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Sharp upper bounds for total π-electron energy of alternant hydrocarbons

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The energy $E(G)$ of a graph G is defined as the sum of the absolute values of all the eigenvalues of the adjacency matrix of the graph G. This quantity is used in chemistry to approximate the total π-electron energy of molecules and in particular, in case G is bipartite, alternant hydrocarbons. In this paper, we show that if $G = (V_1, V_2; E)$ is a bipartite graph with $m \geqslant n_1$ edges and $|V_1| = n_1 \geqslant n_2 = |V_2|$, then

$$E(G) \leqslant \frac{2m}{\sqrt{n_1 n_2}} + 2\sqrt{(n_2 - 1)\left(m - \frac{m^2}{n_1 n_2}\right)}$$

and

$$E(G) \leqslant \sqrt{n_1 n_2}(1 + \sqrt{n_2})$$

must hold.

KEY WORDS: alternant hydrocarbons, energy, upper bound

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1. Introduction

Let G be a graph on n vertices and $A(G)$ be the adjacency matrix of G. The eigenvalues $\lambda_1 \geqslant \lambda_2 \geqslant \cdots \geqslant \lambda_n$ of $A(G)$ are called the eigenvalues of G. The energy of G, denoted by $E(G)$, is defined as

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

In chemistry, the energy of a graph is of interest since it can be used to approximate, the total π-electron energy of a molecule (see [2, 6, 7, 9]).

A graph $G = (V_1, V_2; E)$ is a *bipartite graph* with vertex classes V_1 and V_2 if $V(G) = V_1 \cup V_2$, $V_1 \cap V_2 = \Phi$ and every edge joins a vertex of V_1 to a vertex of V_2.

In 1971, McClelland [13] gave a upper bound for the energy of a conjugated hydrocarbon with n carbon atoms and m carbon–carbon bonds, that is

$$E(G) \leqslant \sqrt{2mn}. \tag{1.1}$$

After McClelland's bound, numerous other bounds for $E(G)$ which contain parameters other than n and m or are restricted to special classes of conjugated hydrocarbons were given (see [1, 4, 5, 8]).

Recent upper bounds for $E(G)$ depending only on n (the number of carbon atoms) and m (the number of carbon–carbon bonds) are as follows:

Koolen et al. [10] proved that for a conjugated hydrocarbon,

$$E(G) \leqslant \frac{2m}{n} + \sqrt{(n-1)\left(2m - \left(\frac{2m}{n}\right)^2\right)} \tag{1.2}$$

and

$$E(G) \leqslant \frac{n(1+\sqrt{n})}{2} \tag{1.3}$$

must hold.

In the case of alternant hydrocarbons, Koolen and Moulton [12] proved that

$$E(G) \leqslant 2\left(\frac{2m}{n}\right) + \sqrt{(n-2)\left(2m - 2\left(\frac{2m}{n}\right)^2\right)} \tag{1.4}$$

and

$$E(G) \leqslant \frac{n}{\sqrt{8}}(\sqrt{2} + \sqrt{n}). \tag{1.5}$$

Note 1. In [11], Koolen and Moulton proved that bound (1.2) is always better than bound (1.1). For a alternant hydrocarbon, by direct calculation, it is easy to see that bound (1.4) is always better than bound (1.2) and bound (1.5) is always better than bound (1.3).

In this paper, we show that for a bipartite graph (corresponding to an alternant hydrocarbon) $G = (V_1, V_2; E)$ with $m \geq n_1$ edges and $|V_1| = n_1 \geq n_2 = |V_2|$, then

$$E(G) \leqslant \frac{2m}{\sqrt{n_1 n_2}} + 2\sqrt{(n_2 - 1)\left(m - \frac{m^2}{n_1 n_2}\right)}$$

and

$$E(G) \leqslant \sqrt{n_1 n_2}\left(1 + \sqrt{n_2}\right).$$

2. Lemmas and results

Lemma 2.1. [3] Let A be a real symmetric matrix with eigenvalues $\mu_1 \geq \mu_2 \geq \cdots \geq \mu_n$. Given a partition $\{1, 2, \ldots, n\} = \Delta_1 \cup \Delta_2 \cup \cdots \cup \Delta_m$ with $|\Delta_i| = n_i > 0$, consider the corresponding blocking $A = (A_{ij})$, so that A_{ij} is an $n_i \times n_j$ block. Let e_{ij} be the sum of the entries in A_{ij} and put $B = \left(\frac{e_{ij}}{n_i}\right)$ (i. e., $\frac{e_{ij}}{n_i}$ is an average row sum in A_{ij}). Then the spectrum of B is contained in the segment $[\mu_n, \mu_1]$.

For any graph G with n vertices and m edges, it is a well-known fact that [3]

$$\lambda_1 \geq \frac{2m}{n}. \tag{2.1}$$

Furthermore, for a bipartite graph, we have the following:

Theorem 2.1. Let $G = (V_1, V_2; E)$ be a bipartite graph on n vertices m edges and suppose that $|V_1| = n_1,\ |V_2| = n_2$. Then we have

$$\lambda_1 \geq \frac{m}{\sqrt{n_1 n_2}} \tag{2.2}$$

and if G is a regular bipartite graph, then the equality holds.

Proof. Without loss of generality, we can assume that

$$V_1 = \{v_1, v_2, \ldots, v_{n_1}\} \text{ and } V_2 = \{v_{n_1+1}, v_{n_1+2}, \ldots, v_n\}.$$

Then $A(G)$ can be written in the following form:

$$A(G) = \begin{bmatrix} O_{n_1} & A_1 \\ A_1^T & O_{n_2} \end{bmatrix},$$

where O_{n_1} is an $n_1 \times n_1$ zero matrix and A_1 is an $n_1 \times n_2$ submatrix of $A(G)$.

Note that the sum of the entries of A_1 is m. Let

$$B = \begin{bmatrix} 0 & \frac{m}{n_1} \\ \frac{m}{n_2} & 0 \end{bmatrix}.$$

By a simple calculation, we have $\rho(B) = \frac{m}{\sqrt{n_1 n_2}}$, where $\rho(B)$ denotes the largest eigenvalue of B. From lemma 2.1, we have $\lambda_1 \geq \frac{m}{\sqrt{n_1 n_2}}$.

If G is a r-regular bipartite graph, then $n_1 = n_2$. Thus, we have $\frac{m}{\sqrt{n_1 n_2}} = r = \lambda_1$. The proof is complete. □

Note 2. Since $n_1 + n_2 \geq 2\sqrt{n_1 n_2}$, it is easy to see that bound (2.2) is always better than bound (2.1).

A $2-(\upsilon, k, \lambda)$-design is a collection of k-subsets or blocks of a set of υ points, such that each 2-set of points lies in exactly λ blocks. The design is called symmetric in case the number of blocks b equals υ. *The graph of a* $2-(\upsilon,k,\lambda)$-*design* is formed in the following way:

the $b+\upsilon$ vertices of the graph correspond to the blocks and points of the design with two vertices adjacent if and only if one corresponds to a block and the other corresponds to a point contained in that block. Clearly the graph is bipartite. Note that the graph of a symmetric $2-(\upsilon,k,\lambda)$-design with $\upsilon > k > \lambda > 0$ has eigenvalues k, $\sqrt{k-\lambda}$ (with multiplicity $\upsilon-1$), $-\sqrt{k-\lambda}$ (with multiplicity $\upsilon-1$) and $-k$ (see [3]).

Lemma 2.2. [3] For the bipartite graph $G=(V_1,V_2;E)$ with $|V_1|=n_1\geq n_2=|V_2|$, we have

$$\eta(G)\geq n_1-n_2,$$

where $\eta(G)$ is the number of 0 as an eigenvalue of G.

Now we can give the main results of this paper.

Theorem 2.2. Let $G=(V_1,V_2;E)$ ($|V_1|=n_1\geq n_2=|V_2|$) be a bipartite graph on n vertices and $m\geq n_1$ edges. Then we have

$$E(G)\leqslant \frac{2m}{\sqrt{n_1n_2}}+2\sqrt{(n_2-1)\left(m-\frac{m^2}{n_1n_2}\right)}. \tag{2.3}$$

Moreover, if $n=2\upsilon$, $2\sqrt{m}<n<2m$ and G is the graph of a symmetric $2-(\upsilon,k,\lambda)$–design with $k=\frac{2m}{n}$ and $\lambda=\frac{k(k-1)}{\upsilon-1}$, then the equality holds.

Proof. If $n_2=1$, then $m=n_1$. By direction calculation, the equality of (2.3) holds. In the following, we always assume that $n_2\geq 2$.

From lemma 2.2 and the *Coulson–Rushbrooke* pairing theorem [3, theorem 3.11], we have

$$E(G)=2\lambda_1+2\sum_{i=2}^{n_2}\lambda_i.$$

Note that $\sum_{i=1}^{n_2}\lambda_i^2=\frac{1}{2}\sum_{i=1}^{n}\lambda_i^2=m$. Using this together with the *Cauchy–Schwartz* inequality, we have

$$\sum_{i=2}^{n_2}\lambda_i\leqslant\sqrt{(n_2-1)\left(m-\lambda_1^2\right)}.$$

Thus, we have

$$E(G)\leqslant 2\lambda_1+2\sqrt{(n_2-1)\left(m-\lambda_1^2\right)}. \tag{2.4}$$

Let $f(x) = 2x + 2\sqrt{(n_2 - 1)(m - x^2)}$. By direct analysis we verify that $f(x)$ is a monotonically decreasing function in the interval $\left(\sqrt{\frac{m}{n_2}}, \sqrt{m}\right)$. In view of $m \geq n_1$, we see that $\sqrt{\frac{m}{n_2}} \leqslant \frac{m}{\sqrt{n_1 n_2}} \leqslant \lambda_1$ must hold. Hence we have from (2.4) and theorem 2.1 that

$$E(G) \leqslant f(\lambda_1) \leqslant f\left(\frac{m}{\sqrt{n_1 n_2}}\right) = \frac{2m}{\sqrt{n_1 n_2}} + 2\sqrt{(n_2 - 1)\left(m - \frac{m^2}{n_1 n_2}\right)}.$$

If G is the graph of a symmetric $2-(\upsilon, k, \lambda)$-design satisfying the conditions of theorem 2.2, by direction calculation, the equality holds. □

Note 3. Let n_1, n_2 and m be integers satisfying that $n = n_1 + n_2 \geq 3, n_1 \geq n_2 \geq 1, m \geq n_1$ and $g(x) = 2x + \sqrt{(n-2)(2m - 2x^2)}$. By direct analysis we verify that the function $g(x)$ monotonically decreases in the interval $\left(\sqrt{\frac{2m}{n}}, \sqrt{m}\right)$. Since $m \geq n_1$, we have $2m \geq 2n_1 \geq n$. Then we have $\frac{m}{\sqrt{n_1 n_2}} \geq \frac{2m}{n} \geq \sqrt{\frac{2m}{n}}$. Thus, $g\left(\frac{m}{\sqrt{n_1 n_2}}\right) \leqslant g(\frac{2m}{n})$, that is

$$\frac{2m}{\sqrt{n_1 n_2}} + \sqrt{(n-2)\left(2m - 2\frac{m^2}{n_1 n_2}\right)} \leqslant 2\left(\frac{2m}{n}\right) + \sqrt{(n-2)\left(2m - 2\left(\frac{2m}{n}\right)^2\right)}.$$

By direct calculation, we have

$$\frac{2m}{\sqrt{n_1 n_2}} + 2\sqrt{(n_2 - 1)\left(m - \frac{m^2}{n_1 n_2}\right)} \leqslant \frac{2m}{\sqrt{n_1 n_2}} + \sqrt{(n-2)\left(2m - 2\frac{m^2}{n_1 n_2}\right)}.$$

From the above two inequalities, we conclude that bound (2.3) is always better than bound (1.4).

Theorem 2.3. Let $G = (V_1, V_2; E)$ $(|V_1| = n_1 \geq n_2 = |V_2|)$ be a bipartite graph on $n \geq 2$ vertices. Then

$$E(G) \leq \sqrt{n_1 n_2}(1 + \sqrt{n_2}). \tag{2.5}$$

Moreover, if $n = 2\upsilon$, and G is the graph of a $2-\left(\upsilon, \frac{\upsilon+\sqrt{\upsilon}}{2}, \frac{\upsilon+2\sqrt{\upsilon}}{4}\right)$–design, then the equality holds.

Proof. By direct calculation, we have the left side of inequality (2.3) – considered as a function of m – is maximized when

$$m = \frac{n_1 n_2 + n_1\sqrt{n_2}}{2}$$

holds. Inequality (2.5) now follows by substituting this value of m into (2.3).

If $n = 2\upsilon$, and G is the graph of a $2-(\upsilon, \frac{\upsilon+\sqrt{\upsilon}}{2}, \frac{\upsilon+2\sqrt{\upsilon}}{4})$-design, it is seen that the equality holds. The proof is complete. □

Note 4. Since $n_1+n_2 \geq 2\sqrt{n_1 n_2}$, it is easy to see that bound (2.5) is always better than bound (1.5).

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