Graphenylene nanotubes: structure, electronic properties and potential applications

by

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Abstract

The electronic properties of a new type of carbon nanotube, based on the graphenylene motif, are investigated using density functional and tight-binding methods. Analogous to conventional graphenebased carbon nanotubes, a two-dimensional graphenylene sheet can be "rolled" into a seamless cylinder in armchair, zigzag, or chiral orientations. The resulting nanotube can be described using the familiar (n,m) nomenclature and possesses four-, six-, and twelve-membered rings. Density functional theory-based geometry relaxations predict that graphenylene nanotubes, like their two-dimensional counterpart, exhibit three distinct bond lengths between carbon atoms, indicating a non-uniform electron distribution. The dodecagonal rings form pores, 3.3 Å in diameter in the two-dimensional case, which become saddle-shaped paraboloids in smaller-diameter graphenylene nanotubes. Electronic structure calculations in density functional theory predict zigzag graphenylene nanotubes to be small-band-gap semiconductors, with a generally decreasing band gap as the diameter increases. Interestingly, the calculations predict metallic characteristics for armchair graphenylene nanotubes with small diameters (< 2 nm), and semiconducting characteristics with a small band gap for armchair graphenylene nanotubes with larger diameters. Similar to conventional carbon nanotubes, graphenylene nanotubes with indices mod(n-m,3)=0 exhibit a band gap approximately equal to that of armchair graphenylene nanotubes with comparable diameters.

Preface

The contributions from this thesis have led to the following publication and presentation:

- A. Koch, A. Khoshaman, H. Fan, G. Sawatzky, A. Nojeh, "Graphenylene nanotubes" J. Phys. Chem. Lett., 2015, 6 (19), pp 3982–3987. DOI: 10.1021/acs.jpclett.5b01707
- A. Koch, S. Motavas, A. Khoshaman, H. Fan, G. Sawatzky, A. Nojeh, "Graphenylene-based nanotubes," Contributed talk and poster, 15th Int'l Conference on the Science and Application of Nanotubes (NT14), Los Angeles, CA, June 2014.

All of the chapters were written by the author with the assistance of Professor Alireza Nojeh. All of the ideas and simulations were conceived by the author with guidance from Professors Alireza Nojeh and George Sawatzky. Ms. Saloome Motavas provided initial help with setting up some of the simulations. The thesis largely builds upon the above publication and presentation. The author analyzed the results in collaboration with Mr. Amir Khoshaman, Mr. Harrison Fan, and Professors Alireza Nojeh and George Sawatzky.

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List of symbols and constants

Variable	Description	Unit or Value	
Symbol	Description		
(n,m)	Chiral indices	(dimensionless)	
а	Normalized lattice vector	m	
<i>a₁, a</i> 2	Lattice vectors	m	
B_{θ}	Magnetic field	Т	
<i>b</i> 1, <i>b</i> 2	Reciprocal lattice vectors	m ⁻¹	
Ch	Chiral vector	m	
<i>С</i> _{<i>i</i>µ}	Coefficients of basis set expansion	(dimensionless)	
d	Tube diameter	m	
Ε	Energy	J or eV	
h	Planck constant	6.626×10 ⁻³⁴ J·s	
Н	Hamiltonian operator	(dimensionless)	
ħ	Reduced Planck constant	1.055×10 ⁻³⁴ J·s	
<i>h</i> _{tube}	Thickness of tube wall	m	
Ι	Spin coefficient	(dimensionless)	
L	Length of chiral vector	m	
L1, L2, L3	Graphenylene bond lengths	m	
m	Mass	kg	
n	Charge density	C/m ³	
Ν	Number of particles in many-body equation	(dimensionless)	
Nunit	Number of 2D unit cells in tube unit cell	(dimensionless)	
q	Charge	С	
R	Nanotube symmetry vector	m	
R	Nanotube radius	m	
r	Position vector	m	
S	Overlap matrix	(dimensionless)	
Т	Translational vector	m	
		1	

General Table of Symbols and Constants

V	Potential	V (volts)
Y	Young's modulus	N/m ²
Ζ	Nucleic charge	C (Coulombs)
α_{curve}	Curvature energy coefficient	eV·Å ² /atom
γ	Chemical hardness function	V/C
ε	Energy eigenvalue	J or eV
\mathcal{E}_{0}	Permittivity of vacuum	$8.854 \text{x} 10^{-12} \text{ F} \cdot \text{m}^{-1}$
ζ	Number of radial functions per pseudo-atomic orbital	(dimensionless)
θ	Chiral angle	radians / degrees
μ	Magnetic moment	μN (nuclear magnetons)
ν	Frequency	Hz
ϕ	Kohn-Sham orbital	(dimensionless)
$arphi_{\mu}$	Basis functions	(arbitrary spatial function)
χ	Spin orbital	(dimensionless)
Ψ	Wave function	(dimensionless)
Ω	Atomic volume	m ³
Φ	Roll angle	radians or degrees

List of abbreviations

Abbreviation	Description	
2D	Two-dimensional	
3D	Three-dimensional	
CBM	Conduction band minimum	
CNT	Carbon nanotube	
DFT	Density functional theory	
DFTB	Density functional theory-based tight-binding	
DOS	Density of states	
FET	Field-effect transistor	
GGA	Generalized gradient approximation	
GNT	Graphenylene nanotube	
KS	Kohn-Sham	
LDA	Local density approximation	
PBE	Perdew-Burke-Ernzerhof	
RF	Radio frequency	
SCC	Self-consistent charge density	
	Spanish Initiative for Electronic Simulations with Thousands of	
SIESTA	Atoms	
ТВ	Tight-binding	
VBM	Valence band maximum	

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Dedication

To my loving and supportive parents, my candid and encouraging brother, my warm and thoughtful grandparents, and my caring and generous aunt Trish.

Chapter 1 – Introduction

1.1. Low-dimensional carbon allotropes

Carbon can exist in the form of a multitude of allotropes, including the familiar diamond and graphite, as well as two-dimensional forms such as graphene and one-dimensional forms such as linear acetylenic carbon. This is due to the ability of the valence electrons of carbon atoms to form sp, sp^2 , and sp^3 hybrid orbitals, and thus a variety of bond angles and nearest neighbor atoms. This also leads to a wide diversity of structural, electronic, and optical properties for different carbon allotropes, easily observed when comparing the optical transparency and extreme hardness of diamond with the opaqueness and softness of graphite. Therefore, an extraordinarily wide array of applications are possible with this one element in its many forms.

Graphene, a two-dimensional hexagonal network of sp^2 -hybridized carbon atoms with fully delocalized π -electrons, is a particular allotrope of carbon which has been the subject of intense interest due to its unique electrical [1], thermal [2], and mechanical [3] properties. Graphene forms the structural motif for a multitude of carbon allotropes of various dimensionalities: conceptually, graphene may be rolled into a fullerene, nanocone, or carbon nanotube, or stacked in layers to form graphite. A section of graphene and a segment of a graphitic carbon nanotube are shown in Figure 1. Further discussion on the lattice parameters of graphene, nanotubes, and related structures will follow in subsequent sections.



Figure 1: (Left) a graphene sheet section. The red box is a unit cell and a_1, a_2 are lattice vectors. (Right) a CNT segment. Note that this segment may be concatenated to form a longer CNT, or terminated by hydrogens.

Due to the attractive properties of graphene and its versatility as a building block for a variety of carbon materials, interest has been sparked in investigating other periodic two-dimensional carbon allotropes [4]. Carbon can form planar networks of various polygons other than the hexagonal (C₆) rings found in graphene, ranging from linear chains to dodecagonal rings. In the case of two-dimensional networks, only the *sp* and *sp*² hybridization states are found, because *sp*³-hybridized carbon lends itself to three-dimensional bonding angles. In the past decade, there has been a rapid expansion in the family of two-dimensional carbon allotropes in literature. Recently investigated two-dimensional carbon networks include α -graphyne, β -graphyne, γ -graphyne [5], graphenylene [6], graphdiyne [7], pentahexoctite [8], and a host of planar carbon allotropes based on graphene with structural defects [9], [10]. A few of these planar carbon allotropes are presented in Figure 2.



Figure 2: Two dimensional carbon allotropes (a) α -graphyne, (b) β -graphyne, and (c) pentahexoctite. Individual atoms have been omitted for simplicity. Red boxes are a unit cells and $\mathbf{a_1}$, $\mathbf{a_2}$ are lattice vectors. While α -graphyne and β -graphyne are comprised of both sp- and sp²-hybridized carbon atoms, pentahexoctite is comprised solely of sp²-hybridized carbon atoms.

Many of these two-dimensional carbon networks have only been investigated theoretically, but remarkably, graphdiyne, a network consisting of C_6 rings (sp^2 carbon) and linear chains (sp carbon) was synthesized in large planar film form via a cross-coupling reaction using hexaethynylbenzene on the surface of copper in 2010 [7]. Notably, although graphdyine film synthesis has been successful, graphdyine has been calculated to be less energetically favorable than many other two-dimensional carbon allotropes [8], including graphenylene, as shown in Figure 3. It is therefore interesting and worthwhile to explore the properties and potential applications of more exotic two-dimensional carbon networks and the related structures based thereupon. Further discussion on relative energies will follow in Chapter 4.



Figure 3: Total energy per atom for various carbon allotropes as a function of difference in average bond angle from graphene (δ_{avg}) . As shown in the figure, the successfully synthesized graphdyine is actually the least energetically favorable structure of those shown. Reprinted with permission from [8].

Carbon nanotubes (CNTs) are particular carbon allotropes based on the structural motif of graphene which have attracted intense interest due to their quasi-one-dimensional nature and vast array of exciting properties [11]. A CNT can be considered heuristically as a rolled-up sheet of graphene, formed by rolling the graphene sheet along a particular axis to form a seamless cylinder, such that all carbon atoms are three-fold coordinated without any dangling bonds. While previous investigations in literature have primarily focused on graphitic nanotubes, in theory a wide variety of nanotubes could be formed based on the structural motifs of various two-dimensional allotropes of carbon. Due to the diversity of material properties of two-dimensional carbon allotropes, further described in the following paragraphs, an even richer variety of structural and electronic properties, and thus potential applications, are possible with non-graphitic nanotubes.

1.2. Graphenylene

Graphenylene, shown in Figure 4, is a periodic two-dimensional network of sp²-hybridized carbon atoms which features four-, six-, and twelve-membered rings, and has recently become the subject of investigation due to its geometry [12], [13], [14]. It is worth noting that in graphene, fullerene, and CNTs, the π -electrons are fully delocalized and roughly homogeneously distributed, and thus all bond lengths are approximately equal. In graphenylene, geometry relaxations in the framework of DFT, including the work presented in this thesis, have predicted a heterogeneous distribution of π -electrons, leading to three distinct bond lengths between each carbon atom at any particular vertex. Each six-membered ring thus contains two distinct, alternating bond lengths, which is quite different from graphene-based structures, which exhibit uniform bond lengths.



Figure 4: Section of two-dimensional graphenylene. The red box is a unit cell and a_1, a_2 are lattice vectors.

Graphenylene can be considered the planar sheet limit of a class of molecules known as [N]phenylenes, which are polycyclic hydrocarbons which consist of N benzene rings separated by N-1 cyclobutadiene units. Small [N]phenylenes, i.e. molecular fragments of graphenylene, have already been successfully synthesized in linear, armchair, and zigzag form [15]. For example, Han et al. [16] synthesized helical chains of [7]-, [8]-, and [9]phenylenes via cobalt-catalyzed cyclotrimerization of triynes, i.e. a series of steps in which multiple triynes react to form aromatic compounds. Figure 5 shows a helical [9]phenylene, which matches the current size limit (N=9) for all phenylenes, synthesized in this manner.

Characterization of [*N*]phenylenes is most commonly performed via proton nuclear magnetic resonance (¹H-NMR) spectroscopy. Briefly, ¹H-NMR spectroscopy is carried out by placing the sample in a strong DC magnetic field (B_0), which induces a splitting of the spin states of the H nuclei into +1/2 and -1/2 states, which have an energy difference proportional to the strength of the external magnetic field. If the sample is irradiated at a radio frequency (RF) energy corresponding to the spin state separation of the hydrogen nuclei, related by Planck's constant *h*, it will cause the excitation of those nuclei in the +1/2 state to the higher -1/2 spin state. This RF frequency relates to the external magnetic field according to Equation (1-1).

$$\nu = \frac{\Delta E}{h} = \frac{\mu B_0}{hI} \tag{1-1}$$

For hydrogen nuclei (spin $\frac{1}{2}$), $I = \frac{1}{2}$, and the magnetic moment $\mu = 2.7927 \ \mu_N$ (units of nuclear magnetons). This RF excitation frequency, in the tens to hundreds of MHz depending on B_0 , will shift slightly depending on the local geometry of the surrounding atoms and the resultant local magnetic field at

the nucleus. This is known as the chemical shift, and it can be precisely measured using an RF spectrometer to determine the local character of the hydrogens that terminate [N]phenylenes. The ¹H NMR spectra can be compared with previously established spectra for lower numbered [N]phenylenes [17] and against well-established spectra for similar benzenoids [18].



Figure 5: Structure of helical [9] phenylene, the largest [N] phenylene synthesis reported. The uneven and unsymmetrical helical turn is presumed to be affected by the presence of the solvating CH₂Cl₂. <i>Reprinted with permission from [16].

[N]phenylenes have so far been only been synthesized for $N \leq 9$, and large-scale synthesis of graphenylene has not yet been achieved experimentally. However, Brunetto et al. [12] have shown through DFT-based molecular dynamics simulations that large-area graphenylene sheets could potentially be synthesized via dehydrogenation of highly ordered porous graphene, a process which results in spontaneous interconversion to graphenylene. Figure 6 shows snapshots of this process according to the aforementioned molecular dynamics simulation. It should be noted that dehydrogenation of ordered porous graphene is within the capabilities of modern synthesis techniques. Significant experimental advances have been achieved in dehydrogenation of ordered defects in hydrocarbons and fullerenes [19], nanographene flakes [20], and even two-dimensional hydrocarbon networks similar to graphenylene [21].



Figure 6: Molecular dynamics simulation by Brunetto et al. [12] showing intermediate steps from (a) dehydrogenated porous graphene to (d) graphenylene. Reprinted with permission from [12]

The electronic properties of graphenylene have been scarcely studied thus far. The band structure is of particular interest, since graphene is a zero-band-gap semiconductor or semimetal [1], which limits its potential electronic applications, as explained in the following section. Song et al. [13] calculated the electronic properties of graphenylene using DFT methods with a variety of exchange-correlation functionals and reported an extremely narrow, direct band gap of 0.025 eV. However, it is understood that DFT tends to significantly underestimate band gap values. For this reason, Brunetto et al. employed DFT-based tight-binding (TB) calculations, which predicted a direct band gap of 0.8 eV. In the present study, both methods are employed to calculate the band gap of graphenylene, as further detailed in Chapter 4.

1.3. Potential applications of graphenylene

The potential applications of graphenylene have been scarcely studied thus far. In this section, the potential applications discussed in literature will be briefly reviewed.

Graphenylene sheets feature dodecagonal rings which result in periodically distributed pores of 3.2 Å in diameter (calculated to be 3.3 Å in this work), when measured from the edge of the electron density isosurface at an isovalue of 0.2 a.u., as described by Song, et al. [13] and as depicted in Figure 7. This pore structure makes graphenylene a potential candidate as a two-dimensional molecular sieve for gas separation applications, much like the similarly structured zeolite SSZ-33 [22] and certain types of porous graphene [23]. Hydrogen gas separation is especially of interest for hydrogen fuel cell applications. Song, et al. [13]

concluded that graphenylene is a promising potential candidate as a membrane for separating H₂ from other gas molecules, such as CO, N₂, CO₂ and CH₄. This is attributed to the pore diameter of graphenylene, which is larger than the kinetic diameter of H₂, but smaller than all of the kinetic diameters of CO, N₂, CO₂ and CH₄, meaning the diffusion of these gas molecules through the pores is dynamically unfavorable, with the exception of H₂. The calculations in the aforementioned study predict an energy barrier of only 0.20 eV, while other molecules exhibit much larger activation energies for diffusion of 0.99, 1.01, 1.05 and 2.28 eV for CO, N₂, CO₂ and CH₄, respectively [24], demonstrating that H₂ can easily diffuse through graphenylene pores under experimental conditions. The selectivity of graphenylene for gas separation can then be estimated according to the Arrhenius equation. The calculations predicted notably high selectivities for hydrogen separation: 10^{12} H₂ over CO (H₂/CO), 10^{13} H₂/CO₂, 10^{14} H₂/N₂, and 10^{34} H₂/CH₄.



Figure 7: Measurement of pores formed by the dodecagonal rings in graphenylene, using the method employed by Song, et al. [13]. In this work, the pores were found to be 3.3 Å in diameter, as discussed in Chapter 4.

Another potential application of two dimensional graphenylene is lithium adsorption, diffusion and storage. In a study by Yu [14], DFT calculations were carried out to investigate lithium adsorption and diffusion on monolayer and bilayer graphenylene. The adsorption of lithium atoms on graphenylene was found to be stronger than that on pristine graphene. Graphenylene was also shown to be a highly promising material for ion diffusion applications, due to the advantages of the dodecagonal holes. In the study by Yu [14], ion transport was demonstrated in a three-dimensional stacked graphenylene material, and it was found that both in-plane and out-of-plane lithium diffusion is achieved by overcoming the energy barriers no higher than 0.99 eV. Notably, lithium atoms can be dispersed remarkably well on graphenylene, respectively, as shown in Figure 8. These reversible capacities are larger than those predicted for graphene and graphyne by Zhang, et al. [25]. The intercalation of lithium atoms was shown to have little effect on the structures of

both monolayer and bilayer graphenylenes, meaning graphenylene-based materials would retain their mechanical properties during charging cycles in lithium-ion battery applications.



Figure 8: Top view and side view of optimized geometries of lithium-intercalated (a) monolayer and (b) bilayer graphenylene. Reprinted with permission from [14].

Graphenylene also has the potential for use in electronic applications where graphene is inadequate. Despite the aforementioned extraordinary properties of graphene and its potential in various applications, using graphene as an electronic material remains challenging due to its lack of a sizable bandgap. While the semimetallic nature of graphene does not compromise its applicability for use in transparent conductive films [26] or high-frequency analog electronics [27], it significantly limits the use of graphene in many applications where semiconductors with an appreciable bandgap are required. For example, graphene fieldeffect transistors (FETs) for digital logic applications have been widely investigated due to their high carrier mobility, reasonably good transconductance, and mechanical stability [28]. However, the lack of a band gap makes it nearly impossible to completely switch off graphene FETs, leading to a very low on/off current ratio typically in the single digits in top-gated graphene FETs [29]. In response, various methods have been developed to generate a bandgap in graphene, with the goal of retaining graphene's extraordinary properties in semiconductor-based applications. These include slicing or patterning graphene sheets into nanoribbons to induce quantum confinement [30], chemical modification or doping to interrupt the π -electron network [31], [32], introducing defects [9], and applying mechanical deformation or strain to graphene [33]. Graphenylene, on the other hand, is predicted to be an intrinsic semiconductor, and is largely unencumbered by these challenges, depending on the size of the true (experimental) band gap.

1.4. Objectives

One possibility which has not yet been thoroughly investigated in literature is a family of carbon nanotubes based on the structural motif of two-dimensional graphenylene. Nanotubes based on graphenylene, which shall henceforth be referred to as graphenylene nanotubes (GNTs) have so far only been described in terms of their geometric configuration. Balaban and Vollhardt [6] described the possibility of their existence only in a qualitative sense, at the level of an artist's impression, as seen in Figure 9.



Figure 9: Stereo views of an armchair GNT, depicted by Balaband and Vollhardt [6] for the purposes of qualitative description (without calculation). Reprinted with permission from [6].

Therefore, until this study, it was previously unknown whether GNTs are actually stable structures which could physically exist without collapsing. It is the purpose of this study to introduce GNTs in a physically meaningful way, and to investigate their structural and electronic properties, and thereby gain insight into their potential applications.

1.5. Thesis outline

Chapter 2 outlines the structural parameters of graphenylene nanotubes, namely the unit cells and vectors, as well as the chiral and translational vectors that define the chirality of the tubes. These mathematics of these parameters are implemented in a MATLAB nanotube generator, which is described in detail later in the chapter. Chapter 3 gives an overview of the calculation methods used in this work,

including a brief introduction to density functional theory and its implementation in the SIESTA method, as well as the density functional theory-based tight-binding method and its implementation in the DFTB⁺ software package. The reasoning behind the choices of each set of parameters in both methods will be explained in detail. Chapter 4 presents the results of these calculations for both methods. The structural properties of graphenylene nanotubes are analyzed, including the evolution in bond length and pore size with tube diameter, as well as the relationship between curvature energy and tube diameter. The electronic structure of graphenylene nanotubes is then examined in terms of energy dispersion, density of states, and overall band gap trends. Chapter 5 outlines the potential applications of graphenylene, including gas separation and storage, lithium ion storage, and electronic devices, based on the results presented in the previous chapter.

Chapter 2 – Structural parameters of graphenylene nanotubes

2.1. Classification of graphenylene nanotubes

Just as a single-wall CNT can be heuristically described as sheet of graphene which is rolled into a seamless cylinder along a particular axis, a single-wall GNT can be described in the same manner, with graphenylene being the structural basis rather than graphene. As in the case of CNTs, the direction of the roll can be chosen almost arbitrarily, a fact which leads to a wide variety of GNT structures. Figure 10 shows three examples of single-wall GNTs constructed by rolling a graphenylene sheet along three different directions. It should be noted that the ends of GNTs can be terminated either by hydrogens or presumably by a "cap" consisting of a hemisphere of a graphenylene-based fullerene, as depicted qualitatively by Balaban and Vollhardt [6]. Since single-wall CNTs can reach lengths on the scale of hundreds of microns and thus exhibit aspect ratios as high as 10⁵, they can be considered as one-dimensional nanostructures; in this work, GNTs will also be considered as such. The GNTs shown in Figure 10 can be considered as sections which can be repeated to form a much longer GNT.



Figure 10: (a) An armchair, (b) zigzag, and (c) chiral GNT, demonstrating the different geometries of GNTs that are possible by choosing different orientations of the roll. (d) A zigzag CNT is shown for comparison.

Like their graphitic counterparts, GNTs may be classified as achiral or chiral. Achiral nanotubes are those whose mirror image has a structure which is identical to the original, and are further categorized into armchair and zigzag nanotubes, as exemplified in Figures 10a and 10b, respectively. Armchair GNTs can be distinguished most readily by the alignment of the dodecagonal rings with the axis of the tube, whereas the dodecagonal rings in zigzag GNTs are aligned with the circumference of the tube. Armchair and zigzag GNTs can also be distinguished by the geometry of the cross-section of the tube, as shown in Table 1 of the following section. Chiral GNTs exhibit spiral symmetry, and their mirror image cannot be transposed onto the original tube. In summary, a wide variety of GNT geometries are available with various chiralities as well as diameters.

2.2. Lattice parameters of two-dimensional graphenylene

The unit cell of graphenylene, i.e. the most basic set of atoms which can be translated periodically to form an infinitely large graphenylene sheet, consists of twelve sp²-carbon atoms. Examining the similarities between graphene and graphenylene (left and middle sections of Figure 11), their crystallographic symmetries appear quite similar. Whereas the unit cell of graphene contains two carbon atoms joined by a single covalent bond, the unit cell of graphenylene contains two phenyl groups joined by a four-membered ring (cyclobutadiene). One key difference, however, is that all carbon atoms in graphene are joined by covalent bonds of equal length, $a_{c-c,graphene} = 1.42$ Å, whereas graphenylene contains three distinct bond lengths L_1 , L_2 , and L_3 , as shown in Figure 11. In this work, these bond lengths are calculated to be $L_1 = 1.38$ Å, $L_2 = 1.47$ Å, and $L_3 = 1.48$ Å, as explained in Chapter 4. In both systems, the unit cell is a rhombus, such that a hexagonal lattice is formed. The unit vectors a_1 and a_2 , i.e. the translational vectors between adjacent unit cells in real space, of graphene and graphenylene are described by the formula:

$$a_1 = \left(\frac{\sqrt{3}a}{2}, \frac{a}{2}\right), \qquad a_2 = \left(\frac{\sqrt{3}a}{2}, -\frac{a}{2}\right)$$
 (2-1)

In graphene, *a* is the distance between second-nearest-neighbor carbon atoms. This can expressed in terms covalent bond length between adjacent carbon atoms: $a_{graphene} = |a_1| = |a_2| = 1.44 \times \sqrt{3} = 2.49$ Å. In graphenylene, *a* is the translational distance between nearest-neighbor twelve-membered rings, which is calculated to be 6.79 Å in this work, as explained in Chapter 4.

The corresponding Brillouin zone, i.e. unit vector in reciprocal space, for this type of lattice is a hexagon, which can be described by the vectors b_1 and b_2 of the reciprocal lattice, which are given by:

$$\boldsymbol{b_1} = \left(\frac{2\pi}{\sqrt{3}a}, \frac{2\pi}{a}\right), \qquad \boldsymbol{b_2} = \left(\frac{2\pi}{\sqrt{3}a}, -\frac{2\pi}{a}\right) \tag{2-2}$$

The hexagonal Brillouin zone of both graphene and graphenylene, indicated by the shaded hexagon in the right panel of Figure 11, contains three points of high symmetry, Γ , K, and M. These correspond to the center (zero momentum), corner, and center of the edge, respectively, of the Brillouin zone. In Chapter 4, the path Γ -M-K- Γ , indicated by the triangle in the right panel of Figure 11, will be used in calculating the energy dispersion relation of two-dimensional graphenylene.



Figure 11: (Left) Unit cell of graphene. (Middle) Unit cell of graphenylene, showing location of three distinct bond lengths. (Right) Brillouin zone and symmetry points of graphene; the Brillouin zone of graphenylene has the same shape and symmetry

2.3. Lattice parameters of graphenylene nanotubes

The structural parameters which have been conventionally used to define CNTs are largely applicable to GNTs. In the remaining sections of this chapter, the conventions for CNT parameters set forth by Saito, et al. [34] shall be used, with a few exceptions where the parameters used for CNTs are not applicable to GNTs.

The structure of a GNT can be considered as a section of a graphenylene sheet which is sliced and rolled to form a seamless cylinder. The circumference of the tube is thus specified by a line segment which is drawn between two crystallographically equivalent points on a graphenylene sheet, depicted as vector \overrightarrow{OA} on Figure 12. Then, by drawing a perpendicular vector \overrightarrow{OB} to an equivalent point on the lattice, the geometry of a GNT can be constructed by taking the slice of the sheet defined by points O, A, B, and B' and rolling the sheet such that points O and A coincide. The vectors \overrightarrow{OA} and \overrightarrow{OB} thereby form the chiral vector C_h can then be expressed as integer multiples of the unit vectors

$$\boldsymbol{C_h} = n\boldsymbol{a_1} + m\boldsymbol{a_2} \equiv (n,m) \tag{2-3}$$

where *n* and *m* are integers with $0 \le |m| \le n$. In Figure 10, these specific integers are (3,3), (5,0), and (4,1) for the graphenylene nanotubes from left to right, respectively, as well as a (10,0) CNT on the right. As indicated in Table 1, an armchair nanotube corresponds to indices where n = m, or $C_h = (n, n)$. Zigzag nanotubes correspond to m = 0, or $C_h = (n, 0)$, and all other cases correspond to chiral nanotubes. The diameter of the resulting tube is then

$$d = \frac{L}{\pi} = \frac{|C_h|}{\pi} = \frac{1}{\pi} \sqrt{C_h \cdot C_h} = \frac{a}{\pi} \sqrt{n^2 + m^2 + nm}$$
(2-4)

The chiral angle θ , shown in in Figure 12, is defined as the angle between the chiral angle C_h and the lattice vector a_1 , i.e. the inner product, as given by the expression:

$$\cos(\theta) = \frac{C_h \cdot a_1}{|C_h||a_1|} = \frac{2n+m}{2\sqrt{n^2+m^2+nm}}$$
(2-5)

In GNTs, this angle corresponds to the tilt angle of the dodecagonal rings with respect to the tube axis. Zigzag (n, 0) nanotubes correspond to $\theta = 0^{\circ}$ and armchair (n, n) nanotubes correspond to $\theta = 0^{\circ}$. Due to the hexagonal symmetry of graphenylene, only angles of $0 \le |\theta| \le 30^{\circ}$ are unique.

Table 1:	Classification	of graphenyl	lene nanotubes
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Туре	θ	C_h	Cross-section
armchair	30°	(n,n)	
zigzag	0°	(n,0)	
chiral	$0^{\circ} < \theta < 30^{\circ}$	(<i>n</i> , <i>m</i>)	various

Since we consider GNTs and CNTs to be quasi-one-dimensional structures, the sole unit vector is the translational vector \vec{T} , which corresponds to the vector \vec{OB} in the unrolled sheet, given by the expression:

$$T = t_1 a_1 + t_2 a_2 \equiv (t_1, t_2) \tag{2-6}$$

where t_1 and t_2 are integers. The expressions for t_1 and t_2 can be derived from the orthogonality of T and C_h and the previous equations in this sections, and are given by:

$$t_1 = \frac{2m+n}{\gcd(2n+m, 2m+n)}$$
(2-7)

$$t_2 = -\frac{m+2n}{\gcd(2n+m,2m+n)}$$
(2-8)

where gcd denotes greatest common divisor. In general, the length of the translation vector T = |T|, i.e. the length of one unit cell of each nanotube, is greatly reduced when *n* and *m* have a common divisor or when (n - m) is a multiple of 3.



Figure 12: An unrolled graphenylene sheet and the geometric parameters of a GNT. Any GNT can be constructed by choosing integers (n, m) and connecting points O and A (and B and B'). The vectors in the figure correspond to $C_h = (4,2), T = (4,-5)$

The unit cell of a GNT defined by vectors C_h and T contains N_{unit} unit cells. The number of unit cells is found by taking the area $|C_h \times T|$ and dividing by the area of a unit cell $|a_1 \times a_2|$:

$$N_{unit} = \frac{|C_h \times T|}{|a_1 \times a_2|} = \frac{2(m^2 + n^2 + nm)}{\gcd(2n + m, 2m + n)}$$
(2-9)

The total number of atoms in the GNT unit cell is then equal to $12 N_{unit}$. For example, the (4,2) GNT shown in Figure 12 contains 336 atoms.

A few of the parameters that have been defined for CNTs do not apply to GNTs due to the irregularities that arise from the 3 distinct bond lengths found in graphenylene. These include any parameters which depend on the symmetry vector \mathbf{R} , which is used to place individual carbon atoms on specific sites on the nanotube. Therefore, an unconventional approach must be taken in order to construct individual GNTs based on chosen chiral indices. This method was implemented in MATLAB and will be discussed in the following section.

2.4. MATLAB graphenylene nanotube generator

GNTs are more challenging to generate than their graphitic counterparts due to the presence of three distinct bond lengths in graphenylene. Instead of placing atoms along site vectors determined by the chirality of the tube as in CNTs, GNTs must be constructed by taking polygon *OAB'B* and rolling it about a central nanotube axis. This was accomplished in the MATLAB R2014b software package using the process outlined in Figure 13.



Figure 13: Block diagram of MATLAB program for generating GNT coordinates.

As indicated in Figure 13, the only input required is the chiral index of the desired GNT. The details of the calculation are described in the following steps:

- The vectors *C_h* and *T* and values *d*, *θ*, and *N_{unit}* are calculated according to equations (2-3), (2-6), (2-4), (2-5), and (2-9), respectively.
- 2. The unit cell is replicated according to unit vectors a_1 and a_2 to form a large planar sheet.
- 3. Polygon *OAB'B* is defined (see Figure 12) and the atoms within it are cut from the sheet using the *inpolygon* function to form the unrolled GNT unit cell.
- 4. This unrolled GNT unit cell is rotated using a rotation matrix method:

$$\begin{bmatrix} \cos(30^\circ - \theta) & -\sin(30^\circ - \theta) \\ \sin(30^\circ - \theta) & \cos(30^\circ - \theta) \end{bmatrix} \begin{bmatrix} x_1 & \cdots & y_1 \\ x_n & \cdots & y_n \end{bmatrix} = \begin{bmatrix} x_1' & \cdots & y_1' \\ x_n' & \cdots & y_n' \end{bmatrix}$$
(2-10)

where x_i and y_i are the spatial coordinates of atom *i* (of n = 12N total atoms in the cell) and x_i' and y_i' are the rotated spatial coordinates of atom *i*. The resulting cell vectors are now aligned with the original *x*-*y* coordinate system, as shown in Figure 14.



Figure 14: Rotated, unrolled unit cell of a (4,2) GNT (blue). The unit cell has been duplicated in x' (yellow) and y' (orange) to show continuity of the roll and of the nanotube unit cell translation, respectively.

5. Now a new three-dimensional set of axes is defined. The cell is rolled about a new z-axis, defined as parallel to the previous y-axis, at a distance of $L/2\pi$ from it (out of the page):

$$\Phi_{i} = \frac{x_{i}'}{2\pi L}, \qquad \begin{bmatrix} \cos(\Phi_{i}) & -\sin(\Phi_{i}) \\ \sin(\Phi_{i}) & \cos(\Phi_{i}) \end{bmatrix} \begin{bmatrix} L/2\pi \\ 0 \end{bmatrix} = \begin{bmatrix} x_{i,tube} \\ y_{i,tube} \end{bmatrix}$$
(2-11)

where Φ_i is defined as the angle between the vector from the origin to atom *i*, and the new *x*-axis. The 3D coordinates of atom *i* in the GNT are now $(x_{i,tube}, y_{i,tube}, z_{i,tube})$ where $z_{i,tube} = y_i'$. These coordinates are the output of the program, as shown in Figure 15.



Figure 15: The output GNT unit cell from the MATLAB GNT generator in blue. A second unit cell (orange) has been stacked to show continuity. The central tube axis is shown in black.

- 6. The coordinates of the resulting GNT unit cell are checked for errors in the following steps:
 - a. The GNT unit cell is replicated once above and once below the original, such that all bonds to the original unit cell are satisfied.
 - b. All atomic distances are calculated using the *pdist* function, and arranged via the *squareform* function, resulting in a matrix with columns corresponding to individual atoms and rows corresponding to atomic distance to each other atom.
 - c. Columns 1 through *n* are extracted to examine the original (middle) unit cell.

- d. Each row is then sorted in ascending order. In each column, rows 2 through 4 now contain the approximate values $\begin{bmatrix} L_1 \\ L_2 \\ L_3 \end{bmatrix}$.
- e. The exact bond lengths L_1 , L_2 , and L_3 are then subtracted from this matrix. If the absolute value of any element in the resulting matrix is found to be greater than a specified tolerance (set to 0.05 Å), an error will be returned.

Despite the irregular structure of graphenylene and the ostensibly messy termination of the unit cells of chiral GNTs, the program has been successfully used for a wide variety of chiral GNTs without error. This program has also been used to generate graphene, graphyne, and pentahexoctite sheets, as shown in Figures 1 and 2, and various CNTs, as shown in Figures 1 and 10.

Chapter 3 – Calculation methods

3.1. Calculation overview

Two approaches were used in calculating the structural and electronic properties of graphenylene nanotubes: density functional theory (DFT) and density functional theory-based tight-binding (DFT-based TB). All geometry relaxations were performed via DFT calculations using the SIESTA software package [35]. However, it is commonly known in the computational physics community that although DFT can dependably predict geometries and some electronic properties, calculating certain excited-state properties remains a challenge. Most notably, DFT is known to underestimate band gaps in semiconductors and insulators by 30-100% [36]. The underestimation of the band gap in DFT has primarily been attributed to the inherent lack of derivative discontinuity [37] and delocalization error [38] in the exchange-correlation functionals. It is also often claimed that, since the band gap is an excited-state property, ground-state DFT calculations were used to calculate band structure using the optimized geometries. DFT-based TB has been shown to reliably describe the electronic properties of carbon-based materials [40] (even though it is not an an *ab initio* method) and was implemented using the DFTB⁺ software package [41]. This method was also used for the purposes of comparison with the graphenylene by Brunetto, *et al.* [12].

In this chapter, a short review of the fundamental physics of DFT is presented, followed by a brief overview of the basic principles of DFT-based TB. A brief description of each software package will also be provided, as well as a detailed description of the parameters used in each calculation.

3.2. Introduction to density functional theory

Density functional theory is perhaps the most successful and widely used method of computing the electronic structure of matter. In this section, the fundamental physics of DFT shall be covered using the conventions in the work of Parr and Yang [42]. DFT is derived from the Schrödinger equation, formulated in the 1920s, for a many-body system.

3.2.1. The many-body Schrödinger equation

The time-independent Schrödinger equation is an eigenvalue problem of the Hamiltonian operator H where total energy E is the eigenvalue and the wave function Ψ , which contains information of the quantum state of a particle, is the eigenfunction. The time-independent, non-relativistic Schrödinger equation in spatial coordinates of r is written as:

$$H\Psi(r) = E\Psi(r) \tag{3-1}$$

The Hamiltonian operator is the sum of the kinetic energy operator and the potential energy of the system. For a single, non-relativistic particle with mass m which is moving through an electric field, this amounts to:

$$H = -\frac{\hbar^2}{2m} \nabla^2 + V(r)$$
(3-2)

where \hbar is the reduced Planck constant $(h/2\pi)$, ∇^2 is the Laplacian function (a differential operator), and V is potential energy. The Schrödinger equation has exact solutions for only a few simple physical systems, namely a particle in a box, simple harmonic oscillator, and a hydrogen atom. For many-body systems of interacting particles, it is impossible to solve the Schrödinger equation exactly, and thus approximations must be used. Consider the case of a system of N electrons and several atomic nuclei. The full Hamiltonian can be written as:

$$H = -\frac{\hbar^2}{2m_e} \sum_{i} \nabla_i^2 - \sum_{i,I} \frac{Z_I e^2}{r_{i,I}} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{r_{ij}} - \frac{\hbar^2}{2M_I} \sum_{I} \nabla_I^2 + \sum_{I,J} \frac{Z_I Z_J e^2}{R_{IJ}}$$
(3-3)

where $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ (the distance between electrons *i* and *j*), $R_{IJ} = |\mathbf{R}_I - \mathbf{R}_J|$ (the distance between nuclei *I* and *J*), Z_I is the charge of nucleus *I*, and M_I is the mass of nucleus *I*. In order of appearance, the five terms in the operator define the kinetic energy of all electrons, the interaction potential energy between electrons and nuclei, the electron-electron interaction energy, the kinetic energy of all nuclei, and lastly the interaction energy between nuclei.

In order to simplify this problem, the spatial and temporal evolution of the electrons and the nuclei are separated into two terms, in what is commonly known as the Born-Oppenheimer approximation. In this approximation, the nuclei are assumed to be moving so slowly relative to the electrons that they are considered to be stationary. The total wave function for the many-body system is then:

$$\Psi_i = \Psi_{elec}(\boldsymbol{r}_i, \{\boldsymbol{R}_J\}) \Psi_{nuc}(\{\boldsymbol{R}_J\})$$
(3-4)

where r_i corresponds to positions of electrons and $\{R_J\}$ the parameterized positions of the nuclei, respectively. The "fixed-nuclei" Hamiltonian is now:

$$H = -\frac{\hbar^2}{2m_e} \sum_{i} \nabla_i^2 - \sum_{i,I} \frac{Z_I e^2}{r_{i,I}} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{r_{ij}} + \sum_{I,J} \frac{Z_I Z_J e^2}{R_{IJ}}$$
(3-5)

where the last term (the nucleus-nucleus interaction) is now a constant. Although the Schrödinger equation for a many-body system is now greatly simplified by the Born-Oppenheimer approximation, the electronic part of equation (3-5) is still only numerically solvable by introducing further approximation, as explained in the following section.

3.2.2. The Hartree and Hartree-Fock approximations

One natural approach to further approximate the many-body Schrödinger equation is the Hartree approximation. In this method, the many-body problem is transferred to a single-particle problem by approximating the wave function of the many-body system as the product of single-electron wave functions:

$$\Psi(\mathbf{r}_{1}, \mathbf{r}_{2}, \dots \mathbf{r}_{N}) = \Psi_{1}(\mathbf{r}_{1})\Psi_{2}(\mathbf{r}_{2}) \dots \Psi_{N}(\mathbf{r}_{N})$$
(3-6)

However, this approximation fails to satisfy the anti-symmetry requirements of the Pauli exclusion principle, which state that if two spin-position coordinates are interchanged, the wave function must change sign $(\Psi(\mathbf{x}_1, \mathbf{x}_2) = -\Psi(\mathbf{x}_2, \mathbf{x}_1))$, where \mathbf{x} is a coordinate that includes spatial as well as spin degrees of freedom. This issue was solved with the Hartree-Fock approximation, in which the many-body wave function is written in terms of a single Slater determinant of single-particle wave functions. For a system with N electrons, the Slater determinant is written as

$$\Psi(\mathbf{r}_{1},\mathbf{r}_{2},...\mathbf{r}_{N}) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_{1}(\mathbf{x}_{1}) & \chi_{1}(\mathbf{x}_{2}) & \cdots & \chi_{1}(\mathbf{x}_{N}) \\ \chi_{2}(\mathbf{x}_{1}) & \chi_{2}(\mathbf{x}_{2}) & \cdots & \chi_{2}(\mathbf{x}_{N}) \\ \vdots & \vdots & & \vdots \\ \chi_{N}(\mathbf{x}_{1}) & \chi_{N}(\mathbf{x}_{2}) & \cdots & \chi_{N}(\mathbf{x}_{N}) \end{vmatrix}$$
(3-7)

, where $\chi(\mathbf{x})$ are known as spin orbitals, and $\frac{1}{\sqrt{N!}}$ is a normalization factor. This Slater determinant fulfills the Pauli Exclusion principle because no two identical electrons occupy the same orbitals simultaneously, and if any two rows of the determinant are identical, the determinant will vanish. The anti-symmetry principle is fulfilled because the exchange of any two columns changes the sign of Ψ .

In the Hartree-Fock method, the Hamiltonian corresponding to each electron has the form

$$H = T + V + V_H \tag{3-8}$$

, where *T* is the kinetic term, *V* is the potential due to the nuclei, and V_H is the Hartree potential or mean field potential, i.e. the average Coulomb interaction potential between one electron and all other electrons in the system. It can be expressed in terms of average charge density

$$V_{H}(\mathbf{r}) = \frac{e^{2} \int n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^{3}r'$$
(3-9)

According to the Rayleigh-Ritz variational method, the ground state energy eigenvalue E_0 can then be determined by minimizing the expectation value of the Hamiltonian with respect to a trial wave function
$$E_0 = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} \tag{3-10}$$

3.2.3. Density functional theory

In the Hartree-Fock method, the *N*-electron wave function is approximated as a single Slater determinant of single-electron wave functions. In density functional theory, the principal concept is to use the ground state electron density, rather than the many-electron wave function, as the central variable. The fundamental principles behind DFT are the Hohenberg-Kohn theorems, the first of which states that for a system of interacting particles in an external potential, the ground state electron density $n(\mathbf{r})$ fully and uniquely determines the external potential $V_{ext}(\mathbf{r})$. One could alternatively say that a one-to-one mapping exists between electron density and external potential.

In order to use the electron density as the central variable, functionals (i.e. functions of other functions, denoted by square brackets), of the electron density $n(\mathbf{r})$ are used in place of operators. The total energy functional $E[n(\mathbf{r})]$ is thus expressed as

$$E[n(\mathbf{r})] = \int V_{ext}(\mathbf{r})n(\mathbf{r})d\mathbf{r} + F[n(\mathbf{r})]$$
(3-11)

, where $V_{ext}(\mathbf{r})$ is the external potential due to electrons and nuclei and $F[n(\mathbf{r})]$ is given by

$$F[n(\mathbf{r})] = T[n(\mathbf{r})] + E_{ee}[n(\mathbf{r})]$$
(3-12)

 $F[n(\mathbf{r})]$ is the sum of the kinetic energy of electrons, $T[n(\mathbf{r})]$, and the electron-electron interaction energy, $E_{ee}[n(\mathbf{r})]$. It is often called a universal functional because it does not depend on the external potential. The electron-electron interaction term can be expanded as

$$F[n(\mathbf{r})] = T[n(\mathbf{r})] + \frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}[n(\mathbf{r})]$$
(3-13)

, where $E_{xc}[n(\mathbf{r})]$ is the electron exchange-correlation functional. The key drawback of DFT is that there is no exact expression for this exchange-correlation term. In the Hartree-Fock method, the exchange between electrons and the correlated motion of electrons of like spin due to the Pauli principle is taken into account (although correlation resulting from Coulomb repulsion between electrons is absent). In DFT, the exchange-correlation term must be approximated, as described later in this section.

To address this problem, Kohn and Sham [43] developed a set of equations in which the ground state electron density is expressed in terms of a (fictitious) non-interacting system of electrons which has the

exact same electron density $n(\mathbf{r})$ as the original system. For this system, the energy functional of equation (3-11) can be written as

$$E[n(\mathbf{r})] = T_s[n(\mathbf{r})] + \int V_{KS}(\mathbf{r})n(\mathbf{r}) d^3r$$
(3-14)

, where $V_{KS}(\mathbf{r})$ is the unique potential which gives rise to $n(\mathbf{r})$ as its ground state charge density according to the Hohenberg-Kohn theorem. The Kohn-Sham variant of the Schrödinger equation for electrons moving in an effective external potential is then

$$\left[-\frac{\hbar^2}{2m_e}\nabla^2 + V_{KS}[n(\boldsymbol{r})]\right]\varphi_i(\boldsymbol{r}) = \varepsilon_i\varphi_i(\boldsymbol{r})$$
(3-15)

, where the Kohn-Sham effective external potential $V_{KS}(\mathbf{r})$ is given by:

$$V_{KS}[n(r)] = V_{ext}(r) + V_{H}[n(r)] + V_{XC}[n(r)]$$
(3-16)

 $V_{ext(r)}$ is the potential due to atomic nuclei, $V_H(r)$ is the Hartree potential as defined in equation (3-9), and $V_{XC}(r)$ is the exchange-correlation potential, which accounts for the electron-electron interactions not taken into account by the other terms, and has its roots in the quantum-mechanical nature of the electrons as non-static particles with spin, interacting through Coulomb forces. The solutions to this equation are the Kohn-Sham energy eigenvalues ε_i and Kohn-Sham orbitals φ_i . From the solution, the kinetic energy of the system of non-interacting electrons can be calculated

$$T_{s}[n(\mathbf{r})] = \sum_{i} \langle \varphi_{i} | -\frac{\nabla^{2}}{2} | \varphi_{i} \rangle$$
(3-17)

, as well as the density of the non-interacting system, which relates to the probability density of the Kohn-Sham orbitals

$$n_s(\mathbf{r}) = \sum_i |\varphi_i(\mathbf{r})|^2 \tag{3-18}$$

It is usually inefficient to express the orbitals in the basis of a Cartesian grid. To simplify the calculation, the Kohn-Sham orbitals are usually expressed in terms of basis functions. The "basis set" is chosen appropriately based on the system; plane-wave, Gaussian, and linear combinations of atomic orbitals (LCAO) basis sets are commonly used. Consequently, the Kohn-Sham equations are solved for the coefficients in the basis set expansion

$$\varphi_i(\boldsymbol{r}) = \sum_{\mu} c_{i\mu} \phi_{\mu}(\boldsymbol{r}) \tag{3-19}$$

, where $c_{i\mu}$ are the coefficients in the basis set expansion and ϕ_{μ} are the chosen basis functions. It should be noted that, when the basis functions are not orthogonal, an overlap matrix must also be used. The exchange and correlation potential can also be defined as the functional derivative of the exchangecorrelation energy with respect to energy density

$$V_{XC}[n(\mathbf{r})] = \frac{\delta E_{XC}[n(\mathbf{r})]}{\delta n(\mathbf{r})}$$
(3-20)

As stated previously, the most formidable challenge in DFT is that the exact exchange-correlation functional is not known. Two main approximation methods have been developed to approximate this functional: the local density approximation (LDA) and the generalized gradient approximation (GGA). In the LDA, the local exchange-correlation potential at position r for the inhomogeneous system is equal to the exchange-correlation potential for a homogeneous electron gas with that particular density n(r)

$$E_{XC}^{LDA}[n(\mathbf{r})] = \int n(\mathbf{r})\varepsilon_{XC}[n(\mathbf{r})]d^3r \qquad (3-21)$$

where $\varepsilon_{XC}[n(\mathbf{r})]$ is the exchange-correlation energy per particle of a homogeneous electron gas, which is a system with known exchange-correlation energies. $\varepsilon_{XC}[n(\mathbf{r})]$ can be expressed as the sum of the exchange and correlation contributions

$$\epsilon_{XC}[n(\mathbf{r})] = \varepsilon_X[n(\mathbf{r})] + \varepsilon_C[n(\mathbf{r})]$$
(3-22)

For a homogeneous electron gas, the exchange part of this term is known and is given by the exchange part of the Thomas-Fermi-Dirac energy functional [42]

$$\varepsilon_X[n(\mathbf{r})] = -\frac{3}{4} \left(\frac{3n(\mathbf{r})}{\pi}\right)^{1/3}$$
(3-23)

However, no such explicit expression exists for the correlation part, which must be parameterized to be used in DFT calculations. One extension of the LDA is the GGA, where the gradient of the density is considered along with the density itself

$$E_{XC}^{GGA}[n(\mathbf{r})] = \int n(\mathbf{r})\varepsilon_{XC}[n(\mathbf{r}), \nabla n(\mathbf{r})]d^3r \qquad (3-24)$$

Many exchange-correlation functionals have been developed in the LDA and GGA, and they are usually tailored to specific systems. Usually some known behavior of the exact functional is considered as well as empirical parameters. In that sense, DFT is not strictly an *ab initio* method. Further discussion on the selection of exchange-correlation functional in this work will follow in Section 3.4.

3.2.4. Self-consistent solution of the Kohn-Sham equations

Once the exchange-correlation energy has been approximated, the equations in subsection 3.2.3 can be solved iteratively in a self-consistent (SC) loop. In order to solve the Kohn-Sham equations for a many-body system, one must define the Hartree potential $V_H[n(\mathbf{r})]$ and exchange-correlation potential $V_{XC}[n(\mathbf{r})]$,

both of which are functionals of electron density $n(\mathbf{r})$. However, as stated in equation (3-7), the Kohn-Sham orbitals $\varphi_i(\mathbf{r})$ must be known in order to find $n(\mathbf{r})$. Therefore, a common approach is to begin with a trial input density, i.e. an educated guess for $n(\mathbf{r})$, and begin solving the Kohn-Sham equations iteratively, as illustrated in Figure 16. These iterative calculations continue until the electron density converges. That is, each element in the density matrix $D_{\mu\nu} = 2\sum_i c_{\mu i} c_{\nu i}^*$, where where $c_{i\mu}$ are the coefficients in the basis set, is less than a predefined tolerance. This way, the calculations are said to be self-consistent. The final electron density is then considered the ground state electron density, and it can then be used to calculate the total energy of the system.



Figure 16: Flow diagram of self-consistent method of solving the Kohn-Sham equations

3.3. The SIESTA method

SIESTA [35], short for the Spanish Initiative for Electronic Simulations with Thousands of Atoms, is a widely used computational tool to efficiently perform self-consistent Kohn-Sham DFT calculations of molecules and solids. Its efficiency is closely related to the use of localized basis sets, which have cutoff radii such that $\phi_k(\mathbf{r}) = 0$, $|\mathbf{r}| > r_{cutoff}$. SIESTA uses LCAO basis sets, which can be beneficial when analyzing information about specific orbitals. Pseudopotentials are also used in order to exclude the core electrons from the calculation, since the predominant effect caused by the core electrons is screening of the nuclear potential. Further discussion on basis sets and pseudopotentials used in SIESTA calculations can be found in subsections 3.4.2 and 3.4.3.

The SIESTA calculations can be performed using a wide variety of exchange-correlation functionals, in the LDA and GGA, and aside from the standard way of solving the generalized eigenvalue problem by direct diagonalization, it also offers more efficient (yet less precise) order-N algorithms which rely heavily on sparsity of Hamiltonian and overlap matrices. However, the latter feature was not used in the calculations performed in this work. The SIESTA package also provides structural relaxation capabilities, accomplished by minimizing the forces on individual atoms by moving them according to one of several geometry optimization algorithms, e.g. the method of conjugate gradients and the Broyden method [44].

3.4 Density functional theory calculation parameters

The parameters which must be considered in SIESTA DFT calculations of GNTs are as follows:

- 1. Basis set
- 2. Exchange-correlation treatment
- 3. Pseudopotential
- 4. Sampling parameters: real-space grid, k-space grid
- 5. SCF calculation parameters: mixing weight, density tolerance, electronic temperature
- 6. Geometry optimization parameters: algorithm, force tolerance
- 7. Lattice parameters: lattice vectors (inter-nanotube distance)

The first three parameters require detailed discussion, which is presented in the following three subsections. All other parameters are briefly discussed here.

Real-space integrations are performed on a finite 3D grid in SIESTA. The fineness of this grid are determined by its plane-wave cutoff, i.e. all plane waves with kinetic energy below this cutoff are represented on the grid without aliasing. In this work, all calculations were performed on a grid with a cutoff energy of 250 Rydberg, which is equal to or above that of nearly all CNT calculations in SIESTA in literature.

The first Brillouin zone, the unit cell in k-space, is most commonly sampled using a Monkhorst-Pack [45] scheme, which divides the Brillouin zone into an equally spaced grid of points in k-space. Since GNTs are considered to be one-dimensional structures, the Brillouin zone is one dimensional in the direction of the nanotube axis in k-space, and has a length conventionally written in units of π/a , with *a* being the length of the nanotube unit cell (in this case $a = |\mathbf{T}|$). In this work, k-space was sampled using the Monkhorst-Pack scheme, although it is rather arbitrary since the Brillouin zone is one-dimensional. 50 points were taken along the single unit vector in k-space.

All calculations were performed with electronic temperature set to room temperature (300 K). The electron density tolerance for convergence of the SC loop was set to 10⁻⁵. The mixing weight for electron density is defined as

$$n_{ni}(\mathbf{r}) = \alpha_{mix} n_{new}(\mathbf{r}) + (1 - \alpha_{mix}) n_{old}(\mathbf{r})$$
(2-25)

, where α is the mixing weight ($0 \le \alpha_{mix} \le 1$) and $n_{ni}(\mathbf{r})$ is the electron density used in the next SC iteration. For GNTs with less than 200 atoms, a mixing weight of 0.3 was used, but this led to convergence difficulties for GNTs with more than 200 atoms. For larger GNTs, the mixing weight was set to 0.1.

The atomic positions were relaxed using the conjugate gradient minimization until the forces on the atoms were less than 0.01 eV/Å. A trial experiment was conducted using a tighter tolerance (0.005 eV/Å) and it was found to have no significant effect on the structural or electronic properties.

Given that periodic boundary conditions were used in the SIESTA calculations, interactions between tubes were avoided by spacing the tubes at least 15 Å apart from edge to edge. This figure is within the usual range found in computational CNT literature, and it was confirmed in a trial experiment to have no effect on the electronic structure on the GNT. For this trial experiment, the electronic properties of a (*3,0*) GNT were calculated for inter-nanotube spacings from 10 Å to 25 Å. The electronic structure did not change for any of the GNTs except for the one with the smallest spacing (10 Å), as evidenced by the plot of the band gaps in Figure 17. The band gaps shown are relative to the GNT with 25 Å spacing.



Figure 17: Band gap of (3,0) GNTs with various inter-tube spacings, relative to the GNT with the largest spacing (25 Å)

3.4.1 Basis sets

As discussed in the previous section, SIESTA uses basis functions which are linear combinations of atomic orbitals (LCAO). These are numerical atomic orbitals (NAO) which are constructed as a numerical solution of the Kohn-Sham equations of the isolated pseudo-atom on a logarithmic grid which is more dense near the nucleus. The basis function is composed of an adjustable radial component and a well-defined spherical harmonic for a given orbital. The radial part is defined by either a single radial function, ζ , or more, i.e. double- ζ in the case of two radial functions. Additionally, access to higher angular momenta can be introduced by adding artificial polarization functions to the standard minimal basis of the atom. All numerical atomic orbitals in SIESTA are strictly localized, i.e. set to zero beyond a cutoff radius. In this study, a double- ζ basis set with polarization orbitals (DZP basis set was used. This usually means that two radial basis functions were used for each pseudo-atomic orbital, i.e. two of each of the 1s, 2s, 2px, 2py, and 2pz orbitals. However, in this case the basis set is known as a "split-valence" basis set which only uses one function for the core (1s) electrons. Since the highest angular momentum orbital for carbon is the p subshell, the "polarization" of the atom is included by adding a set of d subshell atomic orbital functions.) Cutoff radii of 2.64 Å for the s orbital and 3.31 Å for the p and polarizing d orbitals were used, as determined from an energy shift of 50 meV by localization The general shapes of the s, p, and d orbitals are shown in Figure 18.



Figure 18: General shape of s, p, and d atomic orbitals in their lowest shell, from left to right

3.4.2 Exchange-correlation treatment

The exchange-correlation functional chosen for DFT calculations on GNTs was a variant of the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional parameterized for solids, known as PBEsol, which is used in the generalized gradient approximation (GGA). The PBEsol functional has been used in the literature to calculate the electronic properties of two-dimensional graphenylene [13]. The performance of different functionals for carbon-based structures, including thermodynamics and curvature related properties, have been discussed in the literature [46].

3.4.3 Pseudopotentials

Referring back to equation (3-16), the effective potential $V_{KS}(\mathbf{r})$ for the electronic density $n(\mathbf{r})$ consists of the Hartree potential $V_H(\mathbf{r})$, the exchange-correlation potential $V_{XC}(\mathbf{r})$, and the external potential due to the nuclei $V_{ext}(\mathbf{r})$. In the SIESTA method, the strong nuclear Coulombic potentials are replaced by effective ionic pseudopotentials, which take into account the screening effects of the tightly-bound coreelectrons and exclude them from the calculations. This saves a significant amount of computation, since core electrons are highly localized and therefore require a very dense energy grid in order to calculate. Furthermore, the core electrons contribute little to atomic bonding compared to the valence electrons, and their effect in this regard is usually negligible. Therefore, it is advantageous to replace the potential due to the core electrons with a pseudopotential which has the same effect on the valence electrons [47].

For the GNT calculations, a Troullier-Martins pseudopotential [47] obtained from the Abinit pseudopotential database was used, and is shown in Figure 19. The cutoff radius These types of pseudopotential functions are generated from an all-electron calculation of an atom in some reference state, and this pseudopotential was generated using a PBE (GGA) exchange-correlation functional, which is the

functional used for calculations in this work. It is called a norm-conserving soft pseudopotential because the charge enclosed in the pseudopotential region is equal to the charge enclosed by the same space in the all-electron calculation. This pseudopotential is also fully nonlocal, i.e. different effective potentials are felt by different angular momentum states, as seen in the left panel of Figure 19.



Figure 19: (Left) Potential and (right) charge density with respect to radius from the atomic core for the carbon atom pseudopotential used in the calculations.

3.4.4. Summary of density functional theory calculation parameters

Although the previous subsections provided a detailed explanation of the parameter selection for the SIESTA DFT calculations, it is convenient to summarize, as is presented in Table 2.

Basis set	Double- ζ plus polarization (DZP)
Exchange-correlation	Perdew-Burke-Ernzerhof (GGA), parameterized for solids (PBEsol)
functional	
Pseudopotential	Troullier-Martins, PBE (GGA), fully nonlocal, norm-conserving soft
Real-space grid	250 Rydberg plane-wave equivalent cutoff
k-space grid	50 point sampling along 1D unit vector in k-space
Electronic temperature	300 K
SC density tolerance	10-5
Density mixing weight	0.3 for small GNTs (<200 atom unit cell), 0.1 for larger GNTs
Geometry optimization	Conjugate gradient method
Force tolerance	0.01 eV/Å
Inter-nanotube spacing	>15 Å

Table 2: Parameters used in SEIESTA DFT calculations

3.5 Density functional theory-based tight-binding method

In the tight-binding (TB) method, the band structure of a solid can be computed by solving for a system of superimposed orbitals for isolated, neutral atoms located each atomic site. The single-electron energy eigenvalues ε_i are obtained by solving the secular equation [34]

$$\det[H - ES] = 0 \tag{3-26}$$

, where H is the tight-binding Hamiltonian of the system, E is the energy eigenvalue matrix, and S is the overlap matrix. The following discussion on the background of the tight-binding method and its descendants is based on the works of Frauenheim [48] and Elstner [49]. In the standard TB method, the Hamiltonian is represented in an orthoganalized basis of atomic-like orbitals, where the matrix elements have been parameterized to match the band structure of a suitable reference system. The total energy is written as a function of all atomic coordinates

$$E_{tot} = E_{bs} + E_{rep} \tag{3-27}$$

, where E_{bs} is the sum of the occupied orbital energies and E_{rep} is the short-range repulsive two-particle interaction.

The self-consistent charge density functional tight binding (SCC-DFTB) method is a TB method based on DFT. To solve the SCC-TB equations, the zeroth order, non-SCC system must first be solved (for Hamiltonian H^0). The density $n(\mathbf{r})$ is considered as the sum of neutral atomic densities, i.e. $n_0(\mathbf{r}) =$ $\sum_{\alpha} n_0^{\alpha}(\mathbf{r})$, where α refers to an atomic site. Referring back to the Kohn-Sham variant of the Schrodinger equation (3-14), the Kohn-Sham Hamiltonian (H_{KS}) can be expressed as

$$H_{KS} = -\frac{\hbar^2}{2m_e} \nabla^2 + V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + V_{XC}(\mathbf{r})$$
(3-28)

The Kohn-Sham equations are solved in terms of a suitable LCAO basis set, i.e.

$$\Psi_i(\boldsymbol{r}) = \sum_{\mu} c_{i\mu} \phi_{\mu}(\boldsymbol{r} - \boldsymbol{R}_I)$$
(3-29)

, and ϕ_{μ} enter the calculation of the TB Hamiltonian matrix elements in the LCAO basis as

$$H^0_{\mu\nu} = \langle \phi_\mu | H_{KS}(n_0) | \phi_\nu \rangle \tag{3-30}$$

The diagonal elements are thus $H^0_{\mu\mu} = \varepsilon_{\mu}$, where ε_{μ} is the Kohn-Sham energy eigenvalue for the neutral, isolated atom. The non-diagonal elements are evaluated with a two-center approximation:

$$H^{0}_{\mu\nu} = \langle \phi_{\mu} \left| H_{KS} \left(n^{\alpha}_{0} + n^{\beta}_{0} \right) \right| \phi_{\nu} \rangle$$
(3-31)

The Hamiltonian $H^0_{\mu\nu}$ and overlap $S_{\mu\nu} = \langle \phi_{\mu} | \phi_{\nu} \rangle$ are calculated on a relevant scale (in this work, up to 10 Å) and tabulated.

The self-consistent charge distribution component is accomplished via a second-order expansion of the Kohn-Sham energy functional with respect to density fluctuations

$$E = \sum_{i}^{occ} \langle \Psi_{i} | H_{0} | \Psi_{i} \rangle - \frac{1}{2} \iint \frac{n_{0} n_{0}'}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' d\mathbf{r} + E_{XC}[n_{0}] - \int V_{XC}[n_{0}] n_{0} d\mathbf{r} + \frac{1}{2} \iint \left(\frac{1}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta^{2} E_{XC}}{\delta n \delta n'} \Big|_{\mathbf{n}_{0}} \right) \delta n \delta n'$$
(3-32)

, where the charge density fluctuation $\delta n = n - n_0$ is represented by atomic components $\delta n = \sum_{\alpha} \delta n_{\alpha}$, and δn_{α} is approximated by induced charge fluctuations $\Delta q_{\alpha} = q_{\alpha} - q_{\alpha}^{0}$, computed by Mulliken charge analysis. The integral over the 1/r term and second derivative of E_{XC} is approximated by a function γ , which depends on chemical hardness, yielding the second-order term:

$$E^{2nd} = \frac{1}{2} \sum_{\alpha\beta} \gamma_{\alpha\beta} \Delta q_{\alpha} \Delta q_{\beta}$$
(3-33)

Returning to the generalized eigenvalue problem, for the SCC Hamiltonian the second-order approximations are now included

$$H_{\mu\nu} = H^{0}_{\mu\nu} + \frac{1}{2} S_{\mu\nu} \sum_{\gamma} \Delta q_{\gamma} (\gamma_{\alpha\gamma} + \gamma_{\beta\gamma})$$
(3-33)

The E_{rep} term from equation (3-27) is approximated as a sum of two-body potentials $E_{rep} = \sum_{\alpha\beta} U_{\alpha\beta}$ (see [50] for more details). Finally, the approximate DFTB total energy is

$$E_{tot} = \sum_{i\mu\nu} c_{i\mu}c_{i\nu}H^{0}_{\mu\nu} + \frac{1}{2}\sum_{\alpha\beta}\Delta q_{\alpha}\Delta q_{\beta}\gamma_{\alpha\beta}(R_{\alpha\beta}) + E_{rep}$$
(3-33)

This energy is then minimized to yield the ground state density. It is worth noting that, although DFTB is called a semi-empirical calculation method, no reference to empirical data is made in the whole parametrization procedure, i.e. every step is based on DFT calculations. DFT-based TB has been shown to reliably predict the electronic properties of carbon-based materials, specifically band gap values that are in good agreement with empirical values [51].

3.5.1 DFTB calculation parameters

The DFTB⁺ calculations performed on the GNTs were carried out using the optimized geometries from SIESTA calculations. Atomic and diatomic contributions for the DFTB Slater-Koster parameter sets were calculated from DFT used a PBE (GGA) functional. The charges in the system were calculated using a converged k-point sampling of 48 k-points. The obtained charges were kept fixed, and the one-electron levels were calculated for 25 k-points along the one dimension of the GNT Brilluoin zone. The SCC tolerance for charge density iterations was set to 10⁻⁵ and the electronic temperature was set to room temperature (300 K).

Chapter 4 – Calculation results

4.1. Structural properties of graphenylene nanotubes

The geometry of each GNT was optimized in the SIESTA DFT calculations using a conjugate gradient method. The properties of two-dimensional graphenylene were also calculated in order to use as a point of reference. The structural parameters of GNTs, namely bond lengths and diameters of the pores formed by the dodecagonal rings, deviate from that of two-dimensional graphenylene, more significantly in GNTs with smaller diameters than those with large diameters. In this section, those results are presented in detail.

4.1.1 Bond lengths and charge distribution

First, the relaxed geometry of two-dimensional graphenylene was calculated as a point of reference, and for the purposes of comparison with the studies of Brunetto [12] and Song [13]. As these studies have indicated, graphenylene was found to exhibit three distinct bond lengths, as shown in Table 3 (refer to Figure 11 for the location of these bonds). The relaxed structure of graphenylene thus exhibits alternating bond lengths around each six-membered carbon ring, indicating nonuniformity of the distribution of the π -electrons around the ring, unlike the case in benzene or graphene. As explained in Section 2.2, the 12-atom unit cell of graphenylene leads to a larger lattice constant a_0 , and consequently, larger translational vectors (or alternatively, lengths of nanotube unit cells). $|T_{ZZ}|$ and $|T_{AC}|$ denote lengths of the translational vectors for zigzag and armchair nanotubes, respectively. In both CNTs and GNTs, $|T_{AC}| = a_0$ and $|T_{ZZ}| = \sqrt{3}a_0$.

		Graphenylene		
	Graphene	L_1	L ₂	L ₃
C-C bond length (Å)	1.428	1.378	1.468	1.481
a ₀ (Å)	2.473	6.788		
$ T_{ZZ} $	4.284	11.757		
<i>T_{AC}</i>	2.473	6.788		

Table 3: Bond lengths and unit vectors	for two-dimensional	graphene and	graphenylene,	from DFT	calculations in this work
			0 1 2 2		

GNTs also exhibit three distinct bond lengths, although these are dependent on the diameter of the tube to a small degree. Figure 20 shows the evolution of each bond length with tube diameter. The L_1 and L_2

bonds In smaller diameters tubes, both L_1 and L_2 are larger than they are in 2D graphenylene, and the difference in bond length with respect to the 2D case follows a $1/R^2$ trend (with *R* being the radius of the tube) in both cases, suggesting a curvature dependence. Trendlines for the $1/R^2$ fit and statistical r² values are listed in the figures. Interestingly, the trend in L_3 is different in two ways. First, this bond is actually shorter for small-diameter GNTs than in the 2D case, unlike L_1 and L_2 . Second, the relationship between L_3 and tube radius shows a split between GNTs for which mod(n - m, 3) = 0 and GNTs with all other chiralities. The former category includes all armchair as well as zigzag tubes where *n* is a multiple of 3, and the (4,1) and (5,2) chiral GNTs, while the latter includes the remaining zigzag and chiral GNTs that were studied. This split in the trend of ΔL_1 suggests that there may be a dependence on electronic structure as well as curvature. The stark difference in L_3 between, for example, the (6,0) GNT and its closest zigzag neighbors (5,0) and (7,0), which have similar tube radii and identical bonding angles, is highly suggestive of this additional dependence. It is also worth noting that (3,0) is an outlier in terms of its L_2 bond, further suggesting a dependence on a variable other than geometric configuration.



Figure 20: (Left) bond length and (right) change in bond length with respect to 2D graphenylene, for L_1 , L_2 , and L_3 (from top to bottom, respectively) showing $1/R^2$ trendline and statistical r^2 values.

The presence of three disparate bond lengths in GNTs is a consequence of a heterogeneous distribution of the π -electrons, unlike the fully delocalized π -electron network found in CNTs. The SIESTA DFT calculations confirm this nonuniform charge distribution. Figure 21 shows the electron density of a zigzag

and armchair GNT, plotted at an isovalue of 0.27 $e/Å^3$. A greater electron density (in yellow) can clearly be seen near the L_1 bond, which is not shared with the four-membered rings compared with the L_2 and L_3 bonds, which are shared with the four-membered rings.



Figure 21: Electron density (in light teal) of (left) a (2,2) armchair GNT and (right) a (4,0) zigzag GNT unit cell, at an isosurface value of 0.27 e/Å³.

4.1.2 Pore size evolution

The dimensions of the pores formed by the dodecagonal rings in GNTs change significantly depending on the diameter of the GNT. When graphenylene is rolled into a tube, the pores are bent around the circumference of the tube, resulting in paraboloid or saddle-shaped pores. Smaller-diameter GNTs contain pores which are significantly narrowed in the transverse direction of the tube, while the pores found in larger diameter GNTs approach a circular geometry 3.3 Å in diameter, as in 2D graphenylene. The pores are defined using the method described by Song, *et al.* [13], and are measured in the same manner as 2D graphenylene: a high-resolution image (e.g. Figure 22) is taken and the distance in pixels between the edges of the pore is compared with that of a known distance, such as the distance between opposite atoms of the pore. An example of a saddle-shaped pore formed by the dodecagonal rings in a (4,0) GNT is shown in Figure 22. The pores in this GNT clearly exhibit deviation from the nearly perfect circles found in 2D graphenylene. The pore resembles an ellipse when viewed from the front in a 2D projection, as shown in Figure 22, and the saddle shape can clearly be seen via the pores on the side of the GNT.



Figure 22: Measurement of pores formed by the dodecagonal rings, shown here for a (4,0) GNT, using the method employed by Song, et al. [13], showing the vertical and horizontal axis measurements.

In the relaxed GNT geometry, the pores generally follow the model of a rolled sheet, with some slight deviation. Figure 23 shows the dimensions of the pores formed by the dodecagonal rings, as a function of tube diameter. Each line segment represents a particular GNT, with the top and bottom points being the dimensions in the vertical and horizontal directions, respectively. The dashed and dotted lines represent the dimensions of the pores in the vertical and horizontal dimensions, respectively, of a sheet of graphenylene (using the relaxed geometry from DFT calculations in this work) which is simply wrapped around the circumference of a particular tube. This is accomplished via the MATLAB nanotube generator described in Section 2.4, using the relaxed coordinates of 2D graphenylene. Smaller-diameter zigzag GNTs tend to be elongated in the vertical dimension and narrowed in the horizontal dimension when compared to a rolled sheet of graphenylene. In general, armchair GNTs tend to follow the rolled-sheet model more precisely than zigzag GNTs. For the larger-diameter GNTs in this study (diameter greater than ~2.5 nm), the saddle shape becomes quite negligible and the pores can be approximated by 2D graphenylene.



Figure 23: The dimensions of the pores formed by the dodecagonal rings, with respect to tube diameter. Each line segment represents a particular GNT, with the top and bottom points being the dimensions in the vertical and horizontal axes, respectively. The dashed and dotted lines represent the dimensions of the pores in the vertical and horizontal dimension, respectively, of a sheet of graphenylene

4.1.3 Stability of graphenylene nanotubes

As a fully relaxed structure in the DFT calculations, GNTs are considered to be thermodynamically stable. In order to further examine the stability of GNTs, the total energy per atom for a variety of carbon allotropes was calculated via DFT. Graphene is taken as a reference point in order to avoid the issue of van der Waals interactions. As shown in Table 4, the total energy per atom of two-dimensional graphenylene relative to graphene was calculated to be 0.66 eV/atom, in exact agreement with a previous study [13] for the exchange-correlation functional used in this study (PBEsol). Table 4 also presents the total energy cost relative to graphene for two small-diameter GNTs with similar radii.

Table 4: Total energy per atom for various carbon allotropes in reference to graphene, according to DFT calculations

	Graphene	(5,5) CNT	Graphenylene	(2,2) GNT	(3,0) GNT
Total energy (eV/atom)	0	0.17	0.66	0.76	0.79

Although these values are quite high, it should be noted that the total energies per atom relative to graphene for C_{60} , graphyne, and carbyne have been calculated in literature to be 0.38, 0.70, and 1.13 ev/atom, respectively, using the same functional [13]. More importantly, this value is 0.77 eV/atom for

graphdiyne, which has been successfully synthesized in the form of a large area film [8]. The fact that the thermodynamic instability of most GNTs relative to graphene is less than that of graphdiyne, coupled with the fact that helical molecular fragments of graphenylene have been successfully synthesized (as discussed in Section 1.2), makes it reasonable to assume that GNTs are capable of existing in reality. That being said, it is important to draw the distinction between stability and synthesizability. However, synthesis of complex carbon molecules has historically shown a pattern of abrupt discovery of a facile synthesis method after years of painstaking effort, as in the case of fullerenes and graphdiyne.

4.1.4 Curvature energy

DFT calculations predict the total energy of GNTs to be strictly dependent upon the tube diameter. Shown in Figure 24 is the curvature energy, $E_C = E_{tot,GNT} - E_{tot,Graphenylene}$, i.e. the total energy per atom for each GNT relative to 2D graphenylene. Similarly to what is observed in *ab-initio* studies of CNTs [52], the curvature energy per atom increases with increasing curvature following a classical $1/R^2$ dependence, with *R* being the radius of the GNT. Based on the continuum elastic model, the curvature energy for a carbon tubule can be expressed as [53]:

$$E_C = \frac{Y h_{tube}^3}{24} \frac{\Omega}{R^2} = \frac{\alpha_{curve}}{R^2}$$
(4-1)

, where *Y* is the Young's modulus, h_{tube} is the thickness of the tube wall, and Ω is the atomic volume. This is a classical model of strain energy that considers the tube as a bent bar of 2D carbon (e.g. graphene or graphenylene). Thus, the Young's modulus is calculated for the 2D sheet. The DFT calculations predict energies which correspond precisely to this relationship (with statistical $r^2 = 0.9988$), where $\alpha_{curve} = 1.4746$ eV·Å²/atom. The Young's modulus *Y* can be determined with the appropriate choice of *h*. If *h* for GNTs is considered to be approximately equal to that of CNTs (a reasonable assumption because both consist of a cylinder of a single layer of carbon atoms), then the Young's modulus of graphenylene is approximately 69% of the value predicted for graphene (2.14 eV·Å²/atom) [52].



Figure 24: Curvature energy, i.e. total energy per atom for graphenylene nanotubes relative to two-dimensional graphenylene, which follows closely a $1/R^2$ relationship, where R is the GNT tube radius.

4.2 Electronic structure from density functional theory calculations

GNTs share many characteristics with CNTs in their electronic structure; this is particularly evident in the differences between the band structures of armchair versus zigzag GNTs, and in the armchair-like characteristics in the case of GNTs with indices where mod(n - m, 3) = 0. This section provides a detailed description of the behavior of the electronic structure of GNTs of various chiral indices.

4.2.1 Energy dispersion and density of states

For 2D graphenylene, DFT calculations in this work predict a direct and narrow band gap of 0.033 eV, as shown in Figure 25. Like graphene, both the valence band maximum (VBM) and conduction band minimum (CBM) located at the *K* point of the Brillouin zone (see Figure 11). Unlike graphene, the bands do not form sharp Dirac points at the *K* point, but rather smooth bands with a slope of zero and direct gap at this point. Since DFT calculations tend to underestimate band gaps by 30-100%, as explained in Section 3.1, it is reasonable to assume that the actual (experimental) band gap value is significantly larger, and that graphenylene is thus a semiconductor with a direct band gap.



Figure 25: Band structures of (a) graphene (b) graphenylene from DFT calculations, with (c) and (d) showing detail around the K point for (a) and (b), respectively

The band structures of a zigzag and armchair GNTs bear some resemblance to those of conventional carbon nanotubes, as seen in Figure 26, due to the similar crystal symmetry and band structures of their twodimensional counterparts. In zigzag GNTs, the gap is narrowest at the zero-momentum point (Γ), while in armchair GNTs, the gap is narrowest at a nonzero point in k-space.



Figure 26: Band structures of (a) (8,0) zigzag CNT, (b) (8,0) zigzag GNT, (c) (5,5) armchair CNT, and (5,5) armchair GNT, from DFT calculations. Similarities between the band structures of CNTs and GNTs include valence band maxima and conduction band minima at the same points in k-space when comparing zigzag or armchair tubes. Note the different energy scales for CNTs vs GNTs.

The band structures of a few selected zigzag GNTs are shown in Figure 27. As the chiral index n increases, the periodic boundary condition expands and thus more sub-bands are added to the nanotube Brillouin zone. This generally tends to narrow the gap between the valence and conduction bands until it approaches the band gap of the 2D sheet; i.e., a nanotube with an infinitely large index n would have an infinite radius of curvature and would be equivalent to a 2D sheet. As in the case of CNTs, zigzag GNTs where n is a multiple of 3 exhibit smaller band gaps than their nearest zigzag GNT counterparts, which can be observed in the (6,0) band structure in Figure 76. The bottom panel of Figure 27 shows a density of states (DOS) plot for each GNT shown in the top panel. It should be noted that this DOS plot is simply created by taking the energy eigenvalues from the DFT calculations and applying a Gaussian smearing function, which is inputted by the user. In this case, the smearing parameter was chosen to be small (0.01 eV) in order not to obscure the small band gap. The plots show a diminishing gap in the DOS for zigzag GNTs as n increases, with the exception of (6,0), where a nonzero DOS can be observed at the Fermi level, indicating metallic character.



Figure 27: (Top) band structures and (bottom) density of states plots for a selection of zigzag GNTs, from DFT calculations. The latter are in units of number of states/eV, and are arbitrary due to the selection of Gaussian smearing parameter and energy grid by the user.

Figure 28 shows the band structures of a few selected armchair GNTs. DFT calculations show that the sub-bands nearest to the Fermi level in armchair GNTs cross each other in small diameter nanotubes, as exemplified by the (2,2) and (4,4) band structures in Figure 28. This effect disappears for larger-diameter armchair nanotubes, in which case those sub-bands become separated to form a small band gap, as seen in the (10,0) GNT. This band-bending effect has also been reported in DFT calculations of small diameter zigzag CNTs, and is commonly attributed to $\sigma^*-\pi^*$ rehybridization due to the effects of curvature of the nanotube [54], [55]. The small gap which opens up for larger-diameter armchair tubes results in diminishing states near the Fermi level.



Figure 28: (Top) band structures and (bottom) density of states plots for a selection of armchair GNTs, from DFT calculations

A few chiral GNTs were included in the study, although the overall number of chiral GNTs was limited because the number of atoms in the DFT calculation was capped at 400 due to computation and time budget. The number of atoms per unit cell of chiral GNTs is higher than that of zigzag or armchair GNTs for a given tube radius because of their lower symmetry, and therefore only five chiral tubes were calculated. Figure 29 shows the band structures of the chiral GNTs calculated in this study. Generally, the band gap shrinks as the chiral indices increase, and chiral tubes with indices where mod(n - m, 3) = 0 show an absence of a band gap, indicating metallic character. These characteristics are likewise shared with CNTs.



Figure 29: Band structures of the chiral GNTs in this study, from DFT calculations. The Fermi level is indicated in red for ease of viewing.

4.2.2 Band gap trends

In general, armchair (n,n) GNTs exhibit smaller (or zero) band gap values compared with their zigzag (n,0) GNT counterparts of similar diameter. The band gaps of zigzag GNTs tend to generally decrease as nanotube diameter increases, with the exception of GNTs with index *n* being a multiple of 3, where the band gaps values are similar to those of armchair GNTs with similar diameter. These characteristics, analogous to CNTs, are a consequence of the similar hexagonal Brillouin zone symmetry and location of VBM and CBM in the band structures of graphenylene and graphene. As diameter becomes large, the limits imposed by the circumferential periodic boundary condition become less significant, and the band gap values approach the 0.033 eV value calculated for two-dimensional graphenylene. Small-diameter armchair GNTs have zero band gap due to the band-bending effect of curvature, a phenomenon which is commonly reported in DFT calculations of small diameter zigzag CNTs and attributed to $\sigma^*-\pi^*$ rehybridization [54], [55].The overall trends in GNT band gap values can be seen in Figure 30.



Figure 30: Band gap variation for zigzag (red), armchair (blue) and chiral (purple) GNTs, from DFT calculations. Lines are meant to help guide the eye. The band gap of two-dimensional graphenylene denoted by the dashed line.

4.3 Electronic structure from density functional theory-based tight-binding calculations

For the purposes of comparison with the graphenylene study by Brunetto, et al. [12], SCC-DFTB calculations have also been employed. These calculations generally predict very similar band structures for GNTs as the DFT calculations in the previous subsection, with the key differences being that the band gap values tend to be significantly higher. This is a consequence of the higher band gap predicted by SCC-DFTB for 2D graphenylene, which was calculated to be 0.6 eV in this work, as shown in Figure 31. Brunetto, et al. [12] predicted a band gap of 0.8 eV, but their calculations employed a parameter set which was calculated using a hybrid functional. In this work, the parameter set used was calculated using a PBE (GGA) functional for the purpose of consistency with the DFT calculations, which were used to find the optimized geometries to input into the SCC-DFTB calculations.



Figure 31: Band structure of 2D graphenylene from SCC-DFTB calculations

4.3.1 Energy dispersion and density of states

The band structures of a few zigzag GNTs from SCC-DFTB calculations are shown in Figure 32. The band structures largely resemble those calculated from DFT (Figure 27), although the band gap is significantly larger. This is reflected in the DOS plots, where an absence of states can clearly be observed near the Fermi level. It should be noted that a larger Gaussian smearing parameter was used in obtaining the DOS plots in the SCC-DFTB figures, since the band gaps are larger and thus less prone to obscuring.



Figure 32: (Top) Band structures and (bottom) density of states plots for a selection of zigzag GNTs, according to SCC-DFTB calculations.

Likewise, band structures of armchair GNTs largely resemble those calculated from DFT (Figure 28), although the band gap is significantly larger in every case. Again, this effect is readily observed in the DOS plots, where an absence of states can clearly be seen near the Fermi level. A similar band-bending effect is observed for smaller-diameter armchair GNTs, which is expected due to the DFT-based calculation used in the SCC-DFTB method.



Figure 33: (Top) Band structures and (bottom) density of states plots for a selection of armchair GNTs, according to SCC-DFTB calculations.

4.3.2 Band gap trends

SCC-DFTB calculations show a similar trend in band gap values, as seen in Figure 34, with two key differences. First, the band gap values calculated using this method are consistently larger than those obtained using DFT calculations, as expected. Second, the band-bending effect seen in smaller-diameter armchair GNTs is more severe according to SCC-DFTB calculations. As a result, the band gaps of small diameter zigzag GNTs are lower than expected when compared to DFT calculations.



Figure 34: Band gap variation for zigzag (red), armchair (blue) and chiral (purple) GNTs, from SCC-DFTB calculations. Lines are meant to help guide the eye. The band gap of two-dimensional graphenylene denoted by the dashed line.

Chapter 5 – Potential applications

5.1. Electronic devices

A wide range of electronic and photonic applications of CNTs are possible and have been the subject of intense investigation over the previous two decades due to their geometry, mechanical robustness, and near-ballistic charge transport. CNT-based field-effect transistors (FETs) have been of particular interest due to their potential to out-perform state-of-the art silicon devices [56]. The primary advantages of CNT-based FETs are the extremely high carrier mobility in sp² carbon materials, atomic thickness, and the unique gate geometries that are made possible, such as the wrap-around gate [57]. CNT-based FETs must use semiconducting CNTs as channel material, since metallic CNTs are not capable of serving as a digital switch without a band gap. In addition to the advantages of CNTs previously mentioned, semiconducting CNTs have the advantage of a symmetric band structure near the Fermi level which results in equal effective masses for both electrons and holes, which can lead to symmetric CMOS with potentially very low power consumption as well as a compacted circuit layout.

However, CNT growth is challenging to control, and as-grown CNTs almost invariably contain a mixture of semiconducting and metallic CNTs, the latter of which are not suitable for use in FETs. Some progress has been made in recent years in selective growth of semiconducting CNTs [58], controlled removal of metallic CNTs [59], and CNT separation technology [60], although perfect control of semiconducting CNT growth has not yet been achieved. GNTs, on the other hand, are likely to be purely semiconducting, if the underestimation of the band gap in DFT calculations is taken into account. Therefore, under this assumption, GNTs would likely be the better practical choice of nanotube for use in FETs (as depicted in Figure 35). If a reliable growth technique were to be developed for GNTs, no selection or separation process would be required, and GNTs of virtually any diameter could be used for electronic devices, including very large diameters (assuming a band gap variation as in Figure 34). This presents a distinct advantage over CNTs because large-diameter CNTs are either metallic or have a very small band gap.



Figure 35: Depiction of a GNT-based field-effect transistor

5.2 Gas separation and storage

The pore diameters found in GNTs are similar in scale to the kinetic diameters of a few gases [24], as seen in Figure 36. As a rule of thumb, transport of gases through porous membranes is thermodynamically favorable only if the kinetic diameter of the gas molecule is smaller than that of the pore. The kinetic diameter of a gas molecule is usually determined empirically, but it can also be evaluated in a more quantum mechanical sense by examining the cross-sectional size of its electron density at some predetermined isovalue [61], similar to the way that the pore sizes in GNTs are determined in this work.



Figure 36: Pore diameter of GNTs as a function of tube diameter, with reference to the kinetic diameters of a few gas molecules. Each line segment corresponds to a particular GNT, wherein the top and bottom data points are the dimensions in the longitudinal and transverse directions, respectively.

Large-diameter GNTs contain pores which are approximately equal in dimension to those found in 2D graphenylene, which are larger than the kinetic diameter of H_2 but smaller than the kinetic diameters of O_2 , N_2 , and CO. Consequently, diffusion of O_2 , N_2 , and CO, as well as larger gas molecules, is thermodynamically unfavorable compared with H_2 , making GNTs an attractive candidate for hydrogen storage and separation. Smaller-diameter GNTs offer a range of pore diameters from 1.5 to 3.3 Å in the transverse direction. GNTs thus provide a wide range of selectivities for gas diffusion, dependent upon chiral index.

5.3 Lithium ion batteries

Another potential application of GNTs is in lithium adsorption, diffusion, and storage. This subsection will focus on the potential of GNTs in in the storage of lithium atoms via intercalation for lithium ion battery applications. In the study on 2D graphenylene by Yu [14], it was shown that lithium atoms can be dispersed remarkably well on graphenylene, both in monolayer and bilayer form, and that the intercalation of lithium atoms was shown to have little effect on the structure of graphenylene, meaning graphenylene-based materials would retain their mechanical properties during charging cycles in lithium-ion battery applications.

GNTs offer a very unique and promising structure for lithium storage. Geometry relaxations were performed in SIESTA on a (previously relaxed) (4,0) GNT with four Li atoms located just outside of the nanotube, a few Angstroms radially outward from the center of the dodecagonal rings, in order to determine the equilibrium position of the Li atoms. Interestingly, the relaxed positions of the Li atoms were just inside the nanotube, as shown in Figure 37. This is in contrast to the relaxed positions of the ions near a (10,0) CNT (chosen for its similar diameter) which are located outside of the tube. Therefore, when comparing GNTs and CNTs of the same diameter, Li intercalation is significantly enhanced in GNTs and far greater storage density is possible, the latter due to the smaller volume occupied by the nanotube and Li atoms together. This preliminary study indicates that GNTs may be a promising material for lithium ion battery applications, and further study on lithium adsorption and diffusion (the latter via a molecular dynamics study) is warranted.



Figure 37: Relaxed positions of Li atoms placed outside a (left) (4,0) GNT and (right) a (10,0) CNT. The equilibrium positions of the Li atoms are located inside the GNT but outside the CNT.

Chapter 6 – Summary, conclusion, and future work

Prior to this work, graphenylene nanotubes were described only in a qualitative sense in terms of their geometric configuration [6]. Furthermore, only one chirality of graphenylene nanotubes were described in that previous work, without any indication as to whether their chiral indices could be arbitrarily chosen based on the (n,m) nomenclature. Nothing was known about the relaxed geometry, structural properties, electronic structure, nor could any educated conclusions be drawn about the potential applications of graphenylene nanotubes. Therefore, this work effectively introduces graphenylene nanotubes as a novel family of carbon allotropes.

6.1. Contributions

The contributions of this thesis and their immediate applications are as follows:

- 1. Chapter 2 describes a MATLAB program which builds a unit cell of a GNT of any arbitrary chiral indices inputted by the user, without error. This not only saves significant amounts of time in constructing GNT geometries, but also in terms of geometry relaxation time in the DFT calculations: the program is also flexible in terms of its parameters (bond lengths, lattice vectors), such that the relaxed bond lengths and lattice vectors of a small GNT can be used as a starting point to construct larger GNTs. Moreover, if a different exchange-correlation functional were to be chosen (which results in different bond lengths), the same procedure could be used in order to save a vast amount of computation time for geometry relaxation. This program has also been modified to produce the graphyne and pentahexoctite sheets shown in Figure 2, and a few further simple modifications were added to produce nanotube analogs of these sheets. Therefore, this program lays the groundwork for constructing any nanotube based on any 2D allotrope of carbon for a future study.
- 2. Chapter 4 described the stability, structural properties, and electronic properties of a large number of armchair, zigzag, and chiral GNTs. All of these properties were unknown prior to this work.
- 3. Chapter 5 presented three potential applications of GNTs: GNT-based electronics (specifically GNT-based FETs), gas separation and storage, and lithium ion intercalation and storage. For all of these applications, GNTs have unique qualities which are advantageous over CNTs, making GNTs a very lucrative material system. These assessments of potential applications were made possible by the properties described in Chapter 4, which were unknown prior to this work.

6.2. Conclusion and future work

GNTs exhibit several interesting properties which are advantageous over CNTs. First, GNTs contain dodecagonal carbon rings which form pores that are nominally 3.3 Å in diameter, although the dimensions of the pore are modified in smaller-diameter GNTs. These pores provide the ability to separate and store two very important molecules: hydrogen gas and lithium ions. For the vast majority of GNTs, the diameter of the pores formed by the dodecagonal rings is larger than the kinetic diameter of H₂ but smaller than that of most other significant gases in the atmosphere, which results in high selectivity for hydrogen gas diffusion through the pores. Geometry relaxations in the framework of DFT in this work have shown that lithium ion diffusion through the pores into the interior of the GNT is actually energetically favorable, which is not the case in CNTs, making GNTs highly attractive for lithium ion storage.

Second, GNTs are assumed to be semiconductors with a direct band gap (taking into account the underestimation of band gaps by DFT calculations and assuming the empirical band gaps are closer to SCC-DFTB predictions). If GNT synthesis is successfully achieved in the future, this would render GNTs as the more practical quasi-one-dimensional carbon material, since as-grown CNTs contain a mixture of metallic and semiconducting CNTs, whereas all GNTs are assumed to be semiconducting based on the previously mentioned criteria.

The present study could be expanded in the future in multiple ways, in terms of theoretical studies or synthesis experiments. Three possible future studies are outlined as follows:

- 1. Synthesizing GNTs by introducing vacancies in CNTs using a focused ion beam (FIB) or by other means. In this study, an attempt would be made to introduce controlled vacancies in CNTs under vacuum, such that spontaneous interconversion to GNTs (at least locally) could occur. Several steps have already been taken for this effort, and are presented in Appendix A. In conjunction, a DFT-based molecular dynamics study on this interconversion process in GNTs would be performed in the same framework of the study by Brunetto, et al. [12]. The GNT samples would be characterized using transmission electron microscopy (TEM) or some other atomic-scale microscopy, since the first GNTs to be synthesized in this manner would likely be quite rare among other defected CNTs, and consequently any spectroscopic identifiers would likely be washed out.
- 2. Performing a thorough study of gas selectivity and diffusion through the pores formed by the dodecagonal rings in a variety of different GNTs. This would involve a DFT-based molecular dynamics study of transport of gas molecules through the pores, analyzing the energy barriers to the diffusion of different gas molecules to the pores in GNTs of various chiralities.

3. Performing a thorough study of lithium adsorption, diffusion and storage on GNTs of various chiralities. The results would be analyzed and compared to CNTs. It is hypothesized based on the results of the 2D graphenylene study by Yu [14] and the preliminary results from Section 5.3 that GNTs will exceed CNTs significantly in their ability to be intercalated by Li⁺ ions and to store them. If the results of the first future study are successful, this could even be tested experimentally in a Li⁺ ion cell.

References

- [1] K. S. Novoselov, et al., "Two-dimensional gas of massless Dirac fermions in graphene," *Nature*, vol. 438, pp. 197-200, 2005.
- [2] A. A. Balandin, et al.,"Superior thermal conductivity of single-layer graphene," *Nano Lett.*, vol. 8, pp. 902-907, 2008.
- [3] C. Lee, X. Wei, J. W. Kysar and J. Hone,"Measurement of the elastic properties and intrinsic strength of monolayer graphene," *Science*, vol. 321, pp. 385-388, 2008.
- [4] H. Lu and S.-D. Li, "Two-dimensional carbon allotropes from graphene to graphyne," J. Mat. Chem. C, vol. 1, pp. 3677, 2013.
- [5] V. R. Coluci, S. F. Braga, S. B. Legoas, D. S. Galvão, and R. H. Baughman, "Families of carbon nanotubes: Graphyne-based nanotubes," *Phys. Rev. B*, vol. 68, pp. 35430, 2003.
- [6] A. T. Balaban and K. P. C. Vollhardt, "Heliphenes and related structures," *Open Org. Chem. J.*, vol. 5, pp. 117-126, 2011.
- [7] G. Li, et al., "Architecture of graphdiyne nanoscale films," *Chem. Commun.*, vol. 46, pp. 3256, 2010.
- [8] B. R. Sharma, A. Manjanath and A. K. Singh,"pentahexoctite: A new two-dimensional allotrope of carbon," *Sci. Reports*, vol. 4, pp. 7164, 2014.
- [9] V. H. Crespi, L. X. Benedict, M. L. Cohen and S. G. Louie,"Prediction of a pure-carbon planar covalent metal," *Phys. Rev. B: Condens. Matter*, vol. 53, pp. R13303, 1996.
- [10] F. Banhart, J. Kotakoski and A. V. Krasheninnikov, "Structural defects in graphene," *ACS Nano*, vol. 5, pp. 26, 2011.
- [11] E. T. Thostenson, Z. Ren and T.-W. Chou,"Advances in the science and technology of carbon nanotubes and their composites: a review," *Composites Sci. and Tech.*, vol. 61, pp. 1899-1912, 2001.
- [12] G. Brunetto, et al.,"Nonzero gap two-dimensional carbon allotrope from porous graphene," *J. Phys. Chem. C*, vol. 116, pp. 12810-12813, 2012.
- [13] Q. Song, et al., "Graphenylene, a unique two-dimensional carbon network with nondelocalized cyclohexatriene units," *J. Mater. Chem. C*, vol. 1, pp. 38, 2013.
- [14] Y.-X. Yu, "Graphenylene: a promising anode material for lithium-ion batteries with high mobility and storage," *J. Mater. Chem. A*, vol. 1, pp. 13559-13566, 2013.
- [15] J. M. Schulman and R. L. Disch,"A Theoretical Study of Large Planar [N]Phenylenes," *J. Phys. Chem. A*, vol. 111, pp. 10010-10014, 2007.
- [16] S. Han, et al., "Total syntheses of angular [7]-, [8]-, and [9]phenylene by triple cobalt-catalyzed cycloisomerization: Remarkably flexible heliphenes," *Angew. Chem.*, vol. 114, pp. 3361-3364, 2002.
- [17] S. Han, et al., "Total Syntheses and Structures of Angular [6]- and [7]Phenylene: The First Helical Phenylenes (Heliphenes)," *Angew. Chem.*, vol. 114, pp. 3357-3361, 2002.
- [18] B. Iglesias, A. Cobas, D. Pérez, E. Guitián, and K. P. C. Vollhardt,"Tris(benzocyclobutadieno)triphenylene and its lower biphenylene homologues by palladium-catalyzed cyclizations of 2,3-didehydrobiphenylene," *Org. Lett.*, vol. 6, pp. 3557-3560, 2004.
- [19] G. Otero, et al., "Fullerenes from aromatic precursors by surface-catalysed cyclodehydrogenation," *Nature*, vol. 454, pp. 865-868, 2008.
- [20] M. Treier, et al., "Surface-assisted cyclodehydrogenation provides a synthetic route towards easily processable and chemically tailored nanographenes," *Nat. Chem.*, vol. 3, pp. 61-67, 2011.
- [21] H. Liang, et al., "Two-dimensional molecular porous networks constructed by surface assembling," *Coord. Chem. Rev.*, vol. 1, pp. 2959–2979, 2009.
- [22] S. P. Elangovan, M. Ogura, M. E. Davis and T. Okubo, "SSZ-33: A promising material for use as a hydrocarbon trap," *J. Phys. Chem. B*, vol. 108, pp. 13059-13061, 2004.
- [23] D. Jiang, V. R. Cooper and S. Dai, "Porous graphene as the ultimate membrane for gas separation," *Nano Lett.*, vol. 9, pp. 4019-4024, 2009.
- [24] S. Matteucci, Y. Yampolskii, B. D. Freeman and I. Pinnau," Transport of gases and vapors in glassy and rubbery polymers," *Materials Science of Membranes for Gas and Vapor Separation*, John Wiley & Sons, Ltd: Chichester, UK, 2006.
- [25] H. Zhang, et al., "High mobility and high storage capacity of lithium in sp–sp2 hybridized carbon network: the case of graphyne," *J. Phys. Chem. C*, vol. 115, pp. 8845-8850, 2011.
- [26] S. Bae, et al., "Roll-to-roll production of 30-inch graphene films for transparent electrodes," *Nature Nanotech.*, vol. 5, pp. 574-578, 2010.
- [27] P. Avouris, "Graphene: Electronic and photonic properties and devices," *Nano Lett.*, vol. 10, pp. 4285-4294, 2010.
- [28] G. Lu, K. Yu, Z. Wen and J. Chen, "Semiconducting graphene: converting graphene from semimetal to semiconductor," *Nanoscale*, vol. 5, pp. 1353, 2013.
- [29] F. N. Xia, D. B. Farmer, Y. M. Lin and P. Avouris,"Graphene field-effect transistors with high on/off current ratio and large transport band gap at room temperature," *Nano Lett.*, vol. 10, pp. 715-718, 2010.
- [30] Y.-C. Chen, et al., "Tuning the band gap of graphene nanoribbons synthesized from molecular precursors," *ACS Nano*, vol. 7, pp. 6123-6128, 2013.
- [31] Z. T. Luo, P. M. Vora, E. J. Mele, A. T. C. Johnson, and J. M. Kikkawa,"Photoluminescence and band gap modulation in graphene oxide," Appl. Phys. Lett., vol. 94, pp. 111909, 2009.
- [32] H. T. Liu, Y. Q. Liu and D. B. Zhu,"Chemical doping of graphene," J. Mater. Chem., vol. 21, pp. 3335-3345, 2011.
- [33] V. M. Pereira and A. H. C. Neto,"Strain engineering of graphene's electronic structure," *Phys. Rev. Lett.*, vol. 103, pp. 046801, 2009.
- [34] R. Saito, G. Dresselhaus and M. Dresselhaus,"Physical Properties of Carbon Nanotubes," Imperial College Press: London, 1998.
- [35] J. M. Soler, et al., "The SIESTA method for ab initio order-N materials simulation," *J. Phys. Condens. Matter*, vol. 14, pp. 2745, 2002.
- [36] M. K. Y. Chan and G. Cedar,"Efficient band gap prediction for solids," *Phys. Rev. Lett.*, vol. 105, pp. 196403, 2010.
- [37] L. J. Sham and M. Schlüter,"Density-functional theory of the energy gap," *Phys. Rev. Lett.*, vol. 51, pp. 1888, 1983.
- [38] A. J. Cohen, P. Mori-Sánchez and W. Yang,"Fractional charge perspective on the band gap in density-functional theory," *Phys. Rev. B*, vol. 77, pp. 115123, 2008.
- [39] R. W. Godby, M. Schlüter and L. J. Sham, "Quasiparticle energies in GaAs and AlAs," *Phys. Rev. B*, vol. 35, pp. 4170, 1987.
- [40] D. Porezag, T. Frauenheim, T. Köhler, G. Seifert, and R. Kaschner,"Construction of tightbinding-like potentials on the basis of density-functional theory: Application to carbon," *Phys. Rev. B*, vol. 51, pp. 12947, 1995.
- [41] B. Aradi, B. Hourahine and T. Frauenheim, "DFTB+, a sparse matrix-based implementation of the DFTB method," *J. Phys. Chem. A*, vol. 111, pp. 5678-5684, 2007.
- [42] Robert G. Parr, W. Yang, "Density-Functional Theory of Atoms and Molecules" Oxford: Oxford University Press, 1994.
- [43] W. Kohn and L. J. Sham, "Self-consistent equations including exchange and correlation effects," *Phys. Rev.*, vol. 140, pp. A1133, 1965.
- [44] C. G. Broyden, "A class of methods for solving nonlinear simultaneous equations," Math. Comp., vol. 19, pp. 577-593, 1965.
- [45] H. J. Monkhorst and J. D. Pack, "Special points for Brillouin-zone integrations," *Phys. Rev. B*, vol. 13, pp. 5188, 1976.

- [46] N. Mounet and N. Marzari, "First-principles determination of the structural, vibrational and thermodynamic properties of diamond, graphite, and derivatives," *Phys. Rev. B*, vol. 71, pp. 205214, 2005.
- [47] N. Troullier and J. L. Martins, "Efficient pseudopotentials for plane-wave calculations," *Phys. Rev. B*, vol. 43, pp. , 1991.
- [48] T. Frauenheim, et al., "BOOK CHAPTER: A self-consistent charge density functional based tightbinding method for predictive matierials simulations in physics, chemistry, and biology,", vol., pp.,.
- [49] M. Elstner, et al., "Self-consistent-charge density-functional tight-binding method for simulations of complex materials properties," *Phys. Rev. B*, vol. 58, pp. 7260, 1998.
- [50] W. Foulkes and R. Haydock,"Tight-binding models and density-functional theory," *Phys. Rev. B*, vol. 39, pp. 12520, 1989.
- [51] Z. Peralta-Inga, S. Boyd, J. S. Murray, C. J. O'Connor, and P. Politzer,"Density functional tightbinding studies of carbon nanotube structures," *Struct. Chem.*, vol. 14, pp. 431-443, 2003.
- [52] O. Gülseren, T. Yuldirim and S. Ciraci, "Systematic ab initio study of curvature effects in carbon nanotubes," *Phys. Rev.B*, vol. 65, pp. 153405, 2002.
- [53] D. H. Robertson, D. W. Brenner and J. W. Mintmire,"Energetics of nanoscale graphitic tubules," *Phys. Rev. B*, vol. 45, pp. 12592, 1992.
- [54] L. X. Benedict, E. L. Shirley and S. G. Louie,"Hybridization effects and metallicity in small radius carbon nanotubes," *Phys. Rev. Lett.*, vol. 72, pp. 1878, 1994.
- [55] Y. Matsuda, J. Tahir-Kheli and W. A. Goddard,"Definitive band gaps for single-wall carbon nanotubes," *J. Phys. Chem. Lett.*, vol. 1, pp. 2946–2950, 2010.
- [56] L.-M. Peng, Z. Zhang and S. Wang,"Carbon nanotube electronics: recent advances," *Materials Today*, vol. 17, pp. 433-442, 2014.
- [57] P. Avouris, Z. Chen and V. Perebeinos, "Carbon-based electronics," *Nature Nanotech.*, vol. 2, pp. 605-615, 2007.
- [58] J. H. Li, et al., "Growth of high-density-aligned and semiconducting-enriched single-walled carbon nanotubes: decoupling the conflict between density and selectivity," *ACS Nano*, vol. 8, pp. 554-562, 2014.
- [59] S. H. Jin, et al., "Using nanoscale thermocapillary flows to create arrays of purely semiconducting single-walled carbon nanotubes," *Nature Nanotech.*, vol. 8, pp. 347-355, 2013.
- [60] M. C. Hersam,"Progress towards monodisperse single-walled carbon nanotubes," *Nature Nanotech.*, vol. 3, pp. 387-394, 2008.
- [61] N. Mehio, S. Dai and D. Jiang,"Quantum mechanical basis for kinetic diameters of small gaseous molecules," *J. Phys. Chem. A*, vol. 118, pp. 1150-1154, 2014.

Appendix A – MATLAB code

The following code was used to create graphenylene nanotubes of arbitrary chiral index.

```
clear all
close all
clc
format long
% INPUTS
n = 5;
m = 0;
% Unit cell of graphyne
atoms = 12;
L1 = 1.3776; %bond length 1, Angstroms
L2 = 1.468; %bond length 2, Angstroms
L3 = 1.481; %bond length 2, Angstroms
a = 6.7881; %length of unit vector, Angstroms
% Unit vectors
a1 = [sqrt(3)/2, 1/2]*a; %real space unit vector 1
a2 = [sqrt(3)/2, -1/2]*a; %real space unit vector 2
b1 = [1/3, 1]*2*pi/a; %k space unit vector 1
b2 = [1/3, -1]*2*pi/a; %k space unit vector 1
Theta0 = 30; %degrees
% Define nanotube vectors
Ch = n*a1+m*a2; %Chiral vector
L = a*sqrt(n^2+m^2+n*m); %Length of Ch
Diameter = L/pi %tube diameter
Theta = asin(sqrt(3)*m/(2*sqrt(n^2+m^2+n*m))); %Chiral angle
d = gcd(n,m); %divisor 1
dR = gcd(2*n+m,2*m+n);  %divisor 2
N = 2*(n^2+m^2+n*m)/dR; %Number of 2D unit cells in unrolled sheet
t1 = (2*m+n)/dR; t2 = -1*(2*n+m)/dR; %Translational vector indices
T = t1*a1+t2*a2; %Translational vector
Tlen = sqrt(3)*L/dR %Length of translational vector
% Nanotube Brillouin zone
K1 = 1/N*(-1*t2*b1+t1*b2); %recipricoal lattice vectors of nanotube
K2 = 1/N*(m*b1-n*b2);
% Form unit cell (UPDATE: coordinates from DFT)
g unit(1,:) = [1.19115326,0.73391827];
q unit(2,:) = [-0.00206607, 1.42249396];
g unit(3,:) = [-1.27326162, 0.6887435];
g unit(4,:) = [-1.2732611,-0.68874337];
g unit(5,:) = [-0.0020661,-1.42249417];
g_unit(6,:) = [1.19115345,-0.73391831];
g unit(7,:) = [2.67202462, 0.73404904];
g unit(8,:) = [3.86505294,1.42287425];
g unit(9,:) = [5.13609433,0.68896079];
g_unit(10,:) = [5.13609454,-0.68896137];
g unit(11,:) = [3.86505295,-1.42287472];
g unit(12,:) = [2.67202478,-0.73404924];
unit offset = mean([g unit(1,1),g unit(7,1)]);
g unit(:,1) = g unit(:,1) - unit offset;
% Adjust origin for cleaner unit cell
if m == 0
    tube offset = [0 a1(2)];
```

```
elseif m == n
    tube offset = [0 a1(2)/2];
else
    tube offset = [unit offset 0];
end
% Plot unrolled unit cell
figure()
scatter(g unit(:,1),g unit(:,2),'filled')
grid on
axis equal
hold on
plot([-1*a1(1) 0],[0 a1(2)],'r',[0 a1(1)],[-1*a1(2),0],'r')
plot([-1*a2(1) 0],[0 a2(2)],'r',[0 a2(1)],[-1*a2(2),0],'r')
% Create graphenylene sheet
g unit sheet = g unit + repmat(tube offset, atoms, 1); %offset origin
% Inputs
m sheet = 10; %Sheet size
n sheet = 10; %Sheet size
gsheet = zeros(atoms*m sheet*n sheet,2); %Empty sheet matrix
gsheet(1:atoms,:) = g unit sheet; %First unit cell
for i = 2:n sheet %Replicate unit cell
    for j = 2:m sheet
        gsheet(atoms*(j-1)+1:atoms*j,:)=g unit sheet+(j-
1) * repmat(a1, atoms, 1);
    end
    gsheet(atoms*m sheet*(i-1)+1:atoms*m sheet*i,:) =
gsheet(1:atoms*m sheet,:)+(i-1)*repmat(a2,atoms*m sheet,1);
end
gsheet half = [gsheet; gsheet - repmat(n sheet*a2,length(gsheet),1)]; %Half
sheet
gsheet full = [gsheet half; gsheet half +
repmat(m sheet*al,length(gsheet half),1)]; %Full sheet
% Plot nanotube vectors over sheet
figure()
scatter(gsheet full(:,1),gsheet full(:,2),'filled')
hold on
plot([0 Ch(1)],[0 Ch(2)], 'r',[0 T(1)],[0 T(2)], 'g')
hold on
plot([0 K2(1)],[0 K2(2)],'k')
grid on
axis equal
% Cut polygon OAB'B
nrcorner = Ch+T; %Outermost corner
xv = [0 T(1) nrcorner(1) Ch(1)]; %Polygon x coordinates
yv = [0 T(2) nrcorner(2) Ch(2)]; %Polygon y coordinates
xcol = gsheet full(:,1); %Sheet x coordinates
ycol = gsheet full(:,2); %Sheet y coordinates
in = inpolygon(xcol,ycol,xv,yv); %Select atoms inside polygon
xribbon = xcol(in); yribbon = ycol(in); %Coordinates of atoms in polygon
% Rotate
rot ang = -1*acosd(Ch(1)/L); %Define rotation angle
rotmatz = [cosd(rot ang) -1*sind(rot ang); sind(rot ang) cosd(rot ang)];
%Rotation matrix
ribbon rot = (rotmatz*[xribbon, yribbon]')'; %Rotated ribbon
ribbon concat x = [ribbon rot(:,1) + L, ribbon rot(:,2)];
ribbon concat y = [ribbon rot(:,1), ribbon rot(:,2)+Tlen];
figure()
```

```
scatter(ribbon rot(:,1),ribbon rot(:,2),'filled')
hold on
grid on
axis equal
xlabel(['x^\prime (', char(197), ')'])
ylabel(['y^\prime (', char(197), ')'])
% Visual check for periodicity
scatter(ribbon concat y(:,1),ribbon concat y(:,2),'filled')
scatter(ribbon concat x(:,1), ribbon concat x(:,2), 'filled')
% Roll ribbon into tube
ntube = zeros(length(ribbon rot),3); %Empty 3D tube matrix
ntube(:,3) = ribbon rot(:,2); %z tube = y sheet
for j = 1:length(ribbon rot)
    phi = ribbon rot(j, \overline{1})/L^{*2*pi}; %Define angle relative to center of tube
axis
    rotmatj = [cos(phi) -1*sin(phi); sin(phi) cos(phi)]; %Create rotation
matrix
    ribbon rolled(j,1:2) = (rotmatj*[L/(2*pi);0])'; %Place atom at new
coordinate
end
ntube(:,1:2) = ribbon rolled; %to 3D tube matrix
% CHECK FOR ERRORS
% Step 1: build long tube
ntube above = ntube; ntube above(:,3) = ntube(:,3)+Tlen; %Top nanotube cell
ntube below = ntube; ntube below(:,3) = ntube(:,3)-Tlen; %Bottom nanotube
cell
ntube long = [ntube; ntube above; ntube below]; %Stack nanotube cells
% Step 2: calculate nearest neighbor bond lengths
bonds all = squareform(pdist(ntube long,'euclidean')); %All bond lengths
bonds lunit = bonds all(:,1:length(ntube)); %Bond lengths for middle cell
bonds_lunit = sort(bonds_lunit, 'ascend'); %Sort bond lengths ascending
nearest neighbors = bonds lunit(2:4,:); %Extract nearest neighbors
%Step 3: check nearest neighbors
nn check = nearest neighbors -
repmat([L1;L2;L3],1,length(nearest neighbors));
errormat = abs(nn check)>0.01; %Check if any bond lengths are off
if max(errormat)>0
    disp('Error: some bond lengths incorrect')
end
% Step 4: Check # atoms
    if length(ntube long) ~= atoms*N*3
        disp('Error: wrong number of atoms')
    end
%Plot tube
figure()
scatter3(ntube(:,1),ntube(:,2),ntube(:,3),'filled')
grid on
axis equal
hold on
scatter3(ntube above(:,1),ntube above(:,2),ntube above(:,3),'filled')
line([0 0],[0 0],[0 2*Tlen],'Color',[0 0 0])
xlabel(['x (',char(197),')'])
ylabel(['y (', char(197), ')'])
zlabel(['z (', char(197), ')'])
```