

AN UPPER BOUND FOR THE LARGEST EIGENVALUE OF A GRAPH: EFFECT OF TYPES OF VERTICES

Lemi TÜRKER

Department of Chemistry, Middle East Technical University, Ankara, Turkey

Received 29 October 1991

Abstract

A novel method, based on the topology of the cardinal vertex, is described to find an upper bound for the largest eigenvalue of a graph.

1. Introduction

Graph theory has been shown to be an appropriate tool for the analysis of topologically related molecular properties [1]. In the study of conjugated molecules, a simple Hückel molecular orbital (HMO) treatment [2–4] is entirely equivalent to a graph-theoretical treatment mainly because of the close relation between the HMO Hamiltonian and molecular topology [5]. In particular, the eigenvalues of the adjacency matrix (A) of the graph which possesses the same pattern of connectedness as the molecule under consideration are identical to the HMO energies of the molecule. The totality of eigenvalues of the matrix A is called a spectrum of the graph corresponding to this matrix [6]. Within the framework of HMO theory, graph spectral analysis was carried out analytically for certain classes of conjugated systems such as rings and chains [7], stars and other trees [8–10].

The spectrum of a graph possesses the property that if D_m is the maximal vertex degree of a graph, then the interval in which the eigenvalues λ_i of the graph lie is limited and expressed by the Frobenius theorem [6, 11]:

$$-D_m \leq \lambda_i \leq D_m \quad i = 1, 2, \dots, N.$$

Therefore, for the Hückel graphs [5, 11], the whole spectrum lies in the interval from -3 to $+3$. However, 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 already attracted much attention and have been investigated in some detail [12, 13]. Quite recently, topologically-dependent alternatives of the above-mentioned bounds for alternant hydrocarbons were reported [14]:

$$\lambda_1 \leq \sqrt[4]{e^2 - 2a_4}, \quad (1)$$

$$\lambda_1 \leq \sqrt[8]{e^4 + 4ea_6 + 2a_4^2 - 4e^2a_4 - 4a_8}, \quad (2)$$

where λ_1 is the largest eigenvalue, whereas e and a_k ($k = 4, 6, 8$) stand for the number of edges and the coefficients in the corresponding characteristic polynomial $p(\lambda)$ of the graph, respectively [15,16].

In the present study, a novel upper bound (based on nodal properties of a graph) for the largest eigenvalue is developed.

2. Theory

Formulas (1) and (2) have certain drawbacks. For instance, although the latter is a very realistic bound for λ_1 , the calculation of a_k values might be a tedious task to do. On the other hand, eq. (1) becomes inferior to the bounds given by the Frobenius theorem if the number of edges (e) and vertices (N) of a graph are quite large. For instance, in the case of terylene ($e = 37$, $N = 30$), the bound for λ_1 becomes 3.51, whereas D_m is just 3. Actually, eq. (1) gives better results as long as $e^2 - 2a_4 \leq 81$ or, for benzenoid graphs, $e + V_3 \leq 27$ (see the appendix), where V_3 is the number of vertices having degree three.

To compute the upper bounds of eigenvalues of a given N -row square matrix, there exist many methods and theorems [17]. Of these, Gershgorin's theorem [18] states that all the eigenvalues of an $N \times N$ matrix A lie in the region of the complex plane given by the union of N disks:

$$|b_{ii} - \lambda| \leq \sum_{\substack{J=1 \\ J \neq i}}^N b_{ij}, \quad i = 1, \dots, N. \quad (3)$$

Applied to the adjacency matrix of a given chemical graph where the matrix elements (b_{ij}) are either zero or one, Gershgorin's theorem proves the Frobenius theorem because all the diagonal elements b_{ii} are zero for nonheteroconjugated molecules and the sum of off-diagonal matrix elements row-wise is simply equal to the degree of the vertex associated with a specific b_{ii} element. In that respect, the application of Gershgorin's theorem to the adjacency matrix A has no merit. However, the concept of $T(A)$ graphs (fig. 1) [19] (which are the topological representation of already known $T(A)$ -type square matrices [6,20]), together with the above-mentioned theorem gives an upper bound for the largest eigenvalue dictated mainly by the degrees of a given graph.

In graph theory, the matrix elements b_{ij} can be interpreted as the number of unitary walks between the vertices i and j . Then, the product of two elements of matrix A , $b_{rj} b_{js}$, is equal to 1 if vertex r is connected to vertex j , and the latter in

its turn is connected to vertex s , i.e. between r and s there is a walk of length 2 passing through j . If there is no such walk, the product $b_{rj}b_{js}$ is zero [6].

The square of the matrix A has the element c_{rs} , which is equal to

$$c_{rs} = \sum_{j=1}^N b_{rj}b_{js}. \tag{4}$$

The right-hand side of eq. (4) represents the number of all walks of length 2 connecting vertex r with vertex s . A graph $T(A)$ is the graphical representation of all the off-diagonal as well as diagonal relations of the A^2 matrix [19,20] and it is proved that $T(A)$ graphs of alternant hydrocarbons are decomposable [19] into $T(A^*)$ and $T(A^0)$ mates. Some examples are presented in fig. 1. Note that the number

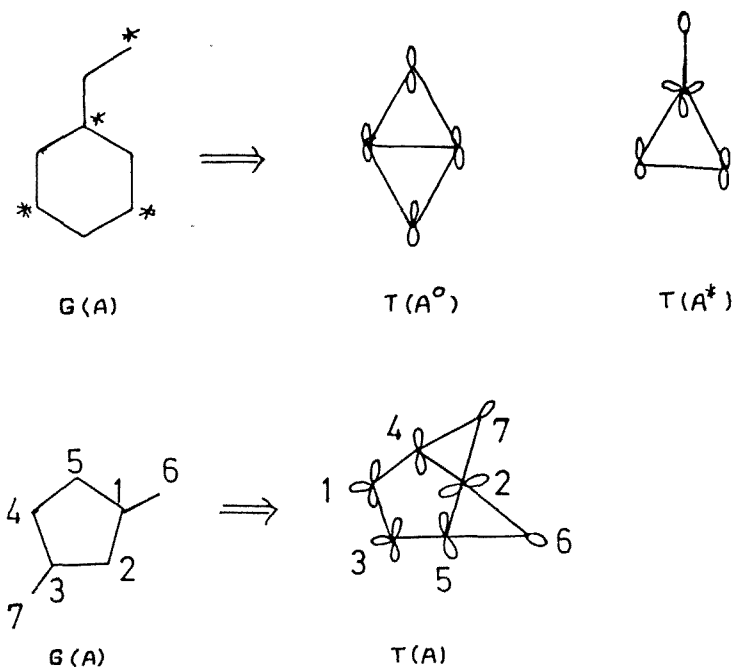


Fig. 1. $T(A)$ graphs of certain systems.

of self-loops on the vertices of a $T(A)$ graph is equal to the degrees of the corresponding vertices of the original graph $G(A)$.

On the other hand, the following equations hold in linear algebra [21] for the adjacency matrix A of a graph:

$$AX = \lambda X, \tag{5}$$

$$A^2X = \lambda^2 X, \tag{6}$$

where X is the invariant vector or, more commonly, eigenvector and λ is an eigenvalue of the graph. Hence, Gershgorin's theorem can be used to obtain the bounds for eigenvalues of the A^2 matrix via $T(A)$ graphs, thus enabling one to evaluate the bounds for the spectrum of the adjacency matrix A .

DEFINITION 1

The cardinal vertex V_c is a vertex having the greatest number of self-loops and, in addition, the greatest number of connections in a $T(A)$ graph. Note that V_c in a $T(A)$ graph is associated with one of the vertices having the greatest degree in the corresponding $G(A)$ graph.

THEOREM 1

In a Hückel graph, the largest eigenvalue cannot be greater than

$$\left(D_m + \sum_{\substack{i=1 \\ i \neq m}}^K c_{mi} \right)^{1/2},$$

which is dictated by the topology of the cardinal vertex.

Proof

Let λ_m be the greatest eigenvalue of a graph $G(A)$ and $\Lambda_m = \lambda_m^2$. Thus, Λ_m is the greatest eigenvalue of the corresponding $T(A)$ graph (or $T(A)$ mates, $T(A)^*$ and $T(A^0)$, in the case of even alternant hydrocarbons). Since $b_{ii} = 0$ in the adjacency matrix A , ineq. (3) becomes

$$|\lambda_m| \leq \sum_{i=1}^N b_{mi}, \quad (7)$$

where the right-hand side of ineq. (7) is equal to the degree D_m of the cardinal vertex which leads to $\lambda_m \leq D_m$. On the other hand, ineq. (3) applied to the corresponding $T(A)$ graph becomes

$$|D_m - \Lambda_m| \leq \sum_{\substack{i=1 \\ i \neq m}}^K c_{mi}, \quad (8)$$

where $\sum_{i=1, i \neq m}^K c_{mi}$ represents the total number of connections of V_c in the corresponding $T(A)$ graph. The upper index K is equal to N and $N/2$ for nonalternant and even alternant systems, respectively, whereas it is equal to $(N+1)/2$ or $(N-1)/2$ for odd alternant systems, depending on which one of the $T(A)$ mates possesses the original cardinal vertex.

By rearranging ineq. (8) and substituting $\Lambda_m = \lambda_m^2$, one obtains

$$\lambda_m \leq \sqrt{D_m + \sum_{\substack{i=1 \\ i \neq m}}^K c_{mi}} \equiv D_T. \quad (9)$$

As long as $D_T < D_m$, the right-hand side of ineq. (9) is a much better bound (D_T) than D_m , which requires that

$$\sum_{\substack{i=1 \\ i \neq m}}^K c_{mi} \leq D_m^2 - D_m. \quad (10)$$

Actually, for Hückel graphs inequality (10) is fulfilled in all cases for $D_m > 1$ (ethylene has $D_m = 1$). For example, the largest eigenvalue of the diphenylmethyl system [22] is 2.236, whereas the bounds given by D_T and D_m are 2.449 and 3, respectively. D_T is obtained as shown in fig. 2.

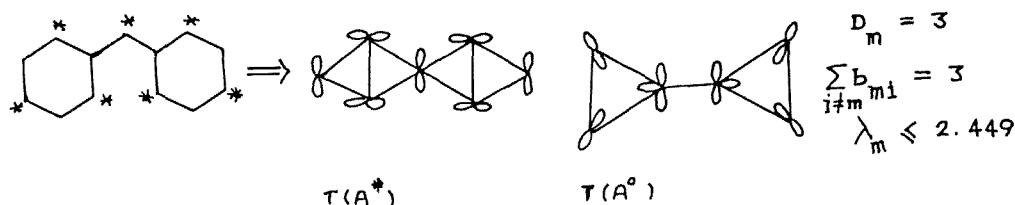


Fig. 2. $T(A)$ graphs of the diphenylmethyl system leading to the upper bound of the largest eigenvalue.

Classification of vertices of $T(A)$ graphs

Vertices of a $T(A)$ graph retain much of the information originally possessed by graph $G(A)$. The degree of any vertex in $G(A)$ as well as the A^2 -relation (walks of length 2) are reflected in a $T(A)$ graph.

DEFINITION 2

Let i and j be the number of self-loops and the number of connections of any vertex in a $T(A)$ graph, respectively. Then any vertex can be described properly by a notation of type $V_{i(j)}$.

Some examples for the classification of vertices are given in fig. 3. The vertex under consideration is labelled with a \blacktriangledown sign.

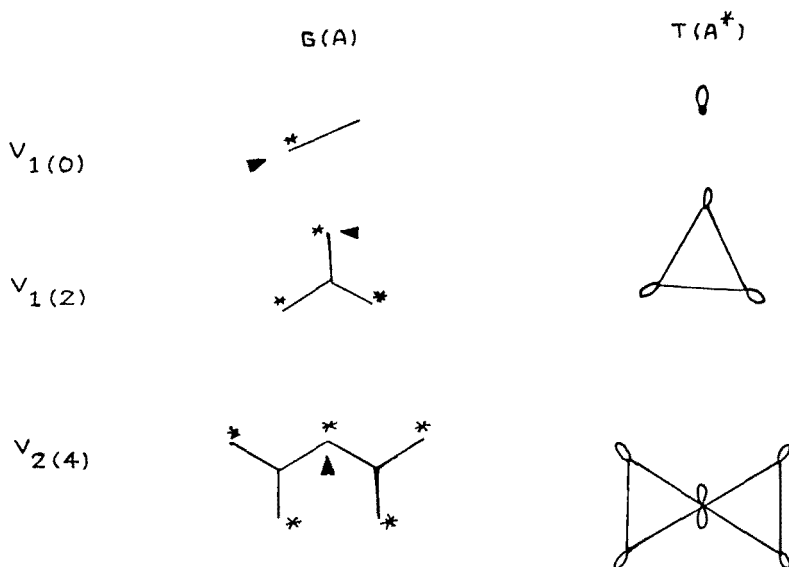
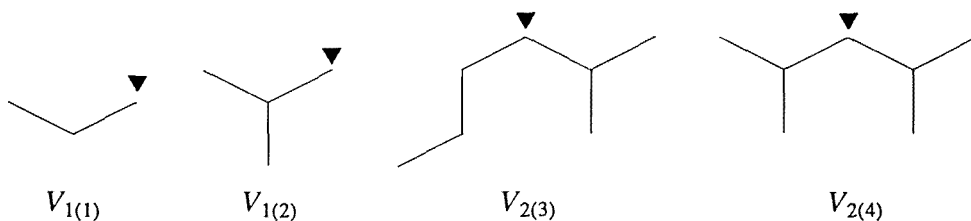


Fig. 3. Some examples for the classification of vertices.

3. Results and discussion

Table 1 tabulates some vertex types which occur in Hückel graphs. As can be seen from tables 1 and 2, when the cardinal vertex is one of the types listed, the bound given by D_T is superior to the Frobenius bound (D_m) except for vertices of type $V_{1(1)}$, $V_{1(2)}$, $V_{2(3)}$, and $V_{2(4)}$. These types of vertices are present (indicated by a \blacktriangledown sign) in one of the following or similar graphs.



However, it is unlikely for these vertices to be a cardinal vertex in a Hückel graph; hence in these systems the bounds are dictated by other types of vertices (cardinal vertex). Thus, the simple method presented here provides one with superior or comparable bounds (D_T) to the Frobenius approach.

The construction of $T(A)$ graphs especially for alternant hydrocarbons is a straightforward process [19] and D_T depends only on the topology of the cardinal vertex, which also possesses some partial information about the fine topology of the

Table 1

Some vertex types in Hückel graphs and the corresponding possible bounds for the largest eigenvalue.

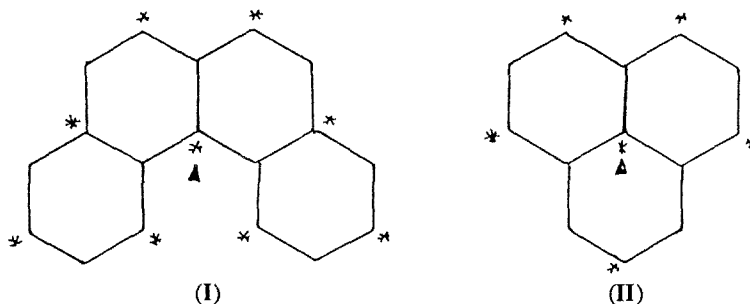
Type	D_m	$\sum_{i=1, i \neq m}^K c_{mi}$	D_T
$V_{1(0)}$	1	0	1.00
$V_{1(1)}$	1	1	1.41
$V_{1(2)}$	1	2	1.73
$V_{2(0)}$	2	0	1.41
$V_{2(1)}$	2	1	1.73
$V_{2(2)}$	2	2	2.00
$V_{2(3)}$	2	3	2.23
$V_{2(4)}$	2	4	2.45
$V_{3(0)}$	3	0	1.73
$V_{3(1)}$	3	1	2.00
$V_{3(2)}$	3	2	2.23
$V_{3(3)}$	3	3	2.45
$V_{3(4)}$	3	4	2.64
$V_{3(5)}$	3	5	2.82
$V_{3(6)}$	3	6	3.00

Table 2

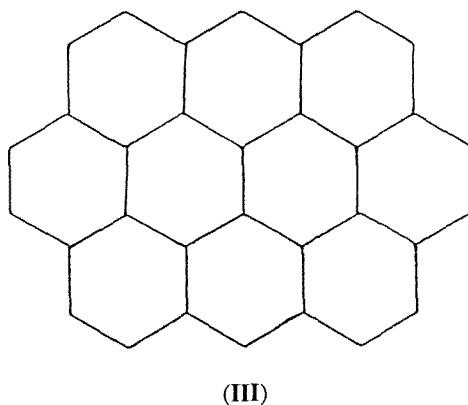
The largest eigenvalue (λ_1) and its upper bounds (D_m and D_T) for some molecules.

Molecule	D_m	D_T	λ_1 [22]
Benzene	2	2.000	2.000
Naphthalene	3	2.645	2.303
Diphenylene	3	2.645	2.532
Biphenyl	3	2.645	2.278
Styrene	3	2.449	2.136
Para-quinodimethane	3	2.449	2.170
Hexatriene	2	2.000	1.802
Phenanthrene	3	2.828	2.435

system. Of course, in some cases different molecules might have the same type of cardinal vertices. For instance, a $V_{3(6)}$ type vertex pattern exists in 3, 4-benzphenanthrene (I) as well as in phenalenyl (II) kernels. Phenanthrene, naphthalene and benzene kernels possess $V_{3(5)}$, $V_{3(4)}$, and $V_{2(2)}$ type cardinal vertices, respectively. Thus,



whenever these systems are embedded in more complex structures, D_T of the initial and former structures will be the same as long as the embedding process does not engender a new cardinal vertex. One should also consider the priority order if more than one type of kernels are embedded. For instance, in the structure of ovalene (III), both naphthelene and phenalenyl kernels (also the 3, 4-benzphenanthrene



kernel (I) exist, which possess $V_{3(4)}$ and $V_{3(6)}$ type vertices, respectively. However, priority has to be given to the phenalenyl kernel (II).

4. Conclusions

The upper bounds for eigenvalues may be found by using various topologically irrelevant approaches [17]. On the other hand, the topological bounds [14], despite their accuracy, require the usage of certain predetermined polynomial coefficients (the characteristic polynomial) which most of the time are difficult to evaluate. The method presented above is a very straightforward one to estimate the range of eigenvalues of a graph. Also, it has to be mentioned that the present method is superior to the Frobenius approach (table 2).

Appendix

For alternant hydrocarbons, the A_4 coefficient is given in ref. [15]:

$$a_4 = \frac{e^2 - e}{2} - V_2 - 3V_3 - 2R_4,$$

where V_2 and V_3 are the numbers of vertices having degree two and three, respectively. The number of four-membered rings is expressed by R_4 . It is known [11, 15] that $V_1 + 2V_2 + 3V_3 = 2e$. Hence, for benzenoid molecules ($V_1 = 0$ and $R_4 = 0$), eq. (1) becomes

$$\lambda_1 \leq \sqrt[4]{3e + 3V_3} \equiv \lambda_u.$$

The condition satisfying $\lambda_u < D_{\max}$ can be obtained easily for Hückel graphs which can have maximum degree of three, that is,

$$e + V_3 \leq 27.$$

References

- [1] I. Gutman and N. Trinajstić, *Topics Curr. Chem.* 42(1975)49.
- [2] K. Ruedenberg, *J. Chem. Phys.* 22(1954)1878.
- [3] H.H. Günthard and H. Primas, *Helv. Chim. Acta* 39(1956)1645.
- [4] H.H. Schmidtke, *J. Chem. Phys.* 45(1966)3920.
- [5] I. Gutman and O.E. Polansky, *Mathematical Concepts in Organic Chemistry* (Springer, Berlin, 1986).
- [6] I.S. Dmitriev, *Molecules Without Chemical Bonds* (Mir, Moscow, 1981).
- [7] E. Hückel, *Z. Phys.* 70(1931)204.
- [8] I. Gutman, *Croat. Chem. Acta* 48(1976)97.
- [9] I. Gutman, *MATCH* 8(1980)291.
- [10] I. Gutman and O.E. Polansky, *MATCH* 8(1980)315.
- [11] A. Graovac, I. Gutman and N. Trinajstić, *Topological Approach to the Chemistry of Conjugated Molecules* (Springer, Berlin, 1977).
- [12] O.E. Polansky and I. Gutman, *MATCH* 5(1979)149.
- [13] I. Gutman, *MATCH* 11(1981)75.
- [14] L. Türker, *MATCH* 25(1990)217.
- [15] L. Türker, *MATCH* 16(1984)83.
- [16] I. Gutman, L. Türker and J.R. Dias, *MATCH* 19(1986)147.
- [17] E. Kreyszig, *Advanced Engineering Mathematics* (Wiley, New York, 1968).
- [18] H.D. Ikramov, *Linear Algebra* (Mir, Moscow, 1983).
- [19] L. Türker, *MATCH* 25(1990)195.
- [20] G.G. Hall, *Mol. Phys.* 33(1977)551.
- [21] I.V. Proskuryakov, *Problems in Linear Algebra* (Mir, Moscow, 1978).
- [22] E. Heilbronner and H. Bock, *The HMO Model and its Application*, Vol. 3 (Wiley, New York, 1976).