Research Article

Zooming in on fullerenes

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Summary. *Carbon does not appear only as diamond and graphite. Fullerenes, forming a third family of allotropes of carbon (C), exist as large stable clusters of C atoms. A trivalent polyhedron P is a cubic graph which may be embedded on a convex 3-D surface of genus zero and a fullerene, Cn, is P with twelve pentagons, the remaining faces being hexagons. We introduce the concept of nut fullerenes, so called because their skeleton is a nut graph that implies one NBO with the charge contributed by the NBO electron being shared among all the C-centres. The charge distribution over all the framework of the molecule has strong chemical consequences. We study the substructures in fullerenes and other trivalent polyhedra, that determine the presence of a NBO. Together with the symmetry group of the graph, they shed new light on singular graphs and polyhedra in particular.*

The Schrödinger wave equation that yields the wave functions specifying the possible energies of a molecule is well known to most scientists. Wave equations and operators are quite complex and still a healthy area of research. Determining the electron (ε) energy levels of a Carbon (C) molecule is, however, relatively easy, owing to the Hückel Molecular Orbital (HMO) theory, for $\pi-\varepsilon-$systems. This approximates the Schrödinger's equation leading to a simpler one $\boldsymbol{Ax}=\lambda\boldsymbol{x}$ where $\boldsymbol{A}$ is the adjacency 0 – 1 matrix of the molecular graph *G* whose structure is the same as that of the molecule with the C-centres as vertices and the σ-bonds as edges. In spite of the errors in the approximations, the values of λ (termed eigenvalues of $\boldsymbol{A}$), for the ε- energy levels of the molecule and those of the vectors $\boldsymbol{x}$ describing the ε-orbitals, that are surprisingly close to those obtained experimentally.

Non-bonding orbitals (NBOs) present in some molecules are characterised by the presence of the *zero* energy level $(\lambda=0)$. The orbital vector $\boldsymbol{x}$ satisfies $\boldsymbol{Ax}=\boldsymbol{0}$ and is said to be a *kernel eigenvector* of $\boldsymbol{A}$ or of *G*. The number of linearly independent vectors $\boldsymbol{x}$ satisfying $\boldsymbol{Ax}=\boldsymbol{0}$ is said to be the *nullity* of $\boldsymbol{A}$.

Fullerenes, discovered in 1987, when an arc was passed through C vapour, form a third family of allotropes of C, in addition to graphite and diamond which were known since the reign of the alchemists. They exist as large stable clusters of C atoms, each having three σ-bonds, forming a spherical or other convex shape.

In (Yoshida *et al.*, 1997) M Yoshida, P.W. Fowler *et al* described the rarely occurring NBOs of a subfamily of fullerenes by comparing the orbital patterns to the four NBOs of the graphite sheet. In (Sciriha 1998a, 1998b), the author was motivated by the same problem for an arbitrary graph. The aim was to discover the structural features that force a graph *G* to be singular. The results point to subgraphs called minimal configuration (mcs) that are present in *G*. An algorithm constructs all possible mcs and a catalogue of the smaller mcs can be found in (Sciriha 1998a) and (Sciriha 1998b). These studies prompt us to ask which part of the molecule of a singular fullerene is responsible for a particular NBO. Are chemical mcs possible?

The characterization of the graphs with eigenvalue zero, known as *singular* graphs, has been a long-standing problem in the sixty-year-old history of graph theory, during which time the latter has emerged as an ever-expanding prolific discipline of mathematics. Each kernel eigenvector $\boldsymbol{x}$ of *G* is an NBO and determines a well-defined *core* which is the singular subgraph induced by the non-zero entries of $\boldsymbol{x}$. Moreover, a core, corresponding to a kernel eigenvector $\boldsymbol{x}$ in a minimal basis (a basis in which the linearly independent vectors have a minimum number of non-zero entries) for the nullspace of $\boldsymbol{A}$, "grows" into a minimal configuration (mc) by adding vertices, which form a *periphery*, until the nullity is reduced to one. Such a mc of nullity one is the subgraph of the singular graph responsible for the presence of the NBO $\boldsymbol{x}$. Thus a mc consists of a core and a periphery.

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If a core happens to have nullity one, then it is a special mc called *nut graph* that needs no periphery. The search for nut molecular graphs has aroused a flurry of interest among chemists because of the strong chemical implications. Nut graphs are unique among molecules with one NBO because each C-centre is charge rich. Moreover the spin and bond-order densities are also spread over the whole π-framework and not on some substructure. We consider the constraints required for a fullerene or other trivalent polyhedron to be a nut graph.

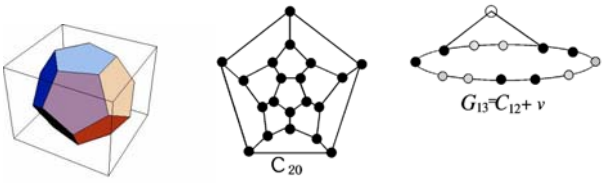

Figure 1

The trivalent fullerene has a planar embedding. Euler's equation $n+f=m+2$ for solids of genus zero relates the number n of C-centres (vertices) with the number m of σ-bonds (edges) and the number f of faces formed by the σ-bonds. Since $2m=3n$, we deduce that a fullerene has exactly twelve pentagons and $\left(\frac{n}{2}-10\right)$ hexagons. The smallest hypothetical fullerene is the well known twenty-vertex Platonic solid, the dodecahedron, C_{20}, consisting of twelve pentagonal faces embedded on a sphere. The nullity of C_{20} is four and it is a core so that each C-centre in a hypothetical C_{20} molecule is charge-rich. The four NBOs correspond to distinct mcs found as subgraphs. Figure 1 shows a 3-D picture and a planar embedding of C_{20} as well as G_{13}, one of the mcs. The smallest fullerene with nullity one is $C_{28}:1$ and the smallest nut fullerene is $C_{36}:14$ shown in Figure 2.

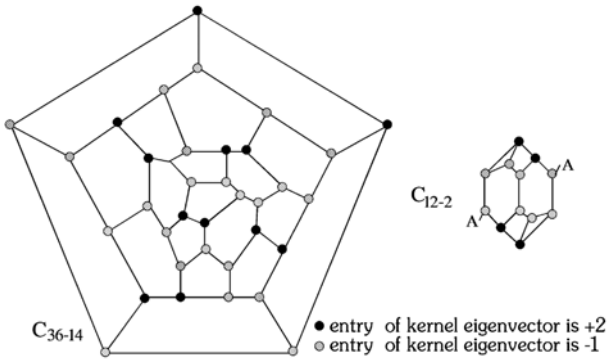

Figure 2

The chemically realizable fullerenes known to date follow the Isolated Pentagon (IP) rule. The smallest is the Buckminster Fullerene C_{60}, which has no NBO and whose spherical structure is that adopted for the football (Figure 3). Adjacent pentagons in a fullerene structure are thought to produce too much strain to allow stability.

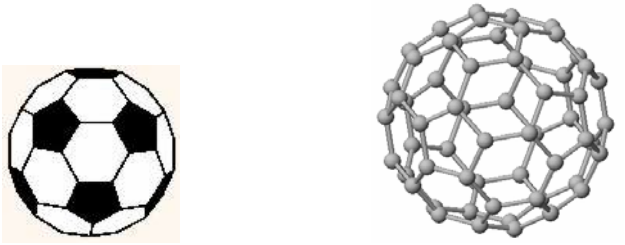

Figure 3

Among the large number of fullerene isomers C_n for n up to 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, although C_{106} and C_{114}, as examples of sporadic closed shell fullerenes, approach "nut graph" status having an energy level very close to but not exactly zero.

Although there exist nut graphs of all orders $n \geq 7$, their frequency seems to be low among graphs of low order. So it was quite surprising that among the trivalent polyhedra a considerable number were found to be nut graphs. For instance, among the 1249 trivalent polyhedra of order 18, there are 285 nut graphs.

As in many areas of science, symmetry plays an important role in revealing physical and chemical behaviour. The symmetry group of the planar embedding of a fullerene enables the vertices (C-centres) to be partitioned into orbits each containing equivalent vertices. Thus vertices in an orbit may be mapped onto each other by a transformation such as a rotation and/or a reflection, preserving adjacencies. Moreover these vertices carry the same charge. Linear algebra and symmetry help to determine easily some of the energy levels of large symmetrical fullerenes, since these are given by the eigenvalues of the much smaller orbit-orbit matrix.

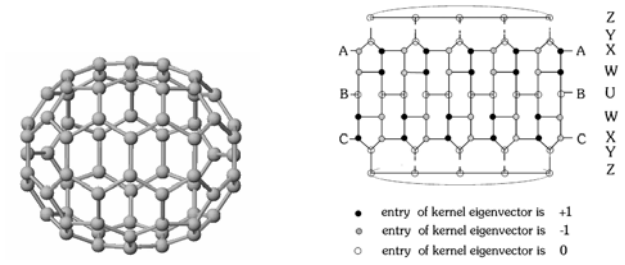

Figure 4

The fullerene C_{70}, for instance, has 5 orbits, $UWXYZ$, containing 10, 20, 20, 10 and 10 vertices respectively as shown in Figure 4. The 5×5 orbit-orbit matrix

$$M = \begin{array}{c} \\ U \\ W \\ X \\ Y \\ Z \end{array} \begin{pmatrix} 1 & 2 & 0 & 0 & 0 \\ 1 & 1 & 1 & 0 & 0 \\ 0 & 1 & 1 & 1 & 0 \\ 0 & 0 & 2 & 0 & 1 \\ 0 & 0 & 0 & 1 & 2 \end{pmatrix}$$

has eigenvalues 3, 2.414, 1.414, -1.414, -1.414 which are among the ε-energy

levels of C_{70}. The core of C_{70} is the union of two cycles C_{20} and a mc is shown in Figure 5. The study of the NBO of C_{70} shows that the unique core may grow into distinct mcs present as subgraphs in the 70-vertex graph. These mcs may even be cospectral.

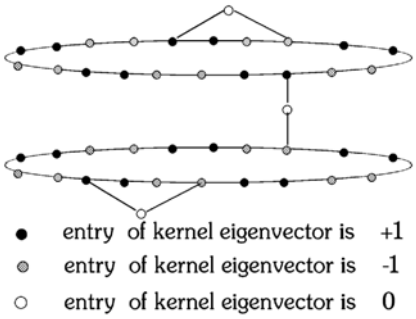

Figure 5

Although C_{70} has nullity one, it is not a mc but contains a mc. If as for C_{70}, the entries of the NBO $\boldsymbol{x}$ are +1, -1 and zero, then $\boldsymbol{Ax = 0}$ requires that even an uncharged C-centre has an uncharged atom adjacent to it. Thus at least two peripheral vertices are adjacent, a situation which is not allowed by mcs. The powerful theories of groups and matrices yield results interesting to chemists. For a highly symmetrical (vertex transitive) one orbit graph, there is equidistributivity of charge from the NBO among all the C-centres. This requires an even number of σ bonds for each C-atom, thus ruling out fullerenes. It follows that trivalent polyhedra with one orbit either have no NBOs or more than one. Two non-degenerate energy levels are sufficient for multi-orbits, so that a trivalent graph with one NBO is multi-orbit.

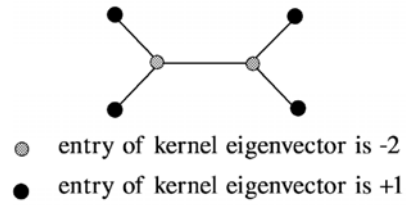

Figure 6

Two interesting examples of two-orbit nut graphs are the trivalent polyhedron and the smallest nut fullerene shown in Figure 2. The entries in the kernel eigenvector are -1 and 2 for both. This demands that the structure has the motif shown in Figure 6 as a factor and that it is made up of disjoint motifs that span the structure. Thus is spanned by two motifs whereas has 6 factors. More complex nut graphs have been identified but it is unlikely that they can be synthesised in the laboratory since to date all have adjacent pentagons.

References

Sciriha I., (1998a), On the Construction of Graphs of Nullity One, *Discrete Math.*, **181**, 193-211.

Sciriha I., (1998b), On the Rank of Graphs, in eds. Y. Alavi *et al*., The Eighth Quadrennial International Conference on Graph Theory, Combinatorics, Algorithms and Applications, Springer-Verlag, II 769-778.

Yoshida M., Fujita M., Fowler P. W., Kirby E. C., (1997), Non-bonding Orbitals in Graphite, Carbon Tubules, Toroids and Fullerenes, *J. Chem. Soc., Faraday Trans.*, **93** (6), 1037-1043.