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ANOTHER UPPER BOUND FOR TOTAL π-ELECTRON ENERGY OF ALTERNANT HYDROCARBONS

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Abstract. A novel upper bound for total π-electron energy of alternant hydrocarbons is derived. Conditions under which the

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present result is better than Türker's upper bound (Match 16, 83 (1984)) are examined.

1. Introduction

In a recent paper [1] one of the present authors derived an upper bound

$$E_L = 2\sqrt{4ma_4 + e}$$

for total π-electron energy of alternant hydrocarbons and showed that his bound is better than that of McClelland

$$E_M = \sqrt{2Ne}$$

namely that the following inequalities hold

$$E_\pi \leq E_L \leq E_M.$$

Here and later E_π denotes the exact value of the Hückel molecular orbital total π-electron energy in β units.

In the present work we shall derive another upper bound, viz.,

$$E_G = 2\sqrt[3]{6\sqrt{-na_6} + 3e\sqrt{4ma_4 + e} - \sqrt{8e^3/N}}$$

and show that for large enough conjugated systems,

$$E_\pi \leq E_G \leq E_L \leq E_M. \tag{1}$$

As a matter of fact, the left- and right-hand side inequalities in (1), namely $E_\pi \leq E_G$ and $E_L \leq E_M$ hold for arbitrary

alternant systems. The conditions under which $E_G \leq E_L$ also holds will be discussed in full length later on. It should be pointed out that violations of $E_G \leq E_L$ exist, but only when the molecular graph has small number of vertices (eight or less). In the great majority of chemically relevant cases $E_G \leq E_L$ and therefore (1) are valid.

The notation used in this paper follows completely that of ref. [1] and will be, therefore, not explained in full detail. In particular, the molecular graph under consideration has N vertices and e edges and the auxiliary quantities m and n are defined as

$$m = \binom{N/2}{2} = N(N-2)/8$$

and

$$n = \binom{N/2}{3} = N(N-2)(N-4)/48.$$

The characteristic polynomial is written in the form

$$P(x) = x^N + a_1 x^{N-1} + a_2 x^{N-2} + \ldots$$

$$\ldots + a_{2k} x^{N-2k} + \ldots + a_{N-1} x + a_N.$$

Since we shall be dealing with even alternant hydrocarbons,

$$a_1 = a_3 = \ldots = a_{N-1} = 0$$

and

$$(-1)^k a_{2k} \geq 0$$

for all $k \geq 0$.

2. The Main Result

In order to obtain our main result, namely

$$E_\pi \leq E_G \tag{2}$$

we need some preparations. Denote the graph eigenvalues by $x_1, x_2, \ldots, x_N$ and label them in non-increasing order. For alternant hydrocarbons (=bipartite graphs), we have then [1]

$$E_\pi = 2 \sum_{i=1}^{N/2} x_i \tag{3}$$

$$e = \sum_{i=1}^{N/2} x_i^2 \tag{4}$$

$$a_4 = \sum_{i<j}^{N/2} x_i^2 x_j^2 \tag{5}$$

$$a_6 = \sum_{i<j<k}^{N/2} x_i^2 x_j^2 x_k^2 . \tag{6}$$

Define, in addition, an auxiliary function Q as

$$Q = 2 \sum_{i=1}^{N/2} x_i^3 . \tag{7}$$

Next one should note that for any non-negative real numbers $a_1, a_2, \ldots, a_p$ the following inequalities

$$p^{-1} \sum_{i=1}^{p} a_i \leq [p^{-1} \sum_{i=1}^{p} a_i^2]^{1/2} \tag{8}$$

$$[p^{-1} \sum_{i=1}^{p} a_i^2]^{1/2} \leq [p^{-1} \sum_{i=1}^{p} a_i^3]^{1/3} \tag{9}$$

as well as the equality

$$6 \sum_{i<j<k}^{p} a_i a_j a_k = [\sum_{i=1}^{p} a_i]^3 - 3[\sum_{i=1}^{p} a_i][\sum_{i=1}^{p} a_i^2] + 2\sum_{i=1}^{p} a_i^3 \tag{10}$$

hold. In particular, the expression (10) is one of the so called Newton´s identities.

Having in mind (9) we can write

$$[(N/2)^{-1} \sum_{i=1}^{N/2} x_i^2]^{1/2} \leq [(N/2)^{-1} \sum_{i=1}^{N/2} x_i^3]^{1/3}$$

from which (4) and (7) yield straightforwardly

$$Q \geq N(2e/N)^{3/2}. \tag{11}$$

Setting p=N/2 and $a_i = x_i$ into (10) and using (3), (4) and (7) we arrive at

$$\sum_{i<j<k}^{N/2} x_i x_j x_k = [(E_\pi/2)^3 - 3eE_\pi/2 + Q]/6. \tag{12}$$

Observe that on the left-hand side of (12) there are exactly $n = \binom{N/2}{3}$ summands of the type $x_i x_j x_k$. Then, as a special case of (8) we have

$$n^{-1} \sum_{i<j<k} x_i x_j x_k \leq [n^{-1} \sum_{i<j<k} (x_i x_j x_k)^2]^{1/2}.$$

Combining the above inequality with (6) and (11) one arrives at

$$(E_\pi/2)^3 - 3eE_\pi/2 + Q \leq 6(-na_6)^{1/2}. \tag{13}$$

Note that eq. (13) was obtained by a reasoning which parallels (but, of course, is not identical to) that of ref. [1], where (8) has been combined with (5) and another of Newton's identities to give the result $E_\pi \leq E_L$. Here, however, a further complication occurs by the appearance of the term Q. In order to eliminate it from (13), use (11) to get

$$(E_\pi/2)^3 - 3eE_\pi/2 + N(2e/N)^{3/2} \leq 6(-na_6)^{1/2}. \tag{14}$$

The above inequality is cubic in E_π and is therefore of little practical applicability. This problem is overcome by replacing E_π in the second term on the left-hand side of (14) by its upper bound E_L:

$$(E_\pi/2)^3 - eE_L/2 + N(2e/N)^{3/2} \leq 6(-na_6)^{1/2}.$$

This latter inequality can be explicitly solved in E_π and results in (2).

3. Is E_G Better than E_L?

In the following table E_π, E_G, E_L and E_M values are collected for a few selected conjugated acyclic and benzenoid

hydrocarbons.

molecule	N	e	E_π	E_G	E_L	E_M
vinylbutadiene	6	5	6.90	7.20	7.14	7.74
2,3-divinylbutadiene	8	7	9.33	9.80	9.93	10.58
3-vinylhexatriene	8	7	9.45	9.95	10.07	10.58
3,4-divinylhexatriene	10	9	11.92	12.65	12.85	13.42
benzene	6	6	8.00	8.16	8.10	8.49
naphthalene	10	11	13.68	14.16	14.35	14.83
coronene	24	30	34.57	36.97	37.40	37.95
hexabenzocoronene	48	60	69.26	74.87	75.35	75.89

As it can be seen, (1) is not obeyed in all cases, vinylbutadiene and benzene being exceptions. In the great majority of cases, however, the inequalities (1) are fulfilled. As a matter of fact, they have been tested for more than a hundred benzenoid hydrocarbons and found to fail only in the case of benzene. They hold also for all even cycles with N vertices, N>6.

We demonstrate now that violations of (1) will not occur if the alternant conjugated system considered is large enough. According to our experience "large enough" here means "ten or more conjugated centers".

Suppose now that the molecular graph has large N and e values, but a finite e/N ratio. Then we may write

$$a_4 \sim (e^2-Ae)/2 \tag{15}$$

$$a_6 \sim -(e^3-3Be^2)/6 \tag{16}$$

where $\sim$ means asymptotically equal. The constants A and B depend in a certain way on the structure of the graph considered. In Appendix 1 will be shown that for a molecular graph having V_2 vertices of degree 2, V_3 vertices of degree 3 and R_4 four-membered cycles,

$$A \sim 1 + 2(V_2 + 3V_3 + 2R_4)/e \tag{17}$$

$$B \sim A - \frac{2}{3}(1/e^2) \sum_{i=1}^{N/2} x_i^6. \tag{18}$$

Taking into account only terms of the order $N \sim e \sim (Ne)^{1/2}$ and $N^{-1} \sim e^{-1} \sim (Ne)^{-1/2}$ and neglecting terms of order $N^{-2} \sim e^{-2} \sim (Ne)^{-1}$ and smaller, we prove by routine but somewhat laborous calculation that

$$E_L - E_G \sim (2e/N)^{-1/2}(2B-A-2e/N)/2. \tag{19}$$

It is now evident that the relation $E_L \geq E_G$ (and therefore (1)) will be fulfilled if the right-hand side of (19) is positive. Hence

$$2B-A \geq 2e/N \tag{20}$$

must hold in order to be able to give a positive answer to the question posed in the title of the present section.

The relations (17)-(19) are asymptotically correct, that is they hold in the limit when N and e tend to infinity. The inequality (20) gives, thus, conditions for the validity of $E_G \leq E_L$ also in this limit case. It is, however, clear that (17)-(19)

will be "almost" correct if N and e are large enough and, consequently, (20) can be applied for large enough molecular graphs too. What "large enough" means is not clear from the present discussion. As already mentioned, our numerical experience indicates that (17)-(19) are applicable as acceptable approximations for molecular graphs with more than ten vertices.

Consider first the following two examples. For the path graph (with N vertices and e=N-1 edges),

$$a_4 = \binom{N-2}{2} \sim (e^2-3e)/2$$

and

$$a_6 = -\binom{N-3}{3} \sim -(e^3-9e^2)/6.$$

Hence A=B=3. Since $e/N \sim 1$, relation (20) is obviously fulfilled.

For the cycle (with N vertices and e=N edges),

$$a_4 = \frac{N}{N-2}\binom{N-2}{2} = (e^2-3e)/2$$

and

$$a_6 = -\frac{N}{N-3}\binom{N-3}{3} \sim -(e^3-9e^2)/2$$

and we reach the same conclusions as above.

In the last part of the subsequent section the validity of (20) for (large) benzenoid hydrocarbons will be demonstrated.

4. Discussion

An important feature of the upper bounds E_L and E_G is that they depend on the coefficients of the characteristic polynomial. Whereas E_L depends on a_4 and $a_2 = -e$, E_G is a function of a_6, a_4 and a_2. Therefore a better understanding of the dependence of E_L and E_G (and thus also of E_π) on molecular topology requires the examination of the topological dependence of the coefficients a_4 and a_6.

Both E_L and E_G exhibit a fairly perplexed, but analytically well defined dependence on a_4 and a_6. It is not difficult to see that E_L is a monotonously increasing function of a_4 whereas E_G is a monotonously increasing function of both a_4 and $-a_6$.

The problem of a_4 is relatively simple and has been (independently) solved by each of the present authors [1], [2], [3]. Hence it has been shown that for molecular graphs

$$a_4 = \binom{e}{2} - 2R_4 - V_2 - 3V_3 \tag{21}$$

where (as before) R_4 stands for the number of four-membered cycles and V_i counts the vertices of degree i. A generalization of eq. (21) is

$$a_4 = \binom{e}{2} - 2R_4 - V_2 - 3V_3 - 6V_4 - 10V_5 - \ldots$$

For benzenoids, (21) reduces to

$$a_4 = (e^2-9e + 6N)/2 \tag{22}$$

showing that both a_4 and E_L depend solely on the parameters e and N and are therefore unable to distinguish isomers. This latter conclusion holds for acyclic molecules as well.

The problem of a_6 is considerably more difficult. We point out some results along these lines [4].

The coefficient a_6 for the path and the cycle with N vertices is given by

$$a_6 = -(e-4)(e-3)(e-2)/6 + (e-4)\delta-2R_6 \tag{23}$$

where δ=0 for the path and δ=1 for the cycle. Here and later R_6 denotes the number of six-membered cycles.

For any set of benzenoid hydrocarbon isomers, the differences in a_6 are equal to the differences in the number of concave bay regions (N_b) [3]. For example, the anthracene molecule has no bay region (N_b=0) and a_6 = -296. The phenanthrene molecule has one bay region (N_b=1) and a_6 = -297 [5]. Thus $a_6 + N_b$ is a graphical invariant for benzenoid hydrocarbon isomers.

Assuming that the term $a_6 + N_b$ has the same form as in the case of the path and the cycle, eq. (23), we write

$$a_6 + N_b = -(e-4)(e-3)(e-2)/6 + \alpha e_i^2 + \beta e_i + \gamma -2R_6$$

where e_i is the number of internal edges bounded by two fused rings and α, β and γ are parameters to be determined from known data for benzenoid hydrocarbons [4,5]. The solution of α, β and γ

gives then

$$a_6 = -(e^3-27e^2 + 158e + 48)/6 - \\ - 3N(e-8) - N_b. \tag{24}$$

Using (22) and (24) it is possible to confirm the validity of (20) in the case of (large) benzenoids. For large e and N, eqs. (22) and (24) result in

$$a_4 \sim [e^2 - (9-6N/e)e]/2$$

and

$$a_6 \sim -[e^3 - 3(9-6N/e)e^2]/6.$$

Bearing in mind (15) and (16) we see that

$$A = B = 9 - 6N/e$$

and therefore $E_L \geq E_G$ whenever

$$9 - 6N/e \geq 2e/N. \tag{25}$$

The solution of (25) reads $0.8 \leq e/N \leq 3.7$, which is obviously fulfilled for all benzenoids. This explains why the new upper bound (E_G) is found to be superior to the old one (E_L) in all benzenoid systems with two hexagons or more. (Benzene also satisfies (25), but fails to satisfy the relation $E_G \leq E_L$. This is, of course, no contradiction because for the applicability of (25) it was required that the benzenoid system is large enough.)

Appendix 1

Derivation of eqs. (17) and (18)

In order to deduce formula (17) rewrite (15) in the form

$$A \sim (e^2 - 2a_4)/e$$

and insert into it eq. (21).

Note that by the Newton's identity,

$$\sum_{i=1}^{N/2} x_i^4 = e^2 - 2a_4 .$$

Therefrom we conclude that

$$A \sim (1/e) \sum_{i=1}^{N/2} x_i^4 . \tag{26}$$

Eq. (18) is obtained starting with another Newton's identity, viz.,

$$\sum_{i=1}^{N/2} x_i^6 = e^3 - 3e\, a_4 + 3a_6$$

and combining it with the definition (16) of B, namely

$$B \sim (e^3 - 6a_6)/(3e^2)$$

and with eq. (21).

For $e \to \infty$ the right-hand side of (26) is finite. Therefore the limit of

$$(1/e^2) \sum_{i=1}^{N/2} x_i^8$$

is finite and consequently the term

$$(1/e^2) \sum_{i=1}^{N/2} x_i^6$$

vanishes as e tends to infinity. Consequently, for sufficiently large molecular graphs,

$$A = B.$$

Appendix 2

An Upper Bound for B

In addition to (8) and (9) the following inequality

$$p^{-1} \sum_{i=1}^{p} a_i \leq [p^{-1} \sum_{i=1}^{p} a_i^6]^{1/6}$$

holds. Identifying the numbers a_i with the first N/2 graph eigenvalues one obtains

$$E_\pi/N \leq [\frac{2}{N} \sum_{i=1}^{N/2} x_i^6]^{1/6}$$

where, of course, eq. (3) was used. Since $E_\pi \geq N$ [6], we conclude that

$$\sum_{i=1}^{N/2} x_i^6 \geq N/2.$$

By inserting this inequality into the expression for B, eq. (18), we get finally

$$B \leq 1 + 2\,(V_2 + 3V_3 + 2R_4)/e - N/(3e^2).$$

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