Spiral Codes and Goldberg Representations of Icosahedral Fullerenes and Octahedral Analogues

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An icosahedral fullerene may be considered as a tessellation of the sphere specified by an ordered pair of integers, or as a tightly wound spiral of faces. Explicit analytical relations for interconverting the two representations are given, enabling the canonical spiral code to be constructed for an icosahedral fullerene of any size. Analogous relations hold for the octahedral square + hexagon polyhedra that have been mentioned as possible candidates for boron−nitride "fullerenes".

INTRODUCTION

A useful method of generating and representing fullerene polyhedra, now enshrined in IUPAC nomenclature for the molecules,[1] is based on face spirals.[2] With some[3−8] manageable[9] exceptions, a fullerene C_n, which by definition has exactly 12 pentagonal and $(n/2 - 10)$ hexagonal rings, can be peeled as a continuous, tightly wound spiral strip of faces. This is made into a canonical code by taking the lexicographically minimal such sequence, regarded as an $(n/2 + 2)$-digit integer made up of 5's and 6's for the two face types. The adjacency information implicit in the spiral code can be used to reconstruct the graph, embed it in three-dimensional space, assign point-group symmetry and model electronic structure, vibrational and NMR spectra, relative energies, interconversion and growth mechanisms of fullerene isomers,[3] and even predict patterns of chemical reactivity.[10] It is known that the original spiral algorithm is complete for, among other subsets, all 5- and 6-fold symmetric fullerenes[11] and so gives a code for all those belonging to icosahedral point groups.

The aim of the present paper is to show that this versatile code can be constructed explicitly for any member of the icosahedral class, given only its Goldberg[3,12,13] parameters. Spirals for octahedrally symmetric polyhedra,[12] which are not themselves classical fullerenes but are described by the same Goldberg parameters, are obtained as useful byproducts.

THE GOLDBERG CONSTRUCTION

Any fullerene can be regarded as a cubic (≡three-regular, ≡trivalent) covering of the sphere by combinatorial pentagons and hexagons and can therefore be generated from its *net* drawn on the lattice of face centers of the graphite sheet or vertices of its dual, the triangulation of the plane. The vertices of the net correspond to pentagon centers in the fullerene, where folding of the graphite sheet introduces the defect by cutting out a 60° wedge of the plane. This construction is particularly simple in icosahedral symmetry, where the whole net is fixed in both size and orientation by choice of a single lattice vector, or equivalently an ordered pair of integer components[3,12,13] (Figure 1).

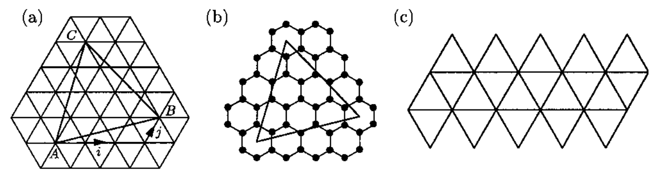

Figure 1. Goldberg[12,13] construction of icosahedral fullerenes: (a) a master equilateral triangle superimposed on the regular triangular lattice is specified by the vector *AB* formed by taking *i* steps in a straight line, turning through 60°, and taking *j* more steps; (b) the master triangle *ABC* includes $(i^2 + ij + j^2)$ vertices (carbon atoms) of the dual graphite lattice; (c) 20 copies of the triangle *ABC* make up the net of the master icosahedron whose vertices are fullerene pentagon centers and which, by dualization, contains $20(i^2 + ij + j^2)$ atoms as a fullerene.

From this *Goldberg construction*, it follows that an icosahedral fullerene C_n exists for all distinct integer solutions (i, j) of

$$n = 20(i^2 + ij + j^2) \qquad (1)$$

Solutions are made canonical by imposing the conditions $i \geq j$, $i + j > 0$, and the pair of integers so obtained is an encoding of a wealth of symmetry, geometric and electronic structural information about the fullerene. For $i = j$ or $j = 0$, the net folds to yield an I_h polyhedron, but otherwise the point-group symmetry will be I. When $i - j$ is divisible by three, the fullerene is a *leapfrog*[14] of a smaller structure and has a properly closed-shell π configuration, with bonding HOMO and antibonding LUMO within the simple Hückel model.[15] Leapfrog fullerenes support fully symmetric Clar and Fries valence-bond structures and have low-lying acceptor levels spanning the translational and rotational representations in the point group.[16] When $i - j$ is *not* divisible by three, the fullerene includes a single dodecahedral orbit of 20 atoms and in Hückel theory would have an open-shell π configuration with two electrons in a 4-fold degenerate level.

The new result here is that the integers i and j also determine in a straightforward way the spiral code for the fullerene.

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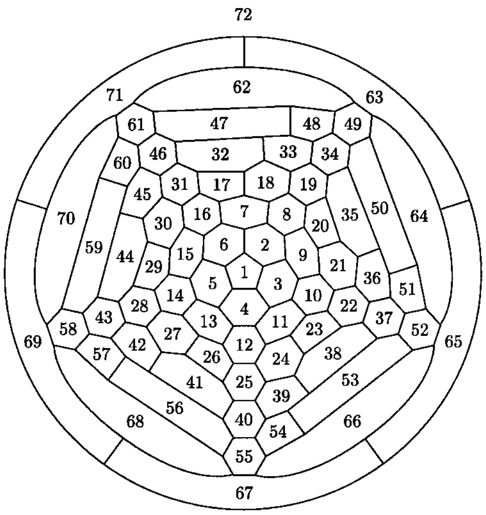

Figure 2. Schlegel diagram of C_{140}, the smallest chiral icosahedral fullerene. The numbers indicate the sequence of faces in the canonical spiral code. Note especially the presence of "hidden" faces 62, 64, 66, 68, and 70 (see text).

THE CANONICAL SPIRAL CODE

Every icosahedral fullerene has a spiral that starts at one pentagon and finishes at its antipodal partner after winding around the connecting C_5 axis.[11] In fact, the trivial symmetry of the spiral dictates that if there is one, there will be 120 (60) copies for an I_h (I) fullerene. An example is shown in Figure 2, where the sequence of visited faces is marked on the Schlegel diagram for the I fullerene with $n = 140$ and Goldberg parameters $(i, j) = (2, 1)$. As the centers of the 12 pentagons of an I or I_h fullerene lie at the vertices of a regular icosahedron, this special spiral can be described as a path on a sphere: it starts out from the North Pole and winds down to a tropical circle that includes the next five pentagons, through the all-hexagon equatorial region, then into the second tropic, finally reaching the South Pole at the last pentagon. Although a given fullerene may have others, this mandatory spiral is clearly lexicographically minimal in I_h cases, as it starts with a 5 and is then fully determined—all 10 combinations of second and third faces 2 and 3 being equivalent. For an I fullerene there is a choice for face 3, as the route may make a left or right turn from the second face, but if both possibilities lead to a legal spiral, one will reach the second pentagon sooner and will be canonical.

From the geographical analogy it is also clear that the spiral takes the form

$$5(6)^{\alpha}(5(6)^{\beta})^4 5(6)^{\gamma}(5(6)^{\delta})^4 5(6)^{\epsilon}5 \qquad (2)$$

where the exponent notation denotes repetition of a bracketed sequence. Clearly, $\beta = \delta$, from the equal spacing of pentagons within the circuits of five in the northern and southern hemispheres.

The connection between the spiral parameters α to ϵ and the Goldberg parameters (i, j) is established by induction based on an analysis of the way the spiral is built up.[11] From the point of view of the initial pentagon at the North Pole, the local environment is a conical array of concentric rings of hexagons (Figure 3). Successive circumscribing layers of 5, 10, 15, ... hexagons grow out uniformly from the pentagon until the first layer that includes (five) pentagons is encountered. The spiral completes a whole number, $i + j - 1$, of

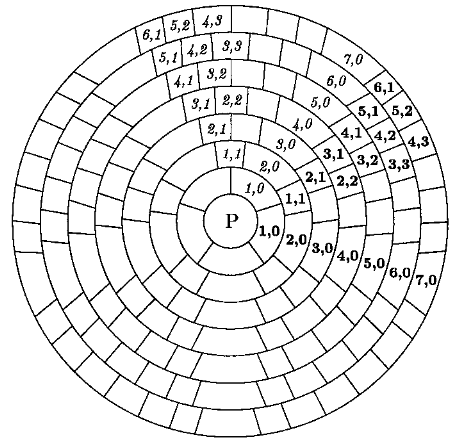

Figure 3. Goldberg parameters and the cap structure of an icosahedral fullerene (i, j). Starting from a central pentagon, the spiral continues through concentric rings of hexagons until one containing the second (italic), third (bold), and next three pentagons is reached. Beyond this ring, the adjacencies of conical graphite are perturbed. The first three pentagons are the apexes *A*, *B*, *C* of the master triangle of Figure 1a.

hexagon circuits and enters the pentagon-containing layer, either $j - 1$ (for $j \neq 0$) or $i - 1$ (for $j = 0$) faces before the first pentagon of that layer. Thus the formula for α is

$$\alpha = \frac{5}{2}(i + j)^2 - \frac{5}{2}i - \frac{3}{2}j - 1 + i\delta_{j0} \qquad (3)$$

where δ_{j0} is the Kronecker symbol, equal to 1 when $j = 0$ and 0 otherwise.

In the second section of the spiral, $(5(6)^{\beta})^4$, the pentagon plus β succeeding hexagons span one-fifth of the $(i + j)$th circumscribing ring, and thus

$$\beta = \delta = i + j - 1 \qquad (4)$$

Beyond the first layer containing pentagons, the exact appearance of the Schlegel diagram depends on the placing of these pentagons, as discussed in section 3 of ref 11. With due account taken of "hidden faces" (i.e., faces that appear between two whole layers in the final conical section of the spiral, such as 62, 64, 66, 68, and 70 for C_{140} shown in Figure 2), expressions for the remaining parameters of the spiral are easily found to be

$$\gamma = (5i + 1)(i - 1) + j(5i - 3) \qquad (5)$$

and

$$\epsilon = \frac{5}{2}i^2 + \frac{15}{2}j^2 - \frac{3}{2}i - \frac{7}{2}j - i\delta_{j0} \qquad (6)$$

A simple check on these expressions is that they fulfill the sum rule for the total number of hexagonal faces:

$$\alpha + 4\beta + \gamma + 4\delta + \epsilon = \frac{n}{2} - 10 = 10(i^2 + ij + j^2 - 1) \quad (7)$$

The canonical spiral is thus specified completely by the values of i and j. Table 1 lists the spiral parameters and spiral counts for I and I_h fullerenes with $n < 1000$ vertices.

The two smallest icosahedral fullerenes C_{20} and C_{60} share two interesting characteristics. First, both have palindromic canonical spirals, i.e., with $\alpha = \epsilon$ as well as $\beta = \delta$. The analytical expressions in eqs 3 and 6 show that this property

Table 1. Canonical Spirals and Spiral Counts for Icosahedral Fullerenes C_n ($n < 1000$)[a]

i	j	n	α	β	γ	δ	ϵ	N_t
1	0	20	0	0	0	0	0	120
1	1	60	5	1	2	1	5	360
2	0	80	6	1	11	1	5	360
2	1	140	15	2	18	2	11	840
3	0	180	17	2	32	2	15	480
2	2	240	31	3	25	3	30	1080
3	1	260	30	3	44	3	22	1560
4	0	320	33	3	63	3	30	960
3	2	380	51	4	56	4	41	2160
4	1	420	50	4	80	4	38	2100
5	0	500	54	4	104	4	50	1560
3	3	540	77	5	68	5	75	1440
4	2	560	76	5	97	5	57	3000
5	1	620	75	5	126	5	59	2760
6	0	720	80	5	155	5	75	1920
4	3	740	107	6	114	6	91	3720
5	2	780	106	6	148	6	78	3720
6	1	860	105	6	182	6	85	3840
4	4	960	143	7	131	7	140	2880
5	3	980	142	7	170	7	112	4800
7	0	980	111	6	216	6	105	2640

[a] (i, j) are the Goldberg parameters, and α to ϵ define the spiral as in eq 2. N_t is the total number of successful spiral starts; the number of distinct spirals is found by dividing by the order of the group. Note that C_{20}, C_{60}, C_{140}, and C_{260} are omnispiral.

is not shared by any other icosahedral fullerene: many fullerenes have palindromic spirals, but no other icosahedral fullerene has a palindromic *canonical* spiral. The second property shared by C_{20} and C_{60} is that of omnispirality. A fullerene C_n has $6n$ putative spiral starts, as each may begin with the triple of faces around any vertex taken in any order. In the four omnispiral icosahedral fullerenes C_{20}, C_{60}, C_{140}, and C_{260} (Table 1), all such starts lead to legal spiral codes, of which $n/20$ (I_h) or $n/10$ (I) are distinct. Uniquely, for C_{20} all $6n$ are canonical. As the table shows, omnispiral fullerenes may be chiral or achiral.

In the subset of I fullerenes, it turns out that both distinct spiral starts from a pentagon lead to legal codes. The noncanonical member of the pair is easily shown by induction to be

$$5(6)^{\alpha'}(5(6)^{\beta})^4 5(6)^{\gamma'}(5(6)^{\delta})^4 5(6)^{\epsilon'}5 \tag{8}$$

with

$$\alpha' = \alpha + i - j \tag{9}$$

$$\gamma' = \gamma - 2j \tag{10}$$

$$\epsilon' = \epsilon - i + 3j \tag{11}$$

Finally, the Goldberg construction can also be applied to find trivalent polyhedra based on the octahedron and tetrahedron, where all nonhexagonal faces are then respectively square (and six in number) or triangular (and four in number). A given (i, j) pair specifies a graph with

$$n = 4r/(6 - r)(i^2 + ij + j^2) \tag{12}$$

vertices and

$$f_6 = n/2 - 2r/(6 - r) \tag{13}$$

hexagons for $r = 3, 4, 5$.

For $r = 4$, an extension of the reasoning in ref 11 shows that all the square + hexagon polyhedra with axes of 4-fold rotational symmetry have at least one spiral, and a version of the inductive argument used for fullerenes gives the canonical spiral of the O and O_h members of this series as

$$4(6)^{\alpha''}(4(6)^{\beta})^3 4(6)^{\epsilon''}4 \tag{14}$$

with β as before, and

$$\alpha'' = 2(i + j)^2 - 2i - j - 1 + i\delta_{j0} \tag{15}$$

$$\epsilon'' = 2i^2 + 2j^2 - i - 2j - i\delta_{j0} \tag{16}$$

These octahedral structures are alternants and have been considered as plausible candidates for BN analogues of the fullerenes.[17,18] Any classical fullerene must have at least six homonuclear bonds when decorated with $n/2$ B and $n/2$ N atoms. The octahedral structures offer one solution to the problem,[17−20] but the energetic balance between chemical and steric frustration may still favor the classical structures.

When $r = 3$ the spiral construction fails early, at the 36-vertex T_d polyhedron $(i, j) = (3, 0)$.[8] Exploration of all Goldberg triangle + hexagon tetrahedral polyhedra with up to 2000 vertices shows that most have no spiral. This is perhaps not surprising, given the existence of four triangular "traps" in these graphs.[7] All those in the range with spirals have Goldberg parameters (i, i) or $(i, i - 1)$, apart from the two small cases (2, 0) and (3, 1). The spiral construction is therefore not a natural one for these polyhedra. For $r = 4$ and 5, however, the parameter pair (i, j) is all that is needed to find the spiral and derive a wealth of chemical information.

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