

# The Leapfrog Principle: A Rule for Electron Counts of Carbon Clusters

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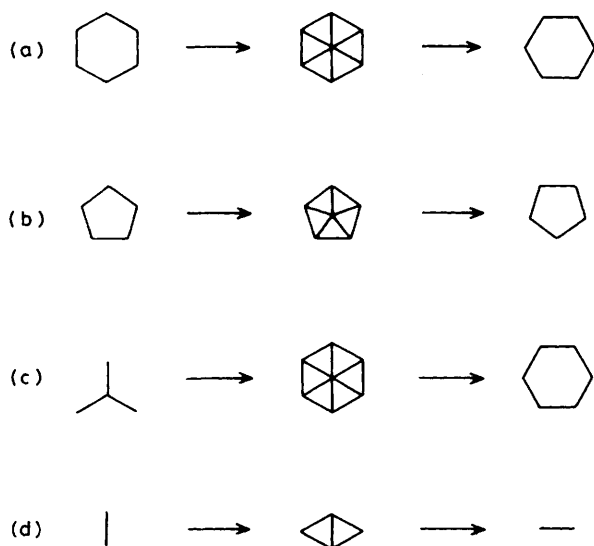
Pseudospherical carbon clusters  $C_n$  with  $n = 60 + 6k$  and  $k$  equal either to zero or to any integer greater than one are expected to have closed electronic shells; a simple rule predicts the symmetries of the bonding orbitals of these 'leapfrog' clusters.

Laser irradiation of graphite produces a range of novel carbon species, amongst them the now famous  $C_{60}$  molecule.<sup>1-3</sup> It has been postulated that the longer-lived fragmentation products with even numbers of carbon atoms are *pseudo*-spherical clusters.<sup>3</sup> In particular, the sixty-carbon fragment is thought to have a truncated icosahedral structure.<sup>1</sup> Calculations from simple Hückel<sup>4</sup> to *ab initio* SCF<sup>5</sup> levels confirm that icosahedral  $C_{60}$  would have a closed-shell electronic configuration with substantial delocalisation energy, and would occupy at least a local minimum on the potential energy surface. A seventy-carbon species also shows special stability.<sup>2</sup> Theoretical studies of a number of hypothetical molecules suggests that  $C_{60}$  and  $C_{70}$  may be members of a larger series of stable clusters.<sup>6,7</sup> Indeed, an infinite series of closed-shell clusters of icosahedral symmetry is predicted by Hückel theory.<sup>8</sup> The present paper widens the discussion still further. All 3-connected carbon frameworks that satisfy certain general conditions are predicted here to give closed shells. To generate these structures we use the leapfrog principle<sup>8</sup> described below.

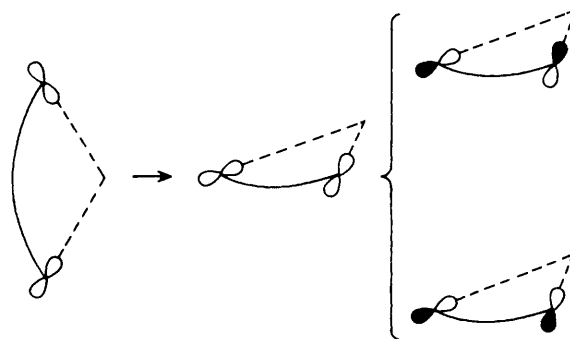
The various theoretical treatments make some plausible assumptions about the shapes of large carbon clusters. They are thought to be 3-connected, pseudospherical polyhedra with 12 pentagonal faces and all other faces hexagonal. Exactly 12 pentagons are necessary to give a geometrically closed shape. Other ring sizes are less likely because they reduce the delocalisation energy. At least one such  $n$ -vertex polyhedron exists for all even  $n \geq 20$  with the sole exception<sup>9</sup> of  $n = 22$ . The number of hexagonal faces is  $(n/2) - 10$ , and in

a sense these polyhedra are finite analogues of the infinite graphite layer. When  $n$  is small the polyhedra are unique, but the number of distinct combinations of atoms grows rapidly with increasing nuclearity. For example, there is only one pentagon + hexagon cluster with  $n = 24$  but over 80 for  $n = 44$ .<sup>10,11</sup> In qualitative M.O. theory these clusters are considered to be held together by  $\sigma$  and  $\pi$  bonds. Using a set of  $sp^2$  hybrids on each atom, one two-electron bond is constructed for each of the  $(3n/2)$  edges of the polyhedron. A  $\pi$  framework is built up from the remaining  $n$  radial p orbitals. A closed-shell cluster is thus one where precisely  $(n/2)$  of the  $\pi$  M.O.s are bonding.

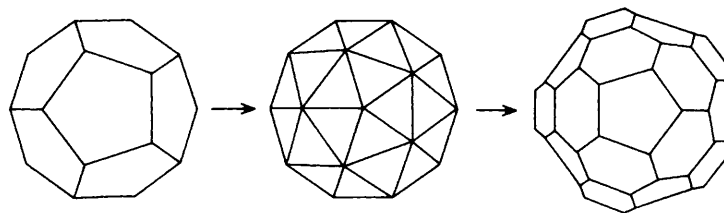
From any pentagon + hexagon polyhedron we may generate another containing three times as many atoms. This is done by the leapfrog operation<sup>8</sup> which is carried out as follows. First, all faces of the original polyhedron P are capped to produce a deltahedron D (= a polyhedron with all faces triangular). Then the dual is taken (the dual is a polyhedron where each face-centre of the original becomes a vertex, and each vertex is replaced by the centre of a face. Thus a cube and an octahedron are duals, an icosahedron and a dodecahedron are duals, and a tetrahedron is self-dual). The final polyhedron L is termed the leapfrog of P. It is easy to show by Euler's rule that the final polyhedron has  $3n$  vertices, and  $12$  pentagonal and  $(3n/2) - 10$  hexagonal faces. It is also evident that a polyhedron and its leapfrog belong to the same point group (except when by accident of bondlengths the leapfrog has higher symmetry). Leapfrogging may be repeated so that, from an original  $n$ -vertex cluster, polyhedra with  $3n$ ,  $9n$ ,  $27n$  etc. vertices are produced. As shown in Figure 1, to each face of the original polyhedron corresponds a geometrically similar but rotated face in the leapfrog. In addition each vertex of the original is replaced by a hexagon in the leapfrog. Some use has been made of the leapfrog operation<sup>8</sup> but here we introduce an important new point. The abstract mathematical concept of



**Figure 1.** Transformation of components of a polyhedron P under the leapfrog operation: (a) a hexagon in P is replaced by a hexagonal cap rotated through  $30^\circ$  (and surrounded by hexagons); (b) a pentagon in P gives a pentagon in L but rotated through  $36^\circ$ ; (c) a vertex of P is surrounded by 3 capping atoms and gives a new hexagonal face in L; (d) an edge of P gives an edge rotated through  $90^\circ$  in L.



**Figure 2.** Bonding and antibonding localised orbitals of a leapfrog polyhedron. The arrow represents the leapfrog operation. An edge of the original polyhedron corresponds to a transverse edge in the leapfrog for which the radial p-orbitals give one antibonding (upper) and one bonding (lower) combination.



**Figure 3.** The simplest example of the leapfrog operation. A dodecahedron ( $C_{20}$ ) has 12 pentagonal faces. Each of these is capped, becoming a pentagonal pyramid, to give a 32-vertex 60-face deltahedron: the omnicapped dodecahedron ( $B_{32}$ ). In the second stage of the leapfrog operation the dual is taken. Each triangle is replaced by a 3-coordinate vertex, each capping atom becomes the centre of a pentagon, and each 6-coordinate vertex the centre of a hexagon. The final polyhedron is thus the truncated icosahedron ( $C_{60}$ ).

the leapfrog has an implication for cluster bonding: any leapfrog of a 3-connected pentagon + hexagon cluster corresponds to a closed-shell neutral carbon cluster.

To see this, consider the effect of the leapfrog operation on an edge of the original polyhedron (Figure 1d). Corresponding to each edge in the original is one rotated through  $90^\circ$  in the leapfrog. Of the  $(9n/2)$  edges of the leapfrog, one third are derived in this way from the edges of the original. Every vertex of the leapfrog is contained in just one such edge. Because the polyhedron is 3-connected an electron-precise  $\sigma$  framework can be constructed from  $sp^2$  hybrids. Remembering that each vertex also carries a radial p orbital, we can assign one local  $\pi$ -bond and one  $\pi$ -antibond to each derived edge (Figure 2). Interaction between the local orbitals will produce delocalised M.O.s and will alter their energies but will not change the total number of bonding and antibonding combinations. We can therefore expect  $(3n/2)$  bonding and  $(3n/2)$  antibonding M.O.s in the  $\pi$ -system. Hence the leapfrog has a closed shell with  $3n$   $\pi$ -electrons occupying  $(3n/2)$  orbitals.

Since pentagon + hexagon polyhedra exist with 20, 24, 26, 28 . . . vertices, this reasoning predicts closed shells for  $C_n$  where  $n = 60, 72, 78, 84$  . . . (but not 66), *i.e.* for equation (1), where  $k$  is either zero or an integer greater than one. This is an analogue of the famous  $4n + 2$  rule of Hückel, and it is equivalent to a statement that, whenever a structure L can be made by leapfrogging a small cluster P, the larger molecule has a closed shell. It has nothing to say about non-leapfrog structures. Vertex numbers not satisfying equation (1) may or may not give closed shells. For example,  $C_{70}$  does not satisfy equation (1) but is closed-shell, albeit with an empty nonbonding orbital.<sup>6</sup> Furthermore, clusters with a vertex number satisfying equation (1) but which are not geometrically leapfrogs may or may not be closed-shell. For example, of several possible shapes for  $C_{120}$  some have closed and some open shells; only when they are leapfrogs of  $C_{40}$  is the closed shell guaranteed by equation (1). The rule (1) is borne out by calculations on a range of carbon clusters  $C_n$  with  $n$  ranging from 20 to several hundred. All leapfrogs tested so far have been found to be closed-shell. These calculations will be reported in detail in a later paper.

$$n = 60 + 6k \quad (1)$$

One interesting feature of the leapfrog procedure is that it never generates adjacent pentagons.  $C_{60}$ , the smallest leapfrog, is also the smallest cluster where every pentagonal face is surrounded by hexagons. On general chemical grounds we would expect that the pentagons would be well-separated in stable clusters, and we would also expect highly symmetrical structures to be particularly stable. Icosahedral clusters satisfy both of these expectations, as they have the highest possible symmetry and maximise the distance between pentagons.<sup>8</sup> However, they do not all have closed shells.

$C_{22}$  does not exist as a pentagon + hexagon polyhedron and so  $C_{66}$  cannot be made as a leapfrog. A rather irregular 66-vertex cluster of  $D_3$  symmetry has an open shell. Its leapfrog,  $C_{198}$ , has a closed shell. The second member of the series (1) is a  $C_{72}$  structure which is the leapfrog of the unique  $C_{24}$  polyhedron and turns out to be the same molecule as the 'carbon pillow'.<sup>3</sup>

A useful analogy can be drawn between the unsaturated carbon clusters and the saturated polyhedranes. An  $m$ -vertex 3-connected polyhedron can serve as the carbon framework of an electron-precise  $C_mH_m$  cluster. The three lobes of a set of  $sp^2$  hybrids give one local  $\sigma$ -bond per edge and hence a closed-shell configuration. A one-to-one correspondence exists between the  $\sigma$ -bonding orbitals of a  $C_mH_m$  cluster (or the edges of the  $C_m$  polyhedron) and the  $\pi$ -bonding orbitals of the leapfrog  $C_{3m}$ . A group theoretical version of this correspondence runs as follows. The symmetry spanned by the  $\pi$ -bonding M.O.s of a leapfrog cluster L is the same as the reducible representation of the edges of the original polyhedron P, see equation (2). Thus we have not only a criterion

$$\Gamma_{3n/2}(\text{bonding M.O.s of L}) = \Gamma_{3n/2}(\text{edges of P}) \quad (2)$$

for predicting closed shells but also a prediction of the symmetry labels of the electronic configuration. To take a simple example,  $C_{60}$  is the leapfrog of  $C_{20}$  (Figure 3) and therefore the bonding  $\pi$  M.O.s of  $C_{60}$  should span the same symmetry as the 30 edges of a dodecahedron, *i.e.* equation (3).

$$\Gamma_{30} = A_g + T_{1u} + T_{2u} + G_g + G_u + 2H_g + H_u \quad (3)$$

This is correct.<sup>6</sup> Similarly the 90 edges of  $C_{60}$  span the symmetry in equation (4), and this is the reducible representa-

$$\Gamma_{30} + \Gamma_{60} = 2A_g + T_{1g} + 3T_{1u} + T_{2g} + 3T_{2u} + 3G_g + 3G_u + 5H_g + 3H_u \quad (4)$$

$$\Gamma_{30} + 2\Gamma_{60} + \Gamma_{120} = 4A_g + A_u + 5T_{1g} + 8T_{1u} + 5T_{2g} + 8T_{2u} + 9G_g + 9G_u + 13H_g + 10H_u \quad (5)$$

tion of the 90 bonding M.O.s of  $C_{180}$ , the leapfrog<sup>8</sup> of  $C_{60}$ . In turn the 270 edges of  $C_{180}$  span equation (5), and match in symmetry the bonding  $\pi$  M.O.s of  $C_{540}$ .<sup>8</sup> All the  $\Gamma_m$  are  $\sigma$  representations, generated by permutation of a set of equivalent points (*e.g.* bond centres). For further explanation of the symbols see ref. 12.

The new electron-counting rule subsumes an earlier one for  $I$  and  $I_h$  clusters. It has been shown<sup>8</sup> that icosahedral clusters with  $60m$  atoms have closed shells, those with  $60m + 20$  atoms have open shells. Here  $m$  is an integer of the form  $(a^2 + ab + b^2)$ . Each closed-shell  $I$  or  $I_h$  cluster is the leapfrog of an open-shell structure of the same symmetry but with only  $20m$

atoms. Thus all closed-shell icosahedral clusters are special cases of the new  $60 + 6k$  rule with  $k = 10$  ( $a^2 + ab + b^2 - 1$ ).

Finally we consider some hypothetical  $C_{120}$  clusters. Dualising the various proposals of Brown and Lipscomb<sup>13</sup> for  $B_{22}$  structures (Figures Xa, Xb, and Xc of ref. 13), we may construct  $C_{40}$  frameworks of  $T_d$ ,  $D_{5d}$ , and  $C_{2v}$  symmetry. A second  $D_{5d}$  structure can be made from two half-dodecahedra joined by two belts of hexagons. All give either open shells or closed shells with empty bonding M.O.s. On leapfrogging we obtain four properly closed-shell  $C_{120}$  structures with delocalisation energies of 0.56332, 0.56336, 0.56331, and 0.56338  $\beta$ /atom, respectively. (The second  $D_{5d}$  value was given incorrectly in ref. 8 where the structure illustrated is actually  $D_{5h}$  and open-shell.) Although the assumption of a single  $\beta$  value introduces some uncertainty into the comparison, it is clear that all four are plausible structures for  $C_{120}$ , substantially more stable than the 'Archimedene' (non-leapfrog) proposal<sup>14</sup> with its delocalisation energy of 0.48810  $\beta$ /atom. A forthcoming paper will present possible structures for a large number of carbon clusters.

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