

ATOMIC AND ELECTRONIC STRUCTURE OF MINI-FULLERENES: FROM FOUR TO TWENTY

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Abstract. It is customary to assume that fullerenes are the carbon molecules having a shape close to a spherical surface which can be composed of regular pentagons combined with regular hexagons. Earlier we developed a method for calculating electronic and atomic structure for such fullerenes. Now we suppose that the restriction on fullerenes construction only from pentagons and hexagons is unnecessary. In other words, we take the term “*fullerene*” in a broad sense to mean any shape inscribed into to a spherical surface which can be composed of carbon atoms, each atom having three nearest neighbors, whenever discussing hollow carbon clusters. In addition to this definition, we suppose that not only atoms but also shared electron pairs, forming covalent bonds, are located on one and the same sphere. From this it follows that the geometry of both the electronic structure as well as of the atomic structure of fullerenes can be most conveniently constructed and studied with the help of *spherical geometry*. We enlarged here the approach developed earlier for usual fullerenes. The procedure created reveals the *hidden symmetry* of the shared electron pairs located on the same sphere as that of carbon atoms. The most interesting result is that we have found *structural isomers* of some fullerenes which differed in their surface electronic density.

1. Definitions and main postulates

“A knowledge of the relative positions in space of the atoms in a molecule has acquired grater importance recently for two reasons: first, because they are fundamental in determining the possibility of resonance among different structures; and secondly, from the point of view of chemical dynamics, since we now realize that the heat of activation is largely the energy required to bring the atoms into their proper position for reaction” (Bakerian Lecture ‘Stereochemical types and valency groups’ by N.V. Sidgwick F.R.S. and H.M. Powell, 1940 [1]).

After such pre-statement we pass on to fullerenes. It is customary to assume that fullerenes are the carbon molecules having a shape close to a spherical surface which can be composed of regular pentagons combined with regular hexagons. From this it follows that the least fullerene has twenty atoms forming twelve pentagons. We suppose that this restriction is unnecessary. In other words, we take the term “*fullerene*” in a broad sense to mean any shape inscribed into a spherical surface which can be composed of atoms, each atom having three nearest neighbors, whenever discussing carbon clusters. Remember the main notions of spherical geometry [2] which can be used in what follows. Any plane which intersects a sphere gives in a cross section a circle. If a secant plane goes through the sphere center, the

cross section is a *great circle*. A small circle parallel to a great circle can be considered as a *parallel*. Other notions will be given as needed.

The geometrical approach alone can give possible forms of the broad-sense fullerenes. However, if we wish to gain a more penetrating insight into their nature, we need to take into consideration, along with the atomic structure of these spherical molecules, their electronic structure. For this purpose we will use an enlarged version of the theory developed by Sidgwick and Powell [1] in 1940. As it was discussed in details [3], Sidgwick and Powell formulated the following rule:

- geometry of a molecule is dictated by the arrangement of electron pairs in the valence shell of atoms;
- each shared electron pair, forming a covalent bond, can be considered as a point charge;
- all the electron pairs of a molecule arrange themselves into such configuration which ensures their maximal removing from each other.

For example, two point charges on a sphere surface give a linear configuration; three point charges form an equilateral triangle, and four point charges must be put into the vertices of a regular tetrahedron (Fig. 1, up). Each configuration at a given number of point charges can form its own space molecular structure. Denote the central atom of a molecule by letter A, and a noncentral atom by X. Then a molecule AX_2 will be linear, e.g. beryllium chloride in a gas phase. Analogously, any molecule AX_3 must have an equilateral triangle configuration, e.g. trifluoro boron; and a molecule AX_4 exists in the form of a regular tetrahedron, e.g. methane (Fig. 1, bottom).

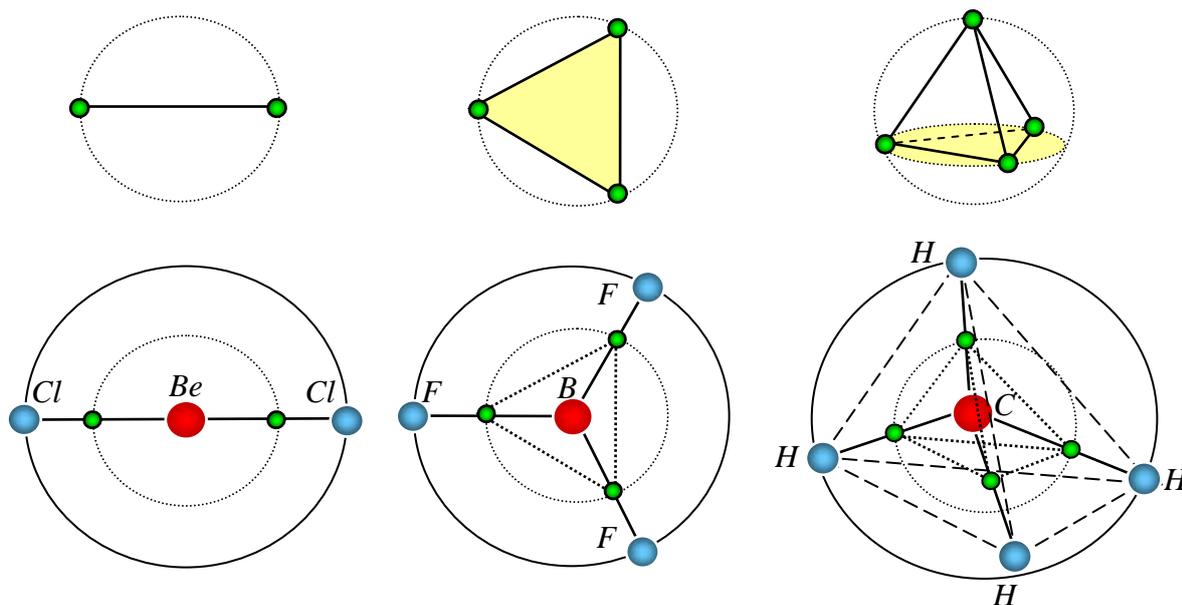


Fig. 1. Point charges with maximum mutual removal on a sphere surface (up) and the corresponding configurations of molecules (bottom). Here the large circles represent atoms; the smaller ones refer to the electron pairs located at the centers of covalent bonds.

Sidgwick–Powell’s theory allowed explaining and predicting stereochemical properties of many simple molecules (more than 1500 [1]). This theory was extended and applied to cyclic molecules such as cyclohexane [4] and usual fullerenes [5], which have no a central atom. The all-important result of such extension consists in the following: the *hidden symmetry of special electronic pattern does not coincide with that of atomic one*. However, it is precisely this electronic pattern that defines the atomic structure and explains, e.g. why a cyclohexane molecule has such unusual forms as a chair and a boat.

In this contribution we modified the approach developed in [4] and applied it to the broad-sense fullerenes. Contrary to the previous approaches [1, 4], where atoms and electron pairs had their own spheres, the main innovation is an additional postulate: we suppose that atoms and shared electron pairs, forming covalent bonds, are located *on one and the same sphere*. From this it follows that the geometry of both the electronic structure as well as of the atomic structure of fullerenes can be most conveniently constructed and studied with the help of *spherical geometry*. A preliminary study has justified this assertion [6, 7].

2. Tetrahedral fullerene C_4

The least carbon volume cluster which can be inscribed into a sphere is a regular tetrahedron. It contains four atoms. It should be emphasized that any three atoms can be laid on one and the same parallel (Fig. 2a); and it is possible to circumscribe only one great circle which passes through any two atoms lying on a sphere (Fig. 2b).

Let us modify the theory of Sidgwick and Powell so as to apply it for fullerenes. According to their theory, the shared electron pairs are thought of as point charges repelling each other. However, in contrast with their stereometry and according to our postulate, we will use spherical geometry. Therefore, since we have six point charges, all these charges should be located on the great circles which pass through any two atoms connected by a respective electron pair (Fig. 3).

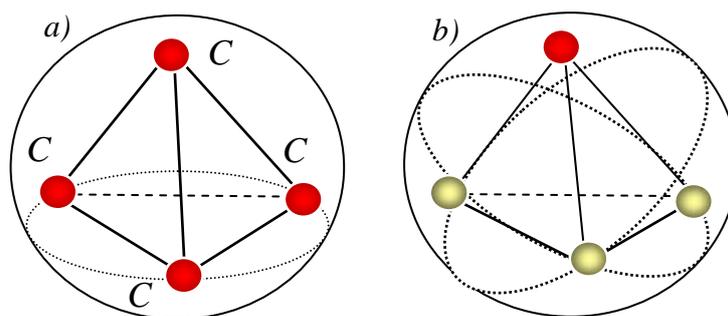


Fig. 2. Carbon tetrahedron inscribed into a sphere. Here (a) any three atoms lie on one and the same parallel; (b) only two great circles from six possible ones are shown.

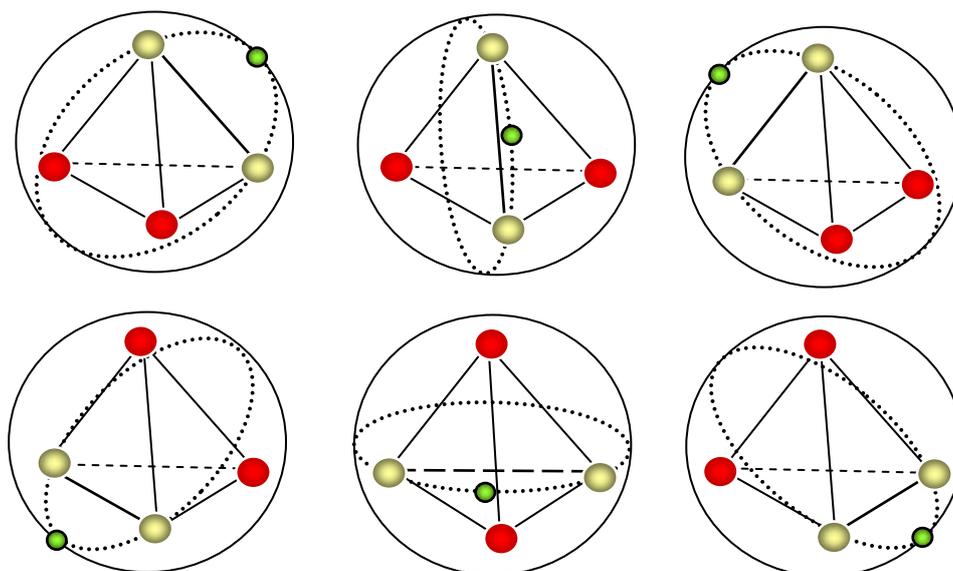


Fig. 3. Shared electron pairs of a tetrahedral fullerene.

In other words, the shared electron-pair-bond must be represented not as a straight line (Fig. 1), but as a small arc of a *geodesic line* (Fig. 4a). It is worth noting that a geodesic line on a sphere is just the same as a great circle, and a small arc of it, which is less than a semicircle, is the least path between the ends of this arc [2].

As a consequence of this procedure, we obtain an *octahedron* inscribed into the sphere which apexes are the shared electron pairs (Figs. 4b and 4c). The all-important result is that such procedure reveals the *hidden symmetry* [4] of the shared electron pairs located on the same sphere as that of the carbon atoms.

It is of interest to note that, in spite of different approaches, the electronic configuration of this mini-fullerene coincides with that of an ordinary molecule having a central atom and six electron pairs in its valence shell [8]. According to [8] an octahedron is the only stable configuration for six electron pairs.

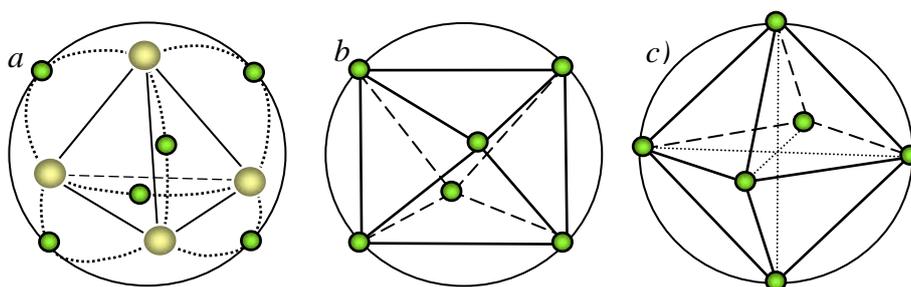


Fig. 4. Shared electron pairs. Here (a) their position on geodesic lines; (b) shared-electron-pairs octahedron corresponding to (a); (c) more usual form of this octahedron.

3. Triangular prismatic fullerene C_6

The next in size carbon cluster, each atom of it having three nearest neighbors, which can be inscribed into a sphere, is a triangular prism. Here three atoms of each base can be laid on one and the same parallel (Fig. 5a). Besides, it is possible to circumscribe only one great circle which passes through any two nearest-neighbor atoms lying on a sphere (Figs. 5b, c).

Similar to the previous procedure for a tetrahedral fullerene, we obtain for the nine shared electron pairs of a triangular prismatic fullerene the following configuration which contains nine points with maximum removal from each other (Fig. 5d).

Again the electronic configuration of this mini-fullerene coincides with that of an ordinary molecule having nine electron pairs in its valence shell [8]. For this reason we will use the terminology accepted in molecular geometry. According to [8] this configuration is named a three-cap trigonal prism.

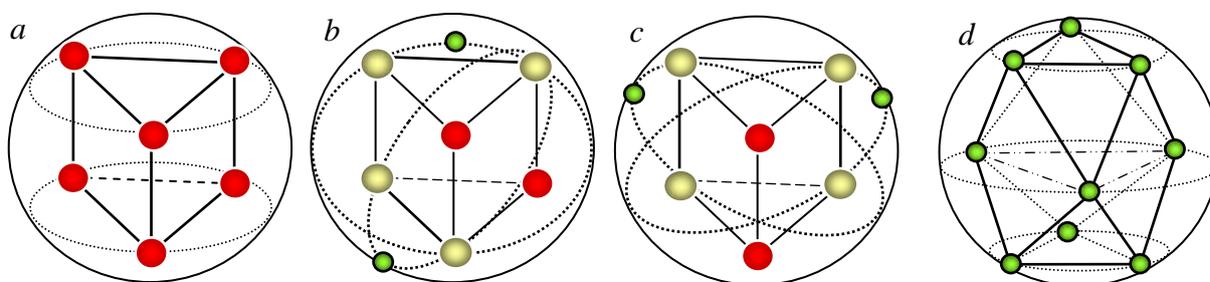


Fig. 5. Carbon triangular prism inscribed into a sphere. Here (a) three atoms of two bases lie on one and the same parallel; (b–c) four great circles from nine possible ones are shown; (d) nine shared electron pairs on a sphere surface with maximum removal from each other, so called a three-cap trigonal prism.

4. Cubic fullerene C_8

The next in size carbon cluster, each atom of it having three nearest neighbors, which can be inscribed into a sphere, is a cube (Fig. 6a). Here twelve shared electron pairs on a sphere surface form an icosahedron (Fig. 6b). It has 20 triangular faces, 30 edges and 12 apices [2].

As in two previous cases, the electronic configuration of this mini-fullerene coincides with that of an ordinary molecule having twelve electron pairs in its valence shell [8].

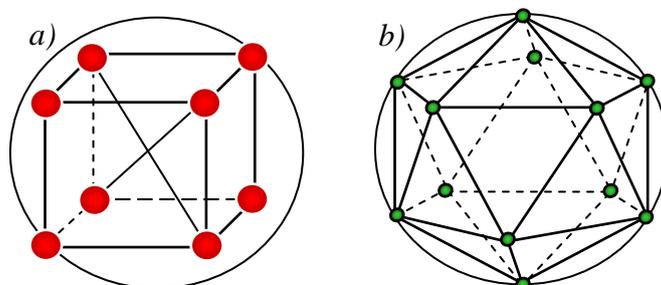


Fig. 6. Carbon cube inscribed into a sphere (a); twelve shared electron pairs on a sphere surface with maximum removal from each other forming an icosahedron (b).

5. Pentagonal prismatic fullerene C_{10}

The next in size carbon cluster, each atom of it having three nearest neighbors, which can be inscribed into a sphere, is a pentagonal prism. Here five atoms of each base can be laid on one and the same parallel (Fig. 7a). Similar to the previous procedure for a triangular prismatic fullerene, we obtain for the 15 shared electron pairs of a pentagonal prismatic fullerene the following configuration which contains fifteen points with maximum removal from each other (Fig. 7b). Up to this carbon cluster we observed similarity of the electronic configurations of mini-fullerenes and ordinary molecules. Now we have no such analogy, so we are compelled to introduce new designations. By analogy with [8] this electronic configuration could be named a five-cap pentagonal prism. It has 20 triangular faces, 2 pentagonal faces, 35 edges and 15 apices.

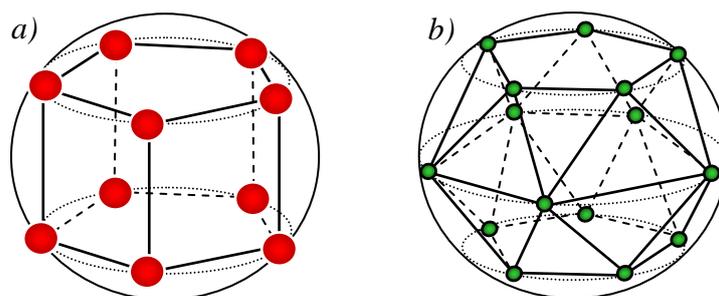


Fig. 7. Carbon pentagonal prism inscribed into a sphere (a) and fifteen shared electron pairs on a sphere surface forming a five-cap pentagonal prism (b).

6. Fullerene of twelve carbon atoms C_{12}

Here we confront with a new phenomenon, namely, different forms of carbon hollow molecules. We can imagine four structural isomers of this fullerene.

a) Hexagonal prism. It is the simplest form that can be thought of. Here six atoms of each base are laid on one and the same parallel (Fig. 8a). Similar to the previous cases, we obtain for the shared electron pairs the following configuration which contains eighteen points with maximum removal from each other (Fig. 8b). By analogy with [8] this

configuration could be named a six-cap hexagonal prism. It has 24 triangular faces, 2 hexagonal faces, 42 edges and 18 apices.

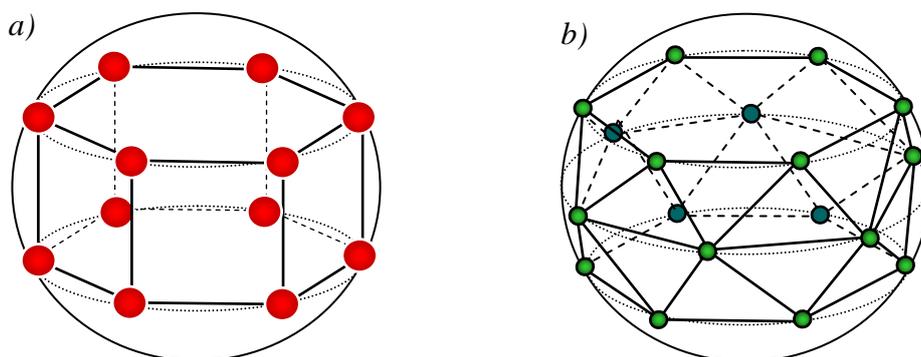


Fig. 8. Hexagonal prism inscribed into a sphere (a) and eighteen shared electron pairs on a sphere surface forming a six-cap hexagonal prism (b).

b) Twisted hexagonal prism. It is a rather exotic form that can be thought of (Fig. 9a). The algorithm for obtaining the shared electron pairs in equilibrium state is analogous to the considered above. The electronic structure obtained consists of triangles, squares and pentagons (Fig. 9b). It could be named a six-cap twisted hexagonal prism.

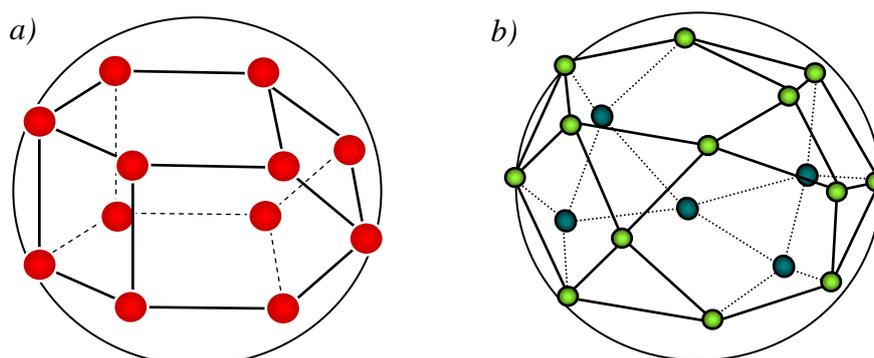


Fig. 9. Twisted hexagonal prism inscribed into a sphere (a) and eighteen shared electron pairs on a sphere surface forming a six-cap twisted hexagonal prism (b).

c) Truncated tetrahedron. It is a more complex shape which can be obtained from a tetrahedral fullerene. In the previous cases we have used the method of great circles for obtaining the electronic structure of mini-fullerenes realizing this algorithm with the help of a special program [6]. Compared to the previous cases, we modified this method in the following way. At first a truncated tetrahedron was inscribed into a sphere (Fig. 10a). Then the point charges (electron pairs) were put on the middles of edges of this tetrahedron (Fig. 10b). Thereafter the electronic structure obtained was subjected to radial expansion. As a result, the electron pairs which do not belong to the triangle edges found themselves on a sphere in equilibrium positions (Fig. 10c).

The next step is to displace nonequilibrium point charges to the sphere surface so as to obtain their maximum removal from each other and from the point charges which are in equilibrium positions (Figs. 11-3 and 11-4). The final electronic configuration consists of distorted hexagons and rather regular triangles (Figs. 11-5, 11-6, and 11b).

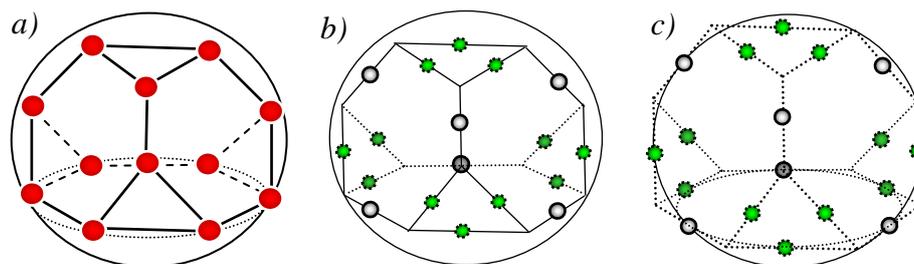


Fig. 10. Truncated tetrahedron inscribed into a sphere (a); eighteen shared electron pairs in a truncated tetrahedron (b); extension of the truncated tetrahedron together with shared electron pairs (c). The electron pairs which are in nonequilibrium state are denoted by dark (green) circles.

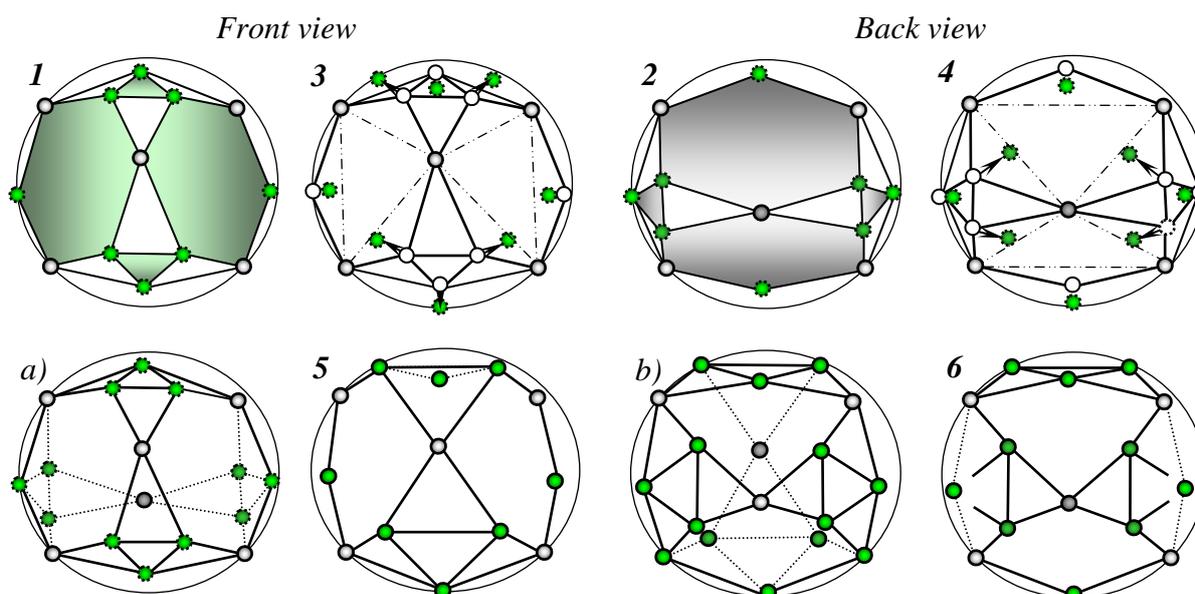


Fig. 11. Algorithm for obtaining the shared electron pairs in equilibrium. Initial nonequilibrium electron pairs configuration (a, 1, and 2); displacement of nonequilibrium electron pairs (3 and 4); final equilibrium electron pairs configuration (b, 5, and 6).

c) **(Tri-penta₃)₂ polyhedron** (Fig. 12). It is a rather sophisticated shape which resembles a barrel or a rugby ball. However it can be treated in a way similar to the previous case. The final electronic configuration consists of rather regular pentagons and triangles (Fig. 13). It is less distorted than the previous electronic structure and has the more uniform distribution of point charges.

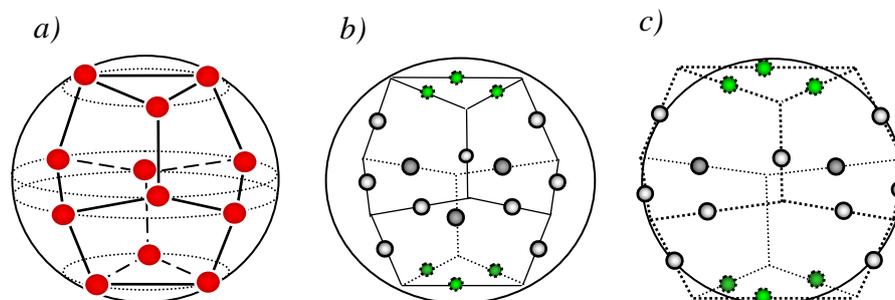


Fig. 12. (Tri-penta₃)₂ polyhedron inscribed into a sphere (a); 18 shared electron pairs of the polyhedron (b); uniform extension of the polyhedron together with its shared electron pairs (c). The electron pairs which are in nonequilibrium state are denoted by dark (green) circles.

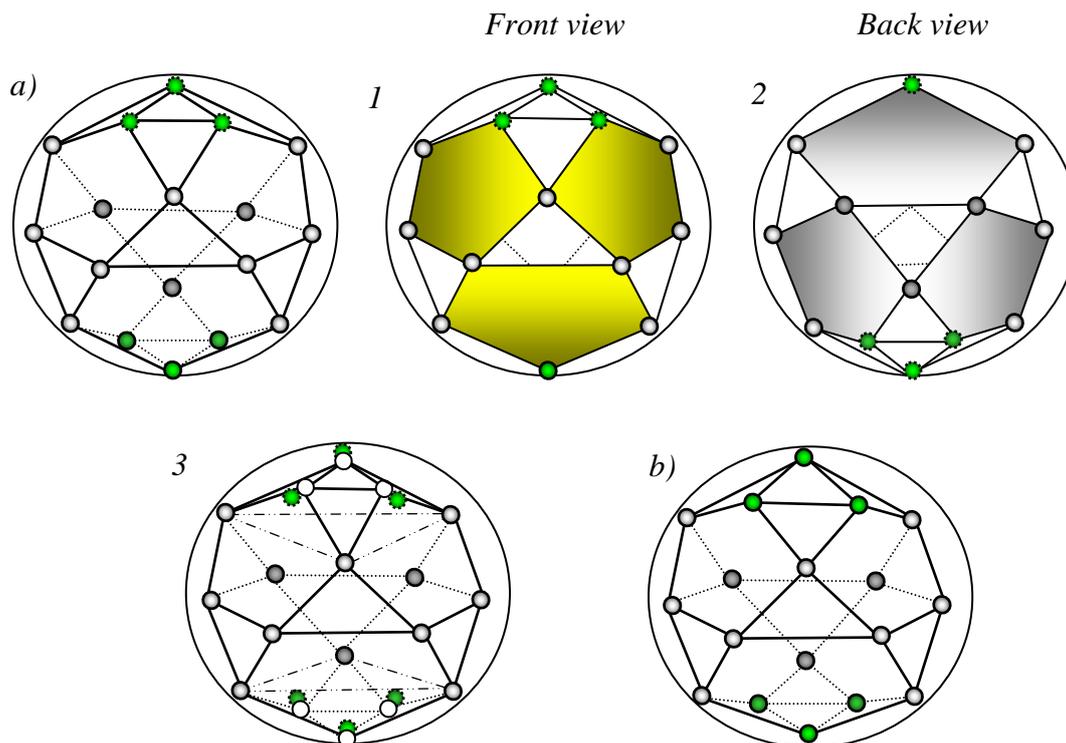


Fig. 13. Algorithm for obtaining the shared electron pairs in equilibrium state. Initial nonequilibrium electron pairs configuration (*a*, *1*, and *2*); displacement of nonequilibrium electron pairs (*3*); final equilibrium electron pairs configuration (*b*).

It is known that for molecules, having a large number of electron pairs, there are some of the structures with close energy [8]. At this, there are a wide variety of factors that can appear to be the reason of accidental stabilization of one of these structures. We suppose that the same situation takes place for the isomers of mini-fullerenes considered.

7. Fullerene of fourteen carbon atoms C_{14}

We can imagine two structural isomers of this fullerene.

a) Tetragonal trefoil-pair (or shamrock-pair) polyhedron (Fig. 14). The algorithm for obtaining the shared electron pairs in equilibrium state is analogous to the considered above. The electronic structure consists of triangles, squares, and bent hexagons (Fig. 15).

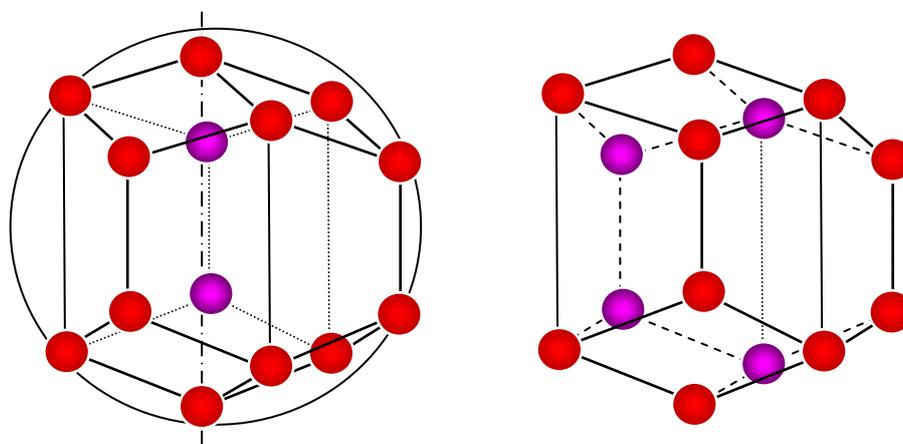


Fig. 14. Tetragonal trefoil-pair polyhedron inscribed into a sphere.

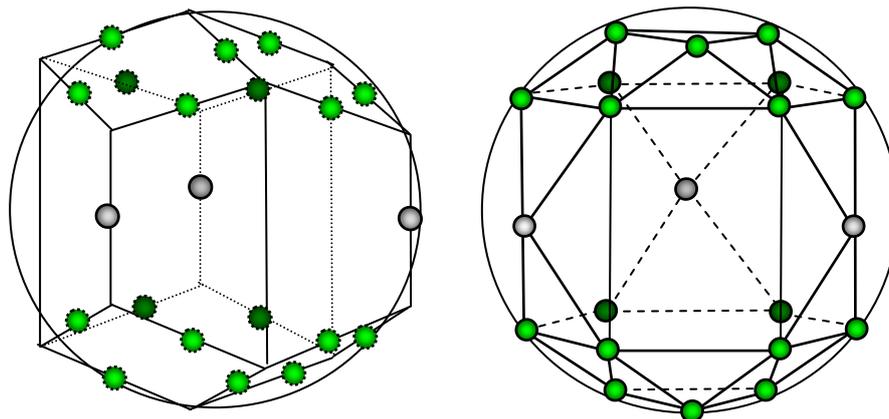


Fig. 15. Twenty-one shared electron pairs on a sphere surface forming a five-cap hexagonal prism (two vertical and three horizontal caps).

b) Base-truncated triangular bipyramid (Fig. 16). The algorithm for obtaining the shared electron pairs in equilibrium state is analogous to the considered above. The electronic structure consists of triangles, squares, and pentagons (Fig. 17).

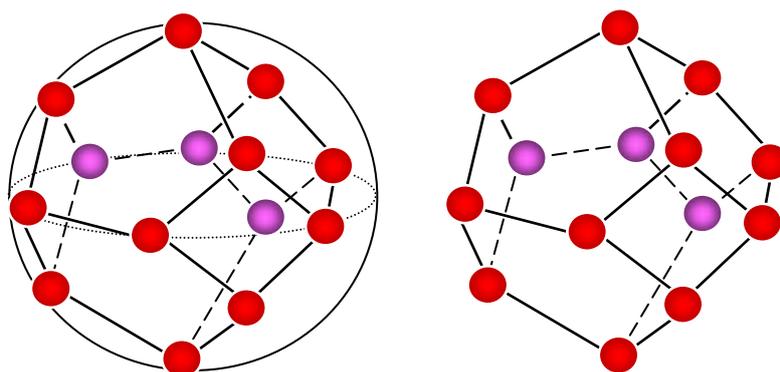


Fig. 16. Base-truncated triangular bipyramid inscribed into a sphere.

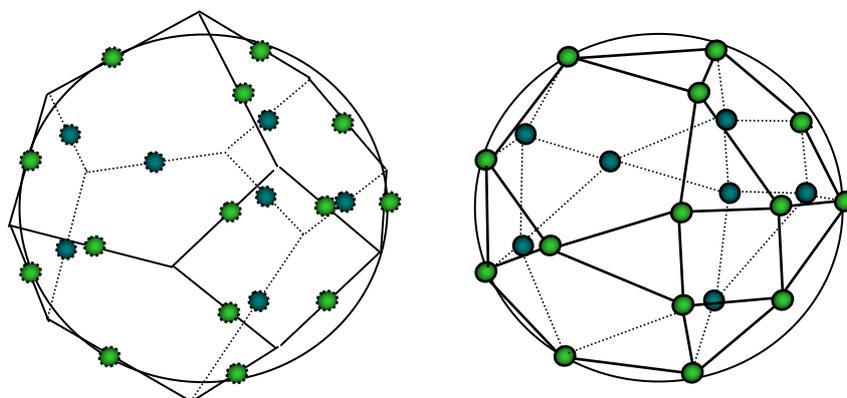


Fig. 17. Twenty-one shared electron pairs on a sphere surface of a base-truncated triangular bipyramid fullerene of fourteen atoms.

8. Fullerene of sixteen carbon atoms C_{16}

There are two structural isomers of this fullerene.

a) Half-truncated cube. The atomic configuration has much in common with that of a truncated tetrahedron fullerene. It consists of triangles and hexagons (Fig. 18). The algorithm for obtaining the shared electron pairs in equilibrium state is analogous to the considered above and is shown in Fig. 19. The final electronic configuration consists of bent hexagons and rather regular triangles.

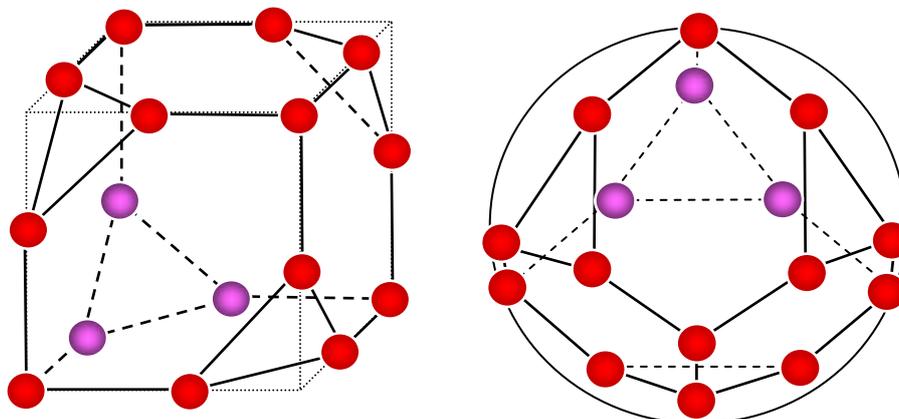


Fig. 18. Half-truncated cube inscribed into a sphere.

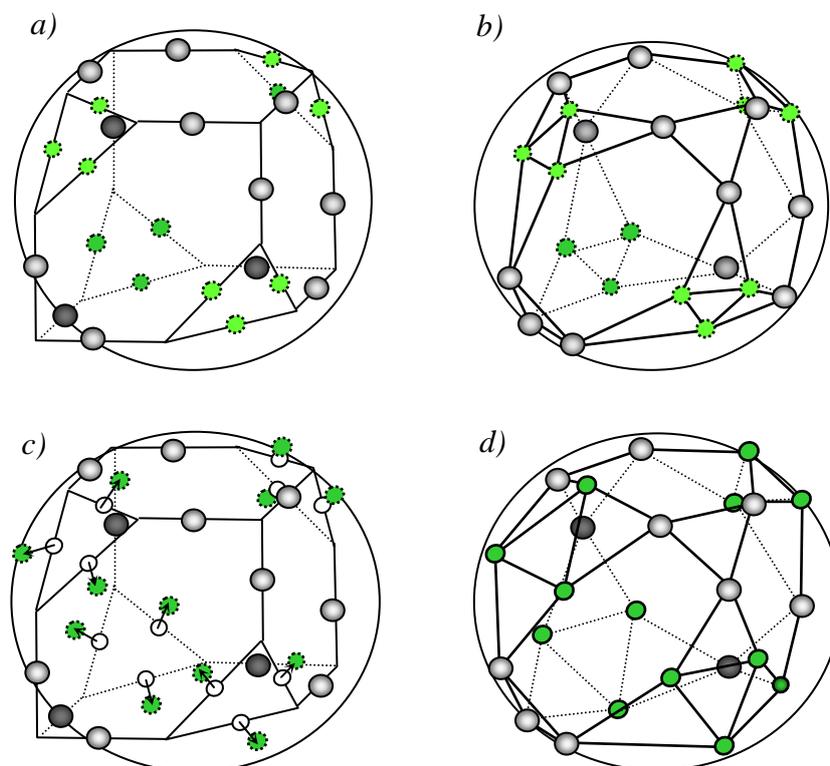


Fig. 19. Algorithm for obtaining the shared electron pairs in equilibrium state. Initial nonequilibrium electron pairs configuration (*a*, *b*); displacement of nonequilibrium electron pairs (*c*); final equilibrium electron pairs configuration (*d*).

b) (Tetra-penta₄)₂ polyhedron. The atomic configuration has much in common with that of a (tri-penta₃)₂ polyhedron, which resembles a barrel or a rugby ball. It is formed from two squares and eight pentagons (Fig. 20a). The algorithm for obtaining the shared electron pairs in equilibrium state is analogous to the considered above and is shown in Fig. 20b. The final electronic configuration consists of regular pentagons, triangles, and squares. It closely resembles that of a (tri-penta₃)₂ polyhedron. It should be emphasized that the difference between the non-equilibrium and equilibrium configurations is so small that it cannot be noticed graphically. For this reason only one configuration is shown (Fig. 20c).

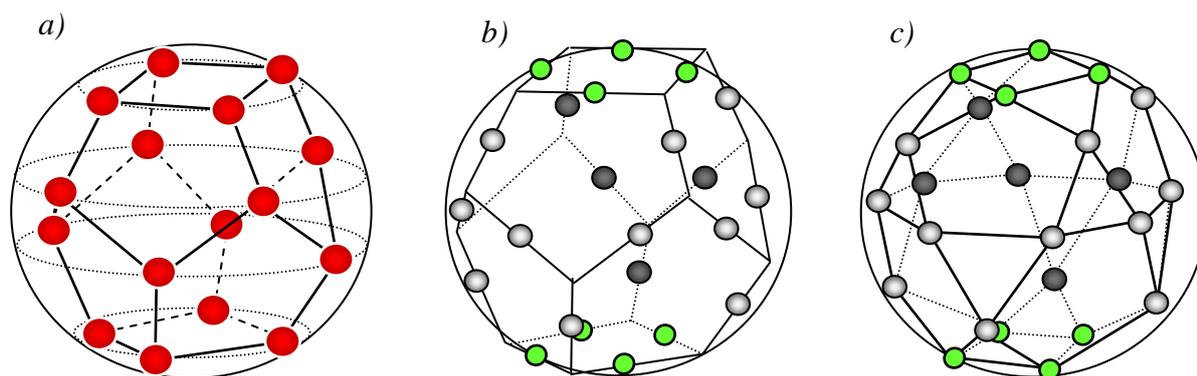


Fig. 20. (Tetra-penta₄)₈ polyhedron inscribed into a sphere (a); twenty four shared electron pairs in the polyhedron (b); final equilibrium electron pairs configuration (c).

9. Fullerene of eighteen carbon atoms C₁₈

There are two structural isomers of this fullerene.

a) Truncated triangular bipyramid (Fig. 21). The algorithm for obtaining the shared electron pairs in equilibrium state is analogous to the considered above. The electronic structure consists of triangles, squares, and hexagons (Fig. 22).

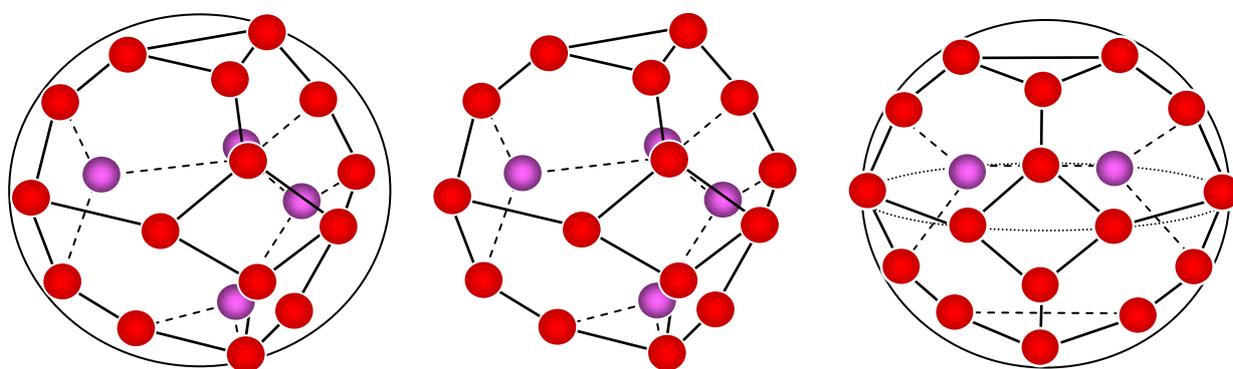


Fig. 21. Truncated triangular bipyramid inscribed into a sphere.

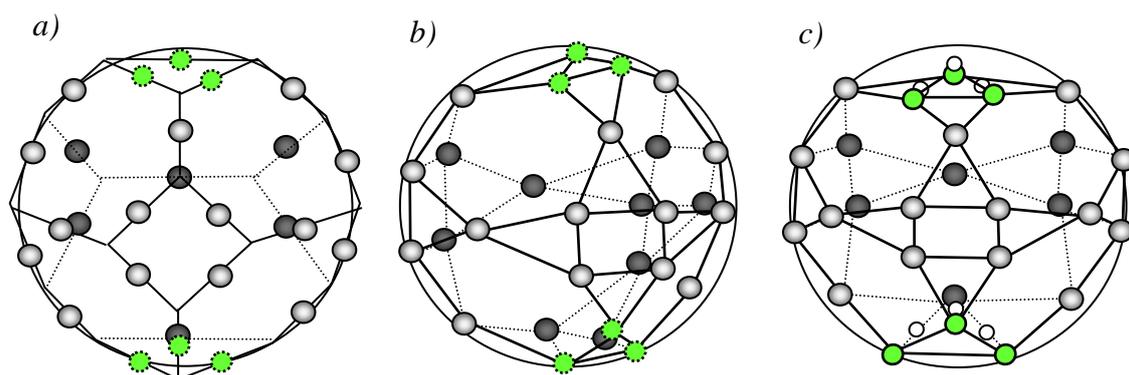


Fig. 22. Twenty-eight shared electron pairs of the truncated triangular bipyramid of eighteen atoms on a sphere surface: initial non-equilibrium electron pairs configuration (*a*, *b*); displacement of non-equilibrium electron pairs and final equilibrium configuration (*c*).

b) (Tri-penta₃)₂-hexa₃ polyhedron. It should be emphasized that contrary to all the previous shapes of fullerenes this configuration can be inscribed only into an ellipsoid of revolution (Fig. 23). The algorithm for obtaining the shared electron pairs in equilibrium state is analogous to the considered above and is shown in Fig. 24. The electronic structure consists of triangles, pentagons, and bent hexagons.

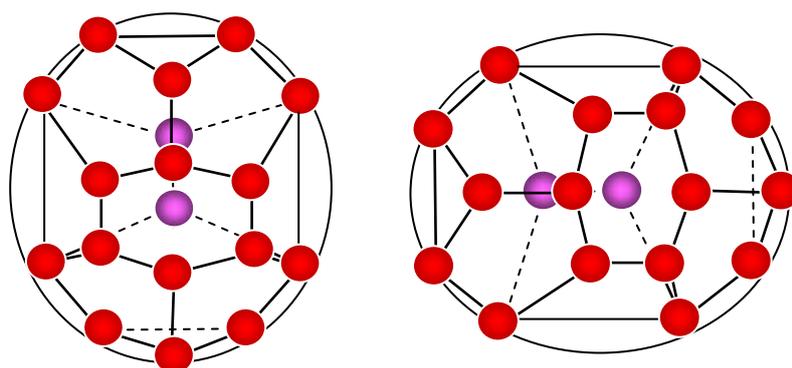


Fig. 23. (Tri-penta₃)₂-hexa₃ polyhedron inscribed into an ellipsoid of revolution.

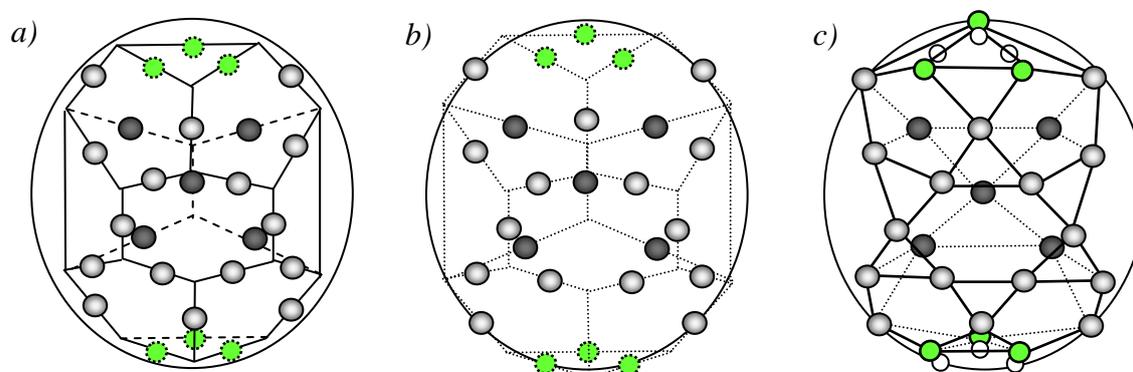


Fig. 24. Twenty seven shared electron pairs of the polyhedron inscribed into an ellipsoid (*a*); extension of the polyhedron together with shared electron pairs (*b*); displacement of nonequilibrium electron pairs and final equilibrium configuration (*c*).

10. Fullerene of twenty carbon atoms C_{20}

There are three structural isomers of this fullerene.

a) Dodecahedron. The atomic configuration is a regular polyhedron (Fig. 25). It consists of twelve pentagons. The algorithm for obtaining the shared electron pairs in equilibrium state is analogous to the considered above and is shown in Fig. 26. The final electronic configuration consists of regular pentagons and triangles. It should be emphasized that for obtaining the equilibrium configuration it is enough only to do uniform expansion.

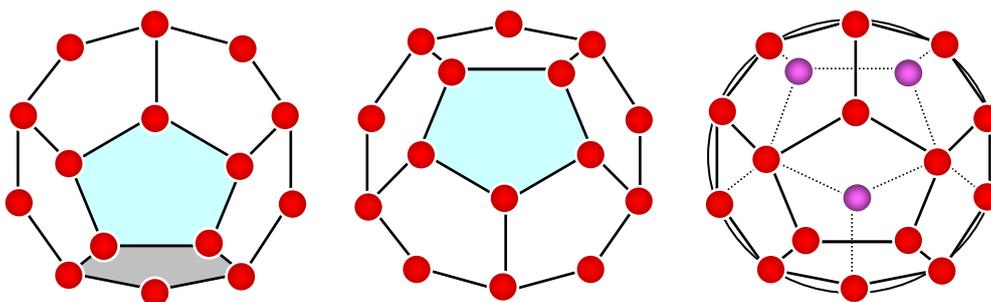


Fig. 25. Dodecahedron: front and rear view; inscribed into a sphere.

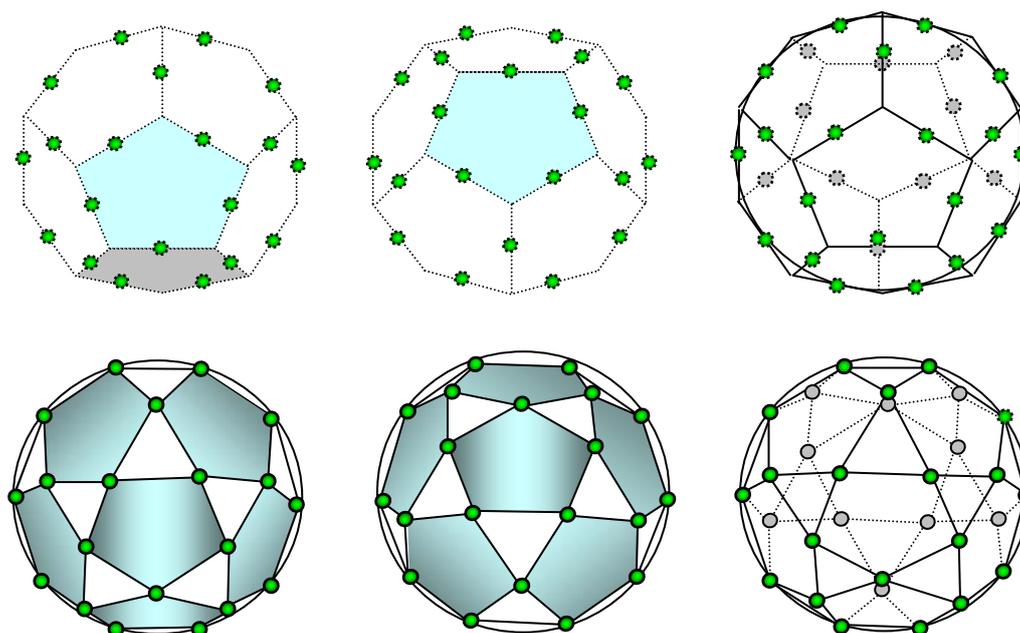


Fig. 26. Algorithm for obtaining the shared electron pairs in equilibrium state: initial electron pairs configuration (*above*); uniform expansion of the initial configuration leads to an equilibrium configuration (*below*).

b) (Tetra-penta-hexa)₄ polyhedron. The atomic configuration consists of four rhombs, four pentagons and four hexagons (Fig. 27). The algorithm for obtaining the shared electron pairs in equilibrium state is analogous to the considered above and is shown in Fig. 28. The final electronic configuration consists of regular triangles, squares, pentagons, and hexagons. It should be emphasized that the difference between the non-equilibrium and equilibrium configurations is so small that it cannot be noticed graphically.

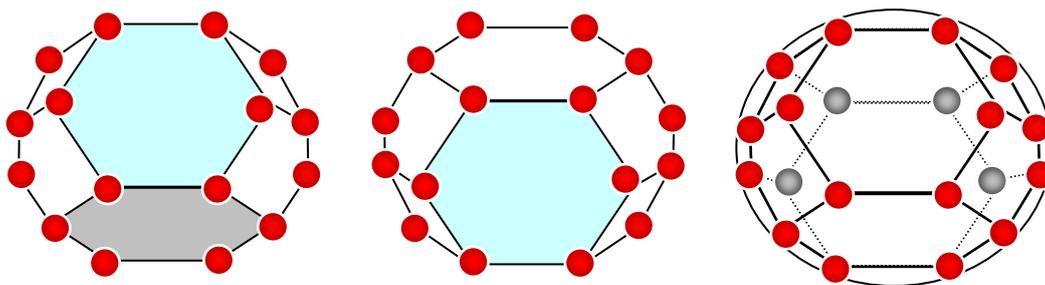


Fig. 27. (Tetra-penta-hexa)₄ polyhedron: front and rear view; inscribed into a sphere.

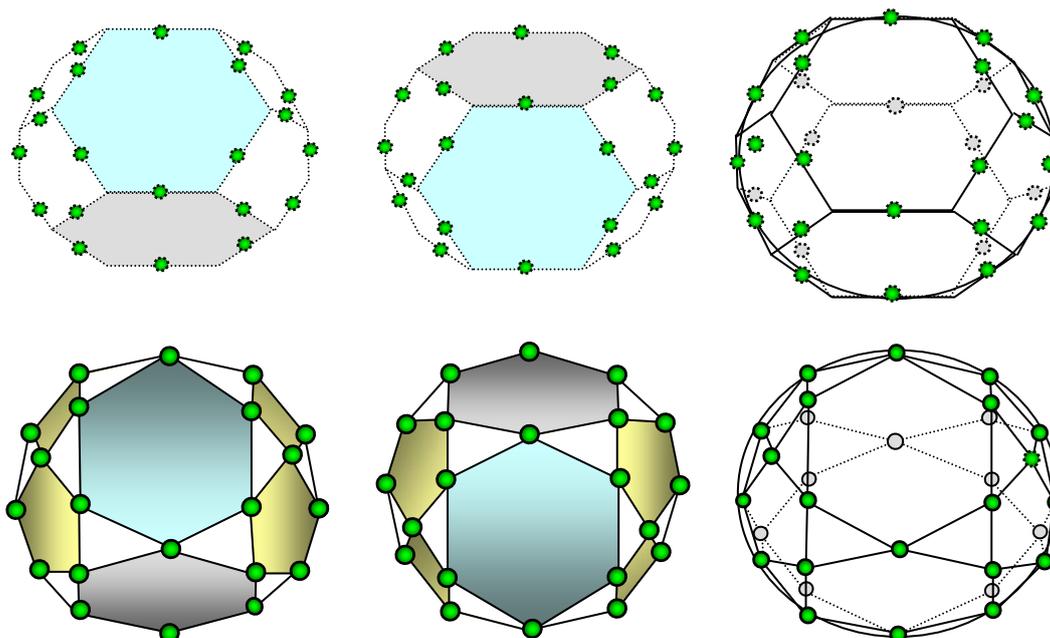


Fig. 28. Algorithm for obtaining the shared electron pairs in equilibrium state: initial electron pairs configuration (*above*); uniform expansion of the initial configuration leads to an equilibrium configuration (*below*).

c) **(Tetra-hexa)₃-penta₆ polyhedron.** The atomic configuration consists of three squares, three hexagons and six pentagons (Fig. 29). The algorithm for obtaining the shared electron pairs in equilibrium state is analogous to the considered above and is shown in Fig. 30. The final electronic configuration consists of regular pentagons, triangles, and squares. It should be emphasized that the difference between the non-equilibrium and equilibrium configurations is so small that it cannot be noticed graphically.

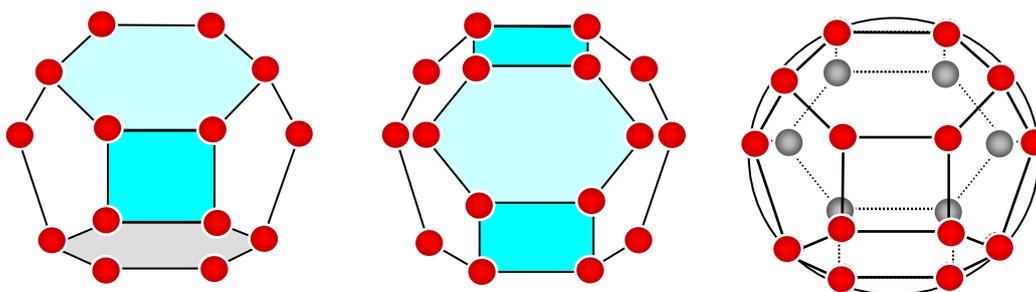


Fig. 29. (Tetra-hexa)₃-penta₆ polyhedron: front and rear view; inscribed into a sphere.

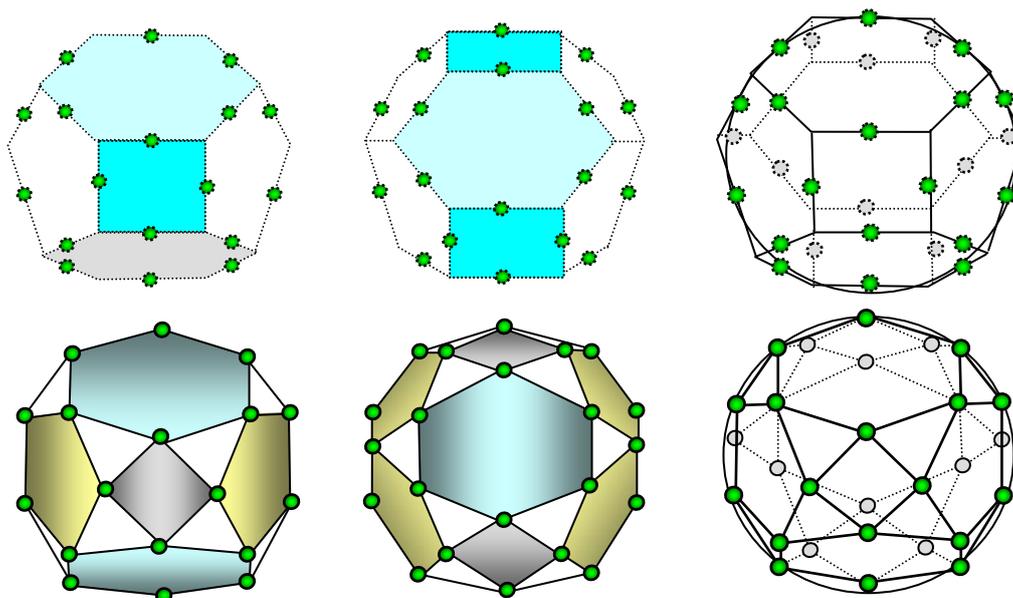


Fig. 30. Algorithm for obtaining the shared electron pairs in equilibrium state: initial electron pairs configuration (*above*); uniform expansion of the initial configuration leads to an equilibrium configuration (*below*).

11. Conclusion

We have developed a method for calculating electronic and atomic structure of fullerenes. Here we took the term “*fullerene*” in a broad sense to mean any hollow shape inscribed into a spherical surface which can be composed of carbon atoms, each atom having three nearest neighbors. In addition to this definition, we supposed that not only atoms but also shared electron pairs, forming covalent bonds, were located on one and the same sphere. In this case the geometry of both the electronic structure as well as of the atomic structure of the fullerenes should be most conveniently constructed and studied with the help of *spherical geometry*. The procedure created revealed the *hidden symmetry* of the shared electron pairs located on the same sphere as that of carbon atoms. The most interesting result was that we have found *structural isomers* of some fullerenes which differed in their surface electronic density.

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