MATCH
Communications in Mathematical and in Computer Chemistry

MATCH Commun. Math. Comput. Chem. **61** (2009) 383-394

ISSN 0340 - 6253

The fourth maximal energy of acyclic graphs[1]

Shuchao Li[a] and Xuechao Li[b,2]

[a]Faculty of Mathematics and Statistics, Central China Normal University, Wuhan 430079, P. R. China

[b]Division of Academic Enhancement, The University of Georgia, Athens, GA 30602, USA

(Received August 23, 2007)

Abstract. The energy of a graph is defined as the sum of the absolute values of all eigenvalues of the graph. Recently, Gutman, Radenković, Li and Li [Extremal energy trees, MATCH Commun. Math. Comput. Chem. 59 (2008) 315-320] conjecture the acyclic graphs with the fourth-maximal energy among n-vertex trees. In this paper, we show that this conjecture is true.

1 Introduction

All graphs in this paper are finite, undirected and simple. Let G be a graph on n vertices. The *characteristic polynomial* of G, denoted here by $P(G,x)$, is defined as $P(G,x) = \det(xI - A)$, where I is the identity matrix of order n and $A(G)$ is the adjacency matrix of G. The eigenvalues $x_1, x_2, \ldots, x_n$ of the adjacency matrix of G are called the *eigenvalues* of G. The *energy* of G, denoted by $E(G)$, is defined as

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

[1]The research is partially supported by National Science Foundation of China (Grant No. 10671081)

[2]Corresponding author. Email address: xcli@uga.edu (X. Li), lscmath@mail.ccnu.edu.cn (S. Li)

Historically chemists used the model in which the experimental heats of formation of conjugated hydrocarbons are closely related to the total π-electron energy. Today such a model is over-simplistic, but nevertheless HMO has some value because it points to that part of the experimental heats of formation of conjugated hydrocarbons that can be viewed as due to molecular connectivity (molecular topology). The calculation of the total π-electron energy in a conjugated hydrocarbon can be reduced (within the framework of the HMO approximation; see, e.g, [4, 5]) to $E(G)$ of the corresponding graph G). There are a lot of results on $E(G)$. Also, till now, some results have been known for graphs with extremal energies [see 3, 6-21].

Let $P_n(i)m$ denote the graph obtained by joining the terminal vertex of P_m to the i-th vertex of P_n, where $1 \leqslant i \leqslant \lceil \frac{n}{2} \rceil$. For convenience we shall denote $P_n(i)m$ in an abbreviated manner as $n(i)m$. For a graph G, let $m(G,k)$ be the number of the k-matchings of G, $k \geqslant 1$, and define $m(G,0) = 1$. If G is an acyclic graph on n vertices, then the energy of G can be expressed in terms of the Coulson integral formula [5] as

$$E(G) = \frac{2}{\pi} \int_0^{+\infty} \frac{1}{x^2} \ln \left(\sum_{k=0}^{\lfloor n/2 \rfloor} m(G,k) x^{2k} \right) dx, \tag{1}$$

where

$$P(G,x) = x^n - m(G,1)x^{n-2} + m(G,2)x^{n-4} - \cdots + (-1)^k m(G,k)x^{n-2k} \tag{2}$$

is the characteristic polynomial of the corresponding acyclic graph G. n is the number of vertices in G.

Thus, by (1), $E(G)$ is a strictly monotonically increasing function of $m(G,k)$, $k = 1, \ldots, \lfloor n/2 \rfloor$. This observation led Gutman [2] to define a *quasi-order* over the set of all acyclic graphs: if G_1 and G_2 are two acyclic graphs, then

$$G_1 \succeq G_2 \Leftrightarrow m(G_1,k) \geqslant m(G_2,k) \text{ for all } k \geqslant 1.$$

If $G_1 \succeq G_2$, and there is a j such that $m(G_1,j) > m(G_2,j)$, then we write $G_1 \succ G_2$. Therefore,

$$G_1 \succ G_2 \Rightarrow E(G_1) > E(G_2).$$

If neither $G_1 \preceq G_2$ nor $G_2 \preceq G_1$, then G_1 and G_2 are said to be *incomparable.* This increasing property of energy has been used in the study of extremal values of energy over some significant classes of graphs. For instance, Gutman [2] determined trees with minimal, second-minimal, third-minimal and fourth-minimal energies; Zhang and Li characterized the trees with minimal energy [18] and maximal energy [19], respectively, among the trees with perfect matchings. Recently, N. Li and S. Li [9] characterized the trees with third maximal energy and fourth-, fifth-, sixth-minimal energies among the trees of n vertices. In [3], Gutman et al. proposed the following conjecture.

Conjecture 1.1. *For $n \leqslant 5$ there is no fourth-maximal tree. For $n = 6, n = 7, n = 8, n = 11$, and $n = 13$ the fourth-maximal trees are T_{15}, T_{16}, T_{17}, T_{18}, and T_{19} respectively, depicted in Figure* 1. *For $n = 9$ there are two cospectral trees, T_{20} and T_{21} sharing the fourth- and fifth-maximal position. For $n = 10$ and $n = 12$ and $n \geq 14$ the fourth-maximal tree is $P_{n-2}(7)2$.*

By [1], it is straightforward to check that the conjecture is true for $n \leqslant 10$. In this paper, our work is to show that the conjecture is also true for $n \geqslant 11$. We verify this conjecture in Section 3.

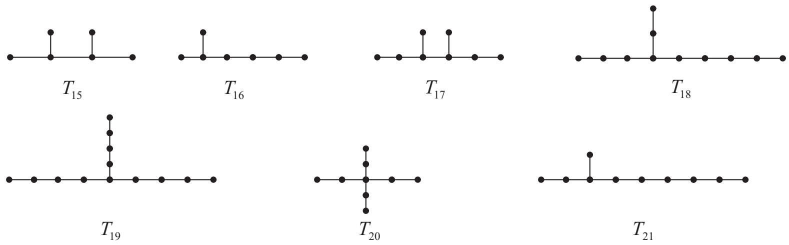

Figure 1: Graphs $T_{15}, T_{16}, T_{17}, T_{18}, T_{19}, T_{20}$ and T_{21}.

2 Some previous results

The following four facts belong to I. Gutman [2].

Fact 1. Let T be a tree with n vertices and uv an edge of T. Then $m(T,k) = m(T-uv,k)+m(T-u-v,k-1)$, especially if v is a pendent vertex of T with pendent edge uv, then $m(T,k) = m(T-v,k)+m(T-u-v,k-1)$ where $k = 1,\dots,\lceil\frac{n-1}{2}\rceil$.

Fact 2. $n-1(i)1 \prec n-1(3)1$ if $i \neq 1,3$ and $1 \leq i \leq \lceil\frac{n-1}{2}\rceil$.

Fact 3. $P_l \succ P_2 \cup P_{l-2} \succ \cdots \succ P_{2k} \cup P_{l-2k} \succ P_{2k+1} \cup P_{l-2k-1} \succ P_{2k-1} \cup P_{l-2k-1} \succ \cdots \succ P_1 \cup P_{l-1}$, where $l = 4k+r, 0 \leq r \leq 3$.

Fact 4. P_n ($n-2(3)2$, respectively) is the tree with maximal (second-maximal, respectively) energy among n-vertex trees.

Lemma 2.1 ([2]). *Let G be a forest of order $n(n>1)$ and G' be a spanning subgraph (respectively, a proper spanning subgraph) of G, then $G \succeq G'$ (respectively, $G \succ G'$).*

Lemma 2.2 ([9]). *$n-2(5)2$ has the third-maximal energy tree of all n-vertex trees.*

3 Tree with fourth maximal energy

In this section we give a tree with fourth maximal energy on n vertices, $n \geqslant 11$. Before giving the proof the of main result, we need some lemmas for preparation.

Lemma 3.1. *$n-1(i)1 \prec n-2(7)2$, if $i \neq 1, n-1$ and $n-2(g)2 \prec n-2(7)2$ for $g = 4,6,8$.*

Proof. We need only to show that $n-1(3)1 \prec n-2(7)2$ by Fact 2. By Fact 1, it is obvious that

$$m(n-1(3)1,k) = m(p_2 \cup (n-3)(3)1,k) + m(n-4(3)1,k-1), \tag{3}$$

$$m(n-2(4)2,k) = m(P_2 \cup n-3(3)1,k) + m(P_{n-3},k-1), \tag{4}$$

$$\begin{aligned} m(n-2(7)2,k) &= m(n-2(7)1,k) + m(p_{n-2},k-1) \\ &= m(P_{n-2},k) + m(P_6 \cup P_{n-9},k-1) + m(P_{n-2},k-1), \end{aligned} \tag{5}$$

$$\begin{aligned} m(n-2(4)2,k) &= m(n-2(4)1,k) + m(P_{n-2},k-1) \\ &= m(P_{n-2},k) + m(P_3 \cup P_{n-6},k-1) + m(P_{n-2},k-1), \qquad (6) \\ m(n-2(g)2,k) &= m(n-2(g)1,k) + m(P_{n-2},k-1) \\ &= m(P_{n-2},k) + m(P_{g-1} \cup P_{n-g-2},k-1) + m(P_{n-2},k-1). \end{aligned}$$

Since P_n is of maximal energy of all trees on n vertices, by equations (3) and (4), we have $n-1(3)1 \prec n-2(4)2$. By equations (5) and (6) together with Fact 3, $n-2(4)2 \prec n-2(7)2$. Thus $n-1(3)1 \prec n-2(7)2$. Note that $g-1$ is odd, by Fact 3, $P_{g-1} \cup P_{n-g-2} \prec P_6 \cup P_{n-6}$, thus $n-2(g)2 \prec n-2(7)2$. □

Lemma 3.2. *Let T_1, T_2, T_3, T_4, T_5 be the trees as in Figures 2-4. Then $T_2 \prec T_1 \prec T_4 \prec T_3 \prec T_5$.*

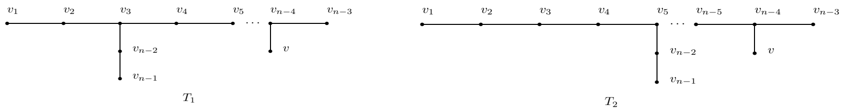

Figure 2: Graphs T_1 and T_2.

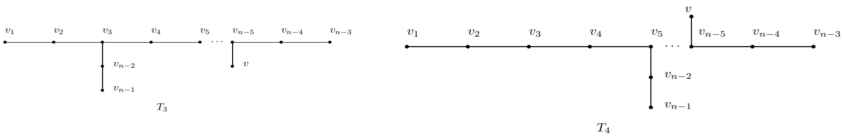

Figure 3: Graphs T_3 and T_4.

Proof. By Fact 1, we have

$$\begin{aligned} m(T_1,k) &= m(T_1 - v,k) + m(T_1 - v - v_{n-4},k-1) \\ &= m(n-3(3)2,k) + m(n-5(3)2,k-1), \\ m(T_2,k) &= m(T_2 - v,k) + m(T_2 - v - v_{n-4},k-1) \\ &= m(n-3(5)2,k) + m(n-5(5)2,k-1), \end{aligned}$$

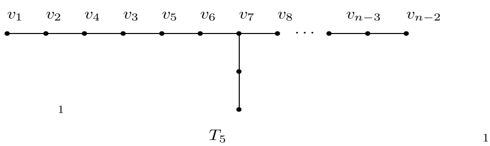

Figure 4: Graph T_5.

1

1

$$
\begin{aligned}
m(T_3,k) &= m(T_3-v,k)+m(T_3-v-v_{n-5},k-1)\\
&= m(n-3(3)2,k)+m(P_2\cup n-6(3)2,k-1),\\
m(T_4,k) &= m(T_4-v,k)+m(T_2-v-v_{n-5},k-1)\\
&= m(n-3(5)2,k)+m(P_2\cup n-6(5)2,k-1).
\end{aligned}
$$

By Fact 4 and Lemma 2.2, $m(n-i(3)2,j)>m(n-i(5)2,j)$ ($i=3,5,6$ and $j=k-1,k$), we have that $T_2\prec T_1, T_4\prec T_3$ immediately. Next we are to show that $T_1\prec T_4$, and $T_3\prec T_5$.

Again, by Fact 1, we have

$$
\begin{aligned}
& m(T_1,k)\\
= \ & m(T_1-v,k)+m(T_1-vv_{n-4},k-1)\\
= \ & m(n-3(3)2,k)+m(n-5(3)2,k-1)\\
= \ & [m(n-3(3)2-v_{n-5}v_{n-4},k)+m(n-3(3)2-v_{n-5}-v_{n-4},k-1)]\\
& +[m(n-5(3)2-v_1v_2,k-1)+m(n-5(3)-v_1-v_2,k-2)]\\
= \ & m(n-4(3)2,k)+m(n-5(3)2,k-1)+[m(n-5(3)1,k-1)+m(P_{n-5},k-2)]\\
= \ & [m(n-5(3)2,k)+m(n-6(3)2,k-1)+m(n-5(3)2,k-1)]\\
& +[m(n-5(3)1,k-1)+m(P_{n-6},k-2)+m(P_{n-7},k-3)]\\
= \ & m(n-5(3)2,k)+[m(P_2\cup n-8(3)2,k-1)+m(n-9(3)2,k-2)]+m(n-5(3)2,k-1)]\\
& +[m(n-5(3)1,k-1)+[m(P_{n-8},k-2)+m(P_{n-8},k-3)+m(P_{n-9},k-3)]+m(P_{n-7},k-3)]\\
= \ & [m(n-5(3)2,k)+m(P_2\cup n-8(3)2,k-1)+m(n-5(3)2,k-1)+m(n-5(3)1,k-1)\\
& +m(P_{n-7},k-3)]+m(n-9(3)2,k-2)+m(P_{n-8},k-2)+m(P_{n-8},k-3)+m(P_{n-9},k-3)\\
= \ & S^*+S_{T_1},
\end{aligned}
$$

where $S^*=[m(n-5(3)2,k)+m(P_2\cup n-8(3)2,k-1)+m(n-5(3)2,k-1)+m(n-5(3)1,k-1)+m(P_{n-7},k-3)]$ and $S_{T_1}=m(n-9(3)2,k-2)+m(P_{n-8},k-2)+m(P_{n-8},k-3)+m(P_{n-9},k-3)$.

$$
\begin{aligned}
m(T_4,k) &= m(T_4-v,k)+m(T_4-v-v_{n-5},k-1)\\
&= m(n-3(5)2,k)+m(P_2\cup n-6(5)2,k-1)\\
&= [m(n-3(5)2-v_2v_3,k)+m(n-3(5)2-v_2-v_3,k-1)]\\
&\quad +[m(n-6(5)2-v_2v_3,k-1)+m(n-6(5)2-v_2-v_3,k-2)]\\
&\quad +[m(n-6(5)2-v_2v_3,k-2)+m(n-6(5)2-v_2-v_3,k-3)]\\
&= m(P_2\cup n-5(3)2,k)+m(n-5(3)1,k-1) \qquad (\textit{note that } n-6(2)2=n-5(3)1)\\
&\quad +m(P_2\cup n-8(3)2,k-1)+m(n-7(3)1,k-2) \qquad (\textit{note that } n-8(2)2=n-7(3)1)\\
&\quad +m(P_2\cup n-8(3)2,k-2)+m(n-7(3)1,k-3) \qquad (\textit{note that } n-8(2)2=n-7(3)1)\\
&= m(n-5(3)2,k)+m(n-5(3)2,k-1)+m(n-5(3)1,k-1)\\
&\quad +m(P_2\cup n-8(3)2,k-1)+m(P_{n-7},k-2)+m(P_2\cup P_{n-10},k-3)\\
&\quad +m(n-8(3)2,k-2)+m(n-8(3)2,k-3)+m(P_{n-7},k-3)+m(P_2\cup P_{n-10},k-4)
\end{aligned}
$$

$$
\begin{aligned}
&= m(n-5(3)2,k)+m(n-5(3)2,k-1)+m(n-5(3)1,k-1)+m(P_2\cup n-8(3)2,k-1)\\
&\quad +m(P_{n-7},k-3)+m(P_{n-7},k-2)+m(P_2\cup P_{n-10},k-3)+m(n-8(3)2,k-2)\\
&\quad +m(n-8(3)2,k-3)+m(P_2\cup P_{n-10},k-4)\\
&= S^*+S_{T_4},
\end{aligned}
$$

where

$$
\begin{aligned}
S_{T_4} &= m(P_{n-7},k-2)+m(P_2\cup P_{n-10},k-3)+m(n-8(3)2,k-2)\\
&\quad +m(n-8(3)2,k-3)+m(P_2\cup P_{n-10},k-4)\\
&= [m(P_{n-8},k-2)+m(P_{n-9},k-3)]+m(P_2\cup P_{n-10},k-3)+m(n-8(3)2,k-2)\\
&\quad +m(n-8(3)2,k-3)+m(P_2\cup P_{n-10},k-4)
\end{aligned}
$$

Now $T_1 \prec T_4$ if and only if $S_{T_1} < S_{T_4}$. So we are to show that $S_{T_1} < S_{T_4}$ by comparing each item of S_{T_1} with that of S_{T_4}. Since $m(n-9(3)2,k-2)$ ($m(P_{n-8},k-3)$, respectively) in S_{T_1} is smaller than $m(n-8(3)2,k-2)$ ($m(n-8(3)2,k-3)$, respectively) in S_{T_4}, and each of the rest of the items are identical in both S_{T_1}, S_{T_4}, we have that $S_{T_1} < S_{T_4}$.

Next we consider $m(T_5,k)$ and $m(T_3,k)$.

$$
\begin{aligned}
m(T_5,k) &= m(T_5-v_2v_3,k)+m(T_5-v_2-v_3,k-1)\\
&= m(P_2\cup n-4(5)2,k)+m(n-5(4)2,k-1)\\
&= m(n-4(5)2,k)+m(n-4(5)2,k-1)+m(n-5(4)2,k-1)\\
&= m(n-4(5)2-v_2v_3,k)+m(n-4(5)2-v_2-v_3,k-1)\\
&\quad +m(n-4(5)2-v_2v_3,k-1)+m(n-4(5)2-v_2-v_3,k-2)+m(n-5(4)2,k-1)\\
&= m(P_2\cup n-6(3)2,k)+m(n-6(3)1,k-1)\\
&\quad +m(P_2\cup n-6(3)2,k-1)+m(n-6(3)1,k-2)+m(n-5(4)2,k-1)\\
&= S_1+S_{T_5},
\end{aligned}
$$

where $S_1=m(P_2\cup n-6(3)2,k)+m(P_2\cup n-6(3)2,k-1)$, $S_{T_5}=m(n-6(3)1,k-1)+m(n-6(3)1,k-2)]+m(n-5(4)2,k-1)$.

$$
\begin{aligned}
m(T_3,k) &= m(n-3(3)2,k)+m(P_2\cup n-6(3)2,k-1)\\
&= m(n-3(3)2-v_{n-5}v_{n-4},k)+m(n-3(3)2-v_{n-5}-v_{n-4},k-1)\\
&\quad +m(P_2\cup n-6(3)2,k-1)\\
&= m(n-5(3)2,k)+m(n-5(3)2,k-1)+m(n-6(3)2,k-1)\\
&\quad +m(P_2\cup n-6(3)2,k-1)\\
&= [m(n-6(3)2,k)+m(n-7(3)2,k-1)]+m[n-6(3)2,k-1]+m(n-7(3)2,k-2)\\
&\quad +n-6(3)2,k-1)+m(P_2\cup n-6(3)2,k-1)\\
&= [m(n-6(3)2,k)+m(n-6(3)2,k-1)]+m(P_2\cup n-6(3)2,k-1)\\
&\quad +[m(n-6(3)2,k-1)+m(n-7(3)2,k-1)+m(n-7(3)2,k-2)]
\end{aligned}
$$

$$\begin{aligned}
&= m(P_2 \cup n-6(3)2, k) + m(P_2 \cup n-6(3)2, k-1)\\
&\quad +[m(n-6(3)2, k-1) + m(n-7(3)2, k-1) + m(n-7(3)2, k-2)]\\
&= S_1 + S_{T_3},
\end{aligned}$$

where $S_{T_3} = [m(n-6(3)2, k-1) + m(n-7(3)2, k-1) + m(n-7(3)2, k-2)]$. So, $T_3 \prec T_5 \Leftrightarrow S_{T_3} < S_{T_5}$. Next, we need to observe S_{T_3} and S_{T_5} more sophisticatedly. Note that $n-p(2)2 = n-p+1(3)1$ where p is positive integer.

$$\begin{aligned}
S_{T_5} &= m(n-6(3)1, k-1) + m(n-6(3)1, k-2)] + m(n-5(4)2, k-1)\\
&= [m(P_{n-6}, k-1) + m(P_2 \cup P_{n-9}, k-2)] + [m(P_{n-6}, k-2) + m(P_2 \cup P_{n-9}, k-3)]\\
&\quad +[m(n-6(3)2, k-1) + m(n-6(3)1, k-2)]\\
&= [m(P_{n-6}, k-1) + m(P_2 \cup P_{n-9}, k-2)] + [m(P_{n-6}, k-2) + m(P_2 \cup P_{n-9}, k-3)]\\
&\quad +[m(n-6(3)2, k-1)] + [m(P_{n-6}, k-2) + m(P_2 \cup P_{n-9}, k-3)]\\
&= [m(P_{n-7}, k-1) + m(P_{n-8}, k-2)] + [m(P_{n-9}, k-2) + m(P_{n-9}, k-3)]\\
&\quad +[m(P_{n-7}, k-2) + m(P_{n-8}, k-3)] + [m(P_{n-9}, k-3) + m(P_{n-9}, k-4)]\\
&\quad +[m(n-6(3)2, k-1)] + [m(P_{n-7}, k-2) + m(P_{n-8}, k-3)] + [m(P_{n-9}, k-3) + m(P_{n-9}, k-4)].
\end{aligned}$$

Note that $m(P_{n-8}, k-2) + m(P_{n-9}, k-3) = m(P_{n-7}, k-2)$ and $m(P_{n-8}, k-3) + m(P_{n-9}, k-4) = m(P_{n-7}, k-3)$ in above equation, so

$$\begin{aligned}
S_{T_5} &= m(n-6(3)2, k-1) + m(P_{n-7}, k-1) + m(P_{n-7}, k-2) + m(P_{n-9}, k-2)\\
&\quad +2m(P_{n-9}, k-3) + 2m(P_{n-7}, k-2) + m(P_{n-7}, k-3) + m(P_{n-9}, k-4).
\end{aligned}$$

$$\begin{aligned}
S_{T_3} &= [m(n-6(3)2, k-1) + m(n-7(3)2, k-1) + m(n-7(3)2, k-2)]\\
&= m(n-6(3)2, k-1) + [m(n-7(3)1, k-1) + m(P_{n-7}, k-2)] + [m(n-7(3)1, k-2)\\
&\quad +m(P_{n-7}, k-3)]\\
&= m(n-6(3)2, k-1) + [m(P_{n-7}, k-1) + m(P_2 \cup P_{n-10}, k-2)] + m(P_{n-7}, k-2)\\
&\quad +[m(P_{n-7}, k-2) + m(P_2 \cup P_{n-10}, k-3)] + m(P_{n-7}, k-3)\\
&= m(n-6(3)2, k-1) + m(P_{n-7}, k-1) + m(P_{n-7}, k-2) + m(P_{n-10}, k-2)\\
&\quad +2m(P_{n-10}, k-3) + m(P_{n-7}, k-2) + m(P_{n-7}, k-3)] + m(P_{n-10}, k-4).
\end{aligned}$$

By Lemma 2.1 and fact that $m(P_{n-9}, i) > m(P_{n-10}, i)$, we compare each item of the last expressions of S_{T_3} with that of S_{T_5}, we have $S_{T_3} < S_{T_5}$, hence $T_3 \prec T_5$. □

For the sake of convenience, let $\mathscr{H}_n = \{P_n, n-2(3)2, n-2(5)2, n-2(7)2\}$ and denote $\{G_1, \cdots, G_t\} \prec G$ if each $G_i \prec G$.

Lemma 3.3. *Let T_1' and T_2' be the trees exhibited in Figure 5 Then $T_2' \prec T_1' \prec n-2(7)2$.*

Proof. Since

$$\begin{aligned} m(T_2',k) &= m(T_2'-v,k)+m(T'-2-v-v_2,k-1) \\ &= m(n-2(5)2,k)+m(n-5(3)2,k-1) \\ &\quad < m(n-2(3)2,k)+m(P_{n-3},k-1) \\ &= m(T_1',k). \end{aligned}$$

So $T_2' \prec T_1'$. Next we show that $T_1' \prec n-2(7)2$.

By the expression of $m(T_3,k)$ in Lemma 3.2, we have

$$\begin{aligned} m(n-3(3)2,k) &= m(P_2\cup n-6(3)2,k)+m(n-6(3)2,k-1)+m(n-7(3)2,k-1) \\ &\quad +m(n-7(3)2,k-2). \end{aligned}$$

Thus,

$$\begin{aligned} m(T_1',k) &= m(T_1'-v,k)+m(T_1'-v-v_2,k-1) \\ &= m(n-3(3)2,k)+m(P_3,k-1) \\ &= m(P_2\cup n-6(3)2,k)+m(n-6(3)2,k-1)+m(n-7(3)2,k-1)+m(n-7(3)2,k-2) \\ &\quad +m(P_3,k-1) \\ &= m(P_2\cup n-6(3)2,k)+m(n-6(3)2,k-1)+m(n-7(3)2,k-1)+m(n-7(3)2,k-2) \\ &\quad +m(P_3\cup P_{n-6},k-1)+m(P_2\cup P_{n-7},k-2) \\ &= m(P_2\cup n-6(3)2,k)+m(n-6(3)2,k-1)+m(n-7(3)2,k-1)+m(n-7(3)2,k-2) \\ &\quad +m(P_{n-6},k-1)+2\times m(P_{n-6},k-2)+m(P_{n-7},k-2)+m(P_{n-7},k-3) \\ &= S^*+S^*_{T_1'}, \end{aligned}$$

where $S^* = m(P_2\cup n-6(3)2,k)+m(n-6(3)2,k-1)+m(n-7(3)2,k-1)+m(n-7(3)2,k-2)+2m(P_{n-6},k-2)$ and

$$\begin{aligned} S^*_{T_1'} &= m(P_{n-6},k-1)+m(P_{n-7},k-2)+m(P_{n-7},k-3) \\ &= m(P_{n-6},k-1)+m(P_{n-7},k-2)+m(P_2\cup P_{n-9},k-3)+m(P_{n-10},k-4). \end{aligned}$$

From the expressions of $m(T_5,k)$ and S_{T_5} in Lemma 3.2, where $T_5 = n-2(7)2$, we have that

$$\begin{aligned} m(T_5,k) &= m(P_2\cup n-6(3)2,k)+m(n-6(3)2,k-1) \\ &\quad +m(P_2\cup n-6(3)2,k-1)+m(n-6(3)1,k-2)+m(n-5(4)2,k-1) \\ &= m(P_2\cup n-6(3)2,k)+m(n-6(3)2,k-1)+m(n-6(3)2,k-1)+m(n-6(3)2,k-2) \\ &\quad +m(n-6(3)1,k-2)+[m(n-6(3)2,k-1)+m(n-6(3)1,k-2)] \\ &= m(P_2\cup n-6(3)2,k)+m(n-6(3)2,k-1) \\ &\quad +[m(n-7(3)2,k-1)+m(n-8(3)2,k-2)]+[m(n-7(3)2,k-2)+m(n-8(3)2,k-3)] \\ &\quad +2\times[m(P_{n-6},k-2)+m(P_2\cup P_{n-9},k-3)]+m(n-6(3)2,k-1) \\ &= S^*+S^*_{T_5}, \end{aligned}$$

where

$$\begin{aligned} S^*_{T_5} &= m(n-8(3)2,k-2)+m(n-8(3)2,k-3)+2m(P_2\cup P_{n-9},k-3)+m(n-6(3)2,k-1) \\ &= m(n-8(3)2,k-2)+m(n-8(3)2,k-3)+2m(P_2\cup P_{n-9},k-3)+m(n-6(3)2,k-1) \\ &\quad +[m(P_{n-6},k)+m(P_2\cup P_{n-9},k-3)+m(P_{n-6},k-2)]. \end{aligned}$$

Note that $m(n-6(3)2,k-1) = m(n-6(3)1,k-1)+m(P_{n-6},k-2)$. So $T_1' \prec T_5 \Leftrightarrow S^*_{T_1'} < S^*_{T_5}$. Now we are to compare $S^*_{T_1'}$ and $S^*_{T_5}$. By Fact 3 and Lemma 3.1, and facts that $m(P_i,k-1) \leq m(P_i,k-2)$, $m(P_{n-7},k-2) < m(P_{n-6},k-2)$, and $m(P_{n-10},k-4) < m(P_1\cup P_{n-9},k-3)$, it is easy to see that $S^*_{T_1'} < S^*_{T_5}$. Thus $T_1' \prec n-2(7)2$. □

By looking at the Appendix of tables of graph spectra in *Spectra of graphs* by D. Cvetokvić, M.Doob and H. Sachs, we need to consider cases for $|T| = 11, 12, 13$ first.

We denote by $\mathcal{J}_{m,n}$ the set of trees of order n with m pendent vertices.

Lemma 3.4. *$n-1(2)1$ has the minimal energy in $\mathcal{J}_{3,n}$.*

Proof. We prove it by induction. It is true for $|T| \leq 10$ by Appendix of tables of graph spectra in the book: Spectra of Graphs[1]. Assume that the statement is true for smaller value of $|T|$. Now we consider $|T| = n$ where $T \in \mathcal{J}_{3,n}$. Since $m(T,k) = m(T-v_{n-1},k)+m(T-v_{n-1}-v_{n-2},k-1)$, while $n-1(2)1-v_{n-1} = n-2(2)1$ is of minimal energy in $\mathcal{J}_{3,n-1}$ and $n-1(2)1-v_{n-1}-v_{n-2} = n-3(2)1$ is of minimal energy in $\mathcal{J}_{3,n-2}$, by induction hypothesis, our statement holds. □

Lemma 3.5. *Let $T_m \in \mathcal{J}_{m,n}$ and $T_3 \in \mathcal{J}_{3,n}$, then $T_m \prec T_3$ where $m \geq 4$.*

Proof. It is true for $|T| \leq 10$ by Appendix of tables of graph spectra in the book: Spectra of Graphs[1]. Assume the result is true for smaller value of $|T|$. Now consider $|T| = n$. For T_3, we could carefully chose a pendent edge vw of T_3 with v is a pendent vertex such that $T_3 - v \in \mathcal{J}_{3,n-1}$ and $T_3 - v - w \in \mathcal{J}_{3,n-2}$. Then we carefully chose a pendent edge v^*w^* of T_m with v^* a pendent vertex such that $T_m - v^* \in \mathcal{J}_{m',n-1}$ and $T_m - v^* - w^* \in \mathcal{J}_{m'',n-2}$ where $m' \geq 4$ and $m'' \geq 4$ except one particular tree T^{4*} which obtained from P_{n-2} by adding two pendent edges: one pendent edge be added to vertex v_2 with pendent vertex v and another pendent edge be added to vertex v_{n-3} with pendent vertex w. For the former case, by induction hypothesis, and by $m(T_m,k) = m(T_m - v^*,k) + m(T_m - v^* - w^*, k-1)$, we have $T_m \prec T_3$. For the later case, $m(T^{4*},k)$ $= m(T^{4*}-v,k)+m(T^{4*}-v-v_2,k-1) = m(n-2(2)1,k)+m(n-4(2)1,k-1)$. By Lemma 3.4, $n-2(2)1$ ($n-4(2)1$, respectively) is of minimal energy in $\mathcal{J}_{3,n-1}$ ($\mathcal{J}_{3,n-3}$,respectively). So our statement holds. □

From previous two Lemmas, we have that the tree of order n with fourth maximal energy must be in $\mathcal{J}_{3,n}$. By checking each characteristic polynomial of trees in $\mathcal{J}_{3,n}$ for $n = 11, 12, 13$, we obtain that $n-2(4)2$ is the tree of fourth maximal energy when $n = 11, 12$ and $9(5)4$ is the tree of fourth maximal energy when $n = 13$.

Now we are ready to prove our main results.

Theorem 3.6. *Let T be a tree on n vertices, and $T \notin \mathscr{H}_n$, then $T \prec n-2(7)2$ where $|T| = n \geq 14$.*

Proof. For $|T| = 14, 15$, by Lemma 3.5, the result can be checked by looking at their characteristic polynomials in $\mathscr{J}_{3,14}, J_{3,15}$. We suppose the result holds for smaller value of $|T|$. Now consider $|T| = n$, we shall show that $T \prec n-2(7)2$ if $T \notin \mathscr{H}_n$. Let v be an end vertex of a longest path of T, then this v must be a pendent vertex. Let w be the vertex adjacent to v. If $T - v = P_{n-1}$, i.e., $T = n-1(2)1$ by the choice of v, then by Lemma 3.1, $T \prec n-2(7)2$. If $T - v = n-3(3)2$, then $T = n-2(4)2$ or T_1 (see Figure 2) or T_1'(see Figure 5) by the choice of v. By the proof of Lemma 3.1, Lemma 3.2 and Lemma 3.3, $\{n-2(4)2, T_1, T_1'\} \prec n-2(7)2$. If $T - v = n-3(5)2$, then T must be $n-2(6)2$ or T_2 (see Figure 2) or T_2' (see Figure 5). Again by Lemma 3.1-3.3 $\{n-2(6)2, T_2, T_2'\} \prec n-2(7)2$. If $T - v = n-3(7)2$ by the choice of v, T must be $n-2(8)2$ or T_6 or T_6' (see Figure 5). By Lemma 3.1, $n-2(8)2 \prec n-2(7)2$. Note that T_6 is obtained from $n-3(7)2$ by adding an edge to v_{n-4} with pendent vertex v, while T_6' is obtained from $n-3(7)2$ by adding an edge to v_2 with pendent vertex v.

$$\begin{aligned}
m(T_6, k) &= m(T_6 - v, k) + m(T_6 - v_{n-4} - v, k-1) \\
&= m(n-3(7)2, k) + m(n-5(7)2, k-1), \\
m(T_6', k) &= m(T_6' - v, k) + m(T_6' - v_2 - v, k-1) \\
&= m(n-3(7)2, k) + m(n-5(5)2, k-1), \\
m(n-2(7)2, k) &= m(n-2(7)2 - v_{n-2}, k) + m(n-2(7)2 - v_{n-3} - v_{n-2}, k-1) \\
&= m(n-3(7)2, k) + m(n-4(7)2, k-1), \\
m(n-2(7)2, k) &= m(n-2(7)2 - v_1, k) + m(n-2(7)2 - v_1 - v_2, k-1) \\
&= m(n-3(6)2, k) + m(n-4(5)2, k-1).
\end{aligned}$$

By Lemma 2.1, $m(n-5(7)2, k-1) < m(n-4(7)2, k-1)$, $m(n-5(5)2, k-1) < m(n-4(5)2, k-1)$, thus $\{T_6, T_6'\} \prec n-2(7)2$. So, we assume that $T - v \notin \mathscr{H}_n$. Note that the order of $T - v$ is $n-1$, then by the induction hypothesis, we have $T - v \prec n-3(7)2$. Next we consider $T - v - w$. If $T - v - w = P_{n-2}$, then $T = n-2(3)2$ or P_n by the choice of v, a contradiction to that $T \notin \mathscr{H}_n$. If $T - v - w = n-4(3)2$, note that $T \neq n-2(5)2$, so T must be either T_7, or T_7' (see Figure 5). Since $T_7 - v_{n-4} \notin \mathscr{H}_{n-1}$ and $T_7 - v_{n-4} - v_{n-5} \notin \mathscr{H}_{n-2}$, by our induction hypothesis, we have $m(T_7, k) = m(T_7 - v_{n-4}, k) + m(T_7 - v_{n-4} - v_{n-5}, k-1) < m(n-3(7)2, k) + m(n-4(7)2, k-1) = m(n-2(7)2, k)$. Hence $T_7 \prec n-2(7)2$. Similarly we have that $T_7' \prec n-2(7)2$. If $T - v - w = n-4(5)2$, by the choice of v, T must be one of $\{T_8, T_9, T_{10}, T_{11}\}$ exhibited in Figure 5. Using a similar argument to that in a previous discussion, we have

$$\begin{aligned}
m(T_i, k) &= m(T_i - v_{n-4}, k) + m(T_i - v_{n-4} - v_{n-5}, k-1) \qquad (i = 8, 9) \\
&\quad < m(n-3(7)2, k) + m(n-4(7)2, k-1) \\
&= m(n-2(7)2, k), \\
m(T_j, k) &= m(T_j - v_1, k) + m(T_j - v_1 - v_2, k-1) \qquad (j = 10, 11) \\
&\quad < m(n-3(7)2, k) + m(n-4(7)2, k-1) \\
&= m(n-2(7)2, k).
\end{aligned}$$

If $T - v - w = n-4(7)2$, by the choice of v, T must be one of $\{T_{12}, T_{13}, T_{14}\}$ exhibited in Figure 5. By induction hypothesis, $m(T_i, k) = m(T_i - v, k) + m(T_i - v - w, k-1) < m(n-3(7)2, k) + m(n-4(7)2, k-1) = m(n-2(7)2, k)$ since $T_i - v \notin \mathscr{H}_{n-1}$, and $T_i - v - w \notin \mathscr{H}_{n-2}$ where $i = 12, 13, 14$.

Now we could assume that $T - v - w \notin \mathscr{H}_{n-2}$. Hence $m(T, k) = m(T - v, k) + m(T - v - w, k-1) < m(n-3(7)2, k) + m(n-4(7)2, k-1) = m(n-2(7)2, k)$ by induction hypothesis. Thus, $T \prec n-2(7)2$. Therefore, the theorem holds. Hence we have completed the proof of conjecture. $\square$

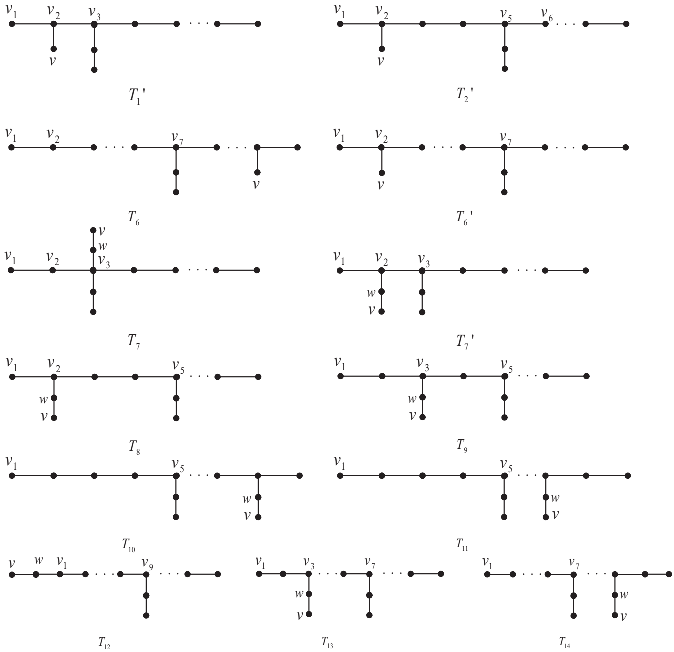

Figure 5: $T_1', T_2', T_6, T_6', T_7, T_7', T_8, T_9, T_{10}, T_{11}, T_{12}, T_{13}$ and T_{14}.

References

[1] D. Cvetković, M. Doob, H. Sachs, Spectra of Graphs – Theory and Applications, Academic Press, New York, 1980.

[2] I. Gutman, Acyclic systems with extremal Hückel π-electron energy, Theoret. Chim. Acta. 45 (1977) 79-87.

[3] I. Gutman, S. Radenkovic, N. Li and S. Li, Extremal energy trees, MATCH Commun. Math. Comput. Chem. 59 (2008) 315-320.

[4] I. Gutman, The energy of a graph: old and new results, in: A. Betten, A. Kohnert, R. Laue, A. Wassermann (Eds.), Algebraic Combinatorics and Applications, Springer-Verlag, Berlin, 2001, pp. 196-211.

[5] I. Gutman, O.E. Polansky, Mathatical Concepts in Organic Chemistry, Springer, Berlin, 1986.

[6] I. Gutman, B. Furtula, H. Hua, Bipartite unicyclic graphs with maximal, second-maximal, and third-maximal energy, MATCH Commun. Math. Comput. Chem. 58 (2007) 85-92.

[7] H. Hua, On minimal energy of unicyclic graphs with prescribed girth and pendent vertices, MATCH Commun. Math. Comput. Chem. 57 (2007) 351-361.

[8] H. Hua, Bipartite unicyclic graphs with large energy, MATCH Commun. Math. Comput. Chem. 58 (2007) 57-83.

[9] N. Li and S. Li, On the Extremal Energies of Trees, MATCH Commun. Math. Comput. Chem. 59 (2008) 291-314.

[10] S. Li, X. Li, and Z. Zhu, On tricyclic graphs with minimal energy, MATCH Commun. Math. Comput. Chem. 59 (2008)397-419.

[11] S. Li, X. Li, and Z. Zhu, Minimal energies and Hosoya indices of unicyclic graphs, Accepted by MATCH Commun. Math. Comput. Chem.

[12] S. Li, Z. Zhu, Minimal energies and Hosoya indices of bicyclic graphs, preprint.

[13] W. Yan, L. Ye, On the minimal energy of trees with a given diameter, Appl. Math. Lett. 18 (2005) 1046-1052.

[14] W. Yan, L. Ye, On the maximal energy and the Hosoya index of a type of trees with many pendent vertices, MATCH Commun. Math. Comput. Chem. 53 (2005) 449-459.

[15] L. Ye, X. Yuan, On the minimal energy of trees with a given number of pendent vertices, MATCH Commun. Math. Comput. Chem. 57 (2007) 193-201.

[16] L. Ye, X. Yuan, On the minimal energy of trees with a given number of pendent vertices, MATCH Commun. Math. Comput. Chem. 57 (2007) 193-201.

[17] A. Yu, X. Lv, Minimum energy on trees with k pendent vertices, Linear Algebra Appl. 414 (2006) 625-633.

[18] F.J. Zhang, H.E. Li, On acyclic conjugated molecules with minimal energies, Discr. Appl. Math. 92 (1999) 71-84.

[19] F.J. Zhang, H.E. Li, On maximal energy ordering of acyclic conjugated molecules, in: P. Hansen, P. Fowler, M. Zheng (Eds.), Discrete Mathematical Chemistry, Am. Math. Soc., Providence, 2000, pp. 385-392.

[20] J. Zhang, B. Zhou, On bicyclic graphs with minimal energies, J. Math. Chem. 37 (2005) 423-431.

[21] B. Zhou and F. Li, On minimal energies of trees of a prescribled diameter, J. Math. Chem. 39 (2006) 465-473.