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On the minimal energy of unicyclic Hückel molecular graphs possessing Kekulé structures

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ABSTRACT

Let G be any unicyclic Hückel molecular graph with Kekulé structures on n vertices where $n \geq 8$ is an even number. In [W. Wang, A. Chang, L. Zhang, D. Lu, Unicyclic Hückel molecular graphs with minimal energy, J. Math. Chem. 39 (1) (2006) 231–241], Wang et al. showed that if G satisfies certain conditions, then the energy of G is always greater than the energy of the radialene graph. In this paper we prove that this inequality actually holds under a much weaker condition.

1. Introduction

Let G be a graph with n vertices and $A(G)$ be the adjacency matrix of G. The characteristic polynomial of G is defined as that of $A(G)$

$$\phi_G(\lambda) = \det(\lambda I - A(G)) = \sum_{i=0}^{n} a_i(G)\lambda^{n-i},$$

where I is the n by n identity matrix. Similarly, the eigenvalues of $A(G)$ are defined to be the eigenvalues of G. Since $A(G)$ is symmetric, all eigenvalues are real numbers. Let $\lambda_1, \lambda_2, \ldots, \lambda_n$ denote those eigenvalues, then the energy of G is defined as

$$\mathcal{E}(G) = \sum_{i=1}^{n} |\lambda_i|.$$

The energy of a graph defined this way is a pure mathematical concept. But when a molecular graph is used to model a π-electron system, the energy of the graph has been shown to be a good approximation of the binding energy of the π-electrons. Here we just briefly review the motivation of this definition which has been well explained in [1]. Interested readers should refer to [1] for more details. Within the framework of Hückel Molecule Orbit model, the total molecular orbital energy of all π-electrons in a molecule is given by

$$E_\pi = n_e\alpha + \beta \sum_{j=1}^{n} \eta_j \lambda_j,$$

where $n_e\alpha$ corresponds to the energy of n_e isolated p-electrons, β is a constant, η_j is the number of π-electrons in the jth molecular orbital, and λ_j's are the eigenvalues of the corresponding molecular graph. Since we are only interested in the

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binding energy of the π-electrons, the only non-trivial part is $\mathcal{E} = \sum_{j=1}^{n} \eta_j \lambda_j$. For most conjugated π-electron systems of chemical interest, all bonding molecular orbitals are doubly occupied and all antibonding molecular orbitals are unoccupied. This leads to the fact that $\eta_j = 2$ if $\lambda_j > 0$ and $\eta_j = 0$ if $\lambda_j < 0$. Hence $\mathcal{E} = 2\sum_{\lambda_j > 0} \lambda_j$. Notice that for a simple graph, $\sum_{j=1}^{n} \lambda_j = \mathrm{trace}(A(G)) = 0$, then $\mathcal{E} = \sum_{j=1}^{n} |\lambda_j|$.

The energy problems of some special graphs have been extensively investigated. For example, minimal energy problems have been studied for the classes of acyclic conjugated molecules [10], trees with a given number of pendant vertices [9], and trees with a given maximum degree [3], etc. Minimal energy problems of unicyclic graphs, i.e., graphs that contain exactly one cycle, are usually harder than those of acyclic graphs. Hou [2] first considered it for general unicyclic graphs. Later Li and Zhou studied this problem for bipartite unicyclic graphs with a given partition [4]. Recently, there have been two papers [5,8] concerning the minimal energy of unicyclic molecular graphs with a perfect matching and several interest findings have been presented.

Conjugated hydrocarbon molecules studied in the Hückel Molecule Orbit theory are usually represented by the carbon-atom skeleton graphs whose maximum degree is less than four. In this paper, we study unicyclic Kekuléan Hückel molecular graphs which in graph theory are simple unicyclic connected graphs with a perfect matching and maximum degree less than four. The minimal energy problem of such molecular graphs was investigated in [7] and some partial results were obtained (summarized in Section 2). The goal of this paper is to present a much stronger result.

Before proceeding, we introduce some notations. A *matching* in a graph is a set of edges with no shared end-vertices. A matching is *perfect* if it consists of $\frac{n}{2}$ edges. A *k-matching* is a matching with k edges. The *degree* of a vertex is the number of edges incident with it. As usual, C_l denotes a cycle with l vertices. $\Delta(G)$ and $E(G)$ denote the maximum degree and the edge set of a graph G, respectively. We use $\mathcal{H}_n$ to denote the set of unicyclic Kekuléan Hückel molecular graphs with n vertices. Let G be a unicyclic graph with the unique cycle C_l. $G - C_l$ is the graph obtained from G by deleting the vertices of C_l. For any graph G and positive integer k, $\mathcal{M}(G, k)$ and $m(G, k)$ represent the set and the number of k-matchings of G, respectively. Therefore if $G \in \mathcal{H}_n$, then $\mathcal{M}(G, \frac{n}{2}) \neq \emptyset$ and $m(G, \frac{n}{2}) \geq 1$. For convenience, we define $m(G, 0) = 1$ and $m(G, k) = 0$ for negative integer k. For $G \in \mathcal{H}_n$, we use M_G to denote one arbitrarily selected perfect matching of G. Let $\phi \subset E(G) - M_G$, $N_M(\phi)$ denotes the set of edges of M_G that are adjacent to ϕ. Two special graphs of $\mathcal{H}_n$ are needed. Here we follow the notations used in [7]. $S_n^{\frac{n}{2}}$ represents the graph obtained by attaching one pendant edge to each vertex of $C_{\frac{n}{2}}$, which is known as the radialene graph in chemistry. $R_n^{\frac{n}{2}+1}$ denotes the graph obtained by attaching one pendant edge to all but two consecutive vertices of $C_{\frac{n}{2}+1}$.

2. Preliminaries

It is not easy to directly analyze each eigenvalue of a graph G. The Coulson integral formula [1] is a convenient tool to overcome this difficulty

$$\mathcal{E}(G) = \frac{1}{\pi} \int_0^\infty \frac{1}{x^2} \ln \left[\left(\sum_{i=0}^{[n/2]} (-1)^i a_{2i}(G) x^{2i} \right)^2 + \left(\sum_{i=0}^{[n/2]} (-1)^i a_{2i+1}(G) x^{2i+1} \right)^2 \right] \mathrm{d}x.$$

Let $b_i(G) = |a_i(G)|$. For unicyclic graphs, it can be shown [2] that

$$\mathcal{E}(G) = \frac{1}{\pi} \int_0^\infty \frac{1}{x^2} \ln \left[\left(\sum_{i=0}^{[n/2]} b_{2i}(G) x^{2i} \right)^2 + \left(\sum_{i=0}^{[n/2]} b_{2i+1}(G) x^{2i+1} \right)^2 \right] \mathrm{d}x.$$

Given two unicyclic graphs G and H, a sufficient condition for $\mathcal{E}(G) > \mathcal{E}(H)$ is to have $b_i(G) \geq b_i(H)$ for all i while $b_i(G) > b_i(H)$ for some i. All current results on extremal energies of unicyclic chemical graphs are based on this condition [2,7,8,11].

However, sometimes this sufficient condition is too strong to be applicable. We will need a simple weaker sufficient condition for our purpose. For any $G \in \mathcal{H}_n$, define the polynomial

$$F_G(x) = \left(\sum_{i=0}^{\frac{n}{2}} b_{2i}(G) x^{2i} \right)^2 + \left(\sum_{i=0}^{\frac{n}{2}-1} b_{2i+1}(G) x^{2i+1} \right)^2.$$

Clearly, if $F_G(x) > F_H(x)$ for all $x > 0$, then $\mathcal{E}(G) > \mathcal{E}(H)$.

A lot of research have been carried out on generating the coefficients of the characteristic polynomial from the structure of a graph. Among them the most elegant one is probably the method of Sachs [6]:

$$a_i(G) = \sum_{S \in \mathcal{L}_i} (-1)^{k(S)} 2^{c(S)},$$

where $\mathcal{L}_i$ denotes the set of Sachs graphs of G with i vertices, $k(S)$ is the number of components of S, and $c(S)$ is the number of cycles contained in S.

A Sachs graph S is defined as a subgraph of G whose every component is either a K_2 or a cycle. Using this fact, the following useful relation between matching numbers and $b_i(G)$ can be shown.

Lemma 2.1 ([2,7]). *Let G be a unicyclic graph on n vertices with a cycle C_l.*
(1) *If $l = 2r$, then $b_{2k}(G) = m(G, k) + 2(-1)^{r+1}m(G - C_l, k - r)$ and $b_{2k+1}(G) = 0$;*
(2) *If $l = 2r + 1$, then $b_{2k}(G) = m(G, k)$ and $b_{2k+1}(G) = \begin{cases} 2m(G - C_l, k - r), 2k + 1 \geq l; \\ 0, 2k + 1 < l. \end{cases}$*

For any $G \in \mathcal{H}_n$ we let $\hat{G}$ denote the graph obtained from G by deleting the perfect matching M_G first and then deleting the isolated vertices. Since each k-matching ϕ of G can be decomposed into two parts ϕ_1 and ϕ_2 where $\phi_1 \subset E(\hat{G})$ and $\phi_2 \subset M_G - N_M(\phi_1)$ (ϕ_1 and ϕ_2 could be $\emptyset$). It is easy to see that

$$m(G, k) = \binom{\frac{n}{2}}{k} + \sum_{i=1}^{k} \sum_{\phi_1 \in \mathcal{M}(\hat{G}, i)} \binom{\frac{n}{2} - |N_M(\phi_1)|}{k - i}, \tag{1}$$

where we use the convention $\binom{0}{0} = 1$ and $\binom{p}{q} = 0$ for any $p < q$. Clearly, for $\phi_1 \in \mathcal{M}(\hat{G}, i)$, we have $|N_M(\phi_1)| \leq 2i$. While if $G \cong S_n^{\frac{n}{2}}$, then $|N_M(\phi_1)| = 2i$.

The main results of [7] can be summarized as follows. Assume that $n \geq 6$, $S_n^{\frac{n}{2}} \ncong G \in \mathcal{H}_n$, and G contains a cycle C_l. Then if one of the following conditions holds: (1) $\frac{n}{2} \equiv l \equiv 1 \pmod 2$ and $l \leq \frac{n}{2}$, (2) $l \not\equiv \frac{n}{2} \equiv 0 \pmod 4$, (3) $\frac{n}{2} \equiv l \equiv 2$ (mod4) and $l \leq \frac{n}{2}$, then $\mathcal{E}(G) > \mathcal{E}\left(S_n^{\frac{n}{2}}\right)$. It is also proved in [7] that for $n \geq 6$, if $\frac{n}{2} \equiv 3 \pmod 4$, $l \not\equiv 0 \pmod 4$, and $l > \frac{n}{2}$, then $\mathcal{E}(G) > \mathcal{E}\left(R_n^{\frac{n}{2}+1}\right)$. However it is not clear whether $\mathcal{E}(R_n^{\frac{n}{2}+1}) > \mathcal{E}(S_n^{\frac{n}{2}})$ under those conditions.

In next section, we are going to show that the above conditions can be significantly weakened. Essentially for $n \geq 8$, $S_n^{\frac{n}{2}} \ncong G \in \mathcal{H}_n$, and G contains a cycle C_l. As long as $l \not\equiv 0 \pmod 4$, we have $\mathcal{E}(G) > \mathcal{E}\left(S_n^{\frac{n}{2}}\right)$. We will also show that $\mathcal{E}\left(R_n^{\frac{n}{2}+1}\right) > \mathcal{E}\left(S_n^{\frac{n}{2}}\right)$ in general.

3. Main results

Lemma 3.1. *If $n \geq 6$ is an even number and $S_n^{\frac{n}{2}} \ncong G \in \mathcal{H}_n$, then there exists a 2-matching $\phi \in \hat{G}$ both edges of which are adjacent to a common edge of M_G.*

Proof. Let $C_l = u_1, u_2, \ldots, u_l = u_0$ be the unique cycle of G. We consider the following three cases.
Case 1: $M_G \cap E(C_l) = \emptyset$.

Since M_G is a perfect matching, there exist l vertices $v_1, v_2, \ldots, v_l \notin C_l$ such that $u_iv_i \in M_G$. Notice that $\Delta(G) \leq 3$ and $G \ncong S_n^{\frac{n}{2}}$, then there is a vertex $w \notin C_l$ adjacent to some v_i. Clearly $\phi = \{u_{i-1}u_i, wv_i\}$ is a 2-matching of $\hat{G}$ and both $u_{i-1}u_i$ and wv_i are adjacent to $v_iu_i \in M_G$.

Case 2: $M_G \cap E(C_l) \neq \emptyset$ and $l = 3$.

Without loss of generality, we assume that $u_1u_2 \in M_G$.

If $d(u_1) = 3$, then there exists a vertex $v \notin C_l$ and $vu_1 \in \hat{G}$. Hence $\phi = \{vu_1, u_2u_3\}$ is a 2-matching of $\hat{G}$, and both vu_1 and u_2u_3 are adjacent to $u_1u_2 \in M_G$.

If $d(u_2) = 3$, the claim can be similarly proved.

If $d(u_1) = d(u_2) = 2$, then $d(u_3) = 3$. So there exists a vertex $v \notin C_l$ such that $vu_3 \in M_G$. Since $n \geq 6$, then $d(v) > 1$. Let $w \in N(v)/\{u_3\}$. Then $\phi = \{wv, u_1u_3\}$ is a 2-matching of $\hat{G}$ and both wv and u_1u_3 are adjacent to $vu_3 \in M_G$.

Case 3: $M_G \cap E(C_l) \neq \emptyset$ and $l \geq 4$.

Assume that $u_iu_{i+1} \in M_G$. Then $\phi = \{u_{i-1}u_i, u_{i+1}u_{i+2}\}$ is a 2-matching of $\hat{G}$, and both $u_{i-1}u_i$ and $u_{i+1}u_{i+2}$ are adjacent to $u_iu_{i+1} \in M_G$. ■

From Lemma 3.1 we immediately have the following result.

Corollary 3.2. *If $n \geq 6$ is an even number and $S_n^{\frac{n}{2}} \ncong G \in \mathcal{H}_n$, then there is a 2-matching $\phi \in \hat{G}$ such that $|N_M(\phi)| \leq 3$.*

It was shown that $S_n^{\frac{n}{2}}$ is the minimal graph of $\mathcal{H}_n$ in terms of matching numbers.

Lemma 3.3 ([7]). *If $n \geq 6$ and $G \in \mathcal{H}_n$, then $m(G, k) \geq m\left(S_n^{\frac{n}{2}}, k\right)$ for all k.*

But we need a stronger inequality for our analysis.

Lemma 3.4. *If $n \geq 8$ is an even number and $S_n^{\frac{n}{2}} \ncong G \in \mathcal{H}_n$, then for $2 \leq k \leq \frac{n}{2} - 1$ we have*

$$m(G, k) \geq m\left(S_n^{\frac{n}{2}}, k\right) + \binom{\frac{n}{2} - 3}{k - 2}.$$

Proof. From the proof of Lemma 2 of [7] we know $m\left(\hat{G}, i\right) \geq m\left(\hat{S}_n^{\frac{n}{2}}, i\right)$ for all i. Now we take a closer look at $m\left(\hat{G}, 2\right) - m\left(\hat{S}_n^{\frac{n}{2}}, 2\right)$. Since $\Delta(G) \leq 3$, then $\Delta(\hat{G}) \leq 2$. Therefore every component of $\hat{G}$ is either a path or a cycle. Because $G \ncong S_n^{\frac{n}{2}}$ so $\hat{G} \ncong C_{\frac{n}{2}}$. Hence at least one component of $\hat{G}$ is a path. Every edge of $\hat{G}$ is adjacent to at most two other edges while a pendant edge of a path is adjacent to at most one other edge. On the other hand, every edge of $\hat{S}_n^{\frac{n}{2}} = C_{\frac{n}{2}}$ is adjacent to exactly two other edges. Hence $m\left(\hat{G}, 2\right) \geq m\left(\hat{S}_n^{\frac{n}{2}}, 2\right) + 1$.

Then it follows from (1) and $|N_M(\psi)| = 2i$ for $\psi \in M(S_n^{\frac{n}{2}}, i)$that

$$m(G,k) - m\left(S_n^{\frac{n}{2}}, k\right) = \sum_{i=1}^{k} \sum_{\phi\in\mathcal{M}(\hat{G},i)} \binom{\frac{n}{2} - |N_M(\phi)|}{k-i} - \sum_{i=1}^{k} \sum_{\psi\in\mathcal{M}\left(\hat{S}_n^{\frac{n}{2}},i\right)} \binom{\frac{n}{2}-2i}{k-i}$$

$$= \sum_{i=1}^{k} \sum_{\phi\in\mathcal{M}(\hat{G},i)} \binom{\frac{n}{2} - |N_M(\phi)|}{k-i} - \sum_{i=1}^{k} m\left(\hat{S}_n^{\frac{n}{2}}, i\right) \binom{\frac{n}{2}-2i}{k-i}.$$

Let ϕ_1 be the special 2-matching of $\hat{G}$ mentioned in Corollary 3.2. We then have

$$\begin{aligned}
& m(G,k) - m\left(S_n^{\frac{n}{2}}, k\right) \\
&\geq \sum_{i=1}^{k} \sum_{\phi\in\mathcal{M}(\hat{G},i),\phi\neq\phi_1} \binom{\frac{n}{2} - |N_M(\phi)|}{k-i} + \binom{\frac{n}{2}-3}{k-2} - \sum_{i=1}^{k} m\left(\hat{S}_n^{\frac{n}{2}}, i\right)\binom{\frac{n}{2}-2i}{k-i} \\
&\geq \sum_{i=1,i\neq 2}^{k} m\left(\hat{G}, i\right)\binom{\frac{n}{2}-2i}{k-i} + \left(m\left(\hat{G},2\right)-1\right)\binom{\frac{n}{2}-4}{k-2} + \binom{\frac{n}{2}-3}{k-2} - \sum_{i=1}^{k} m\left(\hat{S}_n^{\frac{n}{2}}, i\right)\binom{\frac{n}{2}-2i}{k-i} \\
&\geq \sum_{i=1,i\neq 2}^{k} m\left(\hat{G}, i\right)\binom{\frac{n}{2}-2i}{k-i} + m\left(\hat{S}_n^{\frac{n}{2}}, 2\right)\binom{\frac{n}{2}-4}{k-2} + \binom{\frac{n}{2}-3}{k-2} - \sum_{i=1}^{k} m\left(\hat{S}_n^{\frac{n}{2}}, i\right)\binom{\frac{n}{2}-2i}{k-i} \\
&\geq \sum_{i=1,i\neq 2}^{k} \left(m\left(\hat{G}, i\right) - m\left(\hat{S}_n^{\frac{n}{2}}, i\right)\right)\binom{\frac{n}{2}-2i}{k-i} + \binom{\frac{n}{2}-3}{k-2} \\
&\geq \binom{\frac{n}{2}-3}{k-2}. \quad \blacksquare
\end{aligned}$$

Now we can prove our main results.

Theorem 3.5. *If $n \geq 8$ is an even number, $S_n^{\frac{n}{2}} \ncong G \in \mathcal{H}_n$, and the length l of the cycle of G satisfies $l \not\equiv 0 \pmod 4$, then $\mathcal{E}(G) > \mathcal{E}\left(S_n^{\frac{n}{2}}\right)$.*

Proof. We consider three cases.

Case 1: $\frac{n}{2} \equiv 0 \pmod 4$.

See [7] for proof.

Case 2: $\frac{n}{2} \equiv 1$, or $3 \pmod 4$. That is $\frac{n}{2} \equiv 1 \pmod 2$.

Since $n \geq 8$, $\frac{n}{2} = 2h+1$ for some $h \geq 2$. From Lemma 2.1(2) we have $b_{2k}\left(S_n^{\frac{n}{2}}\right) = m\left(S_n^{\frac{n}{2}}, k\right)$ for all k, $b_{2h+1}\left(S_n^{\frac{n}{2}}\right) = 2$. Since $S_n^{\frac{n}{2}} - C_l$ consists of $\frac{n}{2}$ isolated vertices, by Lemma 2.1(2) again, we have $b_{2k+1}\left(S_n^{\frac{n}{2}}\right) = 0$ for $k \neq h$.

Since $l \not\equiv 0 \pmod 4$, then by Lemmas 2.1 and 3.3 we get $b_{2k}(G) \geq m(G,k) \geq b_{2k}\left(S_n^{\frac{n}{2}}\right) \geq 0$ for all k. Moreover, considering $k = h$ and $k = h+1$, from Lemma 3.4 we have

$$b_{2h}(G) - b_{2h}\left(S_n^{\frac{n}{2}}\right) \geq m(G,h) - m\left(S_n^{\frac{n}{2}}, h\right) \geq \binom{2h-2}{h-2} > 1,$$

and

$$b_{2h+2}(G) - b_{2h+2}\left(S_n^{\frac{n}{2}}\right) \geq m(G,h+1) - m\left(S_n^{\frac{n}{2}}, h+1\right) \geq \binom{2h-2}{h-1} > 1.$$

Therefore for any $x > 0$,

$$\begin{aligned} F_G(x) &= \left(\sum_{k=0}^{2h+1} b_{2k}(G)x^{2k}\right)^2 + \left(\sum_{k=0}^{2h} b_{2k+1}(G)x^{2k+1}\right)^2 \\ &\geq \left(\sum_{k=0}^{2h+1} b_{2k}(G)x^{2k}\right)^2 \\ &\geq \left(\sum_{k=0,k\neq h,h+1}^{2h+1} b_{2k}(G)x^{2k} + b_{2h}(G)x^{2h} + b_{2h+2}(G)x^{2h+2}\right)^2 \\ &> \left(\sum_{k=0,k\neq h,h+1}^{2h+1} b_{2k}(S_n^{\frac{n}{2}})x^{2k} + (b_{2h}(S_n^{\frac{n}{2}})+1)x^{2h} + (b_{2h+2}(S_n^{\frac{n}{2}})+1)x^{2h+2}\right)^2 \\ &\geq \left(\sum_{k=0}^{2h+1} b_{2k}\left(S_n^{\frac{n}{2}}\right)x^{2k} + x^{2h} + x^{2h+2}\right)^2 \\ &\geq \left(\sum_{k=0}^{2h+1} b_{2k}\left(S_n^{\frac{n}{2}}\right)x^{2k} + 2x^{2h+1}\right)^2 \quad \left(\text{since } x^{2h}+x^{2h+2} \geq 2x^{2h+1}\right) \\ &\geq \left(\sum_{k=0}^{2h+1} b_{2k}\left(S_n^{\frac{n}{2}}\right)x^{2k}\right)^2 + \left(2x^{2h+1}\right)^2 \\ &= F_{S_n^{\frac{n}{2}}}(x), \end{aligned}$$

which leads to $\mathcal{E}(G) > \mathcal{E}\left(S_n^{\frac{n}{2}}\right)$.

Case 3: $\frac{n}{2} \equiv 2 \pmod 4$.

Since $n \geq 8$, $\frac{n}{2} = 4h+2$ for some $h \geq 1$. From Lemma 2.1(1) we know that $b_{2k+1}\left(S_n^{\frac{n}{2}}\right) = 0$ for all k, and

$$\begin{aligned} b_{2k}\left(S_n^{\frac{n}{2}}\right) &= m\left(S_n^{\frac{n}{2}}, k\right) + 2m\left(S_n^{\frac{n}{2}} - C_{\frac{n}{2}}, k-2h-1\right) \\ &= \begin{cases} m\left(S_n^{\frac{n}{2}}, k\right), & k \neq 2h+1, \\ m\left(S_n^{\frac{n}{2}}, 2h+1\right) + 2, & k = 2h+1. \end{cases} \end{aligned}$$

On the other hand, because $l \not\equiv 0 \pmod 4$, we have $b_{2k}(G) \geq m(G,k)$. Hence from Lemma 3.3 we know that if $k \neq 2h+1$, then $b_{2k}(G) \geq m(G,k) \geq m\left(S_n^{\frac{n}{2}}, k\right) = b_{2k}\left(S_n^{\frac{n}{2}}\right)$. While if $k = 2h+1$, then by Lemma 3.4 we have

$$\begin{aligned} b_{4h+2}(G) &\geq m(G, 2h+1) \\ &\geq m\left(S_n^{\frac{n}{2}}, 2h+1\right) + \binom{4h-1}{2h-1} \\ &> m\left(S_n^{\frac{n}{2}}, 2h+1\right) + 2 \\ &= b_{4h+2}\left(S_n^{\frac{n}{2}}\right). \end{aligned}$$

So $\mathcal{E}(G) > \mathcal{E}\left(S_n^{\frac{n}{2}}\right)$. ■

In [7], $\mathcal{E}\left(R_n^{\frac{n}{2}+1}\right)$ was also used as a lower-bound for the energies of some graphs in $\mathcal{H}_n$. But it was not clear in [7] whether $R_n^{\frac{n}{2}+1}$ is a better candidate than $S_n^{\frac{n}{2}}$ as the minimal energy graph of $\mathcal{H}_n$. We have the following result.

Theorem 3.6. *If $n \geq 8$ is an even number, then $\mathcal{E}\left(R_n^{\frac{n}{2}+1}\right) > \mathcal{E}\left(S_n^{\frac{n}{2}}\right)$.*

Proof. Note that $R_n^{\frac{n}{2}+1}$ contains a cycle $C_{\frac{n}{2}+1}$. If $\frac{n}{2}+1 \not\equiv 0 \pmod 4$, then from Theorem 3.5 we have $\mathcal{E}\left(R_n^{\frac{n}{2}}+1\right) > \mathcal{E}\left(S_n^{\frac{n}{2}}\right)$.

Now we assume that $\frac{n}{2}+1 \equiv 0 \pmod 4$. Since $n \geq 8$, then $\frac{n}{2} = 4h+3$ for some $h \geq 1$.

From Lemma 2.1(1), we know that $b_{2k+1}\left(R_n^{\frac{n}{2}+1}\right)=0$ for all k and

$$b_{2k}\left(R_n^{\frac{n}{2}+1}\right) = m\left(R_n^{\frac{n}{2}+1},k\right)-2m\left(R_n^{\frac{n}{2}+1}-C_{\frac{n}{2}+1},k-(2h+2)\right) = \begin{cases} m\left(R_n^{\frac{n}{2}+1},k\right), & k\neq 2h+2,\\ m\left(R_n^{\frac{n}{2}+1},2h+2\right)-2, & k=2h+2.\end{cases}$$

Again from Lemma 2.1, we have $b_{2k}\left(S_n^{\frac{n}{2}}\right)=m\left(S_n^{\frac{n}{2}},k\right)$ for all k and

$$b_{2k+1}\left(S_n^{\frac{n}{2}}\right)=2m\left(S_n^{\frac{n}{2}}-C_{\frac{n}{2}},k-(2h+1)\right)=\begin{cases}0, & k\neq 2h+1,\\ 2, & k=2h+1.\end{cases}$$

Now we compare $b_{2k}\left(R_n^{\frac{n}{2}+1}\right)$ and $b_{2k}\left(S_n^{\frac{n}{2}}\right)$. Using Lemma 3.3 we get $b_{2k}\left(R_n^{\frac{n}{2}+1}\right)\geq b_{2k}\left(S_n^{\frac{n}{2}}\right)$ for $k\neq 2h+2$. Considering $k=2h+1$ and $k=2h+2$, by Lemma 3.4 we have

$$b_{4h+2}\left(R_n^{\frac{n}{2}+1}\right)-b_{4h+2}\left(S_n^{\frac{n}{2}}\right)=m\left(R_n^{\frac{n}{2}+1},2h+1\right)-m\left(S_n^{\frac{n}{2}},2h+1\right)\geq\binom{4h}{2h-1}>1,$$

and

$$b_{4h+4}\left(R_n^{\frac{n}{2}+1}\right)-b_{4h+4}\left(S_n^{\frac{n}{2}}\right)=m\left(R_n^{\frac{n}{2}+1},2h+2\right)-m\left(S_n^{\frac{n}{2}},2h+2\right)-2\geq\binom{4h}{2h}-2>1.$$

Therefore for any $x>0$,

$$\begin{aligned} F_{R_n^{\frac{n}{2}+1}}(x) &= \left(\sum_{k=0}^{4h+3} b_{2k}\left(R_n^{\frac{n}{2}+1}\right)x^{2k}\right)^2\\ &> \left(\sum_{k=0}^{4h+3} b_{2k}\left(S_n^{\frac{n}{2}}\right)x^{2k}+x^{4h+2}+x^{4h+4}\right)^2\\ &\geq \left(\sum_{k=0}^{4h+3} b_{2k}\left(S_n^{\frac{n}{2}}\right)x^{2k}+2x^{4h+3}\right)^2\\ &\geq \left(\sum_{k=0}^{2h+1} b_{2k}(S_n^{\frac{n}{2}})x^{2k}\right)^2+(2x^{4h+3})^2\\ &= F_{S_n^{\frac{n}{2}}}(x),\end{aligned}$$

which leads to $\mathcal{E}\left(R_n^{\frac{n}{2}+1}\right)>\mathcal{E}\left(S_n^{\frac{n}{2}}\right)$. ■

Remark. The assumption $l\not\equiv 0 \pmod 4$ in Theorem 3.5 cannot be dropped. As a simple example, consider the following graph. For any even number $n\geq 6$, let A_n denote the graph obtained by attaching a path with $n-4$ edges onto C_4. Clearly, $A_n\in\mathcal{H}_n$. Direct calculations with n up to 24 show that $\mathcal{E}(A_n)<\mathcal{E}\left(S_n^{\frac{n}{2}}\right)$ when $6\leq n\leq 16$, while $\mathcal{E}(A_n)>\mathcal{E}\left(S_n^{\frac{n}{2}}\right)$ when $n\geq 18$. Based on the numerical findings, we conjecture that $\mathcal{E}(A_n)-\mathcal{E}\left(S_n^{\frac{n}{2}}\right)$ is an increasing function of n. We leave this conjecture and the goal of fully solving the case when l is divisible by 4 as our future research topics.

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