The Shape of Bucky Onions

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Abstract

The morphology of Bucky onions is investigated by ab initio calculations using Yang’s new $O(N)$ method. It is found that for large single shell fullerenes with $I_h$ symmetry, the spherical morphology has the lower energy than that of polyhedrons. The formation energy per atom follows a simple scaling law. Including an estimate of inter-shell van de Waals interactions leads to the conclusion that spherical multiple shell Bucky onions are likely the most stable structure of large carbon clusters. These results are in good agreement with recent observation.
The exciting discovery of concentric spherical graphitic shells by Ugarte raises several intriguing questions. Most fundamentally, it suggests that multi-shell fullerenes — so called Bucky onions — are the most stable structures of finite carbon clusters. This, and the remarkable spherical shape of these onions call for theoretical studies. For cluster size up to $N = 240$ carbon atoms, Adams et al. have performed first principle calculations and showed that “ball shaped” fullerenes have a lower energy than that of tube-shaped. However, based either on empirical potentials calculations, geometric consideration and elastic theory, it has been concluded by several groups that for large fullerenes the morphology is polyhedrally faceted. This appears to contradict the experimental observation of spherical shells.

In this letter, we report results of first principle calculations for carbon clusters up to 1,000 atoms by the “divide-and-conquer” method of Yang. These are the first ab initio calculations for such large molecules. The results unequivocally demonstrate that for single shell fullerenes the spherical morphology has a lower energy than those of polyhedrons. Furthermore we show that the leading $N$ dependence of the total energy obtained can be understood in term of the Hückel theory. Including the inter-shell van de Waals interactions leads to the conclusion that the multi-shell concentric spherical Bucky onions are likley the most stable structure of large carbon clusters, as observed in recent experiments.

Most methods of first principle calculations are limited to molecules of small or modest size. Recently one of us has developed an efficient $O(N)$ algorithm, designed specifically for large molecules. The method has been implemented for general molecular computations and tested in small systems against the traditional Kohn-Sham density-functional theory. The tests performed were molecular bonding energetic, molecular internal rotation potential barriers, and total electronic density of states. In our present calculations, a cluster is divided into subsystems with one atom each, and the local basis set for each subsystem used includes the atomic orbitals of the atom as well as those up to the third nearest neighbors. We use the local density approximation(LDA) for the exchange and correlation energy and numerical LDA solutions of a spherical carbon atom for the atomic orbitals. To reduce the computational effort the non-selfconsistent Harris functional is employed as well as the $I_h$
symmetry. Using this new method we are able to carry out \textit{ab initio} calculations for carbon clusters up to 1,000 atoms. Selective results are summarized in Table I.

We restrict our investigation to Goldberg type I fullerenes\cite{4}, in which the number of atoms in $n$th shell is $N(n) = 60n^2$ and the average radius can be approximated by $\bar{R}_n \approx 2.4\bar{b} n$, where $\bar{b}$ is the average C-C bond length. Thus, the inter-shell spacing is close to the inter-layer distance in the graphite, giving rise to the maximum inter-shell van de Waals attraction. For the smallest member $C_{60}$, all sites are equivalent, the shape can be classified equally well as spherical or polyhedral. The next shell $C_{240}$ has three independent atomic sites (Fig.1). The $I_h$ symmetry reduces the independent variables to seven. A global search for the minimum is out of reach of our present computational capabilities. We have investigated four most likely morphologies. 1) Sphere (S), in which all three sites are assumed to be on a spherical surface. 2) Icosahedrally (I) faceted, here all three sites are assumed to be on a faceted surface. A generalization of this morphology to large fullerenes is an Icosahedron\cite{5}. 3) Truncated Icosahedron (TI), this is an inflated version of $C_{60}$, in which site 1 and 2 (Fig.1) are assumed to be on the pentagonal facet while 2 and 3 are on a hexagonal facet. 4) The low energy morphology obtained by Yoshida and Osawa (YS)\cite{4}. This morphology is neither spherical nor simply faceted. However, as measured by the deviation from a sphere it is very close to (TI).

For the morphologies (S), (I) and (TI) the total energy was minimized with respect to two independent bond lengths (Fig.1). For the (YS) shape we take the ratios of various bond lengths to be the same as that given by Ref.4. Table I lists the formation energy and corresponding geometric parameters obtained. As one can see, the formation energy for S-$C_{240}$ is significantly smaller than that of I-$C_{240}$, TI-$C_{240}$ and YO-$C_{240}$. Therefore, our results demonstrate that for $C_{240}$ the spherical morphology has a lower energy than that of polyhedrons. This conclusion remains unchanged when the calculations were repeated using the atomic orbitals from up to fourth nearest neighbor atoms.

Included in Table I are also results of similar investigations for $C_{540}$. Again it is found that the spherical morphology has significant lower energy. Strong evidence in favor of
the spherical shape is the fact that in all cases the formation energy is correlated with the sphericity as measured by the standard deviation (SD) from a perfect sphere (Table I). The more spherical is the morphology the lower is the energy. Based on these results we conclude that for large single-shell fullerenes the spherical shape is the preferred morphology.

To understand the $N$ dependence of the formation energy several more clusters are examined. Plotted in Fig. 2 are the formation energy per atom $E_c$ versus $1/N$. $E_c$ decreases monotonically with increasing fullerene size $N$. A straight line fitting to the four largest fullerenes calculated leads to

$$E_c(N) = -7.178(1.0 - \frac{4.69}{N}) \text{ eV}.$$  \hfill(1)

Thus, $E_c(\infty) = -7.178$ eV is the extrapolated cohesive energy per atom for single graphitic layer. This number is close to that found by other calculations and by experiments.\(^\text{9}\)

The simple $1/N$ dependence can be understood in terms of the Hückel theory. In the nearest neighbor (n.n.) tight binding calculation there are two contributions to the energy difference between a fullerene and that of a graphitic layer. The first is due to the finite size of the fullerene. Exact calculation shows that the tight binding energy increases linearly with $1/N$, $E_t(N) = -1.574t(1 - \frac{0.835}{N})$, where $t$ is the n.n. hoping integral.\(^\text{11}\) This relation should reflects the approximate $N$ dependence of $\sigma$ bonding energy. The second, and more important contribution comes from the fact that for $\pi$ orbitals the n.n. overlaps depends on the molecular size.\(^\text{8}\) For spherical morphology $t_\pi$ is proportional to the $\cos(\phi)$, where $\phi$ is the radial angle spanned by the nearest neighbor C-C bond, $t_\pi = t_o \cos(\phi) = t_o \cos(2 \arcsin(\frac{b}{2R_N}))$ where $R_N$ is the radius of the sphere and $t_o$ is the limiting value for the graphitic plane. Taking $R_N \approx 2.4b\sqrt{N/60}$ and expanding in $1/N$ to the leading order one gets

$$t_\pi \approx t_o(1.0 - \frac{5.21}{N}).$$  \hfill(2)

Compared with Eq. 1 one sees the dominant contribution to the $N$ dependence of the cohesive energy is due to the change in $p_\pi$ orbital overlaps.

We now discuss the energetics of multi-shell Bucky onions and their morphology. Here one needs to include the inter-shell interactions. In Goldberg type I fullerenes the spacing
between successive shells, \( \sim 3.4\text{Å} \), is almost the same as that of interlayer spacing in graphite. Therefore one expects that interactions are dominated by the van de Waals force. In solid \( C_{60} \), the intermolecular interactions have been successfully modeled using the van de Waals interactions \cite{10}. There it was found that 90\% of cohesion energy can be calculated by simply summing over all the inter-fullerenes C-C interactions using the Lennard-Jones potential. For Bucky onions, this method should be an even better approximation as the inter-shell spacing are uniform. Therefore we use the same Lennard-Jones potential (\( \epsilon = 2.964 \text{meV} \), \( \sigma = 3.407\text{Å} \)) to evaluate the inter-shell interactions.

The fact that \( R_{n+1} - R_n \sim \sigma \) suggests that the inter-shell attraction is the largest when both shells have the spherical shape. Indeed numerical calculations show that the attractive interactions in the sphere morphology is significantly larger than that of polyhedrons, because the non-uniform spacing between shells in the latter. For example, the attraction between \( C_{240} \) and S-\( C_{540} \) (-17.7 eV, see Table II) is significantly larger than that between I-\( C_{240} \) and I-\( C_{540} \) (-12.3 eV). Thus, the inter-shell interactions also favor the spherical shape. Therefore we conclude that \textit{the shape of a multi-shell Bucky onion is spherical}. This is in agreement with experimental observation of spherical shaped multi-shell concentric Bucky onions \cite{1}. In Fig.3 a non-perspective view of a five shell Bucky onion is shown.

From Table II the van de Waals interactions between the \( n \)th and \((n + 1)\)th shell is found to be well described by \( V_{n,n+1} = -3.0n(n + 1) \text{eV} \). Using the extrapolated energy Eq.1 for the single shell fullerene, one can estimates that when \( n \geq 3 \) two shell Bucky onion with \( N(n) + N(n+1) \) atoms is more stable than a single shell fullerene with the same total number of atoms. The first case where the number \( N(n) + N(n+1) \) also belongs to a type I Goldberg fullerene is when \( n = 3 \). Thus our calculations suggest that energetically \( C_{(540,960)} \) is more stable than \( C_{1500} \). This result is rather different from earlier calculation where the crossover was found to occur at \( N \sim 6000 \). Finally, it is clear that for large clusters the dense Bucky onions are most stable. This is because the van de Waals attraction is \( \sim l^3 \) for a \( l \) shell onion, while the cost is \( \sim l \) compared with a single shell fullerene.
In conclusion, we have shown that the shape of large fullerenes are spherical regardless whether it is single or multiple shell. By including the van de Waals interactions between shells it is demonstrated that spherical dense Bucky onions are likely the most stable structure for large carbon clusters. This is in good agreement with recent experimental observations of these concentric spherical shells. The possibility of forming a lattice of Bucky onions should open up a new area of fullerene research and many interesting physical properties can be expected.

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11 If all nearest neighbor hoping are identical, caculations show that all type I Goldberg series are close-shelled, namely the HOMO are completely occupied. This is generally not true for type II in which \( N(n) = 20n^2 \).

12 In the case of spherical morphology, it is found that the rotational barrier of inner shell vs outer shell is very small. Thus, free rotation is expected at room temperature. In contrast, for polyhedron morphologies the barriers are very high.

13 The next occurrence for the identity \( n^2 + (n + 1)^2 = m^2 \) is when \( n = 20, m = 29 \). In this case \( N = 50460 \), the van de Waals attraction \( V_{20,21} = 1261 \text{ eV} \) is large and the two-shell onion is more stable.
FIGURES

FIG. 1. Asymmetric part of large fullerene structures. (a) $C_{240}$, shown are three independent sites and two bond labeling (see text). (b) Similar drawing for $C_{540}$.

FIG. 2. The formation energy vs $1/N$. The straight line (Eq.1) is the least square fit into the four points $N = 180, 240, 540, 960$.

FIG. 3. A non-perspective view of the five shells dense Bucky onion $C_{(60,240,540,960,1500)}$. For clarity, only portion of each shell is shown.
TABLES

TABLE I. Formation energies per atom for various fullerenes with different morphologies: S – spherical, I – Icosahedron faceted, TI – truncated Icosahedron, YO – the structure given in Ref.4. 

\( \bar{b} \) – average bond length, \( \bar{R} \) – Average radius, SD – standard deviation from a perfect sphere.

|         | \( E_c \) (eV) | \( \bar{b}(\text{Å}) \) \((b_1, b_2)\) | \( \bar{R}(\text{Å}) \) | SD (Å) |
|---------|----------------|--------------------------------------|----------------|--------|
| S-C\(_{240}\) | -7.05          | 1.43 (1.43, 1.43)                   | 7.12           | 0.00   |
| I-C\(_{240}\) | -6.90          | 1.45 (1.46, 1.42)                   | 7.27           | 0.39   |
| TI-C\(_{240}\) | -6.92          | 1.46 (1.47, 1.43)                   | 7.09           | 0.18   |
| YO-C\(_{240}\) | -6.97          | 1.45 (1.45, 1.40)                   | 7.03           | 0.17   |
| S-C\(_{540}\) | -7.09          | 1.41 (1.42, 1.41)                   | 10.5           | 0.00   |
| I-C\(_{540}\) | -6.86          | 1.43 (1.44, 1.40)                   | 10.4           | 0.52   |

TABLE II. The van de Waals interactions between the first five shells of a dense spherical Bucky onion.

| \( V_{ij} \) (eV) | \( C_{240} \) | \( C_{540} \) | \( C_{960} \) | \( C_{1500} \) |
|-------------------|--------------|--------------|--------------|---------------|
| \( C_{60} \)      | -5.57        | -0.81        | -0.20        | -0.07         |
| \( C_{240} \)     |              | -17.7        | -2.34        | -0.55         |
| \( C_{540} \)     |              |             | -35.9        | -4.28         |
| \( C_{960} \)     |              |              |             | -59.9         |