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ARS MATHEMATICA CONTEMPORANEA

Also available at http://amc.imfm.si
ISSN 1855-3966 (printed edn.), ISSN 1855-3974 (electronic edn.)
ARS MATHEMATICA CONTEMPORANEA 5 (2012) 99–105

HL-index of a graph

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Received 15 November 2010, accepted 26 April 2011, published online 12 December 2011

Abstract

Let G be a simple, connected graph with n vertices and eigenvalues $\lambda_1 > \lambda_2 \geq \ldots \geq \lambda_n$. If n is even, define $H = n/2$ and $L = H + 1$. If n is odd, define $H = L = (n+1)/2$. Define the HL-index of G to be $R(G) = \max(|\lambda_H|, |\lambda_L|)$. The eigenvalues λ_H and λ_L appear in chemical graph theory in the study of molecular stability. In this paper, bounds on HL-index for chemical and general graphs are studied. It is shown that there exist graphs with arbitrarily large HL-index.

Keywords: HL-index, graph spectrum, HOMO-LUMO map.

Math. Subj. Class.: 15A18, 05C50, 05C90

1 Introduction

First, recall the definition of the graph spectrum. Let G be a simple, connected graph on n vertices and $A(G)$ its adjacency matrix. The collection of eigenvalues of $A(G)$ is called the spectrum, spec(G), of G. Since $A(G)$ is a symmetric matrix, its spectrum is real and can be described as follows: spec$(G) = \{\lambda_1, \lambda_2, \ldots, \lambda_n\}$, where $\lambda_1 > \lambda_2 \geq \ldots \geq \lambda_n$. Since $A(G)$ has a zero diagonal, $\sum_i \lambda_i = 0$. To indicate eigenvalue multiplicities, spec(G) can be rewritten as

$$\text{spec}(G) = \left\{[\mu_1]^{a_1}, [\mu_2]^{a_2}, \ldots, [\mu_s]^{a_s}\right\},$$

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where $\mu_1 > \mu_2 > \ldots > \mu_s$ are distinct eigenvalues of $A(G)$ and $a_1, a_2, \ldots, a_s$ are their multiplicities. Note that $a_1 = 1$ for connected graphs, since they have a simple principal eigenvalue.

In linear algebra and in spectral graph theory, particular attention is paid to the principal (Perron) eigenvalue λ_1. In graph theory, the minimal eigenvalue λ_n and the second eigenvalue, λ_2, have also been studied. Apart from classical bounds, not much is known in general about the remaining eigenvalues, although there has been a great deal of work on spectra of specific classes of graphs of importance in chemistry and elsewhere [4, 10, 5, 3].

In theoretical chemistry the middle eigenvalues play an important role in the Hückel model of π-electron systems. For even n we define $H := n/2$ and $L := H + 1$. If n is odd, we define $H := L := (n + 1)/2$. In chemical graph theory, the eigenvalue difference $\lambda_H - \lambda_L$ is called the HOMO-LUMO gap of G and is related to the kinetic stability of a molecule. HOMO and LUMO denote Highest Occupied Molecular Orbital and Lowest Unoccupied Molecular Orbital, respectively. There is a direct correspondence between eigenvalues and the corresponding eigenvectors of the molecular graph and the orbital energies and molecular orbitals in the Hückel model.

Given the set of eigenvalues, the ground-state electron configuration of the molecule and hence of the graph is determined by application of three rules: the Aufbau Principle (fill orbitals in order of decreasing eigenvalue), the Pauli Principle (no orbital may contain more than two electrons), and Hund's Rule of Maximum Multiplicity (no orbital receives a second electron before all orbitals degenerate with it have each received one). A molecule and its graph are open shell if any orbitals/eigenvectors are partially occupied, and closed shell otherwise. For neutral molecules, the order of the molecular graph, n, is equal to the number of electrons in the π system. The (fully or partly) occupied orbital of highest energy (corresponding to eigenvalue λ_H) is the HOMO. The (partly or fully) occupied orbital of lowest energy (corresponding to eigenvalue λ_L) is the LUMO. If there are partially occupied orbitals, HOMO and LUMO coincide; a partially occupied orbital is also known as a SOMO (singly occupied molecular orbital).

The pair of HOMO-LUMO eigenvalues (λ_H, λ_L) may be represented as a point in a plane. Thus, for a family of graphs $\mathcal{G}$ we get a set of points. Such a diagram in the HOMO-LUMO plane is called the HOMO-LUMO *map* of $\mathcal{G}$ (see [7, 8]). Furthermore, the right triangle T_C with vertices $(-1, -1), (1, -1), (1, 1)$ is called the *chemical triangle*. A connected graph with maximum valence at most 3 is a *chemical graph*. Experimental evidence shows that most chemical graphs are mapped into the chemical triangle [7]. For instance, in [8] the authors verify this for many fullerenes ([9]), and in particular, it can be proved to be true for chemical trees, i.e., trees with maximal valence ≤ 3. However, it is not true that all chemical graphs possess this property. The smallest counterexample is the Heawood graph, a well-known 3-regular graph that is the Levi graph of the Fano plane, the 6-cage, and the skeleton of the smallest "polyhedral" polyhex torus. Its spectrum is: $\left\{[3]^1, [\sqrt{2}]^6, [-\sqrt{2}]^6, [-3]^1\right\}$ (see, e.g., [1, 2]). Hence the Heawood graph falls outside the chemical triangle T_C. So far, this is the only chemical graph that we know to fall outside T_C. Exhaustive search reveals no other example with 19 or fewer vertices, and no other exception amongst 3-regular graphs with 24 or fewer vertices. Once the degree constraint is relaxed, graphs G with $R(G) > 1$ appear in large numbers (2 for $n = 6$, 119 for $n = 8$, 37 for $n = 9$, 151062 for $n = 10$, see [7]).

The HOMO-LUMO *radius* or *HL-index* ([7]) is defined as

$$R(G) := \max\left\{|\lambda_H|, |\lambda_L|\right\}.$$

The theorem about chemical trees can be restated as follows.

Theorem 1.1 ([7]). *For each chemical tree T, the HL-index is bounded by* 1,

$$R(T) \leq 1.$$

For general graphs, no such bound is known. By the Gerschgorin and Cauchy interlacing theorems one can easily prove that the HL-index of a graph is bounded by its maximal degree or the average valence [4]. For bipartite and pseudo-bipartite graphs, tighter bounds were obtained in [7]. (A pseudo-bipartite graph is not bipartite, but like a bipartite graph it has $\lambda_H = -\lambda_L$.)

Theorem 1.2 ([7]). *Let G be a bipartite or pseudo-bipartite graph with n vertices and m edges, and let $\bar{d} := 2m/n$ denote its average degree. Then*

$$0 \leq R(G) \leq \sqrt{\bar{d}}.$$

Thus, in particular, if G is a chemical bipartite or pseudo-bipartite graph,

$$0 \leq R(G) \leq \sqrt{3}.$$

Now let $\mathcal{G}$ be a family of graphs. Define the HL-index of $\mathcal{G}$, $R(\mathcal{G})$, to be the maximum value of $R(G)$ for $G \in \mathcal{G}$.

Theorem 1.3. *Let $\mathcal{G}_D$ be the family of graphs with maximal degree at most D. Then*

$$0 \leq R(\mathcal{G}_D) \leq D.$$

The equality in the lower bound is reached for many graphs, whilst the equality in the upper bound is reached only for the complete graph K_2.

Proof. The lower bound is obvious from the non-negativity of the HL-index. The equality is reached for the complete bipartite graph $K_{2,2}$, amongst many others. The Gerschgorin theorem yields the upper bound. Here, equality is obviously reached for the complete graph on 2 vertices K_2. There are no other such graphs. In such a case, the absolute value of the "middle" eigenvalue λ_H or λ_L should be D. But since $|\lambda_i| \leq D$ for all i, at least half of the eigenvalues should be equal to D or $-D$. Since by the Perron-Frobenius theorem for simple connected graphs the Perron eigenvalue is simple, this is possible only for $n = 2$ and the graph K_2. □

Since for the Heawood graph G, $R(G) = \sqrt{2}$, the upper bound is in general at least $\sqrt{2}$ and less than 3 for chemical graphs.

Theorem 1.4. *Let $\mathcal{C} = \mathcal{G}_3$ be the family of chemical graphs. Then*

$$\sqrt{2} \leq R(\mathcal{C}) < 3.$$

2 Main result

The HL-index of a family of graphs is bounded from above by a function of its maximum degree. Here we show that the HL-index may be arbitrarily large.

Theorem 2.1. *For each positive constant $K > 0$ there exists a connected graph $G(K)$ such that the HL-index of $G(K)$ is greater than K,*

$$R(G(K)) > K.$$

Proof. We will use Paley graphs and their spectral properties (see, e.g., [1, 2]). Let $q = p^m$ be a prime power of the form $q = 4t + 1$, $t \in \mathbb{N}$. The graph $P(q)$ is defined on the finite field $F(q)$ with q elements. Its vertex set is $F(q)$, and two vertices are adjacent if and only if their difference is a square in the field. The Paley graph $P(q)$ is self-complementary and strongly regular. The eigenvalues of the Paley graph $P(q)$ are

$$\left\{ \left[\frac{q-1}{2}\right]^1, \left[\frac{-1+\sqrt{q}}{2}\right]^{\frac{q-1}{2}}, \left[\frac{-1-\sqrt{q}}{2}\right]^{\frac{q-1}{2}} \right\}.$$

Hence $R(P(q)) = \lambda_H = \lambda_L = (\sqrt{q} - 1)/2$. Take $q > (2K + 1)^2$, and the proof is concluded. □

A Paley graph has an odd number of vertices and hence $\lambda_H = \lambda_L$ by definition. One can ask a natural question: Is it possible to find a sequence of even-order connected graphs with increasing HL-index? The answer to this question is in the affirmative.

For instance, take any connected, regular, bipartite graph G that has exactly 4 distinct eigenvalues. Cvetković, Doob, and Sachs [4, p. 166] proved that G has to be a Levi graph of a symmetric $2 - (v, k, \lambda)$ design. Its spectrum is (see [6])

$$\left\{ [k]^1, \left[\sqrt{k-\lambda}\right]^{v-1}, \left[-\sqrt{k-\lambda}\right]^{v-1}, [-k]^1 \right\},$$

and therefore its HL-index is equal to $\sqrt{k-\lambda}$. For $k = n + 1$, $v = n^2 + n + 1$, $\lambda = 1$, the designs are finite projective planes, which exist for prime powers $n = p^m$. Hence $\sqrt{k-\lambda} = \sqrt{n}$ is arbitrarily large.

3 Questions

Let us conclude the paper with some interesting questions.

1. Is the Heawood graph the only chemical graph outside the chemical triangle T_C?
2. Let $\mathcal{C} = \mathcal{G}_3$ be the family of chemical graphs. By Thm. 1.4, $\sqrt{2} \leq R(\mathcal{C}) < 3$. How large can $R(\mathcal{C})$ be?
3. It would be interesting to determine the graphs G on n vertices with maximal HL-index $R(G)$. For small numbers of vertices, n, the graphs maximizing $R(G)$ (or if there are many, the numbers of such graphs) are listed in Table 1, and examples are shown in Figure 1.

   Here $G_{6,1}$ is the pentagonal pyramid (wheel with 5 spokes), $G_{8,1}$ is the two-dimensional subdivision of the tetrahedron, and $G_{10,1}$ is the complement of the Petersen

n	$R(G)$	graphs
2	1	K_2
3	1	K_3
4	1	$K_4 - e, K_4$
5	1	$G_{5,1}, G_{5,2}, G_{5,3}, G_{5,4}, G_{5,5} = K_5$
6	$\sqrt{6} - 1$	$G_{6,1}$
7	1	109 graphs, the one with most edges being K_7
8	$\phi = (1 + \sqrt{5})/2$	$G_{8,1}$
9	$\sqrt{2}$	$G_{9,1}, G_{9,2}, G_{9,3}$
10	2	$G_{10,1}$

Table 1: Graphs on n vertices with maximal HL-index.

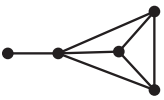
graph. When the maximal HL-index for a given n is equal to 1, the complete graph K_n achieves that maximum (as spec$(K_n) = \{[n-1]^1, [-1]^{n-1}\}$), and clearly is the unique graph with the maximal number of edges m that does so.

4. Determine the graphs G with n vertices and m edges with maximal HL-index $R(G)$.
5. Since the number of adjacency matrices of chemical graphs is countable, the same holds for the image of the HOMO-LUMO map. Does there exist a simply connected region with positive area in the chemical triangle that contains no points (λ_H, λ_L)?

4 Acknowledgements

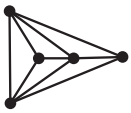
GJ and TP thank ARRS for a grant P1-294. PWF thanks the Royal Society for an award under the RS/Wolfson Research Merit Scheme. TP thanks Peter Šemrl for a fruitful discussion.

$G_{5,1}$



$G_{5,2}$

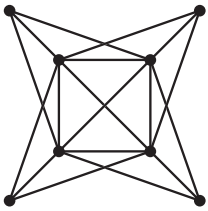
$G_{5,3}$



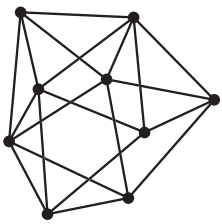
$G_{5,4}$

$G_{5,5}$

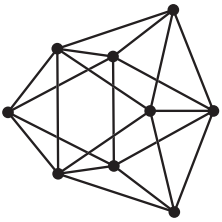
$G_{6,1}$



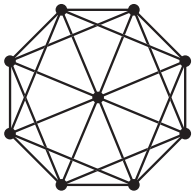
$G_{8,1}$



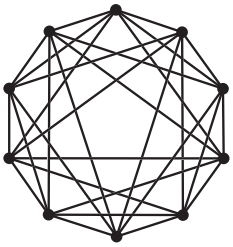
$G_{9,1}$



$G_{9,2}$



$G_{9,3}$



$G_{10,1}$

Figure 1: Graphs $G_{n,i}$ with maximal HL-index.

References

[1] A. E. Brouwer, A. M. Cohen and A. Neumaier, *Distance-regular Graphs*, Ergebnisse der Mathematik 3.18, Springer, Heidelberg, 1989.

[2] A. E. Brouwer, Graph descriptions, http://www.win.tue.nl/~aeb/graphs/index.html, (last accessed 12.11.2010).

[3] F. R. K. Chung, *Spectral Graph Theory*, CBMS Regional Conference Series in Mathematics, American Mathematical Society, 1997.

[4] D. M. Cvetković, M. Doob and H. Sachs, *Spectra of Graphs*, V.E.B. Deutscher Verlag der Wissenschaften, Berlin, 1979.

[5] D. Cvetković, P. Rowlinson and S. Simić, *An Introduction to the Theory of Graph Spectra*, London Mathematical Society Student Texts, Cambridge University Press, 2009.

[6] E. R. van Dam, Regular graphs with four eigenvalues, *Linear Algebra Appl.* **226-228** (1995) 139–162.

[7] P. W. Fowler and T. Pisanski, HOMO-LUMO maps for chemical graphs, *MATCH Commun. Math. Comput. Chem.* **64** (2010), 373–390.

[8] P. W. Fowler and T. Pisanski, HOMO-LUMO maps for fullerenes, *Acta Chim. Slov.*, **57** (2010), 513–517.

[9] P. W. Fowler and T. Pisanski, Leapfrog fullerenes and Clar polyhedra, *J. Chem. Soc., Faraday Trans.* **90** (1994), 2865–2871.

[10] I. Gutman and O. Polansky, *Mathematical Concepts in Organic Chemistry*, Springer, Berlin, 1986.