MATCH
Communications in Mathematical and in Computer Chemistry

MATCH Commun. Math. Comput. Chem. **56** (2006) 113-129

ISSN 0340 - 6253

MOMENTS AND π-ELECTRON ENERGY OF HEXAGONAL SYSTEMS IN 3-SPACE

J. A. de la Peña[1] and L. Mendoza[2]

[1] Instituto de Matemáticas, UNAM. Cd. Universitaria, México 04510 D.F.
e-mail: jap@matem.unam.mx Correspondent author.

[2] Departamento de Matemáticas, Facultad de Ciencias, Univ. de los Andes, Mérida, Venezuela.
e-mail: lmendoza@ula.ve

(Received December 15, 2005)

Abstract

Let G be a finite hexagonal system with boundary embedded in the 3-dimensional space. We consider the dependence of the spectral moments $M_k(G)$ and the total π-electron energy $E_\pi(G)$ on the molecular structure of G. Our formulas involve the classical structural invariants of G and the rank of the fundamental group $\pi_1(G)$, which is a (non-abelian) free group. Our results generalize the benzenoid formulas (where $\pi_1(G) = 0$).

A *hexagonal system* is a finite connected graph, in the 3-dimensional space, with all edges lying on regular hexagons. Hexagonal systems have been extensevely studied as natural representations of benzenoid hydrocarbons, in case the system is planar, (see for example [6, 5]); the recent development of nanotechnology requires the consideration of tubes, cones and other spacial structures (see [11]), and more interesting from the mathematical point of view, the synthesis of new hydrocarbons including knotted rings and linked rings (catananes), Möbius strips and other topologicaly relevant structures is a booming field [4, 14, 15].

In the Hückel theory the total π*-electron energy* of a bipartite graph G is defined as the sum $E_\pi(G) = \sum_{i=1}^{n} |\lambda_i|$ of the absolute values of the eigenvalues $\lambda_1 \leq \lambda_2 \leq \cdots \leq \lambda_n$ of the adjacency matrix $A(G)$ of G. This energy is in good correlation with the observed heats of formation of the corresponding conjugated hydrocarbons and it is related with other chemical invariants [6, 5].

The k-th *spectral moment* of G is defined as $M_k(G) = \sum_{i=1}^{n} \lambda_i^k$, for k even. Since the pioneering work of Hall [9], spectral moments found multiple applications in quantum chemistry, solid state physical chemistry, the calculation of π-electron energy (see for example [5, 7, 16, 17, 8]). A problem considered in detail is the dependence of $M_k(G)$

and $E_\pi(G)$ on the molecular structure of G. This dependence was resolved for $k \leq 12$ in any benzenoid system. Not much seems to be known for other types of hexagonal systems.

Let G be a hexagonal system with boundary in the 3-dimensional space. Recently, we introduced the consideration of the *fundamental group* $\pi_1(G)$ of G which is a free (non-abelian) group of rank $\mathrm{rk}\,(G)$, [2, 3]. If $\mathrm{rk}\,(G) = 0$, the system G is planar and hence G represents a benzenoid hydrocarbon. For $\mathrm{rk}\,(G) > 0$, we shall provide expressions for $M_k(G)$, $k = 2, 4, 6, 8$, depending on the structure of G. In particular, showing that

$$\mathrm{rk}\,(G) = \frac{1}{12}(M_4(G) - 3M_2(G)) - h(G) + 1,$$

where $h(G)$ denotes the number of hexagons in the system G. Our formulas generalize the equations obtained in [16, 17, 18].

We shall consider the problem of evaluation of $E_\pi(G)$ for hexagonal systems G with $\mathrm{rk}\,(G) > 0$. Among other things, we prove that the bounds

$$\left(\frac{16}{27}\right)^{1/2} \sqrt{2n(G)m(G)} \;\leq\; 2\sqrt{2}m(G)\sqrt{\frac{m(G)}{M_4(G)}} \;\leq\; E_\pi(G) \;\leq\; \sqrt{2n(G)m(G)}$$

given by McClelland [12] and the authors [1] in the benzenoid case, still hold for our more general setting, where $n(G)$ (resp. $m(G)$) denotes the number of vertices (resp. of edges) of G.

Moreover, we consider the approximation of $E_\pi(G)$ by the truncated expansions $E_\pi(L) = \sum_{q=0}^{L} \alpha_{2q} M_{2q}(G) - \alpha_0 \sigma(L)$, where $\sigma(L)$ is the number of zero eigenvalues of $A(G)$, as calculated in [17]. We shall give explicit expressions for $E_\pi(L)$, $L = 0, 1, 2, 3, 4$, for (regular) hexagonal systems, generalizing known formulas (3.2).

According to Hückel theory $E_\pi(G)$ measures the energy in the local bonds between neighbouring carbons, but examples show (section 3) that spectral moments and energy may be 'blind' with respect to the global structure of G. In forthcoming work we shall propose the introduction of the *interlacing energy* which depends on the knot structure of the valued graph (Δ_G, v_G) associated to G according to [3].

1. Spacial hexagonal systems: structure and invariants.

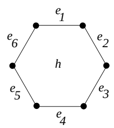
1.1. A *hexagonal system* $G = (G_0, G_1, \mathcal{H}(G))$ is given by a set of vertices G_0, a set of edges $G_1 \subset G_0^2$ and a set $\mathcal{H}(G) \subset G_1^6$ of hexagons, satisfying:

(H1) each edge $e = \{x, y\} \in G_0^2$, satisfies $x \neq y$ and belongs to a hexagon (that is, there is $e' \in G_1^5$ with $(e, e') \in \mathcal{H}(G)$);

(H2) each vertex $x \in G_0$, belongs to at most 3 edges in G (that is, the *degree* $d(x) \leq 3$);

(H3) each hexagon $\{e_1, e_2, \dots, e_6\}$ is formed by pairwise different edges with $e_i \cap e_{i+1}$ a single vertex, for $i = 1, \dots, 6$ and $e_7 = e_1$. Moreover, two hexagons have at most one edge in common.

For a sextuple $e_i = \{x_i, x_{i+1}\} \in G_0^2$, $1 \leq i \leq 6$ and $x_1 = x_7$, in case $h = \{e_1, e_2, \dots, e_6\} \in \mathcal{H}(G)$ we draw the picture:



We denote by $n(G)$ (resp. $m(G), h(G)$) the number of vertices (resp. edges, hexagons) of the system G.

1.2. Let $G = (G_0, G_1, \mathcal{H}(G))$ be as above. Fix (s, t) an orientation of the edges of G, that is, $e = \{x, y\} = \{s(e), t(e)\}$ and write an arrow $s(t) \xrightarrow{e} t(e)$ and its inverse $t(e) \xrightarrow{e^{-1}} s(e)$.

Recall from [2] the definition of the *fundamental group* $\pi_1(G)$:

Fix a vertex $x_0 \in G_0$. Consider the group $W(G, x_0)$ of all closed walks in G starting and ending at x_0 (the trivial walk τ_{x_0} is the identity). Define a *homotopy relation* $\sim$ in $W(G, x_0)$ induced by:

(a) If $e = \{x, y\} \in G_1$, then $ee^{-1} \sim \tau_{t(e)}$ and $e^{-1}e \sim \tau_{t(e)}$;

(b) If $\{e_1, \dots, e_6\} \in \mathcal{H}(G)$, choose $\varepsilon_i \in \{1, -1\}$ such that $e_1^{\varepsilon_1} \dots e_6^{\varepsilon_6}$ is an oriented path, then

$$e_i^{\varepsilon_i} e_{i+1}^{\varepsilon_{i+1}} \dots e_6^{\varepsilon_6} e_1^{\varepsilon_1} \dots e_{i-1}^{\varepsilon_{i-1}} \sim \tau_{x_i} \text{ with } x_i \in \{s(e_i), t(e_i)\};$$

(c) If $u \sim v$, then $wuw' \sim wvw'$, whenever the products make sense.

We set $\pi_1(G, x_0) = W(G, x_0)/\sim$ which inherits the group structure of $W(G, x_0)$ and does not depend on the choice of x_0. Hence $\pi_1(G) = \pi_1(G, x_0)$.

Theorem [2, 3] *Let G be a hexagonal system with boundary. The following holds:*

a) *there is a graph $\Delta_G \hookrightarrow \mathbb{R}^3$ such that $\pi_1(G) = \pi_1(\Delta_G)$ and $\pi_1(G)$ is therefore a free (non-abelian) group with rank* $\mathrm{rk}\,(G) = m(G) - h(G) - n(G) + 1$*;*

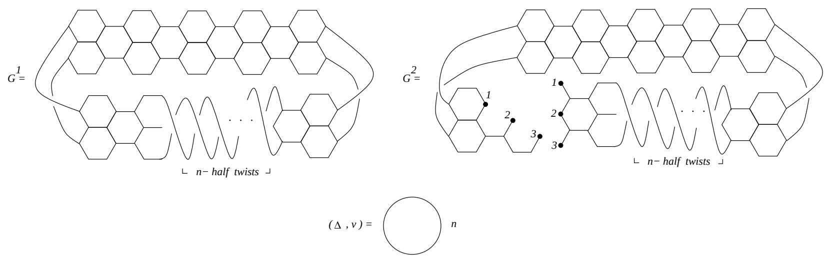
b) *the graph Δ_G is 3-regular with $2(\mathrm{rk}\,(G) - 1)$ vertices;*

c) *there are knot configurations $G_1, \ldots, G_s$ (with $s = \mathrm{rk}\,(G)$) induced by full subgraphs of G, such that, choosing c^i a closed walk in the boundary of G_i ($1 \leq i \leq s$) we get a system of generators of $\pi_1(G)$;*

d) *the valuation $v_G(c_i) = m_i$ counts the number of half-twists of G_i.*

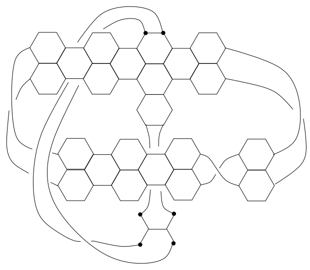
1.3. *Examples:*

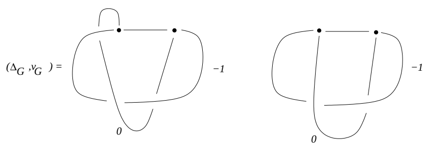
(1) The following hexagonal systems:



are called *n-conic configurations.* If the twists are in the opposite direction, we called them $(-n)$-conic configurations. The associated graph with valuation is (Δ, v) in both cases.

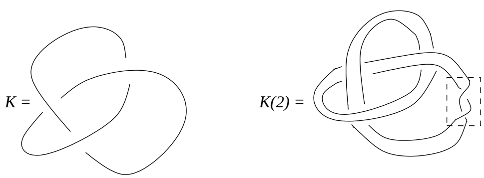
(2)

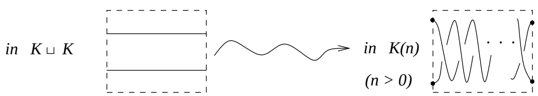




The graph $\Delta_G \hookrightarrow \mathbb{R}^3$ can be transformed in the second graph via Reidemeister moves [19]. We say that Δ_G is a knotted graph.

(3) Given any knot K and a number $n \in \mathbb{Z}$, we consider the link $K(n)$ formed as in the following example for the trifoil knot and $n = 2$:

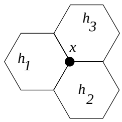




That is, in the link formed by two copies of K, an interval $[0,1]\coprod[0,1]$, as the enclosed in the dotted square, is substituted by the link with n half-twists. The crossings are the opposites if $n < 0$. The CW-complex associated to $K(n)$, denoted by $cw(K(n))$, is defined in the obvious way.

Any hexagonal system G whose associated CW-complex $cw(G)$ is homeomorphic to $cw(K(n))$ for a link $K(n)$ is called a *knot configuration* (of type n). Examples (2) and (3) are particular instances of knot configurations.

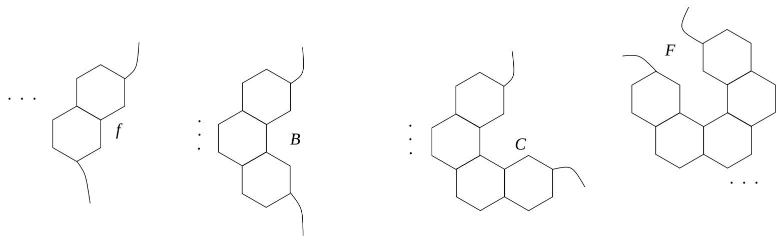
1.4. We shall consider a hexagonal system $G = (G_0, G_1, \mathcal{H}(G))$ with boundary. We say that $x \in G_0$ is an *interior vertex* if there are edges $a_i = \{x, y_i\}$ belonging to hexagons h_i, $i = 1, 2, 3$, as in the picture



We denote by $i(G)$ the number of interior vertices of G. We say that G is a *cata-condensed system* if $i(G) = 0$. For rk$\,(G) = 0$ and $i(G) = 0$, we get a *catacondensed benzenoid* G and the following well-known formulae hold:

$$\begin{aligned} n(G) &= 4h(G) + 2, \quad m(G) = 5h(G) + 1, \\ M_2(G) &= 10h(G) + 2, \quad M_4(G) = 42h(G) - 6, \quad M_6(G) = 214h(G) - 82 + 6b, \end{aligned}$$

where the invariant $b = B(G) + 2C(G) + 3F(G)$ counts (in a weighted form) the number of *bay regions* of G: B (bays), C (coves) and F (fjords) defined as in the picture where f is the number of *fissures*.



For benzenoid systems (that is rk$\,(G) = 0$), the following holds [5]:

$$M_2(G) = 2m(G),\ M_4(G) = 18m(G) - 12n(G),\ M_6(G) = 158m(G) - 144n(G) + 48 + 6b$$

Observe that a fissure is determined by a sequence of vertices (x_1, x_2, x_3) on the boundary with degrees $(2,3,2)$, similarly $B(G)$ (resp $C(G)$, $F(G)$) is the number of sequences of vertices on the boundary with degrees $(2,3,3,2)$ (resp $(2,3,3,3,2)$, $(2,3,3,3,3,2)$). For a general hexagonal system G we shall define $B_s(G)$ the number of *generalized bay regions* of type $(2,3,3,\ldots,3,3,2)$ determined by sequences of $s+2$ vertices on the boundary, s of those of degree 3. In particular $B_1(G) = f(G)$, $B_2(G) = B(G)$, etc. We shall consider the invariant $t(G) = \sum_{s\geq 1} B_s(G)$.

Lemma. *Let G be a hexagonal system with boundary and denote*

$$m_{ij}(G) = |\{e = \{x,y\} \in G_1 \colon d(x) = i \text{ and } d(y) = j\}|.$$

Then the following hods:

$$\begin{aligned} m_{22}(G) &= n(G) - 2h(G) + 2(1 - \mathrm{rk}\,(G)) - t(G), \\ m_{23}(G) &= 2t(G), \\ m_{33}(G) &= 3h(G) - 3(1 - \mathrm{rk}\,(G)) - t(G). \end{aligned}$$

Proof: By definition of the bay regions, we have $m_{23}(G) = 2t(G)$.

By [3, (1.5)], $n_3(G) = 2[h(G) - (1 - \mathrm{rk}\,(G))]$. Since $3n_3(G) = m_{23}(G) + 2m_{33}(G)$, we get the expression for m_{33}. Finally, using that $m_{22}(G) + m_{23}(G) + m_{33}(G) = m(G)$ and by (1.2.a), $m(G) = h(G) + n(G) - (1 - \mathrm{rk}\,(G))$, we get the equation for $m_{22}(G)$. $\square$

Relations between m_{ijk} and structural properties of G can be found in [13].

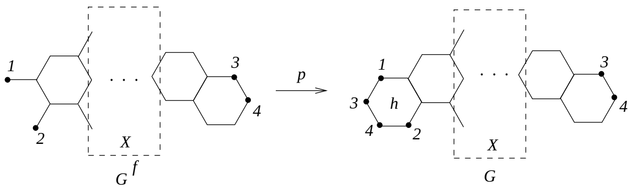
1.5. Proposition. *Let G be a hexagonal system with boundary. The following holds:*

(1) $$n(G) + i(G) = 4h(G) + 2(1 - \mathrm{rk}\,(G))$$

(2) $$m(G) + i(G) = 5h(G) + (1 - \mathrm{rk}\,(G)).$$

Proof: By induction on $i(G)$. Assume $i(G) = 0$, then every hexagon $h \in \mathcal{H}(G)$ has an edge on the boundary. We proceed by induction on $\mathrm{rk}\,(G)$. The case $\mathrm{rk}\,(G) = 0$, yields a catacondensed benzenoid system and the result follows from (1.4).

Suppose $s := \mathrm{rk}\,(G) > 0$, then there exists a covering $p \colon K \to G$ determined by the action of $\mathbb{Z}$. We may choose a fundamental domain G^f in K as in [3, (2.1)], to



get the situation depicted in the diagram. Completing G^f to a hexagonal system $\bar{G}$ we have

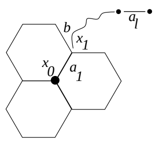
$$n(\bar{G}) = n(G) + 2,\ m(\bar{G}) = m(G) + 1,\ h(\bar{G}) = h(G) \text{ and } \mathrm{rk}\,(\bar{G}) = \mathrm{rk}\,(G) - 1.$$

Moreover, by induction hypothesis,

$$n(\bar{G}) = 4h(\bar{G}) + 2(1 - \mathrm{rk}\,(\bar{G})) \text{ and } m(\bar{G}) = 5h(\bar{G}) + (1 - \mathrm{rk}\,(\bar{G})),$$

and a substitution yields the result in this case.

Assume $i(G) > 0$. We claim that there is a hexagon h with an edge $e = \{x, y\}$ and a vertex z such that e lies on the boundary and z is a interior vertex. Indeed, for each interior vertex x, let $\ell(x)$ be the length of a minimal walk $x = x_0 \xrightarrow{a_1} x_1 \longrightarrow \cdots \xrightarrow{a_\ell} x_\ell$ with a_ℓ an edge on the boundary. Let x_0 be an interior vertex with minimal $\ell(x_0)$ $(=: \ell)$ and let $x = x_0 \xrightarrow{a_1} x_1 \longrightarrow \cdots \xrightarrow{a_\ell} x_\ell$ be such that a_ℓ is on the boundary.



Since $\ell(x_1) < \ell(x_0)$, then x_1 is not an interior vertex. Then b is an edge on the boundary.

Define now the hexagonal system G' formed by deleting those edges of h on the boundary (with the corresponding vertices). Then

$$n(G') = n(G) - j,\ m(G') = m(G) - (j+1),\ h(G') = h(G) - 1 \text{ and } \mathrm{rk}\,(G') = \mathrm{rk}\,(G),$$

for some $1 \leq j \leq 3$. Moreover, $i(G') = i(G) - (4-j)$. The induction hypothesis implies the result. □

Corollary. [2, (2.3)] *Let G be a hexagonal system with boundary. Then*

$$\mathrm{rk}\,(G) = m(G) - h(G) - n(G) + 1.$$

□

2. Moments.

2.1. Let $A = (a_{ij})$ be the $(n \times n)$ *adjacency matrix* of (G_0, G_1). Observe that $d(i) = \sum_{j=1}^{n} a_{ij}$ is the degree of a vertex i and $w(i) = \sum_{j=1}^{n} a_{ij} d(j)$ is called the *weight* of i.

Let $A^k = (a_{ij}^{(k)})$ be the k-th power of A. Then

$$M_k(G) = \mathrm{tr}\,(A^k) = \sum_{i=1}^{n} a_{ii}^{(k)}$$

Proposition.

(a) $M_2(G) = 2m(G)$;

(b) $M_4(G) = 6n_2(G) + 15n_3(G)$, *where* $n_k(G) = |\{i \in G_0 \colon d(i) = k\}|$;

(c) $M_4(G) = 18m(G) - 12n(G)$.

(d) $M_4(G) = 42h(G) + 6(\mathrm{rk}\,(G) - 1) - 6i(G)$.

Proof: (a): $M_2(G) = \sum_{i=1}^{n} a_{ii}^{(2)} = \sum_{i=1}^{n} d(i) = 2m(G)$;

(b): $a_{ii}^{(4)} = d(i)^2 + \sum_{j=1}^{n} a_{ij}(d(j) - 1) = d(i)^2 + w(i) - d(i)$. Then

$$M_4(G) = \sum_{i=1}^{n} a_{ii}^{(4)} = \sum_{i=1}^{n} (d(i)^2 - d(i)) + \sum_{i=1}^{n} w(i) = \sum_{i=1}^{n} [2d(i)^2 - d(i)].$$

The last equality due to $\sum\limits_{i=1}^{n} w(i) = \sum\limits_{i,j,k} a_{ij}a_{jk} = \sum\limits_{j} \left(\sum\limits_{i,k} a_{ji}a_{jk} \right) = \sum\limits_{j} d(j)^2$.

Finally, $M_4(G) = \sum\limits_{d(i)=2} [2d(i)^2 - d(i)] + \sum\limits_{d(i)=3} [2d(i)^2 - d(i)] = 6n_2(G) + 15n_3(G)$.

(c): Observe that $n(G) = n_2(G) + n_3(G)$ and $2m(G) = 2n_2(G) + 3n_3(G)$. The claim follows from (b). (d) follows directly from (1.2.a) and (c). $\square$

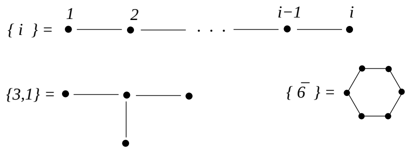
2.2. Proposition. *Let G be a hexagonal system with boundary such that every hamiltonian cycle $x_0 \xrightarrow{a_1} x_1 \xrightarrow{a_2} \cdots \xrightarrow{a_6} x_7 = x_0$ in G ($x_i \neq x_j$ for $i,j = 1,2,\ldots,7$) defines a hexagon in $\mathcal{H}(G)$. Then the following holds:*

$$M_6(G) = 146m(G) - 126n(G) + 12(1 - \mathrm{rk}\,(G)) - 6t(G).$$

Proof: We proceed as in [18], showing that

$$M_6(G) = 2N_{\{2\}} + 12N_{\{3\}} + 6N_{\{4\}} + 12N_{\{3,1\}} + 12N_{\{\bar{6}\}},$$

where N_Δ denotes the number of full subgraphs in G isomorphic to Δ and



In [18], it is also shown $N_{\{2\}} = m(G)$, $N_{\{3\}} = 4m(G) - 3n(G)$, $N_{\{3,1\}} = 2m(G) - 2n(G)$ and $N_{\{\bar{6}\}} = h(G)$ by hypothesis.

To prove the equation, we shall estimate $N_{\{4\}}$. Namely, a full embedding u of $1 \;\text{——}\; 2 \xrightarrow{\alpha} 3 \;\text{——}\; 4$ in G is of one of the following types:

(i) $d(u(2)) = d(u(3)) = 2$, then $u(\alpha)$ is of type m_{22} and this happens exactly once for every edge of type m_{22};

(ii) $d(u(2)) = 2$ and $d(u(3)) = 3$ (or symmetrically), then $u(\alpha)$ is of type m_{23} and this happens in exactly 2 different ways for every edge of type m_{23};

(iii) $d(u(2)) = 3 = d(u(3))$, then $u(\alpha)$ is of type m_{33}. This happens in exactly 4 different ways for every edge of type m_{33}. Suming up:

$$N_{\{4\}} = m_{22}(G) + 2m_{23}(G) + 4m_{33}(G) = n(G) + 10h(G) - 10(1 - \mathrm{rk}\,(G)) - t(G)$$

Substituting this value of $N_{\{4\}}$ in the first identity for $M_6(G)$ and using (1.4), we get our equation. $\square$

We shall say that a hexagonal system G with boundary such that every closed walk of length 6 defines a hexagon in $\mathcal{H}(G)$ is a *regular system.*

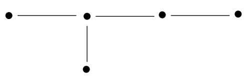
2.3. For the consideration of the moment $M_8(G)$ we introduce the following notation:

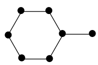
$$m_{ijk}(G) = |\{(e, e') \in G_1^2 \colon e = \{x, y\}, e' = \{y, z\} \text{ and } d(x) = i, d(y) = j, d(z) = k\}|.$$

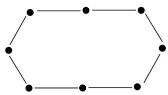
According to the method presented in [18], the moment $M_8(G)$ can be calculated counting the number of certain subgraphs in the following way:

$$\begin{aligned} M_8(G) = \;& 2N_{\{2\}} + 28N_{\{3\}} + 32N_{\{4\}} + 72N_{\{3,1\}} + 8N_{\{5\}} \\ & + 16N_{\{4,1\}} + 96N_{\{\bar{6}\}} + 16N_{\{\bar{6},1\}} + 16N_{\{\bar{8}\}}, \end{aligned}$$

where the graphs $\{4, 1\}$, $\{\bar{6}, 1\}$ and $\{\bar{8}\}$ are as follows:

{4,1} = 

{$\bar{6}$, 1 }= 

{ $\bar{8}$ } = 

Observe that for $\mathrm{rk}\,(G) = 0$, as noted in [18], $N_{\{\bar{8}\}} = 0$. In case $\mathrm{rk}\,(G) > 0$, the formula in [18] already takes into account all tree subgraphs of G and only the cyclic subgraphs have to be additionally considered. It is interesting to note that a full subgraph C of G of type $\{\bar{8}\}$ is a hamiltonian cycle which yields a non trivial element $1 \neq [C] \in \pi_1(G)$.

Proposition. *Let G be a regular hexagonal system with boundary. Then the following holds:*

$$\begin{aligned} M_8(G) = \;& 1186m(G) - 1140n(G) + 192(1 - \mathrm{rk}\,(G)) - 96t(G) \\ & + 8f(G) + 8m_{222}(G) + 16N_{\{\bar{8}\}}(G). \end{aligned}$$

Proof: We estimate the different N_Δ (omitting the reference to G):

- $N_{\{5\}} = m_{222} + 2m_{223} + 2m_{233} + m_{232} + 4m_{323} + 4m_{333}$.

  Moreover $m_{223} = 2(m_{22} - m_{222})$; $m_{233} = 4t - 2f$; $m_{232} = f$; $2m_{333} = 4m_{33} - m_{233}$.

  Also, $3m_{23} = 2(m_{323} + m_{232}) + m_{223} + m_{233}$ and $m_{323} = 2h - n - 2(1 - \mathrm{rk}\,(G)) + 2t + m_{222}$.

  This yields: $N_{\{5\}} = 24h - 24(1 - \mathrm{rk}\,(G)) - 4t + f + m_{222}$.

- $N_{\{4,1\}} = m_{23} + 4m_{33} = 12h - 12(1 - \mathrm{rk}\,(G)) - 2t$.

- $N_{\{\bar{6},1\}} = 6h - m_{222} - m_{223} - m_{323} = 8h - n - 2(1 - \mathrm{rk}\,(G))$.

  Suming up the above equatities and using (1.2) and (2.2), we get the value of $M_8(G)$. □

Remark: The expression for $M_6(G)$ and $M_8(G)$ generalize the previous results for benzenoid hydrocarbons, [17, 18]. Our formulas use parameters slightly different than [18], and therefore yield new formulas for benzenoid cases when $\mathrm{rk}\,(G) = 0$.

3. Energy of a hexagonal system with boundary.

3.1. One of the applications of spectral moments has been the approximated calculation of the total π-energy $E_\pi(G)$ of a benzenoid hydrocarbon system G. In [1], we introduced some simple arithmetic inequalities which yield lower bounds for $E_\pi(G)$. These bounds hold 'mutatis mutandis' for general hexagonal systems.

Proposition. *Let G be a hexagonal system, then the following hold:*

a) *If q, t, s are positive integers, q even and $4q = t + s + 2$, then*

$$M_q^2 (M_t M_s)^{-1/2} \leq E_\pi(G)$$

b) *In particular, for $(2, 2, 4)$ and $(4, 6, 8)$, we get:*

$$2\sqrt{2}m\sqrt{\frac{m}{M_4}} \leq E_\pi(G) \text{ and } \frac{M_4^2}{\sqrt{M_6 M_8}} \leq E_\pi(G)$$

c) $(16/27)^{1/2}\sqrt{2nm} \leq E_\pi(G)$. □

The inequality (c) was first proved by McClelland [12] for benzenoid hydrocarbons.

3.2. In [17], a method to linearly approximate $E_\pi(G)$ by spectral moments was given. Truncated expansions $E_\pi(L)$ are defined, which converge to $E_\pi(G)$ as $L \to \infty$, with the form

$$E_\pi(L) = \sum_{q=0}^{L} \alpha_{2q} M_{2q}(G) - \alpha_0 \sigma(G),$$

where $\sigma(G)$ is the number of zero eigenvalues of $A(G)$ and

$$\alpha_0 = \frac{1}{\pi}\frac{6}{2L+1}\,, \quad \alpha_{2q} = (-1)^{q+1}\frac{1}{\pi}\frac{2^{2q+1}}{3^{2q-1}}\frac{(L+q)!}{(2L+1)(2q-1)(2q)!(L-q)!}$$

For a regular hexagonal system G and $L = 2, 3, 4$ the approximations are:

$$\begin{aligned} E_\pi(2) &= -0.02515041076 M_4 + 0.5092958178 M_2 + 0.3819718633 M_0 \\ &\quad -0.38197186\sigma(G) \end{aligned}$$

or

$$E_\pi(2) = 0.56588424m + 0.68377679n - 0.38197186\sigma(G).$$

For $L = 3$

$$\begin{aligned} E_\pi(3) &= 0.0047905544 M_6 - 0.0898228956 M_4 + 0.7275654545 M_2 \\ &\quad +0.2728370452 M_0 - 0.27283704\sigma(G) \end{aligned}$$

or

$$\begin{aligned} E_\pi(3) &= 0.53773973m + 0.747101193n + 0.057486653(1 - \mathrm{rk}\,(G)) \\ &\quad -0.028743326t - 0.27283704\sigma(G). \end{aligned}$$

For $L = 4$

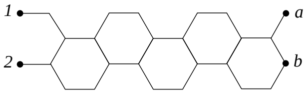
$$\begin{aligned} E_\pi(4) &= -0.0011828529 M_8 + 0.026081907 M_6 - 0.20958675 M_4 \\ &\quad +0.94314040 M_2 + 0.21220659 M_0 - 0.21220659\sigma(G) \end{aligned}$$

or

$$\begin{aligned} E_\pi(4) &= 0.5188140m + 0.7893796n + 0.08587512(1 - \mathrm{rk}\,(G)) - 0.04293756t \\ &\quad -0.0094628235(f + m_{222}) - 0.018925646 N_{\{\bar{8}\}} - 0.21220659\sigma(G). \end{aligned}$$

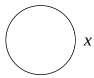
Which generalize the corresponding expression for benzenoid hydrocarbons given in [18]. In most instances, $E_\pi(4)$ is already a good approximation to $E_\pi(G)$ as the following examples confirm.

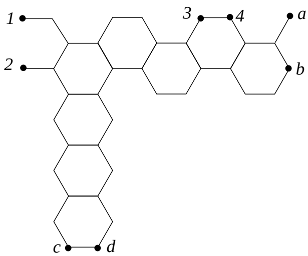
3.3. ***Examples:*** Consider the following regular hexagonal systems (obtained by identifying the vertices marked with the same numbers). We indicate the corresponding valued graph (Δ_G, v_G).



(I) a=1, b=2, x=0.

(II) a=2, b=1, x=1.

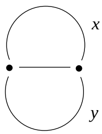


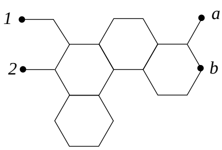


(III) a=1, b=2, c=3, d=4. x=0, y=0.

(IV) a=1, b=2, c=4, d=3. x=0, y=1.

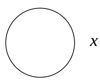
(V) a=2, b=1, c=4, d=3. x=1, y=1.





(VI) a=1, b=2. x=0.

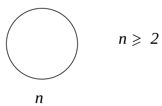
(VII) a=2, b=1. x=1.



	(I)	(II)	(III)	(IV)	(V)	(VI)	(VII)
$m(G)$	30	30	44	44	44	25	25
$n(G)$	24	24	34	34	34	20	20
$\sigma(G)$	0	0	0	0	0	0	0
$\mathrm{rk}\,(G)$	1	1	2	2	2	1	1
$t(G)$	6	7	10	10	11	4	5
$f(G)$	0	2	4	4	5	0	1
$m_{222}(G)$	0	0	0	0	0	2	2
$N_{\{\bar{8}\}}$	0	0	0	0	0	7	6
$M_4(G)$	252	252	384	384	384	210	210
$M_6(G)$	1320	1314	2068	2068	2062	1106	1100
$M_8(G)$	7644	7564	12304	12304	12216	6594	6490
$\sqrt{\frac{32nm}{27}}$	29.21	29.21	42.107	42.107	42.107	24.343	24.343
$2m\sqrt{\frac{2m}{M_4}}$	29.27	29.27	42.126	42.126	42.126	24.398	24.398
$E_\pi(2)$	33.387	33.387	48.147	48.147	48.147	27.823	27.823
$E_\pi(3)$	33.890	33.861	48.717	48.717	48.688	28.271	28.242
$E_\pi(4)$	34.252	34.190	49.114	49.114	49.061	28.435	28.401
$E_\pi(G)$	34.435	34.405	49.349	49.289	49.255	28.599	28.646

We observe that the parameters involved in $M_q(G)$, $0 \leq q \leq 8$ for the hexagonal systems (III) and (IV) are the same. In fact, $M_q(G_{\mathrm{III}}) = M_q(G_{\mathrm{IV}})$ for $0 \leq q \leq 12$ and only $M_{14}(G_{\mathrm{III}}) \neq M_{14}(G_{\mathrm{IV}})$.

More problematic is to consider hexagonal systems G_n obtained from the same underlying graph as (I) and (II) but with valued graph (Δ_G, v_G) given by



If n is even, then the adjacency matrix $A(G_n) = A(G_0)$ and all spectral moments $M_q(G_n) = M_q(G_0)$ and energy $E_\pi(G_n) = E_\pi(G_0)$. Similarly, if n is odd, $A(G_n) = A(G_1)$ and moments and energy coincide for G_n and G_1. This means that the spectral theory of graphs is 'blind' with respect to the global knot structure of the graphs. In a forthcoming paper we shall introduce the *interlacing energy* $E_i(G)$ of the system G, which takes into account the knot structure of the valued graph (Δ_G, v_G).

References

[1] J.A. de la Peña, L. Mendoza and J. Rada. *Comparing momenta and π-electron energy of benzenoid molecules.* Discrete Math. 302 (2005) 77–84.

[2] J.A. de la Peña and L. Mendoza. *The fundamental group of a hexagonal system in* 3*-space.* To appear.

[3] J.A. de la Peña and L. Mendoza. *The structure of hexagonal systems in* 3*-space.* To appear.

[4] C. Dietrich-Buchecker and J.P. Sauvage. *A synthetic molecular trefoil knot.* Angew. Chem. Int. Ed. Engl. 28 (1989) 189–192.

[5] I. Gutman. *Total π-electron energy of benzenoid hydrocarbons.* In Topics Curr. Chem. 162 (1992) 29–63.

[6] I. Gutman and O. Polanski. *Mathematical concepts in Organic Chemistry.* Springer, Berlin (1986).

[7] I. Gutman and V. Rosenfeld. *Spectral moments of polymer graphs.* Theor. Chim. Acta 93 (1996) 191–197.

[8] I. Gutman. The energy of a graph: Old and new results. In: A. Betten, A. Kohnert, R. Loue, A. Wassermann (Eds.), *Algebraic Combinatorics and Applications.* Springer-Verlag, Berlin (2001) 196–211.

[9] G.G. Hall. *The bond orders of alternant hydrocarbon molecules.* Proc. Roy. Soc. A 229 (1955): 251–259.

[10] G.G. Hall. *The evaluation of moments for polycyclic hydrocarbons.* Theor. Chim. Acta 70 (1986): 323–332.

[11] P.J.F. Harris. *Carbon Nanotubes and Related Structures. New materials for the Twenty-first Century.* Cambridge Univ. Press, Cambridge (1999).

[12] B.J. McClelland. *Properties of the latent roots of a matrix: The estimation of π-electron energies.* J. Chem. Phys 54 (1971): 640–643.

[13] J. Rada. *Second order Randic index of benzenoid systems.* Ars Combinatoria 72 (2004) 77–88.

[14] D. Walba, R. Richards and C. Haltiwanger. *Total synthesis of the first molecular Möbius band.* J. Am. Chem. Soc. 104 (1982) 3219–3221.

[15] E. Wasserman. *Chemical topology.* Sci. Am. 207 (1962) 94–100.

[16] Y. Yiang and A. Tang. *Evaluation of moments and their application in Hückel molecular orbital theory.* Theor. Chim. Acta 66 (1984) 183–192.

[17] Y. Yiang, H. Zhu, H. Zhang and I. Gutman. *Moment expansion of Hückel molecular energies.* Chem. Phys. Lett. 159 (1989) 159–164.

[18] Y. Yiang, X. Qian and Y. Shao. *The evaluation of momenta for benzenoid hydrocarbons.* Theor. Chim. Acta 90 (1995) 135–144.

[19] Y. Yokota. *Topological invariants of graphs in* 3*-space.* Topology 35 (1996) 77–87.