the interior, the resulting annular patch admits exactly one perfect internal Kekulé structure (of the matching edge color) which then extends to an internal Kekulé structure for the entire patch.

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