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Formation of general fullerenes by their projection on a honeycomb lattice

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We propose the use of a projection method based on a honeycomb lattice to enhance the geometrical understanding of general fullerenes. An arbitrary fullerene consisting of pentagonal and hexagonal arrangements of carbon atoms is completely specified by the distribution of twelve pentagonal *defects* on an otherwise hexagonal honeycomb lattice. Utilizing this projection method, we demonstrate the geometric specification of icosahedral hyperfullerenes and general chiral fullerene tubules suitably capped on each end.

The discovery of new aromatic molecules based on C_{60} (Refs. 1 and 2) has aroused great scientific activity not only for their exceptional properties but also for their potential for applications to physics, chemistry, biotechnology, and materials science. A major focus at present is the study of how and why fullerenes form in such elegant structures and the search for new stable fullerenes.

The basic structure of C_{60} is a hollow truncated regular icosahedron. If we preserve the icosahedral symmetry and add hexagons between pentagons of C_{60}, the series of giant fullerenes C_{240}, C_{540}, C_{960}, ..., C_{60n^2} is obtained.[2–4] Fowler[5] pointed out that more general icosahedral fullerenes are possible, corresponding to Goldberg polyhedrons,[6] which are spherical polyhedrons[5,7] and have $20(m^2+mn+n^2)$ atoms where m and n are non-negative integers. Possible cage structures for lower symmetry molecules are discussed by several authors.[8,9] If the geometrical constraint of including only hexagonal and pentagonal faces is relaxed, other icosahedral hyperfullerenes also can be obtained, like the Archimedene.[10]

Another interesting generalization of fullerenes is to extend C_{60} in only one direction to form graphene tubules which have hemispheres of C_{60} on both ends.[11] An oval-shaped C_{70} fullerene is the simplest example of symmetry lowering of C_{60}. The existence and structure of C_{70} is already well established. Stimulated by the experimental observation of graphite tubules,[12–14] researchers have already discussed their electronic properties theoretically.[15–18] To nucleate cylindrical growth, some defects are needed during the early formation stage. The geometrical approach described here for general fullerene tubules provides a convenient method for the construction of caps suitable for nucleating such tubules.

In this paper we propose a projection method for describing fullerenes on a honeycomb lattice or a graphene sheet (a single layer of graphite), thereby providing a geometrical understanding of the formation of general fullerenes. We show that the geometrical construction can be applied to any fullerene consisting of hexagons and pentagons of carbon atoms. In this construction, a pentagon is regarded as a defect on the honeycomb network of carbon atoms, since a conical surface forms around each pentagonal defect. We first apply this projection method to icosahedral fullerenes and demonstrate their *icosapod* structure (i.e., a truncated cone of graphene with pentagonal cross section). Further we apply this

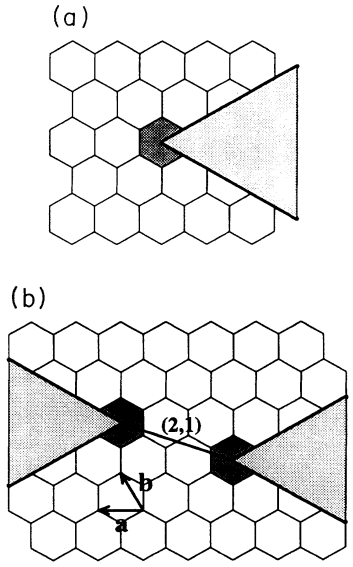

FIG. 1. (a) Formation of a pentagonal defect in a honeycomb lattice removes the area designated by the shaded outlined triangle. (b) The vector (m,n) which connects two pentagonal defects fully specifies the icosahedral hyperfullerene. The diagram is constructed for $(m,n)=(2,1)$.

projection to the formation of suitably capped fullerene tubules with arbitrary chirality.

First let us examine the role of a single pentagon in a hexagonal honeycomb lattice. If we prepare a honeycomb sheet as shown in Fig. 1(a), then remove the 60° wedge of the dark-shaded hexagon, and connect the two edges along the dark lines from the center, then we form a truncated cone with a pentagonal cross section projecting out of the plane of the hexagonal network. The apical pentagon can be regarded as a defect in the honeycomb lattice.

Next we put a second pentagonal defect on the sheet as shown in Fig. 1(b). In this figure we define a vector $(m,n) \equiv m\mathbf{a}+n\mathbf{b}$ connecting the two pentagonal defects using two basis vectors of the honeycomb lattice $\mathbf{a}$ and $\mathbf{b}$. Since in icosahedral symmetry we have a fivefold axis around the first defect, we then must put five pentagons equivalently at 72° intervals (or 60° on the honeycomb lattice) around the first defect. These six defects together with their surrounding hexagons form a hemisphere derived from the honeycomb lattice. Finally we can form a closed cage with icosahedral symmetry by joining two identical hemispheres so that the twelve defects align icosahedrally.

The vector (m,n) defined in Fig. 1(b) is thus sufficient for specifying a general icosahedral fullerene.[5,6] The connectivity of the twelve pentagons relative to the honeycomb lattice is shown by considering C_{140} in Fig. 2. Here we see that relative to the honeycomb lattice, all the defects are distributed on a triangular lattice whose characteristic vector is $(2,1)$ or $(1,2)$, since all icosahedral fullerenes are generated by connecting twenty regular (equilateral) triangles. The C_{140} fullerenes with $(2,1)$ and $(1,2)$ are related to each other by mirror symmetry. The total number of atoms for the vector (m,n) is given by $20(m^2+mn+n^2)$, corresponding to the total area of the planar surface. For example, the series C_{60}, C_{240}, ..., C_{60n^2} are assigned to the vectors $(1,1)$, $(2,2)$, ..., (n,n), respectively. When $m=n$ or $mn=0$ the fullerenes have I_h symmetry, but in other cases the fullerenes have I symmetry which is a subgroup of I_h without the inversion operation.

In Fig. 3 we show two examples of icosahedral fullerenes with $(m,n) = (2,0)$ and $(2,1)$ which correspond to the molecules C_{80} with I_h symmetry and C_{140} with I symmetry, respectively. The difference from the spherical Goldberg polyhedrons[5–7] is that our icosahedral fullerenes form conical surfaces around the pentagons. However, the joining of pentagonally truncated cones requires a slight rearrangement of atoms relative to those on exact conical surfaces, for otherwise the surfaces on adjacent defects would be connected by a kink. Several authors have discussed the nonspherical nature of the larger icosahedral fullerenes[2,19] and have suggested that the icosapodlike fullerenes might be energetically more favorable than the spherical fullerenes because the carbon atoms which are far from each defect should form a flat sheet, i.e., graphite.

Since the atoms are confined to a single surface in our model, it is probable that the strain near the pentagons where the curvature is the largest would be relaxed to minimize the total energy, but would still retain the same icosahedral symmetry as before. The Kekulé pattern is not applicable for general icosahedral hyperfullerenes except for the case where m^2+mn+n^2 or $m-n$ is a multiple of 3, because the Kekulé structure gives a three sublattice pattern on a honeycomb lattice. Fowler showed by simple Hückel theory that when $m-n$ is a multiple of 3 the fullerene molecules have filled levels at the Fermi energy, giving rise to a semiconductor; otherwise the molecules have partly filled levels.[5] In the former case, the fullerene should undergo a Jahn-Teller distortion to

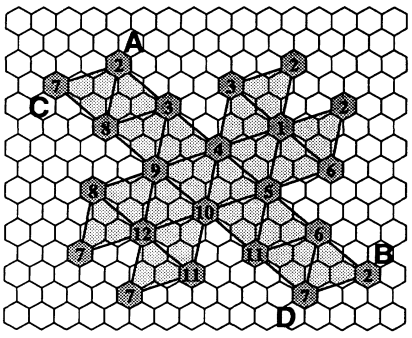

FIG. 2. Expanded surfaces of C_{140} with $(m,n) = (2,1)$. The twelve pentagonal defects are indicated by 1–12. The C_{140} fullerene is obtained by superimposing pentagons with the same number.

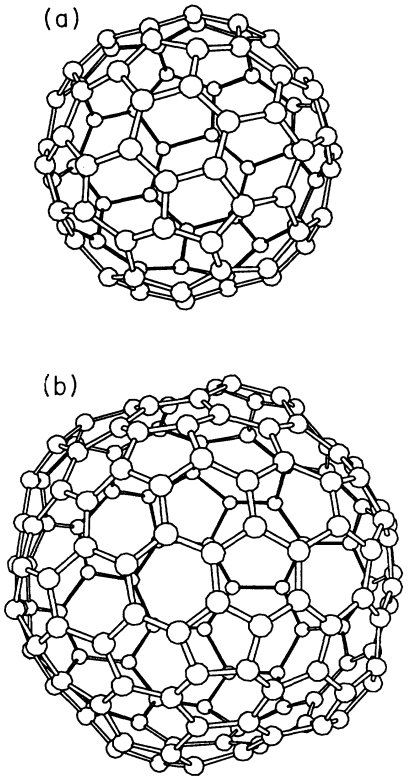

FIG. 3. Icosapod hyperfullerene molecules of (a) C_{80} and (b) C_{140}, corresponding to $(m,n)=(2,0)$ and $(2,1)$, respectively.

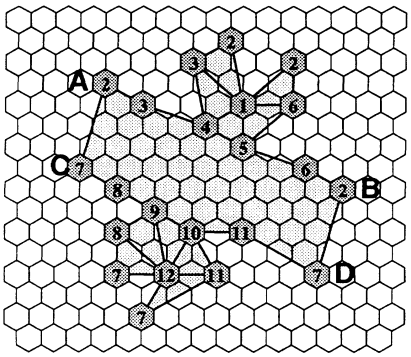

FIG. 4. An example of the projection of the capped tubule with the chiral vector $\mathbf{d}_{AB} = (7, 5)$. Different caps are constructed for the two ends of the fiber to illustrate the multiple possibilities for nucleating a given fiber.

form the Kekulé pattern as is seen in C_{60}. With regard to the latter case, we are now investigating whether or not the molecule is stabilized by a Jahn-Teller distortion, and if so, what kind of texture may appear.[20]

The method given here for icosahedral fullerenes can be generalized to classify fullerenes of lower symmetry, for example, C_{70}. We can also apply this method to produce graphene tubules from icosahedral hyperfullerene molecules in the same way as we can make armchair and zigzag fibers from cuts of the C_{60} molecule.[11] This is done by increasing the size of sides BD and AC of the parallelogram $ABCD$ in Fig. 2 to form the tubules, while retaining the lengths of AB and CD in order to fit the tubules perfectly to their adjacent fullerene hemispherical caps. The number of carbon atoms $T_{m,n}$ for the fullerene tubules is given by $10(m^2+mn+n^2)+10pI$ $(I = 1, 2, \ldots)$ where $10p$ is the number of carbon atoms along the $\mathbf{d}_{AB}$ vector and p is the greatest common factor of m and n, except for the case when $n(m)=0$, for which $p = m(n)$. Thus the spiral graphene tubules[17] with the chiral vector $\mathbf{d}_{AB}=(5m, 5n)$ can be capped by an icosahedral hemisphere. We note that $(m, n)=(2, 1)$ and $(1, 2)$ give tubules with left-handed and right-handed chirality, respectively, and are therefore expected to be optically active.

The projection in Fig. 2 can be generalized to specify caps for chiral fibers without fivefold symmetry. Once the chiral vector $\mathbf{d}_{AB}$, which specifies both the fiber diameter and chirality, is given, the problem of finding the cap of the tubule can be reduced to finding the distribution of five defects, for example, defects 2, 3, 4, 5, and 6 in Fig. 2. If these five defects are arranged so as to keep the condition that at each defect the 60° wedge is missing on the honeycomb lattice, this projection can form a cap for a tubule with a given $\mathbf{d}_{AB}$. Nonequilateral triangles can be used to form a general fiber cap. We show in Fig. 4 an example of caps for a graphene tubule with $\mathbf{d}_{AB}=(7, 5)$. Different caps are constructed for the two ends of the fiber to illustrate the multiple possibilities for nucleating and terminating a given fiber.

In this paper we have demonstrated a projection method for specifying general fullerenes on a honeycomb lattice. We show that any fullerene which consists of twelve pentagons and any number of hexagons of carbon atoms can be specified by arrangement of the twelve pentagonal defects on a honeycomb lattice. With this projection, we demonstrate the *icosapod* of icosahedral fullerenes as well as general graphene tubules capped on their edges. The coordinates of carbon atoms on the icosapod provide a good starting point for investigating the structual stability of the fullerene. Special attention in future work should be directed toward new physics, such as the left and right optical activity, that is expected from molecules described by the symmetry group I.

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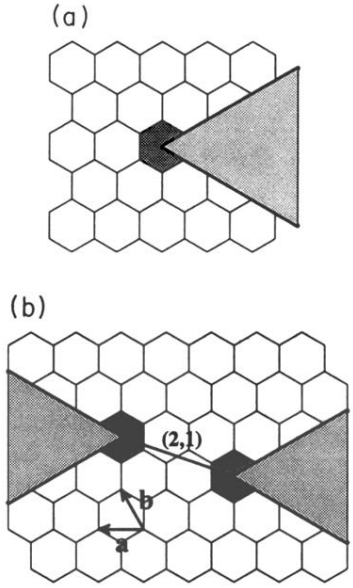

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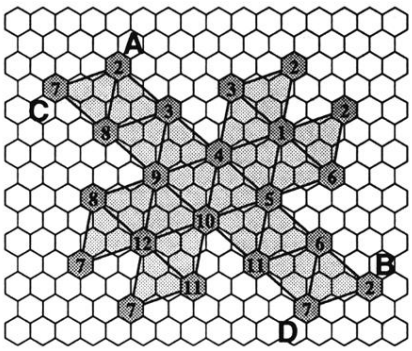

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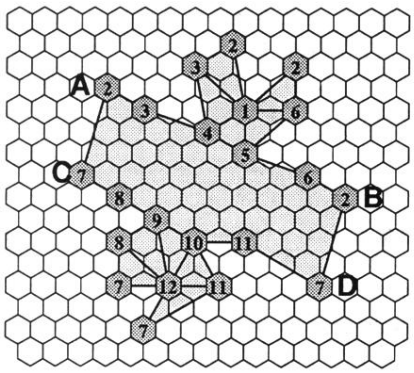

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