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Distributed Curvature and Stability of Fullerenes

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Abstract

Energies of non-planar conjugated π systems are typically described qualitatively in terms of the balance of π stabilisation and the steric strain associated with geometric curvature. Curvature also has a purely graph-theoretical description: combinatorial curvature at a vertex of a polyhedral graph is defined as one minus half the vertex degree plus the sum of reciprocal sizes of the faces meeting at that vertex. Prisms and antiprisms have positive combinatorial vertex curvature at every vertex. Excluding these two infinite families, we call any other polyhedron with everywhere positive combinatorial curvature a PCC polyhedron. Cubic PCC polyhedra are initially common, but must eventually die out with increasing vertex count; the largest example constructed so far has 132 vertices. The fullerenes C_n have cubic polyhedral molecular graphs with n vertices, 12 pentagonal and $(n/2 - 10)$ hexagonal faces. We show that there are exactly 39 PCC fullerenes, all in the range $20 \leq n \leq 60$. In this range, there is only partial correlation between PCC status and stability as defined by minimum pentagon adjacency. The sum of vertex curvatures is 2 for any polyhedron; for fullerenes the sum of squared vertex curvatures is linearly related to the number of pentagon adjacencies and hence is a direct measure of relative stability of the lower ($n \leq 60$) fullerenes. For $n \geq 62$, non-PCC fullerenes with a minimum number of pentagon adjacencies minimise mean-square curvature. For $n \geq 70$, minimum mean-square curvature implies isolation of pentagons, which is the strongest indicator of stability for a bare fullerene.

Introduction

A quarter of a century after fullerenes were first obtained in synthetically useful quantities,^{1,2} the factors selecting the relatively few experimentally observed nuclearities and isomers¹⁻⁶ from the mass of mathematical possibilities⁷ for these molecules are still only partly known. It is clear that competing π -electronic and σ -steric factors are significant for the relative kinetic and thermodynamic stabilities of fullerene isomers.^{7,8} Exhaustive *ab initio* optimisation of *all* mathematically distinct structural isomers to determine their relative energies is a strategy that

soon runs into difficulties, given the rapid growth in isomer count,^{7,9-12} and input from more qualitative methods is therefore an essential aid to identification of general classes of stable fullerenes.^{7,13-15} Correlations for the lower fullerenes (C_n with $n \leq 60$)¹⁶ point to the number of pentagon adjacencies, N_p , as an important first estimator of stability. Each additional pentagon adjacency carries an energy penalty of *ca* 1 eV.^{16,17} Minimisation of N_p correlates well with low energy for the small fullerenes.⁷ For $n \geq 70$, where isolation of pentagons ($N_p = 0$) is possible, it appears that all experimentally characterised neutral fullerenes obey the isolated-pentagon rule (IPR).^{18,19} Separation of σ and π systems is not strictly preserved in curved systems such as fullerenes, but still gives a useful framework for discussing qualitative effects of curvature. Pentagon adjacencies are disfavoured on both π and σ criteria: they introduce energetically unfavourable ‘anti-aromatic’ 8π circuits and also concentrate local curvature, with resulting hybridisation strain, an effect that is captured in geometric models such as POAV.^{13,20} These various considerations give ample reason for the common practice of using N_p as a proxy for both steric strain and overall stability of fullerene isomers.

There is a close association between closed-shell π configurations and isolation of pentagons. Until recently, it was tacitly assumed that that isolation of pentagons was *necessary* if a fullerene was to have all its bonding π orbitals occupied in the Hückel model; occasional counterexamples to this belief have been found from C_{120} onwards, but they have LUMOs that are bonding by only tiny amounts.²¹ Stability rules for functionalised, endohedral or charged fullerene species are apparently more complicated.²²⁻²⁷ and, even in bare fullerenes, cross-cage interactions may destabilise some IPR isomers, as in the notorious case of the sole IPR isomer of the elusive C_{72} , where the bare-fullerene isomer of highest stability is believed to be one with a single pentagon adjacency²⁸⁻³⁰

The present investigation revisits the assumed general connection between stability and distribution of local curvature for fullerenes. We first reprise combinatorial definitions of curvature, Positive Combinatorial Curvature, and PCC polyhedra (PCCP). We identify the PCC fullerenes, and exhibit relationships between new mathematical and established chemical measures of steric strain in fullerenes and other cubic polyhedra. Finally, we place isolated-pentagon fullerenes in the context of combinatorial measures of curvature, giving a new interpretation of the IPR. The key point here is that IPR isomers have a precise characterisation in terms of curvature: they minimise mean-square combinatorial curvature.

Background

The mathematical definition of curvature at a vertex i of a polyhedral graph is^{31,32}

$$\varphi(i) = 1 - \frac{1}{2}d_i + \sum_{j=1}^{d_i} \frac{1}{f_{ij}} \quad (1)$$

where d_i is the degree of the vertex i , and f_{ij} is the size of the j th of the d_i faces incident on vertex i .

This combinatorial definition is motivated by the Euler theorem for spherical polyhedra:

$$n + f = m + 2, \quad (2)$$

where n , f and m are respectively the total numbers of vertices, faces and edges. Within definition (1), the *global* curvature, i.e., vertex curvature (1) summed over all vertices, is equal to the Euler characteristic, which is two for the sphere:

$$\sum_{i=1}^n \varphi(i) = \sum_{i=1}^n \left\{ 1 - \frac{1}{2}d_i + \sum_{j=1}^{d_i} \frac{1}{f_{ij}} \right\} = n - m + f = 2. \quad (3)$$

Here the summations of the three terms on the RHS of (1) follow from simple counting of vertices, from double counting of edges by adding up vertex degrees, and from noting that each face of size r contributes $1/r$ at each of its r vertices.

All spherical polyhedra have the same global total curvature, but what may distinguish them is the *distribution* of that curvature over the vertices. One natural limiting case is of polyhedra with everywhere positive combinatorial curvature, i.e., where every vertex of the polyhedron has a strictly positive value of $\varphi(i)$. The two infinite series of polyhedral graphs with everywhere positive combinatorial curvature are the prisms and antiprisms. It is usual to use the term *PCC polyhedra* to describe those polyhedra that have everywhere positive combinatorial curvature but are neither prisms nor antiprisms. The number of PCC polyhedra is finite³³ and it is of interest to determine their maximum order (i.e., vertex count). Devos and Mohar³³ asked for a largest PCC polyhedral graph and proved that it has at least 120 and at most 3444 vertices; Zhang³⁴ reduced the upper bound, showing that the maximum vertex count is less than 580. For the lower bound, Réti *et al.*³¹ gave an example of a PCC polyhedron with 138 vertices, which was further improved to 208 vertices by Nicholson and Sneddon,³⁵ both examples containing a mixture of degree-3 and degree-4 vertices. The best bounds currently available for largest PCC polyhedral graphs of general degree are therefore

$$208 \leq n_{max} < 580. \quad (4)$$

If we are interested in polyhedra that can model all-carbon hollow cages, vertex degree is limited to three (*cubic* polyhedra, also known as *trivalent* polyhedra). Ten combinations of sizes for faces meeting at a degree-3 vertex (the ten *vertex types*) lead to a combinatorially flat vertex (Table 1). Conversely, all vertex types that lead to positive curvature at a degree-3 vertex are listed in Table

2. A similar table for general degrees is given in Ref. 34. A cubic PCC polyhedron has have vertex types drawn from Table 2 (only).

Cubic polyhedra

Computer search of cubic polyhedral graphs in the range $4 \leq n \leq 28$ (generated with the plantri program³⁶) gives the counts listed in Table 3. Cubic PCC polyhedra are common for small n . The observed monotonic reduction in the percentage of PCC polyhedra for small n , $14 \leq n \leq 28$, is consistent with their inevitable eventual disappearance for large cubic polyhedra. The two smallest non-PCC cubic polyhedra have the 14-vertex graphs shown in Figure 1. A much larger cubic PCC polyhedron is the I_h -symmetric great rhombicosidodecahedron,³⁷ once suggested as the framework for a possible C_{120} all-carbon cage,³⁸ in which each of the 120 vertices occurs at the junction of a 4-gon, 6-gon and 10-gon, and hence contributes $1/60$ to the curvature. The lower bound³³ of 120 on n_{\max} for cubic polyhedra derived from this example was improved to 132 by Réti *et al.*³¹ who subdivided opposite edges of six of the square faces of the great rhombicosidodecahedron in a pattern that preserves T_h point-group symmetry. The resultant 132-vertex polyhedron has 36 square, 20 hexagonal and 12 11-sided faces, with vertex curvatures of $1/11$ for the twelve new vertices created by the subdivision, and $1/132$ for the rest. This gives the best published lower bound for cubic polyhedra.

Fullerene polyhedra

For the particular subset of cubic polyhedra comprised by the fullerenes, the situation is much simpler, as the only allowed face sizes are 5 and 6, which fact leads to an easy upper bound on n_{\max} for this class. Fullerene vertices occur at junctions of three faces according to the vertex types 555, 556, 566, or 666 (Figure 2), with counts of n_{555} , n_{556} , n_{566} , and n_{666} , and with decreasing vertex curvatures $\varphi(i) = 1/10$, $1/15$, $1/30$ and 0. Geometric measures of strain follow the same decreasing order, from the highly pyramidal triple-pentagon to the flat triple-hexagon sites. For example, the POAV (π -orbital axis vector) measure²⁰ calculated with nominal bond angles gives pyramidalisation angles 20.9° , 16.7° , 11.6° and 0° for the four cases. With two exceptions, all fullerenes contain a mixture of vertex types. The curvature sum rule $\sum_{i=1}^n \varphi(i) = 2$ derived from the Euler formula implies values of $n = 20$, 30, and 60 for the exceptional all-555, all-556 and all-566 fullerenes. Of these, the first and third cases are uniquely realised in C_{20} and $I_h C_{60}$. The second case is impossible: any hypothetical all-556 C_{30} would require each of its five hexagons to be surrounded by pentagons, but no isolated-hexagon fullerenes exist for $n > 28$.

An upper bound on the number of vertices of a PCC fullerene is easily established. Every fullerene vertex with positive curvature is in at least one pentagon. A fullerene has exactly 12 pentagonal faces, and hence at most 60 vertices in pentagons. Any fullerene with $n > 60$ vertices must have at least one vertex of type 666, and hence a PCC fullerene has at most 60 vertices. The bound is sharp: the experimentally observed icosahedral isomer of C_{60} is vertex-transitive, with all vertices therefore having equal curvature of $2/60 = 1/30$. The smallest possible fullerene is the vertex-transitive dodecahedron, with 20 vertices of type 555, hence curvature $1/10$ at all vertices. The range of existence of PCC fullerenes is therefore $20 \leq n_{\max} \leq 60$. There are 5770 fullerene isomers in this range,⁷ and straightforward exhaustive search yields a total of exactly 39 PCC fullerenes, as listed in Table 4 and Figure 3. The smallest non-PCC fullerene is $C_{32:5}$, with two 666 vertices (Figure 4). There are no PCC fullerenes on 46, 48, 52, 54, 56 or 58 vertices, and, of course, none on more than 60 vertices.

The PCC set forms a vanishingly small fraction of mathematically possible fullerene isomers, but, in view of the earlier discussion of curvature and steric strain, it is of interest to ask whether the PCC property correlates with stability. As noted above, an indicator of overall energetic stability for the lower fullerenes is N_p , the number of pentagon adjacencies.^{7,16-20} Counting vertices, vertices in pentagons, and pentagon-pentagon edges gives three relations amongst the counts of the four vertex types and the number of pentagon adjacencies for a general fullerene on n vertices:

$$n_{555} + n_{556} + n_{566} = n - n_{666}, \quad (5)$$

$$3n_{555} + 2n_{556} + n_{566} = 60, \quad (6)$$

$$3n_{555} + n_{556} = 2N_p. \quad (7)$$

Taking the numbers of pentagon adjacencies, N_p , and fused pentagon triples (n_{555}) as the known quantities, the remaining three vertex counts are determined:

$$n_{556} = 2N_p - 3n_{555}, \quad (8)$$

$$n_{566} = -4N_p + 3n_{555} + 60, \quad (9)$$

$$n_{666} = 2N_p - n_{555} - 60 + n. \quad (10)$$

The necessary and sufficient condition for a PCC fullerene is that $n_{666} = 0$, and hence (10) gives a relationship between measures of pentagon crowding in PCC fullerenes:

$$\text{(PCC)} \quad 2N_p - n_{555} = 60 - n. \quad (11)$$

Thus, for a PCC fullerene ($n_{666} = 0$), all vertex counts are fixed once N_p and n are given:

$$\text{(PCC)} \quad n_{555} = 2N_p - 60 + n, \quad (12)$$

$$\text{(PCC)} \quad n_{556} = -4N_p + 180 - 3n, \quad (13)$$

$$\text{(PCC)} \quad n_{566} = 2N_p - 120 + 3n. \quad (14)$$

As all terms on the RHS of each equation (12) – (14) are even, all three counts n_{555} , n_{556} and n_{566} take *even* values in a PCC fullerene, though not necessarily in a general fullerene.

Note that PCC status does not imply that N_p should be minimized for the given value of n . By (11), in a PCC fullerene, N_p may take values greater than the minimum if compensated by larger n_{555} . A non-minimum value of either of these two invariants for a fullerene isomer is taken as an indicator of instability,¹⁵ and so PCC fullerenes are not necessarily stable fullerenes, and since integer solutions of equation (11) do not lead to constructible PCC fullerenes for all vertex numbers between 20 and 60, stable fullerenes in this range are not necessarily PCC. However, inspection of Table 4 shows that at those values where a PCC fullerene exists: (a) at least one PCC isomer realises the minimum value of N_p for n -vertex fullerenes, and (b) the set of PCC isomers includes the most stable n -vertex isomer as predicted by tight-binding calculations.³⁹

Stability and general curvature measures

We have seen that PCC character and steric strain (as expressed in fullerenes by N_p) are only partially correlated (Table 4). The requirement that $\varphi(i) > 0$ for all vertices i does not uniquely pick out the fullerenes with minimum N_p , but some other measures based on combinatorial curvature have greater success.

Following Réti and Bitsay,⁴⁰ generalised curvature-like invariants with different exponents in the face-size term can be defined for arbitrary powers s : for vertex i , with degree d_i and where f_{ij} is the size of the j -th of the d_i incident faces,

$$\varphi_s(i) = 1 - \frac{1}{2}d_i + \sum_{j=1}^{d_i} f_{ij}^s, \quad (15)$$

where the usual combinatorial curvature defined in (1) corresponds to $s = -1$. In principle, Réti and Bitsay,⁴⁰ allow s to be an arbitrary real number, although in fact they use only integer values $s \geq -1$, as do we in what follows. Moments of the generalised curvatures (15) are then defined as

$$\mu_{s,q} = \frac{1}{n} \sum_{i=1}^n [\varphi_s(i)]^q. \quad (16)$$

In the remainder of this section we examine the behaviour of the moments $\mu_{s,q}$ when they are specialised to fullerenes. For a fullerene, the generalised curvatures for the vertex types 555, 556, 566, 666 are respectively $3 \times 5^s - 1/2$, $2 \times 5^s + 1 \times 6^s - 1/2$, $1 \times 5^s + 2 \times 6^s - 1/2$, and $3 \times 6^s - 1/2$. It is a peculiar feature of the definition of these ‘curvatures’ that all vertices of cubic polyhedra have positive generalised curvature for all integers $s > -1$; there are no ‘flat’ vertices in fullerenes or other cubic polyhedra for these values of s .

The first moments $\mu_{s,1}$ for any of the generalised curvatures depend at most on n and s , via the formula

$$n \mu_{s,1} = \sum_{i=1}^n \varphi_s(i) = \frac{1}{2} n (6^{s+1} - 1) - 60(6^s - 5^s). \quad (17)$$

derived using the curvatures given above for the four vertex types and the expressions (8) to (10) for the counts of each vertex type. Hence only the standard curvature ($s = -1$) has a constant sum for all fullerenes; for higher values of s , the total increases in linear fashion.

The second moment of the standard curvature, $\mu_{-1,2}$, detects pentagon adjacencies in fullerenes, since, from the definition (16),

$$n \mu_{-1,2} = \frac{1}{100} n_{555} + \frac{1}{225} n_{556} + \frac{1}{900} n_{566} + 0 n_{666}, \quad (18)$$

and substitution using (8) and (9) reduces this to

$$n \mu_{-1,2} = \sum_{i=1}^n [\varphi_{-1}(i)]^2 = \frac{1}{15} + \frac{1}{225} N_p. \quad (19)$$

The second moment $\mu_{-1,2}$ is a linear function of the number of pentagon adjacencies and hence correlates well with stability for lower fullerenes.¹⁷ All higher moments of $\varphi_{-1}(i)$ have a linear dependence on both n_{555} and N_p , with general expression

$$30^q n \mu_{-1,q} = 30^q \sum_{i=1}^n [\varphi_{-1}(i)]^q = \alpha n_{555} + \beta N_p + 60, \quad (20)$$

where $\alpha = 3(3^{q-1} - 2^q + 1)$ and $\beta = 4(2^{q-1} - 1)$. The third moment is given by

$$n \mu_{-1,3} = \frac{1}{4500} n_{555} + \frac{1}{2250} N_p + \frac{1}{450}, \quad (21)$$

Taken together, moments $\mu_{-1,2}$ and $\mu_{-1,3}$ (or $\mu_{-1,2}$ and any $\mu_{-1,q}$ with $q > 2$) carry the same information as n_{555} and N_p .

Curvature measures and the π -electronic energy spectrum

Finally, it is interesting to note that these relations for curvature moments lead to a direct connection between the *steric* property of curvature and the π *electronic* property of the graph spectrum. If the adjacency matrix has eigenvalues $\{\lambda_i\}$, then the q -th spectral moment, defined by $M_q = \sum_{i=1}^n \lambda_i^q$, counts self-returning walks of length q in the graph. For a fullerene C_n , the first seven spectral moments are functions of n only, but the eighth and ninth can distinguish isomers with different values of n_{555} and N_p , since a fused pentagon pair implies an 8-circuit and a fused triple implies a 9-circuit. Hence,⁴¹

$$M_8 = \sum_{i=1}^n \lambda_i^8 = 639 n - 1920 + 16 N_p, \quad (22)$$

and

$$M_9 = \sum_{i=1}^n \lambda_i^9 = 18360 + 18 n_{555} - 36 N_p. \quad (23)$$

All moments of the standard curvature $\varphi_{-1}(i)$ are therefore determined by the Hückel spectrum of the fullerene, e.g., from (20) and (22),

$$\sum_{i=1}^n \left[\varphi_{-1}(i) \right]^2 = \frac{1}{3600} M_8 - \frac{71}{400} n + \frac{3}{5}. \quad (24)$$

(Note that (11) and (23) together also give a characterisation of PCC fullerenes as those fullerenes for which M_9 is equal to $17280 + 18n$.)

From a chemical point of view, this direct relationship between an apparently ‘steric’ and an apparently ‘electronic’ property is intriguing. Pentagon adjacency has at least two obvious disadvantages in a bare carbon cage: it introduces an 8-circuit, which in conjugated-circuit models has an adverse effect on the π -resonance energy, and it leads to higher local curvature and hence bond-angle strain. It is perhaps not a coincidence that surviving molecular models from the early fullerene era often show structural failure at precisely such points of high curvature. The forms of equations (22) to (24) show that the steric and electronic effects of these destabilising motifs are linked, even at the purely graph-theoretical level. Local curvature is correlated with pyramidalisation angle, as we have seen, and (24) therefore implies a connection between the effect per pentagon adjacency on orbital energies and this measure of steric strain.

Non-conventional choices of exponents for the face sizes in the definition of curvature have the same information content for fullerenes since all moments $\mu_{s,q}$ are linear functions of n_{555} , n_{556} , n_{566} and n_{666} , and hence of the three variables n_{555} , N_p and n . For example, using $s = 1$ instead of $s = -1$ in the definition (15) would give

$$n \mu_{1,1} = \frac{35}{2} n - 60, \quad (25)$$

$$n \mu_{1,2} = \frac{1225}{4} n + 4 N_p - 2040 \quad (26)$$

$$n \mu_{1,3} = \frac{42875}{8} n + 198 N_p - 6n_{555} - 52035 \quad (27)$$

for fullerenes, and yet another way of relating curvature, strain and the Hückel spectrum. These simple relations can account for many initially surprising correlations. Réti et al.⁴⁰ plot various combinations of moments for fullerenes with 60 vertices, and show one intriguing case where the strange combination

$$\Lambda(1) = 100 \left\{ \left(1 + \sqrt{\mu_{1,2}} \right) / \left(1 + \sqrt{(\mu_{1,1})^2} \right) \right\} - 1 \quad (28)$$

gives an apparently perfect correlation with N_p ($R^2 = 1$ is reported). Power series expansion shows how this (in fact approximate) linearity for fixed n arises from (25) and (26).

Beyond the lower fullerenes

In the range $62 \leq n \leq 68$, full isolation of pentagons is not possible, but isomers that have at most pairing of pentagons and also minimise N_P can be constructed.⁷ These have $n_{555} = 0$ by definition and N_P values of 3 for C_{62} , and 2 for C_{64} to C_{68} . They also minimise n_{666} , the number of ‘flat’ vertices, and the mean square curvature as measured by either φ_{-1} or φ_1 . Interestingly, the most stable isomer of C_{62} is expected to be a non-classical cage with a single heptagonal and 13 pentagonal faces;⁴² this cage has three flat vertices of type 666 and hence is not PCC.

Generalised curvature measures: selection of fullerenes from cubic polyhedra

The generalised curvatures proposed by Réti and Bitay⁴⁰ can also be used to give a new view of a previous proposal for a function that successfully picks out fullerenes from the general mass of cubic polyhedra. Some years ago, Domene *et al.*⁴³ suggested that the well known Euler-based relation for cubic polyhedra

$$\sum_r (6-r)f_r = 12 \quad (29)$$

(where f_r is the number of faces of size r) might usefully be generalised to

$$F = \sum_r (6-r)^2 f_r. \quad (30)$$

as a way of selecting fullerenes and near-fullerenes from the mass of cubic polyhedral candidate carbon cages. It is straightforward to show that $F \geq 12$ for all cubic polyhedra. We have from (29) and (30)

$$F = 9f_3 + 4f_4 + f_5 + 0f_6 + f_7 + 4f_8 + 9f_9 + \dots \quad (31)$$

$$12 = 3f_3 + 2f_4 + f_5 + 0f_6 - f_7 - 2f_8 - 3f_9 + \dots \quad (32)$$

and hence

$$F - 12 = 6f_3 + 2f_4 + 2f_7 + 6f_8 + 12f_9 + \dots \quad (33)$$

As all $f_r \geq 0$, we have $F \geq 12$. In fact, $F = 12$ if and only if the polyhedron is a fullerene. The proof is easy. In one direction, for a fullerene only f_5 and f_6 may be non-zero, and $F = f_5 = 12$. In the other, if $F = 12$, (33) implies that all f_r other than f_5 and f_6 are zero, and we have a fullerene.

This old measure F is related to the recently defined generalised curvature with $s = 1$, since

$$\begin{aligned} F &= \sum_r (6-r)^2 f_r = \sum_r (36f_r - 12rf_r + r^2 f_r) \\ &= 36f - 24m + \sum_{i=1}^n \sum_{j=1}^{d_i} f_{ij} = 72 - \frac{35}{2}n + n \mu_{1,1}. \end{aligned} \quad (34)$$

Hence, the sum $\sum_{i=1}^n \varphi_1(i) = n \mu_{1,1}$ carries no more information than the previously defined F . Minimisation of either quantity picks out fullerenes from other cubic polyhedra, and finds near-fullerene polyhedra for the values of n where fullerenes are not possible.

Conclusions

The mathematical definitions of combinatorial curvature and allied quantities have been applied to make connections between curvature and stability in polyhedral candidates for conjugated carbon frameworks. One attractive idea is that, since curvature adds up over the polyhedral surface to a fixed sum, the thinnest possible distribution, in which every vertex has a positive contribution to the total, could have energetic advantages. It turns out that distribution of curvature as thinly as possible over the surface of a fullerene is not a particularly good recipe for stability. The small set of PCC fullerenes includes both stable and unstable isomers, and misses out many relatively stable lower fullerenes.

However, combinatorial curvature(s) can yield chemically significant correlations. Straightforward summation of the generalised vertex curvature φ_1 is sufficient to distinguish fullerenes from non-fullerenes through (34); this turns out to be equivalent to a calculation based on minimisation of mean departure of face size from the hexagonal ideal, which was the motivation behind the older F function.⁴³ More usefully, minimisation of the sum of squares of the standard combinatorial curvature φ_{-1} separates more stable from less stable lower fullerenes, as shown by (19), and also gives a guide to stable isomers in the problem intermediate region $62 \leq n \leq 68$ where pentagon isolation is not possible.

Curvature is also shown to be directly linked to models of π -electron energies through the relationship (24) between the same mean-square measure and the moment expansion for the eigenvalues of the adjacency matrix.

Finally, we note that consideration of combinatorial curvature and moments of curvature casts a sidelight on the isolated-pentagon rule. An IPR fullerene C_n has $n_{566} = 60$ and $n_{666} = n - 60$. Thus, by (19), the sum of squared curvature over all vertices of an IPR fullerene is $\frac{1}{15}$. In a well defined sense, all IPR fullerenes are closest to PCC character in that they have the maximum possible number of vertices with positive combinatorial curvature. Hence for fullerenes in general, minimisation of the mean square curvature is equivalent to application of the *minimum pentagon adjacency* rule.^{7,18}

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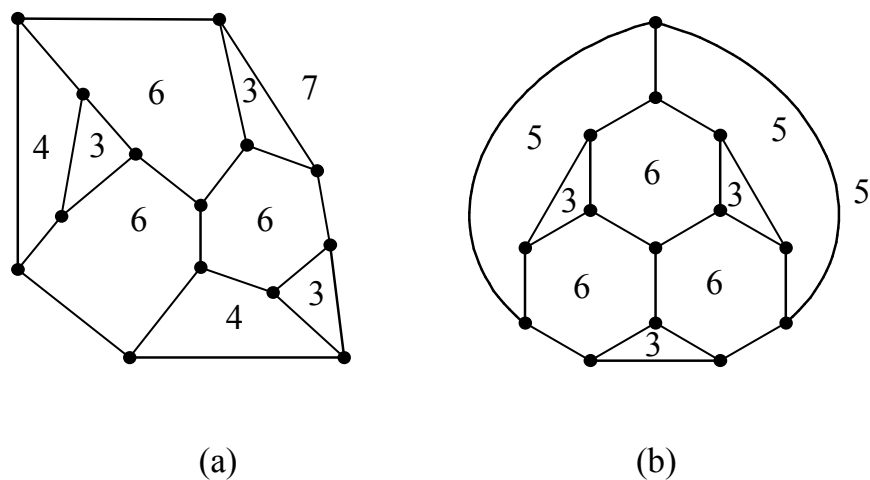


Figure 1. The two smallest cubic polyhedra that do not have everywhere positive combinatorial curvature, shown as Schlegel diagrams. In each case, the polyhedron has 13 vertices of positive and one of zero combinatorial curvature where three faces of size 6 meet.

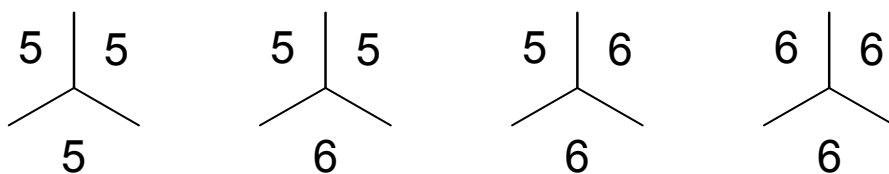


Figure 2. The four fullerene vertex types.

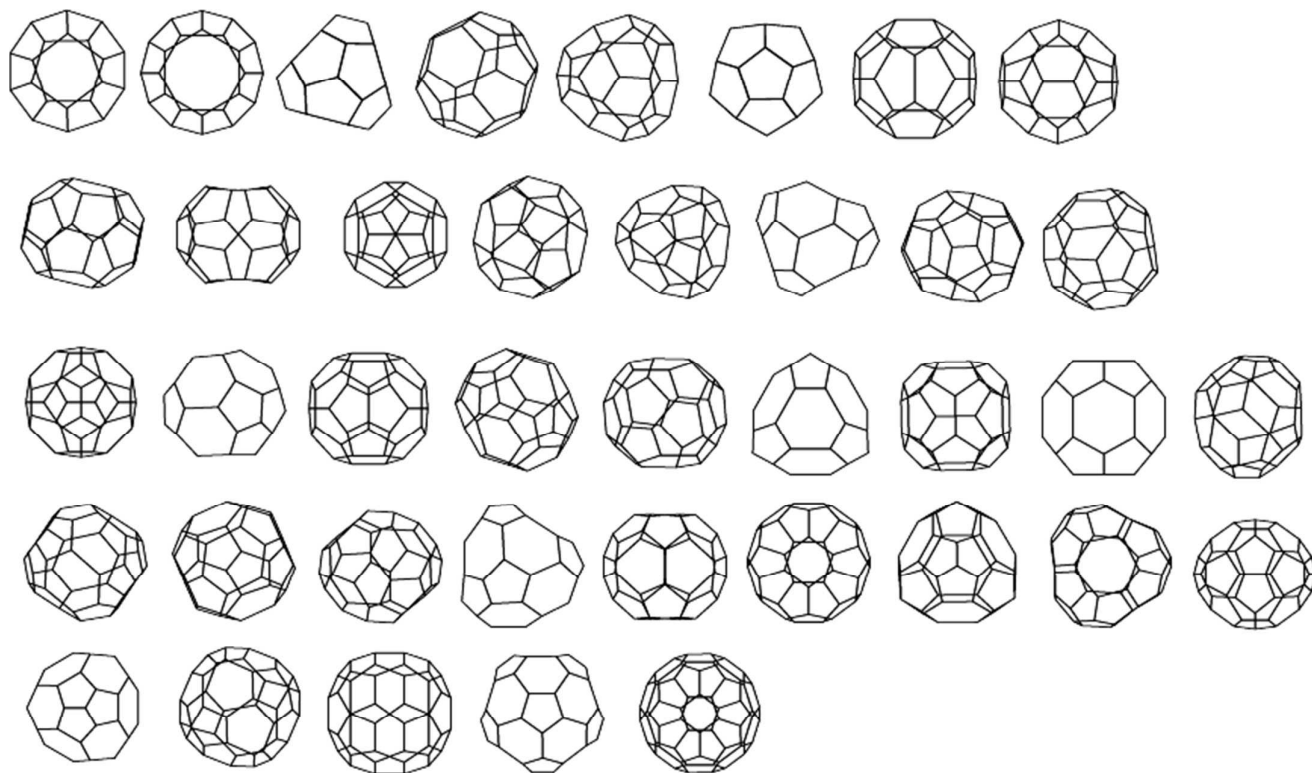


Figure 3. The 39 PCC fullerenes, listed in the order used in Table 4 and drawn to exhibit maximum symmetry.

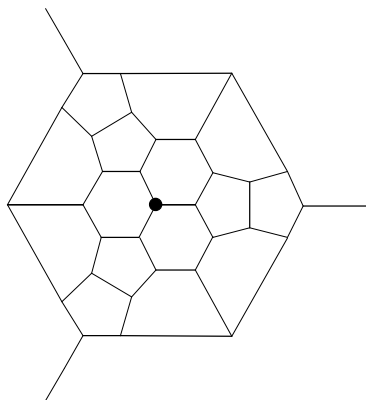


Figure 4. The smallest non-PCC fullerene, C₃₂ (isomer 5),⁷ has D_{3h} symmetry and antipodal 666 vertices (one at the centre and one at infinity in this Schlegel-like representation).

Table 1: The ten combinations of sizes $f_1 \leq f_2 \leq f_3$ for faces meeting at a vertex i of a cubic polyhedron that produce $\varphi(i) = 0$, i.e., a ‘flat’ vertex.

f_1	f_2	f_3
3	7	42
3	8	24
3	9	18
3	10	15
3	12	12
4	5	20
4	6	12
4	8	8
5	5	10
6	6	6

Table 2: The fifteen cases for sizes for faces meeting at a vertex i of a cubic polyhedron that produce positive curvature at the vertex. When the two smallest face sizes are fixed at f_1 and f_2 , the third has the range f_2 to f_{high} , where in some cases (denoted by an infinity sign in the table) f_{high} may be arbitrarily large (controlled only by the limit on the total number of vertices). Note that although the arithmetic condition $\varphi(i) > 0$ would apparently allow $f_1 = f_2 = 3$ and $f_{\text{high}} > 3$, the requirement that a polyhedron be 3-connected implies that the only cubic polyhedral graph with two or more adjacent triangular faces is the tetrahedron, and hence $f_{\text{high}} = 3$ here. Bounds on curvature for each possibility are given in the final column.

f_1	f_2	f_{high}	Curvature
3	3	3	$\varphi = \frac{1}{2}$
3	4	∞	$1/12 < \varphi \leq 1/3$
3	5	∞	$1/30 < \varphi \leq 7/30$
3	6	∞	$0 < \varphi \leq 1/6$
3	7	41	$1/1722 \leq \varphi \leq 5/42$
3	8	23	$1/522 \leq \varphi \leq 1/12$
3	9	17	$1/306 \leq \varphi \leq 1/18$
3	10	14	$1/210 \leq \varphi \leq 1/30$
3	11	13	$1/858 \leq \varphi \leq 1/66$
4	4	∞	$0 < \varphi \leq 1/4$
4	5	19	$1/380 \leq \varphi \leq 3/20$
4	6	11	$1/132 \leq \varphi \leq 1/12$
4	7	9	$1/252 \leq \varphi \leq 1/28$
5	5	9	$1/90 \leq \varphi \leq 1/10$
5	6	7	$1/105 \leq \varphi \leq 1/30$

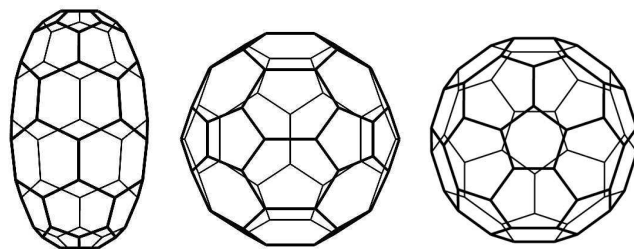
Table 3: The numbers of PCC cubic polyhedra with $n \leq 28$ vertices. The columns show n , the number of vertices and at each n , $N(\text{iso})$, the number of combinatorially distinct cubic polyhedra; $N(\text{PCC})$, the number of combinatorially distinct PCC cubic polyhedra, and $\% \text{PCC}$, the percentage of PCC polyhedra..

n	$N(\text{iso})$	$N(\text{PCC})$	$\% \text{PCC}$
4	1	1	100
6	1	0	0
8	2	1	50
10	10	9	90
12	14	13	93
14	50	47	94
16	233	209	91
18	1249	1068	86
20	7595	6183	81
22	49565	38700	78
24	339721	253349	75
26	1507869	1080509	72
28	17490240	12120318	69

Table 4: The 39 PCC fullerenes. The number of vertices is n , and p is the position in the spiral order of fullerene isomers.⁷ Numbers of pentagon adjacencies (N_p), fused pentagon triples (n_{555}) and remaining vertex types (n_{556} and n_{566}) are listed. A fullerene has $n/2-10$ hexagonal faces. A PCC fullerene has $n_{666} = 0$. An asterisk against N_p or n_{555} indicates the minimum for the given n ; against the code $n:p$ it indicates the isomer with lowest total energy in calculations of Zhang et al.³⁹

$n:p$	N_p	n_{555}	n_{556}	n_{566}	Face Spiral
20:1*	30*	20*	0	0	1 2 3 4 5 6 7 8 9 10 11 12
24:1*	24*	12*	12	0	1 2 3 4 5 7 8 10 11 12 13 14
26:1*	21*	8*	18	0	1 2 3 4 5 7 9 11 12 13 14 15
28:2	18*	4*	24	0	1 2 3 5 7 9 10 11 12 13 14 15
28:1*	20	8	16	4	1 2 3 4 5 7 10 12 13 14 15 16
30:3*	17*	4*	22	4	1 2 3 4 7 10 11 12 13 14 15 16
30:2	18	6	18	6	1 2 3 4 5 7 11 13 14 15 16 17
30:1	20	10	10	10	1 2 3 4 5 6 12 13 14 15 16 17
32:6*	15*	2*	24	6	1 2 3 5 7 9 10 12 14 16 17 18
32:4	16	4	20	8	1 2 3 4 7 10 11 12 14 15 17 18
32:1	17	6	16	10	1 2 3 4 5 7 12 14 15 16 17 18
32:2	18	8	12	12	1 2 3 4 5 8 12 13 15 16 17 18
32:3	18	8	12	12	1 2 3 4 5 9 12 13 14 16 17 18
34:5*	14*	2*	22	10	1 2 3 5 7 10 11 13 15 16 18 19
34:2	15	4	18	12	1 2 3 4 5 12 13 14 15 16 17 18
34:4	15	4	18	12	1 2 3 4 7 11 12 13 15 16 17 19
36:14*	12*	0*	24	12	1 2 4 7 9 10 12 13 14 16 18 20
36:15	12*	0*	24	12	1 2 4 8 9 10 12 13 14 15 18 20
36:9	13	2	20	14	1 2 3 4 11 12 13 14 15 16 17 18
36:11	13	2	20	14	1 2 3 5 7 10 12 15 16 18 19 20
36:12	13	2	20	14	1 2 3 5 10 11 13 14 15 16 17 19
36:6	14	4	16	16	1 2 3 4 7 10 12 15 17 18 19 20
36:8	14	4	16	16	1 2 3 4 7 11 12 15 16 18 19 20
36:13	15	6	12	18	1 2 3 6 10 11 12 14 15 16 18 20
38:17*	11*	0*	22	16	1 2 4 7 9 10 12 13 15 18 20 21
38:10	12	2	18	18	1 2 3 5 7 10 12 15 17 19 20 21
38:13	12	2	18	18	1 2 3 5 10 11 13 15 16 19 20 21
40:38*	10*	0*	20	20	1 2 4 7 9 11 13 15 17 19 20 22
40:39	10*	0*	20	20	1 2 4 7 9 11 13 15 18 19 21 22
40:29	11	2	16	22	1 2 3 5 10 13 14 15 16 18 19 22
40:31	11	2	16	22	1 2 3 5 10 13 15 16 18 19 20 22
40:40	12	4	12	24	1 2 6 9 10 12 13 15 16 18 20 22
42:45*	9*	0*	18	24	1 2 4 7 9 12 13 16 18 19 21 22
44:75*	8*	0*	16	28	1 2 4 7 9 12 13 16 18 21 23 24
44:89	8*	0*	16	28	1 2 4 9 12 13 14 16 17 19 22 24
44:55	9	2	12	30	1 2 3 5 10 13 15 16 19 21 23 24
44:72	9	2	12	30	1 2 3 10 11 13 14 16 17 20 22 24
50:271*	5*	0*	10	40	1 2 9 10 12 14 15 17 20 22 24 26
60:1812*	0*	0*	0	60	1 7 9 11 13 15 18 20 22 24 26 32

Graphical Abstract



$$\begin{array}{ccccccc} \mu_{-1,2} & 7/45 & > & 17/225 & > & 1/15 \\ N_p & 20 & > & 2 & > & 0 \end{array}$$

Combinatorial measures of curvature can be used to distinguish stable from unstable fullerenes, and fullerenes from the mass of cubic polyhedral cages.