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BOUNDS FOR THE LARGEST EIGENVALUE IN ALTERNANT HYDROCARBONS A TOPOLOGICAL APPROACH

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Abstract. Certain topological upper and lower bounds for the largest eigenvalue of alternant hydrocarbons are derived.

1. Introduction

The eigenvalue-eigenvector problem of the adjacency matrix of a graph has attracted the attention of graph theoreticians over a considerable period of time[1]. For certain classes of graphs, within the framework of Hückel Molecular Orbital (HMO) theory , the graph spectrum can be solved in a closed analytical form, most frequently using the symmetry properties of a graph[2]. Thus, graph spectral-structural analysis was carried out analytically for rings[3], chains[3], stars and other trees[4,5,6] etc.

The interval in which the eigenvalues X_j of a graph lie is limited and given by Frobenius theorem[2,7],

$$-d_{max} \leq X_j \leq d_{max} \qquad j= 1,2...N$$

where, d_{max} is the maximal vertex degree in a graph. Therefore, for the Hückel graphs[1,2] the whole spectrum lies in the interval from -3 to +3 . In the linear polyenes and annulenes the eigenvalues lie in the interval from -2 to +2. The largest and the smallest eigenvalues of a molecular graph have been already investigated in some detail.[8,9] In the present study ,topologically dependent alternatives of the abovementioned bounds are given.

2.Theory.

Suppose, G is an undirected planar graph, having r rings, e edges and N vertices such that the degree (d_i) of every vertex in G is $1 \leqslant d_i \leqslant 3$ (i.e. G is a Hückel graph[1,2]). Furthermore, let N be an even number and P(X) be the corresponding characteristic polynomial ,

$$P(X) = X^N + a_1 X^{N-1} + a_2 X^{N-2} + \ldots\ldots + a_{N-1} X + a_N \qquad (1)$$

For alternant hydrocarbons the graph eigenvalues appear in pairs $\pm X_1$, $\pm X_2$,....., $\pm X_{N/2}$ and P(X) can be written in the form of,

$$P(X) = (X^2-X_1^2)(X^2-X_2^2)\ldots\ldots(X^2-X_{N/2}^2) \qquad (2)$$

We assume : $X_1 \geqslant X_2 \geqslant \ldots\ldots \geqslant X_{N/2}$. The quantity we are concerned with in the present paper is the largest eigenvalue, X_1. Within the HMO theory X_1 corresponds to the

energy of the lowest occupied molecular orbital. It is easy to see that the following equations hold[10,11,12],

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

$$a_4 = \sum_{i<j}^{N/2} x_i^2 x_j^2 \tag{4}$$

$$e^2 = \sum_{i=1}^{N/2} x_i^4 + 2a_4 \tag{5}$$

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

$$a_8 = \sum_{i<j<k<l}^{N/2} x_i^2 x_j^2 x_k^2 x_l^2 \tag{7}$$

On the other hand, the following holds ,

$$\sum_{i\neq j\neq k}^{N/2} x_i^4 x_j^2 x_k^2 = \sum_{i=1}^{N/2} x_i^4 (a_4 - x_i^2 (e - x_i^2)) \tag{8}$$

$$\sum_{i\neq j\neq k}^{N/2} x_i^4 x_j^2 x_k^2 = a_4 \sum_{i=1}^{N/2} x_i^4 - e \sum_{i=1}^{N/2} x_i^6 + \sum_{i=1}^{N/2} x_i^8 \tag{9}$$

By using eq.5 , eq.9 is changed into,

$$\sum_{i\neq j\neq k}^{N/2} x_i^4 x_j^2 x_k^2 = a_4 (e^2 - 2a_4) - e \sum_{i=1}^{N/2} x_i^6 + \sum_{i=1}^{N/2} x_i^8 \tag{10}$$

Now, squaring both sides of eq.4 one gets,

$$a_4^2 = \sum_{i<j}^{N/2} x_i^4 x_j^4 + 2\sum_{i\neq j\neq k}^{N/2} x_i^4 x_j^2 x_k^2 + 6\sum_{i\neq j\neq k\neq l}^{N/2} x_i^2 x_j^2 x_k^2 x_l^2 \qquad (11)$$

Inserting eqs.7 and 10 into eq.11 and noting that[11],

$$\sum_{i=1}^{N/2} x_i^6 = e^3 - 3ea_4 + 3a_6 \qquad (12)$$

one obtains,

$$\sum_{i<j}^{N/2} x_i^4 x_j^4 = 5a_4^2 - 8ea_4 + 2e^4 + 6ea_6 - 2\sum_{i=1}^{N/2} x_i^8 - 6a_8 \qquad (13)$$

Multiplying eqs.3 and 6 side by side, one gets,

$$ea_6 = \sum_{i=1}^{N/2} x_i^4 (a_4 - x_i^2(e - x_i^2)) + 4a_8 \qquad (14)$$

$$ea_6 = a_4 \sum_{i=1}^{N/2} x_i^4 - e\sum_{i=1}^{N/2} x_i^6 + \sum_{i=1}^{N/2} x_i^8 + 4a_8 \qquad (15)$$

Using eqs.5 ,12 ,15 and one has,

$$\sum_{i=1}^{N/2} x_i^8 = 4ea_6 - 4e^2 a_4 + 2a_4^2 - 4a_8 + e^4 \qquad (16)$$

Then eq.13 becomes,

$$\sum_{i<j}^{N/2} x_i^4 x_j^4 = a_4^2 - 2ea_6 + 2a_8 \qquad (17)$$

On the other hand, it is evident that, $x_1^8 < \sum_{i=1}^{N/2} x_i^8$ and $x_1^4 <$

$\sum_{i=1}^{N/2} x_i^4$. Then by using eqs.16 and 5 one gets,

$$x_1 < \sqrt[8]{e^4 + 4ea_6 + 2a_4^2 - 4e^2a_4 - 4a_8} \equiv x_U \qquad (18)$$

$$x_1 < \sqrt[4]{e^2 - 2a_4} \qquad (19)$$

The right hand side of inequalities 18 and 19 represent two different upper bounds of x_1 of which the former one is denoted by x_U .

Now, consider eq.17. Since, $\sum_{i<j}^{N/2} x_i^4 x_j^4 > \sum_{i=2}^{N/2} x_1^4 x_i^4$,

$$\sum_{i=2}^{N/2} x_1^4 x_i^4 \leqslant a_4^2 - 2ea_6 + 2a_8 \qquad (20)$$

Note that, $\sum_{i=2}^{N/2} x_i^4 = \sum_{i=1}^{N/2} x_i^4 - x_1^4$. Then ineq.20 becomes,

$$x_1^4 (\sum_{i=1}^{N/2} x_i^4 - x_1^4) \leqslant a_4^2 - 2ea_6 + 2a_8 \qquad (21)$$

and because of eq.5 one obtains

$$(e^2 - 2a_4) x_1^4 - x_1^8 \leqslant a_4^2 - 2ea_6 + 2a_8 \qquad (22)$$

Ineq.22 can be rearranged as,

$$x_1^8 - (e^2 - 2a_4) x_1^4 + (a_4^2 - 2ea_6 + 2a_8) \geqslant 0 \qquad (23)$$

what implies ,

$$X_1 > \sqrt[4]{0.5((e^2 - 2a_4) + \sqrt{(e^4 + 8ea_6 - 8a_8 - 4e^2a_4)})} \qquad (24)$$

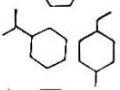
Obviously, the right hand side of the above inequality represents a lower bound, X_L for X_1. Note that, X_L is an upper bound for X_2.

3.Conclusion.

The upper and lower bounds for eigenvalues may be found by using various topologically irrelevant mathematical approaches[13]. The topological bounds X_U and X_L derived in the present work estimate the upper and lower bounds of the largest eigenvalue X_1 of alternant hydrocarbons much better (Table 1). The other upper bound expressed by ineq.19 is much easier to evaluate than X_U (ineq.18) but it is obviously less sensitive to topological changes occuring in the molecular structures. Since, the coefficients a_8 and a_{10} may reflect the fine details of the topology of a given system, X_U and X_L values should generally be different for isomeric alternant hydrocarbons (see Table 1).

TABLE 1. The Bounds For The Largest Eigenvalue, x_1, of Various Alternant Systems.

The lower bound, x_L, is given by eq.18 and the upper bound, x_U by eq.24. The x_1 values are excerpted from Ref.14.

Molecule	a_2	a_4	a_6	a_8	x_1	x_U	x_L
	-3	1	0	0	1.618	1.618	1.618
	-5	6	-1	0	1.802	1.813	1.801
	-7	13	-7	1	2.095	2.103	2.093
	-9	26	-30	13	2.170	2.183	2.151
	-6	9	-4	0	2.000	2.001	1.997
	-7	13	-7	0	2.101	2.106	2.096
	-8	19	-16	4	2.136	2.146	2.127
	-8	18	-13	1	2.194	2.199	2.185
	-8	18	-12	0	2.175	2.185	2.165
	-8	18	-12	1	2.170	2.183	2.162
	-9	25	-25	8	2.193	2.214	2.178
	-10	33	-44	24	2.214	2.243	2.181
	-9	22	-16	1	2.355	2.365	2.350
	-11	41	-65	43	2.303	2.322	2.259

References

1. I.Gutman and O.E.Polansky , "Mathematical Concepts in Organic Chemistry" Springer-Verlag,Berlin, 1986.
2. A.Graovac,I.Gutman and N.Trinajstic, "Topological Approach to The Chemistry of Conjugated Molecules" Springer-Verlag Berlin,1977.
3. E. Hückel, Z.Physik,70,204 (1931).
4. I. Gutman, Croat .Chem.Acta, 48,97 (1976).
5. I.Gutman, Match 8,291 (1980).
6. I.Gutman and O.E.Polansky, Match 8,315 (1980).
7. I.S.Dmitriev , "Molecules Without Chemical Bonds", Mir, Moscow, 1981.
8. O.E.Polansky and I.Gutman ,Match 5, 149 (1979).
9. I.Gutman, Match 11, 75 (1981).
10. L.Türker, Match, 16,81 (1984).
11. I.Gutman, L.Türker and J.R. Dias, Match,19,147 (1986).
12. A. Kurosh, "Higher Algebra" Mir ,Moscow,1975.
13. E.Kreyszing,"Advance Engineering Mathematics", Wiley ,New York, 1967.
14. A.Streitwieser.Jr,and J.I.Brauman,"Supplemental Tables of Molecular Orbital Calculations",Pergamon Press,Oxford,1965.