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Symmetry aspects of leapfrog and truncated polyhedra

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Abstract

A leapfrog polyhedron is constructed by capping a parent polyhedron on every face and taking the dual of the result. General relationships between the symmetries spanned by vertices, edges and faces of parent and leapfrog are derived and extended to arbitrarily high local angular momentum. Symmetry relationships between leapfrogs of dual polyhedra are found. Leapfrogging the dual of a polyhedron is equivalent to truncating the original. The eigenvalue spectrum of a truncated trivalent polyhedron is given as a function of the spectrum of the parent, and the consequences for electronic structure of polyhedral carbon cages are discussed in terms of localised and Clar models of π bonding. All truncated fullerenes are closed-shell in Hückel theory, each with the same formal π electronic configuration as the leapfrog of the same parent, though unlikely to be either sterically or electronically optimal.

1. Introduction

The leapfrog transformation was first defined in the context of the theoretical chemistry of fullerenes as a way of generating the structures of larger members of the fullerene series from smaller parents [1-3]. A fullerene [4] is a trivalent pseudospherical polyhedral cage consisting of n carbon atoms linked in 12 pentagonal and $(n/2 - 10)$ hexagonal rings. The leapfrog process of omnicapping followed by taking the dual of the polyhedron results in the conversion of a fullerene C_n to a fullerene C_{3n}. (Each vertex of the parent generates a new hexagonal face in the leapfrog, each face and edge of the parent survives in rotated form in the leapfrog.) The operation is of chemical interest [2] because it yields a molecule with a properly closed π shell in the qualitative Hückel description of electronic structure used for these unsaturated all-carbon systems. This property can be given a mathematical description as follows. Let the eigenvalues λ_i of the adjacency matrix of a polyhedron P be arranged in descending order. Then, if the polyhedron is a leapfrog fullerene $P = C_n$, its eigenvalue spectrum is not only *closed-shell* ($\lambda_{n/2} \neq \lambda_{n/2+1}$) but

also *properly closed* ($\lambda_{n/2} > 0; \lambda_{n/2+1} \leq 0$), corresponding in Hückel theory to occupation of all bonding molecular orbitals by the n π electrons of the cage. More generally, if P is the leapfrog of any trivalent polyhedron then its spectrum is either closed or properly closed [5]. Symmetry aspects of fullerene leapfrogging have been studied: the permutation representations of the edges, faces and vertices of the leapfrog are all predictable from those of the parent [6].

More generally, *any* polyhedron can be leapfrogged and the resulting polyhedron is always trivalent. This fact is used in the present note to recast the symmetry relations in a form that allows prediction of permutation representations for the leapfrog of any parent polyhedron. Relations connecting the properties of leapfrogs of dual polyhedra, and eigenvalue theorems for truncations of trivalent polyhedra are also derived. All trivalent polyhedra are of at least potential chemical interest as candidates for stable carbon frameworks.

2. Leapfrogging a general polyhedron

Define three polyhedra: P, the parent, O its omnicap, and L its leapfrog (i.e. the dual of O). The numbers of vertices, faces and edges of these polyhedra are v_P, f_P, e_P, v_O, f_O, e_O, v_L, f_L and e_L, respectively. The definitions of O and L imply

$$\begin{aligned} &v_O = v_P + f_P; \qquad f_O = 2e_P; \qquad e_O = 3e_P \\ &v_L = f_O = 2e_P; \qquad f_L = v_O = v_P + f_P = e_P + 2; \qquad e_L = e_O = 3e_P \end{aligned} \tag{1}$$

L is trivalent by construction, and v_L, f_L, e_L are indeed related as for a trivalent polyhedron ($e_L = (3/2)v_L$; $f_L = (1/2)v_L + 2$). If P is also trivalent, then leapfrogging triples the number of vertices as $v_L = 3v_P$ when $v_P = (3/2)e_P$.

Now define permutation representations $\Gamma_\sigma(v,P)$, $\Gamma_\sigma(f,P)$ and $\Gamma_\sigma(e,P)$ for the sets of components of the polyhedra P and L. The object is to derive the representations appropriate to L from those for P. P, O and L all belong to the same point group.

The faces of the leapfrog have centres coinciding with the face centres and the vertices of the parent:

$$\Gamma_\sigma(f,L) = \Gamma_\sigma(f,P) + \Gamma_\sigma(v,P) \tag{2}$$

Every edge of P gives rise to a perpendicular edge in L [3] and together these derived edges exhaust the vertices of L, so that the permutation representation of the

vertices of L can be constructed by taking an in-phase and an out-of-phase combination along every derived edge [6] i.e.

$$\Gamma_\sigma(v, L) = \Gamma_\sigma(e, P) + \Gamma_\perp(e, P) \tag{3}$$

where $\Gamma_\perp(e, A)$ is the representation of a set of tangential vectors perpendicular to the edges of polyhedron A [7]. For any polyhedron A the perpendicular representation is related to those of vertices and faces by [7]

$$\Gamma_\perp(e, A) = \Gamma_\sigma(v, A) \times \Gamma_\epsilon + \Gamma_\sigma(f, A) - \Gamma_0 - \Gamma_\epsilon \tag{4}$$

where Γ_0 and Γ_ϵ are the totally symmetric and antisymmetric representations, respectively. Thus the vertex representation of the leapfrog is related to edge, face and vertex representations of the parent by

$$\Gamma_\sigma(v, L) = \Gamma_\sigma(e, P) + \Gamma_\sigma(f, P) + \Gamma_\sigma(v, P) \times \Gamma_\epsilon - \Gamma_0 - \Gamma_\epsilon. \tag{5}$$

As L is trivalent, its edge representation can be derived from those of its vertices and faces by [7]

$$\Gamma_\sigma(e, L) = \Gamma_\sigma(f, L) \times \Gamma_T - \Gamma_T - \Gamma_R \tag{6}$$

where Γ_T and $\Gamma_R = \Gamma_T \times \Gamma_\epsilon$ are the translational and rotational representations, respectively. Equations (2), (5) and (6) generalise previous expressions which were derived for trivalent parent polyhedra [6].

3. Leapfrogs of dual polyhedra

Consider four polyhedra: P, its dual $\overline{P}$, its leapfrog $L(P)$ and the leapfrog of its dual $L(\overline{P})$. Leapfrogging can be described as omnicapping followed by taking the dual, as above, or as omnitruncation of the dual. It follows from the latter description that $L(P)$ and $L(\overline{P})$ are related as truncations of a dual pair of polyhedra, since $L(P)$ is the truncation of $\overline{P}$ and $L(\overline{P})$ of P. Thus, for example, the leapfrog of the Platonic dodecahedron is the truncated icosahedron and the leapfrog of the icosahedron is the truncated dodecahedron. The two polyhedra $L(P)$ and $L(\overline{P})$ are equal in respect of vertex, face and edge counts, as shown by the symmetry of v_L, f_L and e_L in (1) under exchange of v_P and f_P.

The permutation representations of the structural components of P and $\overline{P}$, $L(P)$ and $L(\overline{P})$ are also related. For two dual polyhedra we have

$$\Gamma_\sigma(v, P) = \Gamma_\sigma(f, \overline{P}),$$

$$\Gamma_\sigma(f,P) = \Gamma_\sigma(v,\overline{P}), \tag{7}$$
$$\Gamma_\sigma(e,P) = \Gamma_\sigma(e,\overline{P}),$$

and because of the rotation of edges on taking the dual, the parallel and perpendicular edge representations swap over as

$$\begin{aligned}\Gamma_\perp(e,P) &= \Gamma_\perp(e,\overline{P}) \times \Gamma_\epsilon = \Gamma_\parallel(e,\overline{P}),\\ \Gamma_\parallel(e,P) &= \Gamma_\parallel(e,\overline{P}) \times \Gamma_\epsilon = \Gamma_\perp(e,\overline{P}).\end{aligned} \tag{8}$$

It follows from the general relations (2) and (6) between a leapfrog and its parent that $L(P)$ and $L(\overline{P})$ have equal face and equal edge representations

$$\Gamma_\sigma(f,L(P)) = \Gamma_\sigma(f,L(\overline{P})) \tag{9}$$

$$\Gamma_\sigma(e,L(P)) = \Gamma_\sigma(e,L(\overline{P})) \tag{10}$$

but not in general equal vertex representations since, from (3),

$$\Gamma_\sigma(v,L(P)) = \Gamma_\sigma(e,P) + \Gamma_\perp(e,P) \tag{11}$$

$$\Gamma_\sigma(v,L(\overline{P})) = \Gamma_\sigma(e,P) + \Gamma_\parallel(e,P) \tag{12}$$

which lead to the weaker condition

$$\Gamma_\sigma(v,L(P)) \times [\Gamma_0 + \Gamma_\epsilon] = \Gamma_\sigma(v,L(\overline{P})) \times [\Gamma_0 + \Gamma_\epsilon] \tag{13}$$

In the case of a *chiral* polyhedron P, i.e. one having only proper rotational symmetry elements, the distinction between Γ_0 and Γ_ϵ vanishes and $L(P)$ and $L(\overline{P})$ share face, edge and vertex representations.

Chirality of P is sufficient but not necessary to ensure equality of vertex representations of $L(P)$ and $L(\overline{P})$. For example, the sixty equivalent vertices of the leapfrog of the Platonic dodecahedron span exactly the same symmetry as those of the leapfrog of the icosahedron, and this can be traced back to the equality of parallel and perpendicular edge representations in each parent, which in turn stems from the fact that the two mirror planes bisecting each parent edge are equivalent (Figure 1).

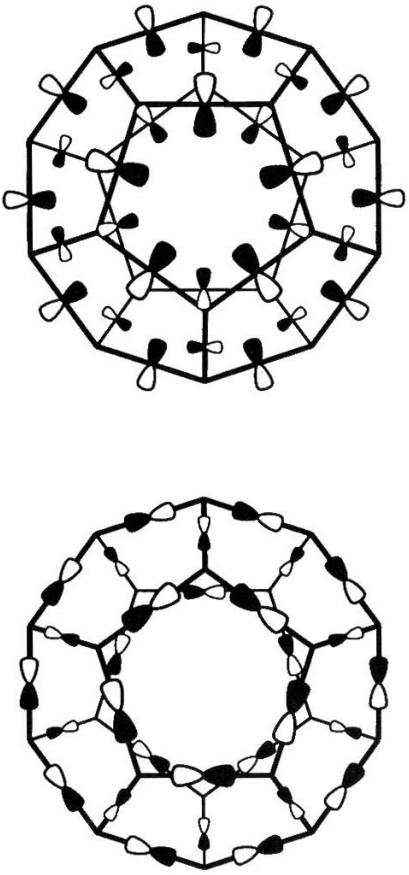


Figure 1: Parallel and perpendicular edge vectors of a dodecahedron span the same reducible representation of the icosahedral group ($T_{1g}+T_{2g}+G_g+H_g+T_{1u}+T_{2u}+G_u+H_u$), which also describes the parallel and perpendicular edge vectors of the icosahedron.

4. Leapfrogging as truncation of the dual

Equations (9) to (12) describe the symmetry consequences of the leapfrog operation for general polyhedra. A special case of interest in chemical applications occurs when P is a trivalent polyhedron and $\overline{P}$, its dual, is therefore a deltahedron. The structural components of the leapfrog polyhedron $L(P)$ then have reducible representations [6]

$$\begin{aligned}
\Gamma_\sigma(v, L(P)) &= \Gamma_\sigma(e, P) + \Gamma_\sigma(v, P) \times \Gamma_T \times \Gamma_\epsilon - \Gamma_\sigma(e, P) \times \Gamma_\epsilon, \\
\Gamma_\sigma(e, L(P)) &= \Gamma_\sigma(e, P) + \Gamma_\sigma(v, P) \times \Gamma_T, \\
\Gamma_\sigma(f, L(P)) &= \Gamma_\sigma(f, P) + \Gamma_\sigma(v, P),
\end{aligned} \tag{14}$$

and $L(\overline{P})$, the leapfrog of the dual deltahedron, equivalent to the truncation T of the original trivalent polyhedron, has structural components spanning $\Gamma_\sigma(e, L(\overline{P})) = \Gamma_\sigma(e, L(P))$, $\Gamma_\sigma(f, L(\overline{P})) = \Gamma_\sigma(f, L(P))$ and

$$\Gamma_\sigma(v, L(\overline{P})) = \Gamma_\sigma(v, P) \times \Gamma_T = \Gamma_\sigma(v, P) + \Gamma_\pi(v, P) \tag{15}$$

Each vertex of P is replaced by a triangle of vertices (a triangular 'facet') in T, with the triangles connected to each other as the original vertices.

(As an aside, if the original polyhedron P were pentavalent, the truncated polyhedron $L(\overline{P})$ would have vertices spanning $\Gamma_\sigma(v, L(\overline{P})) = \Gamma_\sigma(v, P) + \Gamma_\pi(v, P) + \Gamma_\delta(v, P)$, which holds, for example, for P = icosahedron, $\overline{P}$ = dodecahedron, $L(\overline{P})$ = truncated icosahedron, where in maximal symmetry the polyhedra span the 12, 20 and 60 orbits of the I_h group, respectively.)

In particular, then, the application of the leapfrog operation to a fullerene C_n generates another fullerene C_{3n}, but the application of the same operation to its dual produces a truncated fullerene, also with $3n$ vertices, composed of n triangular, 12 decagonal and $(n/2 - 10)$ dodecagonal faces. The eigenvalue spectra of truncated trivalent polyhedra are discussed in section 6 of this paper.

5. Representations for higher local angular momentum

The σ representation is appropriate to the permutation of structureless points on a pseudospherical surface, or more generally of objects or local functions that have cylindrical symmetry with respect to the radius vector. When the functions to be permuted are pairs of tangential dipoles, quadrupoles, or other objects that correspond to nonzero angular momentum about the radius vector, they generate members of the series

$\Gamma_\pi, \Gamma_\delta, \Gamma_\phi, \ldots \Gamma_\lambda \ldots$ Each of these higher representations can be derived from Γ_σ by a bootstrap procedure [8]:

$$\begin{aligned} \lambda = 1: &\qquad \Gamma_\pi = \Gamma_\sigma \times \Gamma_T - \Gamma_\sigma, \\ \lambda = 2: &\qquad \Gamma_\delta = \Gamma_\pi \times \Gamma_T - \Gamma_\pi - \Gamma_\sigma \times (\Gamma_0 + \Gamma_\epsilon), \\ \lambda \geq 3: &\qquad \Gamma_\lambda = \Gamma_{\lambda-1} \times \Gamma_T - \Gamma_{\lambda-1} - \Gamma_{\lambda-2}. \end{aligned} \tag{16}$$

The first few members of the series have applications in the theory of molecular vibrations and in electronic structure theory [9-15].

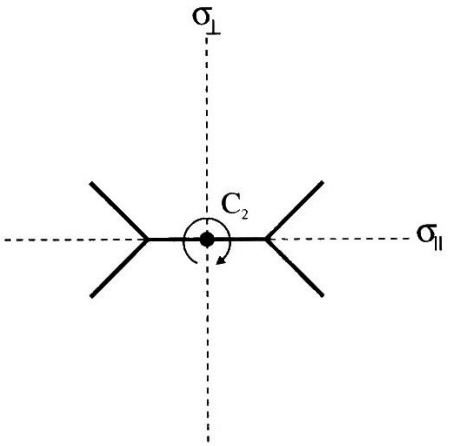
Given the σ representations $\Gamma_\sigma(f, L)$, $\Gamma_\sigma(v, L)$, and $\Gamma_\sigma(e, L)$ for the leapfrog polyhedron, all higher representations appropriate to decoration of the faces, vertices and edges of L can be calculated from (14). Alternatively, the additive structure of each leapfrog representation allows calculation from the corresponding higher representations of the parent polyhedron if these are available. The generalisations of equations (2), (5) and (6) to arbitrary values of angular momentum are

$$\begin{aligned} \Gamma_\lambda(f, L) &= \Gamma_\lambda(f, P) + \Gamma_\lambda(v, P), \\ \Gamma_\lambda(v, L) &= \Gamma_\lambda(e, P) + \Gamma_\lambda(f, P) + \Gamma_\lambda(v, P) \times \Gamma_\epsilon - F_\lambda \times (\Gamma_0 + \Gamma_\epsilon), \\ \Gamma_\lambda(e, L) &= \Gamma_\lambda(f, L) \times \Gamma_T - F_\lambda \times (\Gamma_T + \Gamma_R), \end{aligned} \tag{17}$$

where the intermediate quantity F_λ is found by the formal device of calculating Γ_λ according to (14) but taking Γ_σ to be Γ_0. Thus, $F_\sigma = \Gamma_0$, $F_\pi = \Gamma_T - \Gamma_0$, $F_\delta = \Gamma_T \times \Gamma_T - 2\Gamma_T - \Gamma_\epsilon$ and $F_\lambda = F_{\lambda-1} \times \Gamma_T - \Gamma_{\lambda-1} - \Gamma_{\lambda-2}$ for $\lambda \geq 3$.

More detailed considerations show that use of the full machinery of (15) can be avoided in many cases. For example, a general formula for $\Gamma_\lambda(e, A)$ can be found for the edges of *any* polyhedron A as follows. An edge of any polyhedon has a site symmetry C_{2v} or lower (C_2, C_s, C_1) and can therefore be decorated in at most four symmetry-distinct ways with a local function (Figure 2). Assuming for the moment that all edges are in C_{2v} sites, the global reducible representation of the set of local functions is that induced in G, the point group of the polyhedron, by ascent from C_{2v}. Thus $\Gamma_\sigma(e, A)$ is induced by A_1, $\Gamma_\pi(e, A)$ by $B_1 + B_2$, and $\Gamma_\delta(e, A)$ by $A_1 + A_2$ on $C_{2v} \uparrow G$. Beyond Γ_δ the representations repeat, with $\Gamma_\lambda = \Gamma_\pi$ (λ odd) or $\Gamma_\lambda = \Gamma_\delta$ (λ even), and all Γ_λ ($\lambda > 0$) can be calculated from Γ_σ and one half of Γ_π alone, since

$$\begin{aligned} \Gamma_\lambda(e, A) = \Gamma_\pi(e, A) &= \Gamma_\perp(e, A) \times (\Gamma_0 + \Gamma_\epsilon) \qquad (\lambda \quad \text{odd}) \\ \Gamma_\lambda(e, A) = \Gamma_\delta(e, A) &= \Gamma_\sigma(e, A) \times (\Gamma_0 + \Gamma_\epsilon) \qquad (\lambda \quad \text{even}) \end{aligned} \tag{18}$$



	E	C_2	$\sigma_{\parallel}$	$\sigma_{\perp}$		
A_1	+1	+1	+1	+1		σ
A_2	+1	+1	-1	-1		$\delta_{\parallel\perp}$
B_1	+1	-1	+1	-1		$\pi_{\parallel}$
B_2	+1	-1	-1	+1		$\pi_{\perp}$

Figure 2: Decorations of an edge in a pseudospherical polyhedron. The edge is transformed into itself under at most four symmetry operations (the identity, twofold reflection about the radial vector to its midpoint, reflection in one of two planes containing the radial vector) and therefore has maximal site group C_{2v}. A maximum of four symmetry-distinct decorations is possible, as shown, and therefore all edge permutation representations, of whatever angular momentum, can be given in terms of these four primitives.

The perpendicular edge representation $\Gamma_\perp$ can be deduced from face and vertex permutation representations for any polyhedron using (4), so no explicit calculation of higher representations by (14) is necessary for the edges of any polyhedron. If some or all of the edges are in sites of lower symmetry, the same general expressions apply but $\Gamma_\perp$ and Γ_σ may no longer be distinct.

Similar treatments are possible for vertices and faces of special types of polyhedron. In a trivalent polyhedron, such as a leapfrog, a vertex has at most C_{3v} site symmetry and the same line of argument about induced representations leads to

$$\begin{aligned} \Gamma_\lambda(v,A) &= \Gamma_\pi(v,A) = \Gamma_\delta(v,A) && (\lambda \neq 0 \bmod 3) \\ \Gamma_\lambda(v,A) &= \Gamma_\sigma(v,A) \times (\Gamma_0 + \Gamma_\epsilon) && (\lambda = 0 \bmod 3) \end{aligned} \tag{19}$$

valid for trivalent polyhedra and $\lambda > 0$ only. $\Gamma_\pi(v,A)$ is easily calculated from $\Gamma_\sigma(v,A)$ using (14). Thus all vertex representations of any trivalent polyhedron are available without recursion once the permutation representation is given. Only for the face representations is the full machinery needed.

For a deltahedron $\overline{A}$ the relations for face representations are found by dualising the vertex representations (17)

$$\begin{aligned} \Gamma_\lambda(f,\overline{A}) &= \Gamma_\pi(f,\overline{A}) && (\lambda \neq 0 \bmod 3) \\ \Gamma_\lambda(f,\overline{A}) &= \Gamma_\sigma(f,\overline{A}) \times (\Gamma_0 + \Gamma_\epsilon) && (\lambda = 0 \bmod 3) \end{aligned} \tag{20}$$

valid for deltahedra and for $\lambda > 0$ only. For deltahedra it is now the vertex representations that require the full machinery.

6. Eigenvalue spectra of truncated polyhedra

The eigenvectors of the adjacency matrix of a polyhedron are equisymmetric with the vertices themselves. Hence, from the equations given earlier, the symmetries of the vertices for a truncated trivalent polyhedron $T = T(P) = L(\overline{P})$ can be derived from those of the parent P. It turns out that the eigen*values* can also be derived from those of P.

The spectra of a typical fullerene and its truncation are shown in Figure 3. The fullerene, as a non-alternant trivalent polyhedron, has eigenvalues λ in the range $+3 \geq \lambda > -3$. The truncated polyhedron has eigenvalues t in the range $+3 \geq t > -2$. Highly degenerate eigenvalues at $t = 0$ and $t = -2$ are immediately obvious, but closer inspection shows that the other eigenvalues occur in pairs $t, 1-t$ ($+3$ is paired to one copy of -2),

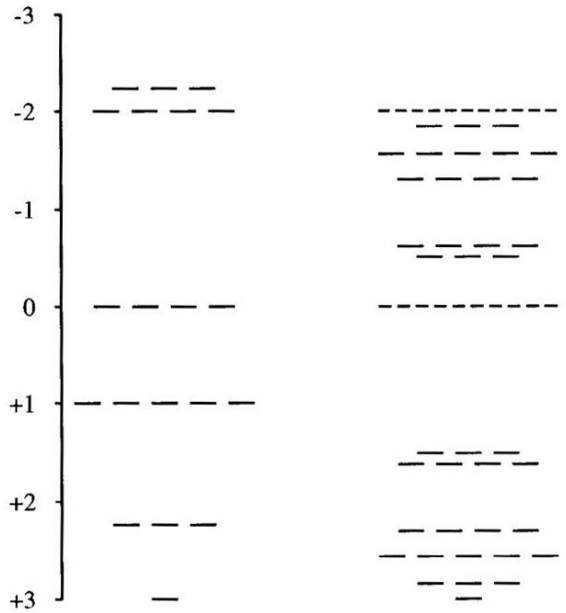


Figure 3: Eigenvalue spectra of a fullerene and its truncate. The spectrum of dodecahedral C_{20} (left) consists of eigenvalues (with multiplicities in brackets) $+3(1)$, $+\sqrt{5}(3)$ $+1(5)$, $0(4)$, $-2(4)$, $-\sqrt{5}(3)$ and the eigenvalues of the truncated dodecahedron (right) are therefore $+3, -2(1)$ $1/2\pm\sqrt{\sqrt{5}+13/4} \approx 2.8422, +0.8422(3)$, $1/2\pm\sqrt{17/4} \approx 2.5616, -1.5616(5)$, $1/2\pm\sqrt{13/4} \approx 2.3028, -1.3028(4)$, $1/2\pm\sqrt{5/4} \approx 1.6180, -0.6180(4)$, $1/2\pm\sqrt{13/4-\sqrt{5}} \approx 1.5069, -0.5069(3)$, plus $20/2 = 10$ extra eigenvalues at 0 and -2.

and in fact the spectrum of the truncated fullerene contains two distorted copies of the original, one squeezed into the range +3 to +1 and the other inverted and squeezed into the range 0 to −2. These relationships turn out to hold for all truncated fullerenes. It can be shown (see Appendix for proofs) that truncation of a general trivalent polyhedron P on n vertices leads to a spectrum with the following characteristics:

(i) $n/2 + 1$ eigenvalues $t = -2$;

(ii) $n/2 + \delta$ eigenvalues $t = 0$ ($\delta = 1$ for an alternant parent P, $\delta = 0$ for non-alternant P);

(iii) For every eigenvalue $-3 < \lambda < 3$ of P, a pair of eigenvalues (one positive and one negative) $t = (1 \pm \sqrt{4\lambda + 13})/2$, thus giving two compressed copies of the original spectrum reproducing its pattern of degeneracies, one inverted with $-2 \leq t \leq 0$, one the right way up and with $1 \leq t \leq 3$: the lower bounds are realised only for alternant P;

(iv) a single eigenvalue $t = +3$ (for any trivalent P);

(v) a single eigenvalue $t = +1$ (for alternant P).

The chemical consequences of this spectral structure are straightforwardly worked out. If we take a carbon framework realising the polyhedron T, it will have n strictly bonding, $n/2 + \delta$ nonbonding and $3n/2 - \delta$ strictly antibonding π molecular orbitals in the Hückel model. The truncation of an alternant parent will therefore give an open-shell electronic configuration for the C_{3n} neutral carbon cage. Truncation of a non-alternant will give a formally closed-shell configuration in which all $n/2$ non-bonding orbitals are occupied.

The electronic structure of such a carbon cage can be rationalised by localised models for the parentage of the Hückel eigenvectors, as done for the leapfrog cages in ref. 16. Truncation of P leads to a 'Clar polyhedron' [17] in which the n disjoint triangular facets derived from vertices of P exhaust the vertices of T. With each triangular facet we can associate a local cyclopropenium bonding scheme of one bonding σ and two antibonding π combinations of radial p orbitals. In the non-interacting limit each triangular facet holds two electrons. The n strictly bonding orbitals orbitals of T are derived by interaction of these local bonding combinations, which changes their energy but not their symmetry or

number. The strictly bonding molecular orbitals of the carbon cage on T are therefore predicted to span $\Gamma_\sigma(v,P)$, and the ion C_{3n}^{n+} to have a properly closed π shell.

The origin of the nonbonding molecular orbitals of the cage can be traced in an alternative localised bonding scheme. Of the $9n/2$ edges of T, $3n/2$ derive from edges of P, and as a set they exhaust the vertices of T. Each of these derived edges can be assigned local bonding and antibonding π orbitals. The local bonds span $\Gamma_\sigma(e,P)$ and on interaction generate the bonding and nonbonding molecular orbitals of T. Since we already know the symmetry of the strictly bonding orbitals, combination of the two models predicts that the non-bonding orbitals of T should span $\Gamma_\sigma(e,P) - \Gamma_\sigma(v,P)$.

We remark that this latter expression always has a well defined meaning for P a non-alternant polyhedron, since in that case the symmetry of the edges always contains that of the vertices. The proof is as follows: We can map the edge space $\Gamma_\sigma(e,P)$ of P to the vertex space $\Gamma_\sigma(v,P)$ of P by sending an edge $\{v_i,v_j\}$ to $v_i + v_j$, and extending by linearity to a linear map $X : \Gamma_\sigma(e,P) \to \Gamma_\sigma(v,P)$. Consider a vertex v_1 of P. We can find a path

$$v_1 \to v_2 \to v_3 \to \ldots v_n \to v_1$$

where n is odd. This can be done by choosing any path from v_1 to an odd face of P, a non-alternant, going around the face and returning to v_1 by the same path. But then the combination

$$(v_1 + v_2) - (v_2 + v_3) + (v_3 + v_4) \ldots - (v_n + v_n) + (v_n + v_1) = 2v_1$$

and so v_1 is in the image of the function X. This holds for all vertices v of P and hence X maps $\Gamma_\sigma(e,P)$ onto $\Gamma_\sigma(v,P)$. This means that $\Gamma_\sigma(v,P)$ is isomorphic to a subspace of $\Gamma_\sigma(e,P)$ and in fact is the complimentary subspace of the kernel of X.

It is easy to see that in the case of an alternant, there is always at least one vertex combination that cannot be matched in nodal pattern by a combination of edges, and therefore will be impossible to match in symmetry in some point groups: this is the fully alternating combination in which any two neighbouring vertices are taken with opposite sign.

The occupied orbitals of T are predicted to span the symmetry of the edges of the parent, which is also the symmetry of the bonding orbitals of the *leapfrog* carbon cage

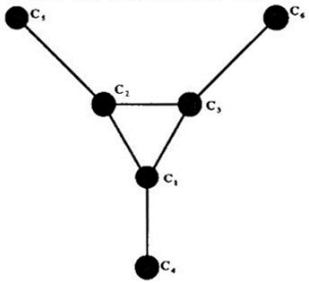
derived from P [2]. Thus, the same π electronic configuration is predicted for the leapfrog of a non-alternant trivalent polyhedron and for the leapfrog of its dual. The presence of at least n triangular faces in T implies, of course, considerable steric strain, and the occupation of $n/2$ non-bonding orbitals points to a highly non-optimal electronic structure; a cage T would be expected to distort to some other trivalent cage in which triangular faces have opened up and nonbonding orbitals have been become bonding. From the point of view of π-electronic stability, the leapfrog fullerenes are still the best choice for carbon cages with $60 + 6k$ ($k \neq 1$) atoms. Steric factors, however, often favour other members of the set of isolated-pentagon fullerenes.

Appendix

Let P be a trivalent polyhedron with n vertices and T its truncation with $3n$ vertices. Corresponding to each vertex v_i in P are three vertices $v_{i,1}, v_{i,2}, v_{i,3}$ in T. Corresponding to each edge of P is an edge of T. Construct an n-dimensional vector space V with basis $e_1, e_2, \ldots, e_n$ corresponding to the vertices on P, and similarly construct an $3n$-dimensional vector space W with basis $e_{1,1}, e_{1,2}, e_{1,3}, e_{2,1}, e_{2,2}, e_{2,3}, \ldots, e_{n,1}, e_{n,2}, e_{n,3}$ corresponding to the vertices of T. Let A be the $3n \times 3n$ vertex adjacency matrix of T. The special features of the spectrum of T noted in section 6 will now be proved in turn.

Let W_λ be the λ-eigenspace of W.

1. Here we want to find the dimension of W_0.



For any $w = (c_1, c_2, c_3, c_4, c_5, c_6, \ldots)$ in W_0, let α_i be the sum of the c_j from the vertices of T corresponding to the vertex v_i of P.

$Aw^t = (\alpha_1 - c_1 + c_4, \alpha_1 - c_2 + c_5, \alpha_1 - c_3 + c_6, \ldots)^t$. Thus

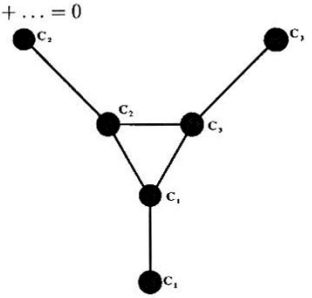
$$\begin{aligned} \alpha_1 - c_1 + c_4 &= 0 \\ \alpha_1 - c_2 + c_5 &= 0 \\ \alpha_1 - c_3 + c_6 &= 0 \end{aligned} \tag{A1}$$

But if we suppose that c_4 corresponds to v_4, c_5 corresponds to v_5 and c_6 corresponds to v_6, we get by symmetry that

$$\begin{aligned} \alpha_4 - c_4 + c_1 &= 0 \\ \alpha_5 - c_5 + c_2 &= 0 \\ \alpha_6 - c_6 + c_3 &= 0 \end{aligned} \tag{A2}$$

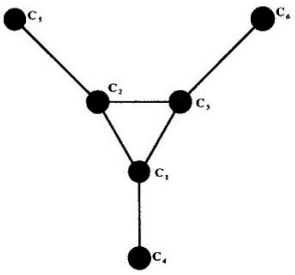
This implies that $\alpha_1 = -\alpha_4 = -\alpha_5 = -\alpha_6$. By chasing around the "original" vertices of P, this forces that each $\alpha_i = 0$ etc. unless P is an alternant. In the case that P is an alternant the edges of P can be directed so that they point from the positive vertices($\alpha_i = \alpha > 0$) to the negative vertices($\alpha_i = -\alpha < 0$). This direction is inherited by the corresponding edges in T. Then we get that $c_i - c_j = \alpha$ whenever $v_i \rightarrow v_j$, i.e. the two vertices v_i, v_j of T are joined by an original edge of P with the arrow towards v_j. Then $\sum c_i - \sum c_j = 3n\alpha/2$ where i runs over the vertices of T corresponding to positive vertices of P, and j runs over the vertices of T corresponding to negative vertices of P.

But also $\sum c_j = -n\alpha/2$ where j runs over the vertices of T corresponding to negative vertices of P and $\sum c_i = n\alpha/2$ where i runs over the vertices of T corresponding to positive vertices of P. So that also $\sum c_i - \sum c_j = n\alpha$. This means $3n\alpha/2 = n\alpha$ which forces $\alpha = 0$. So $\alpha = 0$ in both the alternant and non-alternant cases. Then W_0 is contained in the subspace $3n/2$-dimensional subspace Y of W spanned by the $e_{i,j} + e_{s,t}$ where $v_{i,j}$ and $v_{s,t}$ are joined by an original edge of P. The only additional type of constraint then is of the form $c_1 + c_2 + c_3 + \ldots = 0$



If E is the $n \times n$ adjacency matrix of the vertices of P and G is the $n \times 3n/2$ vertex-edge incidence matrix of P, then $GG^t = 3I + E$, which is an $n \times n$ matrix of rank n if P is a non-alternant and rank =n- 1 if P is an alternant. Thus the rank of G is n in the non-alternant case and is $\geq n - 1$ in the alternant case. But the 'alternating' sum of the rows of G is zero in the alternant case, so the rank of G is then $n - 1$. But G is the matrix of constraints so the dimension of W_0 is $3n/2 - n = n/2$ if P is a non-alternant and $3n/2 - (n - 1) = n/2 + 1$ if P is an alternant.

2. Here we find the dimension of W_{-2}.

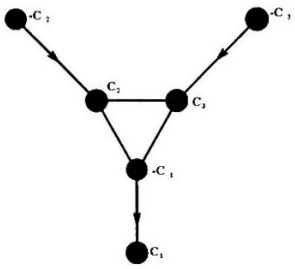


For any $w = (c_1, c_2, c_3, c_4, c_5, c_6, \ldots)$ in W_0, let α_i be the sum of the c_j from the vertices of T corresponding to the vertex v_i of P.

$Aw^t = (\alpha_1 - c_1 + c_4, \alpha_1 - c_2 + c_5, \alpha_1 - c_3 + c_6, \ldots)^t$. Thus

$$\begin{aligned} \alpha_1 - c_1 + c_4 &= -2c_1 \\ \alpha_1 - c_2 + c_5 &= -2c_2 \\ \alpha_1 - c_3 + c_6 &= -2c_3 \end{aligned} \tag{A3}$$

This implies that $c_4 + c_1 = c_2 + c_5 = c_3 + c_6 = \ldots = -\alpha$. Hence adding up about all the original vertices of P, $\sum c_i = n\alpha$. But adding up about all the original edges of P gives $\sum c_i = -3n/2\alpha$. So $\alpha = 0$. Hence W_{-2} is contained in the $3n/2$-dimensional subspace R of W spanned by the $e_{i,j} - e_{s,t}$ where $v_{i,j}$ and $v_{s,t}$ are joined by an original edge of P.



Suppose that $w = (-c_1, c_2, c_3, c_1, -c_2, -c_3, \ldots)$ is in W_{-2}. Then the only additional constraints are

$$\begin{aligned} c_2 + c_3 + c_1 &= 2c_1 \\ -c_1 + c_3 - c_2 &= -2c_2 \\ -c_1 + c_2 - c_3 &= -2c_3 \end{aligned} \tag{A4}$$

These yield: $c_2 + c_3 - c_1 = 0$. But let F be the directed edge-vertex incidence matrix of P, then $F^tF = 3I - E$, which has rank $n-1$. Thus the rank of F is $\geq n-1$. The sum of the rows of F is zero, thus the rank of F is $n-1$. But F is also the constraint matrix, thus

$$\mathrm{Dim}(W_{-2}) = 3n/2 - (n-1) = n/2 + 1 \tag{A5}$$

3. We define a linear map $\mu : V \to W$ by $\mu(e_i) = e_{i,1} + e_{i,2} + e_{i,3}$. Let $\hat{v} = \mu(v)$. Let A, E also represent the transformations induced on V, W by the adjacency matrices of P and T respectively. Let $\widetilde{u}$ be as before. Then it is easy to see that

$$A\hat{e}_i = 2\hat{e}_i + \widetilde{\hat{e}}_i$$

and so by linearity

$$A\hat{v} = 2\hat{v} + \widetilde{\hat{v}} \tag{A6}$$

for all v in V.

Also

$$A\widetilde{e}_i = \hat{Ee}_i - \widetilde{\hat{e}}_i + \hat{e}_i$$

and so by linearity

$$A\widetilde{\hat{v}} = \hat{Ev} - \widetilde{\hat{v}} + \hat{v} \tag{A7}$$

for all v in V. Now if v is an eigenvector of E with eigenvalue λ then by (A7)

$$A\widetilde{\hat{v}} = \hat{\lambda v} - \widetilde{\hat{v}} + \hat{v}$$

so

$$A\widetilde{\hat{v}} = (\lambda + 1)\hat{v} - \widetilde{\hat{v}} \tag{A8}$$

Equations (A6) and (A8) means that the space $\langle \hat{v}, \widetilde{\hat{v}} \rangle$ is A invariant and so A diagonalises on it. If β is an eigenvalue of A on this space then

since the matrix of A on $\langle \hat{v}, \widetilde{\hat{v}} \rangle$ is

$$\begin{pmatrix} -1 & \lambda + 1 \\ 1 & (k-1) \end{pmatrix}$$

$\beta^2 - \beta - (\lambda + 3) = 0$. The roots of this equation are then

$$\beta_1, \beta_2 = (1 \pm \sqrt{1 + 4(\lambda + 3)})/2 \qquad (A9)$$

So each eigenvalue λ of E gives rise to two eigenvalues, β_1, β_2 of A, except in two possible degenerate cases. These occur if the dimension of $\langle \hat{v}, \widetilde{\hat{v}} \rangle$ is one, or equivalently $\widetilde{\hat{v}} = \pm \hat{v}$, which occurs for $\lambda = 3$ and also, if P is an alternant, for $\lambda = -3$. Corresponding to $\lambda = 3$ we get $\beta_1 = 3$. Corresponding to each $-3 < \lambda < 3$ we get two eigenvalues β_1, β_2 of A, with $1 < \beta_1 < 3$ and $\beta_1 + \beta_2 = 1$. If P is an alternant then corresponding to $\lambda = -3$ we get $\beta_1 = 1$.

4. To sum up, for P a non-alternant there are $n/2$ zero eigenvalues for A, $n/2+1$ eigenvalues -2, one eigenvalue +3, $n-1$ eigenvalues β_1 in the range $1 < \beta_1 < 3$ and $n-1$ eigenvalues β_2 in in the range $-2 < \beta_2 < 0$, with $\beta_1 + \beta_2 = 1$.

For P an alternant there are $n/2 + 1$ zero eigenvalues for A, $n/2 + 1$ eigenvalues -2, one eigenvalue +1, one eigenvalue +3, $n-2$ eigenvalues β_1 in the range $1 < \beta_1 < 3$ and $n-2$ eigenvalues β_2 in in the range $-2 < \beta_2 < 0$, with $\beta_1 + \beta_2 = 1$.

5. The above theorem generalises to an arbitrary k-valent polyhedron P. The proof is essentially identical to the 3-valent case and so we omit it. The corresponding conclusion for a k-valent polyhedron P is:

For P a non-alternant there are $(k-2)n/2$ zero eigenvalues for A, $(k-2)n/2+1$ eigenvalues -2, one eigenvalue +k, $n-1$ eigenvalues β_1 in the range $k-2 < \beta_1 < k$ and $n-1$ eigenvalues β_2 in in the range $-2 < \beta_2 < 0$, with $\beta_1 + \beta_2 = k-2$.

For P an alternant there are $(k-2)n/2+1$ zero eigenvalues for A, $(k-2)n/2+1$ eigenvalues -2, one eigenvalue $k-2$, one eigenvalue k, $n-2$ eigenvalues β_1 in the range $k-2 < \beta_1 < k$ and $n-2$ eigenvalues β_2 in in the range $-2 < \beta_2 < 0$, with $\beta_1 + \beta_2 = k-2$.

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