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COILED CARBON NANOTUBES: A SIMPLE MODEL

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1. Introduction

Synthesis of regularly coiled carbon nanotubes has been reported fifteen years ago [1]. Techniques of growth at high yield have been developed, and electrical, mechanical and magnetic properties of the coiled nanotubes have been experimentally investigated [2]. However, geometric structure and other theoretical aspects of these tubes remain unresolved because extremely large number of atoms per unit cell makes conventional numerical methods inapplicable. Here we try to overcome this difficulty with the help of symmetry.

Symmetry transformations of a helically coiled carbon tube, gathered into a line group [3], generate the whole tube from the unit cell of the corresponding straight carbon nanotube. Therefore, modified group projector technique, implemented into POLSym code [4], makes possible calculations which takes into account only unit cell atoms of the straight nanotube. Number of such atoms increases with diameter, and therefore, in order to facilitate the calculations, we do not study thick tubes.

2. Symmetry

First theoretical consideration [1] of the structure of helically coiled carbon nanotubes has been founded on the topological Euler theorem (tacitly assuming rigid bonds), according to which coil is related to occurrence of the pentagon/heptagon pairs at the opposite sides. Such a pair induces a knee, with angle depending on the radius of the tube, and special regular arrangements of the knees produce seemingly helical coils. However, this model gives a number of possible structures, while the experimental data show many different helical coils, most of them being regular smooth helices without emphasized knees. In addition, study of elastic energy of graphene based tubular structures [5] shows that besides straight also helical conformation are stable, without introducing pentagon/heptagon defects.

Hence, we propose a model with atoms forming only hexagonal net which is slightly deformed in a way to produce helical coil (Fig. 1). It should be recalled that straight single wall carbon nanotube (n_1, n_2) consists of identical hexagons (though lengths of the bonds of an atom to its three nearest neighbors differ). It is convenient [6] to introduce coordinate system (related to the

straight nanotube), in which *z*-axis is the tube axis, while *x*-axis is perpendicular to it passing through the centre of a hexagon. Then the coiled nanotube $(n_1,\ n_2)\_(R,\ \chi,\ \varphi_0)$ we obtain as follows. Take the helix of the radius R around central vertical *Z*-axis and inclination angle χ. Pull on it single wall carbon nanotube $(n_1,\ n_2)$ in a way that *z*-axis coincides with the helix. We define *X*-axis as perpendicular to the *Z*-axis through the origin *S* of the coordinate system related to the coiled tube. Angle φ_0 is the angle between *X* and *x*-axis, and it describes rotation of the tube around the helix.

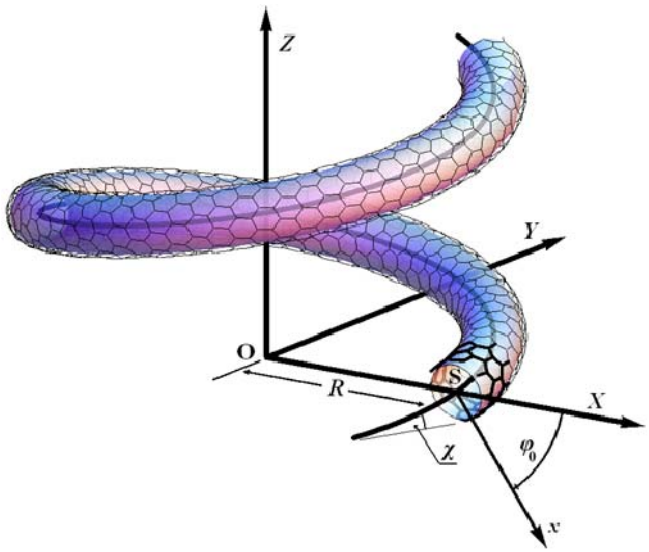

Fig. 1. Configuration of the helically coiled nanotube. Incommensurate coiled carbon nanotube (8,2)_(25.1, 0.17, 0.63) with line group $\mathbf{L} = \mathbf{T}_{24.6}(0.11\text{nm})\mathbf{C}_1$ is presented. Bolded bonds emphasize symcell of the coiled nanotube (i.e. unit cell of the straight single wall carbon nanotube), with 56 atoms. Single turn of the helix cointains slightly more than 28 such periods, i.e. more than 1568 atoms.

As this helical systems obviously do not posses neither mirror nor glide plane symmetry and since nontrivial rotation around the *Z*-axis cannot be the symmetry transformation, the relevant line group is either from the first or (when $\varphi_0 = 0$) from the fifth family (i.e. $\mathbf{L}^1 = \mathbf{T}_Q(F)\mathbf{C}_1$ or $\mathbf{L}^5 = \mathbf{T}_Q(F)\mathbf{D}_1$ [3]). To find *Q* and *F*, we note that one translational period of single wall carbon nanotube is exactly the minimal part which generates the whole helically coiled nanotube by action of the symmetry group **L**. This length a has vertical and horizontal projections F and $2\pi R/Q$, giving: $F = a\sin\chi,\quad Q = 2\pi R/a\cos\chi$. Consequently, symcell of the coiled nanotube contains $N = 4\left(n_1n_2 + n_1^2 + n_2^2\right)/GCD\left(2n_1 + n_1n_2 + 2n_2\right)$ atoms which is the number of atoms in the single wall carbon nanotube unit cell. It should be noted that period *a* is the only parameter of the line group of the straight tube which is also the symmetry parameter of the coiled nanotube. For rational values of *Q*, coiled nanotube is translationally periodic. Then $Q = q/r$ (where q and r are coprime integers, $q \geq r$), and the translational period is $A = qF$.

3. Results

A sample of seventy helically coiled nanotubes with generic straight single wall nanotubes with diameter from 0.5 nm to 3 nm is considered. It includes series of zig-zag $(n,0)$ (for $n=10,\ldots 26$) and armchair (n,n) (for $n=7,\ldots 21$) tubes, as well as the arrays $(2n,n)$ and $(3n,n)$. However, no rule could be derived for the relaxed parameters R and χ; if this is the consequence of density functional tight-binding method applied, more precise methods like molecular mechanics, full density functional [7,8] might reveal such rule (however, then the problem of too many atoms per elementary cell appears). Indeed, for majority of the tubes relaxed radius R is greater than the initial one, while angle χ is increased in the relaxation, but there are exceptions of all kinds (both or only one of the parameters decrease). This is illustrated in Fig. 2. Note also that straight nanotube is obtained for $\chi=\pi/2$ and/or $R=\infty$. Numerically, when we take the initial configuration with sufficiently large R and/or χ close to $\pi/2$, the relaxation gives uncoiled, perfectly straight nanotube; this not only justifies consistency of the method, but shows that in this region of parameters there is no other local minima.

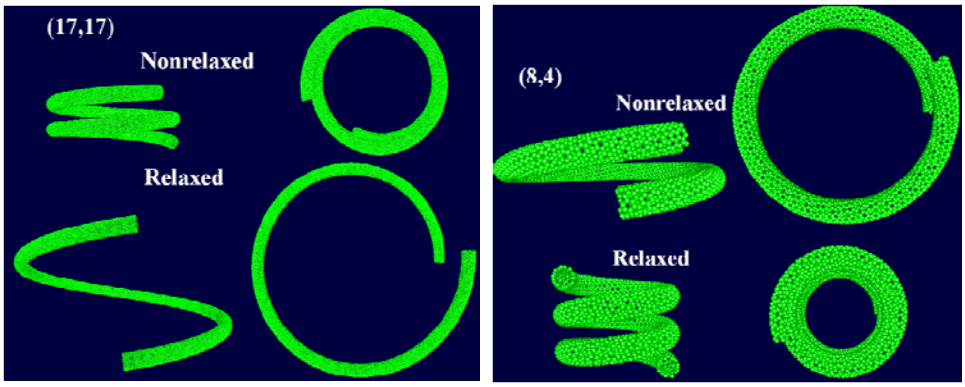

Fig. 2. Initial and relaxed configurations of the helically coiled carbon nanotubes. The typical case is illustrated by helically coiled (17,17) nanotube, which when relaxed becomes less tightly coiled. On the other hand, as shown at the right panel, relaxation makes (8,4) nanotube more tightly coiled (i.e. radius and inclination of the coil are decreased).

We also calculated electronic band structure of the relaxed nanotubes (Fig. 3). Using POLSym code, the energies are assigned by the helical quantum numbers. As rotational group is trivial, the only value of the helical angular momentum quantum number is zero. When $\varphi_0=0$, due to the U-axis symmetry, the energies are double degenerate and interval $[0,\pi/F]$ is irreducible domain of the Brillouin zone; also, there is additional parity quantum number which characterizes states edges of the irreducible domain. Consequently, according to the Landau's noncrossing rule, energy bands cannot cross. Only for $\varphi_0=0$, different bands ending with opposite parity can be joined at the edges of the irreducible domain. The electronic energy bands are calculated within tight-binding density functional method, with full symmetry implementing POLSym code [4]. Each

atom contributed by four sp^3 orbitalls. Roughly, electronic bands of helically coiled nanotubes are similar to those of the generic straight nanotubes as far as the energy range and shape of the band structure as a whole are considered. Still, the number of bands of the coiled nanotubes is much larger because of the greater number of the orbital per unit length is included. The main difference is that vast majority of the HCCNTs are conductive, with significant density of states at Fermi level.

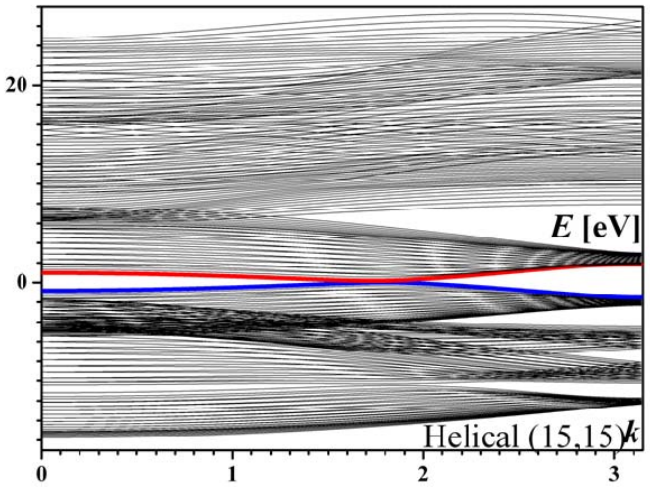

Fig. 3. Electronic bands of helically coiled (15,15) nanotube within sp^3 atomic orbital model. When Fermi level region is enlarged it can be seen that tinny secondary gap arises as noncrossing rule becomes effective, due to the symmetry breaking

4. Summary

A sample of helically coiled nanotubes is analyzed, using symmetry arguments and density functional numerical methods. Due to full symmetry implementation, our model allows only seven relaxation parameters: period and coordinates of a conventional single wall carbon nanotube (a, r, φ and z), radius and inclination of the helix of the coil (R and χ) and position of the tube relative to the helix (φ_0). This simple model gives correct hint of the electronic structure. It confirms that vast majority of the helically coiled nanotubes are conductive with a considerable larger electronic density of states at Fermi level than the conventional straight counterparts.

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