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B a l k a n i c a

New Series Vol. 18, 2004, Fasc. 1-2

A Spectral View of Fullerenes

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Fullerenes, a third family of allotropes of carbon (C), exist as large stable clusters of C atoms. The eigenvalues of the adjacency matrix **A** of a graph, with the same structure as a fullerene, estimate the energies of the π-electrons in these unsaturated systems and the eigenvectors of **A** model the π-molecular orbitals. The eigenvalue zero of **A** indicates the presence of NBOs with no net stabilization or destabilization. Zero energy levels are rare in fullerenes. We study the substructures in fullerenes and other trivalent polyhedra that determine the presence of the eigenvalue zero. Together with the symmetry group of the graph, they shed new light on singular graphs and on singular polyhedra in particular.

AMS Subj. Classification: 92E10, 05C25, 05C50, 05C90, 20F28.
Key Words: Non-bonding orbital (NBO), core, fullerenes, adjacency matrix, minimal configuration (mc), nut graph, automorphism group.

1. Introduction

In addition to graphite and diamond, a third family of allotropes of C exists as large stable clusters of C atoms. The Hűckel molecular orbital (HMOT) theory gives an approximation for the $\pi-$molecular orbitals $\{\mathbf{x}\}$ of a molecule (or $\pi-$system) as a solution to a simplified **Schrődinger equation,** $\mathbf{Ax} = \lambda\mathbf{x}$, that determines the molecular orbital energies λ, where **A** is the adjacency matrix of the **molecular graph** whose structure is the same as that of the molecule.

In [5], the authors rationalised the NBOs in some fullerenes and other C allotropes by looking for an "orbital pattern" similar to one of the four NBOs of the graphite sheet. In [3, 4], the author was motivated by the same question directed at an arbitrary graph: Which structural features force a graph to be singular? The linearly independent kernel eigenvectors, in a minimal basis (in which the vectors have a minimum number of non-zero entries) for the nullspace of **A**, determine subgraphs called mcs which may be chosen from an established list. This leads to the queries: 1. which part of the molecule of a singular fullerene is responsible for a particular NBO?
2. are there any chemical minimal configurations? In section 3 we investigate the substructures (mc, core, periphery) that make a singular graph and settle a query raised in [3]. In section 4 we investigate the cores of trivalent polyhedra.

In section 5 we see that simple (non-degenerate) eigenvalues and symmetry can be crucial in characterising nut graphs, which imply equidistributivity of the π-electron charge density, from among the singular graphs.

By inspecting the sign of the kernel eigenvector entries, we identify, in section 6, interesting substructures that help to classify singular graphs. Applied to trivalent polyhedra, these ideas yield fruitful results. In section 7, we see that vertex transitivity inhibits the formation of a simple kernel eigenvector and that it is impossible to have a mc (and hence a nut graph) with the (+1,-1,0)-kernel eigenvector, the one shared by the isolated pentagon (IP) tubular fullerenes. We end up by noting the relevance of these results to the chemistry of fullerenes.

2. Chemical graphs

A graph $H(\mathcal{V}, \mathcal{E})$ having a vertex set $\mathcal{V}(H) = \{v_1, v_2, \ldots, v_n\}$ and a set $\mathcal{E}$ of $m(H)(= m)$ edges joining distinct pairs of vertices, is said to be of order $n(H)(= n)$. In a molecular graph, the vertices represent the C atoms and the edges, the σ bonds.

The valency val(v) of a vertex v is the number of edges incident to v. The complete graph K_n has n vertices and an edge between every pair of distinct vertices. The complement $\overline{H}$ of H is the graph with vertex set $\mathcal{V}$ and edge set $\mathcal{E}(K_n)\backslash\mathcal{E}(H)$. The cycle C_n has n vertices, is connected and the valency of each vertex is two. The graph $G(X, Y, \mathcal{E})$ is bipartite if $X \dot{\cup} Y$ is a partition of its vertex set so that each edge joins a vertex of X to a vertex of Y. The graph $K_{r,s}$ is the complete bipartite graph with $|X| = r$, $|Y| = s$ and every vertex of X adjacent to every vertex of Y.

A **fullerene** is an allotrope of carbon which like graphite is built of sp^2-hybridised atoms, but unlike graphite need not have a zero HOMO-LUMO gap in the distribution of the π–energy levels of its electrons. In 3D, fullerenes can be embedded on a sphere, ellipsoid or other convex surface. The molecular graph of a fullerene has a planar embedding, its faces consist of pentagons and hexagons and each C atom forms three bonds.

Euler's Polyhedral Formula: *Let G be a connected planar graph with f faces (regions). If $n \geq 3$, then $n + f = m + 2$.*

Lemma 2.1 *A fullerene has exactly 12 pentagons and an even number of C atoms.*

3. Singular graphs

A graph is singular if its adjacency matrix $\mathbf{A}$ has the eigenvalue zero. There exist $\eta(G)(= \eta)$ non-zero vectors $\mathbf{x}$, called **kernel eigenvectors** in the nullspace $\mathcal{E}_0$ of $\mathbf{A}$, satisfying $\mathbf{Ax} = \mathbf{0}$. The multiplicity η of the zero eigenvalue of $\mathbf{A}$ is said to be the **nullity** of $\mathbf{A}$ and corresponds to the number of NBOs in

HMOT. The **rank** of G, denoted by $r(G)$, is the rank of its adjacency matrix $\mathbf{A}$ which is $n(G) - \eta(G)$.

Definition 3.1. *Let* $\mathbf{x_0}$ *be a kernel eigenvector of a singular graph* G*, of order* $n \geq 3$*. A subgraph of* G *induced by the vertices corresponding to the non-zero entries of* $\mathbf{x_0}$ *is said to be a* **core**[2]**,** χ *(w.r.t* $\mathbf{x_0}$*), (sometimes also denoted by* χ_p*, or* $\chi_{\mathbf{x_0}}$*), where* p *is the number of vertices of the core, called the* **core order**.

Definition 3.2. *A singular graph* Γ *of order* $n \geq 3$*, having a core* χ_p *and periphery* $\mathcal{P} := \mathcal{V}(\Gamma) - \mathcal{V}(\chi_p)$*, is said to be a* **minimal configuration,** *of core order* p*, if the following conditions are satisfied: (i)* $\eta(\Gamma) = 1$,
(ii) $\mathcal{P} = \emptyset$ *or* $\mathcal{P}$ *induces an empty graph (with no edges), and*
(iii) $\eta(\chi_p) = 1 + |\mathcal{P}|$.

Lemma 3.3. *The order of a mc having a core* χ_p *is* $p + \eta(\chi_p) - 1$.

(1) A graph G is a core if G is singular graph of nullity at least one, having a kernel eigenvector with each entry being non-zero.
(2) The core of a graph of nullity one is unique.
(3) Condition (iii) in Definition 3.2 is a consequence of the Interlacing Theorem and requires that the nullity is decreased by one with each addition, to χ, of a vertex of P.
(4) A mc Γ is "grown" from χ by adding $\eta(\chi_p) - 1$ mutually disconnected (independent) vertices.
(5) If $\mathbf{x_i}$ is a vector in a minimal basis of $\mathcal{E}_0$, then there exists a subgraph Γ of G with core $\chi_{\mathbf{x_i}}$.
(6) The core-order is a maximum when $\eta(\chi_p) = 1$ and $n(G) = p$. It is a minimum when $\eta(\chi_p) = p$ and the core $(\overline{K_p})$ is empty.
(7) If α is the maximum number of independent vertices in G, then $\overline{K_\alpha}$ is a subgraph of G. By interlacing, if the nullity of G is η, then $p_+ + \eta \geq \alpha$ and $p_- + \eta \geq \alpha$, p_+ (p_-) being the number of positive (negative) eigenvalues of G.

Definition 3.4. *A singular graph is said to be a* **nut graph** *if each entry of* **every** *kernel eigenvector is non-zero.*

A nut graph is a mc with $\mathcal{P} = \emptyset$ and is equal to its core. It is so termed by connotation with the core and the absence of a periphery.

Proposition 3.5. *A mc* Γ *is bipartite if and only if its core is induced by a set of* $(n+1)/2$ *independent vertices.*

Because of its odd cycles, a fullerene is not bipartite. However there are fullerenes (e.g. $C_{32} : 5^1$ of Figure 1) which are singular because they have a bipartite mc as a subgraph.

[2] The core is sometimes referred to as the 'support' of the eigenvector in the literature.
[1] Fullerenes are indexed in spiral order[2].

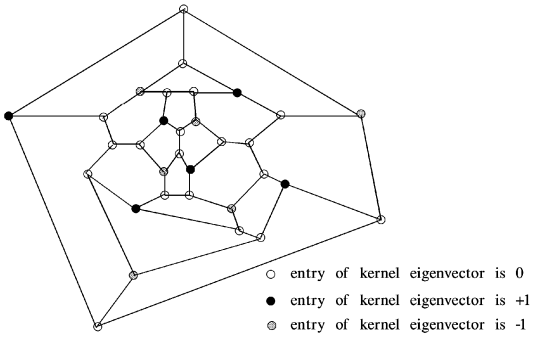

Figure 1: The singular fullerene $C_{32} : 5$ with core $12K_1$.

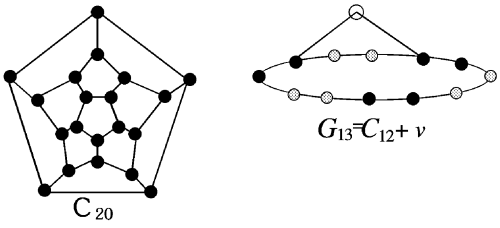

Figure 2: A mc G_{13} with core C_{12} in C_{20}.

4. Cores in fullerenes

The smallest fullerene cage, the dodecahedron, is the molecular graph G of $\mathbf{C_{20}}$, which is the cubic planar graph (regular of valency 3) on 20 vertices, that has 12 pentagonal faces. The nullity of $\mathbf{C_{20}}$ is four and it is a core. The four NBOs correspond to distinct mcs, found as subgraphs, for the four kernel eigenvectors in a minimal basis for the nullspace of G. Two of the mcs are P_{15} with core $\overline{K_8}$ and each of the other two is the bicyclic graph G_{13} of Figure 2 having cycle C_{12} as core. The fullerene $C_{32} : 5$ has $12K_1$ as a core. A possible mc is the path P_{23}.

The chemically realizable fullerenes known to date satisfy the isolated pentagon rule (IPR): no two pentagonal faces share a common edge. The smallest fullerene to follow the IP rule is C_{60} which has no NBO. By introducing a cycle of hexagons between the two caps of the fullerene C_{60}, we obtain C_{70}.

The NBO of IP C_{70} is characterised by the core $2C_{20}$ of a minimal configuration, which has 43 vertices. Since $70 = n(C_{70}) > 43$, there may be various possible mcs which are subgraphs of C_{70}. In fact, those found in C_{70} show us that **these mcs may even be non-cospectral**.

An infinite family of tubular fullerenes, C_n, with hemi-C_{60} caps and

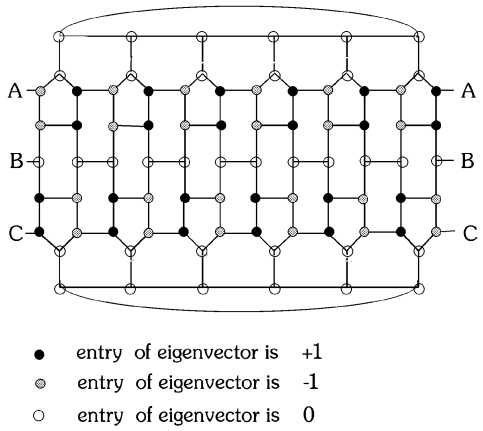

Figure 3: The fullerene C_{70}.

nullity one, has members at $n = 70 + 30k$, $(k = 0, 1, 2, \ldots)$ with overall fivefold symmetry. The core of these fullerenes consists of the disjoint union of $k \geq 2$ copies of C_{20}. A minimal configuration is a $20k + 2k - 1$-vertex-subgraph of the fullerene. A second family has members at $n = 84 + 36k$, $(k = 0, 1, 2, \ldots)$, with hemi-C_{72} caps, overall six-fold symmetry and nullity one for $k > 0$, the fullerene C_{84} with $k = 0$ having nullity 3. For $k > 0$, the core consists of the disjoint union of $k \geq 2$ copies of C_{24}. A minimal configuration is a $24k + 2k - 1$-vertex-subgraph of the fullerene. One of the cores of the fullerene C_{84} is also $2C_{24}$. In addition it has more cores and only 12 vertices do not belong to any core.

Another interesting property of the structure of tubular fullerenes of nullity one is that in building up the fullerene from a mc, **each vertex addition leaves the rank of the adjacency matrix fixed.**

Proposition 4.1. *Sufficient conditions that the rank of the adjacency matrix of a graph G remains unchanged with the addition of a vertex v to G are that*
1. the vector $\mathbf{r}$ *of neighbours of v is in the orthogonal complement of the nullspace $\mathcal{E}_0(A(G))$.*
2. the vertex v does not belong to a new mc in $G + v$.

Each of the 27 vertices added to a mc to form C_{70} satisfies the sufficient conditions in Proposition 4.1.

5. Symmetry

The **automorphism group** $\Gamma(G)$ of a graph G is the group of permutations (symmetries) that act on the vertices and preserve adjacencies.

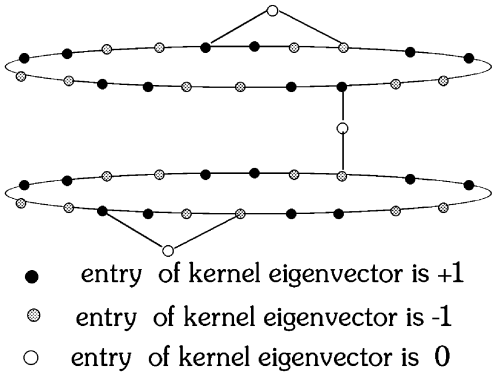

Figure 4: A mc with core $2C_{20}$ in the fullerene C_{70}.

Lemma 5.1. *Let i, j be vertices in G. For all $\gamma \in \Gamma(G)$, $\{i,\ j\}$ is an edge of $G \iff \{\gamma(i),\ \gamma(j)\}$ is also an edge.*

Immediate consequences are:
1. non-edges are sent to non-edges by $\gamma \in \Gamma(G)$
2. val(i)=val($\gamma(i)$)
3. $\Gamma(G) = \Gamma(\overline{G})$

Let Σ be a subgroup of $\Gamma(G)$. The possible 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 $\Omega_i = \{\gamma(i) : \gamma \in \Sigma\}$.

A graph G is said to be **vertex transitive** if it has only one orbit; that is $\forall i, j \in \mathcal{V}(G), \exists \gamma \in \Gamma(G)$ such that $\gamma(i) = j$.

Theorem 5.2. *If $\gamma \in \Gamma(G)$ and 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.*

Theorem 5.3. *Let G be a connected vertex-transitive graph. If $\lambda \neq \rho$ is a simple eigenvalue with λ-eigenvector $\mathbf{x} = (x_1, x_2, \ldots, x_n)$, then*
(1) $|x_1| = |x_2| = \ldots = |x_n|$
(2) the number of positive entries in the λ–eigenvector is $n(G)/2$
(3) $n(G)$ is even
(4) $\lambda = 2q - \rho \in Z$, where q is the valency of the regular subgraph induced by the vertices corresponding to the positive (or negative) entries of the λ–eigenvector.

6. Symmetry in singular graphs

If $\mathbf{x}$ is a kernel eigenvector of a singular graph G, then we identify three disconnected subgraphs G^+, G^- and G^0, induced by the vertices corresponding

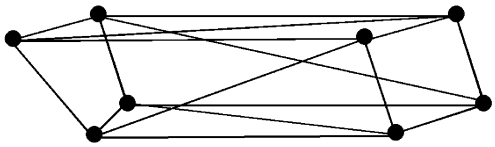

Figure 5: A vertex transitive nut graph.

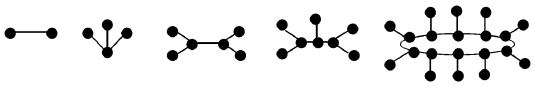

Figure 6: Substructures of G^0 in a cubic graph with a $(+1,-1,0)$–kernel eigenvector (e.g.$C_{32}:5$).

to the positive, negative and zero entries of $\mathbf{x}$ respectively, whose vertices partition $\mathcal{V}(G)$. The vertex-transitive nut graph G in Figure 5 has $G^+ = G_- = C_4$.

Remark 6.1. There are no nut graphs of order less than seven but there exist nut graphs of all orders $n \geq 7$. The occurrence of nut graphs is not so common among graphs of low order. Proposition 6.2 suggests that symmetry tends to help towards the formation of the kernel eigenvector required for a nut graph.

Proposition 6.2. *Let G be a connected vertex-transitive graph of valency ρ. If zero is a simple eigenvalue, then (1) G is a nut graph*
(2) $n(G)$ is even and ρ is even
(3) G^+ is $\frac{\rho}{2}$–regular on $n/2$ vertices.

Proposition 6.3. *Let G be a singular vertex-transitive graph. Then*
(1) G is regular
(2) G is a core.

The triangular prism is such a vertex-transitive graph of nullity two and is a core.

Proposition 6.4. *The following are separately sufficient conditions for a multi-orbit-vertex graph: (1) two simple eigenvalues in a ρ-regular graph, when ρ is odd*
(2) two simple eigenvalues of different parity in a ρ-regular graph, when ρ is even
(3) a trivalent graph of nullity one
(4) a singular graph of nullity one with a kernel eigenvector having entries of different absolute value.

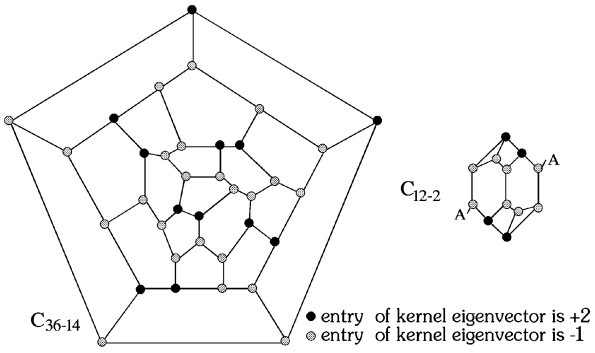

Figure 7: $C_{36} : 14$ and $C_{12} : 2$

Corollary 6.5. *Let the kernel eigenvector of a mc G have an entry which is zero. Then*
(1) G is not vertex-transitive
(2) the vertices of the core belong to a union of orbits disjoint from those to which the periphery belong.

7. Cubic polyhedra

From Proposition 6.2 we deduce:

Proposition 7.1. *A vertex-transitive cubic graph G is either non-singular or has nullity more than one.*

The IP fullerene C_{70} has a kernel eigenvector with the entries being +1, -1 and 0.

Lemma 7.2. *If the entries of a kernel eigenvector of a cubic graph are +1, -1 and 0, then*
(1) the valency of the vertices of G^0 are 1 or 3.
(2) the core is the union of cycles and K_1s.

Proposition 7.3. *A cubic graph G of nullity one with a $(+1, -1, 0)$–kernel eigenvector is not a mc.*

Proposition 7.4. *If a cubic polyhedron is a nut graph, then it is multi-orbit.*

Polyhedron $C_{12} : 2^2$ of Figure 7 have a $(+1, +1, -2)$–kernel eigenvector. The fullerene $C_{44} : 14$ is an example of a nut graph with several distinct entries in its kernel eigenvector.

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

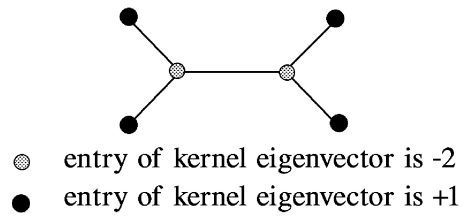

Figure 8: Factor (motif) in a nut fullerene with a $(+1, +1, -2)$–kernel eigenvector.

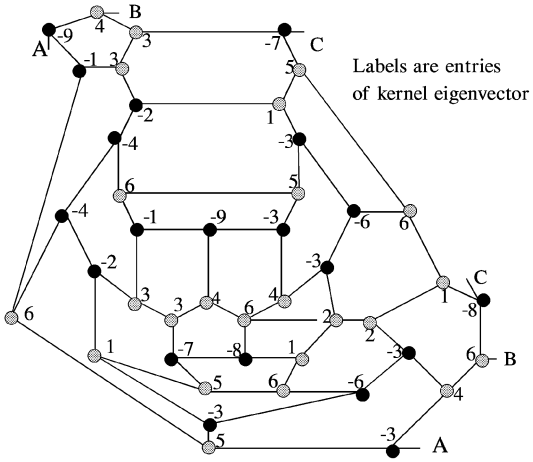

Figure 9: The nut fullerene C_{44} : 14.

Lemma 7.5. *If a cubic nut graph has a* $(+1, +1, -2)$*–kernel eigenvector, then*
(1) G^+ *is the union of cycles*
(2) G^- *is the union of* K_2*s.*

Proposition 7.6. *If a cubic nut graph* G *has a* $(+1, +1, -2)$*–kernel eigenvector, then*
(i) $n(G) = 6k,\ k \geq 2$.
has the motif in Figure 10 as a factor (i.e. there are $n/6$ *disjoint motifs spanning* G*).*

8. Conclusion

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 a nut graph whereas they are concentrated into the core-substructure not affecting the periphery when the latter is not empty. There are 13 nut fullerenes for $n \leq 70$. There are fullerenes of nullity more than one, such as the dodecahedron and $C_{36:15}$ both of which are cores. Other singular fullerenes of nullity more than one, such as $C_{36:13}$, have vertices which correspond to zero entries in each possible kernel eigenvector since they do not belong to any core. These vertices have no contribution to charge from the NBO electron(s).

There are ten singular IP fullerenes for $n \leq 120$ all of nullity one except C_{84} isomer 24 which has nullity three. None of them are nut graphs, as examples of 'sporadic' closed shell fullerenes [2], though C_{106} and C_{114} approach "nut graph" status as they each have an eigenvalue very close to but not exactly zero.

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Received 30.09.2003