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A symmetrized Hückel analysis of carbon cages of I_h point group symmetry

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Some new aspects of qualitative molecular-orbital theory are developed within the context of group theory and a symmetrized Hückel approximation. Conclusions concerning the eigenvalue sums for sets of eigenfunctions of the same symmetries, the occurrence of repetitions of symmetry-adapted projections and the relations between eigenvalues of Γ_g and Γ_u symmetries are exemplified using the C_{120} cage structure of I_h point symmetry. The implications of the orbit-by-orbit approach are outlined for larger clusters.

0. Introduction

Node counting, within the molecular-orbital approximation, is well known as a technique for the identification of the qualitative ordering of molecular-orbital energies for structures giving rise to constant overlap integrals within the LCAO approximation [1,14,16,23]. The carbon cages, of which the fullerenes form the prime example [10,19], provide a variety of structures for which the constant overlap condition is not too bad an approximation and facilitate, in this report, the development of some novel details of qualitative molecular-orbital theory within a Hückel approximation. Because of the form of the regular representation of the I_h point group, the C_{120} cage structure is used as the example upon which these ideas are demonstrated. Larger clusters can be built from the allowed geometric orbits of the I_h group and this type of construction and the procedure for larger clusters is illustrated for the C_{320} cage.

1. Eigenvalue sums

Consider P to be a graph associated with a point symmetry group G realised in a regular geometric orbit, such as the I_{120} cage and A to be a matrix, such as the Hückel-type adjacency matrix of such a structure, which commutes with G in its action on the vector space with basis the set of vertices of G. This vector space can

be identified with a complex group algebra *CG*, whose basis is the set of elements of G, so that A can be regarded as acting on the elements of G. If G can be regarded to act by left (or right) multiplication on *CG*, then it turns out that A corresponds to right (or left) multiplication on *CG* by $g_1 + g_2 + \cdots + g_r$ for some distinct elements $g_1, g_2, \ldots, g_r$ of the group. This conclusion follows from a more general result about semi-simple algebras and arbitrary operators b which commute with the regular action, but it can be validated also from inspection of the geometry of the edges of the graph and the relating of this geometry to the action of A on the group elements.

In the identification of the regular orbit of vertices with the elements of G, an arbitrary vertex ν_0 can be chosen to be the identity element of G corresponding to $+1$. Then for any g_i, causing the transformation of ν_0 to ν_i, the vertex ν_i is associated with the group element g_i. It is easy to see that the $g_1 + g_2 + \cdots + g_r$, whose left multiplication produces the same action as A, is made of the group elements which move ν_0 to its adjacent vertices $\nu_1, \nu_2, \ldots, \nu_r$. If an element g_i appears then so does its inverse g_i^{-1} (not necessarily distinct from g_i itself), since, if g_1 is the symmetry transformation from ν_0 to the adjacent vertex ν_1, then g_1^{-1} transforms the pair (ν_1, ν_0) to (ν_0, ν_{-1}). The number r is the degree of the vertices of the graph P.

The possibility of a weighted adjacency matrix being required to represent some difference in properties of the paths from vertex to vertex would mean that A would be represented by $\alpha_1 g_1 + \alpha_2 g_2 + \cdots + \alpha_r g_r$ with α, the weight associated with the edge from ν_0 to ν_i, and $\alpha_i = \alpha_j$ if $g_i^{-1} = g_j$.

It follows that the trace of A on the component of the regular space of irreducible character Γ of the group is

$$\Gamma(1)\big(\Gamma(g_1) + \Gamma(g_2) + \cdots + \Gamma(g_r)\big)$$

or, in the weighted case,

$$\Gamma(1)\big(\alpha_1\Gamma(g_1) + \alpha_2\Gamma(g_2) + \cdots + \alpha_r\Gamma(g_r)\big).$$

Hence the sum of the eigenvalues corresponding to the distinct types of Γ-spaces (ignoring the multiplicity of the dimension of each Γ-space) is

$$\Gamma(g_1) + \Gamma(g_2) + \cdots + \Gamma(g_r)$$

or

$$\alpha_1\Gamma(g_1) + \alpha_2\Gamma(g_2) + \cdots + \alpha_r\Gamma(g_r).$$

For the cases of some common molecular graphs the sums found for unweighted and weighted cases are given in table 1. Many graphs can be made on a regular orbit by varying the edges, but usually there is, at least, a common one associated with some regular or semi-regular polyhedral structure.

The foregoing analysis can be extended to a graph wherein the vertices form an orbit of a normal subgroup, H, of the given symmetry group G. The matrix A is still represented by left multiplication on the group algebra *CH* by $h_1 + h_2 + \cdots + h_r$

Table 1
The results of a group theory analysis for some point groups giving the eigenvalue sums for the cases of unweighted and weighted adjacency matrices of trivalent polyhedra spanning the regular orbit.

Group	Graph	g_i	Γ	Eigenvalue sum	Weighted sum
I_h	120 cage	α, β, γ	A_g	3	$\alpha+\beta+\gamma$
	(great rhombicosidodecahedron or	σ, σ, σ	A_u	-3	$-\alpha-\beta-\gamma$
	truncated icosidodecahedron [5])		T_{1u}	3	$\alpha+\beta+\gamma$
			T_{1g}	-3	$-\alpha-\beta-\gamma$
			T_{2u}	3	$-\alpha-\beta-\gamma$
			T_{2g}	-3	$-\alpha-\beta-\gamma$
			H_u	-3	$-\alpha-\beta-\gamma$
			H_g	3	$\alpha+\beta+\gamma$
			G_u	0	0
			G_g	0	0
T_d	24 cage	α, β, γ	A_1	3	$\alpha+\beta+\gamma$
	(truncated octahedron [5])	σ_d, σ_d, σ_d	A_2	-3	$-\alpha-\beta-\gamma$
			E	0	0
			T_1	-3	$-\alpha-\beta-\gamma$
			T_2	3	$\alpha+\beta+\gamma$
T_h	24 cage	α, α, β	A_g	3	$2\alpha+\beta$
	(truncated cube [5])	C_3, C_3^2, σ_d	A_u	1	$2\alpha-\beta$
			$E_g[\Gamma]$	0	$-\alpha+\beta$
			$[\Gamma^*]$	0	$-\alpha+\beta$
			$E_u[\Gamma]$	-2	$-\alpha-\beta$
			$[\Gamma^*]$	-2	$-\alpha-\beta$
			T_g	-1	$-\beta$
			T_u	1	β
O_h	48 cage	α, β, γ	A_{1g}	3	$\alpha+\beta+\gamma$
	(great rhombicuboctahedron or	σ_d, σ_d, σ_h	A_{1u}	-3	$-\alpha-\beta-\gamma$
	truncated cuboctahedron [5])		A_{2g}	-1	$\alpha+\beta-\gamma$
			A_{2u}	1	$-\alpha-\beta+\gamma$
			E_g	4	$2\alpha+2\beta$
			E_u	-4	$-2\alpha-2\beta$
			T_{1g}	-3	$-\alpha-\beta-\gamma$
			T_{1u}	3	$\alpha+\beta+\gamma$
			T_{2g}	1	$\alpha+\beta-\gamma$
			T_{2u}	-1	$-\alpha-\beta+\gamma$

($h_i \in H$) but the trace of the matrix on the Γ-type subspaces takes a different form owing to the difference between the central idempotents or projection operators in *CG* compared to those in *CH*. If the stabilizer (site group) [12] of the vertex ν_0 in G is $1, g_2, \ldots, g_s$, then the trace of A on the Γ-type subspaces is

$$\frac{\Gamma(1)}{s}\left(\sum_{i,j}\Gamma(h_i g_j)\right).$$

Table 2
Eigenvalue sums for weighted and unweighted common trivalent cases over orbits of $g/2$ vertices of groups of order g.

Group	Graph	g_i	Γ	Eigenvalue sum	Weighted sum
$G = \mathrm{I_h}$	60 cage	α, α, β	$\mathrm{A_g}$	3	$2\alpha+\beta$
$H = \mathrm{I}$	(truncated icosahedron [5])	$\mathrm{C_5}$ $\mathrm{C_5}$ $\mathrm{C_2}$	$\mathrm{T_{1u}}$	$\frac{3+\sqrt{5}}{2}$	$\alpha\frac{3+\sqrt{5}}{2}$
		σ, σ, σ	$\mathrm{T_{1g}}$	$\frac{-3+\sqrt{5}}{2}$	$\alpha\frac{-1+\sqrt{5}}{2}-\beta$
			$\mathrm{T_{2u}}$	$\frac{3-\sqrt{5}}{2}$	$\alpha\frac{3+\sqrt{5}}{2}$
			$\mathrm{T_{2g}}$	$\frac{-3-\sqrt{5}}{2}$	$\alpha\frac{-1-\sqrt{5}}{2}-\beta$
			$\mathrm{H_u}$	-1	$-\alpha$
			$\mathrm{H_g}$	2	$\alpha+\beta$
			$\mathrm{G_u}$	-1	$-\alpha$
			$\mathrm{G_g}$	-1	$-\alpha$
$G = \mathrm{O_h}$	24 cage	α, α, β	$\mathrm{A_{1g}}$	3	$2\alpha+\beta$
$H = \mathrm{O}$	(truncated cube [5])	$\mathrm{C_3}$ $\mathrm{C_3}$ $\mathrm{C_2}$	$\mathrm{A_{2u}}$	1	$2\alpha-\beta$
		σ_d, σ_d, σ_h	$\mathrm{E_g}$	0	$-\alpha+\beta$
			$\mathrm{E_u}$	-2	$-\alpha-\beta$
			$\mathrm{T_{1g}}$	-2	$-\alpha-\beta$
			$\mathrm{T_{1u}}$	1	α
			$\mathrm{T_{2g}}$	1	α
			$\mathrm{T_{2u}}$	0	$-\alpha+\beta$
$G = \mathrm{O_h}$	24 cage	α, α, β	$\mathrm{A_{1g}}$	3	$2\alpha+\beta$
$H = \mathrm{O}$	(truncated octahedron [5])	$\mathrm{C_4}$ $\mathrm{C_4}$ $\mathrm{C_2}$	$\mathrm{A_{2g}}$	-3	$-2\alpha-\beta$
		σ_d, σ_d, σ_d	$\mathrm{E_g}$	0	0
			$\mathrm{T_{1g}}$	-1	$-\beta$
			$\mathrm{T_{1u}}$	-2	2α
			$\mathrm{T_{2g}}$	1	β
			$\mathrm{T_{2u}}$	-2	-2α
$G = \mathrm{T_d}$	12 cage	α, α, β	$\mathrm{A_1}$	3	$2\alpha+\beta$
$H = \mathrm{T}$	(truncated tetrahedron [5])	$\mathrm{C_3}$ $\mathrm{C_3}$ $\mathrm{C_2}$	E	0	$-\alpha+\beta$
		σ_d, σ_d, σ_d	$\mathrm{T_1}$	-2	$-\alpha-\beta$
			$\mathrm{T_2}$	1	α

In most of the examples $s = 2$ and so in these case the formula reduces to

$$\frac{\Gamma(1)}{2}\big(\Gamma(h_1)+\Gamma(h_2)+\cdots+\Gamma(h_r)+\Gamma(h_1g_2)+\Gamma(h_2g_2)+\cdots+\Gamma(h_rg_2)\big).$$

As before, if the multiplicity, $\Gamma(1)$, is dropped the formula further reduces to

$$\frac{1}{2}\big(\Gamma(h_1)+\Gamma(h_2)+\cdots+\Gamma(h_r)+\Gamma(h_1g_2)+\Gamma(h_2g_2)+\cdots+\Gamma(h_rg_2)\big)$$

or, in the weighted case,

$$\frac{1}{2}\big(\alpha_1\Gamma(h_1)+\alpha_2\Gamma(h_2)+\cdots+\alpha_r\Gamma(h_r)+\alpha_1\Gamma(h_1g_2)+\alpha_2\Gamma(h_2g_2)+\cdots+\alpha_r\Gamma(h_rg_2)\big).$$

Of course, knowledge of the trace of the powers of A, allows one to calculate the eigenvalues of A on this subspace and our method can be extended to do just that. A not dissimilar method was used before to solve the Hückel problem for C_{60} analytically [2,3] but did not exploit the explicit realization of A in regular-type representations, as multiplication by the appropriate group elements.

The character-based approach [2,3] to the solution of the Hückel problem for structures corresponding to regular orbits will be discussed elsewhere [8].

2. Repetitions

Consider a collection of points on the unit sphere exhibiting the point symmetry G. These points form the basis of a vector space, V, acted on by G. A central function, when evaluated at these points, yields a vector which transforms under the group in the same way as the central function. If we take an irreducible subspace of type Γ, then this projects in same manner into the space, V, to give either 0 or a subspace of type Γ (by Schur's lemma).

There is, however, no guarantee that the projections obtained by using the first sufficient number of central functions will lead to projections on all the distinct subspaces. For instance, there might be two subspaces of Γ in V, but the two projections obtained might be in the same subspace. It would appear that there are definite cases when the problems of repetitions can be handled easily by inspection and this is so in the case of the I_{120} cage.

In table 3 the direct sums of the I_h irreducible representations obtained from the irreducible subspaces of R_3 are listed for all l levels up to 15 which is the first value at which the direct sum includes the determinantly anti-symmetric irreducible representation, A_u, and is therefore necessary for a complete treatment of the regular representation.

The vertices of the I_{120} cage generate the regular representation, Γ_R, of the I_h point group

$$\Gamma_R = A_g \oplus A_u \oplus 3T_{1g} \oplus 3T_{1u} \oplus 3T_{2g} \oplus 3T_{2u} \oplus 4G_g \oplus 4G_u \oplus 5H_g \oplus 5H_u.$$

The complicated nature of the group is seen when A_g occurs two or more times in the decomposition of the central function subspaces on the I_h cage. For I_h, there is the trivial occurrence at $l = 0$, but the direct sum decomposition involves A_g, also, at levels l equal 6 and 10.

Thus, if any central function $f(x, y, z)$ of degree l is taken and multiplied by the A_g functions from levels 6 or 10, the result corresponds to an $l + 6$ or level $l + 10$ function of the same symmetry type, but not one that is distinct. The projections into V of $f(x, y, z)$ and these higher level functions, do not produce distinct copies of the symmetry.

The occurrences of redundant repetitions, for the projections of the icosahedral harmonics of the I_{120} cage, are listed in table 4.

Table 3
The irreducible symmetries of the icosahedral harmonics formed as linear combinations of the general spherical harmonics at each level l.

l-value of the general harmonic	Direct sums in I_h
0	a_g
1	t_{1u}
2	h_g
3	$t_{2u} \oplus g_u$
4	$g_g \oplus h_g$
5	$h_u \oplus t_{1u} \oplus t_{2u}$
6	$a_{1g} \oplus g_g \oplus t_{1g} \oplus h_g$
7	$t_{2u} \oplus g_u \oplus h_u \oplus t_{1u}$
8	$t_{2g} \oplus 2h_g \oplus 3g_g$
9	$2g_u \oplus h_u \oplus t_{1u} \oplus t_{2u}$
10	$a_g \oplus t_{1g} \oplus t_{2g} \oplus g_g \oplus 2h_g$
11	$2t_{1u} \oplus t_{2u} \oplus 2h_u \oplus g_u$
12	$a_g \oplus t_{1g} \oplus t_{2g} \oplus 2g_g \oplus 2h_g$
13	$t_{1u} \oplus 2t_{2u} \oplus 2g_u \oplus 2h_u$
14	$t_{1g} \oplus t_{2g} \oplus 2g_g \oplus 3h_g$
15	$1a_u \oplus 2t_{1u} \oplus 2t_{2u} \oplus 2g_u \oplus 2h_u$

Table 4
The occurrence of repetitions of the irreducible representations of the central icosahedral harmonics projected onto the I_{120} cage. The asterisk indicates when the projection into V of that function produces a subspace dependent on the earlier ones.

Type	l						
T_{1u}	1	5	7^*	9			
T_{1g}	6	10	12^*	14			
T_{2u}	3	5	7				
T_{2g}	8	10	12				
G_u	3	7	9	9^*	11		
G_g	4	6	8	10^*	12		
H_u	5	7	9	11	11^*	13	
H_g	2	4	6	8	8^*	10	10^*

3. Node counting and the C_{120} structure

The I_h symmetry of C_{120} provides a good example for the illustration of the foregoing analysis. The Hückel energies, under the assumption that the radial carbon p-orbitals exhibit constant overlap with neighbours so that there is only one Hückel parameter in the adjacency matrix, are given in table 5.

A comparison of the predictions in table 1 for the eigenvalue sums and the results in table 5 shows complete agreement and for each type of irreducible symmetry, the sums of the traces of three reflections are seen to be equal to the eigenvalue sums.

Table 5
The Hückel eigenvalues for the linear combinations of the radial p-orbitals of the C_{120} structure giving rise to the corresponding eigenfunctions.

Symmetry	E values				
a_g	3.000				
a_u	−3.000				
t_{1u}	2.902	1.000	−0.902		
t_{1g}	0.902	−1.000	−2.902		
t_{2u}	2.176	1.000	−0.176		
t_{2g}	0.176	−1.000	−2.176		
g_u	2.545	0.439	−0.830	−2.154	
g_g	2.154	0.830	−0.439	−2.545	
h_u	1.828	0.466	−0.685	−1.888	−2.721
h_g	2.721	1.888	0.685	−0.466	−1.828

Another detail of the results in table 5 is that the Γ_g and Γ_u pairs of eigenvalue sets appear in pairs of opposite sign. This occurs because the framework is an even alternant, i.e., star labels can be attached to half of the cage vertices in such a way that every starred vertex is surrounded by unstarred neighbours and vice versa. Any eigenvector of eigenvalue Γ, therefore, can be converted to one at eigenvalue $-\Gamma$ by reversing the relative phase of the starred and unstarred sets. The inversion operation exchanges starred and unstarred sets in the I_{120} cage, hence the association of the parity change in the eigenfunction with the change in sign of the eigenvalue.

Node counting to generate a qualitative correlation diagram between the number of nodes in the central harmonic function (the l value) and the Hückel molecular-orbital energies of table 5 works as long as the data in table 4 are used to pick the l level of the LCAO-MOs. For each set (ν) of harmonic projections of a given symmetry, rendered mutually orthogonal on the I_{120} cage, the Hückel adjacency matrix (A) can be block-diagonalized using the transpose, ν^t, of V in the product $\nu^t A \nu$. The sets of basic projections are chosen using the data in table 4 and it can be seen in figure 1 that there is a reasonable correlation between the numbers of nodes and the Hückel energies especially when the relation, too, between the Γ_g and Γ_u eigenfunctions is exploited. In the absence of this extra consideration of redundant repetitions, it is to be emphasized that the correlation between 'node counting' and the Hückel results in table 5 would not be found.

4. Large clusters

A considerable literature concerning group theoretical and Hückel analyses of hypothetical large carbon clusters exibiting icosahedral point group symmetry has accumulated [6,15,17,18,21,22,25–29]. Basic to these analyses are constructions of the cluster as a whole, that are based either on folding up nets drawn on the plane triangular tessellation or its dual the graphite sheet, or on propagation over the surface of the

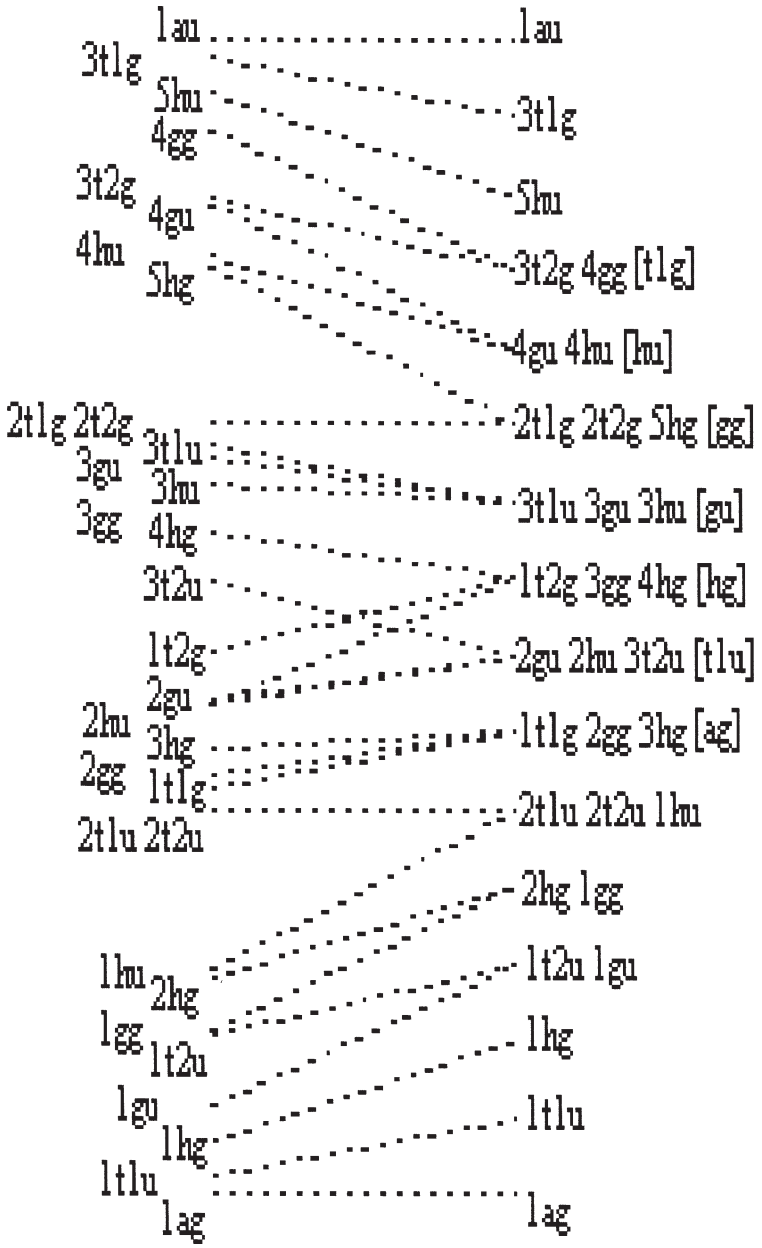

Figure 1. A correlation diagram of the Hückel MO eigenvalues of each symmetry for C_{120}, on the left, with the nodal character of the icosahedral harmonics upon which the final block-diagonalization of the adjacency matrix is accomplished. Note that without the recognition that repetitions (Γ) of the icosahedral harmonics, as products of the form A_g(at $l = 6$) $\otimes \Gamma$ occur on the 120 cage, little agreement with the 'node counting' proposition would be seen. In the diagram the conventional Mullikan notation has been used. Thus, for example, $4g_u$ is the symbol used to identify the fourth set of four g_u eigenfunctions of the Hückel calculation, rather than four sets of g_u symmetry as in expressions for reducible representations.

unit sphere of (for full I_h symmetry) 120 copies of a primitive spherical triangle that joins poles of neighbouring C_2, C_3 and C_5 axes. The orbit-based analysis and procedure of symmetry-based diagonalisation of the adjacency matrix offer a complementary perspective on the other methods.

Icosahedral fullerene structures, I_n, can be constructed for all distinct solutions of the integer relation

$$n = 20\big(i^2 + ij + j^2\big),$$

where $i \geqslant j$, $i > 0$, $j \geqslant 0$ and (i, j) is a lattice vector on the equilateral triangulation of the plane that is used to specify one of the twenty faces of the master icosahedral net [4,6,9,10,15,18]. The cases $i = j$ and $j = 0$ give rise to clusters with full I_h symmetry, and all others, i.e., $i \neq j \neq 0$ give rise to clusters with only the rotational-subgroup symmetry I.

A general result in Hückel theory [6], which turns out to be a special case of the leapfrog theorem for the π structures of fullerenes [13], is that icosahedral fullerenes, I_n, in which n is a multiple of 60 (i.e., when $i - j$ is a multiple of 3) have properly closed shells, with exactly $n/2$ bonding and $n/2$ anti-bonding eigenvectors and ten electrons in the fivefold degenerate HOMO, whereas, in all other icosahedral cases, it is $n - 20$ that is a multiple of 3 and such fullerenes are open shell with two electrons in a fourfold degenerate HOMO level. The closed-shell cases have totally symmetric 'Fries' Kekule structures in which all pentagon edges are single and the maximum number of hexagons are benzenoid [7]; they are also Clar polyhedra [11].

The orbit-by-orbit breakdown of the cage and, hence, the constitution of the primitive spherical triangle can be related simply to the parameters i and j. Trivalency implies that any icosahedral cage can be decomposed into at most three types of orbit as $a\,O_{20} + b\,O_{60} + c\,O_{120}$ with

$$n = 20a + 60b + 120c.$$

For the cages of I symmetry, c is always zero, $a = 1$ for $i - j \neq 0 \bmod 3$ and 0 otherwise, and b follows by subtraction as $(i^2 + j^2 + ij - a)/3$. For the cages of I_h symmetry, $a = 1$ for $j = 0$, $i = 0 \bmod 3$, but zero for $i = j$, and $b = i$ for both $j = 0$ and $i = j$, leaving c to follow by subtraction as $(i^2 + ij + j^2 - a - 3b)/6$.

Thus the first few icosahedral fullerenes C_{20}, C_{60}, C_{80}, C_{140}, C_{180}, C_{240}, C_{260}, ... have decompositions $(a, b, c) = (1, 0, 0)$, $(0, 1, 0)$, $(1, 1, 0)$, $(1, 2, 0)$, $(0, 3, 0)$, $(0, 2, 1)$, $(1, 4, 0)$, ... corresponding to their signatures $(i, j) = (1, 0)$, $(1, 1)$, $(2, 0)$, $(2, 1)$, $(3, 0)$, $(2, 2)$, $(3, 1)$, ... and symmetries I_h, I_h, I_h, I, I_h, I_h, I, ... All the cages with $a = 1$ have open and all with $a = 0$ closed π shells.

For example, the C_{320} structure of I_h symmetry comprises one 20-point, three 60-point, and one 120-point orbit as shown in figure 2. These orbits are propagated from the basic spherical triangular patch from two vertices lying on the line between C_5 and C_3 axes, one on the C_3 axis itself, and one in the general position in the interior of the triangle. With the exception of the O_{20} orbit, corresponding to occupation of the C_3 poles on the unit sphere, there is considerable freedom in the angular dispo-

Figure 2. The C_{320} carbon cage structure and the component geometric orbits of the I_h point group. The complete structure and the separate orbits are shown as Mollweide projections [4,9]. Note that the O_{20} is included in the projections of the other orbits to emphasize the manner in which these orbits can be considered to be decorations of the O_{20} vertices, which are the locations on the unit sphere of the C_3 axes of the I_h point group.

Table 6
Direct-sum irreducible components of the permutation characters on the orbits of the I_h point group.

Orbit	Site group	Direct sum
O_{12}	C_{5v}	$A_g \oplus T_{1u} \oplus T_{2u} \oplus H_g$
O_{20}	C_{3v}	$A_g \oplus T_{1u} \oplus T_{2u} \oplus G_g \oplus G_u \oplus H_g \oplus H_u$
O_{30}	C_{2v}	$A_g \oplus T_{1u} \oplus T_{2u} \oplus G_g \oplus G_u \oplus 2H_g \oplus H_u$
O_{60}	C_s	$A_g \oplus T_{1g} \oplus 2T_{1u} \oplus T_{2g} \oplus 2T_{2u} \oplus 2G_g \oplus 2G_u \oplus 3H_g \oplus 2H_u$
O_{120}	C_1	$A_g \oplus A_u \oplus 3T_{1g} \oplus 3T_{1u} \oplus 3T_{2g} \oplus 3T_{2u} \oplus 4G_g \oplus 4G_u \oplus 5H_g \oplus 5H_u$

sition of the points of the other orbits; each 60-orbit has one degree of freedom and each 120-orbit a further two even when points are all constrained to lie on the unit sphere, and thus, for example, the number of structural parameters and the number of A_g breathing vibrations of an icosahedral cage are simple functions of a, b and c or, equivalently, the i, j signature.

Because of this rotational freedom, the 60 orbits of vertices are not always obvious recognisable copies of the C_{60} fullerene; each isolated-pentagon fullerene has one copy of the orbit wherein the vertices are connected as pentagonal rings, but can have other, disconnected copies. The pentagons can adopt the same orientation as in C_{60} itself, with edges perpendicular to the C_5/C_3 line, or point directly at one another, or be found in any orientation in between. The truncated dodecahedron is also a realisation of the 60-orbit and, in leapfrog fullerenes beyond C_{60}, there is always one copy of the C_{60} orbit, in which the second-neighbour links between vertices form 20 triangles centred of the C_3 axes.

Calculations of Hückel energies in such structures have been carried out by direct diagonalisation [6,18] or by setting up the secular equations for the different symmetry types of eigenfunctions [22,25–29] or by solving the factor characteristic [21,22] equations which can be derived using the Lanczos technique [15] for sparse matrices.

The proposed approach in this report presents an alternative route to the eigenvalues and eigenfunctions of large carbon cages which is very easy to program. As in the other two symmetry-based techniques, the dimensions of the final entities to be transformed to return the eigenvalues and eigenvectors of any cage are simply the numbers corresponding to the occurrences of the direct sum irreducible combinations in each contributing orbit summed over the cage.

This orbit-by-orbit approach has the advantage that it facilitates the identification of the contributions made by particular radial carbon p-orbitals sets to Hückel eigenfunctions of a given symmetry as long as the *proviso* concerning repetitions is observed. The direct sum representations for the orbits of the I_h point group are given in table 6. For C_{320} and all I_h polyhedral carbon cages on more that 180 atoms, there is at least one copy of the 120-point orbit, and all a_u orbitals must be localised on the vertices of the 120-orbit. In C_{320}, the presence of a copy of O_{20} ensures an open-shell configuration for the neutral, with the HOMO–LUMO gap of the closed shell di-cation falling between g_u- and g_g-type eigenvalue subspaces.

Figure 3. The Hückel eigenfunctions, as amplitudes on the cage vertices for representative linear combinations of the sets $6g_u$ and $6g_g$ corresponding to the HOMO and LUMO sets, and the $1a_u$ linear combination localized on the C_{120} case, since only for the regular representation A_u is found to be a component of the direct sum. For clarity, the circles representing individual local amplitudes have been scaled by a factor of 100.

Representative Hückel eigenfunctions of the part-filled $6g_u$ HOMO of C_{320} and the completely empty $6g_g$ LUMO are shown in figure 3, together with the Hückel eigenfunction of a_u symmetry confined to non-zero amplitudes only on the vertices corresponding to the single O_{120} orbit of the icosahedral group. In the HOMO, maximum/minimum wave function amplitudes are found on the first of the O_{60} orbits of figure 2, especially, for carbon atoms near the yz great circle of the unit sphere while the absolute amplitudes of the components in the representative LUMO are relatively large on the other orbits as well and when large are to be found on regions of the cage near the xz great circle. The a_u Hückel eigenfunction in figure 3 (bottom) is confined to vertices of the I_{120} orbit and the constant absolute value of the amplitude changes sign from neighbour to neighbour. Thus it is determined fully by symmetry in this case, where there is only one copy of the regular orbit. Moreover, because the vertices of the 120-orbit are pairwise adjacent, the eigenvalue of the a_u orbital is -1.

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