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Breaking of Icosahedral Symmetry: C_{60} to C_{70}

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Abstract

We describe the existence and structure of large fullerenes in terms of symmetry breaking of the C_{60} molecule. Specifically, we describe the existence of C_{70} in terms of breaking of the icosahedral symmetry of C_{60} by the insertion into its middle of an additional H_2 decagon. The surface of C_{70} is formed by 12 regular pentagons and 25 regular hexagons. All 105 edges of C_{70} are of the same length. It should be noted that the structure of the molecules is described in exact coordinates relative to the non-orthogonal icosahedral bases. This symmetry breaking process can be readily applied, and could account for and describe other larger cage cluster fullerene molecules, as well as more complex higher structures such as nanotubes.

Introduction

Fullerenes are molecules composed entirely of carbon, taking the form of a cage or tube. The family of cage cluster fullerenes is also commonly referred to as buckyballs. The most stable and commonly occurring member of this family is the molecule C_{60}, which consists of 60 carbon atoms arranged in a structure of truncated icosahedrons, made of hexagons and pentagons, with carbon atoms at the corners of each hexagon and a bond along each edge (creating the well-known soccer ball structure - Fig. 1). This structure has been investigated and determined experimentally in both the solid state [1] and in the gas phase [2]. The second most commonly occurring cage structure fullerene is the molecule C_{70}, composed of 70 carbon atoms. Electron diffraction and theoretical studies have verified that this molecule possesses a "rugby ball" structure with a pinching of the waist as the bond lengths follow a simple pattern determined by their relationship to the 5- and 6-membered rings [2,3] - Fig. 2.

Much effort has been directed to answer why the fullerenes C_{60} and C_{70} are so stable and which other higher fullerenes with different sizes and shapes can be formed as stable entities [2,4–6]. With respect to the C_{60} molecule, its stability and its position as the most commonly occurring buckyball can be attributed, at least in part, to its high degree of symmetry [7]. In addition to C_{60} and C_{70}, many other larger fullerenes have been observed, while theoretical calculations have indicated that all fullerenes with an even number of carbon atoms can exist [8]. Significant amounts of work have gone towards elucidating the structure of these higher fullerenes. For example, the structures of C_{84}, as well as C_{60} and C_{70} have been identified through spectroscopy studies [9–12], and by chemical derivatization [13,14], while others have been proposed theoretically [15].

In the present work we consider the existence and structure of higher fullerenes as a symmetry breaking problem, starting from the C_{60} molecule which possesses the highest degree of symmetry. Guided by the common practices in particle physics, we consider the description specifically of the C_{70} molecule as a symmetry breaking problem, with the additional twist that the usual branching rule for the icosahedral symmetry group H_3 to the dihedral symmetry group H_2 is enhanced by adding to it one more decagonal term. The group H_2 is the lowest noncrystallographic finite reflection group. We consider the icosahedral symmetry group H_3 of order 120 of certain carbon molecules as the exact symmetry that is broken to its subgroup H_2 or order 10 dihedral symmetries. We also suggest within this framework how higher order structures such as nanotubes may naturally arise. This provides a framework for understanding of the observed even carbon number rule and for predicting higher order structures which may be assembled.

The paper is unique in providing exact coordinates of the vertices of the fullerenes thus eliminating any additional numbering conventions used elsewhere [16]. This opens the possibility of defining special functions of 3 variables generated by the vertices (see Example 3), to study their possible orthogonality, and conceivably even the corresponding orthogonal polynomials defined by the fullerene structures.

Icosahedral bases in $\mathbb{R}^3$

In order to get exact coordinates of polytopes related to icosahedral symmetry, one has to use bases in the real 3-dimensional space $\mathbb{R}^3$ that reflects the symmetry, namely the simple roots α_1, α_2, α_3 of the icosahedral group and their duals [17]. The geometric relations of the vectors in the α-basis are described by the matrix of scalar products
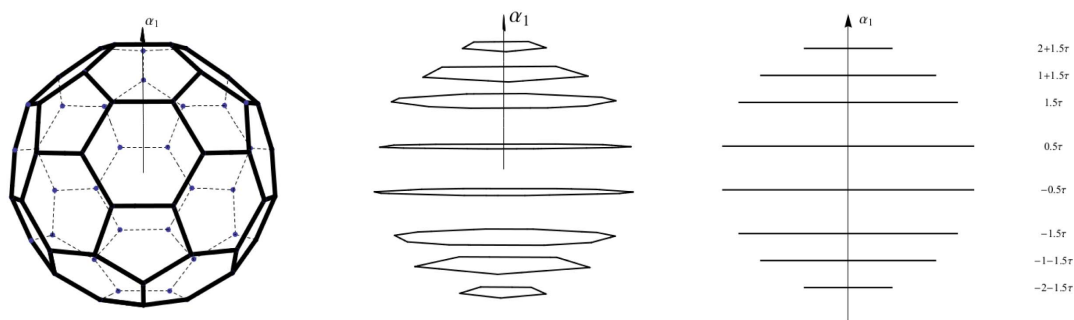
Figure 1. The structure of the C_{60} molecule. (a) The polytope C_{60} is formed by 60 vertices equidistant from its center. Its surface consists of 12 regular pentagons and 20 regular hexagons. All 90 edges are of the same length. (b) The C_{60} polytope viewed in the direction almost parallel to the plane spanned by ω_2 and ω_3, which makes the H_2 orbits (pentagons and decagons) easy to identify. (c) The C_{60} polytope viewed in the direction parallel to the H_2 plane spanned by ω_2 and ω_3. Surface edges of C_{60} are omitted in (b) and (c). Horizontal segments are projections of the H_2 orbits. The number in a row shows the α_1 coordinate of the H_2 orbit. The vertical direction is that of α_1.
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$$C = (C_{jk}) = (\langle \alpha_j, \alpha_k \rangle) = \begin{pmatrix} 2 & -1 & 0 \\ -1 & 2 & -\tau \\ 0 & -\tau & 2 \end{pmatrix}, \quad \tau = \frac{1}{2}(1+\sqrt{5}). \quad (1)$$

The dual or reciprical ω-basis is defined by

$$\langle \alpha_j, \omega_k \rangle = \delta_{jk}, \quad j,k = 1,2,3. \quad (2)$$

The inverse matrix to C is calculated as follows,

$$C^{-1} = (\langle \omega_j, \omega_k \rangle) = \frac{1}{\det C} \begin{pmatrix} 3-\tau & 2 & \tau \\ 2 & 4 & 2\tau \\ \tau & 2\tau & 3 \end{pmatrix}$$
$$= \frac{1}{2} \begin{pmatrix} 2+\tau & 2+2\tau & 1+2\tau \\ 2+2\tau & 4+4\tau & 2+4\tau \\ 1+2\tau & 2+4\tau & 3+3\tau \end{pmatrix}. \quad (3)$$

It follows from Eq.(2) that the α- and ω-bases are related by the matrix equality $\alpha = C\omega$, and $\omega = C^{-1}\alpha$. Explicitly we have

$$\alpha_1 = 2\omega_1 - \omega_2 \qquad \omega_1 = (1 + \frac{1}{2}\tau)\alpha_1 + (1+\tau)\alpha_2 + (\frac{1}{2}+\tau)\alpha_3$$
$$\alpha_2 = -\omega_1 + 2\omega_2 - \tau\omega_3 \quad \omega_2 = (1+\tau)\alpha_1 + (2+2\tau)\alpha_2 + (1+2\tau)\alpha_3$$
$$\alpha_3 = -\tau\omega_2 + 2\omega_3 \qquad \omega_3 = (\frac{1}{2}+\tau)\alpha_1 + (1+2\tau)\alpha_2 + (\frac{3}{2}+\frac{3}{2}\tau)\alpha_3 \quad (4)$$

For the ω-basis of H_2 we choose ω_2 and ω_3 of H_3. By Eq.(2), the direction orthogonal to the plane spanned by ω_2 and ω_3, is that of α_1.

The reflections r_1, r_2, and r_3 in $\mathbb{R}^3$ generate the icosahedral group of order 120. Their action on any vector $x \in \mathbb{R}^3$ is given by

$$r_k x = x - \langle x, \alpha_k \rangle \alpha_k, \quad k = 1,2,3, \quad x \in \mathbb{R}^3. \quad (5)$$

In particular, $r_k 0 = 0$ and $r_k \alpha_k = -\alpha_k$, and also $r_k \omega_j = \omega_j - \delta_{jk} \alpha_k$.

C_{60}

Repeated application of the three reflections to the seed point $(1,1,0) = \omega_1 + \omega_2$ of C_{60}, according to Eq.(5), yields the 60 vertices of C_{60} in the ω-basis:

Figure 2. The structure of the C_{70} molecule. (a) The polytope C_{70} has 105 edges and 12 pentagonal and 25 hexagonal faces. (b) C_{70} viewed from a direction almost parallel to the plane of ω_2 and ω_3. (c) The H_2 structure of C_{70} viewed from a direction parallel to the plane of ω_2 and ω_3. The column of numbers shows the α_1-coordinate of the H_2 orbits of vertices of C_{70}. The inserted decagon has the α_1-coordinate equal to 0. Surface edges are omitted in (b) and (c).
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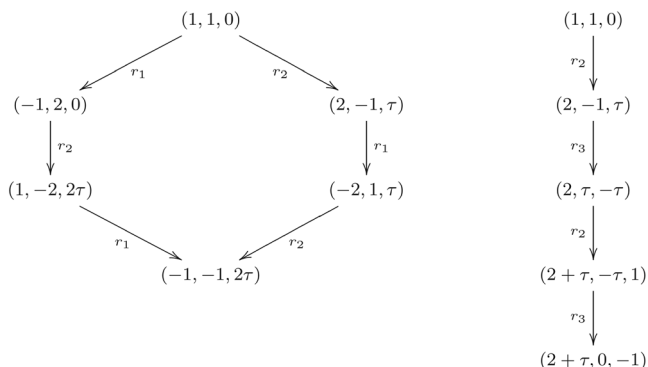|				
$\boxed{\pm(1,1,0)}$	$\boxed{\pm(-1,2,0)}$	$\pm(2,-1,\tau)$	$\pm(1,-2,2\tau)$	$\boxed{\pm(-2,1,\tau)}$
$\pm(-1,-1,2\tau)$	$\pm(-2,2+\tau,-\tau)$	$\pm(2+\tau,-\tau,1)$	$\pm(1,2\tau,-2\tau)$	$\pm(-1,1+2\tau,-2\tau)$
$\pm(\tau,-2-\tau,1+2\tau)$	$\boxed{\pm(-2-\tau,2,1)}$	$\boxed{\pm(2+\tau,0,-1)}$	$\pm(1+2\tau,-2\tau,2)$	$\pm(2\tau,-1-2\tau,2+\tau)$
$\pm(-\tau,-2,1+2\tau)$	$\pm(\tau,2\tau,-1-2\tau)$	$\pm(-2-\tau,2+\tau,-1)$	$\boxed{\pm(-1-2\tau,1,2)}$	$\boxed{\pm(1+2\tau,0,-2)}$
$\pm(-2\tau,-1,2+\tau)$	$\pm(2\tau,\tau,-2-\tau)$	$\pm(-\tau,3\tau,-1-2\tau)$	$\pm(3\tau,-2\tau,1)$	$\pm(0,-2-\tau,3\tau)$
$\pm(-1-2\tau,1+2\tau,-2)$	$\pm(-2\tau,3\tau,-2-\tau)$	$\boxed{\pm(3\tau,-\tau,-1)}$	$\pm(0,1+2\tau,-3\tau)$	$\pm(2,\tau,-\tau)$

(6)

The points in which both the second and third coordinates are non-negative are the dominant points of the H_2 orbits (pentagons and decagons). Boxed points in which the second and third coordinates are positive dominate the decagons. The boxed points, which have 0 as their second or third coordinate, are the dominant points of H_2 pentagons.

Example 1

The hexagon faces of C_{60} come up naturally from the classification of its 2-faces [18] as one orbit of the seed hexagon. The symmetry group of the seed hexagon is generated by the reflections r_1 and r_2. Similarly the pentagon faces of C_{60} come up naturally from the classification of its 2-faces as one orbit of the seed pentagon. The symmetry group of the seed pentagon is generated by the reflections r_2 and r_3.

Let us illustrate the construction of the seed hexagon and of the seed pentagon, starting from the dominant point of C_{60}:

(hexagon diagram)
$(1,1,0)$ →r_1 $(-1,2,0)$, →r_2 $(2,-1,\tau)$
$(-1,2,0)$ →r_2 $(1,-2,2\tau)$
$(2,-1,\tau)$ →r_1 $(-2,1,\tau)$
$(1,-2,2\tau)$ →r_1 $(-1,-1,2\tau)$ ←r_2 $(-2,1,\tau)$

(pentagon diagram)
$(1,1,0)$ →r_2 $(2,-1,\tau)$ →r_3 $(2,\tau,-\tau)$ →r_2 $(2+\tau,-\tau,1)$ →r_3 $(2+\tau,0,-1)$

The vertices of a hexagon and pentagon of the surface of C_{60} adjacent to the dominant point of C_{60} are shown here in the ω-basis.

Example 2

The three simple roots, α_1, α_2, α_3, of the icosahedral group form a special basis in $\mathbb{R}^3$. Their relative angles and lengths are read from the matrix C (Eq.(1)). Those values define the icosahedral group H_3. Therefore they take special positions also in C_{60}.

Let us show that (i) the straight line containing $\pm\alpha_1$ passes through the center of opposite pentagons on the surface of C_{60}. To show it, one needs to take the hexagon generated by r_1 and r_2, and add its vertices to verify that coordinates of the sum are zero in the plane spanned by ω_2 and ω_3.

$$\alpha_1 \sim (1,1,0)+(2,-1,\tau)+(2,\tau,-\tau)$$
$$+(2+\tau,-\tau,1)+(2+\tau,0,-1)=(9+2\tau,0,0)$$

(ii) The straight line containing $\pm\alpha_2$ passes through the center of opposite edges on the surface of C_{60} that separate two hexagons.

$$\alpha_2 \sim (1,1,0)+(-1,2,0)=(0,3,0)$$

(iii) The straight line containing $\pm\alpha_3$ passes through the center of opposite hexagons on the surface of C_{60}.

$$\alpha_3 \sim (1,1,0)+(-1,2,0)+(2,-1,\tau)$$
$$+(1,-2,2\tau)+(-2,1,\tau)+(-1,-1,2\tau)=(0,0,6\tau)$$

Example 3

In this example let us view each point λ of Eq.(6) as an exponential function, $\lambda \to e^{2\pi i\langle\lambda,x\rangle}$, where $x \in \mathbb{R}^3$, and then add up all 60 such exponentials. Call such a sum $C(\lambda,x)$. Since each λ comes with both signs in Eq.(6), we have $C(\lambda,x)$ equal to the sum of 30 cosines $\cos(2\pi\langle\lambda,x\rangle)$. Properties of $C(\lambda,x)$ deserves further study. The function 'remembers' the structure of C_{60} in the entire 3-space and shows intricate interferences of the cosines with a clear maximum when x is at the origin of R^3. On the spherical surface of the C_{60} shell, the function $C(\lambda,x)$ depends periodically on the radius of C_{60}.

C_{70}

The general idea, we pursue here for the modification $C_{60} \to C_{70}$, is first to decompose C_{60} into the sum of 8 orbits of H_2, then to insert another H_2 decagon into its middle. In Fig. 3 it can be seen that the upper and lower half of C_{60} are connected by a ring of 5 hexagons. Replacing that ring by a larger one that is
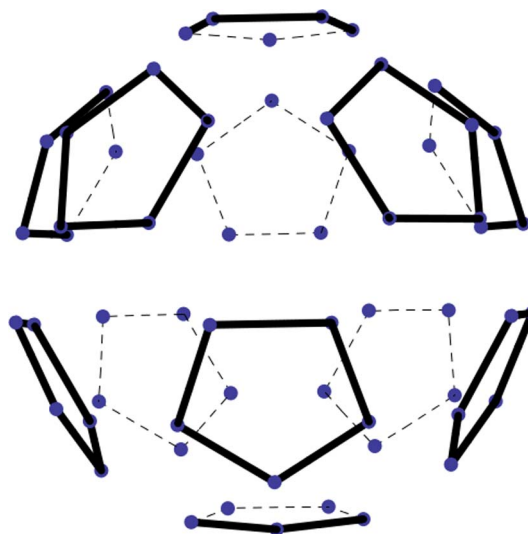

Figure 3. The 12 pentagons of the surface of C_{60} are shown without the hexagons. The 60 dots are the vertices of C_{60}. The polytope is oriented as in Fig. 1.
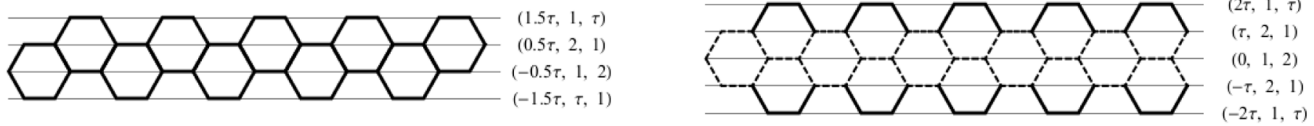doi:10.1371/journal.pone.0084079.g003

Figure 4. A ring of hexagons from the middle of the surface of C_{60} and C_{70} unwrapped into the plane. Horizontal lines indicate positions of the four H_2 decagons in C_{60} and five H_2 decagons in C_{70}. The dominant points identify the H_2 decagons relative to the basis $\{\alpha_1, \omega_2, \omega_3\}$. Dashed lines are the boundaries of the ring of five inserted hexagons.
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made out of 10 hexagons (see Fig. 4), one gets the polytope C_{70}. It is shown in Fig. 2 in three different views analogous to the presentation of C_{60} in Fig. 1.

Symmetry breaking

The H_3 symmetry gets broken when the additional decagon is inserted into the middle of its decomposition into H_2-orbits. The H_2 symmetry remains exact.

$$C_{70}: \qquad 5+5+10+10+\boxed{10}+10+10+5+5, \qquad (7)$$

$\boxed{(\pm(2+2\tau),1,0)}$	$(\pm(2+2\tau),-1,\tau)$	$(\pm(2+2\tau),\tau,-\tau)$	$(\pm(2+2\tau),-\tau,1)$	$(\pm(2+2\tau),0,-1)$
$\boxed{(\pm(1+2\tau),2,0)}$	$(\pm(1+2\tau),-2,2\tau)$	$(\pm(1+2\tau),2\tau,-2\tau)$	$(\pm(1+2\tau),-2\tau,2)$	$(\pm(1+2\tau),0,-2)$
$\boxed{(\pm2\tau,1,\tau)}$	$(\pm2\tau,-1,2\tau)$	$(\pm2\tau,2+\tau,-\tau)$	$(\pm2\tau,1+2\tau,-2\tau)$	$(\pm2\tau,-2-\tau,1+2\tau)$
$(\pm2\tau,-\tau,-1)$	$(\pm2\tau,-2\tau,1)$	$(\pm2\tau,\tau,-2-\tau)$	$(\pm2\tau,2\tau,-1-2\tau)$	$(\pm2\tau,-1-2\tau,2+\tau)$
$\boxed{(\pm\tau,2,1)}$	$(\pm\tau,-2,1+2\tau)$	$(\pm\tau,2+\tau,-1)$	$(\pm\tau,3\tau,-1-2\tau)$	$(\pm\tau,-2-\tau,3\tau)$
$(\pm\tau,-1,-2)$	$(\pm\tau,-1-2\tau,2)$	$(\pm\tau,1,-2-\tau)$	$(\pm\tau,1+2\tau,-3\tau)$	$(\pm\tau,-3\tau,2+\tau)$
$\boxed{(0,1,2)}$	$(0,1+2\tau,-2)$	$(0,-1,2+\tau)$	$(0,-1-2\tau,3\tau)$	$(0,3\tau,-2-\tau)$
$(0,-2,-1)$	$(0,2,-1-2\tau)$	$(0,-2-\tau,1)$	$(0,-3\tau,1+2\tau)$	$(0,2+\tau,-3\tau)$

$$(8)$$

The enlarged structure is C_{70} which has lost the spherical symmetry of C_{60}. It has 70 vertices, and in the middle of it there are 5 consecutive parallel decagons centered at the α_1-axis.

There are still two questions to be answered however before one can call it C_{70}. The answers to these questions must assure that the exterior surface of C_{70} is composed of pentagons and hexagons of the same size as it is for C_{60}. From Fig. 3 we see that the upper and lower halves of C_{60} are bound by a ring of hexagons. (i) What are the distances between the five decagons, and (ii) what is the orientation of the inserted decagon in the ω_2, ω_3 plane?

The answers to the questions are found by making two observations from Fig. 4, where the additional decagon is placed in the middle, so that its α_1 coordinate is zero.

(i) In order to keep the distances between the five decagons of C_{70} equal to what they are in C_{60}, we have to shift correspondingly the upper and the lower halves of what used to be C_{60}. Their α_1 coordinates are increased and decreased by 0.5τ respectively.

(ii) The first row of hexagons in Fig. 4 (right). belonged to the upper half of C_{60}. The second row in Fig. 4 (right) is situated as was the second row in Fig. 4 (left). There it was the top row for the lower part of C_{60}. In Fig. 4 (right) it is the inserted middle row of C_{70}. The third row of hexagons in Fig.4 (right) is the top row of the lower half of C_{70}. The third row of hexagons in Fig. 4 (right) is the top row of the

lower half of C_{60}. However, its position matches the hexagons of the first row. Hence the dominant points of the first and third rows differ by the sign of the first coordinate only.

Summarizing, below are the exact coordinate of the 70 vertices of C_{70} in the basis $\{\alpha_1, \omega_2, \omega_3\}$:

According to [19] the carbon polytope C_{70} is slimmer in the middle. Such data can be matched by choosing a smaller radius for the decagon $(0,1,2)$ in Eq.(8) in the middle of C_{70}. Also the edges leading to that decagon may have to be changed correspondingly. The boxed points in Eq.(8) are the dominant points.

In the present work we have described the existence of the molecule C_{70} in terms of a symmetry breaking process of the insertion of an H_2 decagon (or equivalently inserting a ring of surface hexagons), thus breaking the icosahedral symmetry of C_{60}. There is nothing to prevent however, the insertion of three or more rings of hexagons into the C_{60} structure creating ones that are larger and more complex. Thus the mechanism enables the creation from C_{60}, the fullerenes C_{70}, C_{80}, C_{90} and so on. From the continuation of the process of the insertion of hexagon rings in this fashion, it can also readily be seen that it enables the creation of nanotubes of any length.

Author Contributions

Conceived and designed the experiments: MB JP MS. Performed the experiments: MB JP MS. Analyzed the data: MB JP MS. Wrote the paper: MB JP MS.

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