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On nut and core singular fullerenes

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Abstract

A graph G is singular of nullity $\eta(>0)$, if its adjacency matrix $\mathbf{A}$ is singular, with the eigenvalue zero of multiplicity η. A singular graph having a 0-eigenvector, $\mathbf{x}$, with no zero entries, is called a core graph. We place particular emphasis on nut graphs, namely the core graphs of nullity one. Through symmetry considerations of the automorphism group of the graph, we study relations among the entries of $\mathbf{x}$ which lead to interesting implications in chemistry. The zero eigenvalue is rare in a fullerene graph. We show that there are possible nut fullerenes with relatively simple structures.

MSC: 92E10; 05C25; 05C50; 05C90; 20F28

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1. Introduction

The graphs we consider are simple, i.e. without loops or multiple edges. A graph G is *singular* if its adjacency matrix $\mathbf{A}$ is singular. The dimension of the nullspace of $\mathbf{A}$, i.e. the number of linearly independent *kernel eigenvectors* $\mathbf{x}$ satisfying $\mathbf{Ax} = \mathbf{0}$, is the *nullity* η of $\mathbf{A}$ (and of G). Since $\mathbf{A}$ describes G completely up to isomorphism, we use terminology for G and $\mathbf{A}$ interchangeably.

A graph on n vertices is said to be of order n. The *valency* $\mathrm{val}(v)$ of a vertex v in a graph is the number of edges incident to v. Trivalent (cubic) polyhedra are 3-regular connected planar graphs. A fullerene is a trivalent polyhedral carbon cage, C_n, with 12 pentagonal and $(n/2 - 10)$ hexagonal faces. It is the purpose of this paper to study relations among the entries of a kernel eigenvector by focusing on the symmetries of the graph. Our motivation is to investigate singular fullerenes and singular cubic polyhedra. This yields immediate results concerning the electronic structure and predicted chemistry of molecules with these molecular graphs.

In Section 2, we discuss the relations among a core graph, a core with respect to a kernel eigenvector and a nut graph. The symmetries of a graph, considered in Section 3, help to deduce properties of the entries of kernel eigenvectors that

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in turn yield information on the structure of the graph. In Section 4, we investigate the structure of nut fullerenes. We conclude by discussing in Section 5 the chemical implications of these results.

2. Core graphs

If a graph G is singular, then there exists a kernel eigenvector $\mathbf{x} \in \mathbb{R}^n$, such that $\mathbf{Ax} = \mathbf{0}$. We direct our attention to the entries of $\mathbf{x}$.

Definition 2.1. A *core graph* is a singular graph having a kernel eigenvector with no zero entries.

Lemma 2.2. *Let G be a singular graph and $\mathbf{x}$ a kernel eigenvector of G. The subgraph induced in G by the vertices corresponding to the non-zero entries of $\mathbf{x}$ is a core graph.*

Proof. Without any loss of generality, we may label the vertices of G such that only the first s entries of $\mathbf{x} = (\mathbf{x}_s, \mathbf{0})$ are non-zero. If $\mathbf{A}_s$ is the principal $s \times s$ submatrix, then $\mathbf{A}_s\mathbf{x}_s = 0$ and the graph corresponding to $\mathbf{A}_s$ is a core graph. □

Definition 2.3. Let $\mathbf{x_0}$ be a kernel eigenvector of a singular graph G. A subgraph of G induced by the vertices corresponding to the s non-zero entries of $\mathbf{x}$ is said to be the K (*w.r.t* $\mathbf{x}$), where s is the number of vertices of the core graph, called the *core order*.

Thus a core graph is a singular graph of nullity at least one, having a core of order η. This also means that none of the graph angles for the nullspace is zero (see [5]). In general, the core is disconnected, in which case the nullity is necessarily more than one. In [7,8], the author has investigated the extent to which the core of a graph of nullity one extends through the graph. For $n \geqslant 7$, maximally extending core graphs of nullity one are shown to exist (see [9]).

Definition 2.4. A singular graph is said to be a *nut graph* if it is a core graph with nullity one.

Remark 2.5. For a nut graph, each entry of a kernel eigenvector is non-zero.

3. Symmetry considerations

Let the graph $G = G(\mathscr{V}, \mathscr{E})$ have vertex set $\mathscr{V}$ and edge set $\mathscr{E}$. The *automorphism group* $\Gamma(G)$ of a graph G is the group of permutations (symmetries) that act on $\mathscr{V}$ and preserve adjacencies. If $\mathbf{P}$ is a permutation matrix representing a permutation p and $\mathbf{A}$ is the adjacency matrix of G, then $\mathbf{A} = \mathbf{P}^t\mathbf{AP}$. Recall that for all $p \in \Gamma(G)$, $\{i, j\}$ is an edge of G if and only if $\{p(i), p(j)\}$ is also an edge.

Immediate consequences are that non-edges are sent to non-edges by $p \in \Gamma(G)$ and $\mathrm{val}(i) = \mathrm{val}(p(i))$.

Remark 3.1. The action of p on the set $\mathscr{V}$ of vertices of G is just a relabelling of $\mathscr{V}$ that leaves the overall structures intact. The automorphism group of K_n is the symmetric group S_n. In general, the automorphism group of an n-vertex graph is a subgroup of S_n.

Definition 3.2. Let Σ be a subgroup of $\Gamma(G)$. The images of a vertex i of G under the permutations of Σ are said to form the *orbit* Ω_i of i induced by Σ. Thus $\Omega_i = \{p(i) : p \in \Sigma\}$.

Remark 3.3. Here we consider the orbits induced by $\Gamma(G)$ itself. The orbits form a partition of the vertex set of G into subsets of *equivalent* vertices of the same valency and are easily determined by representing the permutations in $\Gamma(G)$ as a product of disjoint cycles.

Definition 3.4. A graph G is said to be (*vertex*) *transitive* if it has only one orbit; that is for all $i, j \in \mathscr{V}(G)$, there exists p in $\Gamma(G)$ such that $p(i) = j$.

It what follows non-transitive graphs are called multi-orbit.

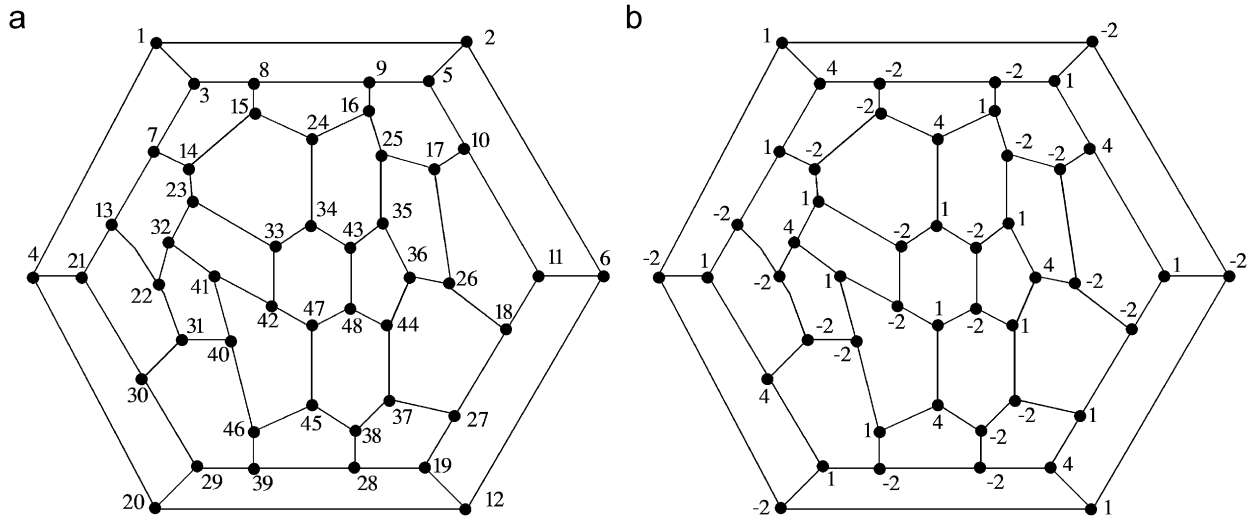

Fig. 1. The fullerene C_{48} : 169: vertex labelling and entries in the generating kernel eigenvector.

3.1. Orbit spectrum

Let G have n vertices and r orbits $Y_1, Y_2, \ldots, Y_d$. Let $\mathbf{X} = (x_{ij})$ be the $n \times d$ indicator matrix that partitions $\mathscr{V}$ into orbits, such that $x_{ij} = 1$ if vertex i lies in orbit Y_j. If $\mathbf{A}$ is the adjacency matrix of G, then $\mathbf{AX} = \mathbf{XQ}$, where $\mathbf{Q} = (q_{ij})$ is a $d \times d$ matrix and each $v \in Y_i$ has q_{ij} neighbours in Y_j. The matrix $\mathbf{Q}$ is the adjacency matrix of the quotient graph G/E; then E is said to be an *equitable* partition of the vertices into orbits and $\mathbf{Q}$ corresponds to a directed graph where q_{ij} arcs go from orbit i to orbit j.

Proposition 3.5. *Eigenvalues of the orbit–orbit matrix* $\mathbf{Q}$ *are also eigenvalues of* G.

Proof. Let $\mathbf{y}$ be an eigenvector of $\mathbf{Q}$ corresponding to eigenvalue λ. Then

$$\mathbf{Qy} = \lambda\mathbf{y} \Longrightarrow \mathbf{AXx} = \mathbf{XQx} = \lambda\mathbf{Xx}.$$

Hence λ is an eigenvalue of $\mathbf{A}$ with at least the same multiplicity as for $\mathbf{Q}$ since the columns of $\mathbf{X}$ are linearly independent. □

Definition 3.6. A cubic polyhedron is a *balanced nut graph* if it is a nut graph in which all the entries of a kernel eigenvector are of the form $(-2)^r$, $r \in \mathbb{Z}^+ \cup \{0\}$. In addition, a balanced nut graph is said to be *a uniform nut graph* if the entries of a kernel eigenvector are in $\{1, -2\}$. Then the graph is said to have a $(1, 1, -2)$-kernel eigenvector.

We now give some examples to show the usefulness of these results.

Example. Fig. 1 shows a labelling and the associated entries of the kernel eigenvector for C_{48} : 169, the smallest balanced but non-uniform nut fullerene.[1] The kernel eigenvector has entries $\{4, -2, 1\}$. The automorphism group has 12 orbits, namely {{1, 12, 34, 47}, {2, 20, 33, 48}, {3, 19, 24, 45}, {4, 6, 42, 43}, {5, 23, 29, 44}, {7, 16, 27, 46}, {8, 15, 28, 38}, {9, 14, 37, 39}, {10, 30, 32, 36}, {11, 21, 35, 41}, {13, 18, 25, 40}, {17, 22, 26, 31}}, each containing

[1] Fullerenes are indexed according to the spiral convention [6].

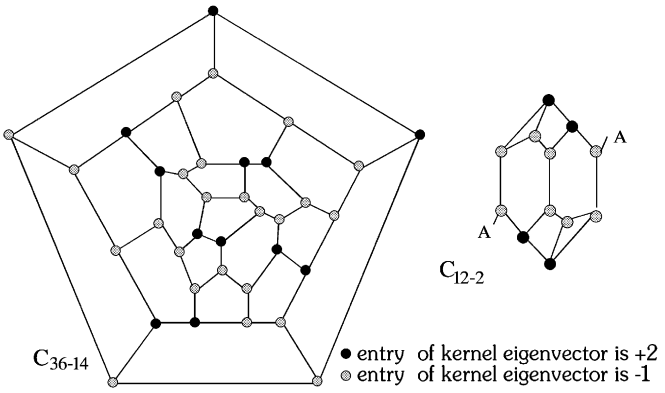

Fig. 2. The fullerene $C_{36}:14$ and the trivalent polyhedron $C_{12}:2$.

four equivalent vertices. The eigenvalues of

$$\mathbf{Q}=\begin{pmatrix}
0&1&1&1&0&0&0&0&0&0&0&0\\
1&0&0&1&1&0&0&0&0&0&0&0\\
1&0&0&0&0&1&1&0&0&0&0&0\\
1&1&0&0&0&0&0&0&0&1&0&0\\
0&1&0&0&0&0&0&1&1&0&0&0\\
0&0&1&0&0&0&0&1&0&0&1&0\\
0&0&1&0&0&0&1&1&0&0&0&0\\
0&0&0&0&1&1&1&0&0&0&0&0\\
0&0&0&0&1&0&0&0&0&1&0&1\\
0&0&0&1&0&0&0&0&1&0&1&0\\
0&0&0&0&0&1&0&0&0&1&0&1\\
0&0&0&0&0&0&0&0&1&0&1&1
\end{pmatrix}$$

are $0, 3, -1.618, 0.618, 1.317, 2.278, -1.891, -0.705, 0.763, 2.055, -2.583, -1.235$ which are indeed eigenvalues of $C_{48}:169$.

For the uniform trivalent nut graphs in Fig. 2, $\mathbf{Q}=\left(\begin{smallmatrix}2&1\\2&1\end{smallmatrix}\right)$ has eigenvalues 3 and 0 while a vertex transitive trivalent graph[2] has $\mathbf{Q}=(3)$ with eigenvalue 3. Though not particularly informative, the latter two cases agree with the result of Proposition 3.5.

3.2. Orbits and entries of eigenvectors

Theorem 3.7. *If λ is a simple eigenvalue of G, then the entries of the λ-eigenvector corresponding to the vertices in an orbit have the same absolute value.*

Proof. Let $p\in\Gamma(G)$, $\mathbf{P}$ be the corresponding $n\times n$ permutation matrix and $\mathbf{x}=(x_1,x_2,\ldots,x_n)^{\mathrm{t}}$ be an eigenvector in the λ-eigenspace $\mathscr{E}_\lambda$, which is of dimension one. Then $\mathscr{E}_\lambda$ is generated by $\mathbf{x}$, for λ of multiplicity one. Since $\mathbf{x}$, $p\mathbf{x}\in\mathscr{E}_\lambda$, then $\mathbf{Px}=\mu\mathbf{x}$ for some $\mu\in\mathbb{R}$. If $c=(1\ 2\ldots k)$ is a cycle in p , then the vertices $1, 2, \ldots, k$ lie in the same orbit. Also if

[2] The trivalent polyhedra are indexed according to the plantri program of Brinkmann and McKay [1].

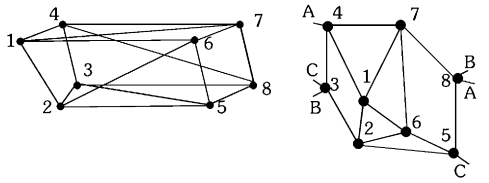

Fig. 3. A (vertex) transitive nut graph.

the matrix $\mathbf{C}$ represents the permutation c, then $\mathbf{C}^k = I$ and $\mathbf{C}^k\mathbf{x}' = \mu^k\mathbf{x}'$ where $\mathbf{x}' = (x_1, x_2, \ldots, x_k)^{\mathrm{t}}$ is the restriction of $\mathbf{x}$ to $\mathbb{R}^k$. Thus $\mu = \pm 1$, so that $|x_1| = |x_2| = \cdots = |x_k|$. □

Definition 3.8. An eigenvector $\mathbf{x}$ of $\mathbf{A}$ is said to be *equidistributive* if the entries of $\mathbf{x}$ have the same absolute value on equivalent vertices, i.e. vertices in the same orbit.

Corollary 3.9. *A kernel eigenvector of a nut graph is equidistributive.*

Proof. The result follows from Theorem 3.7, since a nut graph has zero as a simple eigenvalue. □

3.3. Signs of entries of eigenvectors

If $\mathbf{x}$ is a kernel eigenvector of a singular graph G of nullity one, then we identify three disjoint subgraphs G^+, G^- and G^0 (if it exists), induced by the vertices corresponding to the positive, negative and zero entries of $\mathbf{x}$, respectively. (Clearly their vertex sets partition $\mathscr{V}(G)$). Note that G^+ and G^- can exchange roles.

Remark 3.10. There are no nut graphs of order less than seven but there exist nut graphs of all orders $n \geqslant 7$. The occurrence of nut graphs is not so common among graphs of small order. However, among the singular cubic polyhedra of higher order, a considerable number are nut graphs. For instance, there are 285 nut graphs among the 1249 trivalent polyhedra of order 18.

Theorem 3.11. *Let G be a connected transitive graph (Fig. 3). If $\lambda \neq \rho$ is a simple eigenvalue with λ-eigenvector $\mathbf{x} = (x_1, x_2, \ldots, x_n)^{\mathrm{t}}$, then*

(1) $|x_1| = |x_2| = \cdots = |x_n|$;
(2) *the number of positive entries in* $\mathbf{x}$ *is* $n(G)/2$;
(3) $n(G)$ *is even*;
(4) $\lambda = 2q - \rho \in \mathbb{Z}$, where $q \in \mathbb{Z}^+$;
(5) *the valency q of each of the regular subgraphs G^+ and G^- is* $\frac{1}{2}(\rho + \lambda)$.

Proof. Since G has one orbit (1) follows by Theorem 3.7. Recall that $Aj = \rho j$ where j is the all-one vector. If $\mathbf{x} = (x_1, x_2, \ldots, x_n)^{\mathrm{t}}$ generates $\mathscr{E}_\lambda$, then $\mathbf{x}^{\mathbf{t}}.\mathbf{j} = \sum_{i=1}^{n} x_i = 0$, since eigenvectors of distinct eigenvalues are orthogonal when $\mathbf{A}$ is real and symmetric. By (1), the number of positive entries of $\mathbf{x}$ is the same as the number of negative entries, that is $n(G)/2$, so that (2) follows. From (2), it is clear that $n(G)$ is even, thus proving (3). Let G^+ and G^- be the disjoint subgraphs induced by the vertices corresponding to the $n/2$ positive and $n/2$ negative entries of $\mathbf{x}$, respectively. If vertex i has q neighbours in G^+ and $\rho - q$ in G^-, then,

$$\mathbf{Ax} = \lambda\mathbf{x} \Longrightarrow \sum_{j\sim i} x_j = \lambda x_i, \quad 1 \leqslant i \leqslant n,$$

where the summation runs over the neighbours $\{j\}$ of i

$$\Longrightarrow qx_i + (\rho - q)(-x_i) = \lambda x_i, \quad 1 \leqslant i \leqslant n$$

$$\Longrightarrow \lambda = 2q - \rho \in \mathbb{Z}.$$

Hence (4) follows. Since $-\mathbf{x}$ is also an eigenvector, G^+ and G^- can change roles. The value of q is dependent only on λ and ρ. Hence G^+ and G^- have the same degree and (5) follows from (4). □

From Theorem 3.7, we deduce:

Proposition 3.12. *If G is a singular graph of nullity one with a kernel eigenvector having entries of different absolute value, then G is non-transitive.*

From Theorem 3.11, we deduce other sufficient conditions for non-transitivity.

Proposition 3.13. *Each of the following is a sufficient condition for an n-vertex, connected, ρ-regular graph G to be non-transitive*:

(1) *n is odd and G has two simple eigenvalues*;
(2) *n is even and G has a simple even eigenvalue $\lambda \neq \rho$ and ρ is odd, or G has a simple odd eigenvalue $\lambda \neq \rho$ and ρ is even.*

Proof. Suppose G is transitive. If n is odd, then by Theorem 3.11(3), ρ is the only simple eigenvalue, proving (1). For n even, a simple eigenvalue λ satisfies $\lambda = 2q - \rho$, where q is the valency of each of the regular subgraphs G^+ and G^-. Thus λ and ρ have the same parity thus proving (2). □

Proposition 3.14. *Let G be a connected transitive graph of valency ρ. If zero is a simple eigenvalue, then*

(1) *G is a nut graph*;
(2) *the generator of the nullspace is a kernel eigenvector with each entry being* ± 1;
(3) *$n(G)$ is even and ρ is even*;
(4) *each of the subgraphs G^+ and G^- is $(\rho/2)$-regular on $n/2$ vertices.*

Proof. Since G is transitive, $\mathscr{V}(G^0) = \emptyset$. Hence G is a ρ-regular nut graph, thus proving (1). By Theorem 3.11(1), result (2) follows. By Theorem 3.11(3), n is even and by Theorem 3.11(4), $\lambda = 2q - \rho = 0$, so that $\rho = 2q$, and (3) follows. Since $\mathscr{V}(G) = \mathscr{V}(G^+) \dot{\cup} \mathscr{V}(G^-)$, $|\mathscr{V}(G^+)| = |\mathscr{V}(G^-)| = n/2$, by Theorem 3.11(2). Also $\lambda = 0$ so that $\rho = 2q$, proving (4). □

Proposition 3.15. *Let G be a singular transitive graph. Then G is a regular core graph.*

Proof. A transitive graph is regular since an automorphism preserves adjacencies. The case is settled for $\eta(G) = 1$, since by Proposition 3.14, G is a nut graph (which is a core graph) and by Theorem 3.11, G has a kernel eigenvector with each entry equal to ± 1.

Let the eigenvalue zero of G be repeated and $\mathbf{x} = (x_1, x_2, \ldots, x_n)^{\mathrm{t}}$ be a kernel eigenvector with $\mathbf{x}_i \neq 0$ and $\mathbf{x}_j = 0$. There exists $\gamma \in \Gamma(G)$ such that $\gamma(i) = j$, so that the kernel eigenvector $\gamma\mathbf{x}$ has the jth entry non-zero. Thus there exists a kernel eigenvector which is a linear combination of the basis vectors of the nullspace with each entry being non-zero. Thus G is a core graph. □

Example. The triangular prism of Fig. 4 is a transitive graph of nullity two and is a core graph.

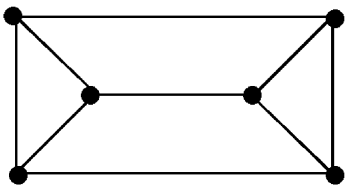

Fig. 4. A trivalent transitive core graph.

4. Nut fullerenes

Consider first cubic graphs. From Proposition 3.14, we deduce:

Proposition 4.1. *A transitive cubic graph G is either non-singular or has nullity more than one.*

Proposition 4.2. *A cubic nut graph G is non-transitive and has a kernel eigenvector with entries having distinct absolute values.*

Proof. Suppose, for contradiction, that G is transitive. Then by Proposition 3.14(2) a $(1, -1)$-kernel eigenvector exists. Thus for $i \in G^+$, $\sum_{j\sim 1} x_j$ is ± 3 or ± 1, contradicting $\mathbf{Ax} = \mathbf{0}$. □

4.1. Uniform nut fullerenes

Remark 4.3. Fig. 2 shows two uniform nut graphs, that is graphs having a $(1, 1, -2)$-kernel eigenvector. The first graph is the smallest nut fullerene, $C_{36} : 14$, while the second is the trivalent nut polyhedron $C_{12} : 2$.

Lemma 4.4. *If a cubic nut graph has a* $(1, 1, -2)$*-kernel eigenvector, then*

(1) G^+ *is* 2*-regular* (*the union of cycles*).
(2) G^- *is* 1*-regular* (*the union of disjoint edges*)

or vice versa.

Proof. If x_1, x_2, x_3 denote the entries of $\mathbf{x}$ corresponding to the neighbours of vertex i, then $\sum_{j\sim i} x_j = 0$. Thus without any loss of generality, $x_1 = x_2 = 1, x_3 = -2$. Hence,

for $i \in G^+$, ρ_+ is 2 (possible structures of G^+ are the union of cycles);
for $i \in G^-$, ρ_- is 1 (possible structures of G^- are the union of disjoint edges).
It is clear that G^+ and G^- may switch roles. □

We notice that the nut fullerene $C_{36} : 14$ of Fig. 2 can be covered by the six-vertex motifs M given in Fig. 5, such that all the vertices are covered. Moreover, the weights attached to the vertices of the motif coincide with the entries of the kernel eigenvector. More generally the same happens in any nut cubic graph with a $(1, 1, -2)$-kernel eigenvector and girth at least 5.

Proposition 4.5. *If a cubic nut graph G, of girth at least* 5*, has a* $(1, 1, -2)$*-kernel eigenvector, then*

(i) $n(G) = 6k,\ k \geqslant 2$.
(ii) *G has the motif M of Fig.* 5 *as a factor* (*i.e. there are* $n/6$ *disjoint motifs M spanning G*).

Proof. Every induced subgraph K_2 in G^- has a unique set of four vertices of G^+ incident to it. There is no vertex of G^+ which is not adjacent to a vertex of G^- and vice versa. Thus the six-vertex motif M spans G. □

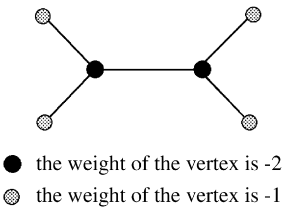

Fig. 5. The motif M in a nut fullerene with a $(1, 1, -2)$-kernel eigenvector.

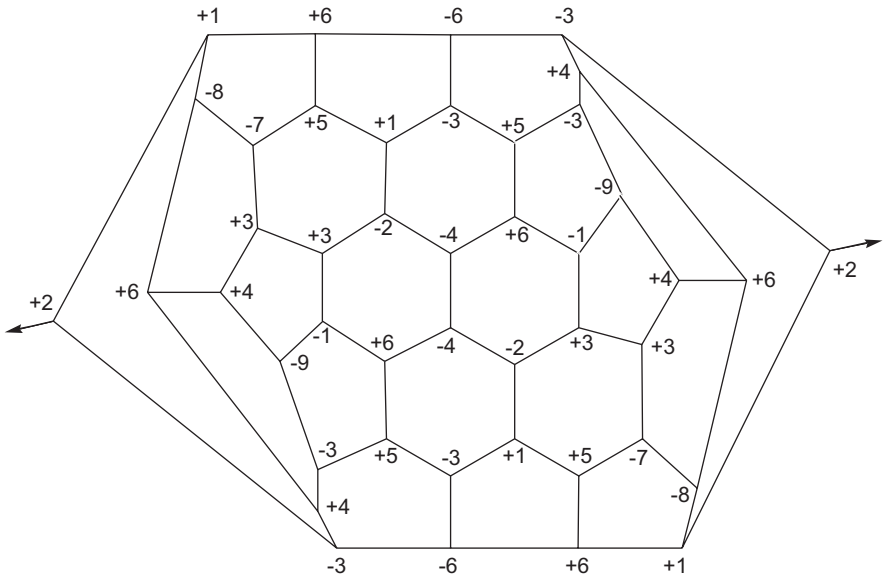

Fig. 6. The nut fullerene C_{44} : 14.

The fullerene C_{36} : 14 of Fig. 2 is an example of a nut fullerene with a $(1, 1, -2)$ kernel eigenvector, while the fullerene C_{44} : 14 of Fig. 6 is an example of a multi-orbit nut graph with several distinct entries in its kernel eigenvector.

4.2. Balanced nut graphs

Remark 4.6. Balanced nut fullerenes are a generalization of uniform nut fullerenes, where the generator of the kernel eigenvector has entries in $\pm\{1, -2, 4, -8, \ldots, (-2)^r, \ldots\}$, $r \in \mathbb{Z}^+ \cup \{0\}$.

Lemma 4.7. *Let G be a balanced nut graph with kernel eigenvector* $\mathbf{x}$. *Let $n_1, n_{-2}, \ldots, n_{(-2)^k}$ denote, respectively, the number of entries $1, -2, \ldots, (-2)^k$ that appear in* $\mathbf{x}$. *Then*

$$n_1 - 2n_{-2} + 4n_4 - \cdots + (-2)^k n_{(-2)^k} = 0. \tag{1}$$

Proof. The eigenvectors belonging to distinct eigenspaces of G are orthogonal. Thus if $\mathbf{j} = (1, 1, \ldots, 1)^{\mathrm{t}}$, then $\mathbf{x}^{\mathrm{t}}.\mathbf{j} = 0$ and the result follows. □

Theorem 4.8. *Let G be a balanced nut graph with kernel eigenvector* $\mathbf{x}$. *If k is the largest integer r that appears in the entries $(-2)^r$ of* $\mathbf{x}$, *then all the integers from 0 to k appear in the entries*; *i.e. the entries of* $\mathbf{x}$ *are $1, -2, 4, \ldots, (-2)^k$, possibly with repetitions.*

Proof. If j is the least integer , $1 \leqslant j \leqslant k$ such that $(-2)^j$ is missing from the entries of $\mathbf{x}$, then for a suitable labelling of G,

$$\mathbf{x} = (\underbrace{1, \ldots}, \underbrace{-2, \ldots}, \underbrace{4, \ldots}, \ldots, \underbrace{(-2)^{j-1}, \ldots}, \underbrace{(-2)^{j+q}, \ldots}, \ldots, .$$

It is clear that two linearly independent kernel eigenvectors can be found, namely

$\mathbf{x_1} = (1, \ldots, -2, \ldots, 4, \ldots, (-2)^{j-1}, \ldots, 0, \ldots, 0)$ and

$\mathbf{x_2} = (0, \ldots, 0, \ldots, (-2)^{j+1}, \ldots, (-2)^k, \ldots,)$, a contradiction. □

5. Chemical implications of nuts and core graphs

In Hűckel molecular orbital theory, the eigenvalues of **A** estimate the energies of the π-electrons in conjugated unsaturated systems, while the eigenvectors of **A** model the π-molecular orbitals.

As used in the chemical model, **x** is usually normalized to unit length. In the present paper we have taken entries in **x** to be normalized to some suitable but usually non-unit length, chosen where possible to have all entries integer, with no overall common factor, and with arbitrary overall sign. Statements about entries in **x** are therefore to be taken modulo sign and an overall normalization factor.

For $\eta = 1$, a kernel eigenvector **x** generating the nullspace of **A** describes the non-bonding orbital (NBO) of a π-conjugated molecule whose C-skeleton is the same as that of G, according to the Hűckel molecular orbital model applied to a simplified Schrődinger equation. The entries of **x** determine the distribution of the electron(s) occupying the NBO: from them follow the charges on the atoms, the bond-orders and, in the case of single occupation, the net spin density at each site.

For a labelling of G, a zero entry in the ith position of **x** indicates a lack of charge at the ith C-centre. The NBO-charge is distributed among the C-atoms in proportion to the square of the entries of **x**. Thus the charge is concentrated in the substructure, the *core* with respect to **x**, that corresponds to the non-zero entries of **x**.

The eigenvalue zero of **A**, for a molecular graph G, indicates the presence of a NBO, **x**, with no net stabilization or destabilization [10]. For the graph G, with the same structure as a molecule, the eigenvalues of **A** estimate the energies of the π-electrons in these unsaturated systems, while the eigenvectors of **A** model the π-molecular orbitals. Computer searches up to $n = 120$ show that zero energy levels are rare in fullerenes. The non-zero entries of the corresponding eigenvectors of **A** determine the substructures in fullerenes (and other trivalent polyhedra) responsible for the presence of the NBOs. We place particular emphasis on polyhedral structures which are nut graphs, implying equidistributivity and the absence of zeroes in the corresponding π-electron charge/spin density, and those which are core graphs where each C-centre carries π density. Through symmetry considerations of the automorphism group of the graph, by studying relations among the entries of **x**, we showed in Sections 3 and 4 that there are hypothetical nut fullerenes with relatively simple structures. Moreover, these results yield information on the chemical properties of trivalent polyhedral carbon cages, in general.

From Corollary 3.9 we deduce:

Proposition 5.1. *A NBO of a nut fullerene is equidistributive.*

Since fullerenes have odd valency, it follows, by Proposition 3.14, that there are no nut fullerenes which are transitive.

We deduce from Proposition 4.2:

Proposition 5.2. *A nut fullerene is multi-orbit and has a kernel eigenvector with entries having distinct absolute values.*

Nut graphs differ from other graphs of nullity one in that contributions by an NBO-electron to charge, net spin and bond-order take place at vertices and edges over the whole π-framework of the graph whereas, in other graphs, they are concentrated into the core-substructure (not affecting the atoms with zero graph angles which correspond to the zero-entries in all possible kernel eigenvectors).

There are 13 nut fullerenes for $n \leqslant 70$ and only 41 in the 10,190,782 fullerene isomers on up to 120 vertices. Nut graphs are quite common amongst small trivalent polyhedra; they constitute about 35% of the 177,758 non-bipartite polyhedra on up to 24 vertices.

There are also fullerenes of nullity more than one, such as the dodecahedron and $C_{36} : 15$, both of which are core graphs. There exist other singular fullerenes, of nullity more than one, which are not core graphs, such as $C_{36} : 13$, and which have vertices corresponding to zero-entries in each possible kernel eigenvector, since these vertices do not belong to any core. To such vertices there correspond zero angles relative to the eigenspace $\mathscr{E}_0$ and therefore no charge contribution from the NBO electron(s).

In the chemically realizable bare, empty fullerenes known to date, the pentagons do not share common edges. The smallest isolated-pentagon (IP) fullerene is the icosahedrally symmetric C_{60} (buckminsterfullerene), which has no NBO. Among the large number of fullerene isomers for up to $n = 120$, there are only nine singular IP fullerenes of which $C_{84} : 24$ has three NBOs whereas the other eight have one NBO. None of them are nut graphs. Some larger

fullerenes, e.g. isomers of C_{106} and C_{114}, as examples of 'sporadic' closed shell fullerenes [6], approach 'nut graph' status as they each have an eigenvalue very close to but not exactly zero.

The uniform nut fullerenes have a (1, 1, −2) NBO. By Proposition 4.5, we deduce:

Proposition 5.3. *In a uniform nut fullerene* C_n, *there is a cover by* $n/6$ *disjoint motifs M.*

Remark 5.4. Equidistributivity for the eigenvectors associated with a *multiple* (degenerate) eigenvalue λ fails but the total charge density of the λ-eigenspace is conserved. Thus if, for instance, a transitive graph G, of order n, has an eigenvalue of multiplicity two, with orthogonal normalized eigenvectors (a_j) and (b_j), then for all j, $(a_j)^2 + (b_j)^2 = 2/n$, so that the charge is the same on every atom. Since there cannot be two linearly independent real eigenvectors in which equivalent vertices have the same fixed entry, when a degenerate set of eigenvectors is only partially occupied, the inability to maintain total symmetry on equivalent vertices can give rise to symmetry breaking. This relation between degenerate eigenvalues and the inability to preserve symmetry in the separate orbitals, explains phenomena such as the Jahn–Teller effect [3] in molecular physics and the Peierls effect [2] in solid state physics.

In [4], it is shown that extensions to domains, other than the real field, are necessary to represent eigenvectors that reflect symmetry preservation. Different bases of the λ-eigenspace vectors in complex, and quaternionic domains are shown to represent total symmetry of charge distributions even at the level of the individual eigenvectors. In the case of the two-fold multiplicity, the complex realizations, $\mathbf{x_1} = (x_{1i})_{1 \leqslant i \leqslant n} = ((a_k) + i(b_k))/\sqrt{2}$ and $\mathbf{x_2} = (x_{2i})_{1 \leqslant i \leqslant n} = ((a_k) - i(b_k))/\sqrt{2}$ in the complex field, yield $|x_{1j}| = |x_{2j}| = ((a_{kj})^2 + (b_{kj})^2)/2 = 1/n$ for all j, as required. This representation of the eigenvectors can be justified experimentally: the two orbitals are those isolated in the presence of external magnetic fields for certain molecules with twofold eigenvalue multiplicity. For multiplicities of higher order, quantum mechanics acting in extended Hilbert spaces is conceivable mathematically but to date has not been linked to physical phenomena.

References

[1] ⟨http://cs.anu.edu.au/~bdm/plantri/plantri-guide.txt⟩.
[2] S.L. Altmann, Band Theory of Solids: An Introduction from the Point of View of Symmetry, Clarendon Press, Oxford, 1991.
[3] I.B. Bersuker, V.Z. Polinger, Vibronic Interactions in Molecules and Crystals, Springer, Berlin, 1989.
[4] A. Ceulemans, P.W. Fowler, M. Szopa, Quaternions and Equidistributive Eigenvectors of Symmetric Graphs, Math. Proc. Roy. Irish Acad. 98A (1998) 139–151.
[5] D.M. Cvetković, P. Rowlinson, S. Simić, Eigenspaces of Graphs, Encyclopedia of Mathematics and its Applications, vol. 66, Cambridge University Press, Cambridge, 1997.
[6] P.W. Fowler, P.W. Manolopoulos, An Atlas of Fullerenes, Clarendon Press, Oxford, 1995.
[7] I. Sciriha, On the construction of graphs of nullity one, Discrete Math. 181 (1998) 193–211.
[8] I. Sciriha, On the rank of graphs, in: Y. Alavi et al., (Eds.), The Eighth Quadrennial International Conference on Graph Theory, Combinatorics, Algorithms and Applications, vol. II, Springer, Berlin, 1998, pp. 769–778.
[9] I. Sciriha, I. Gutman, Nut graphs—maximally extending cores, Utilitas Math. 54 (1998) 257–272.
[10] M. Yoshida, M. Fujita, P.W. Fowler, E.C. Kirby, Non-bonding orbitals in graphite, carbon tubules, toroids and fullerenes, J. Chem. Soc., Faraday Trans. 93 (6) (1997) 1037–1043.