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NEW BOUNDS AND APPROXIMATIONS FOR TOTAL π-ELECTRON ENERGY – A CRITICAL TEST

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ABSTRACT. The quality and correlating ability of some recently deduced bounds and approximate formulas for total π-electron energy are tested on a sample of 106 Kekuléan benzenoid hydrocarbons. It was found that not a single new approximate formula and not a single new bound is better than those from the 1970s.

1 Introduction

The total π-electron energy, calculated by mens of the the Hückel molecular orbital (HMO) approximation, is a quantum–theoretical characteristics of conjugated molecules that has been extensively studied in the last 50 or more years [4, 7]. It is attracting the attention of theoretical chemists and mathematicians thanks to its explicit, but mathematically non-trivial, dependence on molecular topology [13]. In the same time, total the π-electron energy is one of the most reliable results that can be deduced from HMO theory, and is in reasonably good agreement with experimentally determined thermodynamic properties of conjugated molecules, especially their enthalpies [6, 10].

When the HMO total π-electron energy is expressed in the units of the HMO carbon–carbon resonance integral β, then it is directly related to the eigenvalues of the molecular graph [4, 10]. For the majority of conjugated hydrocarbons (including the benzenoid systems studied in the present work), the total π-electron energy satisfies the following expression, which in the same time serves as the definition of graph energy [13]:

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

In Eq. (1), G is the molecular graph (for details see [10]), whose eigenvalues are λ_i , $i = 1, 2, \ldots, n$. In what follows, the number of vertices and edges of the graph G will be denoted by n and m, respectively. It should never be forgotten that n is the number of carbon atoms of the underlying conjugated hydrocarbon, whereas m is the number of its carbon–carbon bonds.

By $\mathbf{A}$ we denote the adjacency matrix of the graphs G (for details see [10]).

Within the theory of total π-electron energy, numerous bounds and approximate expressions for E have been discovered, many of which in terms of n, m, and $\det \mathbf{A}$. The first upper and lower bounds for E were obtained in 1971 by McClelland [14]:

$$E(G) \leq \sqrt{2mn} \tag{2}$$

and

$$E(G) \geq \sqrt{2m + n(n-1)|\det \mathbf{A}|^{2/n}} \tag{3}$$

and are valid for all graphs. Eventually, these bounds were improved in 1974 as [5]

$$E(G) \leq \sqrt{2m(n-1) + n\,|\det \mathbf{A}|^{2/n}} \tag{4}$$

$$E(G) \leq \sqrt{2m(n-2) + 2n\,|\det \mathbf{A}|^{2/n}} \tag{5}$$

and

$$E(G) \geq \sqrt{4m + n(n-2)|\det \mathbf{A}|^{2/n}} \tag{6}$$

where the upper bound (4) holds for all graphs, whereas the bounds (5) and (6) are applicable only to bipartite graphs.

The fact that there exists an excellent linear correlation between E and the McClelland upper bound (2), was the starting point for designing approximate formulas

for E [7, 14]. These approximations are of the form $E \approx a\, E^* + b$, where E^* is some upper or lower bound for E. The coefficients a and b are determined by least squares fitting, and are adjusted for a particular class of molecular graphs (usually benzenoid hydrocarbons). A large number of such approximate formulas was investigated, and their comparative studies can be found in our earlier works [6, 9, 11]. In particular, in [9], 10 (n, m)-type approximate formulas for E were tested. In [6], 24 (n, m)-type and additional 15 (n, m, K)-type formulas were examined. In [11], a total of 44 (n, m)-type approximations for E were dealt with.

Quite recently, a number of new bounds and approximate expressions for E were established [1–3]. In [3], the following lower bound was obtained

$$E(G) \geq \frac{2m}{n} + n - 1 + \ln\left(\frac{n\,|\det \mathbf{A}|}{2m}\right) \tag{7}$$

which requires that $\det \mathbf{A} \neq 0$.

The estimates and approximate formulas (8)–(14) were first time reported in [1]. At this point it should be noted that Eqs. (13) and (14) are erroneous. A correct derivation yields Eqs. (15) and (16), respectively. Therefore, in what follows, Eqs. (13) and (14) will be disregarded, and instead of these, their correct versions (15) and (16) considered.

$$E(G) \geq \sqrt{2m + n(n-1)|\det \mathbf{A}|^{2/n} + \frac{4}{(n+1)(n-2)}\left(\sqrt{\frac{2m}{n}} - \left(\frac{2m}{n}\right)^{1/4}\right)} \tag{8}$$

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

$$E(G) \leq 2m - \frac{2m}{n}\left(\frac{2m}{n} - 1\right) - \ln\left(\frac{n\,|\det \mathbf{A}|}{2m}\right) \tag{10}$$

$$E(G) \leq 2m - \frac{4m}{n}\left(\frac{2m}{n} - 1\right) - \ln\left(\frac{n^2\,|\det \mathbf{A}|}{4m^2}\right) \tag{11}$$

$$E(G) \approx \sqrt{\frac{1}{2}\left(2mn + n^2\,|\det \mathbf{A}|^{2/n}\right)} \tag{12}$$

$$E(G) \approx \frac{\sqrt{2}}{2}\sqrt{2mn} + \frac{n\,|\det \mathbf{A}|^{2/n}}{\sqrt{8}\,m} \tag{13}$$

$$E(G) \approx \sqrt{m + \frac{n-1}{2} + \frac{2m}{n} - \frac{2m^2}{n^2}} \tag{14}$$

$$E(G) \approx \frac{\sqrt{2}}{2}\sqrt{2mn} + \frac{n\sqrt{n}}{4\sqrt{m}}\,|\det \mathbf{A}|^{2/n} \tag{15}$$

$$E(G) \approx m + \frac{n-1}{2} + \frac{2m}{n} - \frac{2m^2}{n^2} \tag{16}$$

The bound (8) is valid for all graphs. The validity of the bound (9) is restricted to bipartite graphs. The bounds (10) and (11) are applicable only for graphs with non-zero determinant of the adjacency matrix. In addition, (11) holds only for bipartite graphs.

What has not been done in the papers [1–3] was the checking of the quality of the bounds (8)–(11), relative to the earlier known bounds, and testing the accuracy of the approximations $a\,E^* + b$, where E^* is an expression on the right–hand side of Eqs. (8)–(12) and (15), (16). We do this in the present work.

2 Testing the new approximate formulas and bounds for total π-electron energy

All earlier tests of approximate formulas for total π-electron energy [6,9,11] were done on a representative set of 106 Kekuléan benzenoid hydrocarbons from the book [15]. We did the same also in the present work.

The molecular graphs of benzenoid hydrocarbons contain no odd-membered cycles and are therefore bipartite [10]. If G is the molecular graph of a benzenoid hydrocarbon, then according to the Dewar–Longuet–Higgins' theorem [4, 8],

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

and therefore

$$|\det \mathcal{A}| = K^2$$

where K is the number of Kekulé structures of the corresponding benzenoid molecule [8]. The sample considered by us consisted of Kekuléan benzenoids, i.e., of benzenoids for which $K > 0$. Therefore, all estimates and approximate expressions for E, mentioned in the preceding section (except, of course, Eqs. (13) and (14)), are applicable for our sample. These estimates and approximate expressions are thus formulas of (n, m)– or (n, m, K)-type, and say something about the dependence of total π-electron energy on the number of carbon atoms (n), carbon–carbon bonds (m), and Kekulé structures (K). Recall that n, m, and K are believed to be the three most important structural parameters, determining the value of total π-electron energy and thus the thermodynamic properties of (strain free) benzenoid hydrocarbons [7, 8, 12]

The results obtained for approximating the total π-electron energy as

$$E \approx a\, E^* + b$$

where E^* is one of the above specified formulas of (n, m)– or (n, m, K)-type, and where a and b are determined by least–squares fitting, are presented in Table 1.

E^*	a	b	R	ARE	GRE
(2)	0.899	0.426	0.99984	0.30	0.96
(3)	1.178	−1.531	0.99593	1.48	5.85
(4)	0.900	0.604	0.99988	0.27	0.93*
(5)	0.902	0.786	0.99991	0.24	0.83*
(6)	1.174	−1.815	0.99636	1.41	5.57*
(7)	1.199	−1.677	0.99704	1.27	5.03*
(8)	1.178	−1.532	0.99593	1.48	5.85
(9)	1.178	−1.533	0.99593	1.48	5.85
(10)	0.612	3.219	0.99772	1.24	3.81*
(11)	0.619	4.398	0.99769	1.29	4.92*
(12)	1.015	−0.314	0.99968	0.41	1.54*
(15)	0.063	16.093	0.97972	3.91	41.26*
(16)	0.814	1.398	0.99979	0.39	1.12*

Table 1. Statistical parameters obtained by approximating the total π-electron energy as $a\, E^* + b$ for the set of 106 benzenoid hydrocarbons from the book [15]. E^* is the expression on the right–hand side of one of the above given relations; R is the correlation coefficient; ARE and GRE are the average and greatest relative errors (in %); asterisk indicates that the (greatest) error of benzene is skipped.

We also tested the quality of the above specified upper and lower bonds for the total π-electron energy. The results obtained are illustrated by the data presented

in Tables 2 and 3. Recall that these all pertain to Kekuléan benzenoid hydrocarbons, which are typical and more often encountered polycyclic conjugated molecules. Therefore, from the examples found in Tables 2 and 3 we may conclude about the quality and applicability of the bounds for E in the case of all chemically relevant graphs.

comp.	n	m	K	E	(2)	(4)	(5)	(10)	(11)
1	20	27	7	25.1012	27.4955	27.2349	26.9718	35.8444	33.5806
2	22	26	17	30.9418	33.8231	33.5719	33.3188	44.5072	42.1442
3	26	31	7	36.1560	40.1497	39.8130	39.4734	55.6754	53.2427
4	26	31	24	36.7953	40.1497	39.9048	39.6584	53.2112	50.7784
5	24	29	13	33.9278	37.3095	37.0243	36.7370	50.3289	47.7877
6	30	36	20	42.1374	46.4785	46.1815	45.8853	63.5240	61.0395
7	28	34	21	39.6950	43.6348	43.3504	43.0640	59.3289	56.7468
8	28	34	24	39.7382	43.6348	43.3600	43.0834	59.0618	56.4797
9	32	39	18	45.0995	49.9600	49.6379	49.3138	69.6063	66.9934
10	36	44	16	50.8226	56.2850	55.9374	55.5876	79.8178	77.1807
11	32	41	50	46.4974	51.2250	50.9331	50.6396	71.1130	68.0501

Table 2. Examples illustrating the quality of the upper bounds (2), (4), (5), (10), (11); 1 = benz[*a*]anthracene, 2 = dibenz[*a,c*]anthracene, 3 = hexacene, 4 = dibenzo[*g,p*]-chrysene, 5 = dibenzo[*b,def*]chrysene, 6 = dibenzo[*a,l*]pentacene, 7 = dibenzo[*a,e*]-perylene, 8 = naphtho[*1,2,3,4-rst*]pentaphene, 9 = naphtho[*8,1,2-cde*]hexacene, 10 = tetrabenzo[*a,de,l,op*]pentacene, 11 = ovalene.

comp.	n	m	K	E	(3)	(6)	(7)	(8)	(9)
1	20	27	7	25.1012	22.6615	22.9740	22.3779	22.6615	22.6617
2	22	26	17	30.9418	28.0804	28.3802	27.6333	28.0804	28.0805
3	26	31	7	36.1560	30.6408	31.0770	30.4074	30.6408	30.6408
4	26	31	24	36.7953	33.4944	33.7858	32.8717	33.4944	33.4944
5	24	29	13	33.9278	30.0739	30.4243	29.6642	30.0739	30.0740
6	30	36	20	42.1374	37.0020	37.3687	36.5160	37.0020	37.0021
7	28	34	21	39.6950	35.1555	35.5057	34.6303	35.1556	35.1556
8	28	34	24	39.7382	35.4740	35.8094	34.8974	35.4740	35.4741
9	32	39	18	45.0995	38.7519	39.1635	38.3273	38.7519	38.7519
10	36	44	16	50.8226	42.4570	42.9139	42.0958	42.4570	42.4570
11	32	41	50	46.4974	41.2267	41.5868	40.4456	41.2267	41.2268

Table 3. Examples illustrating the quality of the lower bounds (3), (6)–(9); the compounds same as in Table 2.

3 Discussion and concluding remarks

From Table 1 we see that the best approximations of the form $E \approx a\,E^* + b$ for the total π-electron energy of benzenoid hydrocarbons are the (n, m)-type McClelland's formula, with E^* given by (2), and its two (n, m, K)-type improvements, with E^* given by (4) and (5). Recall that all these were discovered in the 1970s.

The newly proposed approximations are weaker than these old ones, some slightly, some significantly. Outstandingly bad is the formula with E^* from Eq. (15).

From the data given in Table 2 we see that McClelland's upper bound (2) and its improvements (4) and (5), all from the 1970s, are far better than the upper bounds (10) and (11) put forward in 2013. As expected, (11) is slightly better than (10). Anyway, we may safely conclude that the new upper bounds (10) and (11) are useless (at least for applications in chemistry) and should be ignored in future considerations of both total π-electron energy and graph energy.

The data in Table 3 reveal that the improved McClelland's lower bound (6), from the 1970s, has not been superseded by any of the bounds discovered in 2013. In particular, the lower bound (7) is slightly weaker than the original McClelland's estimate (3) and is thus weaker also than (6). From a purely mathematical point of view, the bound (8) is better than (3), and (9) is better than (8). Numerical tests show that (at least in the case of typical molecular graphs) the improvements of (8) over (3) and of (9) over (8) are insignificant and chemically negligible.

The final conclusion of the present work is that the recently communicated bounds and approximate formulas for total π-electron energy, in spite of their mathematical appeal, are of no practical value for chemical applications, and shed hardly any new light on the dependence of total π-electron energy on molecular structure.

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REFERENCES

[1] K. C. Das, I. Gutman, Estimating the total π-electron energy, *J. Serb. Chem. Soc.* **78** (2013) 1925–1933.

[2] K. C. Das, S. A. Mojallal, Upper bounds for the energy of graphs, *MATCH Commun. Math. Comput. Chem.* **70** (2013) 657–662.

[3] K. C. Das, S. A. Mojallal, I. Gutman, Improving McClellands lower bound for energy, *MATCH Commun. Math. Comput. Chem.* **70** (2013) 663–668.

[4] A. Graovac, I. Gutman, N. Trinajstić, *Topological Approach to the Theory of Conjugated Molecules*, Springer, Berlin, 1977.

[5] I. Gutman, Bounds for total π-electron energy, *Chem. Phys. Lett.* **24** (1974) 283–285.

[6] I. Gutman, Total π-electron energy of benzenoid hydrocarbons, *Topics Curr. Chem.* **162** (1992) 29–63.

[7] I. Gutman, Topology and stability of conjugated hydrocarbons. The dependence of total π-electron energy on molecular topology, *J. Serb. Chem. Soc.* **70** (2005) 441–456.

[8] I. Gutman, S. J. Cyvin, *Introduction to the Theory of Benzenoid Hydrocarbons*, Springer, Berlin, 1989.

[9] I. Gutman, S. Marković, A. V. Teodorović, Ž. Bugarčić, Isomer–undistinguishing approximate formulas for the total π-electron energy of benzenoid hydrocarbons, *J. Serb. Chem. Soc.* **51** (1986) 145–149.

[10] I. Gutman, O. E. Polansky, *Mathematical Concepts in Organic Chemistry*, Springer, Berlin, 1986.

[11] I. Gutman, T. Soldatović, (n, m)-Type approximations for total π-electron energy of benzenoid hydrocarbons, *MATCH Commun. Math. Comput. Chem.* **44** (2001) 169–182.

[12] I. Gutman, N. Trinajstić, C. F. Wilcox, Graph theory and molecular orbitals – X. The number of Kekulé structures and the thermodynamic stability of conjugated systems, *Tetrahedron* **31** (1975) 143–146.

[13] X. Li, Y. Shi, I. Gutman, *Graph Energy*, Springer, New York, 2012.

[14] B. J. McClelland, Properties of the latent roots of a matrix: The estimation of π-electron energies, *J. Chem. Phys.* **54** (1971) 640–643.

[15] R. Zahradník, J. Pancíř, *HMO Energy Characteristics*, Plenum Press, New York, 1970.