

Fullerene graphs with more negative than positive eigenvalues: The exceptions that prove the rule of electron deficiency?

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In rare cases a neutral fullerene has an antibonding HOMO in simple Hückel theory, thus constituting a counter-example to the mathematical conjecture that in all fullerenes the number of positive eigenvalues of the adjacency matrix is greater than or equal to the number of negatives. The examples found here all have at least 628 carbon atoms and leave undisturbed the rule-of-thumb prediction of electron deficiency for the vast majority of fullerenes.

In the classical definition, a fullerene is an all-carbon molecule C_n in the form of a closed, trivalent, polyhedron with 12 pentagonal faces and all other faces hexagonal. Its graph has therefore n vertices (atoms), $3n/2$ edges (σ bonds), $(n/2 - 10)$ hexagonal and 12 pentagonal faces (rings). Extension to other face recipes and topologies to give non-classical fullerenes based on other trivalent polyhedra is possible.^{1–5} This paper deals with the numbers of bonding and antibonding π energy levels to be expected of a classical fullerene, and show that, contrary to mathematical conjecture and extensive numerical experience, a fullerene isomer may have an antibonding HOMO.

The prototypical fullerenes, C_{60} and C_{70} , behave chemically as mildly electron-deficient alkenes⁶ and are induced easily to accept electrons electrochemically.⁷ These properties have been linked to the presence of the 12 statutory five-membered rings demanded by Euler's theorem: as an isolated π system each pentagon would take up readily one extra electron, and in combination they produce six low-lying acceptor orbitals in typical fullerenes.⁸

Chemical observations about electron deficiency of a fullerene translate into mathematical statements about the eigenvalue spectrum of the adjacency matrix of its polyhedron.

Considered as a π system, a neutral fullerene has n electrons to dispose of amongst the $n\pi$ orbitals that result from the Hückel diagonalisation of its adjacency matrix. The orbital energies in simple Hückel theory are $\alpha + \lambda_i\beta$ where α and β are coulomb and resonance integrals, respectively and the $\{\lambda_i\}$ are the adjacency eigenvalues $+3 \geq \lambda_i > -3$. If the eigenvalues are arranged in descending order from $\lambda_1 = +3$, and the orbitals filled according to the Aufbau principle and Hund's rules, then various types of electronic configuration may be envisaged:^{9,10} when $\lambda_{n/2} = \lambda_{n/2+1}$, an open shell is predicted; when $\lambda_{n/2} \neq \lambda_{n/2+1}$, a configuration with all electrons paired is predicted, which may be (i) properly closed, where $\lambda_{n/2} > 0 \geq \lambda_{n/2+1}$; (ii) pseudo-closed, where $\lambda_{n/2} > \lambda_{n/2+1} > 0$; (iii) meta-closed, where $0 \geq \lambda_{n/2} > \lambda_{n/2+1}$.

Of the last three cases, (i) is the optimal situation for π bonding, with all electrons in bonding orbitals and a gap between occupied and empty levels; it is comparatively rare and is exemplified by the leapfrog and carbon-cylinder series of fullerenes.

Case (ii) is the commonest. It is less than optimal from the point of view of π bonding in the neutral, as some bonding capacity is 'wasted' and the structure may be subject to second-order Jahn–Teller distortion,¹¹ but the bonding nature

Table 1 Tetrahedral fullerenes C_n ($n \leq 1000$) with antibonding HOMO levels

n	i	j	k	l	G	λ_{H-1}	λ_H	λ_{H+1}
628	8	3	−1	2	T	0.232 688	−0.000 652	−0.087 510
652	5	7	−1	2	T	0.225 448	−0.001 298	−0.090 597
652	10	0	−1	2	T_d	0.225 190	−0.001 870	−0.093 831
664	9	2	−1	2	T	0.222 680	−0.002 321	−0.093 022
676	7	5	−1	2	T	0.221 662	−0.002 479	−0.086 916
700	8	4	−1	2	T	0.215 618	−0.003 591	−0.090 763
748	6	7	−1	2	T	0.207 816	−0.005 012	−0.085 679
760	7	6	−1	2	T	0.205 180	−0.005 496	−0.087 500
760	11	0	−1	2	T_d	0.207 624	−0.006 144	−0.082 242
772	10	2	−1	2	T	0.205 444	−0.006 423	−0.082 163
808	9	4	−1	2	T	0.199 330	−0.007 264	−0.081 857
820	11	1	−1	2	T	0.195 646	−0.007 444	−0.087 148
844	6	8	−1	2	T	0.192 748	−0.007 835	−0.083 777
844	10	3	−1	2	T	0.192 264	−0.008 022	−0.086 043
868	8	6	−1	2	T	0.190 298	−0.008 625	−0.081 179
892	9	5	−1	2	T	0.185 979	−0.009 097	−0.084 012
940	12	1	−1	2	T	0.182 270	−0.010 724	−0.077 779
952	7	8	−1	2	T	0.179 489	−0.010 358	−0.080 029
964	8	7	−1	2	T	0.177 570	−0.010 547	−0.081 362
964	11	3	−1	2	T	0.179 263	−0.011 079	−0.077 614
1000	13	0	−1	2	T_d	0.173 282	−0.011 287	−0.082 042

(i, j) and (k, l) are the two distinct vectors needed to build the net of the fullerene on the graphite lattice.⁹ G is the maximal point group: within this subclass, G is T_d for $j = 0$, T otherwise. λ_{H-1} , λ_H and λ_{H+1} are the frontier eigenvalues of the adjacency matrix, one below, at and one above the HOMO level, respectively. In all cases examined, λ_{H-1} and λ_H are triply degenerate and λ_{H+1} is doubly degenerate, so that $\lambda_{H-1} = \lambda_{n/2-3} = \lambda_{n/2-2} = \lambda_{n/2-1}$, $\lambda_H = \lambda_{n/2} = \lambda_{n/2+1} = \lambda_{n/2+2}$, $\lambda_{H+1} = \lambda_{n/2+3} = \lambda_{n/2+4}$.

of the LUMO is what might be expected from the presence of the pentagons in the framework, and implies electron deficiency, in that acquisition of extra electrons would lead to increased π stabilisation in simple one-electron theory. However, π stabilisation is only one factor in the overall stability of a fullerene, and, with a very few exceptions for open and properly closed shells, all of the several hundred thousand fullerene graphs with 100 or fewer vertices¹² turn out to be pseudo-closed, so that this can be said to be the typical electronic configuration for a fullerene.

In contrast, no meta-closed fullerene graphs have been identified to date.

Open-shell fullerenes may be further subdivided according to the value of the degenerate eigenvalue $\lambda_{n/2}$. With one exception, every open-shell fullerene in this range of nuclearity has a bonding HOMO; the exception is C_{20} , in which the HOMO and LUMO are exactly non-bonding.

Based on the extensive numerical evidence, therefore, it may seem reasonable to conjecture that every fullerene larger than C_{20} has a bonding HOMO, *i.e.* that

$$\lambda_{n/2} > 0 \quad (C1)$$

for all fullerenes with $n \geq 24$. Let the number of positive, zero and negative eigenvalues of a fullerene graph be n_+ , n_0 and n_- , respectively. Then, as non-alternants, fullerenes may have $n_+ \neq n_-$. The leapfrog fullerenes have $n_+ = n_- = n/2$, the carbon-cylinder closed-shell isomers for $n \neq 84$ have $n_+ = n/2$, $n_0 = 1$, $n_- = n/2 - 1$, pseudo-closed fullerenes have $n_+ > n/2 > n_-$, and so on. In these terms, a plausible conjecture would be that

$$n_+ \geq n_- \quad (C2)$$

for all fullerenes. Conjecture (C2) is one, amongst more than 20 others about fullerene graphs, that was actually made by the Graffiti computer program developed by Fajtlowicz.¹³ The present note points to a series of isomers that serve as counter-examples to both conjectures.

The counter-examples were found during the course of a systematic search of all fullerenes of tetrahedral ($T_+ \equiv T_d$, T_h , T , or, accidentally, I_h , I) symmetry in the range $20 \leq n \leq 1000$. Such fullerenes may be constructed by a modification⁹ of the Goldberg tessellation procedure¹⁴ for icosahedral members of this family of polyhedra. Isomers are constructed as nets drawn onto the triangulated plane, and for T_+ symmetry the net is that of a generalised twisted triangulated truncated tetrahedron made up of 12 scalene and four large and four small equilateral master triangles joining pentagon-centre sites. Two independent lattice vectors, parameterised by four integers i, j, k, l are required to specify the net. The total number of atoms is related to these parameters by

$$n = 4[(i^2 + ij + j^2) + (k^2 + kl + l^2) + 3(il - jk)]$$

A detailed account of the method for compiling at each n a list containing the complete set of independent solutions is given in the Appendix of ref. 9. From the four parameters the adjacency matrix of the fullerene can be constructed and so systematic Hückel calculations may be performed once the list of solutions is given. A similar approach was used in the search for a counter-example to the spiral conjecture which culmi-

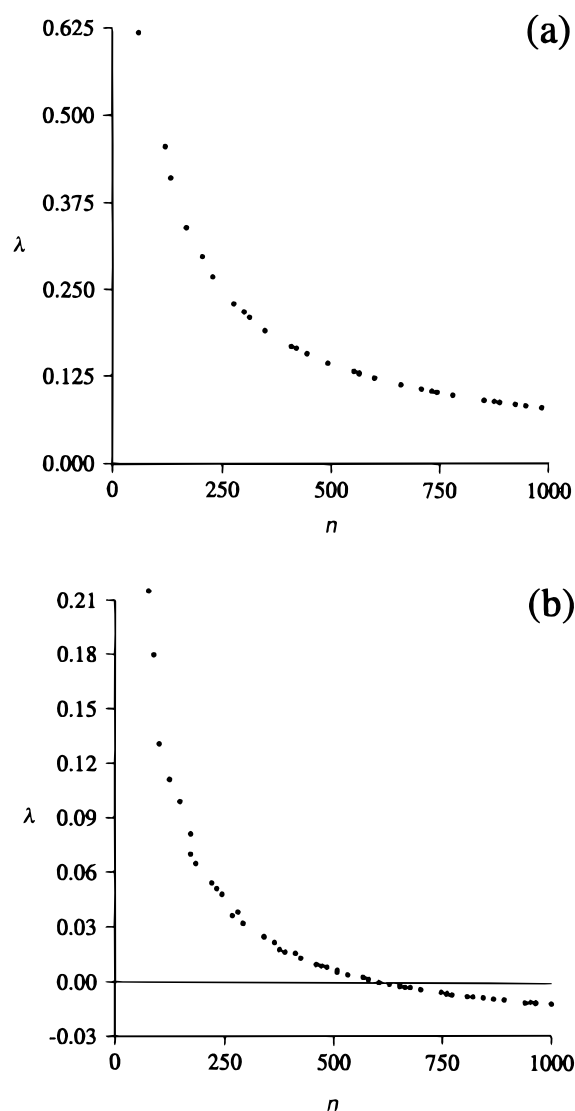
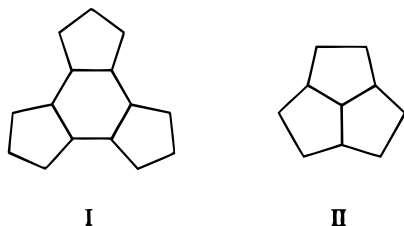


Fig. 1 Variation of the HOMO eigenvalue, λ , with fullerene nuclearity, n , for tetrahedral fullerenes C_n with signature $(i, j, -1, 2)$: (a) leapfrog structures, (b) non-leapfrogs.

nated in the identification of $T C_{380}$ as the smallest known fullerene without a spiral.¹⁵

The systematics of the eigenvalue spectra of the T_+ fullerenes may at some point be described more fully elsewhere. Of interest in the present context is the observation that for a particular sequence of i, j, k, l values the HOMO eigenvalue becomes less positive with increasing n and eventually passes over into negative values for large enough n .

The interesting sequence has $k = -1$, $l = 2$, which corresponds to those tetrahedral fullerenes that contain four copies of the three-pentagon motif I. T_+ fullerenes with four copies of I fall into two sub-classes. In the first ($i - j = 0 \pmod 3$), the fullerene C_n is a leapfrog¹⁶ transformation of a smaller T_+ cage $C_{n/3}$ that had four fused pentagon triples (motif II); as leapfrogs these C_n cages necessarily¹⁷ have properly closed π shells as neutral molecules, with positive HOMO and negative LUMO eigenvalues $\lambda_{n/2}$ and $\lambda_{n/2+1}$, respectively. In the second (with $i - j \neq 0 \pmod 3$), the fullerenes are not leapfrogs of smaller cages, and explicit calculation shows that they would have open π shells as neutral molecules, with two electrons in a triply degenerate HOMO at eigenvalue $\lambda_{n/2} = \lambda_{n/2+1} = \lambda_{n/2+2}$.

All members of both subclasses have isolated pentagons. The first leapfrog fullerene of signature $(i, j, -1, 2)$ is the isolated-pentagon C_{60} and has I_h symmetry. All others of

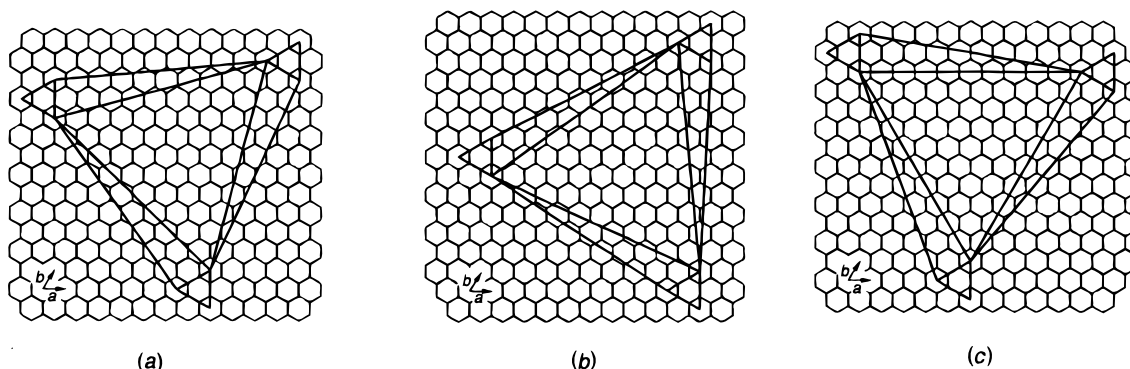


Fig. 2 Net diagrams for the three smallest tetrahedral fullerenes with antibonding HOMO levels. One panel of the master tetrahedron is shown in each case. Values of n and signatures (i, j, k, l) are (a) 628, 8, 3, $-1, 2$; (b) 652, 5, 7, $-1, 2$; (c) 652, 10, 0, $-1, 2$. The signature can be used in conjunction with the unit vectors \mathbf{a} and \mathbf{b} to build the whole net.⁹

both subclasses are of T or T_d symmetry in the absence of Jahn–Teller distortion.

Fig. 1 shows the variation of the eigenvalue $\lambda_{n/2}$ with n for the two classes of fullerenes with signature $(i, j, -1, 2)$. Whilst the behaviour of the leapfrog HOMO is normal, apparently tending asymptotically to zero or a small positive value, the HOMO for the non-leapfrog class has a negative apparent limit. Fig. 2 shows net diagrams for the 628- and the two isomeric 652-vertex fullerenes with antibonding HOMOs, and Table 1 lists all T_+ fullerenes C_n ($n \leq 1000$) for which a negative value of $\lambda_{n/2}$ is found. In each case there is a triple degeneracy

$$\lambda_{n/2} = \lambda_{n/2+1} = \lambda_{n/2+2}$$

so that the π configuration of the neutral cage would be open with an antibonding HOMO; all the examples have the signature $n_+ = n/2 - 1$, $n_0 = 0$, $n_- = n/2 + 1$ and hence $n_+ - n_- = -2$.

Conjectures (C1) and (C2) are therefore falsified. It is possible that smaller counter-examples might exist in some of the lower fullerene symmetry groups, but the examples given in Table 1 are the smallest in tetrahedral or icosahedral symmetries.

It may also be mentioned that the property $n_+ = n_- = n/2$ for a fullerene does not define it uniquely as a leapfrog. A series of so-called sporadic closed-shell fullerenes¹¹ is found for $n \geq 112$ for which a properly closed π shell with a very weakly antibonding LUMO is predicted by simple Hückel theory; as those cages so far investigated in detail have $n_0 = 0$, they too have $n_+ = n_- = n/2$.

What of the rule-of-thumb of electron deficiency of fullerenes? A mathematician would no doubt agree with Sherlock Holmes[†] that a rule with an exception is no rule at all. The existence of fullerenes that would gain π energy by loss of electrons is enough to falsify the proposed rule, at least within the framework of Hückel theory. A chemist will probably prefer to say that the exception proves the rule, taking the ‘loose rhetorical’[‡] sense of the legal maxim. The rarity, large size, probable reactivity and relative instability of the few fullerenes with antibonding HOMOs serve only to highlight the

almost universal electron deficiency of fullerenes as a class, which has its roots in the perturbation of the alternant graphitic lattice by the intervention of 12 pentagonal defects.

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[†] ‘I never make exceptions. An exception disproves the rule.’ A. Conan Doyle, *The Sign of Four*.

[‡] H. W. Fowler, *Modern English Usage*, Oxford, 2nd edn., 1965. Entry under ‘exception’.