ESTIMATION OF BOUNDS OF ORBITAL ENERGIES IN THE HÜCKEL MODEL

MAKOTO ISIHARA

This paper describes an attempt to improve estimation of bounds of orbital energies in the Hückel model. New expressions for handy estimation of the bounds are presented. The handy estimation uses only elementary graph-theoretical quantities as the number of sites and that of bonds. Furthermore, the expressoins are extended to enable us to estimate the bounds, in principle, as exactly as required. Numerical examples for typical π-electron systems are given to illustrate how the expressions work.

1. Introduction

Let us confine ourselves to the simple Hückel model which specifies a system solely by the adjacency of sites. Making a system in the simple Hückel model correspond to a simple graph, we can translate everything in Hückel theory into its counterpart in graph theory. Since the present subject is not inherent only to chemistry, the graph-theoretical terminology is used throughout. No dictionary will be necessary for the translation.

For the present purpose, it is sufficient to consider simple connected graphs. The adjacency matrix of a simple connected graph is irreducible and real-symmetric, consisting of nonnegative components, 0 and 1. The largest eigenvalue is, therefore, positive, nondegenerate, and not exceeded by other eigenvalues of the graph even in absolute value by virtue of Frobenius' theorem. In what follows, simple connected graphs are called graphs for brevity. The whole of eigenvalues of a graph is called the spectrum of the graph.

Throughout this paper, the number of vertices and that of edges of a graph are denoted by n and m, respectively, and n eigenvalues $\{\lambda_j\}$ of the graph are numbered in nonincreasing order as

$$\lambda_1 > \lambda_2 \geq \cdots \geq \lambda_n. \tag{1}$$

The smallest eigenvalue λ_n, being necessarily negative, can be equal to $-\lambda_1$. In such a case, λ_n is nondegenerate and the graph is necessarily bipartite (Lovász, 1993a). Then, the upper bound λ_1 of the spectrum leads us immediately to the lower bound. In general, the upper bound provides a possible approximation of the lower bound by chainging the sign.

It is well-known that the spectrum of a graph is bounded by the largest degree $d_{\max}$ of vertices in the graph as

$$-d_{\max} \leq \lambda_j \leq d_{\max} \qquad (j=1, \cdots, n), \tag{2}$$

which is presumably ascribable to Frobenius (Coulson, 1950). This property has a great conceptual significance, but is not so useful because of its crudeness. It can provide nothing within varieties of graphs of an identical $d_{\max}$.

A remarkable expression for handy estimation of the largest eigenvalue of a graph is known (Hall, 1977). Using the degree d_i of vertex i, we have

$$\lambda_1 \geq \sum_{\text{edge}\, i<j} d_i d_j / \sum_j d_j^2. \tag{3}$$

This provides a good approximation to the largest eigenvalue, but has no direct relation with the bounds of the spectrum naturally.

As a handy estimation of the upper bound with the number of vertices and that of edges, the following is given as an exercise (Lovász, 1993b).

$$\lambda_1 \leq \sqrt{2m(n-1)/n}. \tag{4}$$

Although this leads us to exact bounds for complete graphs, it works quite insatisfactorily within varieties of chemical graphs, that is, rather sparse graphs as Hückel graphs. For example, the right-hand side yields 3.16 for the monohex graph, 4.45 for the dihex one, and 2.89 for the 6-vertex linear chain!

No method for refining estimates of bounds, somehow, seems to have been devised or, at leaset, to be known in prevalent literature. The primary reason for this is probably that our interest concentrates rather in "exact" bounds and that obtaining exact bounds is naturally replaced, for individual graphs, with solving the eigenvalue problem itself.

This paper aims to improve the above-mentioned estimation for bounds of spectra of graphs. New expressions for handy estimation are presented. The handy estimation uses only elementary graph-theoretical quantities as the number of vertices and that of edges. Furthermore, the expressions are extended to enable us to estimate the bounds, in principle, as exactly as required. Numerical examples for typical Hückel graphs are given to illustrate how the expressions work.

2. Handy Estimation

Let $\boldsymbol{A}$ be the adjacency matrix of a graph and denote the trace of the k-th power of $\boldsymbol{A}$ by T_k, which equals the k-th power sum of $\{\lambda_j\}$:

$$T_k = \mathrm{Tr}(A^k) = \sum_{j=1}^{n} \lambda_j^k. \tag{5}$$

The preceding expression (4) is essentially based on the Cauchy-type inequality

$$(T_1 - \lambda_1)^2 \leq (n-1)(T_2 - \lambda_1^2). \tag{6}$$

Here, note that T_1 in the left-hand side necessarily involves a number of negative eigenvalues and that this makes the inequality quite loose. The straightforward way for improvement is, therefore, to use λ_j^2 in place of λ_j. In addition, when the number ν of zero eigenvalues is known, we can make an improvement by taking it into account. Thus, let us take the inequality

$$(T_2 - \lambda_1^2)^2 \leq (\tilde{n}-1)(T_4 - \lambda_1^4) \tag{7}$$

with

$$\tilde{n} = n - \nu. \tag{8}$$

If ν is unknown, we have to content ourselves with neglecting ν. This does not violate the inequality at all, though may degrades it somewhat as the case may be.

Now, for the sake of convenience in description, let us introduce the auxiliary quantity

$$t_k = T_k / \tilde{n}. \tag{9}$$

Then, by a little elementary calculation, the inequality above leads to

$$(\lambda_1^2 - t_2)^2 \leq (\tilde{n}-1)(t_4 - t_2^2). \tag{10}$$

Since the quantity in the parenthesis of the left-hand side is not negative, we can obtain

$$\lambda_1 \leq \sqrt{t_2 + \sqrt{(\tilde{n}-1)(t_4 - t_2^2)}}. \tag{11}$$

As is well known, T_2 is simply equal to $2m$, while T_4 can be evaluated quite easily with n, m, the number r_4 of 4-vertex rings, and the number n_d of vertices of degree d other than 2 and 3 as

$$T_4 = 2(9m - 6n) + 4(n_1 + D) + 8r_4, \tag{12}$$

where the quantity

$$D = \frac{1}{2} \sum_{d=4} (d-2)(d-3) n_d \tag{13}$$

standing for the contribution from vertices of degree larger than 3. When the fourth coefficient a_4 (the coefficient for the (n-4)-th power) of the characteristic polynomial is known ahead, the relationship

$$T_4 = -4a_4 + 2m^2 \qquad (15)$$

immediately gives T_4 (Dias, 1985).

For bipartite graphs, we can or rather must make a further improvement. Since the contribution from λ_n^2 is exactly as large as λ_1^2 itself, it is relevant to treat λ_n^2 as λ_1^2 as

$$(T_2 - 2\lambda_1^2)^2 \leq (\tilde{n} - 2)(T_4 - 2\lambda_1^4), \qquad (16)$$

from which it follows that

$$\lambda_1 \leq \sqrt{t_2 + \sqrt{\left(\frac{\tilde{n}}{2} - 1\right)(t_4 - t_2^2)}}. \qquad (17)$$

Let n vertices of a bipartite graph be partitioned into $n_\bullet$ black and $n_\circ$ white vertices. Denote $n_\bullet - n_\circ$ by ρ and assume ρ to be nonnegative. Unless ρ vanishes, the graph has ρ zero eigenvalues at least. Zero eigenvalues can still exist even if ρ vanishes. Then, it is appropriate, if it is easy, to check whether or not the algebraic structure count vanishes, but no general simple way to know ν seems to have been found (Cvetković, 1979; Trinajstić, 1991). Hence, if ν is unknown, we have to content ourselves to use "the number of zero eigenvalues known to exist" in place of ν, which is often ρ, naturally not less than ρ, and has the same parity as n.

In particular, for bipartite Hückel graphs having neither end vertex nor 4-vertex ring, merely using $\tilde{n}$ and

$$\tilde{d} = 2m/\tilde{n} (= t_2), \qquad (18)$$

the "modified" mean degree of vertices, we have

$$\lambda_1 \leq \sqrt{\tilde{d} + \frac{1}{2}\sqrt{\left(\frac{\tilde{n}}{2} - 1\right)(33 - (9 - 2\tilde{d})^2)}}. \qquad (19)$$

If n and m are fixed with vanishing ν, an identical estimate follows to all. This may be regarded rather as a reflection of the well-known fact that the largest eigenvalues of polyhex graphs consisting of the same number of vertices and the same number of edges are, more or less, close to each other.

3. Exact Estimation

First, let us consider the case where $|\lambda_n|$ differs from λ_1. As a natural extension of the preceding treatment, starting with the inequality

$$(T_{2k}-\lambda_1^{2k})^2 \leq (\tilde{n}-1)(T_{4k}-\lambda_1^{4k}) \tag{20}$$

with an arbitrary natural number k, we have an estimate $b(k)$ for the upper bound of the spectrum of a graph as

$$b(k)=\sqrt[2k]{t_{2k}+\sqrt{(\tilde{n}-1)(t_{4k}-t_{2k}^2)}}. \tag{21}$$

It must be preferable for the purpose here to convert this into

$$b(k)=\sqrt[2k]{T_{2k}\left(\sqrt{\left(1-\frac{1}{\tilde{n}}\right)\left(\frac{T_{4k}}{T_{2k}^2}-\frac{1}{\tilde{n}}\right)}+\frac{1}{\tilde{n}}\right)}, \tag{22}$$

which is ready to show that $b(k)$ approaches λ_1 as k increases, because $\sqrt[2k]{T_{2k}}$ does λ_1 and T_{4k}/T_{2k}^2 unity.

For sufficiently large k, the approximation up to the $4k$-th order of $\{\lambda_j/\lambda_1(j>1)\}$ leads to

$$\frac{b(k)}{\lambda_1}\cong 1+\frac{1}{2k}\left(\eta_{4k}-\frac{\eta_{2k}^2}{\tilde{n}-1}\right) \tag{23}$$

with

$$\eta_{2k}=\sum_{j=2}^{n}(\lambda_j/\lambda_1)^{2k}. \tag{24}$$

The behavior of $b(k)$ is thus found to be remarkably advantageous, compared with that of the "unprocessed" T_{4k}-level estimate $\sqrt[4k]{T_{4k}}$, that is,

$$\sqrt[4k]{T_{4k}}\cong\lambda_1(1+\eta_{4k}/(4k)). \tag{25}$$

However, when n becomes large in sparse graphs, the present estimation loses its efficiency as well. It should be noted that we need not be attentive with the number of zero eigenvalues here.

For bipartite graphs, the modification shown in the preceding section is effective for efficiency. The adjacency matrix $\boldsymbol{A}$ of a bipartite graph can be written in the form

$$\boldsymbol{A}=\begin{pmatrix} \boldsymbol{0} & \boldsymbol{B} \\ {}^{t}\boldsymbol{B} & \boldsymbol{0} \end{pmatrix} \tag{26}$$

with an $n_{\bullet}\times n_{\circ}$ submatrix $\boldsymbol{B}$ and its transpose ${}^{t}\boldsymbol{B}$, so that we have

$$\boldsymbol{A}^{2k}=\begin{pmatrix} (\boldsymbol{B}{}^{t}\boldsymbol{B})^k & \boldsymbol{0} \\ \boldsymbol{0} & ({}^{t}\boldsymbol{B}\boldsymbol{B})^k \end{pmatrix}, \tag{27}$$

where $(\boldsymbol{B}{}^{t}\boldsymbol{B})^k$ and $({}^{t}\boldsymbol{B}\boldsymbol{B})^k$ are, respectively, $n_{\bullet}\times n_{\bullet}$ and $n_{\circ}\times n_{\circ}$ submatrices. Since all nonzero eigenvalues participate in the trace of each submatrix, we may calculate the smaller

$$F_{2k}=\mathrm{Tr}((^t\boldsymbol{BB})^k) \tag{28}$$

in place of T_{2k}. Thus , with

$$\mu=\tilde{n}/2=(n-\nu)/2, \tag{29}$$

we have

$$b(k)=\sqrt[2k]{F_{2k}\left(\sqrt{\left(1-\frac{1}{\mu}\right)\left(\frac{F_{4k}}{F_{2k}^2}-\frac{1}{\mu}\right)}+\frac{1}{\mu}\right)}, \tag{30}$$

which behaves for sufficiently large k as

$$\frac{b(k)}{\lambda_1}\cong 1+\frac{1}{2k}\left(\xi_{4k}-\frac{\xi_{2k}^2}{\mu-1}\right) \tag{31}$$

with

$$\xi_{2k}=\frac{1}{2}\sum_{j=2}^{n-1}(\lambda_j/\lambda_1)^{2k} \tag{32}$$

similarly but much preferably to the nonbipartite case.

In real situation, it is not necessary at all to calculate $b(k)$ successively for every natural number k. Starting with $\boldsymbol{A}$, we can reach the $2s$-th power of $\boldsymbol{A}$ by s times matrix multiplications and, hence, $b(2^{s-2})$. If refinement with very large s is intended, then, to avoid numerical explosion, we should use $\boldsymbol{A}/b_0$ in place of $\boldsymbol{A}$ with a tentative estimate b_0 of λ_1, for example, $d_{\max}$ or $b(1)$ obtainable ahead. Although computational details is left to be devised, it is certain that the expressions above provide a method for estimating bounds of spectra by simple elementary procedure.

4. Numerical Examples and Concluding Remarks

Table 1 and Table 2 show numerical examples for typical Hückel graphs. Table 1 concerns nonbibartite graphs, while Table 2 does bipartite. The tables include $b(k)$'s until the agreement with the largest eigenvalue up to the sixth decimal place. The result of the handy estimation by (11) or (17) is naturally identical with $b(1)$.

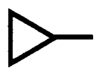
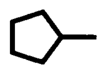
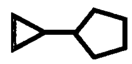
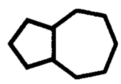
The expressions (11) and (17) work adequately considering its simplicity. Although their estimation is, so to speak, semi-quantitative, they yield even the exact result for small graphs as monotetra and monohex besides complete graphs and star graphs. When the number of vertices in a graph becomes large with its sparsness kept, the expressions will fail to give meaningful estimates. It should be noted that the T_8-level estimate $b(2)$ is clearly better than the T_4-level one $b(1)$. Therefore, if we find an expression of T_8 in terms of elementary graph-theoretical quantities, a good handy estimation follows immediately. As an approximation to the largest eigenvalue, Hall's expression (3) provides much better result than $b(1)$.

The method for exact estimation using (22) or (30) works quite satisfactorily. If the number of vertices contained is not so large, the estimation reaches the "exact" result instantaneously with the use of an ordinary personal computer. However, the present method may suffer from loss of its efficiency for graphs having dense distribution of eigenvalues near the largest as any method for the eigenvalue problem does.

The present method can be extended for application to a general real-symmetric matrix whose components are not only nonnegative. A crucial key for the extension will be how to find or to involve the multiplicity of the largest eigenvalue in computational procedures. Ample room for development is left untouched, in particular, concerning computational devising.

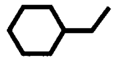
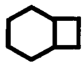
Accepted April 15, 2003

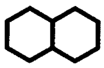
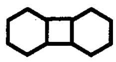
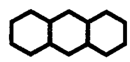
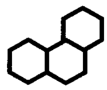
Table 1. $b(k)$'s in Nonbipartite Hückel Graphs

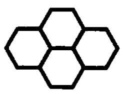
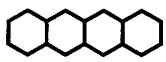
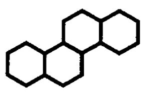
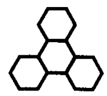
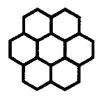
					
$b(1)$	2.236068	2.197368	2.377285	2.640760	2.713189
$b(2)$	2.177743	2.050026	2.193077	2.432218	2.434463
$b(4)$	2.170282	2.004537	2.128298	2.367120	2.336695
$b(8)$	2.170087	2.000072	2.115769	2.359255	2.313051
$b(16)$	2.170086	2.000000	2.114915	2.359029	2.310339
$b(32)$			2.114908		2.310277
d_{max}	3	2	3	3	3
(4) †	2.449490	2.828427	3.162278	3.968627	4.449719
(3) ††	2.111111	2.000000	2.076923	2.333333	2.280000

†) the left-hand side of (4) ††) the left-hand side of (3), an approximation to the largest eigenvalue from the lower side

Table 2. $b(k)$'s in Bipartite Hückel Graphs

					
$b(1)$	1.852161	2.420951	2.676507	2.176835	2.407148
$b(2)$	1.808315	2.414339	2.622767	2.141134	2.359611
$b(4)$	1.802097	2.414214	2.618084	2.135895	2.355726
$b(8)$	1.801938		2.618034	2.135779	2.355674
d_{max}	2	3	3	3	3
(4) †)	2.886751	3.415650	4.183300	3.741657	3.968627
(3) ††)	1.777778	2.411765	2.615385	2.117647	2.333333

					
$b(1)$	2.375064	2.431467	2.632113	2.601340	2.601340
$b(2)$	2.313328	2.323987	2.546276	2.463000	2.472992
$b(4)$	2.303123	2.284176	2.532607	2.420239	2.438279
$b(8)$	2.302776	2.278562	2.532090	2.414366	2.434816
$b(16)$		2.278414	2.532089	2.414214	2.434764
d_{max}	3	3	3	3	3
(4) †)	4.449719	4.882194	5.066228	5.451081	5.451081
(3) ††)	2.280000	2.241379	2.470588	2.368421	2.394737

					
$b(1)$	2.736383	2.768875	2.768875	2.768875	3.055715
$b(2)$	2.575826	2.562980	2.578078	2.586807	2.777311
$b(4)$	2.535312	2.486480	2.512402	2.536290	2.687842
$b(8)$	2.532124	2.468308	2.499755	2.532127	2.675454
$b(16)$	2.532089	2.466750	2.499050	2.532089	2.675131
$b(32)$		2.466732	2.499046		
d_{max}	3	3	3	3	3
(4) †)	5.968668	6.298148	6.298148	6.298148	7.582875
(3) ††)	2.489362	2.411765	2.450980	2.470588	2.615385

†) the left-hand side of (4) ††) the left-hand side of (3), an approximation to the largest eigenvalue from the lower side

References

Coulson, C. A. (1950) "Notes on the Secular Determinant in Molecular Orbital Theory", *Proceedings of the Cambridge Philosophical Society*, Vol. 46, pp.202-205.

Cvetković, D. M., M. Doob, and H. Sachs (1979) *Spectra of Graphs*, p232, Academic Press, New York.

Dias, J. R. (1985) "Properties and Derivation of the Fourth and Sixth Coefficients of the Characteristic Polynomial of Molecular Graphs – New Graphical Invariants", *Theoretica Chimica. Acta*, Vol. 68, pp.107-123.

Hall, G. G. (1977) "On the Eigenvalues of Molecular Graphs", *Molecular Physics*, Vol. 33, pp.551-557.

Lovász, L. (1993a) *Combinatorial Problems and Exercises*, 19(a) in p.81, Elsevier Science Publishers, Amsterdam.

——— (1993b) *Combinatorial Problems and Exercises*, 14(b) in p.81, Elsevier Science Publishers, Amsterdam.

Trinajstić, N. (1991) "Graph Theory and Molecular Orbitals", pp.235-279, in Bonchev, V. and D. H. Rouvray ed. *Chemical Graph Theory, Introduction and Fundamentals*, Abacus Press/Gordon and Breach Science Publishers, New York.