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Computational algorithms for fast-building 3D carbon nanotube models with defects

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ABSTRACT

Algorithms for generating defective carbon nanotubes have been developed and implemented in software. The algorithms were designed to create arrays of carbon atoms that form layers and interconnect. The parameters for construction were the following: Hamada indices that respond to topology (armchair, zigzag or chiral nanotubes) and diameter, the saturated or unsaturated nature of the nanotube, the length and, most importantly, the presence of defects that can be built individually or repetitively by rotating bonds, removing atoms, or adding additional carbon atoms. The output was written in a standard, exportable file format that contained atomic coordinates useful for further computational chemistry work.

1. Introduction

Carbon nanotubes (CNTs) have been recognized as one of the most important materials of the future [1] due to their remarkable properties. They have potential uses in a wide variety of applications, from molecular electronics devices to mechanical, biomedical, medicine, and analytical fields [2–6]. In particular, single-walled CNTs have interesting electronic properties that depend upon factors [7–11] such as chemical constitution, configuration, diameter, and length.

The properties of these nanostructures are drastically modified in the presence of defects such as pentagons, heptagons, rehybridization, vacancies, or dopants. The presence of one or more 5–7 defects (pentagon–heptagon pair) in CNTs has been shown to produce changes in topology that affect the electronic structure [12–14] and mechanical properties of nanotubes, inducing plastic transformations in an otherwise a brittle material [15]. Furthermore, the presence of pentagon–heptagon defects allowed for the heterojunction of nanotubes with different helicities [16,17] that had particular electronic properties that are potentially useful for designing new microelectronic devices [11]. Defects have also been shown to modify the hydrogen adsorption behavior of nanotubes.

Molecular dynamics simulations and density functional theory calculations indicated that defects created on the exterior wall of a (10,10) carbon nanotube enhanced hydrogen adsorption potential. The physisorbed hydrogen molecules remained on the defected nanotube at 300 K, while the hydrogen molecules adsorbed on a perfect nanotube were desorbed [18]. The use of defective nanotubes as an environmental protective agent has been studied using the B3LYP/6-31G(d) method [19]. An interesting application of CNTs with defects involved nitrogen-doped carbon nanotubes used for C—H activation [20,21]. Functionalized [22,23], or doped, nanotubes with a particular distribution of dopants can be useful in many fields and need to be further researched. DFT (density functional theory) calculations of small diameter (∼0.3 nm) nitrogen-containing carbon nanotubes suggested that they could possibly be used as a conducting material for electronic nanodevices [24].

How are these defects produced? It has been observed that when CNTs are formed they are under great tension. One way they released this strain was by a 90° rotation of a C—C bond around its center, creating a Stone–Wales (SW, 5-7-7-5) defect [15]. That defect behaved as a nucleation center for the formation of other defects. Carbon dimers have also been incorporated into nanotubes and formed a new set of defects involving pentagons and heptagons or pentagons and octagons [5,13–15].

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Although many advances in nanotube synthetic methods have been published [25,26], it has always been more convenient to model these new nanostructures to predict their properties before synthesizing them in the laboratory. Molecular modeling offers a practical way to evaluate the potential properties of new materials, such as CNTs, before they are synthesized.

Nanotube molecular design requires structural visualization, information on the atomic coordinates, and consideration of the presence of different nanostructure topologies and geometries. Having appropriate atomic coordinates necessary for computational chemistry work is a challenge, especially for structures with a large number of atoms (i.e., over 300 atoms) bonded with a particular topology, such as defective CNTs. Clearly, an automated computational tool specific, with appropriate user control, for these kind of molecules would be advantageous.

Algorithms for the automated generation of CNTs with a regular hexagonal wall and without any defects are not very complex and have been solved using various tools and software. Most of the solutions [27,28] started with specified (n,m) Hamada indices [10] and utilized a graphene sheet roll-up algorithm to generate single-walled CNTs.

In a related problem, Melchor and Dobado [29] developed software, CoNTub, to solve the problem of joining two arbitrary CNTs. Their nanotube generation algorithm connects both tubes based on a topological algebra. This algebra takes into account a number of combinations and relative orientations between a minimum number of defects using a continuous strip of hexagons containing pentagon and heptagon cycles. However, that software is useful for regular nanotubes, not defective ones.

Stenberg et al. [5,13], using computer simulation tools, inserted molecular moieties of two carbons into a single-walled carbon nanotube to generation bumpy or zipper nanotubes. That approach applied modifications to a previously created nanotube structure; it is not a piece of software that builds defective carbon nanotubes from atomic units.

The algorithms developed in this work were capable of building defect-containing nanotubes, atom by atom, of various topologies and defects. The procedure was implemented as scripts written in the Tcl/Tk language, making it portable to other modeling systems for further property calculations.

2. Computational methods

Instead of using an algorithm oriented towards cutting and rolling up a previously constructed graphene sheet for tube creation, we have created algorithms for nanotube construction by "stacking up" layers or rings, as shown in Fig. 1. A layer is the shorter closed path that begins and ends with the same atom. The number of layers defines the length of the tube, and the number of atoms included in each layer defines its diameter. Nanotube chirality is defined by the particular interconnections between layers. In a single layer, each atom is bound to the previous atom and to the next one. At the same time, each atom has two free valences to connect to both carbon atoms in neighboring layers and hydrogen, if applicable.

Table 1
Relationship between Hamada indices and the number of atoms per layer.

Nanotube configuration	Hamada indexes	x
Zigzag	(n,0)	$2{\cdot}n$
Chiral	(n,m)	$2{\cdot}n+m$
Armchair	(n,n)	$4{\cdot}n$

2.1. Generation of the base layer

Let us consider atoms placed in a two dimensional matrix, R (see Fig. 2) whose size, as expected, depends on the tube length and chirality. Each row, $R[i]$, represents the i layer for the zigzag and armchair topologies, with $R[0]$ being the first row. The number of atoms constituting each layer, x, is related to the Hamada indices, as shown in Table 1. Atoms are consecutively numbered from 1 to x for the first layer. The layers increase in such a way that second layer starts with $x+1$, the third layer starts with $2x+1$ and so on. The first layer is finished when the atom in column x is bound to the atom in column 1. The same is true for the second layer, the atom numbered $3x$ (i.e., $2x+x$) is bound to atom $2x+1$ and so on. Atom numbering is an important factor when writing scripts to define the interconnections between layers as they are built.

2.2. Layer interconnection

Layers were connected in a specific way to generate spatially ordered hexagons of a particular topology according to the following rules:

1. *Zigzag nanotubes*. (i) Odd atoms of an odd row were connected to odd atoms of an anterior row; (ii) even atoms of an even row were connected to even atoms of an anterior row, as is shown in Fig. 2a.
2. *Armchair nanotubes*. For each atom, starting with the first atom of the second row, the corresponding atom identifier number was divided by 4. If the remainder of that division was 0 or 1, a connection with an anterior row was produced in the following way: (i) if the remainder was 1, the atom was connected to an atom of an anterior row having the "same column" plus 1 in matrix R; (ii) if the remainder was 0, connection was made to an atom in an anterior row having the "same column" minus 1 in matrix R, as shown in Fig. 2c.
3. *Chiral nanotubes*. The general procedure was similar to that of zigzag nanotubes except for the closure of the base layer. For a (n,m) tube with a length of l, the size of matrix R was $2n^*(l+m)$, and first atom in row $R[0]$ was bonded with the last atom in row $R[m]$. In general, the last atom in row $R[i+m]$ was bonded with first atom in row $R[i]$. Finally, a cutting away (or atom deletion) step in the initial (top right) and final (bottom left) left-over triangular sections of the nanotube matrix was performed (see Fig. 2b).

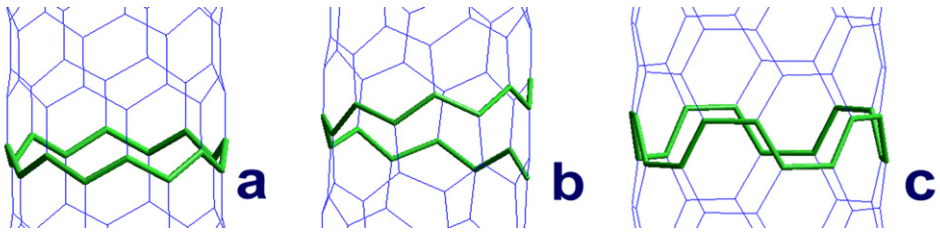

Fig. 1. Base layers (highlighted) for the: (a) zigzag, (b) chiral, and (c) armchair nanotubes.