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## Estimating the total $\pi$ -electron energy

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**Abstract:** The paper gives a short survey of the most important lower and upper bounds for the total  $\pi$ -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  $\pi$ -electron energy; graph energy; HMO theory.

### INTRODUCTION

The total  $\pi$ -electron energy ( $E_\pi$ ), 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.<sup>1–4</sup> In the case of the chemically most relevant conjugated  $\pi$ -electron systems (in particular, benzenoids,<sup>5</sup> phenylenes,<sup>6</sup> fluoranthenes,<sup>7</sup> *etc.*),  $E_\pi$  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:

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

is the structure-sensitive term, depending on the eigenvalues  $\lambda_1, \lambda_2, \dots, \lambda_n$  of the molecular graph  $G$ . The non-trivial part of the theory of total  $\pi$ -electron energy is just the study of the structure-dependency of the quantity  $E$ , which nowadays is referred to<sup>8</sup> 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.<sup>2,5,9</sup>

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,<sup>8</sup> the references cited therein, and recent papers.<sup>10–15</sup>

One of the earliest results in the theory of total  $\pi$ -electron energy are the estimates obtained by McClelland,<sup>16</sup> namely:

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

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<sup>16</sup> that  $a\sqrt{2mn}$ , for  $a \approx 0.9$ , provides an excellent approximation for  $E$ . Comparative testings<sup>5,17–19</sup> 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.<sup>20–23</sup> It was first shown<sup>20</sup> 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,<sup>21</sup> which was further improved<sup>22,23</sup> 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:<sup>24</sup>

$$2\sqrt{m} \leq E(G) \leq 2m \quad (3)$$

and those depending solely on the number of its vertices:<sup>24,25</sup>

$$2\sqrt{n-1} \leq E(G) \leq \frac{n}{2}(\sqrt{n} + 1) \quad (4)$$

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

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

discovered 30 years later<sup>25,26</sup> 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  $\pi$ -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.<sup>27</sup> In particular:

if  $B$  is the molecular graph of a benzenoid hydrocarbon, then:<sup>28,29</sup>

$$\det A(B) = (-1)^{n/2} K(B)^2;$$

if  $F$  is the molecular graph of a fluoranthene, then:<sup>30,31</sup>

$$\det A(F) = (-1)^{n/2} [K(F_1)K(F_2)]^2;$$

where  $F_1$  and  $F_2$  are the „male“ and „female“ fragments of  $F$ ; if  $P$  is the molecular graph of a phenylene, then:<sup>32</sup>

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

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

The dependence of the total  $\pi$ -electron energy on the number of Kekulé structures was much investigated, especially for benzenoids,<sup>33–40</sup> fluoranthenes,<sup>41</sup> and phenylenes.<sup>6</sup> 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  $\pi$ -electron energy. Hitherto, the best such estimates were:<sup>42</sup>

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

valid for general molecular graphs, and

$$\sqrt{4m + n(n-2) |\det A|^{2/n}} \leq E(G) \leq \sqrt{2m(n-2) + 2n |\det A|^{2/n}}, \quad (7)$$

valid for alternant conjugated hydrocarbons. Recently a further upper bound for  $E$  was established:<sup>43</sup>

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

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.<sup>1</sup>

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.*<sup>44</sup> Let  $x_1, x_2, \dots, x_N$  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:

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

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

*Lemma 2.*<sup>45</sup> For a graph  $G$  with  $n$  vertices and  $m$  edges, eigenvalues  $\lambda_1, \lambda_2, \dots, \lambda_n$ , and for  $1 \leq j \leq n$ :

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

*Lemma 3.*<sup>46</sup> 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:

$$E(G) \geq \sqrt{2m + n(n-1) |\det A|^{2/n} + \frac{4}{(n+1)(n-2)} \left[ \sqrt{\frac{2m}{n}} - \left(\frac{2m}{n}\right)^{1/4} \right]^2} \quad (9)$$

*Proof.* From Lemma 1, one obtains:

$$\sum_{i=1}^N x_i \geq N \left( \prod_{i=1}^N x_i \right)^{1/N} + \frac{1}{N-1} \sum_{i < j} (\sqrt{x_i} - \sqrt{x_j})^2 \quad (10)$$

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

$$\begin{aligned} \sum_{j < k} |\lambda_j| |\lambda_k| &\geq \frac{n(n-1)}{2} \left( \prod_{i=1}^n |\lambda_i| \right)^{2/n} + \\ &+ \frac{2}{n^2 - n - 2} \sum_{j < k < r < s} \left( \sqrt{|\lambda_j| |\lambda_k|} - \sqrt{|\lambda_r| |\lambda_s|} \right)^2 \end{aligned}$$

which is the same as:

$$2 \sum_{j < k} |\lambda_j \parallel \lambda_k| \geq n(n-1) |\det A|^{2/n} + \frac{4}{n^2 - n - 2} \sum_{j < k < r < s} \left( \sqrt{|\lambda_j \parallel \lambda_k|} - \sqrt{|\lambda_r \parallel \lambda_s|} \right)^2$$

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:<sup>44</sup>  $\lambda_n \leq -1$ , *i.e.*,  $|\lambda_n| \geq 1$ , one obtains:

$$\begin{aligned} \sum_{j < k < r < s} \left( \sqrt{|\lambda_j \parallel \lambda_k|} - \sqrt{|\lambda_r \parallel \lambda_s|} \right)^2 &\geq \left( \sqrt{|\lambda_1 \parallel \lambda_n|} - \sqrt{|\lambda_{n/2} \parallel \lambda_n|} \right)^2 = \\ &= |\lambda_n| \left( \sqrt{|\lambda_1|} - \sqrt{|\lambda_{n/2}|} \right)^2 \geq \left( \sqrt{\frac{2m}{n}} - \left( \frac{2m}{n} \right)^{1/4} \right)^2 \end{aligned} \quad (11)$$

which combined with:

$$2 \sum_{j < k} |\lambda_j \parallel \lambda_k| + \sum_{j=1}^n |\lambda_j|^2 = \sum_{j=1}^n \sum_{k=1}^n |\lambda_j \parallel \lambda_k| = \left( \sum_{j=1}^n |\lambda_j| \right) \left( \sum_{k=1}^n |\lambda_k| \right) = E^2$$

and bearing in mind that:

$$\sum |\lambda_j|^2 = 2m$$

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

For alternant conjugated hydrocarbons<sup>1,2</sup> (*i.e.*, for bipartite molecular graphs<sup>46</sup>),  $\lambda_j = -\lambda_{n-j+1}$  holds for all  $j = 1, 2, \dots, n$ . 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:

$$\begin{aligned} \sum_{j < k < r < s} \left( \sqrt{|\lambda_j \parallel \lambda_k|} - \sqrt{|\lambda_r \parallel \lambda_s|} \right)^2 &\geq \left( \sqrt{|\lambda_1 \parallel \lambda_n|} - \sqrt{|\lambda_{n/2} \parallel \lambda_{n/2+1}|} \right)^2 = \\ &= (\lambda_1 - \lambda_{n/2})^2 \geq \left( \frac{2m}{n} - \sqrt{\frac{2m}{n}} \right)^2 \end{aligned}$$

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

$$E(G) \geq \sqrt{2m + n(n-1)|\det A|^{2/n} + \frac{4}{(n+1)(n-2)} \left( \frac{2m}{n} - \sqrt{\frac{2m}{n}} \right)^2} \quad (12)$$

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:

$$E(G) \leq 2m - \frac{2m}{n} \left( \frac{2m}{n} - 1 \right) - \ln \left( \frac{n|\det A|}{2m} \right) \quad (13)$$

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:

$$E \leq \lambda_1 + 2m - \lambda_1^2 - \ln |\det A| + \ln \lambda_1 = 2m - \ln |\det A| - f(\lambda_1) \quad (14)$$

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:

$$E(G) \leq 2m - \frac{4m}{n} \left( \frac{2m}{n} - 1 \right) - \ln \left( \frac{n^2 |\det A|}{4m^2} \right) \quad (15)$$

#### 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:

$$E \approx \sqrt{\frac{1}{2}(2mn + n^2 |\det A|^{2/n})} \approx \frac{\sqrt{2}}{2} \sqrt{2mn} + \frac{n |\det A|^{2/n}}{\sqrt{8m}}$$

which, recalling that  $\sqrt{2}/2 \approx 0.707$ , 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  $\pi$ -ЕЛЕКТРОНАИВАН ГУТМАН<sup>1,2</sup> и KINKAR CH. DAS<sup>3</sup>

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Дат је кратак преглед најважнијих доњих и горњих граница за укупну енергију  $\pi$ -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 алтернатне конјуговане угљоводонике.

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## REFERENCES

1. A. Graovac, I. Gutman, N. Trinajstić, *Topological Approach to the Theory of Conjugated Molecules*, Springer, Berlin, 1977
2. I. Gutman, O. E. Polansky, *Mathematical Concepts in Organic Chemistry*, Springer, Berlin, 1986
3. I. Gutman, *J. Serb. Chem. Soc.* **70** (2005) 441
4. M. Perić, I. Gutman, J. Radić-Perić, *J. Serb. Chem. Soc.* **71** (2006) 771
5. I. Gutman, *Topics Curr. Chem.* **162** (1992) 29
6. I. Gutman, A. Stajković, S. Marković, P. Petković, *J. Serb. Chem. Soc.* **59** (1994) 367
7. I. Gutman, J. Đurđević, S. Radenković, A. Burmudžija, *Indian J. Chem., A* **48** (2009) 194
8. X. Li, Y. Shi, I. Gutman, *Graph Energy*, Springer, New York, 2012
9. L. J. Schaad, B. A. Hess, *J. Am. Chem. Soc.* **94** (1972) 3068
10. X. Hu, H. Liu, *MATCH Commun. Math. Comput. Chem.* **66** (2011) 863
11. S. Wagner, *MATCH Commun. Math. Comput. Chem.* **68** (2012) 661
12. E. O. D. Andriantiana, *MATCH Commun. Math. Comput. Chem.* **68** (2012) 675
13. H. Y. Shan, J. Y. Shao, L. Zhang, C. X. He, *MATCH Commun. Math. Comput. Chem.* **68** (2012) 703
14. M. P. Stanić, I. Gutman, *MATCH Commun. Math. Comput. Chem.* **70** (2013) 681
15. K. C. Das, S. A. Mojallal, *MATCH Commun. Math. Comput. Chem.* **70** (2013) 657
16. B. J. McClelland, *J. Chem. Phys.* **54** (1971) 640
17. I. Gutman, S. Marković, A. V. Teodorović, Ž. Bugarčić, *J. Serb. Chem. Soc.* **51** (1986) 145
18. I. Gutman, A. Graovac, S. Vuković, S. Marković, *J. Serb. Chem. Soc.* **54** (1989) 189
19. I. Gutman, T. Soldatović, *MATCH Commun. Math. Comput. Chem.* **44** (2001) 169
20. I. Gutman, *J. Chem. Soc. Faraday Trans.* **86** (1990) 3373
21. L. Türker, *MATCH Commun. Math. Comput. Chem.* **30** (1994) 243
22. I. Gutman, *Croat. Chem. Acta* **68** (1995) 187
23. D. Babić, I. Gutman, *MATCH Commun. Math. Comput. Chem.* **32** (1995) 7
24. G. Caporossi, D. Cvetković, I. Gutman, P. Hansen, *J. Chem. Inf. Comput. Sci.* **39** (1999) 984
25. J. H. Koolen, V. Moulton, *Adv. Appl. Math.* **26** (2001) 47
26. J. H. Koolen, V. Moulton, I. Gutman, *Chem. Phys. Lett.* **320** (2000) 213
27. A. Graovac, I. Gutman, *MATCH Commun. Math. Comput. Chem.* **6** (1979) 49
28. M. J. S. Dewar, H. C. Longuet-Higgins, *Proc. R. Soc. London, Ser. A* **214** (1952) 482



29. I. Gutman, S. J. Cyvin, *Introduction to the Theory of Benzenoid Hydrocarbons*, Springer, Berlin, 1989
30. I. Gutman, *Z. Naturforsch., A* **65** (2010) 473
31. D. Vukičević, J. Đurđević, I. Gutman, *J. Serb. Chem. Soc.* **75** (2010) 1093
32. I. Gutman, *J. Chem. Soc. Faraday Trans.* **89** (1993) 2413
33. G. G. Hall, *Int. J. Math. Educ. Sci. Technol.* **4** (1973) 233
34. I. Gutman, *Chem. Phys. Lett.* **156** (1989) 119
35. I. Gutman, G. G. Hall, *Int. J. Quantum Chem.* **41** (1992) 667
36. I. Gutman, S. Marković, G. G. Hall, *Chem. Phys. Lett.* **234** (1995) 21
37. I. Gutman, S. Marković, D. Vukičević, A. Stajković, *J. Serb. Chem. Soc.* **60** (1995) 93
38. I. Gutman, *Int. J. Quantum Chem.* **74** (1999) 627
39. I. Gutman, S. Radenković, *Chem. Phys. Lett.* **423** (2006) 382
40. S. Radenković, I. Gutman, *J. Serb. Chem. Soc.* **74** (2009) 155
41. J. Đurđević, S. Radenković, I. Gutman, *J. Serb. Chem. Soc.* **73** (2008) 989
42. I. Gutman, *Chem. Phys. Lett.* **24** (1974) 283
43. K. C. Das, S. A. Mojallal, I. Gutman, *MATCH Commun. Math. Comput. Chem.* **70** (2013) 663
44. H. Kober, *Proc. Am. Math. Soc.* **59** (1958) 452
45. R. C. Brigham, R. D. Dutton, *J. Comb. Theory Ser. B* **37** (1984) 228
46. D. M. Cvetković, M. Doob, H. Sachs, *Spectra of Graphs - Theory and Application*, Academic Press, New York, 1980.