Geometries, Electronic Properties, and Energetics of Isolated Single Walled Carbon Nanotubes

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Using the density-functional electronic-structure calculations, we study so-called zig-zag carbon nanotubes. From the complete geometry optimization, it is found that two kinds of bond lengths are considerably different from each other. They possess strong tube-diameter dependence. We determine the bond lengths up to the order of $10^{-2}$ Å and the bond angles to $10^{-2}$ degree. In addition, changes of the electronic band structure upon the geometry relaxation from the uniform bond-length tube are found to be sizable. Also the electronic properties and energetics obtained for optimized geometries are discussed.

KEYWORDS: nanotube, geometric property, bond length, bond angle, band gap, band structure, density functional theory

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1. Introduction

Carbon nanotubes can be regarded as graphiteic cylinders generated just by rolling one sheet of graphite ("graphene") with a finite width.3 They are predicted to become either metal or semiconductor depending on their diameter and chirality.2,3 Such peculiar electronic properties have attracted considerable interest and sparked a large amount of activity from basic to applied research during the last decade. However, details of their structural parameters are not well known yet.

Although all bonds should be equivalent in a graphene sheet, not all the bonds have to be equivalent in carbon nanotubes. It is expected that two or three kinds of bonds will appear in each nanotube, but due to the lack of the crystalline sample of structurally uniform carbon nanotubes, their bond lengths and other structural parameters have not been reported experimentally. The only experimental information about their geometries has been given by the Scanning Tunneling Microscopy measurements, which are enough to discuss the chirality of each nanotube but are not sufficient enough to discuss the detail of the bond lengths.4,5 Therefore the difference between two or three C–C bonds has not been noted so far. It is also expected that the electronic properties of carbon nanotubes may depend on the details of structural parameters. By the tight-binding calculation,2,3 it has been shown that electronic properties of nanotubes depend sensitively on tube diameter and chirality and that nanotubes are categorized into three classes:2 First class becomes metallic, second semiconducting with narrow band gaps, and the third semiconducting with moderate band gaps. From the first-principles electronic-structure study6 it has been pointed out, however, that above classification does not apply to the nanotubes which have very small diameter.

In the present work, we theoretically study the geometrical structure of "zigzag" carbon nanotubes. We discuss bond angles and bond lengths in detail. We also examine the importance of the detailed structure in discussing electronic properties of nanotubes. It has been found that if $n$ is not multiple of 3 for zigzag nanotubes with $5 \leq n < 12$, the energy gap tends to decrease as the tube diameter decreases, being opposite to the tight-binding results.

2. Computational Method and Systems Studied

In the present work, we use the local-density approximation (LDA) in the framework of the density-functional theory (DFT).7,8 The plane-wave basis set with the cutoff energy of 50 Ryd, which is known to be enough for not only the electronic-structure study but also the energetics study of carbon-based solids,9 are used together with the Troullier–Martins pseudopotentials.10 As for the exchange-correlation potential (and functional) in the LDA, we adopt the Ceperley–Alder formula.11,12 We also use the Kleinman–Bylander separable approximation13 for pseudopotentials.

To study how the bond lengths of carbon nanotubes will change from that of an ideal graphene sheet we first have to know the details of geometric parameters of graphite and graphene to be predicted by the present method. We have optimized the bond length of graphite under the experimental interlayer distance of 3.348 Å. The bond length of graphite obtained by this optimization is 1.402 Å, which is 98.7% of the experimental value. This value should be regarded as a scaling factor in the present work to estimate the actual bond lengths from the theoretically optimized values. On the other hand, we should discuss the bond lengths of carbon nanotubes in comparison to a graphene sheet, because a graphene sheet can be regarded as the nanotube thickened to the utmost limit. Therefore we optimized the bond length of a graphene sheet in a supercell with the interlayer distance being 8.5 Å, which can be considered enough to neglect the interlayer interaction. Consequently the optimized bond length of graphene is found to be 1.406 Å (≈ $d_0$). Interestingly, this value is larger than the above graphite value by 0.3%. We discuss the optimized lengths of various bonds of nanotubes in comparison to this graphene value when necessary.

Here, we briefly introduce "zigzag" nanotubes studied in the present work. It is known that structures of nanotubes are identified by a so-called chiral vector, $(n_1, n_2)$.3 Zigzag nanotubes are described by this chiral vector as $(n, 0)$ and they have zigzag edge as shown in Fig. 1. They are called...
“(n, 0) nanotubes” also. It was predicted that if \( n \) is multiple of 3 the energy band of the \((n, 0)\) nanotube is a narrow-gap semiconductor\(^2\) or metallic,\(^3\) and otherwise a moderate or wide gap semiconductor.

All the calculations in this work are carried out in a supercell geometry with a hexagonal array of tubes, with the closest distance between atoms on different tubes being as long as 9 Å to suppress sufficiently the intertube interaction. We optimize the internal coordinates of atoms completely by using the conjugate-gradient method.\(^1\)\(^4\) We also optimize the length of the unit cell along the axes of the tubes by changing the lattice constant \( c \) along the tube axis. In Fig. 2, for example, the calculated values of the total energy of the \((8, 0)\) nanotube are plotted as a function of the \( c \) value. This figure clearly shows a slightly elongated geometry of this nanotube from the ideal one. At each \( c \) value, the optimization of internal coordinates of nanotube have been done.

\[
\Delta E = C_1 \left( \frac{1}{D} \right)^2 + C_2 \left( \frac{1}{D} \right)^4
\]

where \( D \) is a diameter of the tube.\(^1\)\(^5\) In Fig. 3, the calculated values of \( \Delta E \) are plotted as a function of \( 1/D^2 \) for \((n, 0)\) nanotubes with \( n = 5 \rightarrow 12 \). In small diameter cases, spheres plotted deviate downward from the broken line using eq. (3.1), while they deviate upward in large diameter cases. This deviation indicate that the effect of higher order term is not negligible. \( \Delta E \) is an even function of \( 1/D \) because of symmetric properties of the system. Actually the points almost fall on the curve represented by the relation,

\[
\Delta E = C_1 \left( \frac{1}{D} \right)^2 + C_2 \left( \frac{1}{D} \right)^4
\]

with \( C_1 = 6.85eV Å^{-2} \) and \( C_2 = 20.02eV Å^{-4} \). A similar analysis\(^1\)\(^5\) has been performed for the nanotubes studied by using the Tersoff’s model potential. The present \( \Delta E \) value is larger than that of Tersoff’s potential for the tubes with diameter lager than 2.05 Å. Therefore a graphene sheet is slightly harder to bend in the LDA calculation than in the Tersoff’s calculation.
3.2 Detailed geometries

Due to the symmetric properties of zigzag nanotubes, it is expected that two kinds of bond lengths will appear \((d_1 \text{ and } d_2 \text{ in Fig. 1})\). In Fig. 4(a), differences between \(d_0\) and bond lengths in the optimized geometries are plotted as a functions of \(1/D^2\) as in the case of \(\Delta E\). This figure shows that \(d_1 - d_0\) decreases almost proportionally to \(1/D^2\), while \(d_2 - d_0\) increases proportionally to \(1/D^2\):

\[
\begin{align*}
  d_1 &= d_0 + s_1 \left( \frac{1}{D^2} \right) \\
  d_2 &= d_0 + s_2 \left( \frac{1}{D^2} \right)
\end{align*}
\] (3.3)

respectively, where \(s_1 = -0.320 \text{ Å}^3\) and \(s_2 = 0.427 \text{ Å}^3\). They indicate that the bonds parallel to the axes of the tube are shorter than that of graphene. On the other hand, the other type of bonds is longer. The average value of two bonds is given by \(\bar{d} = d_0 + \vec{s}(\frac{1}{D})\) with \(\bar{s} = 0.176 \text{ Å}^3\). In diamond \((sp^3\text{ carbon})\) the bond length is 1.54 Å, which is longer than the bond length in graphite \((sp^2\text{ carbon})\) by 8.4%. In carbon nanotubes, due to the slight bond bending as will be given below, they may possess a slight \(sp^3\) character. This may be the reason why the average value of bond lengths increases with decreasing the diameter.

In the same way, two kinds of bond angles \((\theta_1 \text{ and } \theta_2 \text{ in Fig. 1})\) are plotted also as a function of \(1/D^2\) in Fig. 4(b). The points almost fall on the following lines:

\[
\begin{align*}
  \theta_1 &= \theta_0 + \theta_1 \left( \frac{1}{D^2} \right) \\
  \theta_2 &= \theta_0 + \theta_2 \left( \frac{1}{D^2} \right)
\end{align*}
\] (3.5)

(3.6)

where \(\theta_0 = 120^\circ\), \(\theta_1 = -147.12^\circ\) Å² and \(\theta_2 = 1.18^\circ\) Å². This shows that \(\theta_1\) is proportional to \(1/D^2\) while \(\theta_2\) is almost constant, i.e., almost equal to the ideal bond angle, \(\theta_0\). It should be noted that even in an ideal zigzag carbon nanotube made from a graphene sheet without any structural relaxation, \(\theta_1\) can be smaller than 120, while \(\theta_2\) may remain unchanged. The average bond angle is given by \(\theta_0 + \bar{R}(\theta_0)\) where \(\bar{R} = -48.25^\circ\) Å².

It should be noted here that nanotube diameter, \(D\), can be uniquely obtained if \(d_2, \theta_1, \text{ and } \theta_2\) values are given. Hence, there is a relation to be satisfied by \(d_2, \theta_1, \theta_2\) and \(D\):

\[
\frac{d_2^2 \sin^2 \theta_2}{\bar{d}} + \frac{\sin^2 \theta_1}{\sin^2 \theta_2} = 1
\] (3.7)

Therefore \(s_2, t_1\) and \(t_2\) should satisfy following equation approximately:

\[
s_2 \approx \frac{\pi}{180} \sqrt{\frac{2t_2^2 + 8t_1t_2 - t_1^2}{6(t_1 + 2t_2)}} \sqrt{\frac{\pi}{180\sqrt{3}}} (-t_1 - t_2)
\]

(3.8) is almost satisfied by present \(s_2, t_1\) and \(t_2\) values obtained independently via fitting procedure for \(d_2, \theta_1\) and \(\theta_2\) results, respectively.

The present results, i.e., the presence of two different bond lengths for zig-zag nanotubes, may also be the case for armchair nanotubes. The detailed analysis is now under way.

3.3 Electronic properties

In Fig. 5, the energy gap values obtained are given as a function of \(n\). The present LDA results differ considerably from the tight-binding results.\(^{2,3}\) The \((5,0)\) nanotube is a metal in the present LDA study, while it was predicted to be a moderate-gap semiconductor in the previous tight-binding work.\(^{2,3}\) More importantly, the overall behavior is completely opposite from the tight-binding results. The figure shows that energy gap of moderate-gap semiconductors decreases with decreasing diameter. As has been shown in a previous LDA work,\(^6\) we can see a band near the Fermi level\(\ast\) is lowered in Fig. 5 from the position expected in the tight-binding model. The charge density of this state is found to distribute asymmetrically inside and outside of the nanotube. Therefore, the lowered state is neither pure \(\pi\) nor \(\sigma\) derived state, but contains both \(\pi\) and \(\sigma\) characters.

The band structure obtained is given in Fig. 6 for \(n = 5, 8, 12\) nanotubes. To study the effect of the structural relaxation from an “ideal” rolled graphene, we show the band structure
of not only optimized carbon nanotubes but also that of the initial "ideal" nanotubes. Since the geometrical changes from ideal nanotube structure is larger for a smaller-diameter case, the electronic structure of the optimized (5, 0) nanotube shows the largest difference from that of the initial ideal one.

4. Summary

In summary, we have studied the energetics, geometries and electronic properties of zigzag carbon nanotubes. The total energy per atom can be fitted well by a parabola as a function of $1/D^2$ where $D$ is the tube diameter as has been pointed out by the model potential study previously, while energy loss is found to be larger in the present work. Two kinds of bonds and angles in zigzag nanotubes are both predicted to have sizable differences from each other. All the values are almost fall on a straight line respectively when they are plotted as a function of $1/D^2$. Interestingly in thin nanotubes, overall tendency of the band gap values as a function of the tube diameter is different from that given by previous tight-binding works. The lowered band is confirmed to possess both $\sigma$ and $\pi$ characters. Changes of the electronic band structure from that of the ideal equal-bond length geometry is found to be present and rather large. These results show the importance of the detailed geometric and electronic structure study in this field.

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