MATCH
Communications in Mathematical and in Computer Chemistry

MATCH Commun. Math. Comput. Chem. **65** (2011) 753-774

ISSN 0340 - 6253

Spectral Properties of the He Matrix of Hexagonal Systems

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(Received September 12, 2009)

Abstract

The He matrix, put forward by He and He in 1989 [31], is designed as a means for uniquely representing the structure of a hexagonal system (= benzenoid graph). Observing that the He matrix is just the adjacency matrix of a pertinently weighted inner dual of the respective hexagonal system, we establish a number of its spectral properties. The spectral radius of the He matrix is less than 12, but can be arbitrarily close to 12. In case of catacondensed systems, the spectral radius is less than 6. Based on a computer search, we conjecture that the naphthalene graph is the only hexagonal system whose He matrix has integral spectrum. Some results for the energy of the He matrix are also obtained.

1 Introduction

According to Sachs [46], a *hexagonal system* is defined as follows.

Definition 1.1. A hexagonal unit cell is a plane region bounded by a regular hexagon of side length 1. A hexagonal system is a finite connected plane graph with no cut-vertices in which every interior region is a hexagonal unit cell.

In what follows, instead of "hexagonal unit cell" we will simply say *hexagon*.

Hexagonal systems may be viewed as plane graphs (= graphs embedded in the plane), but also as geometric objects [24]. In the mathematical literature these have been named "hexagonal animals" or "hexanimals" (see e. g., [29]), "honeycomb systems" or "honeycomb graphs" (see e. g., [16, 31]), "polyhexes" (see e. g., [30, 34, 51]), "hexagonal nets" (see e. g., [48]), and "hexagonal polyominoes" (see e. g., [18, 36, 39]). Hexagonal systems are encountered in recreational mathematics, and found application in physics, such as the Ising model, and in polymer science. However, the far greatest interest for these objects is in organic chemistry, since these provide the graph representation of benzenoid hydrocarbons. In chemistry hexagonal systems were extensively studied under the name of "benzenoid graphs" or "benzenoid systems" (see the monograph [25] and the references cited therein); also the name "fusenes" is occasionally used (see e. g., [2, 12]).

In Fig. 1 are found two examples of hexagonal systems.

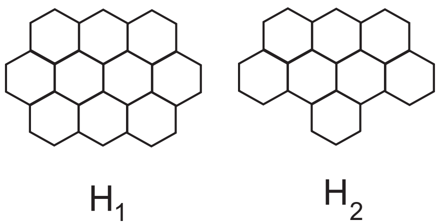


Fig. 1. Hexagonal systems consisting of 10 and 8 hexagons. Their inner duals are shown in Fig. 2.

Definition 1.2. The *inner dual* $ID(H)$ of a hexagonal system H is a graph constructed by placing a vertex in the center of each hexagon of H and by connecting those vertices that are in adjacent hexagons.

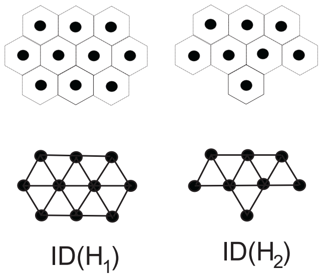


Fig. 2. The inner duals $ID(H_1)$ and $ID(H_2)$ of the hexagonal systems H_1 and H_2 from Fig. 1.

In Fig. 2 are shown the inner duals of the hexagonal systems from Fig. 1. It is easy to realize that these uniquely determine the underlying hexagonal system. However, in the general case, an inner dual may correspond to several different hexagonal systems, as seen from the examples depicted in Fig. 3.

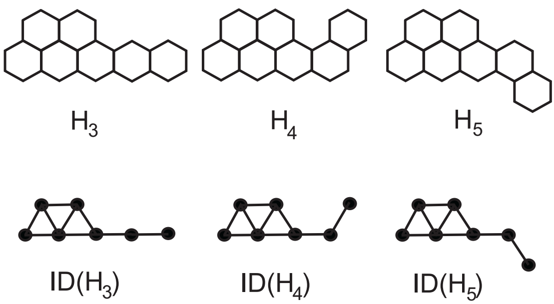


Fig. 3. Three hexagonal systems H_3, H_4, and H_5, whose inner duals $ID(H_3)$, $ID(H_4)$, and $ID(H_5$ (viewed as graphs) are isomorphic. If, however, additional information about the angles between the edges is provided, then the respective diagrams (which then are called "dualist graphs", but which are not graphs) are in a one–to–one correspondence with the underlying hexagonal system.

The fact that an inner dual does not fully characterize the underlying hexagonal systems was notice long time ago [2, 12] and was discussed in due detail in several papers [3, 4, 5, 6, 11] and reviews [7, 8, 9, 10, 19]. The evident solution of this problem was the concept of *dualist graph*, which is constructed in the same manner as the inner dual, except that the angles between the edges are preserved. Initially, the name "characteristic graph" was proposed for this object [12], but in 1977 Balaban changed it into "dualist graph" or simply "dualist" [5]. His motivation was expressed as follows [5]: "*We now prefer to name them dualist graphs, in order to emphasize both the similarity with, and the difference from, dual graphs.*". Nevertheless, the name "characteristic graph" is still used by some authors (see e. g., [6, 31]).

In view of the fact that the dualist graph fully determines the underlying hexagonal system, it was evident that it can be used in connection with the, chemically important, naming, coding, and enumerating of benzenoid hydrocarbons [12]. Approaches of this kind were proposed by Bonchev and Balaban [13] as well as by Cioslowski and Turek [14]; for review see [9]. A few years later He and He [31] put forward a third approach, based on – what He and He themselves called – the *He matrix*. The article [31] remained unnoticed by the majority of scholars involved in research of hexagonal systems, and is not mentioned either in later books and reviews (cf. [10, 19, 25]) or in the extensive monograph [35] on graph–theoretical matrices of chemical relevance.

In this paper we study the He matrix and establish its main mathematical, especially spectral, properties.

2 The He matrix

Provided that the hexagonal systems are drawn so that some of their edges are vertical (as in Figs. 1 and 3), then the edges of the dualist graphs have three different possible directions. We classify them into types (a), (b), and (c), so that an edge e is of type

(a) if the angle between e and the positive horizontal direction is either 0 or π ,

(b) if the angle between e and the positive horizontal direction is either $\pi/3$ or $4\pi/3$, and

(c) if the angle between e and the positive horizontal direction is either $2\pi/3$ or $5\pi/3$.

It should be noted that, according to the above definition, the type of an edge of the dualist graph will not be changed if the entire dualist graph is rotated by 180 degrees.

In Fig. 4 is shown an example of a dualist graph with its edges labeled according to the above specified orientations.

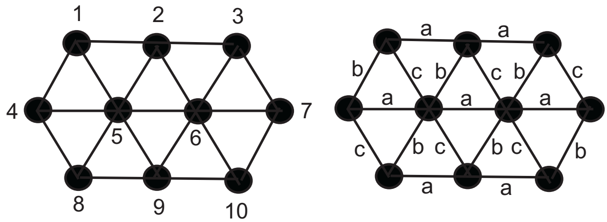


Fig. 4. The dualist graph of the hexagonal system H_1 from Fig. 1, the numbering of its vertices and the labeling of its edges with symbols a, b, and c according to their orientation; for details see text.

He and He have, conventionally, chosen $a = 1$, $b = 2$ and $c = 3$, and have defined the He matrix as follows.

Definition 2.1. Let H be a hexagonal system with n hexagons. Let the vertices of the dualist graph of H be labeled by $1, 2, \ldots, n$. Denote by (rs) the edge of the dualist graph, connecting the vertices r and s. Then the *He matrix* $\mathbf{A}(H)$ of H is a square matrix of order n whose (i,j)-entry is defined as

$$a_{ij} = \begin{cases} 0 & \text{if } i = j \\ 0 & \text{if the vertices } i \text{ and } j \text{ of the dualist graph are not adjacent} \\ 1 & \text{if } (ij) \text{ is an edge of type (a) of the dualist graph} \\ 2 & \text{if } (ij) \text{ is an edge of type (b) of the dualist graph} \\ 3 & \text{if } (ij) \text{ is an edge of type (c) of the dualist graph} \,. \end{cases}$$

The He matrix of the hexagonal system H_1 from Fig. 1, whose dualist graph and the labeling of its vertices are shown in Fig. 4, is given as follows:

$$
\mathbf{A}(H_1) = \begin{pmatrix}
0 & 1 & 0 & 2 & 3 & 0 & 0 & 0 & 0 & 0 \\
1 & 0 & 1 & 0 & 2 & 3 & 0 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 & 0 & 2 & 3 & 0 & 0 & 0 \\
2 & 0 & 0 & 0 & 1 & 0 & 0 & 3 & 0 & 0 \\
3 & 2 & 0 & 1 & 0 & 1 & 0 & 2 & 3 & 0 \\
0 & 3 & 2 & 0 & 1 & 0 & 1 & 0 & 2 & 3 \\
0 & 0 & 3 & 0 & 0 & 1 & 0 & 0 & 0 & 2 \\
0 & 0 & 0 & 3 & 2 & 0 & 0 & 0 & 1 & 0 \\
0 & 0 & 0 & 0 & 3 & 2 & 0 & 1 & 0 & 1 \\
0 & 0 & 0 & 0 & 0 & 3 & 2 & 0 & 1 & 0
\end{pmatrix} .
$$

It is immediately seen that $\mathbf{A}(H)$ is a symmetric matrix with all diagonal elements equal to zero. Therefore its eigenvalues are real, and their sum is equal to zero. The eigenvalues of $\mathbf{A}(H)$ form the spectrum of the He matrix and may be ordered as

$$
\lambda_1(\mathbf{A}(H)) \geq \lambda_2(\mathbf{A}(H)) \geq \cdots \geq \lambda_n(\mathbf{A}(H)) .
$$

In what follows instead of $\lambda_i(\mathbf{A}(H))$ we simply write $\lambda_i(H)$ of, when confusion is not possible, λ_i .

For instance, the eigenvalues of $\mathbf{A}(H_1)$ are 8.036 , 5.325 , 2.006 , 1.416 , -0.151 , -0.261 , -2.598 , -3.794 , -4.881 , and -5.097 .

Assuming that some of its edges are vertical, in the general case a hexagonal system may be drawn in 12 distinct ways. An example is given in Fig. 5. (In case of symmetry [25], this number is smaller, equal to 6, 4, 3, 2, or 1.)

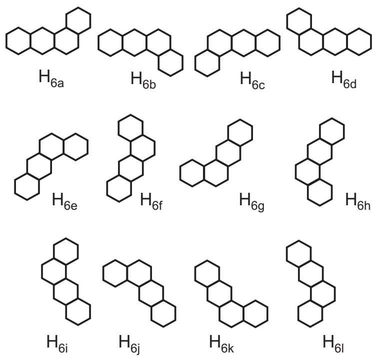


Fig. 5. The twelve distinct ways in which a non-symmetric hexagonal system H_6 can be drawn so that some of its edges are vertical.

Because the type of any edge of the dualist graph is not changed when the dualist graph is rotated by 180 degrees, there exist 6 (= 12/2) non-equivalent He matrices corresponding to one and the same hexagonal system. (Again, in case of symmetry, this number is smaller, equal to 3, 2, or 1.)

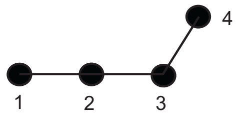


Fig. 6. Numbering of vertices of the dualist graph of the hexagonal system H_6. Depending to the way in which H_6 is drawn (see Fig. 5), six distinct He matrices correspond to this dualist graph.

For example, if the vertices of the dualist graph of H_6 are labeled as indicated in Fig. 6, then the six distinct He matrices of H_6 read as follows:

$$\mathbf{A}(H_{6a}) = \mathbf{A}(H_{6c}) = \begin{bmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 2 \\ 0 & 0 & 2 & 0 \end{bmatrix} \quad , \quad \mathbf{A}(H_{6b}) = \mathbf{A}(H_{6d}) = \begin{bmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 3 \\ 0 & 0 & 3 & 0 \end{bmatrix}$$

$$\mathbf{A}(H_{6e}) = \mathbf{A}(H_{6g}) = \begin{bmatrix} 0 & 2 & 0 & 0 \\ 2 & 0 & 2 & 0 \\ 0 & 2 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix} \quad , \quad \mathbf{A}(H_{6f}) = \mathbf{A}(H_{6h}) = \begin{bmatrix} 0 & 2 & 0 & 0 \\ 2 & 0 & 2 & 0 \\ 0 & 2 & 0 & 3 \\ 0 & 0 & 3 & 0 \end{bmatrix}$$

$$\mathbf{A}(H_{6i}) = \mathbf{A}(H_{6l}) = \begin{bmatrix} 0 & 3 & 0 & 0 \\ 3 & 0 & 3 & 0 \\ 0 & 3 & 0 & 2 \\ 0 & 0 & 2 & 0 \end{bmatrix} \quad , \quad \mathbf{A}(H_{6j}) = \mathbf{A}(H_{6k}) = \begin{bmatrix} 0 & 3 & 0 & 0 \\ 3 & 0 & 3 & 0 \\ 0 & 3 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix}$$

Each of these six matrices has different eigenvalues, namely

$$\lambda_{1,2,3,4}(H_6) = \pm\sqrt{\frac{1}{2}\left[2\,p^2 + q^2 \pm \sqrt{4\,p^4 + q^4}\right]}$$

where

$p = 1\,,\ q = 2$ for H_6 being drawn ass H_{6a} or H_{6c},

$p = 1\,,\ q = 3$ for H_6 being drawn ass H_{6b} or H_{6d},

$p = 2\,,\ q = 1$ for H_6 being drawn ass H_{6e} or H_{6g},

$p = 2\,,\ q = 3$ for H_6 being drawn ass H_{6f} or H_{6h},

$p = 3$, $q = 2$ for H_6 being drawn ass H_{6i} or H_{6l}, and

$p = 3$, $q = 1$ for H_6 being drawn ass H_{6j} of H_{6k}.

Thus, the spectrum of the He matrix depends not only on the underlying hexagonal system, but also on the way in which it has been drawn. This may be considered as a significant weak point of the entire theory of the He matrix.

We denote the characteristic polynomial of $\mathbf{A}(H)$ by

$$\phi(H, \lambda) = \det(\lambda\, \mathbf{I} - \mathbf{A}(H)) = \sum_{k=0}^{n} b_k\, \lambda^{n-k}\ .$$

Evidently, also $\phi(H, \lambda)$ depends both on the hexagonal system H and on the way in which it is drawn. For instance,

$$\phi(H_6, \lambda) = \lambda^4 - (2\,p^2 + q^2)\,\lambda^2 + p^2\,q^2 \qquad (1)$$

where p and q have the values specified above.

For the continuation of this paper it is essential to notice that the He matrix is nothing else than the adjacency matrix of the inner dual, whose edges are weighted by 1, 2, or 3, depending on their (above described) types. Therefore the basic spectral properties of the He matrix are immediate consequences and special cases of results known in spectral graph theory for weighted graphs. The extensions of the spectral properties of simple (non-weighted) graphs to weighted graphs are usually so straightforward that these are not discussed in detail (see, for instance [15]). Yet, in applied sciences there are several works in which spectral properties of weighted graph are considered [35, 40, 41, 42, 44, 50]. For instance, the formula (1) is immediately obtained from the so-called "generalization of Sachs' formula" [41].

The spectral properties of the He matrix have not been studied until now. Therefore the first results obtained along these lines will necessarily be simple and elementary. We, nevertheless, hope that these will pave the way for further, more advanced findings. The ultimate goal of our research is to reveal some concealed properties of the He matrices and/or dualist graphs and/or inner duals and/or hexagonal systems, that would shed more light on the remarkable spectral and combinatorial properties of hexagonal systems. This would make possible to better understand the also remarkable physico–chemical properties of benzenoid hydrocarbons [21, 25, 26]

The rest of the paper is organized is as follows. In Section 3, we state some previously known results related to matrix theory. In Section 4 we present lower and upper bounds on the spectral radius of the He matrix. In Section 5 we consider the question if the spectrum of the He matrix can be integral. In the last section some results on the energy of the He matrix are reported.

3 Lemmas

We list here some previously known results related to matrix theory, that will be needed in the subsequent sections.

Lemma 3.1. (Perron–Frobenius) [17] *A non-negative matrix* $\mathbf{B}$ *always has a non-negative eigenvalue* r *, such that the moduli of all the eigenvalues of* $\mathbf{B}$ *do not exceed* r *. To this "maximal" eigenvalue* r *there corresponds a non-negative eigenvector* $\mathbf{Y}$ *, such that*

$$\mathbf{B}\,\mathbf{Y} = r\,\mathbf{Y} \quad (\mathbf{Y} \geq \mathbf{0}, \quad \mathbf{Y} \neq \mathbf{0}) \ .$$

Lemma 3.2. [33] *Let* $\mathbf{B} = ||b_{ij}||$ *be an* $n \times n$ *irreducible non-negative matrix with spectral radius* $\lambda_1(\mathbf{B})$ *, and let* $R_i(\mathbf{B})$ *be the i-th row sum of* $\mathbf{B}$ *, i. e.,* $R_i(\mathbf{B}) = \sum\limits_{j=1}^{n} b_{ij}$ *. Then*

$$\min\{R_i(\mathbf{B}) : \ 1 \leq i \leq n\} \leq \lambda_1(\mathbf{B}) \leq \max\{R_i(\mathbf{B}) : \ 1 \leq i \leq n\} \ . \tag{2}$$

Moreover, if the row sums of $\mathbf{B}$ *are not all equal, then both inequalities in (2) are strict.*

Lemma 3.3. (Rayleigh–Ritz) [33] *If* $\mathbf{B}$ *is a real symmetric* $n \times n$ *matrix with eigenvalues* $\lambda_1(\mathbf{B}) \geq \lambda_2(\mathbf{B}) \geq \cdots \geq \lambda_n(\mathbf{B})$ *, then for any* $\mathbf{X} \in \mathbf{R}^n$ *, (*$\mathbf{X} \neq \mathbf{0}$*),*

$$\mathbf{X}^t\,\mathbf{B}\,\mathbf{X} \leq \lambda_1(\mathbf{B})\,\mathbf{X}^t\,\mathbf{X} \ .$$

Equality holds if and only if $\mathbf{X}$ *is an eigenvector of* $\mathbf{B}$ *, corresponding to the largest eigenvalue* $\lambda_1(\mathbf{B})$ *.*

Lemma 3.4. (Cauchy) [47] *Let* $\mathbf{B}$ *be same as in Lemma 3.3, and let* $\mathbf{B}_k$ *be its leading* $k \times k$ *submatrix; that is,* $\mathbf{B}_k$ *is the matrix obtained from* $\mathbf{B}$ *by deleting its last* $n-k$ *rows and columns. Then, for* $i = 1, 2, \ldots, k$ *,*

$$\lambda_{n-i+1}(\mathbf{B}) \leq \lambda_{k-i+1}(\mathbf{B}_k) \leq \lambda_{k-i+1}(\mathbf{B}) \ . \tag{3}$$

4 Spectral radius of the He matrix

Let, as before, a_{ij} be the (i,j)-entry of the He matrix $\mathbf{A}(H)$. Let $w_i = \sum_{j=1}^{n} a_{ij}^2$, $i = 1,2,\ldots,n$. Then we have

Lemma 4.1.

$$\sum_{i=1}^{n} \lambda_i^2(H) = \sum_{i=1}^{n} w_i \ .$$

Proof: Let $\mathbf{X} = (x_1, x_2, \ldots, x_n)^t$ be an eigenvector corresponding to the eigenvalue λ_i of $\mathbf{A}(H)$. Then $\mathbf{A}(H)\,\mathbf{X} = \lambda_i\,\mathbf{X}$, that is, $\mathbf{A}^2(H)\,\mathbf{X} = \lambda_i\,\mathbf{A}(H)\,\mathbf{X} = \lambda_i^2\,\mathbf{X}$. But the diagonal elements of $\mathbf{A}^2(H)$ are $w_1\,, w_2\,, \ldots, w_n$. Thus

$$\sum_{i=1}^{n} \lambda_i^2 = \mathrm{Tr}\mathbf{A}^2(H) = \sum_{i=1}^{n} w_i \ .$$

□

Theorem 4.2. *Let H be hexagonal system. Then any eigenvalue λ of the He matrix $\mathbf{A}(H)$ satisfies*

$$-12 < \lambda < 12 \ . \tag{4}$$

Proof: If a hexagon χ of H has six adjacent hexagons, then the vertex of the dualist graph corresponding to χ has degree six, and the edges incident to this vertex have weights 1, 1, 2, 2, 3, and 3, whose sum is 12. Then by Lemmas 3.1 and 3.2, $-12 \leq \lambda \leq 12$.

Since H is finite, its dualist has a vertex of degree strictly less than 6. The corresponding row or column sum of $\mathbf{A}(H)$ is then less than 12. Therefore, by Lemma 3.2 the inequalities in (4) must be strict. □

Corollary 4.3. *The spectral radius of the He matrix may be arbitrarily close to 12.*

Proof: According to Lemma 3.2 the spectral radius of the He matrix $\mathbf{A}(H)$ would be equal to 12 only if all vertices of the dualist graph of H would be of degree 6. This would happen only if H is the (infinite) hexagonal lattice. However, we can easily construct a series of finite hexagonal systems, whose limit is the hexagonal lattice. Consequently, the spectral radii of the corresponding He matrices form a series whose limit value is 12. □

A hexagonal systems is said to be *catacondensed* if its inner dual is a tree [12, 25]. Each vertex of the dualist graph of a catacondensed hexagonal system has degree at most 3. The edges incident to any vertex of degree three have weights 1, 2, and 3, whose sum is 6. The edges incident to a vertex of degree two may have weights 3 and 3, whose sum is also 6. Then in full analogy with Theorem 4.2 and Corollary 4.3 we get:

Corollary 4.4. *Let H be a catacondensed hexagonal system. Then any eigenvalue λ of the He matrix $\mathbf{A}(H)$ satisfies $-6 < \lambda < 6$. The spectral radius of the He matrix of a catacondensed hexagonal system may be arbitrarily close to 6.*

A catacondensed hexagonal systems is said to be a *hexagonal chain* if its inner dual is a path, i. e., has no vertex of degree 3. Then, in analogy to Corollary 4.4, we have:

Corollary 4.5. *Let H be a hexagonal chain. Then any eigenvalue λ of the He matrix $\mathbf{A}(H)$ satisfies $-6 < \lambda < 6$. The spectral radius of the He matrix of a hexagonal chain may be arbitrarily close to 6.*

Theorem 4.6. *Let H be a hexagonal system. Then the spectral radius of its He matrix satisfies*

$$\lambda_1 \leq \max_i \left\{ \frac{1}{d_i} \sum_{j:j\sim i} a_{ij}\, d_j \right\} \tag{5}$$

where d_i is the degree of the vertex i of the dualist graph of H, and where $\sum\limits_{j:j\sim i}$ stands for summation over all vertices j of the dualist graph and all edges (ij) that are incident to the vertex j.

Proof: Consider the matrix $\mathbf{D}^{-1}\mathbf{A}\mathbf{D}$, with $\mathbf{D}$ being the diagonal matrix whose diagonal elements are the degrees of the dualist graph. The (i,j)-th element of $\mathbf{D}^{-1}\mathbf{A}\mathbf{D}$

is equal to

0 if $i = j$, or i is not adjacent to j,

d_j/d_i if (ij) is a type (a) edge of the dualist graph,

$2\,d_j/d_i$ if (ij) is a type (b) edge of the dualist graph, and

$3\,d_j/d_i$ if (ij) is a type (c) edge of the dualist graph.

Inequality (5) follows by applying Lemma 3.2 on $\mathbf{D}^{-1}\mathbf{A}\mathbf{D}$ $\square$

For the hexagonal systems H_1 and H_2 shown in Figure 1, inequality (5) gives $\lambda_1(H_1) \leq 9.33$ and $\lambda_1(H_2) \leq 12.5$. On the other hand, the actual spectral radii are $\lambda_1(H_1) = 8.04$ and $\lambda_1(H_2) = 6.97$.

From these example we see that upper bound (5) is sometimes greater than 12. Since by (4), λ_1 cannot exceed 12, a strengthening of (5) is:

Corollary 4.7.

$$\lambda_1 \leq \min\{12, P\}$$

where P is the expression on the right–hand side of (5).

We now give a lower bound on the spectral radius of the He matrix.

Theorem 4.8. *Let H be a hexagonal system with n hexagons. Then the spectral radius of the He matrix is bounded from below as*

$$\lambda_1 \geq \frac{2\,M_e}{n} \tag{6}$$

where $M_e = \sum_{i \sim j} a_{ij}$ and where $\sum_{i \sim j}$ stands for summation over all edges (ij) of the dualist graph.

Proof: Let $\mathbf{A}(H) = ||a_{ij}||$ be the He matrix corresponding to H. By Lemma 3.3, for any vector $\mathbf{X} = (x_1, x_2, \ldots, x_n)^t$,

$$\begin{aligned} \mathbf{X}^t\,\mathbf{A}(H)\,\mathbf{X} &= \left(\sum_{j:j\sim 1}^{n} x_j\,a_{j1}, \sum_{j:j\sim 2}^{n} x_j\,a_{j2}, \cdots, \sum_{j:j\sim n}^{n} x_j\,a_{j,n} \right)^t \mathbf{X} \\ &= 2 \sum_{i \sim j} a_{ij}\,x_i\,x_j \end{aligned} \tag{7}$$

because $a_{ij} = a_{ji}$. Also,

$$\mathbf{X}^t\,\mathbf{X} = \sum_{i=1}^{n} x_i^2 \,. \tag{8}$$

Using Eqs. (7) and (8), by Lemma 3.3, we obtain

$$\lambda_1 \geq \frac{2\sum\limits_{i\sim j} a_{i,j}\,x_i\,x_j}{\sum\limits_{i=1}^{n} x_i^2} \,. \tag{9}$$

Since (9) is true for any vector $\mathbf{X}$, by putting $\mathbf{X} = (1,1,\ldots,1)^t$ we arrive at the required result (6). $\square$

Given two hexagonal systems H' and H'' and some specified boundary edges in any direction, we can form a new hexagonal system from the disjoint union of H' and H'', by identify these two boundary edges. We say that the new hexagonal systems is a *concatenation* of H' and H''. Two self-explanatory examples of concatenation are found in Fig. 7.

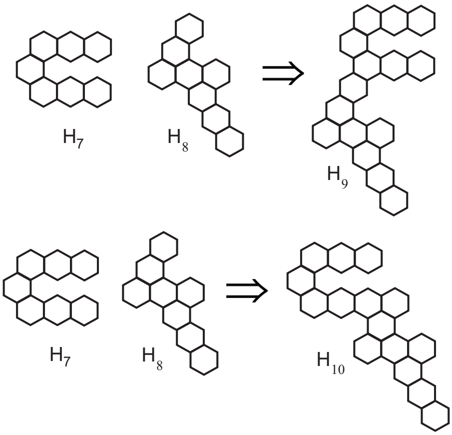


Fig. 7. Examples illustrating the concept of concatenation of hexagonal systems: H_9 and H_{10} are obtained by concatenation of H_7 and H_8.

Let H^* be the concatenation of hexagonal systems H' and H''. Let H^*, H', and H'' have n^*, n', and n'' hexagons, respectively, $n^* = n' + n''$. Then we have the following:

Theorem 4.9. *If H^* is obtained from H' and H'' by identifying a single edge of H' with a single edge of H'', then*

$$\lambda_1(H^*) > \lambda_1(H') \quad \textit{and} \quad \lambda_1(H^*) > \lambda_1(H'') .$$

Proof: By pertinently labeling the vertices of H^*, the respective He matrix is of the form:

$$\mathbf{A}(H^*) = \left[\begin{array}{ccccc|cccc} 0 & * & * & \cdots & * & 0 & 0 & \cdots & 0 \\ * & 0 & * & \cdots & * & 0 & 0 & \cdots & 0 \\ \cdot & \cdot & \cdot & \cdots & \cdot & \cdot & \cdot & \cdots & \cdot \\ * & * & * & \cdots & * & 0 & 0 & \cdots & 0 \\ * & * & * & \cdots & 0 & e & 0 & \cdots & 0 \\ \hline 0 & 0 & 0 & \cdots & e & 0 & * & \cdots & * \\ 0 & 0 & 0 & \cdots & 0 & * & 0 & \cdots & * \\ \cdot & \cdot & \cdot & \cdots & \cdot & \cdot & \cdot & \cdots & \cdot \\ 0 & 0 & 0 & \cdots & 0 & * & * & \cdots & * \\ 0 & 0 & 0 & \cdots & 0 & * & * & \cdots & 0 \end{array}\right]$$

where $e = 1$ or 2 or 3. Let $\mathbf{B}$ be the $(n'+1) \times (n'+1)$ leading submatrix of $\mathbf{A}(H^*)$. Then by Lemma 3.4,

$$\lambda_1(H^*) \geq \lambda_1(\mathbf{B})$$

and

$$\lambda_1(\mathbf{B}) \geq \lambda_1(H') .$$

Thus $\lambda_1(H^*) \geq \lambda_1(H')$. By contradiction, we show that equality in the latter relation never happens.

Suppose that $\lambda_1(H^*) = \lambda_1(H')$. This implies that $\lambda_1(\mathbf{B}) = \lambda_1(H')$. Let $\mathbf{X} = (x_1, x_2, \ldots, x_{n'})^t$ be the eigenvector corresponding to $\lambda_1(H')$. Since H' is connected, $\mathbf{A}(H')$ is an irreducible matrix and hence all the eigencomponents x_i $(i = 1, 2, \ldots, n')$ are positive. From the $(n'+1)$-th equation of $\mathbf{B}\,\mathbf{X} = \lambda_1(H_1)\,\mathbf{X}$, we get

$$\lambda_1(H_1) \cdot 0 = e \cdot x_{n'} \quad (e = 1 \text{ or } 2 \text{ or } 3)$$

implying that $x_{n'} = 0$, Then, however, $\mathbf{X}' = (x_1, x_2, \ldots, x_{n'}, 0)^t$ would be the eigenvector corresponding to $\lambda_1(\mathbf{B})$, a contradiction. Thus $\lambda_1(H^*) > \lambda_1(H')$.

By symmetry, we also get $\lambda_1(H^*) > \lambda_1(H'')$. □

Theorem 4.9 can be extended to the case when the concatenation involves more than one edge (as in the example $H_7 \cup H_8 \Rightarrow H_{10}$ in Fig. 7). Without proof we state:

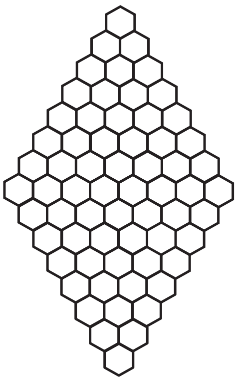
Theorem 4.10. *If H^* is obtained from H' and H'' by identifying k edges of H' with k edges of H'', $k \geq 1$, then*

$$\lambda_1(H^*) > \lambda_1(H') \quad \textit{and} \quad \lambda_1(H^*) > \lambda_1(H'') \ .$$

5 He matrices with integral spectrum

If all the eigenvalues of the He matrix are integers, then its spectrum is said to be integral.

Let H_{11} be the hexagonal systems depicted in Fig. 8. Using Mathematica, we have computed the spectral radius of $\mathbf{A}(H_{11})$ which turns out to be approximately equal to 11.19. So we conclude that the He matrices of all hexagonal systems H which are supergraphs of H_{11}, do not have integral spectrum because, by Theorem 4.2 and Lemma 3.4, $11 < \lambda_1(\mathbf{A}(H)) < 12$.



H_{11}

Fig. 8. A hexagonal system whose He matrix has spectral radius 11.19.

Let H_{12} be the hexagonal system with two hexagons (the "naphthalene graph"), see Fig. 9. The spectrum of its He matrix is either $\{-1, 1\}$ or $\{-2, 2\}$ or $\{-3, 3\}$, depending on the way in which H_{12} is drawn. Thus the spectrum of $\mathbf{A}(H_{12})$ is integral.

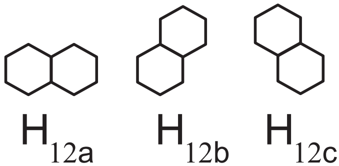


Fig. 9. A hexagonal system whose He matrix has integral spectrum. For the orientations H_{12a}, H_{12b}, and H_{12c}, the spectra of $\mathbf{A}(H_{12})$ are $\{-1,1\}$, $\{-2,2\}$, and $\{-3,3\}$, respectively.

From these observations and after studying many hexagonal systems, we are inclined to state:

Conjecture 1. H_{12} is the only hexagonal system whose He matrix has integral spectrum.

6 Energy of He matrix

The energy of the graph G whose eigenvalues are $\lambda_1, \lambda_2, \ldots, \lambda_n$ is defined as

$$E(G) = \sum_{i=1}^{n} |\lambda_i(G)| \ . \tag{10}$$

This quantity has long known chemical applications and has recently attracted much attention of mathematicians; for chemical and mathematical details see the surveys [20, 23] and [22, 27], respectively; for some recent work on graph energy see [1, 32, 38, 43, 45, 49, 52, 53].

Our intention is to conceive a graph–energy–like quantity, that instead of Eq. (10) would be defined in terms of the eigenvalues of the He matrix. Evidently, if H is a hexagonal system and $\mathbf{A}(H)$ is its He matrix, this "He energy" would be

$$HEE(H) = \sum_{i=1}^{n} |\lambda_i(\mathbf{A}(H))| \ .$$

As explained above, the numerical value of $HEE(H)$ depends on the way in which the hexagonal system H is drawn. Thus, in the general case, a hexagonal system has 6 distinct HEE-values (or 3, 2, 1 in case of symmetry). We are therefore interested in such properties of HEE which are independent of the orientation of the underlying hexagonal system.

Theorem 6.1. *Let H be a hexagonal system with n hexagons. Then the He energy satisfies*

$$HEE(H) \geq \frac{4M_e}{n}$$

where $M_e = \sum\limits_{i\sim j} a_{ij}\,, a_{ij} = 0,\ 1,\ 2,\ or\ 3.$

Proof: We first observe that $HEE(H) \geq 2\,\lambda_1(H)$ with equality holding if and only if $\mathbf{A}(H)$ has at most one positive eigenvalue. By Lemma 4.8, we get the required result.

$\square$

Theorem 6.2. *Let H be a hexagonal system with n hexagons. Then the He energy satisfies*

$$HEE(G) \leq \frac{2M_e}{n} + \sqrt{(n-1)\left(W - \frac{4M_e^2}{n^2}\right)}$$

where, $W = \sum\limits_{i=1}^{n}\sum\limits_{j=1}^{n} a_{ij}^2$ *and* $M_e = \sum\limits_{i\sim j} a_{ij}\,.$

Proof: We just have to emulate Koolen–Moulton's proof [37] of an analogous result for graph energy. $\square$

Using the same notation as in Theorem 4.9, we have:

Theorem 6.3. *If H^* is obtained from H' and H'' by identifying k edges of H' with k edges of H'', $k \geq 1$, then*

$$HEE(H^*) \geq HEE(H') \quad and \quad HEE(H^*) \geq HEE(H'')\ .$$

Proof: We first note that

$$\mathbf{A}(H^*) = \left[\begin{array}{c|c} \mathbf{A}(H') & * \\ \hline * & \mathbf{A}(H'') \end{array}\right]$$

Let $\lambda_i(\mathbf{A}(H_1))$, $i = 1, 2, \ldots, p$, be the positive eigenvalues of $\mathbf{A}(G')$. By Lemma 3.4,

$$\lambda_i(\mathbf{A}(H^*)) \geq \lambda_i(\mathbf{A}(H'))\ ,\ i = 1, 2, \ldots, p\ . \tag{11}$$

Again by Lemma 3.4,

$$\lambda_{n''+i}(\mathbf{A}(H^*)) \leq \lambda_i(\mathbf{A}(H')) \leq 0 \ , \ i = p+1, p+2, \ldots, n'-1, n'$$

i. e.,

$$|\lambda_{n''+i}(\mathbf{A}(H^*))| \geq |\lambda_i(\mathbf{A}(H'))| \ , \ i = p+1, p+2, \ldots, n'-1, n' \ . \tag{12}$$

Thus we have

$$\begin{aligned}
HEE(H^*) &= \sum_{i=1}^{n^*} |\lambda_i(\mathbf{A}(H^*))| \\
&= \sum_{i=1}^{p} |\lambda_i(\mathbf{A}(H^*))| + \sum_{i=p+1}^{n''+p} |\lambda_i(A(H^*))| + \sum_{i=n''+p+1}^{n^*} |\lambda_i(\mathbf{A}(H^*))| \\
&\geq \sum_{i=1}^{p} |\lambda_i(\mathbf{A}(H'))| + 0 + \sum_{i=p+1}^{n'} |\lambda_i(\mathbf{A}(H'))| \quad \text{by (11) and (12)} \\
&= \sum_{i=1}^{n'} |\lambda_i(\mathbf{A}(H')| = HEE(H') \ .
\end{aligned}$$

The proof of $HEE(H) \geq HEE(H'')$ is fully analogous. Hence the theorem follows. □

Acknowledgement. K. Ch. D. and S.-G. L. thank for support by Sungkyunkwan University BK21 Project, BK21 Math Modeling HRD Div. Sungkyunkwan University, Suwon, Republic of Korea. F. M. B. wishes to thank the Department of Mathematics, BK21 project, Sungkyunkwan University for their kind hospitality; also LUMS for travel grant. The work is completed during the visit of F. M. Bhatti as a Visiting Professor at SKKU in August 2009. I. G. thanks for support by the Serbian Ministry of Science (Grant No. 144015G).

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