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Symmetry aspects of bonding in carbon clusters: the leapfrog transformation

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Summary. Starting from any fullerene cage of n carbon atoms it is possible to construct a fullerene cage of $3n$ atoms with a closed electronic shell. This geometrical 'leapfrog' transformation leads to the 'magic numbers' $60+6k$ ($k=0, 2, 3, \ldots$) for neutral carbon clusters. Symmetry relations are derived for the electronic configurations, vibrational modes and numbers of NMR chemical shifts of these closed-shell clusters. All symmetry-related properties of the leapfrog fullerene follow from those of the parent, without the need for explicit construction of the larger cluster.

Key words: Carbon clusters – Leapfrog transformation – Symmetry – Fullerene – C_{60} – C_{70}

1. Introduction

Synthesis of C_{60} and C_{70} in macroscopic amounts [1] has allowed unequivocal determination of the structures of these molecules [2, 3]. Both are examples of fullerenes [4], i.e. of 3-connected polyhedral cages with 12 faces pentagonal and all others hexagonal. Such shapes are especially suitable candidates for carbon cages C_n because they are finite versions of the graphite sheet in which curvature is induced by the pentagons and delocalisation energy is maintained by the hexagons. An infinite series of fullerene cages is mathematically possible – there is at least one for every even value of $n \geqslant 20$ (with the sole exception of $n=22$) and the number of possible geometric isomers grows rapidly with n. As research groups around the world compete to isolate higher fullerenes [5–7] two questions are of basic importance – the atom counts and the shapes of the stable clusters. The present paper deals with one method of predicting these: the so-called leapfrog transformation [8, 9].

Geometrically the leapfrog operation is simple. Take any fullerene structure of n vertices, cap all faces symmetrically and convert to the face dual (Fig. 1). The result is a fullerene of the same symmetry as the original but with $3n$

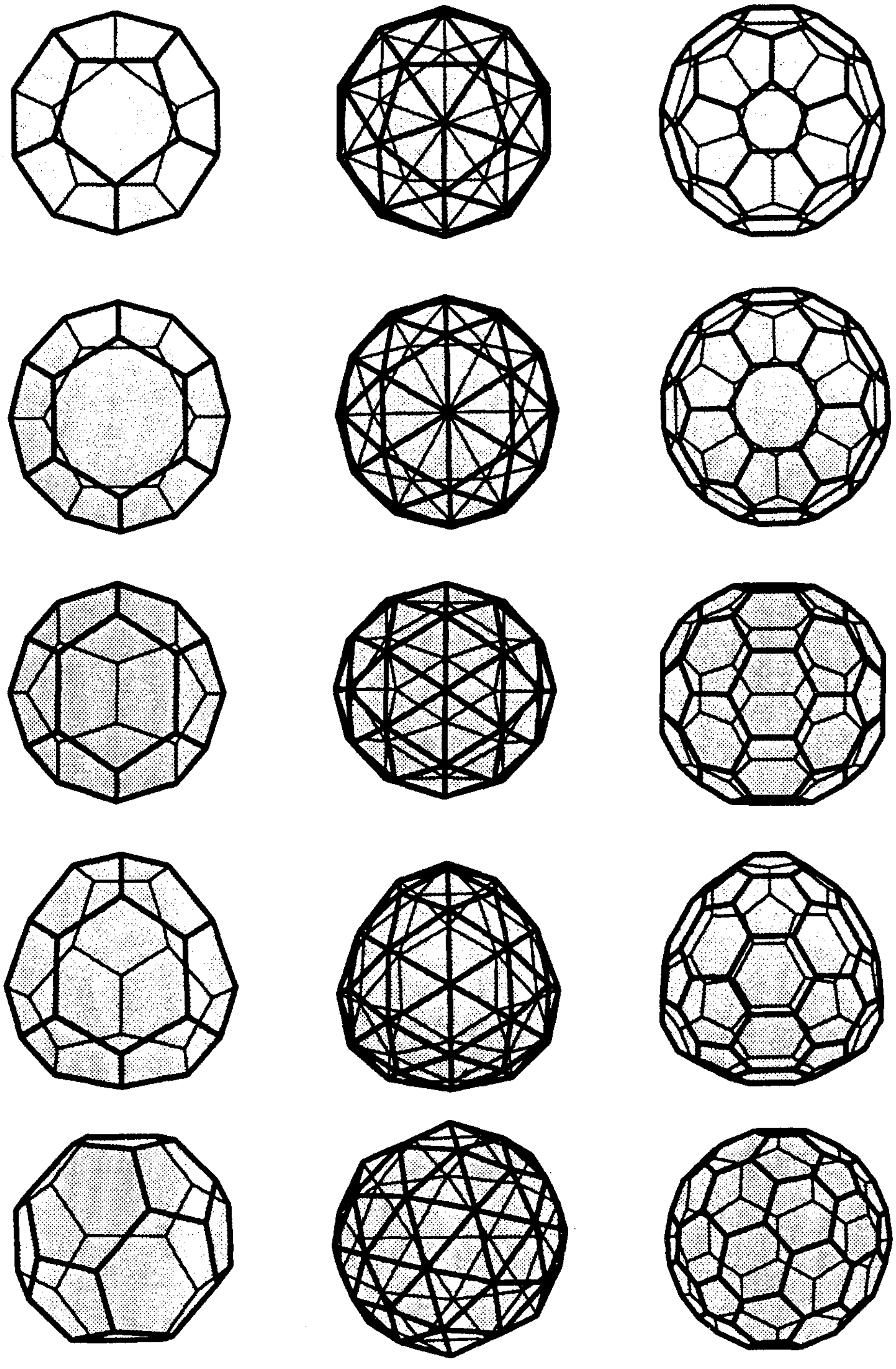

Fig. 1. The first five fullerene polyhedra and their leapfrogs: C_{20}, C_{24}, C_{26}, $C_{28}(T_d)$, $C_{28}(D_2) \Rightarrow B_{32}$, B_{38}, B_{41}, $B_{44}(T_d)$, $B_{44}(D_2) \Rightarrow C_{60}$, C_{72}, C_{78}, $C_{84}(T_d)$, $C_{84}(D_2)$. The intermediate B_n is a deltahedron that would be a suitable candidate for a giant borane framework

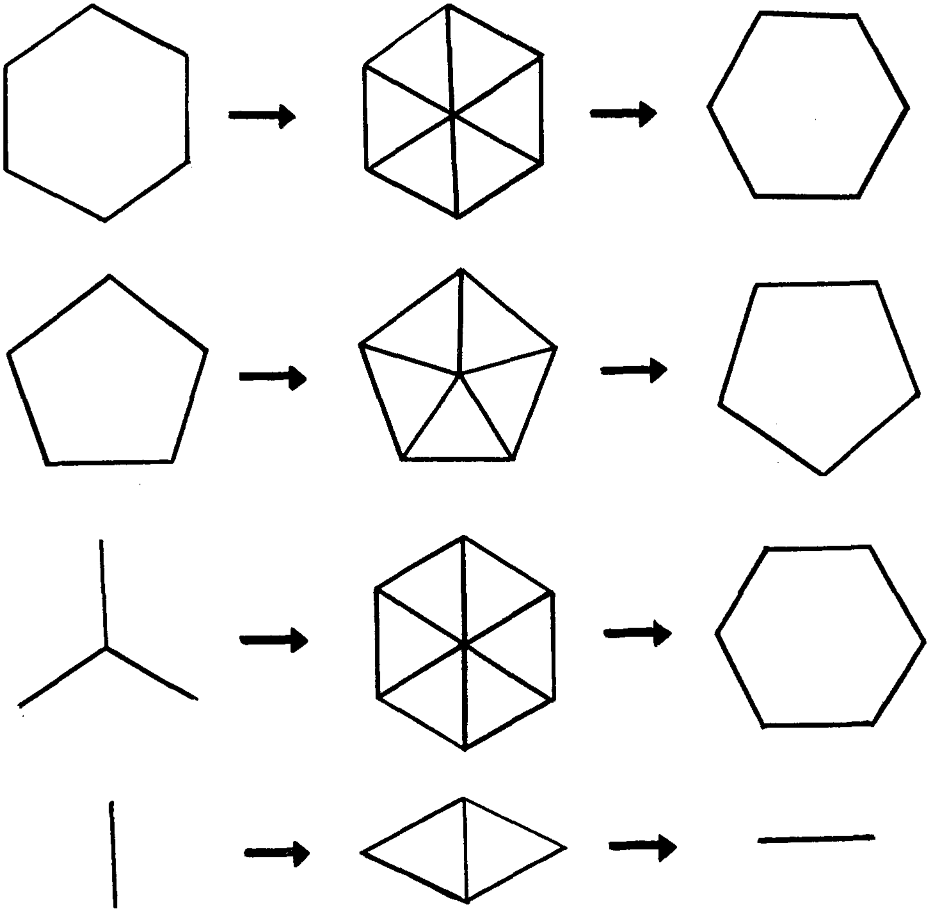

Fig. 2. Effect of the leapfrog operation on structural components (faces, vertices and edges) of a fullerene polyhedron

vertices, obtained by jumping over the intervening $(\frac{3}{2}n + 2)$-vertex deltahedron[1]. Remarkably, this procedure always leads to a fullerene with a closed electronic shell, regardless of the configuration of the starting fullerene [8, 9]. The leapfrog transformation provides partial answers to both questions raised above: closed shells occur for $n = 60 + 6k$ $(k \neq 1)$ in clusters with shapes based on those of $C_{n/3}$, and the number of leapfrog isomers for a given n is the same as the total isomer count for $C_{n/3}$. Leapfrog clusters are guaranteed to have isolated pen-

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[1] Hence the name of this operation taken from the children's game played in many countries but named after different animals (a goat in German (Bocksprung), Dutch (bokjespringen), Swedish (hoppa-bock), Norwegian (hoppe bukk), Danish (buk), Finnish (pukki-hyppy), Czech (skánáni přes kozu) and Swiss German (Böckli-Springä), but a horse in Italian (cavallina), Greek (καβάλλες), Japanese (umatobi) and Irish (caitheamh cliobóg), a sheep in French (saute-mouton), a hare in Flemish (haajse-over) and a frog in English). The Russian (чехарда) and Spanish (churro va) names do not appear to have animal associations.

tagons (Fig. 2) which is also conducive to geometric stability. An argument based on localised bonds [8] suggests that the symmetry of the occupied orbitals of C_n (leapfrog) should be just the edge representation for the parent $C_{n/3}$. In the present note this symmetry aspect is explored further.

It should be noted that the $60 + 6k$ rule is not exclusive; some closed shells occur outside it (notably C_{70}). A subsidiary rule for five- and six-fold symmetric carbon cylinders $n = 2p(7 + 3k)$ where $p = 5$ or 6 and $k = 0, 1, 2, \ldots$ accounts for all known non-leapfrog closed shells obtained in Hückel calculations on fullerenes [10]. Fullerenes with other atom counts may be stable, but do not have properly closed-shell electronic structures within the Hückel approximation [11]. A target for future theoretical work is the integration of electronic and steric factors in a theory that will give uniformly reliable stability predictions for all sizes of cluster.

2. Symmetry and the leapfrog transformation

A fullerene polyhedron P has n vertices, 12 pentagonal faces, $(\frac{1}{2}n - 10)$ hexagonal faces and $\frac{3}{2}n$ edges. The leapfrog polyhedron L has $3n$ vertices, 12 pentagonal faces, $(\frac{3}{2}n - 10)$ hexagonal faces and $\frac{9}{2}n$ edges. Symmetry relations between P and L are now derived.

We may define the vertex-, edge- and face representations of a polyhedron belonging to a point symmetry group G as the permutation (or σ) representations (usually reducible) in G generated by structureless points at all vertices, edge- or face-centres. These positions fall into one or more sets of equivalent points (orbits of G) and so their permutation representations are reducible to sums of the σ representations Γ_σ tabulated in [12]. A convex polyhedron is topologically equivalent to a spherical shape in which all points lie on a surface of arbitrary radius; the distribution of points on this surface determines the symmetry.

It is also useful to define two tangential edge representations $\Gamma_\parallel(e)$ and $\Gamma_\perp(e)$ which are generated by sets of vectors *along* and *across* polyhedron edges, respectively. They sum to the π representation: $\Gamma_\parallel(e) + \Gamma_\perp(e) = \Gamma_\pi(e) = \Gamma_\sigma(e) \times \Gamma_{xyz} - \Gamma_\sigma(e)$ where Γ_{xyz} is the (usually reducible) dipole or cartesian representation in G.

On going from P to L every face is replaced by a similar but rotated polygon on the same centre, and new hexagonal faces appear centred on the vertices of P (Fig. 2). The face representation of L is thus:

$$\Gamma_\sigma(f, L) = \Gamma_\sigma(f, P) + \Gamma_\sigma(v, P) \tag{1}$$

The set of edges of L comprises one edge perpendicular to each old one of P *plus* three new edges around every vertex site of P. The new edges span a $(\sigma + \pi)$ triplet for each old vertex and so the relationship between Γ^α and Γ^π gives the edge representation of L as:

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

Vertices of L can be assigned in pairs to the $3n/2$ edges lying perpendicular to the old edges of P. Taking the in- and out-of-phase combinations for each pair gives:

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

For any 3-connected polyhedron the perpendicular and parallel edge representations are functions of edge and vertex permutation representations (see Eqs. (5′ and 6′) of [13]):

$$\Gamma_{\parallel}(e, P) = \Gamma_{\sigma}(v, P) \times \Gamma_{xyz} - \Gamma_{\sigma}(e, P)$$

$$\Gamma_{\perp}(e, P) = \Gamma_{\parallel}(e, P) \times \Gamma_{\epsilon}$$

where Γ_{ϵ} is the antisymmetric representation. Hence the vertex representations of L is just the sum:

$$\Gamma_{\sigma}(v, L) = \Gamma_{\sigma}(e, P) + \Gamma_{\sigma}(v, P) \times \Gamma_{xyz} \times \Gamma_{\epsilon} - \Gamma_{\sigma}(e, P) \times \Gamma_{\epsilon} \qquad (3b)$$

Thus all three representations can be computed for L once they are known for P. In turn, the tangential representations $\Gamma_{\perp}(e, L)$ and $\Gamma_{\parallel}(e, L)$ follow from the general definitions. Explicit construction of L is not required.

An application of Eqs. (1) to (3) can be made to C_{60}. Truncated icosahedral C_{60} is the leapfrog polyhedron of the 20-carbon dodecahedral cage. The faces, vertices and edges of C_{20} span the orbitals O_{12}, O_{20} and O_{30}, respectively, in the group I_h. Thus for $P_1 = C_{20}$

$$\Gamma_{\sigma}(f, P_1) = \Gamma_{\sigma}(O_{12}, I_h) = A_g + H_g + T_{1u} + T_{2u}$$

$$\Gamma_{\sigma}(v, P_1) = \Gamma_{\sigma}(O_{20}, I_h) = A_g + G_g + H_g + T_{1u} + T_{2u} + G_u$$

$$\Gamma_{\sigma}(e, P_1) = \Gamma_{\sigma}(O_{30}, I_h) = A_g + G_g + 2H_g + T_{1u} + T_{2u} + G_u + H_u$$

Application of Eqs. (1) to (3) together with identities specific to the icoashedral group generates for $L_1 = C_{60}$:

$$\begin{aligned}
\Gamma_{\sigma}(f, L_1) &= \Gamma_{\sigma}(O_{12}, I_h) + \Gamma_{\sigma}(O_{20}, I_h) \\
\Gamma_{\sigma}(v, L_1) &= \Gamma_{\sigma}(O_{30}, I_h) + \Gamma_{\sigma}(O_{20}, I_h) \times \Gamma_{xyz} \times \Gamma_{\epsilon} - \Gamma_{\sigma}(O_{30}, I_h) \times \Gamma_{\epsilon} \\
&= \Gamma_{\sigma}(O_{30}, I_h) + \Gamma_{\sigma}(O_{60}, I_h) \times \Gamma_{\epsilon} - \Gamma_{\sigma}(O_{30}, I_h) \times \Gamma_{\epsilon} \\
&= \Gamma_{\sigma}(O_{60}, I_h) \\
&= A_g + T_{1g} + T_{2g} + 2G_g + 3H_g + 2T_{1u} + 2T_{2u} + 2G_u + 2H_u \\
\Gamma_{\sigma}(e, L_1) &= \Gamma_{\sigma}(O_{30}, I_h) + \Gamma_{\sigma}(O_{20}, I_h) \times \Gamma_{xyz} = \Gamma_{\sigma}(O_{30}, I_h) + \Gamma_{\sigma}(O_{60}, I_h)
\end{aligned}$$

and these agree with the direct symmetry analysis of the 60-vertex cage.

A second example is the 28-vertex fullerene cage which has two isomers (T_d and D_2) each of which can leapfrog to a plausible C_{84} structure [14]. Both have 4 hexagonal and 12 pentagonal faces. For the T_d isomer ($P_2 = C_{28}, T_d$) the structural components span:

$$\begin{aligned}
\Gamma_{\sigma}(f, P_2) &= \Gamma_{\sigma}(O_4, T_d) + \Gamma_{\sigma}(O_{12}, T_d) = 2A_1 + E + T_1 + 3T_2 \\
\Gamma_{\sigma}(v, P_2) &= \Gamma_{\sigma}(O_4, T_d) + 2\Gamma_{\sigma}(O_{12}, T_d) = 3A_1 + 2E + 2T_1 + 5T_2 \\
\Gamma_{\sigma}(e, P_2) &= \Gamma_{\sigma}(O_6, T_d) + \Gamma_{\sigma}(O_{12}, T_d) + \Gamma_{\sigma}(O_{24}, T_d) \\
&= 3A_1 + A_2 + 4E + 4T_1 + 6T_2
\end{aligned}$$

Application of Eqs. (1) to (3) or direct inspection of ($L_2 = C_{84}, T_d$) gives:

$$\begin{aligned}
\Gamma_{\sigma}(f, L_2) &= 5A_1 + 3E + 3T_1 + 8T_2 \\
\Gamma_{\sigma}(v, L_2) &= 4A_1 + 3A_2 + 7E + 10T_1 + 11T_2 \\
\Gamma_{\sigma}(e, L_2) &= 8A_1 + 3A_2 + 11E + 13T_1 + 18T_2
\end{aligned}$$

The corresponding results for the D_2 isomers ($P_3 = C_{28}, D_2$) and ($L_3 = C_{84}, D_2$) are:

$$\Gamma_\sigma(f, P_3) = 4A + 4B_1 + 4B_2 + 4B_3$$

$$\Gamma_\sigma(v, P_3) = 7A + 7B_1 + 7B_2 + 7B_3$$

$$\Gamma_\sigma(e, P_3) = 12A + 10B_1 + 10B_2 + 10B_3$$

$$\Gamma_\sigma(f, L_3) = 11A + 11B_1 + 11B_2 + 11B_3$$

$$\Gamma_\sigma(v, L_3) = 21A + 21B_1 + 21B_2 + 21B_3$$

$$\Gamma_\sigma(e, L_3) = 33A + 31B_1 + 31B_2 + 31B_3$$

All three examples illustrate the general proposition that, given the representations for a polyhedron P, all symmetry properties of its leapfrog L can be deduced. The derived representations have several uses, as now discussed.

3. Properties of the leapfrog cluster

The vertex representation of a polyhedron has several applications in chemistry. First, n_0, the number of copies of the totally symmetric representation in $\Gamma_\sigma(v)$, gives the number of symmetry-distinct nuclei. Hence for a fullerene n_0 would count the distinct chemical shift peaks observable in isotopically dilute (natural-abundance) ^{13}C-NMR spectra.

Multiplication of $\Gamma_\sigma(v)$ by Γ_{xyz} and subtraction of translational and rotational reprsentations yields the vibrational representation Γ_{vib}:

$$\Gamma_{vib} = \Gamma_\sigma(v) \times \Gamma_{xyz} - \Gamma_{xyz} - \Gamma_{xyz} \times \Gamma_\epsilon$$

This, of course, gives the symmetry classification of the normal modes of vibration of the polyhedral structure, and also the number of independent structural parameters n_p for the molecule (n_p is the number of copies of Γ_0 in Γ_{vib}). Similarly the copies of Γ_0 in $\Gamma_\sigma(e)$ correspond to independent nearest-neighbour distances in the polyhedron. Comparison of Γ_{vib} with Γ_{xyz} and $[\Gamma^2_{xyz}]$ gives the number of IR-active, Raman-active and IR/Raman coincident vibrational frequencies. n_p also counts the polarised Raman fundamentals of a molecule. All these quantities for L follow from $\Gamma_\sigma(f, P)$, $\Gamma_\sigma(v, P)$ and $\Gamma_\sigma(e, P)$.

For a polyhedron belonging to a pure-rotation group, Eq. (3) reduces to:

$$\Gamma_\sigma(v, L) = \Gamma_\sigma(v, P) \times \Gamma_{xyz} \qquad C_n, D_n, T, O, I$$

and then the number of NMR signals for L, $n_0(L)$ is simply related to the number of structural parameters of P, $n_p(P)$. In this special case $n_0(L) = n_p(P) + 2n(\mu)$ where $n(\mu)$ is the number of independent components of the dipole moment in G, i.e. the number of Γ_0 symmetries spanned by Γ_{xyz}. This latter relation is valid *only* if G contains no improper operation.

Perhaps the most interesting feature of the leapfrog transformation is that it allows prediction of the symmetries of the occupied orbitals without explicit construction of L. All known leapfrog fullerenes have closed electronic shells, and this has been rationalised (see [8]) by noting that for every L there is at least one localised Kekulé structure that preserves full molecular symmetry and can be constructed by placing a double bond on each of the $3n/2$ edges of L that cross an old edge of P (leading to a network of contiguous benzenoid hexagons centred on every old vertex of P). Interaction amongst the localised orbitals is expected to stabilise the cluster and delocalise the MOs, but not to change the number and symmetry of bonding combinations.

Another, and possibly more convincing argument that leapfrogging will always generate a closed shell can be based on comparison with the bonding in 3-connected saturated cages such as the polyhedranes, C_nH_n. When the carbon skeleton is of the fullerene type we propose to call the hydride a fullerane. The first of the series, $C_{20}H_{20}$, was synthesised a decade ago [15], and the hypothetical C_{60} derivative $C_{60}H_{60}$ has been the subject of *ab initio* calculation [16].

A carbon atom in a 3-connected saturated cluster X has 3 atomic orbitals $(\sigma + \pi)$ available for framework bonding and n such atoms produce $(\frac{1}{2}n + 2)$ strongly and $(n - 2)$ weakly bonding cage orbitals, i.e. $\frac{3}{2}n$ edge-precise single bonds. The total MO representation is:

$$\Gamma_\sigma(v, X) \times \Gamma_{xyz} = \Gamma_\sigma(v, X) + \Gamma_\pi(v, X)$$

and it can be shown [13] that the bonding half of the MOs spans:

$$\Gamma_\sigma(e, X) = \Gamma_\sigma(f, X) + [\Gamma_\pi(f, X) - \Gamma_{xyz} - \Gamma_{xyz} \times \Gamma_\epsilon]$$

whilst the antibonding half spans:

$$\Gamma_\parallel(e, X) = [\Gamma_\sigma(f, X) - \Gamma_0] \times \Gamma_\epsilon + [\Gamma_\sigma(v, X) - \Gamma_0]$$

These equations hold for all 3-connected X.

The link to fullerenes is this. In the 'surface π' system[2] of a fullerene each atom has only a σ radial p orbital instead of the $(\sigma + \pi)$ triplet involved in edge bonding. When X is a leapfrog of some parent P the representation of this basis is, by Eq. (3a):

$$\Gamma_\sigma(v, L = X) = \Gamma_\sigma(e, P) + \Gamma_\perp(e, P)$$

Now, the $n/2$ combinations spanning $\Gamma_\sigma(e, P)$ are wholly contained within $\Gamma_\sigma(e, X)$, and the $n/2$ combinations spanning $\Gamma_\perp(e, P)$ are wholly contained within $\Gamma_\parallel(e, X)$ (note the difference in subscripts here) and so the fullerene subset of the fullerane $(\sigma + \pi)$ basis splits into equal numbers of bonding and antibonding orbitals. Hence the leapfrog cluster has a closed shell.

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[2] There is a potential confusion in notation for carbon clusters. Mathematically, the labels σ, π, δ . . . refer to the nodal characteristics of basis functions defined with respect to a radial vector. Chemically, the same labels are used to describe orbital characteristics with respect to the C–C bond. The framework C–C bonds are then σ, and the bonds formed by lateral overlap of p orbitals are then π. In the mathematical sense, however, the basis functions contributing to the Hückel system span σ representations because they are axially symmetric about a radius. In this paper we use σ and π in the mathematical sense.

In the fullerane the σ lobes are *endo* and in the fullerene they are *exo*, but this does not affect the symmetry argument. The *exo* σ system of the fullerane is stabilised by interaction with the ligating hydrogens, and the resulting C–H bonding combinations can accommodate $2n$ electrons instead of n.

Both arguments lead to the conclusion that the bonding combinations of radial p orbitals of the leapfrog fullerene L span the edge representation of P:

$$\Gamma_{bond}(L) = \Gamma_\sigma(e, P)$$

For example, the full set of radial p orbitals in C_{60} spans $\Gamma_v = \Gamma_\sigma(O_{60}, I_h)$ but the subset of bonding MOs spans $\Gamma_\sigma(O_{30}, I_h)$ which is $\Gamma_\sigma(e)$ for the 20-cage. The full electronic configuration of C_{60} has 60 $1s^2$ cores, 90 σ edge bonds and 30 π edge bonds, i.e. the general formula for the representation spanned by the occupied orbitals is:

$$\Gamma_{occ}(L) = \Gamma_\sigma(v, L) + \Gamma_\sigma(e, L) + \Gamma_\sigma(e, P) = 4\Gamma_\sigma(e, P) + \Gamma_\pi(e, P)$$

where the second identity follows from Eqs. (1) to (3) and a theorem which is valid for 3-connected clusters (see Eq. (7′) in [13]):

$$\text{(3-connected)} \quad \Gamma_\sigma(e) \times \Gamma_{xyz} = \Gamma_\sigma(v) \times \Gamma_{xyz} \times (\Gamma_0 + \Gamma_\epsilon) - \Gamma_\sigma(e) \times \Gamma_\epsilon$$

4. Iteration of the leapfrog transformation

As the leapfrog of a fullerene is itself a fullerene, the procedure may be repeated to generate larger and larger clusters:

$$P(C_n) \rightarrow L(C_{3n}) \rightarrow L'(C_{9n}) \rightarrow L''(C_{27n}) \ldots$$

The icosahedral sequence 20, 60, 180, 540, 1620, ... is of particular interest [17], but is clearly only one of an infinity of possibilities. Every member after the first one has a closed shell, and all symmetry properties of subsequent members are implicit in those of the first. Straightforward iteration of Eqs. (1) to (3) gives the permutation representations of L' in terms of those of P as:

$$\Gamma_\sigma(f, L') = \Gamma_\sigma(f, P) + \Gamma_\sigma(e, P) \times [\Gamma_0 - \Gamma_\epsilon] + \Gamma_\sigma(v, P) \times [\Gamma_0 + \Gamma_{xyz} \times \Gamma_\epsilon]$$

$$\Gamma_\sigma(e, L') = \Gamma_\sigma(e, P) \times [\Gamma_0 + (\Gamma_0 - \Gamma_\epsilon) \times \Gamma_{xyz}] + \Gamma_\sigma(v, P) \times [\Gamma_0 + \Gamma_{xyz} \times \Gamma_\epsilon] \times \Gamma_{xyz}$$

$$\Gamma_\sigma(v, L') = \Gamma_\sigma(e, P) \times [\Gamma_0 - \Gamma_\epsilon] \times [\Gamma_0 - \Gamma_{xyz}] + \Gamma_\sigma(v, P) \times [\Gamma_0 - \Gamma_\epsilon + \Gamma_{xyz}] \times \Gamma_{xyz}$$

Many equivalent forms of these equations can be derived using theorems for 3-connected polyhedra [13] and definitions of Γ_π, Γ_δ etc.

5. Conclusion

The leapfrog transformation offers a systematic way of predicting the shapes, electronic configurations and properties of closed-shell fullerenes. It gives starting guesses for more sophisticated *ab initio* treatments, but can also aid the interpretation of experimental spectroscopic data without the need for explicit construction of the cluster.

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