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BOUNDS FOR THE SMALLEST POSITIVE EIGENVALUE OF A BIPARTITE MOLECULAR GRAPH

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Abstract

Lower and upper bounds (4), (5) and (6) are obtained for the smallest positive eigenvalue of a bipartite molecular graph. Analogous inequalities (7), (8) and (9) hold for the smallest positive zero of the matching polynomial.

The smallest positive eigenvalue h of a bipartite molecular graph is of considerable importance in the topological theory[1] of conjugated π-electron systems since it is closely related with the energy of the highest occupied molecular orbital (as calculated in the Hückel approximation) and with the so called HOMO-LUMO separation. It is a well-known fact that h can be correlated with a number of measurable physico-chemical properties of alternant conjugated hydrocarbons (polarographic oxidation half-wave potential, ionization potential, energy of the first $\pi \rightarrow \pi^*$ transition, energy of the charge-transfer transition of iodine complexes etc.)[2]. In the case of non-alternant hydrocarbons (which are represented by non-bipartite molecular graphs) such correlations are less satisfactory[2,3].

The question how h depends on the structure (i.e. topology) of the conjugated molecule was considered in several recent publications[4,5]. Nevertheless, a complete solution of this problem has not yet been reached. In fact, it is rather little known about the smallest positive eigenvalue of graphs and matrices.

In the present paper we offer lower and upper bounds for h.

If the molecular graph is bipartite, then the per-

tinent conjugated molecule is said to be alternant. A graph is bipartite if and only if it contains no odd cycle.

The eigenvalues of the adjacency matrix of a graph G are called the eigenvalues of this graph; they form the spectrum of G. (For further details on graph spectral theory see the book[6].)

Let G be a bipartite (molecular) graph with N vertices. Let $x_1 \geqslant x_2 \geqslant \cdots \geqslant x_N$ be the eigenvalues of G. According to the Pairing theorem[1],

$$x_j = -x_{N-j+1}$$

for $j = 1,2,\ldots,N$.

In the following we shall consider the class of bipartite graphs for which all eigenvalues differ from zero. It immediately follows from the Pairing theorem that such graphs must have even number of vertices. If $N = 2n$, then the smallest positive eigenvalue of the graph G is x_n, that is $x_n = h$.

In other words[1] we shall restrict our considerations to those alternant conjugated systems which have no non-bonding Hückel molecular orbital.[+] All stable al-

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[+] There exist various graph theoretical procedures by which one can easily determine whether a conjugated molecule has non-bonding molecular orbitals or not.[1,7]

ternant hydrocarbons belong to this class[1,7].

In the subsequent discussion the following spectral properties of the bipartite graphs will be frequently used:

$$\sum_{j=1}^{n} x_j = \frac{1}{2} E \quad , \tag{1}$$

$$\sum_{j=1}^{n} x_j^2 = M \quad , \tag{2}$$

$$\prod_{j=1}^{n} x_j = A \quad , \tag{3}$$

where E, M and A are the total π-electron energy, the number of carbon-carbon bonds and the algebraic structure count, respectively, of the pertinent conjugated hydrocarbon[1]. The number of vertices of the graph considered is 2n. Note that in the case of benzenoid and acyclic conjugated systems, the algebraic structure count A is equal to the number of Kekulé structural formulas[8].

The First Inequality

If a_j and b_j, $j = 1,\ldots,m$ are real numbers, then by the Cauchy inequality[9],

$$\Big(\sum_{j=1}^{m} a_j\, b_j\Big)^2 \leqslant \Big(\sum_{j=1}^{m} a_j^2\Big)\Big(\sum_{j=1}^{m} b_j^2\Big) \quad .$$

By setting $a_j = 1$, $b_j = x_j$ and $m = n-1$ it follows

$$\Big(\sum_{j=1}^{n-1} x_j\Big)^2 \leqslant (n-1)\sum_{j=1}^{n-1} x_j^2 \quad .$$

Taking into account eqs. (1) and (2) and the fact that $x_n = h$, we obtain

$$\Big(\frac{1}{2}E - h\Big)^2 \leqslant (n-1)(M - h^2)$$

i.e.

$$n\,h^2 - E\,h + \frac{E^2}{4} - (n-1)\,M \leqslant 0$$

i.e.

$$\frac{E - Q}{N} \leqslant h \leqslant \frac{E + Q}{N} \quad , \qquad (4)$$

where

$$Q = \sqrt{(n-1)(2MN - E^2)} \quad .$$

This are our first bounds for h.

It should be noted that[10] $2MN - E^2 \geqslant 0$ and thus Q is necessarily real. For certain graphs the lower bound in (4) may be negative. Therefore (4) can be slightly improved as

$$\max\left\{0, \frac{E-Q}{N}\right\} \leqslant h \leqslant \frac{E+Q}{N} \quad .$$

Equality on the both sides of (4) is obtained for the path P_2 with two vertices (for which $h = M = 1$, $N = E = 2$).

The Second Inequality

If a_j, $j = 1,\ldots,m$ are non-negative real numbers, then their geometric mean is not greater than their arithmetic mean[9],

$$\left(\prod_{j=1}^{m} a_j\right)^{\frac{1}{m}} \leqslant \frac{1}{m}\sum_{j=1}^{m} a_j \quad .$$

By setting $a_j = x_j$ and $m = n-1$ and using eqs. (1) and (3) we obtain the inequality

$$(A/h)^{\frac{1}{n-1}} \leqslant (\tfrac{1}{2} E - h)/(n - 1) \quad .$$

Since $\frac{1}{2} E - h < \frac{1}{2} E$, we further deduce

$$(A/h)^{\frac{1}{n-1}} < \frac{E}{2(n - 1)}$$

i.e.

$$h > A \left[\frac{N - 2}{E}\right]^{n-1} \quad .$$

A lower bound for h is obtained if we take into account that h is smaller than or equal to unity (see later). Then $A/h \geqslant A$ and

$$A^{\frac{1}{n-1}} \leqslant (\tfrac{1}{2} E - h)/(n - 1)$$

i.e.

$$h \leqslant \tfrac{1}{2} E - (n - 1) A^{\frac{1}{n-1}} \quad .$$

Consequently, our second bounds for h read

$$A \left[\frac{N - 2}{E}\right]^{n-1} < h \leqslant \tfrac{1}{2} E - (n - 1) A^{\frac{1}{n-1}}. \qquad (5)$$

Equality on the right-hand side of (5) is obtained again for the path P_2 with two vertices.

The Third Inequality

If the algebraic structure count of G is equal to unity, then eq. (3) implies $x_1 x_2 \ldots x_{n-1} h = 1$. Since by definition all the eigenvalues $x_1, x_2, \ldots, x_{n-1}$ are not smaller than h, it is evident that h cannot be greater than unity. Therefore for all bipartite graphs for which $A = 1$, we have

$$h \leqslant 1 \quad . \tag{6}$$

According to the author's opinion the validity of the inequality (6) is much wider. We present here two statements for which no proof is available at the present moment.

CONJECTURE 1. The inequality (6) holds also for bipartite graphs which have $A > 1$.

CONJECTURE 2. The inequality (6) holds for all graphs which have equal number of positive and negative eigenvalues and which have no zero eigenvalue.

Bounds for the smallest positive zero of the matching polynomial

The matching polynomial of a graph was defined within a novel theory of aromaticity[11]. (For details on the

matching polynomial see the review[12].) There exists a far-reaching analogy between the eigenvalues of a bipartite graph and the zeros of the corresponding matching polynomial[12]. If these latter zeros are denoted by $y_1 \geqslant y_2 \geqslant \cdots \geqslant y_N$, then

$$y_j = -y_{N-j+1}$$

for $j=1,2,\ldots,N$. Furthermore, if $N = 2n$, then

$$\sum_{j=1}^{n} y_j = \frac{1}{2} E_R$$

$$\sum_{j=1}^{n} y_j^2 = M$$

$$\prod_{j=1}^{n} y_j = \sqrt{K}$$

where E_R is the reference energy in the topological resonance energy method[11], and K is the number of Kekulé structural formulas of G. Note that the difference between the total π-electron energy and the reference energy is called the topological resonance energy, TRE.

If $y_n = h_R$ is the smallest positive zero of the

matching polynomial, then a fully analogous reasoning as described in the previous sections leads to the inequalities (7)-(9).

$$\frac{E_R - Q_R}{N} \leqslant h_R \leqslant \frac{E_R + Q_R}{N} \qquad (7)$$

where

$$Q_R = \sqrt{(n-1)(2\,M\,N - E_R^2)} \quad .$$

$$\sqrt{K}\left[\frac{N-2}{E_R}\right]^{n-1} < h_R \leqslant \frac{1}{2}\,E_R - (n-1)\,K^{\frac{1}{N-2}} \quad . \qquad (8)$$

For all graphs for which $K = 1$,

$$h_R \leqslant 1. \qquad (9)$$

CONJECTURE 3. The inequality (9) holds also for graphs for which $K > 1$.

The difference $h - h_R$ can be interpreted as the joint effect of all cycles of the conjugated system on the highest occupied MO energy level[5]. Several topological properties of $h - h_R$ have been established[5]. Combining (4) and (7) we can derive also an upper and lower bound for $h - h_R$, namely

$$\frac{TRE - (Q + Q_R)}{N} \leqslant h - h_R \leqslant \frac{TRE + (Q + Q_R)}{N}$$

where

$$TRE = E - E^R \quad .$$

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