Twisting Effects on Carbon Nanotubes: 
A First-Principles Study with Helical Symmetry Operations

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Abstract. We report the energetics and the electronic properties of twisted carbon nanotubes (CNTs). We use a real-space density functional theory with helical-symmetry operation, and apply it for several CNTs with the diameters of around 0.8 nm including the experimentally abundant (6,5) nanotube. By using this computational code, one can now obtain the total energies with enough accuracies to optimize the CNT geometries including quasi-continuous twisting levels for any type of nanotube in principle. As a result, it is found that chiral nanotubes possess twisted geometries at their ground states. The electronic structures of CNTs depend sensitively on twisting levels in this diameter region, and the twisting effects on their fundamental gap values can be judged by the value of mod(n - m, 3), where n and m are the chiral indices.

1. Introduction
Carbon nanotube has been considered to be one of the most important materials in nanoscience and nanotechnology [1]. The reason of this attention mainly comes from their unique electronic properties. It is well known that the electronic transport properties of CNT sensitively depend on the diameter and chirality from the reports by using the tight-binding method [2]. Therefore, it is very important to know the accurate electronic properties of CNTs for any practical electronic application. It is often thought CNT is a perfect cylinder made by rolling up a two-dimensional graphite sheet. In reality, however, there are undeniable possibilities for them to possess structural deformations such as bent, twisted or collapsed region. As for the chiral nanotubes, their ground state geometry may possess intrinsic twisting because of their inherent helical structures. According to the studies by using the density functional theory (DFT), it has been revealed that the electronic structures of CNTs depend sensitively on their geometrical parameters such as bond lengths and bond angles [3 - 5]. Hence, electronic properties of deformed nanotubes should be of high interest and importance. The uniaxial strains of CNTs have been often discussed by using DFT. However, there are no systematic DFT study which has considered twisting effects on CNTs. This is because the most DFT computational codes utilize the translational symmetry together with the plane-waves basis set. The uniaxial strains on CNTs can easily be dealt with by this popular code. On the other hand, applying the twist breaks the original translational symmetry of CNTs and the periodicity of the translational symmetry.
changes significantly depending on the direction and the magnitude of twisting. Hence, it is quite difficult to discuss the twisting effects on CNTs by using the popular DFT code.

2. Computational Details and System Studied

Mintmire et al. reported that all CNTs can be classified by the two kinds of symmetry operations [6]. One is the helical-symmetry operation and the other is the rotational-symmetry operation. By using these symmetry operations not the translational-symmetry but the helical-symmetry, unit cell of any CNT includes only two carbon atoms. In order to implement these symmetry operations to the computational code, we adopt not the plane waves but the real space grids as basis set. Arbitral boundary conditions can be applied by the use of the real space grids, and all quantities are directly calculated on the grid points. Therefore, this DFT code is classified as so-called “real-space” method. In the DFT code, the twist is applied by inclining the translational vector in the expanded plane. The twist angle ($\theta_T$) is defined as the angle between the original translational vector and the declined translational vector. The number of carbon atoms per unit cell does not change by applying the twist unlike the translational unit-cell method. Therefore, we perform the geometrical optimization including the twisting degree of freedom and discuss the electronic properties of all the optimized CNTs in the same computational cost. The present real-space DFT computational code use the local density approximation [7] parametrized by Perdew and Zunger [8, 9]. The norm-conserving pseudopotential proposed by Troullier and Martins is implemented with the separable form [10, 11].

The system studied is shown in figure 1. We choose the several CNTs having the diameters of about 0.8 nm, and focus on the experimentally abundant nanotubes, i.e. (6,5) and (7,5), in the sample produced by using the chemical vapor deposition (CVD) method with the Co-Mo catalyst [12] or the alcohol catalytic CVD method [13].

![Figure 1.](image)

**Figure 1.** $(n, m)$ indices of the systems studied (color online). In each hexagon are written not only the chiral indices but also the number of atoms in the translational unit cell. We discuss the twisting effects of CNTs corresponding to the red-colored hexagons.

3. Results and Discussion

From the structural optimization, it is found that the total energy of the slightly twisted geometry is generally lower than that of the non-twisted geometry in chiral nanotubes. This
Figure 2. Twist-angle dependences of the density of states of (6,5) and (7,5) nanotubes. The black allows show the van Hove singularities corresponding to the $E_{11}$ under $\theta_T = 0$.

result suggests that chiral nanotubes should possess the intrinsic twisting even in their ground state geometry. Among the studied nanotubes, the (6,5) nanotubes is found to have the largest intrinsic-twisting angle. The estimated intrinsic twisting of the (6,5) nanotube should correspond to the half revolution for each $1 \mu m$.

As for the electronic structures, figure 2 represents the twist-angle dependences of the density of states of (6,5) and (7,5) nanotubes. Interestingly, (6,5) and (7,5) show the opposite twist angle dependences. In addition, $E_{11}$ and $E_{22}$ values, the peak-to-peak energy separation between the valence bands and the corresponding conduction bands, also show the inverse twist-angle dependences in each nanotube. When the positive twist is applied on (6,5) nanotube, $E_{11}$ increases while $E_{22}$ decreases. On the other hand, when the same twist is applied on (7,5) nanotube, $E_{11}$ decreases while $E_{22}$ increases. This effect can be understood by the so-called “zone-folding” method which gives the approximate electronic structure of CNT from that of graphene. In that method, the cutting lines which reflect the circumferential boundary conditions play important roles. The two-dimensional first Brillouin zone (FBZ) of graphene is mapped into the one-dimensional FBZ along the cutting lines. The $E_{11}$ and $E_{22}$ values are associated with the nearest and second nearest cutting lines to the “K” point in the FBZ of graphene. These lines lie across the “K” point. At the “K” point, the valence band top and the conduction band bottom touch each other linearly. It is known that the constant-energy surface around the “K” point is similar to the concentric circle in graphene. Therefore, $E_{11}$ and $E_{22}$ values are nearly proportional to the distance between the “K” point and the cutting lines. When the twist is applied, all cutting lines move to the same direction depending on the direction and the magnitude of the twist in a nanotube. Considering this effect, $E_{11}$ and $E_{22}$ values should be inversely affected by the applied twist. When the distance between the “K” point and the nearest cutting line becomes shorter by the twist, the distance between the “K” point and the second nearest cutting line becomes longer. This property can be generalized for the “moderate-gap” semiconducting CNTs by using the value of $\text{mod}(n - m, 3)$, where $n$ and $m$ are the chiral indices. $E_{11}$ and $E_{22}$ values of (7,6), (6,5) and (8,4) show the same twist-angle dependences. On the other hand, their twist-angle dependences of (7,5) and (8,3) show the opposite behavior comparing with the above group. It is also found that the magnitude of change of $E_{11}$ and $E_{22}$ values depends on the chiral angle. Armchair and near armchair
nanotubes show the large twist-angle dependences of about 0.2 eV/degree, while $E_{11}$ and $E_{22}$ values of zigzag nanotubes scarcely depend on the twist angles. They show almost the constant values in the calculated range of the twist angles. It is interesting to note that, when a sizable twist is applied, the original $E_{22}$ line can become closer to the “K” point than the original $E_{11}$ line and $E_{11}$ can be larger than $E_{22}$. Actually, figure 2 shows this situation. In the (6,5) nanotube, the difference between $E_{11}$ and $E_{22}$ values becomes smaller with increasing the positive twist. When the applied positive twist exceeds over two degree, the original $E_{11}$ should be called $E_{22}$ and the original $E_{22}$ should be called $E_{11}$. Also the same exchange is observed in the twisted (7,5) nanotube toward the negative $\theta_T$ direction.

4. Summary
We have investigated the twisting effects on the several CNTs using the real-space DFT computational code which can deal with the geometrical optimization including the twisting degree of freedom. Because we use the helical-symmetry and the rotational-symmetry operations, the computational costs for all CNTs are the same with all twisting conditions in principle. As a result, it is found that the intrinsic twisting should occur in the chiral CNTs, and that the twisting strongly affects the electronic structures of CNTs, inducing the significant variations of not only $E_{11}$ but also $E_{22}$ values. Interestingly, we predict that one should observe the exchange of $E_{11}$ and $E_{22}$ states in the (6,5) and (7,5) with relatively small twisting angles. These twisting effects on the electronic structures should be explained by “zone-folding method”. These results also suggest that the optical properties of CNTs should be changed considerably just by applying the twist.

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