Estimating the total π-electron energy

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Abstract: The paper gives a short survey of the most important lower and upper bounds for the total π-electron energy, i.e., the graph energy (E). In addition, a new lower and a new upper bound for E are deduced, valid for general molecular graphs. The strengthened versions of these estimates, valid for alternant conjugated hydrocarbons, are also reported.

Keywords: total π-electron energy; graph energy; HMO theory.

INTRODUCTION

The total π-electron energy (E_π), as calculated within the simple tight-binding Hückel molecular orbital (HMO) approximation, is one of the most precious pieces of information that can be directly related with molecular structure, by means of spectral graph theory.¹–⁴ In the case of the chemically most relevant conjugated π-electron systems (in particular, benzenoids,⁵ phenylenes,⁶ fluoranthenes,⁷ etc), E_π can be expressed as:

\[ E_\pi = \alpha n + \beta E \]

where \( \alpha \) and \( \beta \) are the standard HMO parameters (constants), \( n \) is the number of carbon atoms (number of vertices of the underlying molecular graph \( G \)), whereas:

\[ E = E(G) = \sum_{i=1}^{n} \lambda_i \]

is the structure-sensitive term, depending on the eigenvalues \( \lambda_1, \lambda_2, \ldots, \lambda_n \) of the molecular graph \( G \). The non-trivial part of the theory of total π-electron energy is just the study of the structure-dependency of the quantity \( E \), which nowadays is referred to⁸ as the energy of the (molecular) graph \( G \). The energy of chemically

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relevant molecular graphs was shown to be quantitatively related with the experimentally determined heats of formation and other measures of thermodynamic stability of the underlying conjugated compounds.\textsuperscript{2,5,9}

In the last 10–15 years, graph energy became a popular topic of mathematical research, resulting in hundreds of published papers. Details on graph energy can be found in a book,\textsuperscript{8} the references cited therein, and recent papers.\textsuperscript{10–15}

One of the earliest results in the theory of total $\pi$-electron energy are the estimates obtained by McClelland,\textsuperscript{16} namely:

$$\sqrt{2m + n(n - 1)} \left| \det A \right|^{2/n} \leq E(G) \leq \sqrt{2mn}$$  \hspace{1cm} (2)

where $n$ is the number of vertices of the molecular graph $G$ (equal to the number of carbon atoms of the underlying conjugated hydrocarbon), $m$ is the number of edges of $G$ (equal to the number of carbon–carbon bonds), and $A = A(G)$ is the adjacency matrix of the graph $G$.

McClelland's upper bound $\sqrt{2mn}$ played a significant role in the theory of the total $\pi$-electron energy, because it was demonstrated\textsuperscript{16} that $a\sqrt{2mn}$, for $a \approx 0.9$, provides an excellent approximation for $E$. Comparative testings\textsuperscript{5,17–19} of the numerous existing $(n,m)$-type approximate formulas for $E$ revealed that not one was better than that of McClelland. This somewhat puzzling result found an explanation after the discovery of McClelland-type lower bounds for energy.\textsuperscript{20–23} It was first shown\textsuperscript{20} that for $g = \sqrt{16/27} = 0.77$, the expression $g\sqrt{2mn}$ is a lower bound for the energy of benzenoid hydrocarbons. Türker obtained $g = 0.5$ for all alternant conjugated hydrocarbons,\textsuperscript{21} which was further improved\textsuperscript{22,23} as $g = \sqrt{32/81} = 0.63$.

Eventually, several other estimates of $E$ were obtained, of which here only those depending solely on the number of edges of the molecular graph are mentioned:\textsuperscript{24}

$$2\sqrt{m} \leq E(G) \leq 2m$$  \hspace{1cm} (3)

and those depending solely on the number of its vertices:\textsuperscript{24,25}

$$2\sqrt{n-1} \leq E(G) \leq \frac{n}{2} \left( \sqrt{n} + 1 \right)$$  \hspace{1cm} (4)

At this point, also an $(n,m)$-type improvement of McClelland's upper bound should be mentioned:

$$E(G) \leq \frac{2m}{n} + \sqrt{(n-1) \left[ 2m - \left( \frac{2m}{n} \right)^2 \right]}$$  \hspace{1cm} (5)

discovered 30 years later\textsuperscript{25,26} than the estimates (2).
By means of the bounds (2)–(5) and McClelland’s approximate expression for $E$, the two most important structural parameters, determining the gross part of total π-electron energy were established: these are $n$ and $m$. The evident next step was to find estimates and approximate expressions for $E$ possessing more than two structural parameters.

Although there is no general agreement about which the third-important structural parameter should be, most attention was paid to the number of Kekulé structures, $K = K(G)$, and to the closely related determinant of the adjacency matrix. In particular:

- if $B$ is the molecular graph of a benzenoid hydrocarbon, then:
  \[
  \det A(B) = (-1)^{n/2} K(B)^2; \]

- if $F$ is the molecular graph of a fluoranthene, then:
  \[
  \det A(F) = (-1)^{n/2} [K(F_1)K(F_2)]^2; \]

where $F_1$ and $F_2$ are the „male“ and „female“ fragments of $F$; if $P$ is the molecular graph of a phenylene, then:

- \[
  \det A(P) = (-1)^{n/2} K(HS)^2 \]

where $HS$ stands for the hexagonal squeeze of $P$.

The dependence of the total π-electron energy on the number of Kekulé structures was much investigated, especially for benzenoids, fluoranthenes, and phenylenes. In view of the above stated relations between the determinant of the adjacency matrix and the number of Kekulé structures, every lower and upper bound for $E$ contains information on the $K$-dependence of the total π-electron energy. Hitherto, the best such estimates were:

- valid for general molecular graphs, and

\[
\sqrt{2m + n(n-1)} \det A^{2/n} \leq E(G) \leq \sqrt{2m(n-1) + n} \det A^{2/n}, \quad (6)
\]

- valid for alternant conjugated hydrocarbons. Recently a further upper bound for $E$ was established:

\[
E(G) \geq \frac{2m}{n} + n - 1 + \ln \left( \frac{n \det A}{2m} \right), \quad (8)
\]

valid under the condition that $\det A \neq 0$, i.e., that no eigenvalue of the molecular graph is equal to zero, i.e., that the respective conjugated molecule has no non-bonding molecular orbitals.

In what follows, two novel $(n, m, \det A)$-type estimates of graph energy were obtained. To realize this, some preparations were required.
PRELIMINARIES

In this section, some previously known results that will be needed in the next two sections are listed.

Lemma 1.\textsuperscript{44} Let $x_1, x_2, \ldots, x_N$ be non-negative numbers, and let:

$$\alpha = \frac{1}{N} \sum_{i=1}^{N} x_i \quad \text{and} \quad \gamma = \left( \prod_{i=1}^{N} x_i \right)^{1/N}$$

be their arithmetic and geometric means. Then:

$$\frac{1}{N(N-1)} \sum_{i<j} \left( \sqrt{x_i} - \sqrt{x_j} \right)^2 \leq \alpha - \gamma \leq \frac{1}{N} \sum_{i<j} \left( \sqrt{x_i} - \sqrt{x_j} \right)^2$$

Moreover, equality holds if and only if $x_1 = x_2 = \cdots = x_N$.

Lemma 2.\textsuperscript{45} For a graph $G$ with $n$ vertices and $m$ edges, eigenvalues $\lambda_1, \lambda_2, \ldots, \lambda_n$, and for $1 \leq j \leq n$:

$$-\sqrt{\frac{2m(j-1)}{n(n-j+1)}} \leq \lambda_j \leq \sqrt{\frac{2m(n-j)}{n j}}$$

Lemma 3.\textsuperscript{46} Let $G$ be a connected graph of order $n$. Then $\lambda_1 \geq 2m/n$, with equality if and only if $G$ is regular.

LOWER BOUND FOR GRAPH ENERGY

Theorem 1. The lower bound in (6) can be improved as:

$$E(G) \geq \sqrt{2m + n(n-1) \left| \det A \right|^{2/n} + \frac{4}{(n+1)(n-2)} \left[ \sqrt{\frac{2m}{n}} - \left( \frac{2m}{n} \right)^{1/4} \right]^2}$$

(9)

Proof. From Lemma 1, one obtains:

$$\sum_{i=1}^{N} x_i \geq N \left( \prod_{i=1}^{N} x_i \right)^{1/N} + \frac{1}{N-1} \sum_{i<j} \left( \sqrt{x_i} - \sqrt{x_j} \right)^2$$

(10)

Substituting in (10) $N = n(n-1)/2$ and $x_i = |\lambda_j| \cdot |\lambda_k|$ for $i = 1, 2, \ldots, n(n-1)/2$, $j = 1, 2, \ldots, n-1$ and $k = j+1, j+2, \ldots, n$, one arrives at:

$$\sum_{j<k} |\lambda_j| |\lambda_k| \geq \frac{n(n-1)}{2} \left( \prod_{i=1}^{n} |\lambda_i| \right)^{2/n}$$

$$+ \frac{2}{n^2 - n - 2} \sum_{j<k<r<s} \left( \sqrt{|\lambda_j| |\lambda_k|} - \sqrt{|\lambda_r| |\lambda_s|} \right)^2$$

which is the same as:
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\[ 2 \sum_{j<k} |\lambda_j \parallel \lambda_k | \geq n(n-1) | \det A |^{2/n} + \frac{4}{n^2 - n - 2} \sum_{j<k<r<s} \left( |\lambda_j \parallel \lambda_k | - |\lambda_r \parallel \lambda_s | \right)^2 \]

By Lemma 2:

\[ \lambda_{n/2} \leq \sqrt{\frac{2m}{n}} \]

whereas by Lemma 3:

\[ \lambda_1 \geq \frac{2m}{n} \]

If, in addition, one takes into account that: \[^{44} \lambda_n \leq -1 \] , i.e., \(|\lambda_n | \geq 1\), one obtains:

\[ \sum_{j<k<r<s} \left( |\lambda_j \parallel \lambda_k | - |\lambda_r \parallel \lambda_s | \right)^2 \geq \left( |\lambda_1 \parallel \lambda_n | - |\lambda_{n/2} \parallel \lambda_{n/2} | \right)^2 = \]

\[ = |\lambda_n | \left( |\lambda_1 | - |\lambda_{n/2} | \right)^2 \geq \left( \sqrt{\frac{2m}{n}} - \left( \frac{2m}{n} \right)^{1/4} \right)^2 \]

which combined with:

\[ 2 \sum j<k |l_j \parallel l_k | + \sum_{j=1}^n |l_j |^2 = \sum_{j=1}^n \sum_{k=1}^n |l_j \parallel l_k | = \left( \sum_{j=1}^n |l_j | \right) \left( \sum_{k=1}^n |l_k | \right) = E^2 \]

and bearing in mind that:

\[ \sum |l_j |^2 = 2m \]

results in a \((n, m, \det A)\)-type lower bound (9).

For alternant conjugated hydrocarbons \(^{1,2} \) (i.e., for bipartite molecular graphs\(^ {46} \)), \( \lambda_j = -\lambda_{n-j+1} \) holds for all \( j = 1, 2, \ldots, n \). In particular, \( \lambda_1 = -\lambda_n \) and \( \lambda_{n/2} = -\lambda_{n/2+1} \). Bearing this in mind, the inequalities in (11) can be strengthened as:

\[ \sum_{j<k<r<s} \left( |\lambda_j \parallel \lambda_k | - |\lambda_r \parallel \lambda_s | \right)^2 \geq \left( |\lambda_1 \parallel \lambda_n | - |\lambda_{n/2} \parallel \lambda_{n/2+1} | \right)^2 = \]

\[ = \left( \lambda_1 - \lambda_{n/2} \right)^2 \geq \left( \frac{2m}{n} - \frac{2m}{n} \right)^2 \]

resulting in the following \((n, m, \det A)\)-type lower bound for total π-electron energy of alternant conjugated hydrocarbons:

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Recall that benzenoids and phenylenes are alternant conjugated hydrocarbons, whereas fluoranthenes are not. It is easy to show that the estimate (12) is better than (9).

**UPPER BOUND FOR GRAPH ENERGY**

_Theorem 2._ Under the condition that \( \det A \neq 0 \), the upper bound in (3) can be improved as:

\[
E(G) \leq 2m - \frac{2m}{n} \left( \frac{2m}{n} - 1 \right) - \ln \left( \frac{n | \det A |}{2m} \right)
\]

(13)

One should compare this result with the lower bound (8).

_Proof._ Consider the function \( f(x) = x^2 - x - \ln x \), which is increasing for \( x \geq 1 \) and decreasing for \( 0 < x \leq 1 \). Thus, for \( x \geq 1 \),

\[
f(x) \geq f(1) = 0, \text{ i.e., } x \leq x^2 - \ln x
\]

with equality holding if and only if \( x = 1 \). Using this result and the definition of graph energy, Eq. (1), one obtains:

\[
E = \lambda_1 + \sum_{j=2}^{n} |\lambda_j| \leq \lambda_1 + \sum_{j=2}^{n} (\lambda_j^2 - \ln |\lambda_j|) = \lambda_1 + 2m - \lambda_1^2 - \ln \prod_{j=1}^{n} |\lambda_j| + \ln \lambda_1
\]

that is:

\[
E \leq \lambda_1 + 2m - \lambda_1^2 - \ln |\det A| + \ln \lambda_1 = 2m - \ln |\det A| - f(\lambda_1)
\]

(14)

Inequality (13) is now obtained by replacing in (14) \( \lambda_1 \) by:

\[
\frac{2m}{n}
\]

This is legitimate since by Lemma 3:

\[
\lambda_1 \geq \frac{2m}{n}
\]

and since:

\[
\frac{2m}{n}
\]

is the average vertex degree, which in molecular graphs is necessarily greater than unity.
By means of arguments analogous to those used for deducing the lower bound (12), in particular, using \( \lambda_1 = -\lambda_n \), for alternant conjugated hydrocarbons without zero graph eigenvalues, the estimate (13) can also be improved as:

\[
E(G) \leq 2m - \frac{4m}{n} \left( 2 \frac{m}{n} - 1 \right) - \ln \left( \frac{n^2 | \det A |}{4m^2} \right)
\]

(15)

DISCUSSION AND CONCLUDING REMARKS

In this paper, our attention was focused on bounds for the HMO total \( \pi \)-electron energy (\( E_\pi \)) of conjugated hydrocarbons, which depend on the number of carbon atoms (\( n \)), the number of carbon–carbon bonds (\( m \)), and the Kekulé structure count (\( K \)). For algebraic reasons, instead of dependence on \( K \), expressions were found in which the determinant of the adjacency matrix (\( \det A \)) is one of the parameters. As explained in the Introduction, for the most important polycyclic conjugated \( \pi \)-electron systems, there are simple relations between \( \det A \) and the Kekulé structure count. Thus, the new estimates reported in this paper, namely (9), (12), (13) and (15), may be viewed as contributions towards a better understanding of the structure-dependency of \( E_\pi \), in particular of its \((n, m, K)\)-dependence.

If \( E_L \) and \( E_D \) is a pair of lower and upper bounds for \( E \), then an approximate expression for \( E \) could be obtained by taking their arithmetic mean: \( 1/2(E_L + E_D) \). However, in view of the algebraic forms of the estimates discussed in this paper, it is better to construct these approximate expressions as \( \sqrt{1/2(E_L^2 + E_D^2)} \). If so, then from the estimates (6), one obtains:

\[
E \approx \sqrt{\frac{1}{2} \left( 2mn + n^2 | \det A |^{2/n} \right)} = \frac{\sqrt{2}}{2} \sqrt{2mn} + \frac{n | \det A |^{2/n}}{\sqrt{8m}}
\]

which, recalling that \( \sqrt{2}/2 = 0.707 \), is evidently a modification of the original McClelland’s formula \( a\sqrt{2mn} \). It is interesting that exactly the same expression was obtained from the improved estimates (7). Equally interesting (and somewhat surprising) is the approximate formula obtained from the estimates (8) and (13):

\[
E \approx \sqrt{m + \frac{n-1}{2} + \frac{2m}{n} - \frac{2m^2}{n^2}}
\]

which is of the \((n, m)\)-type, not containing the logarithm of the determinant of the adjacency matrix, and thus – in contrast to the estimates (8) and (13) – applicable to all molecular graphs.

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ИЗВОД

ГРАНИЦЕ ЗА УКУПНУ ЕНЕРГИЈУ π-ЕЛЕКТРОНА

ИВАН ГУТМАН 1,2 и КИНКАР Ч. ДАС 3

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Дат је кратак преглед најважнијих доњих и горњих граница за укупну енергију π-електрона, тј. енергију графа (E). У наставку су добијене по једна нова доња и горња граница за E, које важе за све молекулске графове. Такође су наведене побољшане верзије тих граница, које важе за алтернантне конјуговане угљоводонике.

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