MATCH
Communications in Mathematical and in Computer Chemistry

MATCH Commun. Math. Comput. Chem. **84** (2020) 239-248

ISSN 0340 - 6253

The Lower Bound of Kekulé Count of Fullerenes

Jin Qian[1,2], Heng Liang[*†1], Fengshan Bai[1]

[1] *Department of Mathematical Sciences, Tsinghua University, Beijing, 100084, P. R. China*
[2] *Department of Mathematics, Northeastern University, Shenyang, 110819, P. R. China*

(Received November 15, 2019)

Abstract

A fullerene graph is a planar cubic graph with only pentagonal and hexagonal faces. It has been proved that fullerene graphs have exponentially many perfect matchings. The lower bound for this number has been studied in the last 20 years. The best known result is $2^{\frac{n-380}{61}}$, which is given in [13] by using the four color theorem. We generalize the structure using in [13] and obtain the improved lower bound $2^{\frac{n-1820}{47.29}}$.

1 Introduction

The fullerenes have been a hot topic over the last 30 years. In the chemical graph theory, the fullerenes could be modeled with graphs. In which, the vertices represent the carbon atoms and the edges represent the bonds between adjacent atoms. This gives cubic graphs, which are planar with only pentagonal and hexagonal faces. The set of double bonds in fullerene is called a Kekulé structure which is also a perfect matching in a fullerene graph. The number of Kekulé structure is called Kekulé structure count, denoted by K, which also represents the number of perfect matching in fullerene graphs. If it is incident with three edges in a perfect matching, the hexagonal face is resonant hexagon in the fullerene graph G. Kekulé structure count is a meaningful index which is related to the stability

*E-mail address: liangh@mail.tsinghua.edu.cn,
†Supported by National Science Foundation of China 11771243 and 11771245

of fullerene [1–6]. If all the pentagons in a fullerene are not adjacent, this is called the isolated-pentagon rule(IPR). Most stable fullerenes meet the isolated-pentagon rule well.

The empirical results suggest that the number of perfect matchings in fullerene graphs increases exponentially with the number of vertices [7]. It was proved that the general lower bounds of Kekulé count are linear in the number of vertices [8]. If fullerene contains a nontrivial cyclic-5-edge cutset, the number of perfect matchings is at least $15 \cdot 2^{\lfloor \frac{n}{20} \rfloor}$ which had been proved by Kutnar and Marušič [9]. A graph is said to be cyclic k-edge-connected, if at least k edges must be removed to disconnect it into two components, each containing a cycle. Such a set of k edges is called a cyclic-k-edge cutset and it is called a trivial cyclic-k-edge cutset if at least one of the resulting two components induces a single k-cycle. And then Došlić and Kardoš et al present that fullerene graphs have exponentially many perfect matchings [10–13]. The best known result is given in [13] as

$$K > 2^{\frac{n-380}{61}} \ . \tag{1}$$

In this paper, we show that the bound can be improved by generalizing the method in [13].

In the next section, we present the detailed proof of the Kekulé count lower bound. In the last section, some discussions will be addressed.

2 Main results

Let G_n be a molecular graph of n carbon atoms Fullerene, G_n^* be the dual graph of G_n. G_n is a 3−regular graph of n vertices and $\frac{3n}{2}$ edges which construct 12 pentagon faces and $(\frac{n}{2} - 10)$ hexagon faces. Such graphs exist on all even $n \geq 20$ except $n = 22$ in the classical definition. The main research graph is G_n^* in this paper. We first introduce three definitions that are used in the proof.

Definition 2.1. *If two vertices $v_i, v_j \in G_n^*$ have an edge connected in the dual graph of fullerene, the **distance** between v_i and v_j is defined as $dist(v_i, v_j) = 1$ in G_n^*; otherwise the $dist(v_i, v_j)$ is defined as the length of the shortest path between v_i and v_j.*

Definition 2.2. *For any hexagonal face f of G_n, the **k-layers neighborhood** $C_k(v)$ of the corresponding vertex v in the dual graph G_n^* is a set of vertex in G_n^*. The set $C_k(v)$ satisfies the following three conditions.*

(1) $dist(v, v') \leq k$, $v' \in C_k(v)$ and $v' \in G_n^*$;

(2) Each corresponding face of v' is a hexagonal face in G_n;

(3) For any pentagon face p of G_n with the corresponding vertex u in the dual graph G_n^*, $dist(v, u) > k$.

Definition 2.3. *For any hexagonal face f of G_n, the* ***Generalized 2k-layers neighborhood*** *$C'_k(v)$ of the corresponding vertex v in the dual graph G_n^* is a set of vertex in G_n^*. The set $C'_k(v)$ satisfies the following two conditions.*

(1) $dist(v, v') \leq 2k$, $v' \in C'_k(v)$ and $v' \in G_n^*$;

(2) For any pentagon face p of G_n with the corresponding vertex $u \in C'_k(v)$ in the dual graph G_n^*, $dist(v, u) > k$.

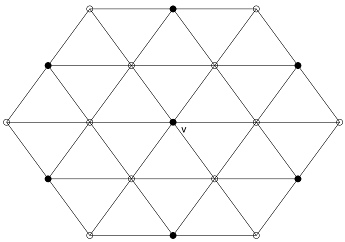

Figure 1. Partially colored two-layer neighborhood.

In a two-layers neighborhood of v, every vertex is a hexagon face of the G_n. The distance between each vertex of the two-layers neighborhood and v is not more than 2. If part of the vertices are colored, other outer vertices can take an arbitrary three colors under the condition that adjacent vertices take different colors [13]. As shown above in Figure 1. In a neighborhood of v where the distance is not more than 5, every vertex is a hexagon face of the G_n. All vertices form a five-layers neighborhood $C_5(v)$. A part of the vertices are colored $c(v)$, as shown below in Figure 2. We want to prove that each v five-layers neighborhood $C_5(v)$ whose part of the vertices are colored also has the same conclusion as two-layers neighborhood.

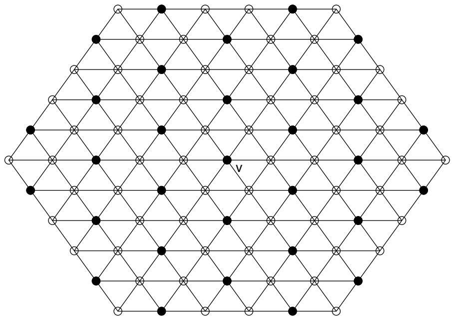

Figure 2. Partially colored five-layer neighborhood.

Then, we will prove our main results. The following Theorem 2.1 and 2.2 illustrative the coloring problem on the outer layer. Based on these conclusions, the improved lower bound of Kekulé count of fullerenes is presented in Theorem 2.3. Theorem 2.4 shows the generalized result.

Theorem 2.1. *Under the condition that the adjacent vertices are colored differently, the non-colored vertices on the outer layer of $C_5(v)$ can choose any other three colors.*

Proof. Six 2-layer neighborhoods located inside 1-6 locations of $C_5(v)$, as shown below in Figure 3. For example: location 1 is the two-layers neighborhood on the upper left and location 2 is the two-layers neighborhood on the upper right in the figure. Considering the two-layers neighborhood of location 1, the non-colored vertices on the outer layer can choose any other three colors. Assume that the color of vertex $D1$ has been selected, the color of the outer layer vertex $D2$ which is adjacent to the vertex $D1$ can be selected from the other two colors of the four colors. Each color of the vertex $D2$ corresponds to a different colored structure. In the two-layers neighborhood of location 2, the color of the outer layer vertex $D1$ has been determined at this time and the color of other peripheral non-colored vertices can be arbitrarily selected. According to the same principle, it can be seen that the non-colored vertices on the outer layer of the five-layers neighborhood $C_5(v)$ can choose any other three colors. ∎

Therefore, by the Four Color Theorem [14–16], we can extend the partially colored five-layers neighborhood to the entire dual graph G_n^*.

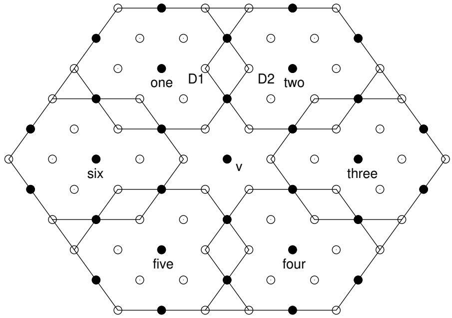

Figure 3. The configuration $C_5(v)$ contains six two-layers neighborhood.

In a neighborhood of any $v \in V$ where the distance is not more than $3k+2$, every vertex is a hexagon face of the G_n. All vertices form a $(3k+2)$-layers neighborhood $C_{3k+2}(v)$. A part of the vertices are colored $c(v)$. The coloring law is as follows. Firstly, the v is colored $c(v)$. In the two-layers neighborhood of v, the colored form of some vertices is shown in Figure 1. Then the just colored vertices are used as the two-layers neighborhood. The colored form of some vertices is shown in Figure 1. Finally, the process will stop until the colored vertices reach the edge of $C_{3k+2}(v)$.

Theorem 2.2. *Under the condition that the adjacent vertices are colored differently, the non-colored vertices on the outer layer $3k+2$ of $C_{3k+2}(v)$ can choose any other three colors.*

Proof. If V is a Generalized $(6k+4)$-layers neighborhood of $\{v\}$, $(3k+2)$-layers neighborhood of any $v \in V$ contains $6k$ two-layers neighborhood that are located between $3k$ layer and $3k+2$ layer. According to Theorem 2.1, it can be seen that the non-colored vertices on the outer layer of the $(3k+2)$-layers neighborhood $C_{3k+2}(v)$ can choose any other three colors. ■

Therefore, by the Four Color Theorem, we can extend the $(3k+2)$-layers neighborhood to the entire dual graph G_n^*.

Theorem 2.3. *If the fullerene graph G_n does not contain the nontrivial cyclic-5-edge cutset structure, the number of perfect matchings is at least $2^{\frac{n-1820}{47.29}}$.*

Proof. Let $U = \{u_1, \cdots, u_{12}\}$ represent the vertex set of the pentagons. We will create a vertex set V of the hexagons which needs to meet two conditions:

(1) When any $v, v' \in V$ and $v \neq v'$, $dist(v, v') \geq 11$;

(2) When any $v \in V$ and $u \in U$, $dist(v, u) \geq 6$.

Assume $V_0 = \phi$, we color the vertices white that the distance from $u_i (i = 1, \cdots, 12)$ is not more than 5. The rest of the vertices are colored black in G_n^*. The number of white vertices colored by each u_i is at most $1 + \sum_{j=1}^{j=5} 5j = 76$. Therefore, the maximum number of white vertices is $12 \cdot 76 = 912$. Choose any black vertex and add it to the creation point set, $V_k := V_{k-1} \bigcup \{v_k\}$. We colore the vertices white that the distance from v_k is not more than 10. The number of white vertices colored by each v_k is at most $1 + \sum_{j=1}^{j=10} 6j = 331$. The process terminates until there is no black vertex. At this time, V_k is V. Then

$$|V| \geq \frac{\frac{n}{2} + 2 - 912}{331} = \frac{n - 1820}{662}. \tag{2}$$

The four colored vertices are marked as A, B, C and D respectively in G_n^*. There are only six edge forms among them: $A - B$, $A - C$, $A - D$, $B - C$, $B - D$ and $C - D$. We mark the edges $A - B$ and $C - D$ as 1, the edges $A - C$ and $B - D$ as 2, the edges $A - D$ and $B - C$ as 3. It has been proved that all the 1 edges constitute a perfect match for G [13]. The same is true for 2 and 3.

Take any point of $v_i \in V$. The points with the distance of v_i no more than 5 constitute a five-layers neighborhood $C_5(v_i)$. The points with the distance of v_i no more than 10 constitute a Generalized ten-layers neighborhood. Each non-colored vertex inside $C_5(v_i)$ is connected to three colored vertices. Known by the dual graph, each point corresponding to a face in the G. The face is a resonant hexagon in one of the three matchings formed by the edges of 1, the edges of 2, and the edges of 3.

The number of resonant hexagons inside $C_5(v_i)$ is $6 + \sum_{j=1}^{j=3} 6j = 42$. So there are a total of $42|V|$ resonant hexagons,

$$42|V| \geq \frac{n - 1820}{662} \cdot 42 = \frac{n - 1820}{331} \cdot 21. \tag{3}$$

Then, the number of resonant hexagons in one of the matchings is at least

$$14|V| \geq \frac{n - 1820}{331} \cdot 7 = \frac{n - 1820}{47.29}. \tag{4}$$

The resonant hexagons in one color class are always disjoint that has been proved [13]. So the number of perfect matchings is at least $2^{\frac{n-1820}{47.29}}$. ■

In the proof process just now, if the set V is regarded as the Generalized ten-layers neighborhood of $\{v_i\}$, V can also choose Generalized $(6k+4)$-layers neighborhood, $k = 0, 1, 2, \cdots$. Now we take the general structure that is the Generalized $(6k+4)$-layers neighborhood to prove the similar conclusion. Follow the same method.

Theorem 2.4. *If the fullerene graph G_n does not contain the nontrivial cyclic-5-edge cutset structure, the number of perfect matchings is at most $2^{\frac{n}{30}}$.*

Proof. Let $U = \{u_1, \cdots, u_{12}\}$ represent the set of vertices of the pentagons. We will create a vertices set V of the hexagons which needs to meet two conditions:

(1) When any $v, v' \in V$ and $v \neq v'$, $dist(v, v') \geq 6k+5$;

(2) When any $v \in V$ and $u \in U$, $dist(v, u) \geq 3k+3$.

Assume $V_0 = \phi$, we color the vertices white that the distance from $u_i (i = 1, \cdots, 12)$ is not more than $3k+2$. The rest of the vertices are colored black in G_n^*. The number of white vertices colored by each u_i is at most

$$1 + (5+10) + \sum_{j=1}^{j=k} 5(3j+3j+1+3j+2) = \frac{45k^2+75k+32}{2}.$$

Therefore, the maximum number to be colored white vertices is

$$12 * \frac{45k^2+75k+32}{2} = 6(45k^2+75k+32).$$

Choose any black vertex and add it to the creation point set, $V_k := V_{k-1} \bigcup \{v_k\}$. We color the vertices white that the distance from v_k is not more than $6k+4$. The number of white vertices colored by each v_k is at most

$$1+(6+12+18+24)+\sum_{j=1}^{j=k} 6(5j+5j+1+5j+2+5j+3+5j+4+5j+5) = 90k^2+180k+61.$$

The process terminates until there is no black vertex. At this time, V_k is V. Then

$$|V| \geq \frac{n+4-12(45k^2+75k+32)}{2(90k^2+180k+61)}. \tag{5}$$

The number of colored vertices in the internal $3k+1$ layer of $C_{3k+2}(v)$ is

$$\sum_{j=1}^{j=k} 6(j+j+j) = 9k^2+9k.$$

The total number of vertices that is in the internal $3k+1$ layer is

$$\sum_{j=1}^{j=3k+1} 6j = 27k^2+27k+6.$$

Then, the number of resonant hexagons is $18k^2+18k+6$. A total number of resonant hexagons is $(18k^2+18k+6)|V|$ in the G. The number of resonant hexagons in one of the matchings is at least

$$(6k^2+6k+2)|V| \geq \frac{n+4-12(45k^2+75k+32)}{90k^2+180k+61}\cdot(3k^2+3k+1). \tag{6}$$

So the number of perfect matchings is $2^{\frac{n+4-12(45k^2+75k+32)}{90k^2+180k+61}\cdot(3k^2+3k+1)}$.

We consider the limit case. When k is large, it is a level of $\frac{n}{30}$. ■

3 Conclusion

In this paper, the number of perfect matchings has been improved by generalizing the method in [13]. Based on our calculation experience on this problem, there may be another way to improve the lower bound by using the relation between Kekulé count and permanents of adjacency matrices of fullerenes. We hope to have a discussion here and as the next research direction.

For an $n\times n$ matrix $A=[a_{ij}]$, the permanent is defined as

$$\mathrm{Per(A)} = \sum_{\sigma\in\Lambda_n}\prod_{i=1}^{n} a_{i\sigma(i)}. \tag{7}$$

where Λ_n denotes the set of all possible permutations of $1,2,\cdots,n$. Though the definition of permanent looks similar to the determinant, the computation of permanent is proved to be a #P-complete problem in counting [17]. Hence, the results about the bound of permanent are abundant. If $A=[a_{ij}]$ is a $k-$regular 0-1 matrix, in which k 1s are in each column and row, the lower bound has been found as [18]

$$\mathrm{Per(A)} \geq \left(\frac{(k-1)^{k-1}}{k^{k-2}}\right)^n. \tag{8}$$

When $k=3$, just corresponding to the adjacency matrix of fullerene molecule graph, the result is

$$\mathrm{Per(A)} \geq \left(\frac{4}{3}\right)^n. \tag{9}$$

which is the best lower bound of permanent for fullerenes till now.

Using the algorithm proposed in [19], we compute the permanent and Kekulé count for all the fullerene isomers with atoms between 20 and 60 and all the IPR structure fullerene isormers with atoms no more than 100. For $C_{20\sim60}$, the ratios of $ln(Perm)/ln(K)$

are between 2.0199 and 2.2378. For $C_{70\sim100}$ IPR structurethe ratios of $ln(Perm)/ln(K)$ are between 2.0739 and 2.1906. If the ratio of $ln(Perm)/ln(K)$ is always no more than 2.5, then

$$K(A) > Perm(A)^{1/2.5} > (4/3)^{n/2.5} \approx 2^{n/6}.$$

An elaborate relation between permanent and Kekulé count is presented in [20] as follows

$$Perm(A) = K(A)^2 + \sum_{s \in S^\bullet} 2^{r(s)}. \tag{10}$$

where $r(s)$ is the number of cyclic components of the Sachs graph s and where the summation goes over the elements of the set $S^\bullet$, namely over the Sachs graphs embracing all vertices of the molecular graph and possessing at least one odd-membered cyclic component.

We hope to obtain the better lower bound of Kekulé count by the relation (10) in future work. Recently, the transfer matrix method is applied to counting perfect matchings in fullerene-like graphs by Behmaram, Došlić and Friedland [21]. We will study the method further and look forward to better results.

References

[1] I. Gutman, O. E. Polansky, *Mathematical Concepts in Organic Chemistry*, Springer, Berlin, 1986.

[2] X. Liu, D. J. Klein, W. A. Seitz, T. G. Schmalz, Sixty–atom carbon cages, *J. Math. Chem.* **12** (1991) 1265–1269.

[3] N. Trinajstić, *Chemical Graph Theory*, CRC Press, Boca Raton, 1992.

[4] S. J. Austin, P. W. Fowler, P. Hansen, D. E. Monolopoulos, M. Zheng, Fullerene isomers of C_{60}. Kekulé counts versus stability, *Chem. Phys. Lett.* **228** (1994) 478–484.

[5] B. Afshin, T. Došlić, S. Friedland, Matchings in m-generalized fullerene graphs,*Ars. Math. Contemp.* **11** (2015) 301–313.

[6] M. B. Ahmadi, V. A. Khorasani, E. Farhadi, Saturation number of fullerene and benzenoid graphs, *MATCH Commun. Math. Comput. Chem.* **77** (2017) 737–747.

[7] D. Cvetković, I. Gutman, N. Trinajstić, Kekulé structures and topology, *Chem. Phys. Lett.* **16** (1972) 614–616.

[8] H. Zhang, F. Zhang, New lower bound on the number of perfect matchings in fullerene graphs, *J. Math. Chem.* **30** (2001) 343–347.

[9] K. Kutnar, D. Marušič, On cyclic edge-connectivity of fullerenes, *Discr. Appl. Math.* **156** (2008) 1661–1669.

[10] T. Došlić, Fullerene graphs with exponentially many perfect matchings, *J. Math. Chem.* **41** (2007) 183–192.

[11] T. Došlić, Leapfrog fullerenes have many perfect matchings, *J. Math. Chem.* **44** (2008) 1–4.

[12] T. Došlić, Finding more perfect matchings in leapfrog fullerenes, *J. Math. Chem.* **45** (2009) 1130–1136.

[13] F. Kardoš, D. Král, J. Miškuf, J. S. Sereni, Fullerene graphs have exponentially many perfect matchings, *J. Math. Chem.* **46** (2009) 443–447.

[14] K. Appel, W. Haken, J. Koch, Every planar map is four colorable. Part I: Discharging, *Illinois J. Math.* **21** (1977) 429–490.

[15] K. Appel, W. Haken, J. Koch, Every planar map is four colorable. Part II: Reducibility, *Illinois J. Math.* **21** (1977) 491–567.

[16] N. Robertson, D. Sanders, P. Seymour, R. Thomas, The four–colour theorem, *J. Comb. Theory B* **70** (1997) 2–44.

[17] L. G. Valiant, The complexity of computing the permanent, *Theor. Comput. Sci.* **8** (1979) 189–201.

[18] A. Schrijver, Counting 1-factors in regular bipartite graphs, *J. Comb. Theory B* **72** (1998) 122–135.

[19] B. Yue, H. Liang, F. Bai, Improved algorithms for permanent and permanental polynomial of sparse graph, *MATCH Commun. Math. Comput. Chem.* **69** (2013) 831–842.

[20] I. Gutman, Permanents of adjacency matrices and their dependence on molecular structure, *Polycyc. Arom. Comp.* **12** (1998) 281–287.

[21] A. Behmaram, T. Došlić, S. Friedland, Matchings in m-generalized fullerene graphs, *Ars Math. Contemp.* **11** (2016) 301–313.