# INVESTIGATION OF THE ELECTRONIC PROPERTIES OF CARBON AND III-V NANOTUBES

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# Abstract

The presence of defects such as impurities and structural defects (vacancies and Stone-Wale defects) particularly affect the electronic properties of nanotubes. Considering various potential applications of nanotubes (e.g. electrical circuits, gas sensors and transistors), we decided to investigate the electronic properties of pure and defected nanotubes (NTs). To this end, *ab* initio calculations usually are the best, specially density functional theory (DFT) based methods. In this regard, various kinds of NTs such as Single-walled (SW) and double-walled (DW) carbon nanotubes (CNT), boron nitride nanotubes (BNNT) and gallium nitride nanotubes (GaNNT) were analyzed.

Boron nitride semiconducting zigzag SWCNT, $B_{cb}N_{cn}C_{1-cb-cn}$, as a potential candidate for making nanoelectronic devices was examined. In contrast to the previous DFT calculations, wherein just one boron and nitrogen doping configuration have been considered, here for the average over all possible configurations, density of states (DOS) was calculated in terms of boron and nitrogen concentrations. It was shown that semiconducting average gap, $E_g$, could be controlled by doping nitrogen and boron. But in contrast to many-body techniques where gap edge in the average DOS is sharp, the gap edge is smeared and impurity states appear in the SWCNT semiconducting gap. For each boron and nitrogen concentrations, also, exact magnitude of the energy gap, $E_g$, was calculated.

Furthermore, Density functional theory (DFT) calculations of the Stone-Wales defected (S-WD) single-walled carbon nanotube (CNT) (10,0) were carried out to understand the effect of S-WD orientations on the electronic properties of CNT. We have considered the influence of supercell approximation on the defect formation energy and the electronic properties of both circumferential and axial S-W

defects in CNT. We found that the probability of S-WD orientation depends on the defect concentration. Density of states of defected CNTs calculations have been applied to indicate the effect of S-WD concentration on the semiconducting energy gap. Utilizing local density of states investigation, also, we explained the reasons of foreign atoms and molecules adsorption on S-WDs .

All BN nanotubes are semiconductor nanostructures regardless of diameter or chirality, in contrast to the carbon nanotubes that have both metallic and semiconducting features. In this case, the electronic properties of defected BNNTs for spin-up and spin-down electrons were explored. We have looked into two types of defects, vacancy and substitution of carbon and oxygen by boron or nitrogen. The formation energy calculation reveals that for both vacancies defected zigzag and armchair BNNTs, the probability of the nitrogen vacancy case is higher than that of the boron one. Also in the carbon doping process of BNNTs, the substitution of boron by carbon is more possible with respect to nitrogen by carbon. In the oxygen doping substitution process, substitution of boron by oxygen is less favorable than nitrogen by oxygen. For the higher-probability cases the spin-up and spin-down band structures show different features. For the first and second cases, the spin-up band structure shows a n-type semiconductor, while the spin-down band structure illustrates a wide band gap semiconductor. But for the oxygen-doped BNNTs case, the spin-up band structure shows a wide band gap semiconductor, while the spin-down band structure illustrates a n-type semiconductor. All defected BNNTs have a 1.0 $\mu_B$ total magnetic moment.

Like BNNTs, GaNNTs, another wide band gap nanostructures, are of interest. Structure and electronic properties of GaN nanotubes (GaNNTs) were studied in our work. The optimized structures (bond-lengths and angles between them) of zigzag GaNNTs (n, 0) and armchair GaNNTs (n, n) ($4 < n < 11$) were calculated by full optimization. The difference between nitrogen ring diameter and gallium ring diameter (buckling distance) and semiconducting energy gap in term of diameter for zigzag and armchair GaNNTs have also been calculated. We observed that buckling distance decreases by increasing nanotube diameter. Furthermore, we have examined the effects of nitrogen and gallium vacancies on structure and electronic properties of zigzag GaNNT (5, 0) using spin dependent density functional theory. By calculating the formation energy, we determined that N vacancy in GaNNT (5, 0) is more favorable than Ga vacancy. The nitrogen vacancy in zigzag GaNNT induces a 1.0 $\mu_B$ magnetization and makes a polarized structure. We realized that in polarized GaNNT a flat band near the Fermi energy splits to occupied spin up and unoccupied spin down levels.

Finally, the electronic properties of DWCNTs were investigated. The DWCNTs were separated into four categories wherein the innerouter nanotubes are metalmetal, metalsemiconductor, semiconductormetal and semiconductorsemiconductor single-wall nanotubes. The band structure of DWCNTs, the local density of states of the inner and outer nanotubes, and the total density of states were calculated. We obtained that for the metalmetal DWCNTs, the inner and outer nanotubes remain metallic for different distances between the walls, while for the metalsemiconductor DWCNTs, decreasing the distance between the walls leads to a phase transition in which both nanotubes become metallic. In the case of semiconductormetal DWCNTs, it is found that at some distance the inner wall becomes metallic, while the outer wall becomes a semiconductor, and if the distance is decreased, both walls become metallic. Finally, in the semiconductorsemiconductor DWCNTs, if the two walls are far from each other, then the whole DWCNT and both walls remain semiconducting. By decreasing the wall distance, first the inner, and then the outer, nanotube becomes metallic.

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# List of Figures

# List of Tables

# Contents

# Chapter 1

# Introduction to Nanostructures

## 1.1 Introduction

Since carbon nanotubes discovery in 1991, nanotubes have generated huge activity in most areas of science and engineering due to their unprecedented physical and chemical properties. No previous material has displayed the combination of superlative mechanical, thermal and electronic properties attributed to them. These properties make nanotubes ideal, not only for a wide range of applications1 but as a test bed for fundamental science. The diverse fields, where in nanotubes are intensely studied and considered to have a huge potential application in all sorts of nanoscale devices, nanostructured materials or instrumentations containing nanoscale components, include computational and experimental nanoscience, theoretical and applied nanotechnology and molecular engineering, theoretical, computational and experimental condensed matter physics and chemistry, and many other fields.

The physics of nanotubes is connected with the exciting fields of computational nano-science, computational nano-technology and computational condensed matter physics. The bases of these fields are numerical modeling and computer-based simulation, to compute the physical properties of nano structures, and nano-scale processes. These new fields of research allows us to exercise a complete control over the structure and functioning of physical matter at the atomistic and molecular scales. Computational nano-scale modelling offers an invaluable tool for the design, fabrication, and quality control of devices and components, and helps clarify the energetics and dynamics of the atoms participating in such structures and the conditions for the final stability of such structures [2].

Computational modeling of properties of nanotubes is based either on the use of methods rooted in the many-body theories of quantum mechanics, such as the density functional theory (DFT) of atoms and molecules, or on the use of methods

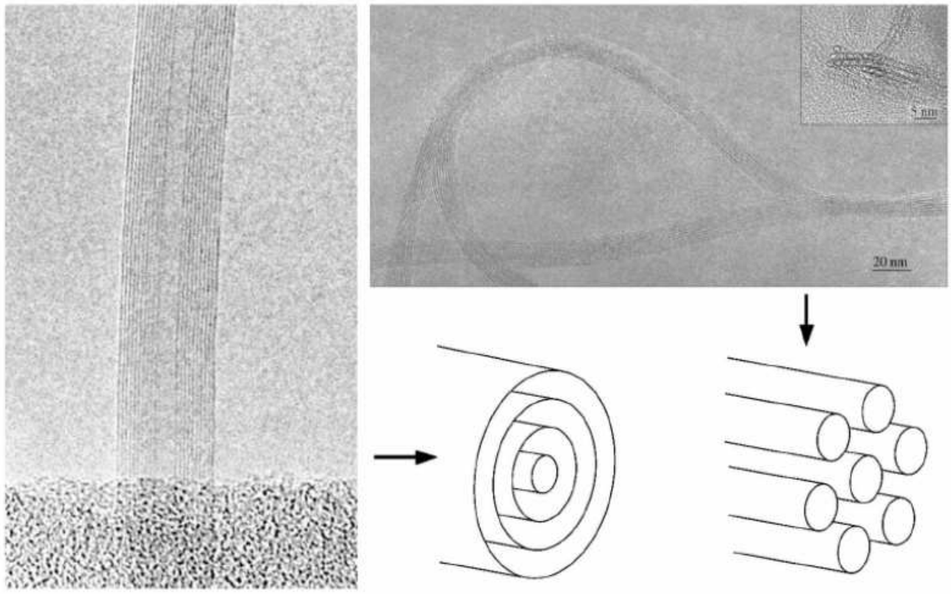


Figure 1.1: High-resolution transmission electron microscopy pictures of a multiwall carbon nanotube (left) and a bundle of single-wall nanotubes(right), illustrating two different possible geometries for nanotubes.

rooted in advanced classical statistical mechanics, such as the molecular dynamics (MD) simulation method. The quantum-mechanical approach allows for an *ab initio*, or first principles, study of nanoscale systems composed of several tens to, at most, several hundreds atoms, with current computational platforms. To be more familiar with different computational techniques in nanoscience, one of the best reference is Ref. [3].

## 1.2 Carbon Nanotubes

### 1.2.1 Structure of carbon nanotubes

Carbon nanotubes were discovered and first characterized in 1991 by Iijima from NEC laboratories (Japan) [4]. The first nanotubes discovered were made of several concentric cylindrical-like shells regularly spaced by an amount of about 3.4$\AA$ as in conventional graphite materials (Fig. 1.2.1, left). These multiwall nanotubes (MWNTs) were first synthesized with diameters ranging from a few nanometers to several hundred nanometers for the inner and outer shells, respectively.

Shortly after the discovery of multiwall carbon nanotubes, single-wall carbon

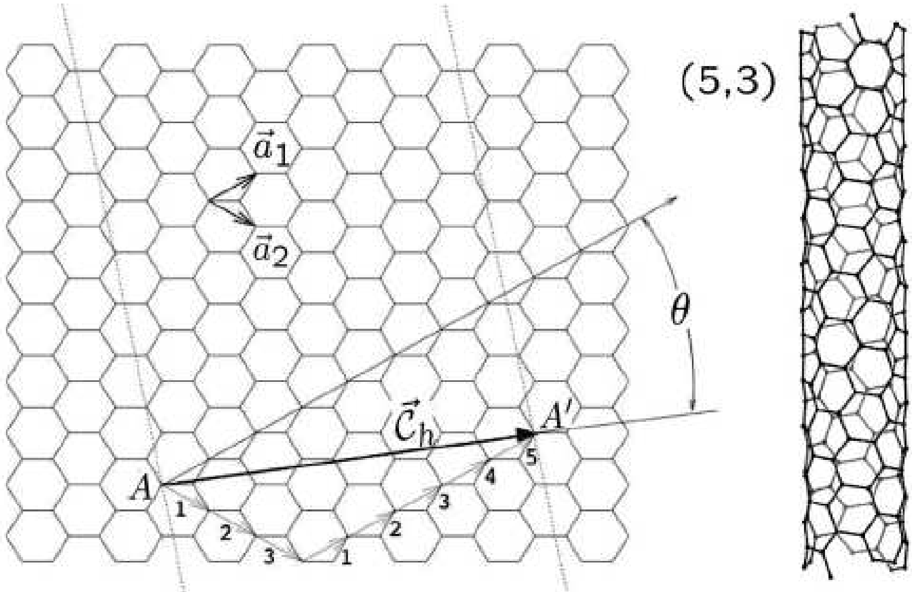


Figure 1.2: Graphene honeycomb network with lattice vectors $\mathbf{a}_1$ and $\mathbf{a}_2$. The chiral vector $\mathbf{c}_h = 5\mathbf{a}_1 + 3\mathbf{a}_2$ represents a possible wrapping of the two-dimensional graphene sheet into a tubular form. The direction perpendicular to $\mathbf{C}_h$ is the tube axis. The chiral angle θ is defined by the $\mathbf{C}_h$ vector and the $\mathbf{a}_1$ zigzag direction of the graphene lattice. In the present example, a (5,3) nanotube is under construction and the resulting tube is illustrated on the right.

nanotubes (SWNTs) were synthesized in abundance using arc-discharge methods with transition-metal catalysts [5, 6]. A carbon naotube made of a single graphite layer (the graphene sheet) rolled up into a hollow cylinder is called a single-wall nanotube. These tubes have quite small and uniform diameter, on the order of $1nm = 10^{-9}m$. Because the microscopic structure of SWNTs is closely related to that of graphene, the tubes are usually labeled in terms of the graphene lattice vectors. As illustrated in Fig. 1.2.1 a single-wall carbon nanotube is geometrically obtained by rolling up a single graphene strip [7]. Its structure can be specified or indexed by its circumferential vector ($\mathbf{C}_h$), as defined by the chiral vector ($AA'$ in Fig. 1.2.1) which connects two crystallographically equivalent sites ($A$ and $A'$) on a graphene sheet. In this way, a SWNT's geometry is completely specified by a pair of integers $(n, m)$ denoting the relative position $\mathbf{C}_h = n\mathbf{a}_1 + m\mathbf{a}_2$ of the pair of atoms on a graphene strip which, when rolled onto each other, form a tube ($\mathbf{a}_1$ and $\mathbf{a}_2$ are unit vectors of the hexagonal honeycomb lattice).

This chiral vector $\mathbf{C}_h$ defines the circumference of the tube. The diameter $d_t$ of the nanotube can thus be estimated from

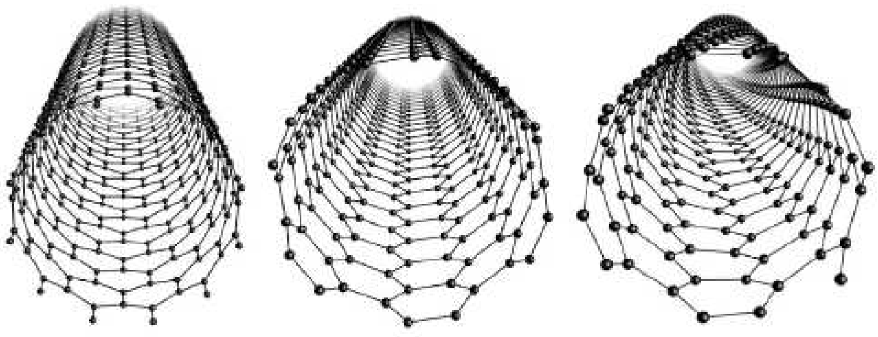


Figure 1.3: Atomic structures of (12,0) zigzag, (6,6) armchair, and (6,4) chiral nanotubes.

$$d_t = |\mathbf{C}_h|/\pi = \frac{a}{\pi}\sqrt{n^2+nm+m^2}, \tag{1.1}$$

where $a$ is the lattice constant of the honeycomb network: $a = \sqrt{3}\times a_{cc}$ ($a_{cc} \simeq 1.42\AA$, the C-C bond length). The chiral vector $\mathbf{C}_h$ uniquely defines a particular (n,m) tube, as well as its chiral angle θ, which is the angle between $\mathbf{C}_h$ and $\mathbf{a}_1$ (zigzag direction of the graphene sheet). The chiral angle θ can be calculated as:

$$cos\theta = \frac{\mathbf{C}_h \cdot \mathbf{a}_1}{|\mathbf{C}_h||\mathbf{a}_1|} = \frac{2n+m}{2\sqrt{n^2+nm+m^2}}. \tag{1.2}$$

The value of θ is in the range $0 \leq |\theta| \leq 30^{\circ}$, because of the hexagonal symmetry of the graphene lattice. This chiral angle θ also denotes the tilt angle of the hexagonal with respect to the direction of the nanotube axis. Nanotubes of type $(n,0)(\theta = 0^{\circ})$ are called zigzag tubes, because they exhibit a zigzag pattern along the circumference. Such tubes display carbon-carbon bonds parallel to the nanotube axis. Nanotubes of the type $(n,n)(\theta = 30^{\circ})$ are called armchair tubes, because they exhibit an armchair pattern along the circumference. Such tubes display carbon-carbon bonds perpendicular to the nanotube axis. Both zigzag and armchair nanotubes are chiral tubes, in contrast with general $(n.m \neq n \neq 0)$ chiral tubes (1.2.1).

The geometry of the graphene lattice and the chiral vector determine not only the diameter of the tube, but also the unit cell and its number of carbon atoms. The smallest graphene lattice vector $\mathbf{T}$ perpendicular to $\mathbf{C}_h$ defines the translational