THE ELECTRONIC PROPERTIES OF HEXAGONAL BORON NITRIDE AND
GRAPHENE NANORIBBONS

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Abstract

The electronic properties of hexagonal boron nitride nanoribbons and graphene nanoribbons will be explored. The goal of studying these properties is to see how these materials pertain to energy storage and device fabrication. Both of these nanostructures are two-dimensional and can be characterized based on their edge shape, either by armchair or zigzag edge. Graphene is normally a semiconductor while boron nitride is known as an insulator.

Theoretical models include the Tight-Binding and Green’s Function Theory. Consequently, the energy band structures, density of states, conductance, and local density of states will be investigated. These results entail the electronic properties which are to be explored. When altering these pure structures, fascinating changes occur and give rise to new electrical behavior. These defects are used to help simulate impurities or contaminated samples in experimental work. Hexagonal Boron Nitride is of importance in this study due to its versatility to contain new electronic properties when an impurity is added.

In addition, Density Functional Theory will be used to compare results to the Tight-Binding Model. This third theory gives a detailed, new perspective on the electronic structure of these nanostructures. It also allows for visualization of their corresponding electron densities and orbitals, where condensed matter physics can be applied. All results are generated using Wolfram Mathematica and ABINIT computational software on the Ball State Beowulf Cluster.
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Chapter 1: Introduction

Here, I will discuss the current perspective in nanoscience and why nanostructures like graphene and hexagonal boron nitride are important and on the rise. This chapter also consists of some literature review and explains the layout for this thesis.

1.1 New Frontiers in Nanoscience

Condensed matter physics is one of the largest fields in theoretical and experimental physics with enormous amounts of practical application. In this field also lies nanoscience, which is a specific sub-field that studies science at the nanometer level. Most nanoscience breakthroughs are related to mechanical, electrical and optical advances that are exhibited in new devices and other technologies. It only makes sense that with time, current technology will become outdated and obsolete – only to be replaced with something more powerful and efficient than its predecessor. Not to mention, most of these new fabrications are often the size of an atom. However, only some of the technology is introduced on a consumer-based level.

For example, solar panels house photovoltaic cells which can be placed upon the roofs of homes in desert regions in the United States to help provide clean, renewable energy [1]. Nanoscale transistors and electronic devices are used in the medical, industrial and engineering fields to aid scientists and engineers in developing new research to solve larger-than-life issues [2]. The need for improved technology is in high demand. In many cases, fabrication of such materials can be costly and fragile to maintain in a pure form. To counter this, computer simulations and modeling are often a first step to manufacture and test the versatility of this brilliant technology.
1.2 Graphene

Graphene was first discovered in 2004 by using a piece of scotch tape to remove layers off graphite until only one layer remained [3, 4]. By cutting a strip out of graphene in either the x-direction or a combination of both x- and y-directions, a graphene nanoribbon (GNR) can be created with a defined edge. These GNRs can possess an armchair or zigzag edge while inheriting a finite width and semi-infinite length.

Figure 1.1 - Schematic diagram of (a) an AGNR with width N dimers and (b) a ZGNR with width N chains.

A schematic of both these edge nanoribbons are shown in Figure 1.1. GNRs consist of carbon atoms laid out in a hexagonal lattice. Neighboring carbon atoms can bond with a sp$^2$ hybridization, leaving p$_z$ orbitals perpendicular to the plane of the sheet. This is due to carbon’s
four valence electrons (2s^2 2p^2) where a hybridized electron configuration is more energetically favorable. Thus, the action sends an electron from the 2s shell into the 2p shell [5, 7, 15].

The carbon atoms are displayed in black in Figure 1.1. Any GNR has a certain width N associated with it. For armchair graphene nanoribbons (AGNRs) like in Figure 1.1(a), N is the number of dimers (pair of atoms) in the transverse direction and for zigzag graphene nanoribbons (ZGNRs) like in Figure 1.1(b), N is the number of chains in the transverse direction.

AGNRs and ZGNRs have fascinating properties that are characteristic of their edge structure. It has been shown that these structures can be both metallic and semiconducting [5, 7, 8]. GNRs have also been a very popular topic of study by countless researchers along with their carbon nanotube (CNT) counterparts [5-14]. This allotrope of carbon has been studied extensively and its mechanical, electrical and optical properties have been heavily exploited for current technology [4-6]. Researchers believe it’d make a good substitute for silicon based transistors and other small-scale technology due to the quasiparticle-like behavior found in its electronic structure [3].

1.3 Hexagonal Boron Nitride

Hexagonal boron nitride is a two-species analog to graphene composed of boron and nitrogen atoms [16]. The boron and nitrogen atoms orient in an alternating pattern spanning the hexagonal lattice. But like graphene, hexagonal boron nitride can be constructed into boron nitride nanoribbons (BNNRs) with an armchair or zigzag edge in the same manner [17]. Due to the electronegativity of nitrogen and the electropositivity of boron, zigzag boron nitride nanoribbons (ZBNNRs) have one edge that’s more negatively charged and one end that is more positively charged. Armchair boron nitride nanoribbons (ABNNR) do not exhibit edge structures
that are purely positively charged or purely negatively charged since there are a mixture of boron and nitrogen atoms that define the edges. Figure 1.2 below shows a schematic diagram of the two possible edge configurations for BNNRs. The boron atoms are denoted with purple color and the nitrogen atoms are denoted with blue color.

![Schematic diagram of BNNRs](image)

**Figure 1.2 – Schematic diagram of (a) an ABNNR with width N dimers and (b) a ZBNNR with width N chains.**

BNNRs are of importance because of their large band gap. This material is an insulator with band gaps ranging from 4.3-6 eV [18-20]. Of course, this presents an issue for semiconductor device fabrication since the band gap is too large. Researchers have found various methods to tune the band gaps and change electronic properties by means of edge functionalization, edge bond termination and by applying stress or strain in the plane [20-23]. If the band gap can be tuned and decreased, BNNRs would be easier fabricated for photovoltaic cells, field-effect transistors and spintronics [2, 19, 24, 25]. However, hexagonal boron nitride
can be used in sheet form or nanotube form as well. This opens up a realm of investigation on creating heterostructures (i.e. materials composed of carbon and boron nitride junctions and other compound interfaces) and attempts to apply external electric fields which create special magnetic and electrical properties [14, 26-28]. It has also been shown that BNNRs are able to become metallic through these techniques [21, 22, 29, 30]. The goal of this thesis is to investigate the basic electronic properties of BNNRs and GNRs (yet the main focus rests on BNNRs). By doing so, an understanding of their potential for device fabrication and energy storage will be developed.

1.4 A Preview of This Thesis

This thesis consists of seven chapters. Chapter 2 explain the theories used for determining electronic properties: the Tight-Binding (TB) Model and Green’s Function Theory. Chapter 3 discusses Density Functional Theory (DFT) as a third method to determine electronic properties. This chapter will also explain the computational methodology of implementing DFT as well as comparisons and differences of DFT to the TB Model. Chapter 4 presents the results from the TB Model, where energy band structures, density of states (DOS), conductance curves and local density of states (LDOS) will be shown. In addition, edge modulation of BNNRs and their effects on band structure, DOS, and conductance will be shown. Finally, the electronic properties of BNNRs will be compared to those of GNRs at the end of the chapter. Chapter 5 is a calibration study of parameters to implement DFT by using ABINIT computational software. This chapter reveals some insight about the inner workings of ABINIT and why certain parameters are chosen to model electronic systems – primarily, those of hexagonal boron nitride in sheet and nanoribbon form. Chapter 6 is a presentation of results obtained through DFT and ABINIT such as band structures, DOS and LDOS calculations, and visualizations through Visual
Molecular Dynamics (VMD) software. Finally, Chapter 7 will offer conclusions based on the results from both models presented and suggest future avenues for further study.
Chapter 2: Tight-Binding Model and Green’s Function Theory

Here, I will introduce the Tight-Binding (TB) Model used to produce energy band structures and density of states. This model is straightforward and effective for obtaining energies by producing Hamiltonian matrix elements. Green’s Function theory is used to calculate conductance and local density of states (LDOS) with the help of the Landauer Formula.

2.1 Tight-Binding Formalism

The Tight-Binding (TB) Model is a quick and efficient method to perform electronic structure calculations. This model is a standard textbook approach to obtain energy band structures and produce Hamiltonian matrix elements, yet it is not an exact calculation [31, 32, 33]. For our application, Huckel Theory is utilized within the TB Model [31]. This theory restricts all interactions to nearest neighbors for a specific set of atomic orbitals. Not only does this restriction ease the calculation, it also keeps the number of matrix elements to a minimum through some approximations. For this work, $p_z$ orbitals are utilized, including their interactions among other $p_z$ orbitals. If other orbitals are to be included, that process would be an example of Extended Huckel Theory [31]. An example of this theory can be seen in Jones’ thesis [7]. In general, the Hamiltonian operator is given by

$$\hat{H} = \sum_i \epsilon_i a_i^\dagger a_i + \sum_{ij} V_{ijk} a_i^\dagger a_j,$$

(2.1)
where $\varepsilon_{ij}$ is the onsite energy of any given $p_z$ orbital, $a_{ij}^+$ and $a_{ij}$ are annihilation and creation operators of sites $i$ and $j$, respectively. Note that the onsite energy is different for each atom and each orbital. For example, $\varepsilon_c$ is the onsite $p_z$ energy of carbon with a value of -8.97 eV. Similarly, $\varepsilon_B$ is -6.64 eV for the onsite energy of boron and $\varepsilon_N$ is -11.47 eV for the onsite energy of nitrogen [31].

$V_{ijk}$ is the hopping parameter which describes the coupling between neighboring $p_z$ orbitals and is given by

$$V_{ijk} = \eta_{ijk} \frac{\hbar^2}{md^2}.$$  \hspace{1cm} (2.2)

Here, $\eta_{ijk}$ is a dimensionless constant describing the $i^{th}$ and $j^{th}$ bond orbital and $k^{th}$ bond type, $m$ is the mass of an electron, $\hbar$ is Planck’s constant (modified) and $d$ is the bond length between neighboring atoms. For the purposes of this thesis, $\eta_{ijk}$ is the same as $\eta_{pp\pi} = -0.81$ for the interaction between two $p_z$ orbitals as a pi ($\pi$) bond (which allows one to say $V_{ijk}$ and $V_{pp\pi}$ are the same). Depending on the bond orbital and bond type used to calculate the hopping parameter, this special constant can change accordingly [15, 31]. In addition, the bond length for a carbon-carbon bond is taken to be 1.42 Å [11] and for a boron-nitrogen bond, 1.43 Å [20]. Note that the bonding parameters to determine matrix elements using Equation 2.2 are approximations using empirical data [31].

Essentially, these two equations are all that one needs to create Hamiltonian matrix elements. Before they can be created, one must think carefully about our nanostructures and their geometry. Since any nanoribbon – graphene or hexagonal boron nitride – can be created from
repeating a primitive unit cell, it is easy to describe a nanoribbon by this primary building block. Thus, it is advantageous to utilize Bloch’s Theorem,

\[ \psi_{nk}(\vec{r}) = e^{i \vec{k} \cdot \vec{r}} u_{nk}(\vec{r}), \]

(2.3)

where \( n \) is a quantum number that indicates the energy band and \( k \) is a quantum number that indicates momentum \( \hbar k \) of the particle. Also, \( u_{nk} \) is a periodic function with associated quantum number and momentum (or wave vector). Bloch’s Theorem says that the wavefunction of an electron in a crystal consists of a plane wave and a periodic function [34]. This theorem is advantageous because it makes the wavefunction simpler to describe. Moreover, all one needs is information about the orbitals in the primitive unit cell in order to apply this theorem. However, one can also think of the wavefunction as being a linear combination of atomic orbitals (LCAO) with the following relation:

\[ |\psi_{nk}\rangle = \sum_{i} C_{i} |\phi_{i}\rangle, \]

(2.4)

where \( C_{i} \) is some constant and \( \phi_{i} \) is one of \( N \) atomic orbitals in the unit cell [31, 32]. The sum in Equation 2.4 encompasses the total number of orbitals of corresponding atoms. Putting all these equations together, one can then satisfy and expand the time-independent Schrodinger Equation,

\[ \hat{H} |\psi_{nk}\rangle = E |\psi_{nk}\rangle. \]

(2.5)

Expanding Equation 2.5 by taking scalar products and using the orthogonality relations [35], a series of equations is generated and can be written in the form of a matrix. An example of this will follow in Section 2.3.
The density of states (DOS) probes the band structure and identifies the amount of states per unit energy [5, 7, 15]. This relationship is given by

\[
\text{DOS} (E) = \sum_{i}^{N} \frac{1}{2\pi} \int \frac{\delta[E_{i}(\vec{k}) - E]}{d\vec{k}},
\]

(2.6)

where \(E_{i}(\vec{k})\) is an energy of band \(i\) with wave vector \(\vec{k}\), and \(E\) is an energy in the 1st Brillouin Zone. Note that the sum is over \(N\) number of points in \(k\)-space and \(1/2\pi\) is the normalization constant. To implement the integral of a Delta function in Equation 2.6, a slightly more approachable form of the following is used [5]:

\[
\text{DOS}(E) \cong \sum_{i}^{N} \frac{1}{2\pi} \sum_{\vec{k}} \frac{K_B T}{[E_{i}(\vec{k}) - E]^2 + (K_B T)^2}.
\]

(2.7)

In Equation 2.7, the \(K_B T\) term is in units of energy (electron-Volt) where \(K_B\) is the Boltzmann constant and \(T\) is the absolute temperature. This energy term is adjustable in efforts to avoid excessive thermal-broadening and is typically set to very low values (below 0.2 eV) [5, 15] given that temperature is near 0 K. Thus, if the energy term is very low, the DOS will reveal sharp, discrete peaks such that the Delta function can spread into an observable continuum. However, if the energy term is relatively high, the DOS will appear more Gaussian-like and will not show discrete peaks.

Replacing the Delta function with a distribution function is desired since computers cannot computationally perform an integral. Thus, discrete sums must be used over all bands and all wave vectors. (Note that the Bloch wavefunction in Equation 2.3 has eigenvector \(\vec{k}\) and by
selecting discrete sums over orbitals means discrete $k$ are selected. The discrete grid can be defined by the smallest k-point taken, which represents the longest wavelength. This same technique will be used in Chapter 5). The DOS is an important calculation for describing the probability of finding electrons at certain energies and accompanies band structures when classifying the electronic properties of a material.

2.2 Green’s Function Theory

A straightforward technique to calculate conductance and local density of states (LDOS) is by using an equilibrium Green’s Function method. This method is designed to model ballistic transport for a material, under the assumption that no scattering occurs at leads when propagating into or out of the conductor [36]. Further, it is best to think of a nanostructure as being divided into three components: a left lead, a conductor, and a right lead. Figure 2.1 illustrates this below. The green highlighted sections represent leads and the orange highlighted section represents the bulk conductor.

Figure 2.1 - Schematic diagram of a nanoribbon modeled with leads and a conductor.
The Green’s Function methodology is taken from Li, et al and Kan, et al [9, 11]. Each piece of the structure in Figure 2.1 has a certain matrix affiliated with it. The conductance is typically derived using the Landauer Formula [5, 7, 36],

\[ G(E) = \frac{2e^2}{h} T(E). \] (2.8)

Here, there is a quantization of \( \frac{2e^2}{h} \) and \( T(E) \) is the transmission function. The transmission function is given in the form,

\[ T(E) = Trace[\Gamma_1 \cdot G_m \cdot \Gamma_2 \cdot G_m^\dagger], \] (2.9)

where \( \Gamma_1 \) and \( \Gamma_2 \) are the coupling functions of the left and right leads to the conductor and \( G_m \) and \( G_m^\dagger \) are the total retarded and total advanced Green’s Functions, respectively. Note that the subscript \( m \) indicates the mode. The advanced Green’s Function represents inward propagation of electrons while the retarded Green’s Function represents outward propagation. The coupling functions can be written as

\[ \Gamma_1 = i[\Sigma_1 - \Sigma_1^\dagger] \]
\[ \Gamma_2 = i[\Sigma_2 - \Sigma_2^\dagger], \] (2.10)

where \( \Sigma_{1,2} \) represents the self-energy matrices from the left and right leads respectively. Self-energy accounts for the potential felt by an electron due to the surrounding medium’s interactions with it. These matrices are calculated through an iterative process [4, 7, 9]. The Green’s Functions are given by

\[ G_m = [EI - H_c - \Sigma_1 - \Sigma_2]^{-1}, \] (2.11)
where $E$ is the total energy, $H_c$ is the Hamiltonian of the conductor and $I$ is the identity matrix.

Note that Equation 2.11 represents the retarded Green’s Function. The advanced Green’s Function can be found by taking the conjugate transpose of that in Equation 2.11. When the retarded Green’s Function is found, the LDOS of atomic site $i$ can be expressed by taking the imaginary part:

$$LDOS_i(E) = \frac{-1}{\pi} Im[G_m(i, i)].$$

(2.12)

The LDOS is a miniature version of the total DOS, except it shows the amount of states at energies for a single atomic site only. To find the total density of states of all the atoms in a periodic unit cell, a summation over all the sites (Green’s Functions) yields Equation 2.6:

$$DOS(E) = \frac{-1}{\pi} Im[Trace[G_m]].$$

(2.13)

Note that Equation 2.13 and Equation 2.6 are equivalent and will produce the same plots. These will be covered in Chapter 4.

### 2.3 Calculating Hamiltonian Matrix Elements

Now, an example calculation to obtain matrix elements for an $N=3$ dimer armchair ribbon of hexagonal boron nitride will be presented. Figure 2.2 below shows the typical set up for this example with each atom numbered in cell I and the three consecutive unit cells (I-1, I, and I+1) are labeled as well. In this case, the primitive unit cell is one complete hexagon, composed of six atoms, as the nanoribbon is infinite in one dimension.
Figure 2.2 - TB set up for an ABNNR with numbered atomic sites and the two nearest neighbor unit cells. Dotted red lines indicate the lattice constant of the unit cell.

Note that the distance between centers of consecutive cells is the lattice constant 3\(a\), where \(a\) is the bond length between neighboring atoms. By geometry, the distance between the dotted red lines in Figure 2.2 is also the lattice constant. In order to obtain matrix elements, it is important to assign each unit cell its own location in relation to an arbitrary point of reference as well as each individual atomic site within that unit cell. Let \(R_I\) denote the location of the \(I^{th}\) unit cell and let \(\tau_J\) denote the locations of each orbital (as phase factors) inside the \(I^{th}\) cell. From Huckel theory, the \(p_z\) orbitals are utilized and thus, the six atomic sites can be viewed as six atomic orbitals. Then, by combining Equation 2.3 and Equation 2.4, a Bloch wavefunction is constructed for the \(I^{th}\) unit cell:

\[
|\psi_{nk}\rangle = \sum_I e^{i\vec{k} \cdot \vec{R}_I} \sum_{J=1}^6 e^{i\vec{k} \cdot \vec{\tau}_J} C_J |\varphi_J\rangle.
\]

(2.14)

Here, the coefficient \(C_J\) is a constant associated with the charge probability amplitude of orbital \(\varphi_J\). The coefficients must be solved analytically in order to satisfy Equation 2.5. Next, the scalar
product of each of the six orbitals in cell I is taken on both sides of Equation 2.5. For this example, only orbital 1 in the Ith cell will be used to calculate its interactions on neighboring orbitals. This process yields

$$\langle \psi_{nk} | \hat{H} | \varphi_{1l} \rangle = \langle \varphi_{1l} | E | \psi_{nk} \rangle,$$

(2.15)

$$C_1 e^{i \vec{k} \cdot (\vec{R}_1 + \vec{t}_1)} \langle \varphi_{1l} | \hat{H} | \varphi_{1l} \rangle + C_2 e^{i \vec{k} \cdot (\vec{R}_1 + \vec{t}_2)} \langle \varphi_{1l} | \hat{H} | \varphi_{2l} \rangle + \cdots + C_6 e^{i \vec{k} \cdot (\vec{R}_1 + \vec{t}_6)} \langle \varphi_{1l} | \hat{H} | \varphi_{6l} \rangle = C_1 e^{i \vec{k} \cdot (\vec{R}_1 + \vec{t}_1)} \langle \varphi_{1l} | E | \varphi_{1l} \rangle.$$

(2.16)

For simplicity, $R_I$ is taken to be at the site of atom 1, which is zero. Since there is a restriction to only nearest neighbor interactions, orbitals 2 and 3 are interacting on orbital 1 (as well as the interaction of orbital 1 with itself). Therefore, any other scalar products not including the nearest neighbor orbitals are shown to be zero using the orthogonality relationship [35]:

$$\langle \varphi_i | \hat{Q} | \varphi_j \rangle = Q \delta_{ij}.$$

(2.17)

In this case, any observable $\hat{Q}$ (i.e. the Hamiltonian) is preserved through a Kronecker delta only if $i=j$. Note that any constants in the place of $\hat{Q}$ can be factored out of Equation 2.17. If $i \neq j$, the entire term vanishes. Thus, any scalar products including orbitals 4, 5, and 6 vanish and the following remains,

$$C_1 e^{i \vec{k} \cdot \vec{r}_1} \langle \varphi_{1l} | \hat{H} | \varphi_{1l} \rangle + C_2 e^{i \vec{k} \cdot \vec{r}_2} \langle \varphi_{1l} | \hat{H} | \varphi_{2l} \rangle + C_3 e^{i \vec{k} \cdot \vec{r}_3} \langle \varphi_{1l} | \hat{H} | \varphi_{3l} \rangle = C_1 e^{i \vec{k} \cdot \vec{r}_1} \langle \varphi_{1l} | E | \varphi_{1l} \rangle.$$

(2.18)

Note that the first term on the left hand side and the right hand side both have the same exponential term. Dividing by this exponential term on both sides leaves
\[ C_1 \langle \varphi_{1l}|\hat{H}|\varphi_{1l}\rangle + C_2 e^{i\vec{k} \cdot (\vec{r}_2 - \vec{r}_1)} \langle \varphi_{1l}|\hat{H}|\varphi_{2l}\rangle + C_3 e^{i\vec{k} \cdot (\vec{r}_3 - \vec{r}_1)} \langle \varphi_{1l}|\hat{H}|\varphi_{3l}\rangle = C_1 \langle \varphi_{1l}|E|\varphi_{1l}\rangle. \]  

(2.19)

It is easy to see that the second and third scalar products in Equation 2.19 include phase factors. The difference in these phase factors as seen in these terms describes the location of orbital \( \tau_j \) in relation to the location of orbital \( \tau_i \). Thus, the orbital interactions \( \langle \varphi_{1l}|\hat{H}|\varphi_{2l}\rangle \) and \( \langle \varphi_{1l}|\hat{H}|\varphi_{3l}\rangle \) both become \( V_{pp\pi} \) (as described using Equation 2.2). This is the hopping parameter in the Hamiltonian from Equation 2.1. There is no phase factor included with the first scalar product, as it represents an orbital interaction with itself. Thus, \( \langle \varphi_{1l}|\hat{H}|\varphi_{1l}\rangle \) can be rewritten as \( \varepsilon_{11} \), which is the onsite energy of orbital 1 in Figure 2.2. Using these facts, the result is a linear equation accounting for all the interactions of orbital 1 in cell I:

\[ \varepsilon_{11} C_1 + V_{pp\pi} C_2 e^{i k a} + V_{pp\pi} C_3 e^{-i k a/2} = E C_1. \]  

(2.20)

The onsite energies and hopping parameters are known values and can be calculated accordingly, as mentioned in Section 2.1. Using Figure 2.2, another simplification can be made: it is important to know that \( \varepsilon_{11} \) is the same as \( \varepsilon_B \), which is the onsite energy of boron. Further, the onsite energy atom 2 is denoted \( \varepsilon_{22} \) which is the same as \( \varepsilon_N \), the onsite energy of nitrogen. These substitutions can be made for each of the onsite energies \( \varepsilon_{ii} \) at site \( i \) depending on if it is a boron or nitrogen atom in this case.

This process of obtaining other matrix elements is similar for all other orbitals in the same unit cell. It is understood that since the hexagon in Figure 2.2 is periodic, atoms 3 and 4 are indeed interacting with neighboring cells, I-1 and I+1, respectively. On the other hand, this analysis can be applied to graphene since the lattice is identical to that of hexagonal boron nitride (except for the bond length and atomic species).
After taking scalar products of all six orbitals, the end result is a system of six linear equations with similar form to that of Equation 2.20. This means the Hamiltonian can be written as a matrix with the coefficients $C_j$ listed as a column vector on the left hand side of Equation 2.20. Likewise, on the right hand side of Equation 2.20, the energy $E$ can be factored out from the column vector of coefficients. The result is an eigenvalue equation where the Hamiltonian matrix can be solved for energies by taking the determinant. The Hamiltonian matrix produced is of the form

$$H = \begin{pmatrix}
\varepsilon_B & V_{pp\pi}e^{ika} & V_{pp\pi}e^{-ika/2} & 0 & 0 & 0 \\
V_{pp\pi}e^{-ika} & \varepsilon_N & 0 & V_{pp\pi}e^{ika/2} & 0 & 0 \\
V_{pp\pi}e^{ika/2} & 0 & \varepsilon_N & V_{pp\pi}e^{-ika} & V_{pp\pi}e^{ika/2} & 0 \\
0 & V_{pp\pi}e^{-ika/2} & V_{pp\pi}e^{ika} & \varepsilon_B & 0 & V_{pp\pi}e^{-ika/2} \\
0 & 0 & V_{pp\pi}e^{-ika/2} & V_{pp\pi}e^{ika} & \varepsilon_B & 0 \\
0 & 0 & 0 & V_{pp\pi}e^{ika/2} & V_{pp\pi}e^{-ika} & \varepsilon_N
\end{pmatrix}.$$  

(2.21)

For a unit cell of six atoms (orbitals) in our particular ABNNR, there will be six eigenvalues in the form of energy as a function of the wave vector in one dimension. These six eigenvalues will correspond to six bands when energy is plotted against the wave vector. In general, N orbitals yield N bands in the energy band structure of a material. Energy band structures and DOS for both BNNRs and GNRs are shown in Chapter 4.

2.4 Summary

The TB Model has been introduced in this chapter. It is not an exact calculation because by using Huckel Theory, only $p_z$ orbitals are used. The interactions of any $p_z$ orbital are restricted to its nearest neighbors. The Bloch wavefunction of an electron is written as a LCAO and
Bloch’s Theorem is applied due to the periodicity of the structure. Then, the Hamiltonian matrix can be obtained by taking scalar products of various orbital interactions. Through this process, the electronic properties of these nanoribbons such as energy band structures and DOS can be found. Green’s Function Theory is used to calculate conductance with the help of the Landauer Formula. Nanoribbons are modeled as ballistic conductors with no scattering at the leads. LDOS can be calculated from the retarded and advanced Green’s Functions. The total DOS can also be found by summing over the individual LDOS of each atomic site. The Tight-Binding Model and Green’s Function Theory are both simple approaches and help us obtain the electronic properties of BNNRs and GNRs.
Chapter 3: Density Functional Theory

In this chapter, I will explain Density Functional Theory (DFT) from the perspective of a user. This theory is similar to that of the TB Model, yet one difference is that the ground state properties of an electronic system can be determined by only knowing the electron density of the system. In addition, this chapter discusses the pros and cons of this theory compared to Tight-Binding and the computational methodology used to calculate such properties.

3.1 Why Density Functional Theory?

Density Functional Theory (DFT) was first established in the mid 1960’s [38-40]. It is a much more careful approach to calculate electronic properties of the ground state. Since the 60’s, the usage of DFT amongst physicists and chemists who perform electronic structure calculations has been steadily increasing in popularity in the scientific community [8, 22, 26, 37]. Its popularity is owed to the ability to simplify the Hamiltonian of an electronic system by reducing a many-body problem to a single-body problem given that one knows information about the electron density. This is achieved through the use of functionals and a series of approximations which will be explained in the following section.

Alternatively, DFT can reign supreme over TB calculations in a few ways. For example, in the previous chapter, a TB Model with Huckel Theory is used, which only uses a single atomic orbital per atom to obtain matrix elements. Recall that the LCAO gives a description about the electronic systems of graphene and hexagonal boron nitride. However, in DFT, a linear combination of plane waves is enough to describe all valence orbitals without restrictions like in the Huckel theory and hence, a more complete picture about the electronic structure can be
formed. Therefore, TB calculations can lack more information than what DFT can provide even though both methods do impose periodic boundary conditions on all systems.

It is also important to take into account the computational time. DFT calculations – as a result of correct parameter settings and system description – can take many hours or days to complete (a supercomputer or computational cluster may come in handy!). For those who only wish to look at basic interactions with no complexity, the TB Model is sufficient with the use of a simple computer program. Note that if one were to use the either model for \(10^{23}\) \(p_z\) orbitals in a given system, there would be \(10^{23}\) positions for each orbital in a single wavefunction with coefficients and eigenvalues that must be solved for simultaneously. Obviously, this is a very difficult endeavor and is realistically impossible to solve. Thus, DFT is an excellent second choice to tackle electronic structure calculations for large and difficult systems.

One of the interesting incentives that DFT offers is the ability to visualize electronic systems. This means one is able to produce visualizations of the electron density, changes in its density, and orbitals, among other things. These visualizations are considered useful when analyzing band structures and DOS. Examples of these visualizations will be shown in Chapter 6.

### 3.2 Describing an Electronic System

#### 3.2.1 The Many Body Hamiltonian

Suppose there is a system of many atoms, with electrons orbiting around their respective nuclei. The Hamiltonian of the system can be properly written as
\[ H = -\frac{\hbar^2}{2m_e} \sum_N \nabla_i^2 - \sum_{i,l} \frac{Z_i e^2}{|\vec{r}_i - \vec{R}_l|} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} - \sum_i \frac{\hbar^2}{2M_i} \nabla_i^2 + \frac{1}{2} \sum_{i \neq j \neq k} \frac{Z_i Z_j e^2}{|\vec{R}_i - \vec{R}_k|}. \]  

(3.1)

Here, the first term describes the kinetic energy of \( N \) electrons, which includes \( m_e \) as the mass of the electron. The second term is an external potential between electron \( i \) and nucleus \( I \) with \( \vec{r}_i \) and \( \vec{R}_l \) being the positions of the electrons and nuclei, respectively; \( Z_i \) is the charge of the nucleus \( I \). The third term is composed of the Coulomb potential between two electrons at positions \( \vec{r}_i \) and \( \vec{r}_j \). The fourth term is the kinetic energy of nucleus \( I \) with \( M_I \) being the mass of the nucleus. The fifth and final term is the potential between nucleus \( I \) and nucleus \( J \), where \( Z_J \) is the charge of another nucleus. This five-term Hamiltonian is bothersome if one were to use it and try to solve the Schrodinger Equation outright. The wavefunction must be a mix of each electron’s position and each nucleus’ position, so Equation 3.1 is very much a many-body problem.

Note that in the fourth term in Equation 3.1, the mass of a nucleus is much more massive compared to the mass of the electron. Then, the motion of nuclei can be treated as stationary compared to the motion of electrons. This means that the nuclei create a net positive, constant potential and the electrons move in this potential. This approximation is known as the Born-Oppenheimer Approximation [35, 40]. To simplify Equation 3.1 further, the nuclear kinetic energy term is removed and the nuclear potential energy term is a constant which is absorbed into a net external potential. For the sake of units, let \( \hbar = m_e = e^2/4\pi\varepsilon_0 = 1 \). This gives,

\[ H = -\frac{1}{2} \sum_N \nabla_i^2 - \sum_{i,l} \frac{Z_i}{|\vec{r}_i - \vec{R}_l|} + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\vec{r}_i - \vec{r}_j|}. \]  

(3.2)
or simply put,

\[ \hat{H} = \hat{T}_e + \hat{V}_{\text{ext}} + \hat{V}_{\text{ee}}. \]  

(3.3)

By using atomic units for the constants listed above, the new unit of energy is known as a Hartree (1 Ha = 27.2 eV) and distance is in Bohr radii (1 Bohr = 0.529 Å) [41-43].

Upon inspection of Equation 3.3, a many-body problem is still present and is not easy to solve. Luckily, two physicists by the names of Hohenberg and Kohn coined two fundamental theorems that provide the framework for DFT. These are known as the Hohenberg-Kohn Theorems [38, 40].

The first theorem says that for any system of interacting particles in an external potential, the potential is determined uniquely by the ground state density. This fact directs us to the second theorem. The second theorem says that there exists a universal functional for the energy \( E[n] \) in terms of the electron density and holds true for any external potential. Thus, the ground state energy of the system is a minimum of this functional and the density that minimizes the functional is the exact ground state density. Using a functional means that electron density depends on position and intuitively, energy depends upon the electron density. So if the ground state wavefunction is given as \( \Psi_0 \) with an associated ground state electron density \( n \), then

\[ E[n] = \langle \Psi_0[n] | \hat{T}_e + \hat{V}_{\text{ext}} + \hat{V}_{\text{ee}} | \Psi_0[n] \rangle. \]  

(3.4)

This expectation value shows that the ground state energy is just

\[ E[n] = T_e[n] + V_{\text{ext}}[n] + V_{\text{ee}}[n]. \]  

(3.5)
3.2.2 The Kohn-Sham Approach

Equation 3.5 gives a relationship between the electron density and the energy. Yet, this isn’t the end of the story. The task is to find an expression for this equation that is suitable to provide the ground state energy (and from minimizing this, solve for the electron density). Another physicist by the name of Sham teamed up with Kohn and suggested that if the real electron density made up of interacting electrons were replaced with a fake density composed of non-interacting, independent electrons, Equation 3.5 can then be solved. This is known as the Kohn-Sham Approach [39, 40].

Through this new model, Kohn and Sham developed an ansatz: suppose the electron density is the sum of the probabilities of orbitals \( \Psi_{nk} \) at point \( \vec{r} \) over \( n \) bands and all wave vectors \( k \):

\[
n(\vec{r}) = \sum_n \sum_k |\Psi_{nk}(\vec{r})|^2 f_{nk}.
\]

Here, \( f_{nk} \) is the occupation of states \( k \) in band \( n \) at position \( r \) and ranges from 0 to 2 to include the effects of spin (Note that spin was not included with wavefunctions in the TB Model and magnetic properties are not of our interest; thus, spin is ignored DFT-based results). The momentum states \( k \) are usually represented in the form of a grid, as Section 3.3 and Section 5.4 will elaborate.

Using this ansatz, Kohn and Sham (KS) were able to write the energy of the new system in the form of
\[ E_{KS}[n] = T_{KS}[n] + \int V_{ext}(\vec{r}) n(\vec{r}) d\vec{r} + E_{Hartree}[n] + E_{XC}[n] + E_{II}. \]  

(3.7)

where \( T_{KS}[n] \) is the kinetic energy of the orbitals, \( V_{ext} \) is the interaction between electrons and nuclei, \( E_{II} \) is the interaction between nuclei. \( E_{Hartree}[n] \) is the Hartree energy, also known as the static charge density energy. This is written as

\[
E_{Hartree}[n] = \frac{1}{2} \int \int \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3r d^3r'.
\]

(3.8)

This, however, is inaccurate because charge densities aren’t static in an electronic system. Thus, \( E_{XC}[n] \), the exchange-correlation (XC) energy, is introduced. It is best to think of this energy as a correction due to using the static charge density energy in Equation 3.7, with the XC term being dependent upon the correlated electron motion. It takes into account small fluctuations or redistributions of charge (i.e. Coulomb repulsion), plus the influence from Fermi statistics (i.e. Pauli Exclusion Principle). The theory of defining the XC energy is discussed in a variety of references and will not be studied in detail [37, 39-43]. However, an XC energy must be defined in Equation 3.7 in order to obtain the ground state energy.

### 3.3 Computational Methodology

Given Equation 3.7, the ground state energy can be solved for. Yet, one must consider the appropriate orbitals in terms of \( n(\vec{r}) \) to solve it. For Kohn and Sham, the final step is to apply a minimization condition with the constraint that orbitals must be normalized. Recall from Chapter 2 that Tight-Binding also uses the normalization condition for orbitals. In order to apply this
energy minimization, one must look to calculus of variations which is explained in detail by others [41-43]. If one minimizes the total energy in Equation 3.7 with respect to the orbitals, the final result is of the form:

$$-\frac{\hbar^2}{2m} \nabla^2 \Psi_{nk}(\vec{r}) + V_{KS}(\vec{r})\Psi_{nk}(\vec{r}) = \varepsilon_{nk} \Psi_{nk},$$

(3.9)

where $\Psi_{nk}(\vec{r})$ is an orbital that gives the ground state density in Equation 3.6 and

$$V_{KS}(\vec{r}) = V_{ext}(\vec{r}) + V_{Hartree}(\vec{r}) + V_{XC}(\vec{r}).$$

(3.10)

where $V_{ext}$ is the external potential caused by the nuclei, $V_{XC}$ is the XC potential. It should be pointed out that the Kohn-Sham potential $V_{KS}(\vec{r})$ can be produced by taking the functional derivative of the energy with respect to the number density [40-43]. Included with these three terms is the Hartree potential that is defined to be

$$V_{Hartree} = \int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3 r',$n

(3.11)

which is the simple electrostatic potential of a charge density at position $r'$.

Equation 3.9 above is referred to as the Kohn-Sham Equation [39, 40], a modified form of the Schrödinger Equation. Note that Equation 3.9 also yields eigenstates $\Psi_{nk}$ and eigenvalues $\varepsilon_{nk}$, just like Equation 2.5 in the TB Model (Chapter 2).
3.3.1 The Self-Consistent Field Cycle

To solve the Kohn-Sham Equation with a computer, a self-consistent process is used and described in Figure 3.1 below.

Figure 3.1 – Flow chart of the self-consistent field cycle used to solve Equation 3.9 (the Kohn-Sham Equation).
Figure 3.1 above gives the flow chart describing the self-consistent field (SCF) cycle used to solve the Kohn-Sham Equation. It is a total of six major steps. First, the user supplies an initial guess for the electron density (which also gives the ‘guessed’ wavefunction). Second, the effective potential is calculated from the external potential, Hartree potential, and the XC potential (by choosing an appropriate functional). Third, the wavefunctions of orbitals are found using the Kohn-Sham Equation. Fourth, the method calculates a probability amplitude of both the new and initially guessed wavefunctions, comparing the two. If the initial and the newly calculated probability amplitudes are not within a certain tolerance, the program goes back to the first step and cycles through until the initial and newly calculated probability amplitudes fall within that tolerance. If the probability amplitudes are within the defined tolerance, the loop proceeds to the last step. The sixth and final step is to calculate the ground state energy using this information. Note that by knowing the probability amplitude of the wavefunction, the electron density is also known. Thus, the fifth step could also be described as a check for a similar electron density.

3.3.2 Issues in Implementing Density Functional Theory

In order to successfully model an electronic system and implement DFT, there are a variety of methods. One commonly used method is the plane-wave pseudopotential method, which is used in this work. Other common methods include the augmented plane-wave method and the localized orbital method to perform DFT calculations [40]. However, these methods are out of the scope of this thesis.

The plane-wave pseudopotential method is useful for periodic systems with small unit cells such as crystals. For modeling BNNRs (which can have widths as small as four atoms) and hexagonal boron nitride as an infinite sheet (where two atoms are all that is needed to replicate a
sheet), this method is perfect since periodic boundary conditions are defined to replicate the overall structure of both materials. In addition, there is no need for a large amount of plane-waves to describe the system. However, if one wishes to use this method with a large unit cell – composed of many orbitals – a large amount of plane-waves would be needed. This also dramatically increases computational time even though it produces an exact result. On the other hand, if a system is not periodic in one or more directions, this approach will require more care, as Chapters 5 and 6 will elaborate.

For this work, ABINIT is the software of choice. ABINIT is a pseudopotential plane-wave expansion package which is used to implement DFT and produce ground state energies and other calculations using the SCF cycle [44]. The software allows the user to define a geometric, periodic system of atoms which are represented by plane waves. The user is able to control any periodic geometry and physical aspects of the system such as the definition of atoms, placement of atoms, and any periodic boundary conditions, among other parameters. Thus, it is a perfect fit if one wishes to model crystalline structures.

In order to use a plane-wave pseudopotential code like ABINIT, one must supply a plane-wave basis set and a pseudopotential. The plane-wave basis set will be explained in this section first. Recall that Equation 2.3 describes the Bloch wavefunction. For the sake of notation, Equation 2.3 can be rewritten as

\[ \Psi_{nk}(\vec{r}) = C_{nk}(\vec{r})e^{i(\vec{k} \cdot \vec{r})}, \]

(3.12)
with crystal momentum $\hbar k$. In the plane-wave pseudopotential implementation of DFT, $C_{nk}(\vec{r})$ is a function with the periodicity of the crystal which can be expanded as a set of plane-waves of the form

$$C_{nk} = \sum_{\vec{G}} c_{n,k+\vec{G}} e^{i(\vec{k}+\vec{G}) \cdot \vec{r}},$$

(3.13)

where $c_{n,k+\vec{G}}$ are constant coefficients and $\vec{G}$ being a reciprocal lattice vector that obeys periodic boundary conditions [34]. Equation 3.13 is the plane-wave basis set ABINIT uses for its calculations. The $G$-vectors are defined by the following connection:

$$\vec{G} \cdot \vec{T} = 2\pi N,$$

(3.14)

where $\vec{T}$ is a translational lattice vector in real space and $N$ is an integer. But which $\vec{G}$ vectors are suitable to satisfy this equation? There are an infinite number of $\vec{G}$ vectors that satisfy Equation 3.14, yet a computer is performing the calculations and cannot count to infinity. The requirement is that there needs to be a maximum $G$-vector that serves as a “cutoff.” Then, a new quantity can be defined, known as the cutoff energy (in units of Hartrees) which is given by,

$$E_{cut} \geq \frac{|k + \vec{G}_{max}|^2}{2}.$$  

(3.15)

Here, $E_{cut}$ is fixed for all $k$, and $G_{max}$ is then determined as the largest $G$-vector for a given wave vector $k$ for which Equation 3.15 is satisfied. The user is able to control the amount of plane waves sent through the periodic electronic system up to some maximum $\vec{G}$ vector [41, 43]. Like Equation 2.3 in Chapter 2, by selecting a finite number of $G$-vectors, this implies a finite
number of bands $n$ and wave vectors $k$ must also be selected. The discussion on this process for selecting a finite number of wave vectors will be explained in Chapter 5. Note that by picking both of these options will lead to the creation of the energy band structure and the DOS by solving Equation 3.9.

Coupled with the plane-wave expansion, pseudopotentials are required in order for ABINIT to calculate a ground state density [44, 46]. Pseudopotentials are fake potentials that remove core electrons, while keeping their effects on valence electrons. The user is able to choose an appropriate pseudopotential for any atomic species, depending upon their desire as how to model the core electrons. A calculation including an all-electron potential, and the huge number of plane-waves needed to get core orbitals, would take an absurd amount of time though it would yield very accurate results. Thus, pseudopotentials enable computational time to be greatly reduced and discourage wasting of computational resources. Studying pseudopotentials is not a focus of this thesis but have been investigated by others in recent years [40-43]. A brief description of the pseudopotentials used for this thesis work will be mentioned in Chapter 5.

3.4 Density Functional Theory vs. Tight-Binding

It is best to put all this into perspective against the TB Model. While the TB Model isn’t a hard calculation, it is still useful for those wishing for a sufficient amount of information to obtain energies, band structures, and DOS by empirical means. Matrix elements are calculated with onsite energies and by the hopping parameter, yet they are restricted to a single valence orbital, meaning that unwanted interactions with other valence orbitals are thrown out. A simple program using Mathematica suffices to get the job done [45]. DFT is a power-house chock full of finely tunable gears which can be adjusted for calculation quality and exact results produced
from a self-consistent calculation. This means matrix elements are calculated exactly between all orbitals in the system when solving the Kohn-Sham Equation and no information is lost. DFT requires however, a great deal of information regarding the electronic system for input whereas TB does not. Yet, both theories solve the Schrodinger Equation in some form or another. DFT branches off from TB in Equation 3.6, where the electron density is written as a sum of wavefunctions. This ansatz is the primary difference between TB and DFT.

The version of DFT mentioned in this work uses a linear combination of plane-waves (LCPW) and expands them to solve for the ground state electron density, which can be used to find the ground state energy of a system. The plane-wave coefficients come from an energy minimization technique which are a priori. TB uses a linear combination of atomic orbitals (LCAO) to solve for the energy based off experimental and/or theoretical findings.

Both of these theories allow us to produce band structures and DOS, as Chapters 4 and 6 will show. In addition, DFT-based results can be a bit more interesting to interpret than those produced from the TB Model. When using the LCPW, more valence orbitals are required for the energy calculation and the use of pseudopotentials freeze out the core electron interactions. With the LCAO, in our particular TB Model, Huckel Theory is used to calculate select interactions using a single valence orbital.

To compare the two methods in a crude manner, let’s think of the TB Model as a conventional toaster oven and DFT as a professional chef-approved oven. The ingredients to bake cookies signify the input parameters and information required about the electronic system to perform the calculation; the ovens represent the mathematical engines and capabilities of both models; and the resulting cookies exhibit the results from both computational programs. Due to the assumptions and lack of exactness with its baking capabilities, the conventional toaster oven
(TB) will produce an under-baked cookie. However, the chef-approved oven (DFT) will produce a highly exceptional cookie that is perfectly baked and appears a bit more interesting than the prior. It is common to understand that researchers try to produce the most accurate results as possible that fit their models. Thus, it is no surprise that most have turned to DFT-based calculations for their work in electronic structure. In the end, the “DFT cookie” will be a more exotic, gourmet treat.

3.5 Summary

In short, DFT is a means to calculate the total energy of a system given the electron density. Through some approximations, the difficult many-body interacting system of electrons was replaced with a simpler, single-body problem. The Hohenberg-Kohn Theorems are the heart of DFT and allow energies to be written in terms of functionals. Kohn and Sham simplified the problem even further by using an ansatz that suggested the electron density is a sum over single-particle, occupied orbitals and all possible spins. The SCF cycle as a means to solve the Kohn-Sham Equation was also introduced. In the plane-wave pseudopotential approach to DFT, the orbitals are a linear combination of plane-waves which solve the Kohn-Sham Equation to arbitrary accuracy (or exactly only if the maximum G-vector goes to infinity), while leaving out no restriction on valence orbital interactions. ABINIT is the plane-wave pseudopotential package of our choice for DFT-implemented calculations. Using DFT and ABINIT, energy band structures and DOS can be produced. Comparisons and differences were also presented regarding DFT versus TB.
Chapter 4: Electronic Properties via Tight-Binding and Green’s Function Theory

Here, I will present the electronic properties from the TB Model and Green’s Function Theory. Results include band structure, DOS, quantized conductance and local density of states (LDOS) for ABNNRs and ZBNNRs. Next, I will investigate band gap engineering via edge modulation of BNNRs which affect both the band structure and DOS. After this, I will show the conductance for various widths with and without edge perturbations. At the end of this chapter, these properties will be compared to properties of GNRs.

4.1 Energy Band Structures and Density of States (BNNRs)

Energy band structures provide a great deal of information regarding the material in question. Typically, one can classify the electronic properties by inspecting the band structure. This allows one to identify the material as a metallic object, semiconductor, or insulator. These calculations are plots of the energy versus the wave vector. It is useful to think of the wave vector as k-space, where k represents the momentum state due to the crystal structure. Using the band structure, we can also obtain the DOS. The DOS reveals the number of states per lattice length per unit energy. Essentially, one can find energy states at which electrons can reside from this plot. The DOS always corresponds to and reflects its appropriate band structure.
4.1.1 Armchair Boron Nitride Nanoribbons

Recall that armchair boron nitride nanoribbons (ABNNRs) have an edge structure as shown in Figure 1.2(a). The unit cell is composed of three dimers with six atoms arranged into a hexagon. Figure 4.1 below shows the band structure and DOS for an ABNNR of N=3 dimers over the 1st Brillouin Zone.

![Figure 4.1](image)

**Figure 4.1** – (a) Band structure and (b) DOS for the unit cell of an ABNNR with N=3 dimers.
In this case, there are only six $p_z$ orbitals in the unit cell so six bands are visible. It is easy to notice that there is symmetry about the Fermi level, which is taken to be 0 eV for the remainder of this thesis. Below the Fermi level, three valence bands are present. Similarly, above the Fermi level, three conduction bands are present. The symmetry represents occupied and unoccupied states that result from using the $p_z$ orbitals from Huckel theory. Also observed in the band structure is a band gap—a primary criterion for classifying a materials’ electronic behavior. Note that since the band gap is large (5.44 eV) at $k=0$, an ABNNR of one complete hexagon (or N=3 dimers) is considered to be an insulator.

If an electron is supplied enough energy in the valence bands and the energy is enough to overcome the band gap, the electron will jump to the conduction bands. However, there are only a certain amount of states that electrons can reside in. Thus, the DOS probes the band structure and identifies the amount of states at certain energies. The flat areas of any band (where the slope is zero) yield a high number of states, exhibited as a sharp peak in Figure 4.1(b). Notice that in the region where the band gap exists, the DOS is zero. Since there are no bands in this region, there are no states available. The amount of states in the outer valence bands and outer conduction bands near ±8 eV in this particular ABNNR are lower compared to states at ±4 eV, other states exist at varying energies.

Recall from solid state physics that for a free particle, energy is related to momentum by

$$E = \frac{\hbar^2 k^2}{2m},$$

(4.1)

where $m$ is the mass of the particle (in our case, the electron) and $k$ is the wave vector. If the bands have a parabolic feature, this indicates that the electrons can freely propagate throughout
the lattice as a Bloch wave. When bands have flat sections with no curvature, this indicates that the denominator in Equation 4.1 must be very large compared to the numerator. Thus, there can be an effective mass of the electron that is infinitely heavy. The flat sections of the bands in Figure 4.1(a) show states consisting of infinitely heavy electrons. Composed of several bands which are observed at roughly ±4 eV, two distinct flat bands can be seen. Electrons virtually cannot move at these energies due to their infinite mass. Consequently, the DOS shows a high response at these energies. Note that for the remainder of this thesis, this “flat band” in ABNNR band structures will be referred to as the “stationary state.” Since \( \pi \) orbitals are utilized in the band structure, it is proposed that the “stationary state” is a state where the orbitals sit on top of the ABNNR, sticking out of the plane (This will be referred to later on in Chapter 6).

If the width of an ABNNR increases, the number of bands increases. Experimentally, nanoribbon widths have been observed with widths ranging from 15 Å to several hundred micrometers by unwrapping boron nitride nanotubes [24]. Figure 4.2 shows the band structure and DOS for an ABNNR of N=9 dimers (~22.3 Å). Here, there are eighteen bands, indicating eighteen \( \pi \) orbitals in the Hamiltonian matrix. The DOS in Figure 4.2(b) has noticeable, sharp peaks at various energies throughout the band structure, indicating that there are high amounts of states at these energies. The DOS also shows that a large number of states lies less than 5 eV from the Fermi energy in both the valence bands and conduction bands. This indicates that more electronic states are kept near the Fermi level of the ABNNR. The band gap found for this particular ABNNR is 4.94 eV so it is also an insulator.
4.1.2 Zigzag Boron Nitride Nanoribbons

ZBNNRs have similar energy band structures in that they too exhibit insulating behavior. For example, Figure 4.3 shows the band structure and DOS for a ZBNNR of N=2 chains. Since a ZBNNR’s smallest repeat unit has four orbitals, there are four bands in the band structure with a relatively low amount of states. There are two states present just above and below the Fermi
level, where the closest band gap is near the edge of the 1\textsuperscript{st} Brillouin Zone. Since this band gap is 4.83 eV between these two bands, we know this particular ZBNNR is an insulator.

Figure 4.3 – (a) Band structure and (b) DOS of ZBNNR of N=2 chains.

Keeping in mind that there are only four orbitals in a ZBNNR unit cell as opposed to six, there are not as many states available in this particular nanoribbon as in Figure 4.1. There is still symmetry about the Fermi level as well. If the width of the ZBNNR is increased, the same trend
can be seen as with ABNNRs: the number of bands increases, corresponding to that many extra orbitals in the Hamiltonian matrix. Figure 4.4 below shows the band structure and DOS for a ZBNNR of N=10 chains (20 atoms in a width of ~42.9 Å).

Figure 4.4 – (a) Band structure and (b) DOS of ZBNNR of N=10 chains.

In this band structure, the bands are rather close to each other, energetically closer to one another than those of the ABNNR of N=9 dimers (see Figure 4.2(a)). Thus, the DOS in Figure 4.4(b) is
high and shows many large peaks at their corresponding energies, indicating longer lifetimes as the energies approach the Fermi level. Notice that there is still a large band gap of 4.83 eV and zero states between the valence bands and conduction bands in the DOS plot, indicating that this ZBNNR is an insulator. Even though the width of the ZBNNR has changed, this has no effect on the band gap. It is important to see that the highest DOS values are near ±4 eV, far from the Fermi level. Upon closer inspection, notice that the highest valence band and the lowest conduction band have flat sections away from k=0. These two bands that split off from the grouping of other valence bands and conduction bands are typical of edge states. However, these edge states are closer to the Fermi level than the bands that meet at the edge of the 1st Brillouin Zone, which is at ±4 eV. Recall that for the ABNNR of N=9 dimers in Figure 4.2(b), the DOS revealed that the “stationary states” were also located at ±4 eV.

So far, we have seen that both types of BNNRs possess insulating electronic behavior due to the large band gap found between the valence bands and conduction bands. The bands are symmetric due to the pₗ orbitals used in Huckel theory and the DOS can be found accordingly. Also, the DOS revealed high amounts of states at specific energies, suggesting there are non-conducting states presents. Therefore, conducting states must contribute at other energies. It is now beneficial to study transport properties of BNNRs.

4.2 Quantized Conductance and LDOS of BNNRs

Recall from Chapter 2 that the transport properties of a system are characterized by its conductance. The Landauer Formula (Equation 2.8) requires us to know the transmission as a function of energy. Thus, conductance can be plotted against energy. Using the imaginary part of
the retarded Green’s function (Equation 2.12) we can also obtain the LDOS plots. The LDOS is the density of states for each individual atom.

4.2.1 Conductance

The conductance plot is shown along with the band structure for an ABNNR of N=9 dimers in Figure 4.5. Often times, an easy way to check conductance plots are by looking at the number of bands that cross at a certain energy. This corresponds to a quantized value of $2e^2/h$. This same connection has been made by Feng, et al [16]. Each band in the band structure can be thought of as a mode of transport for electron propagation.
Figure 4.5 – (a) Band structure and (b) conductance vs. energy for an ABNNR of N=9 dimers.

For example, at ±3 eV in Figure 4.5(a), two bands cross at this energy. Thus, the conductance is $2 \left(\frac{2e^2}{h}\right)$. Likewise, at ±4 eV, there are four bands crossing at this energy, so the conductance is $4 \left(\frac{2e^2}{h}\right)$. Note that in the band gap, the conductance drops to zero. This indicates that no transport occurs in the band gap and agrees with the DOS for this ABNNR (as seen in Figure 4.2). Recall that the “stationary states” occurring at ±4 eV make up a non-conducting band. This is easy to observe since at each value of k, the energy is the same. Due to this non-conducting band, the conductance of the ABNNR relies heavily on degeneracy.
Now, if the width of the ABNNR changes, we would expect the conductance to change as well. The number of bands in the band structure increases by two for each additional dimer. To see this, Figure 4.6 shows conductance vs. energy for different widths of ABNNRs.

![Figure 4.6 - Conductance vs. energy for different widths of ABNNRs.](image)

These conductance curves all show the quantization that’s expected from using the Landauer Formula and also have zero conductance when in the band gap. The larger width ribbons (say N=10 dimers) appear to have a band gap smaller than some of the smaller width ribbons (N=6 for example). The increase in width also allows for more modes of transport, given that the N=10 ABNNR produces a conductance value of $5 \left(\frac{2e^2}{h}\right)$ – a magnitude higher than what was observed in Figure 4.5 with the N=6 ABNNR.

However, ZBNNRs also undergo changes in conductance when width is taken into account. Figure 4.7 shows conductance curves for ZBNNRs of various widths.
ZBNNRs also have a large band gap and the curves in Figure 4.7 all reflect it accordingly. In the N=10 ZBNNR, there were only two flat regions in the band structure (Figure 4.4). Note that the ABNNRs appear to have a smaller band gap as the width increases. From Figure 4.7, it is seen that the conductance for all widths drop to zero as the energies approach the Fermi level and band gap region. This is due to the highest valence band and the lowest conduction band having flat segments away from k=0 (refer to Figure 4.4). So it appears as if the band gap remains constant as the width increases.

4.2.2 Local Density of States

To get a better understanding of the energetics and transport of the system, it is useful to observe the LDOS plots. The LDOS are able to show which atom individually contribute to transport and at which energies they occur. LDOS plots can also be used to confirm the total DOS for any BNNR since the DOS is a sum over all the LDOS of each atom. For this portion, I will explain the LDOS of an ABNNR and then explain it for a ZBNNR.
Figure 4.8 below shows the numbering scheme for atoms for an N=9 dimer (18 atom) ABNNR. The boron atoms are labeled as Atoms 1, 4, 5, 8, 9, 8’, 5’, 4’, 1’ and the nitrogen atoms are labeled Atoms 2, 3, 6, 7, 10, 7’, 6’, 3’, 2’ in the figure. Note that below the fifth dimer pair of the ABNNR, the primed atoms are labeled to differentiate between identical species with a similar numbering scheme for the LDOS plots.

Figure 4.8 - Schematic of an N=9 dimer ABNNR containing 10 unprime and prime numbered atoms to accompany LDOS plots.

Since the system is symmetric, only two full hexagons are necessary to study LDOS. All atoms below the fifth dimer pair (Atoms 9 and 10) are considered a reflection from across the center of
the ABNNR as shown in Figure 4.8. Thus, all corresponding unprime and prime labeled atoms will have the same LDOS characteristics. Figure 4.9 shows several LDOS plots as a function of energy for atoms 1 through 8 in an N=9 dimer ABNNR. The energy range on the x-axis of each plot in Figure 4.9 is the same as the band structure and DOS from Figure 4.2.

The first and most noticeable trait in each of the plots in Figure 4.9 is that the LDOS spikes infrequently at roughly ±4 eV, indicating each atom makes up a part of the non-conducting band as seen in Figure 4.2(a). This confirms what is seen in the band structure for the N=9 ABNNR since the so-called “stationary state” was composed of forbidden band crossings in both the valence bands and the conduction bands.

The second major trait we see is that the LDOS values are much lower than the DOS values in Figure 4.2(b). This is due to the fact that the total DOS (which is uniform and symmetric about the Fermi level) is a contribution from each individual p_z orbital. Now, since each orbital contributes to the total DOS, the LDOS is able to tell us which states are more boron-like or nitrogen-like. The large spike in the LDOS of Atom 1 (Figure 4.9(a)) is present at 4 eV, indicating this state and others surrounding it are boron-rich – which is obvious since the LDOS in this plot is of a boron atom. Similarly, the large spike in the LDOS of Atom 2 (Figure 4.9(b)) is present at -4 eV, indicating that this this state and others surrounding it are nitrogen-rich. The same idea can be applied to the other plots in Figure 4.9. Thus, the valence bands are more nitrogen-rich and the conductance bands are more boron-rich. This also gives a better understanding of the modes of transport as edge atoms have a very high amount of states near the Fermi level (Figure 4.9(a, b)) compared to the inner portions of the ABNNR (Figure 4.9(e, f)). All atoms contribute to transport to an extent, but inner atoms like Atoms 3-8 have states well beyond ±4 eV compared to edge atoms like Atoms 1 and 2. Thus, the inner atoms have more
modes for transport than the edge atoms. Also notice that neighboring atoms seem to have a symmetric reflection in the LDOS – for example, Atoms 7 and 8 are mirror images of each other. This is an example of reflective symmetry and must be due to only using \( p_z \) orbitals in Green’s Function Theory.
Figure 4.9 – LDOS vs. energy for corresponding to Atoms 1-8 for ABNNR in Figure 4.8, presented in (a) through (h) separately.
Since the DOS can be obtained from the LDOS, we expect that summing up all of the LDOS plots for each atom will yield an identical DOS for the N=9 ABNNR system (see Figure 4.2(b)). Figure 4.10 below shows the DOS from using Equation 2.13 from Green’s Function theory.

![Figure 4.10 - DOS vs. energy for N=9 ABNNR using LDOS information.](image)

The DOS in Figure 4.10 has identical shapes and features for the most part compared to Figure 4.2(b). However, the DOS obtained from Green’s Function theory has larger peaks at its most extreme energies (±9 eV) that match the “stationary state” at ±4 eV. This confirms that the DOS calculations agree with each other from both Tight-Binding and Green’s Function theory.

ZBNNRs are not atomically symmetric due to their alternating pattern of boron and nitrogen atoms down the width of the nanoribbon, though the structure itself exhibits symmetry. Another difference is that the edges are composed of one atom where one edge is solely composed of boron atoms and the other edge is solely composed of nitrogen atoms. We can easily expect that the edge atoms and inner atoms of the ZBNNR behave differently and exhibit
comparable properties. For reference, Figure 4.11 shows the numbering scheme for atoms in an
N=10 (20 atom) ZBNNR. The boron atoms are labeled as Atoms 1, 3, 5, 7, 9, 10’, 8’, 6’, 4’, 2’
and the nitrogen atoms are labeled as Atoms 2, 4, 6, 8, 10, 9’, 7’, 5’, 3’, 1’ in the figure.

Figure 4.11 - Schematic of an N=10 chain ZBNNR containing 10 unprime and prime
numbered atoms to accompany LDOS plots.
The unprimed labeled atoms are shown in Figure 4.12 with the LDOS. The primed labeled atoms are not shown, but serve as reflections from their corresponding unprimed atom. The ABNNR studied previously contained a reflective symmetry with each dimer pair in the LDOS plots and the same concept applies to this ZBNNR, but instead the symmetry is down the width of the ribbon. Notice that Atom 8 is a nitrogen atom, but its primed counterpart, Atom 8’, is a boron atom. Thus, the LDOS plots for these two atoms will be reflections of each other from across the Fermi level.

For the sake of simplicity, Figure 4.12 shows the LDOS for the first 8 atoms in Figure 4.11. Immediately noticed are the features that resemble the DOS shown in Figure 4.4(b), yet there are more states available on one side of the Fermi level than the other. Also noticed are the peaks that appear around ±4 eV in most of the plots (except for the LDOS of Atom 1 in Figure 4.12(a)). At this region of energies, most of the bands intersect with each other and exhibit degeneracy, as shown in Figure 4.4(a). It is also another confirmation of the boron-rich behavior of the conduction bands and the nitrogen-rich behavior of the valence bands due to their differing atomic Fermi energies. Note that the edge atom (Atom 1) has its largest peak just beyond 2 eV in Figure 4.12(a). This corresponds to the energy of the first conductance step on the conductance curve shown in Figure 4.7, suggesting that the boron sublattice (Atoms 1, 3, 5, 7, etc.) are responsible for the first mode of transport. Scanning through the rest of the LDOS plots, that same peak decreases with each inward atom of the nanoribbon. This confirms the edge state as described in Figure 4.4 and also indicates that there are more modes for transport with inner atoms, Atoms 2-8 (Figure 4.12(b-h)).
Figure 4.12 - LDOS vs. energy for corresponding to Atoms 1-8 for ZBNNR in Figure 4.11, presented in (a) through (h) separately.
Using the LDOS, one is also able to confirm the total DOS by summing up each of the plots individually. Figure 4.13 below shows the DOS of the N=10 ZBNNR. As expected, the Green’s Function Theory produces nearly the same DOS as shown in Figure 4.4(b).

Figure 4.13 - DOS vs. energy for N=10 ZBNNR using LDOS information.

The conductance and LDOS play a huge role in identifying transport properties and the behavior of such transport. The total DOS can also be produced from the LDOS information and is nearly identical to the DOS plots found in Section 4.1. Thus, both the Tight-Binding DOS and Green’s Function Theory DOS agree nicely.

4.3 Energy Band Structures and Density of States With Small Perturbations (BNNRs)

Since the electronic properties of BNNRs can be characterized by the edge structure (armchair or zigzag), it is intuitive to think about the effects of impurities or perturbation at the
edges once these 2D nanomaterials are fabricated experimentally. This is an important thought because once samples are brought into air or possibly contaminated, the structures themselves as well as the electronic properties can change. Edges and surfaces of BNNRs and GNRs are typically very sensitive to defects [12, 21]. For example, another 2D material – black phosphorus (phosphorene) – is unstable under room temperature conditions when exposed to air and its surface deteriorates [48]. A way to prevent deterioration or imperfection is by functionalizing or terminating edge bonds which preserve the structure and properties of a material. In general, hexagonal boron nitride is vulnerable to defects which are impossible to avoid in the manufacturing process [24, 49]. Hexagonal boron nitride has been studied in sheet, nanoribbon, and nanotube form with defects and researchers have found changes in band gap and electronic properties through these methods [14, 20, 30, 24, 50]. Applying stress or strain to these materials also yield similar effects [16, 23, 48].

For this section, I will focus on a simple method in which the onsite energies of the $p_z$ orbitals of select edge atoms (boron or nitrogen) are adjusted slightly. The adjusted onsite energies are valid only within a range of $\pm 3$ eV from the original energies ($\varepsilon_B = -6.64$ eV and $\varepsilon_N = -11.47$ eV), hence creating a small perturbation effect. Since the ionization energies for an electron in the 2p shell are 8.31 eV for a boron atom and 13.1 eV for a nitrogen atom, small values of perturbation are necessary in order to ensure the system does not become ionized [51, 52]. These small perturbations mimic techniques like edge functionalization or passivation. With these changes, one should expect both the band structure and DOS to change. These results and observations that will be presented are the first step in analyzing methods for tuning band gaps in BNNRs. It should be noted that perturbed BNNRs will be denoted as “imperfect structures.”
4.3.1 Perturbations in Armchair Boron Nitride Nanoribbons

First, the changes in band structure will be shown when perturbations are applied to the top edge boron atoms for a particular ABNNR. The general result holds true for ABNNRs of other widths as well. Figure 4.14 below shows band structures for an N=9 dimer ABNNR with the top edge boron atoms experiencing no perturbation, and perturbations of -1 eV, -2 eV and -3 eV, respectively.

Figure 4.14 - Band structures for an ABNNR of N=9 dimers with top edge boron atoms under (a) no perturbation and perturbations of (b) -1 eV, (c) -2 eV, (d) -3 eV, respectively.

The most noticeable trait is that the conduction bands become distorted and the first conduction band gets pulled down toward the Fermi energy with each increasing strength of perturbation. The energy levels are delocalized, meaning they are less concentrated in a small energy range.
The degeneracy found in Figure 4.14(a) disappears and more forbidden regions appear as the perturbation becomes stronger. The first conduction band finally settles at roughly 1 eV at k=0 (Figure 4.14(d)) compared to 2.5 eV when the ABNNR has no perturbations whatsoever (Figure 4.14(a)). Not only do the conduction bands distort, but the valence bands begin to distort as well. Mathematically, Hamiltonian matrix elements (only the onsite energy of the first boron atom) change due to the presence of the perturbation. This means the eigenvalues of the Hamiltonian change and distorts the band structure as local band gaps become more apparent. This phenomenon is also observed with the DOS as shown in Figure 4.15.

Figure 4.15 shows the DOS for an N=9 dimer ABNNR with the top edge boron atoms experiencing no perturbation, a perturbation of -1 eV, -2 eV and -3 eV, respectively – corresponding to the band structures of Figure 4.14.
Figure 4.15 - DOS for an ABNNR of N=9 dimers with top edge boron atoms under (a) no perturbation, and perturbations of (b) -1 eV, (c) -2 eV, (d) -3 eV, respectively.

Under these small amounts of perturbation, the DOS becomes disrupted from each continuous curve in the lower conduction regions of 7 eV and lower. The DOS also becomes perturbed in the valence bands and increase with magnitude of the perturbation. The degeneracy is also broken and is reflected accordingly in Figure 4.14. The most noticeable change is the “stationary state” at 4 eV in Figure 4.15(a-c) that disappears in Figure 4.15(d), after a perturbation of -3 eV is applied to the top edge boron atoms. This process also occurs when perturbing nitrogen atoms in ABNNRs. Instead, the valence bands will accumulate more distortion than the conduction bands since the valence bands are nitrogen-rich.
4.3.2 Perturbations in Zigzag Boron Nitride Nanoribbons

For ZBNNRs, we also observe similar behavior once perturbations are applied. Figure 4.16 shows the band structures for an N=10 chain ZBNNR with the bottom edge nitrogen atoms experiencing no perturbation, a perturbation of 1 eV, 2 eV and 3 eV, respectively. What is noticeable offhand is that the highest valence band distorts with the band gap steadily decreasing near the edge of the 1st Brillouin Zone (near k=1.2). This appears to be the only band that delocalizes, whilst all the other bands remain intact. Upon close inspection, one can see the valence bands slightly shift upwards toward the Fermi level as the perturbations to the bottom edge nitrogen atoms become stronger. This is a unique feature since ZBNNR edges are composed of solely boron atoms or nitrogen atoms whereas the ABNNR in Figures 4.14 and 4.15 had edges mixed with boron and nitrogen atoms.
Figure 4.16 - Band structures for a ZBNNR of N=10 chains with bottom edge nitrogen atoms under (a) no perturbation, and perturbations of (b) 1 eV, (c) 2 eV, (d) 3 eV.

The disrupted DOS shown in Figure 4.15 for the ABNNR was a result of perturbing top edge boron atoms. However, since ZBNNRs have single atomic species edge compositions, the DOS remains quite intact for this system. The delocalization of the top-most valence band can be seen in Figure 4.17 with the DOS plots for each perturbation of 1 eV, 2 eV and 3 eV, respectively. Note that Figure 4.17 also corresponds to the band structures in Figure 4.16 as shown above.

The top-most valence peak in Figure 4.17(a) shifts upward with each magnitude of perturbation, as seen in Figures 4.14(b), (c) and (d). The majority of the DOS plots remain unaffected except for the upper valence band region, where slight shifts can be seen. The conduction band region does not experience any perturbations in this case, which is different than what was previously seen with the imperfect ABNNR. Both the band structure and DOS for ABNNRs experienced
delocalization in both the valence band and conduction band regions, where band structures and
DOS for ZBNNRs only exhibit delocalization in one region depending on which edge is
perturbed.

Figure 4.17 - DOS for a ZBNNR of N=10 chains with bottom edge nitrogen atoms under (a)
no perturbation, and perturbations of (b) 1 eV, (c) 2 eV, (d) 3 eV, respectively.

4.4 Band Gap Tuning in BNNRs

Now that we have seen the effects of edge atom perturbations on BNNRs and how they
modify the band structures and DOS, we can now discuss the significance of band gap tuning
through this method. Band gaps are essential to nanoelectronic devices – especially
semiconductors – because the purpose of the device is to exploit this band gap. For example,
silicon is used in the form of metal-oxide-semiconductor-field-effect-transistors (or MOSFETs,
for short) and is commonly found in most electronic devices due to its cost effectiveness and small band gap [6].

In general, BNNRs have large band gaps around 4.8-5 eV in their pure forms, without any sorts of defects [2, 17]. However, it has been reported that the band gap in BNNRs can decrease by means of edge functionalization and edge bond termination with oxygen or sulfur atoms where in some cases, ZBNNRs can become semiconducting [20-22]. Some experimentalists have been creative and constructed heterostructures with boron-nitride/graphene interfaces and some go an extra step to additionally apply a transverse electric field to reduce the band gap of the bulk material [17, 25, 27]. Since band gaps in BNNRs can indeed change under a variety of circumstances, let’s take a quick look at how the band gap changes with width as it is the simplest case.

### 4.4.1 Band Gap as a Function of Width

Researchers have also shown that the band gap for ABNNRs decreases and has an oscillatory behavior as the width increases [25]. Figure 4.18 shows the band gap as a function of width (in dimers) for ABNNRs.
Figure 4.18 - Band gap (eV) vs ribbon width (N dimers) for ABNNRs.

The definition of a band gap is the smallest energy difference between the highest valence band and the lowest conduction band. Thus, the band gap can be direct (if the energy difference is from Γ-point to Γ-point) or indirect (if the energy difference is from Γ-point to another momentum state). The band gap in Figure 4.18 asymptotically approaches 4.82 eV as the ribbon width reaches 30 dimers (~74.3 Å) which agrees with Chegel [25]. Band gaps are calculated at k=0 (otherwise known as the Γ-point) for ABNNRs, yet ZBNNRs exhibit a different behavior since their band gaps cannot be calculated at k=0. Recall the imperfect band structures from Figure 4.16 for an N=10 chain ZBNNR. With the TB Model and Huckel theory, the only transitions we are interested in are near the boundary of the 1st Brillouin Zone at k=1.268. Thus, the band gap in ZBNNRs as a function of the width (in chains) is found to be constant at 4.83 eV without any defects. Figure 4.19 shows this relationship.
Even after an enormous width of 30 chains (~128.7 Å), the band gap remains constant. To further investigate band gap tuning, the same method as described in the previous section (Section 4.3) was used for select edge atoms and edges on both ABNNRs and ZBNNRs. To put into perspective with other work, Nakamura, et al. found the band gap for ZBNNRs to decrease slightly as a function of width by first-principles calculations (density functional theory) [54].

4.4.2 Band Gaps Due to Edge Perturbations

The onsite energy of the $p_z$ orbitals for select boron edge atoms or nitrogen edge atoms are adjusted by a small perturbation $V_{B,N}$ in the range of ±3 eV, which causes bands to shift in the band structure and the continuous nature of the DOS is disrupted. Gathering the band gap as a function of the strength of perturbation makes for a useful plot. For the purposes of these next few figures, decreasing the $p_z$ energy of boron or nitrogen atoms refer to $p_z$ energies becoming more negative. On the other hand, increasing the $p_z$ energy of boron or nitrogen atoms refer to $p_z$
energies becoming more positive. Figure 4.20 below shows what happens to the band gap of an N=9 ABNNR when the top edge boron atoms and when top edge nitrogen atoms are modified. An inset is also provided in the figure to highlight which boron atoms or nitrogen atoms were selected, representing a small chunk of the entire ABNNR top edge.

Figure 4.20 - Band gap (eV) vs. perturbation strength applied to (a) top edge boron atoms and (b) top edge nitrogen atoms in an N=9 ABNNR with selected edge atoms circled in green.
Figure 4.20(a) shows the band gap versus the perturbation strength applied to top edge boron atoms and Figure 4.20(b) shows the band gap versus perturbation strength applied to top edge nitrogen atoms for this particular ABNNR. Note that when $V_{B,N}$ is zero, there is no perturbation introduced to the system. As we saw in Figure 4.14 with the conduction bands lowering toward the Fermi energy with negative perturbation strength, the band gap also decreases due to the shifting of the conduction bands. The band gap falls to roughly 3.6 eV (a 27% change) when the boron $p_z$ energy is adjusted by a -3 eV perturbation, the maximum case. However, when $V_{B,N}$ is positive, it has almost no effect on the band gap. Similarly, the opposite is seen for Figure 4.20(b) when the top edge nitrogen atoms are perturbed. The valence bands lift toward the Fermi level with increasing perturbation strength and the band gap decreases due to this shifting. The band gap also falls to about 3.6 eV (also a 27% change) when the nitrogen $p_z$ energy is adjusted by a 3 eV perturbation. Decreasing the nitrogen $p_z$ energy (or when $V_{B,N}$ is negative) has little effect on the band gap. If the range of perturbation is larger, it appears that under extreme circumstances will the ABNNR become semiconducting based off of the definition of the band gap. Intuitively, we should expect that due to symmetry, applying the same perturbations to an ABNNR’s bottom edge will also yield the same results. A band gap of 3.6 eV is comparable to that of Gallium Nitride which is roughly 3.2 eV [18]. Largely, ABNNRs appear to remain as insulators under these sorts of edge modulations.

ZBNNRs also exhibit band gap changes just like ABNNRs since their valence bands and conduction bands are prone to shifting under small perturbations. However, these structures are a little bit more special. Recall that in Figures 4.16 and 4.17 that when the nitrogen edge atoms were perturbed by $V_N$, it only affected the uppermost valence region. A localized effect occurs here due to the compactness of the electronic states (as seen in the DOS) and thus, the upper
valence bands experience the greatest perturbation compared to all other bands surrounding it. Figure 4.21 shows what happens to the band gap of an N=10 ZBNNR when top edge boron atoms or bottom edge nitrogen atoms are modified. An inset is also provided in the figure to highlight which boron atoms or nitrogen atoms were selected, representing a small chunk of the entire ZBNNR edges.

![Figure 4.21](image)

**Figure 4.21** - Band gap (eV) vs. perturbation strength applied to (a) top edge boron atoms and (b) bottom edge nitrogen atoms in an N=10 ZBNNR with selected edge atoms circled in green.
Figure 4.21(a) shows the band gap versus the perturbation strength applied to top edge boron atoms and Figure 4.21(b) shows the band gap versus perturbation strength applied to bottom edge nitrogen atoms for this particular ZBNNR. Note that when $V_{B,N}$ is zero, there is no perturbation introduced to the system. The same reasoning from the imperfect band structures in Figure 4.16 holds as we saw with the ABNNR. When boron atoms on the top edge are perturbed, the conduction bands lower toward the Fermi level and when nitrogen atoms on the bottom edge are perturbed, the valence bands lift toward the Fermi level. Decreasing the boron $p_z$ energy lowers the band gap. At a maximum perturbation strength of -3 eV, the band gap falls to a value of 1.8 eV (a 63% change), which is less than what was found for extreme cases in the ABNNR in Figure 4.20. Raising the boron $p_z$ energy increases the band gap. Similarly, when the nitrogen $p_z$ energy is raised the band gap lowers to 1.8 eV (also a 63% change), entering the semiconducting regime. Note also that this band gap is similar to that of Indium Nitride [18]. By definition of this band gap, this ZBNNR be considered a semiconductor.

It can be inferred that large width BNNRs allow for electronic states to reposition energetically after the edge states are modified. ZBNNRs have more compact states than ABNNRs and have a higher probability of delocalizing. Thus, ZBNNRs have a higher potential to render semiconducting whereas ABNNRs tend to remain insulators under these sorts of edge modulations.

4.5 Quantized Conductance With Small Perturbations

(BNNRs)

Using the same method to perturb edge atoms on BNNRs, the conductance can also be investigated under these small perturbations. These perturbations apply to both the leads and the
conductor of the BNNR (refer to Figure 2.1). One should expect the conductance values to match up with the energies of bands in the band structure. Band gaps should also change accordingly if the conductance experiences these perturbations. I will show results for ABNNRs, followed by ZBNNRs in this section. In addition, the perturbations that will be used for this study are those that contribute to a smaller band gap.

Figure 4.22 below shows the conductance versus energy for an ABNNR of N=9 dimers with the top edge boron atoms under no perturbation and perturbations of -1 eV, -2 eV, and -3 eV, respectively. The legend in the plot below corresponds to these levels of perturbation to the system. The red dotted line represents the conductance under normal conditions without any perturbations.

![Figure 4.22](image)

**Figure 4.22 – Conductance vs. energy of an ABNNR of N=9 dimers with top edge boron atoms under no perturbation and perturbations of -1 eV, -2 eV and -3 eV, as labeled in the legend.**
When the top edge boron atoms are perturbed, recall that the bands in the band structure and DOS become distorted due to the delocalization of the \( p_z \) orbital energies as they approach the Fermi level while the strength of the perturbations increase. The shifting of the bands in Figure 4.14 correspond with the conductance curves in Figure 4.22 above. Notice that as each perturbation is applied, the conductance shifts in the conduction region above the Fermi level. However, below the Fermi energy, there aren’t many shifts in the valence region. The perturbed curves are similar to that of the original conductance under no perturbations with the exception of these shifts. The majority of the disturbances are seen near the Fermi level. Another interesting feature occurs and that is the drop in conductance at various energies with each of the perturbations. For example, under a perturbation of -1 eV, the conductance drops to \( 2 \left( \frac{2e^2}{h} \right) \) at 3.5 eV. This is also observed with each of the curves near -4 eV, as conductance drops from 4 \( \left( \frac{2e^2}{h} \right) \) to \( 2 \left( \frac{2e^2}{h} \right) \) in the valence region. In essence, the modes of transport are disturbed by these perturbations and as a result, some are lost at certain energies. This is also due to a loss of degeneracy where bands cross each other. Instead, forbidden regions open with each of the perturbation strengths applied to the ABNNR. Notice that the band gap also decreases as a function of the perturbation strength.

Figure 4.23 shows the conductance versus energy for the same ABNNR in the previous figure but with the top edge nitrogen atoms under no perturbation and perturbations of 1 eV, 2 eV, and 3 eV, respectively.
Figure 4.23 – Conductance vs. energy of an ABNNR of $N=9$ dimers with top edge nitrogen atoms under no perturbation and perturbations of $-1$ eV, $-2$ eV, and $-3$ eV, as labeled in the legend.

Figure 4.23 appears as a mirror image around the y-axis from Figure 4.22. Recall that if the top edge nitrogen atoms are perturbed, the valence bands become distorted and raise in energy toward the Fermi level. Indeed, Figure 4.23 reflects the same shifting that was observed in Figure 4.22, but in the valence region below the Fermi level. Consequently, the band gap also changes as a function of the perturbation strength. The drops in conductance also occur near 4 eV as a result of degeneracy breaking. By perturbing the top edge nitrogen atoms, the modes of transport reduce.

ZBNNRs can also undergo changes in the conductance. Figure 4.24 shows the conductance versus energy for a ZBNNR of $N=10$ chains with the top edge boron atoms under no perturbation and perturbations of $-1$ eV, $-2$ eV, and $-3$ eV, respectively. The legend in the plot below
corresponds to these levels of perturbation to the system. As in the other figures, the dotted line shows the original conductance under without any perturbations introduced to the system.

Figure 4.24 - Conductance vs. energy of a ZBNNR of N=10 chains with top edge boron atoms under no perturbation and perturbations of -1 eV, -2 eV, and -3 eV, as labeled in the legend.

Just like with was observed with the ABNNRs, the bands shift to different energies and thus the energies for modes of transport shift as well. However, there aren’t a lot of disturbances in the conductance for this particular ZBNNR. With each perturbation, the band gap becomes smaller as seen in Section 4.4.2. This is reflected in the conductance shown in Figure 4.24. Note that the valence region below the Fermi level doesn’t experience many disturbances. Since the top edge boron atoms were perturbed, this affects the first conduction band and hardly affected valence bands. These top edge perturbations do not seem to reduce any modes of transport, where in the ABNNRs (Figures 4.22 and 4.23) the conductance values would drop beyond ±4 eV.
Similarly, the same sort of processes occur in ZBNNRs with the bottom edge nitrogen atoms being perturbed. Figure 4.25 below shows the conductance versus energy for a ZBNNR of N=10 chains with the bottom edge nitrogen atoms under no perturbation and perturbations of 1 eV, 2 eV, and 3 eV, respectively. The legend in the plot below corresponds to these levels of perturbation to the system.

![Graph showing conductance vs. energy](image)

**Figure 4.25 - Conductance vs. energy of a ZBNNR of N=10 chains with bottom edge nitrogen atoms under no perturbation and perturbations of 1 eV, 2 eV, and 3 eV, as labeled in the legend.**

Figure 4.25 is a mirror image of Figure 4.24. Since the bottom edge nitrogen atoms are perturbed, this shifts valence bands and thus, the conductance curves shift for each perturbation strength that’s applied. The band gap also decreases as a result of this shifting, which was observed in Figure 4.24. The conductance curves above the Fermi level do not appear to be affected by these perturbations. ZBNNRs that experience edge perturbations have very localized effects which change the band gap and shift the conductance. Thus, the ZBNNRs are better
candidates for preserving bulk structures as they have localized effects. In both the armchair and zigzag cases, quantization is preserved.

4.6 Comparing Electronic Properties of BNNRs to GNRs

Graphene nanoribbons (GNRs) have been studied by many in the last two decades [4, 5, 7, 8, 11, 12]. These nanoribbons are typically metallic or semiconductors, depending on the edge structure. It has been reported that one-third of AGNRs are metallic with the remaining two-thirds being semiconducting and ZGNRs are metallic always [5, 7]. In most cases, infinite graphene (as a sheet) and AGNRs exhibit a zero-energy band gap and a linear dispersion between valence bands and conduction bands. This linear dispersion may be compared to

\[ E = \hbar k c_{\text{eff}}, \]

where \( c_{\text{eff}} \) is the effective speed of light. Thus, this linear dispersion allows electrons to act like Dirac fermions, indicating they have an effective mass of zero when near the Fermi energy [3, 4, 21]. Graphene is a very special material since it exhibits this property.

Transition metal dichalcogenides (like MoS\(_2\) or WS\(_2\)), 2D planar materials and other heterostructures have been studied for its potential for energy storage and device fabrication as well [6, 26, 27 53, 54]. These layered materials are bound through Van der Waals forces perpendicular to the plane, like both graphene and hexagonal boron nitride. Graphene especially is well-behaved and suitable for charge accumulation inside in the interstitial layers, unlike hexagonal boron nitride [26].
For the purposes of this work, the band structures, DOS, and conductance curves of GNRs will be compared to BNNRs without extensive detail. The reader is referred to theses by Kan and Jones should they be interested in only the electronic properties of GNRs [5, 7].

4.6.1 Band Structure and DOS: Comparisons and Differences

Intuitively, one would expect the band structures and DOS for GNRs should be different than those from BNNRs. First, the comparisons and differences between AGNRs and ABNNRs will be presented, followed by ZGNRs and ZBNNRs, respectively. Note that each of these structures all encompass a common width with their respective edge classifications (armchair or zigzag). For this study, the armchair structures have a width of N=8 dimers and the zigzag structures have a width of N=6 chains. Recall that for N dimers or chains, there are 2N atoms in a nanoribbon which yields 2N bands in the band structure.

Figure 4.26 shows the band structure and DOS for an ABNNR of N=8 dimers and underneath it, the band structure and DOS for an AGNR of N=8 dimers. The first noticeable feature is that the band structure for the AGNR (Figure 4.26(c)) has the linear dispersion in the band gap region. At k=0, there is a linear band crossing. This is the most special feature of graphene and is connected to Equation 4.2. There exist momentum states where the electron can move with a relativistic velocity near the speed of light. Besides this feature, this AGNR is metallic since there is no band gap between the valence bands and conduction bands. The armchair edge states are apparent in both band structures as the features are nearly identical.
Figure 4.26 – Band structures and DOS for ABNNR (a, b) and AGNR (c, d) of N=8 dimers.
For the case of the AGNR, since there is no band gap it is also observed in the DOS in Figure 4.26(d). The DOS from both structures are also nearly identical as well except for the band gap region, where the AGNR has states in this region compared to the ABNNR.

Figure 4.27 shows the band structures and DOS for a ZBNNR and a ZGNR, both of width N=6 chains. The features from both band structures (Figure 4.27(a, c)) are nearly identical except for the presence of a band gap in the ZBNNR. Since the band gap isn’t present in the ZGNR, the DOS in Figure 4.27(d) shows a large spike at the Fermi energy of 0 eV. The DOS for the ZBNNR in Figure 4.27(b) doesn’t exhibit this property and is expected for materials with band gaps. Both of the DOS plots reflect their respective band structures. The upper conduction bands and lower valence bands become degenerate the edge of the 1st Brillouin Zone. One can infer that the zigzag edge state is the primary source of the metallic behavior in ZGNRs. This is clearly visible by the highest valence band and the conduction band in Figure 4.27(c) meeting near the end of the 1st Brillouin Zone. The ZBNNR band structure in Figure 4.27(a) shows this edge state being preserved, yet these bands meet at the Fermi level in the case of the ZGNR. Thus, bands that result from certain edge states can have higher energies than bound states. Essentially, it costs energy to create an edge if one were to cut a ribbon out of an infinite sheet of graphene or hexagonal boron nitride.
Figure 4.27- Band structures and DOS for ZBNNR (a, b) and ZGNR (c, d) of N=6 chains.
4.6.2 Conductance: Comparisons and Differences

Like with the band structures and DOS, the conductance for both materials should differ as well. LDOS for GNRs will not be compared since it has been investigated by others [5, 7]. Recall that conductance reveals information about the electronic transport of a system and is typically quantized. For this comparison, I will show the results of armchair structures with a width of N=8 dimers and the zigzag structures with a width of N=6 chains.

Figure 4.28 shows the conductance versus energy for an ABNNR and AGNR, both of width N=8 dimers respectively. Note that these conductance curves should also reflect the band structures in Figure 4.26. The conductance curve for the ABNNR (Figure 4.28(a)) shows a band gap, indicating that conductance goes to zero. The band gap from this plot matches that of Figure 4.26(a). Similarly, the conductance curve for the AGNR (Figure 4.28(b)) indicates no band gap and a steady conductance value of $1$ ($2e^2/h$) in the band gap region. Recall this is due to the linear dispersion that was seen in Figure 4.26(c) and reflects the metallic nature of the material. It’s also interesting that even though these two nanoribbons are of the same width, both materials possess the same maximum conductance value of $4$ ($2e^2/h$). Note that both conductance curves are indeed quantized, yet the AGNR has larger steps in the conductance compared to the ABNNR.
Figure 4.28 - Conductance vs. energy for (a) ABNNR and (b) AGNR, both of width N=8 dimers.

The conductance for ZBNNRs and ZGNRs should also differ though their band structures were very similar. Figure 4.29 shows the conductance versus energy for a ZBNNR and ZGNR, both of width N=6 dimers respectively.
Figure 4.29 - Conductance vs. energy for (a) ZBNNR and (b) ZGNR, both of width N=6 chains.

These conductance curves reflect the band structures found in Figure 4.27 for zigzag structures. It is easy to see the band gap in Figure 4.29(a) for the ZBNNR, where no transport occurs. However, the ZGNR in Figure 4.27(b) has no band gap (as we expect) and a value of 1 \((2e^2/h)\) in the band gap region surrounding the Fermi energy. Since the bands in the band structure do not overlap, the maximum conductance is 6 \((2e^2/h)\) for both structures. This is verified by the band structures in Figure 4.27 as well. Both of the conductance curves have a similar shape but since
the ZBNNR has a band gap, there is one extra conductance step in Figure 4.29(a), going from zero modes of transport to one mode of transport \((1 \frac{2e^2}{h})\) just beyond \(\pm 2\) eV. On the contrary, the ZGNR’s metallic nature in Figure 4.29(b) is characterized by a single mode of transport \((1 \frac{2e^2}{h})\) in the band gap region surrounding the Fermi energy.

In general, the conductance reflects the band structures for both BNNRs and GNRs. The metallic nature of GNRs is shown accordingly where there is no conductance value of zero in the region of the Fermi energy. BNNRs have a wide band gap and this fact reinforces the insulating properties of these materials. In essence, the electrical properties of these materials are reinforced by the conductance.

4.6.3 Band Gap Tuning via Edge Modulation: Comparisons and Differences

It is known that all ZGNRs are metallic and one-third of AGNRs are metallic as well, with the remaining two-thirds being semiconducting [12]. It is common to know that in order to be a semiconductor, there must be a small band gap. This next study compares the method of band gap tuning by applying perturbations to the edge atoms and consequently alter the onsite energies of the \(p_z\) orbitals in GNRs. This was the same method used in Section 4.4.2 as a result of altering band structures, but instead, it will be applied to GNRs. After this, the band gap with the perturbation strength between ABNNRs/AGNRs and ZBNNRs/ZGNRs will be compared, respectively.

Figure 4.30 on the next shows the band gap vs. perturbation applied to top edge carbon atoms for an AGNR of \(N=8\) dimers and a ZGNR of \(N=6\) chains. The strength of the perturbation that changes the onsite energy is indicated by \(V_c\).
Figure 4.30 - Band gap vs. perturbation strength for top edge carbon atoms in (a) AGNR of N=8 dimers and (b) ZGNR of N=6 chains.

Figure 4.30 indicates that both of these GNRs are metallic under normal conditions without any perturbation. As soon as a perturbation is applied to the AGNR or ZGNR, an intersection of bands must split and a band gap is created. The AGNR in Figure 4.30(a) experiences the same perturbation strengths used in Section 4.4.2 and a monotonic increase in the band gap is
observed, yet the maximum band gap change is slightly larger than 0.4 eV (a 4% change). The small band gap opening that occurs indicates that this particular AGNR can become a semiconductor rather easily. Even at a perturbation of ±3 eV, the band gap is still smaller what the ZGNR in Figure 4.30(b) is capable of. Figure 4.30(b) shows the band gap as a function of the perturbation strength for a ZGNR of N=6 chains. Every nonzero perturbation strength is significant in creating a band gap which is much larger than what was seen for the AGNR. There is a linear relationship between the perturbation strength and the band gap in this particular ZGNR. Thus, this ZGNR is also able to render semiconducting as well. It is expected that applying these same perturbations to the opposite edge of both GNRs will indeed yield the same results.

It is best to put these results into perspective with those of BNNRs and their band gap capabilities. Figure 4.31(a) shows the band gap versus the perturbation strength for ABNNRs and AGNRs and Figure 4.31(b) shows the band gap versus the perturbation strength for ZBNNRs and ZGNRs. Figure 4.31 is essentially Figure 4.30 with ABNNRs/AGNRs and ZBNNRs/ZGNRs of same width with the same perturbations to corresponding edge atoms. The armchair edge structures (both materials) have a width of N=8 dimers and the zigzag edge structures (both materials) have a width of N=6 chains, which is different from those of Figures 4.20 and 4.21.

Recall from Section 4.4.2 that ABNNRs were under perturbations of select boron edge atoms or nitrogen edge atoms where the smallest resulting band gap was identical. The smallest band gap achieved by perturbing the top edge boron atoms is 3.6 eV for the ABNNR, which is still very much in insulating territory. However with the AGNR, its metallic behavior is disrupted with the perturbations applied to top edge carbon atoms and a tiny band gap opens up compared to the
ABNNR. The ZBNNR and ZGNR in Figure 4.31(b) show significant changes in the band gap when the bottom edges are perturbed. The ZGNR band gap opens up linearly with each of the perturbations applied to bottom edge carbon atoms while the ZBNNR band gap decreases with positive perturbation strengths when applied to bottom edge nitrogen atoms.

Figure 4.31 - Band gap vs. perturbation strength for (a) top edge atoms in ABNNRs/AGNRs of width N=8 dimers and (b) bottom edge atoms in ZBNNRs/ZGNRs of width N=6 chains, respectively.
We can conclude that ZBNNRs and ZGNRs are easier to manipulate when it comes to modulating a band gap. ZGNRs with these edge modulations can become semiconducting while ZBNNRs can also become semiconducting. With the armchair structures, AGNRs experience less disruption than ABNNRs when experiencing these sorts of edge perturbations. AGNRs have the capability to become semiconducting and ABNNRs are still far into the insulating region after these edge modulations.

4.7 Summary

The electronic properties using the Tight-Binding (TB) Model and Green’s Function Theory were studied in this chapter. The TB Model allows us to calculate the band structures and density of states (DOS). The conductance and local density of states (LDOS) comes from the Green’s Function Theory, where the nanoribbon is modeled with a conductor and left/right leads. The band structures and DOS show the electronic properties and allow one to make a classification on the material where the conductance and LDOS reveals the transport properties, in agreement with the band structures and DOS.

The band structures and DOS were presented for ABNNRs and ZBNNRs, followed by the conductance and LDOS. BNNRs are always insulators under normal conditions with a large band gap. Next, the band structures and DOS were presented for BNNRs with small perturbations introduced to edge atoms, mimicking experimental techniques where defects are introduced. Since the electronic properties are prone to change when defects or impurities are introduced, a study on band gap tuning was presented. ABNNRs have oscillatory band gaps that decay asymptotically as a function of width and ZBNNRs have a constant band gap for all widths. When edge perturbations are applied, ABNNRs have band gap tuning capabilities that
lower up to 27% from the original band gap of ~4.8 eV, nearing towards the semiconducting region. ZBNNRs are able to end up as semiconductors with band gaps as low as 1.83 eV, up to a 63% change when under no perturbations. This phenomenon is due to the delocalization of $p_z$ orbitals in edge atoms. ZBNNRs have electronic states that are much closer energetically compared to ABNNRs. It is inferred that edge atoms in ZBNNRs have a higher probability of delocalizing than those in ABNNRs. After band gap tuning was studied, the perturbed conductance was studied. The same perturbations used to modify onsite edge energies were used in calculating the conductance of both ABNNRs and ZBNNRs. These results reflected the perturbed band structures as previously seen and quantization was still evident. The perturbations were applied along the edges of both the conductor and leads, thus shifting the modes of transport to different energies. At higher energies away from the Fermi level were regions where the conductance would drop and fluctuate between different quantized values of $2e^2/h$. It turns out that transport heavily relies on degeneracy and when degeneracy is broken, it reduces the possible modes of transport for the system.

Lastly, the band structures, DOS and conductance were studied for GNRs and compared to those of BNNRs. AGNRs especially exhibited a linear dispersion that relates to electrons to behave like massless Dirac fermions, one of the signature features of graphene in general. Band gap modulation was also studied for GNRs and compared to results for BNNRs previously explored. GNRs have the ability to become semiconducting under edge perturbations where AGNRs exhibit a 4% change in band gap and ZGNRs exhibit a linear increase in band gap.
Chapter 5: Convergence Testing For Implementing Density Functional Theory

To implement DFT within ABINIT, the computational method requires testing and calibration for various sets of parameters that describe the electronic system in reality. Thus, parameters can be checked for energy convergence in the SCF cycle as mentioned in Chapter 3 to provide accurate representations and results. This chapter reports the results of said calibration for producing band structure and DOS with ABINIT.

5.1 The Importance of Converging the Total Energy

There exist factors which affect the calculation quality and accuracy of obtaining a ground state density (and subsequently, the ground state energy) for an electronic system. Since ABINIT utilizes the SCF cycle outlined in Figure 3.1, there are a variety of parameters that must be fine-tuned and tested to ensure this result is obtained accurately. A few questions arise if we are to produce this outcome:

1. How well does an arbitrary model represent the atomic/electronic system?
2. How much information does one need to provide?
3. How accurate can one calculate the ground state density and ground state energy?

Luckily, the ABINIT user is able to influence the answers to these three questions. The user is able to set up a model to their preference that contains all the necessary pseudopotentials, XC functionals, definition of the atoms, and periodic boundary conditions. The user can also control the size of the basis set that solves the Kohn-Sham Equation and pick a feasible k-point grid to
yield accurate electron densities. Above all, the user is able to set the algorithm tolerance which constitutes as an end point for the SCF cycle. In ABINIT, these parameters are listed as input variables.

Recall that the SCF cycle explained in Chapter 3 (Figure 3.1) ends when the newly calculated ground state density converges within some tolerance related to the previously calculated ground state density. The outcome of this SCF loop produces the final, converged total energy of the electronic system. Typically, total energy can be considered converged if it falls within 1 milli-Hartree (0.0272 eV) between consecutive SCF cycles. This criterion ensures chemical accuracy required to do further calculations. The convention also serves chemists as a basic convention to create quantum chemical models [41, 60]. In addition, tolerance conditions in the SCF cycle are set to $10^{-7}$ Hartrees to minimize any chances of an improper convergence.

For users, there are many important variables which impact this SCF cycle and for the purpose of this thesis, only four will be discussed. The four input variables are the amount of vacuum between periodic cells, the cutoff energy, the amount of k-points and shape of the k-point grid, and the lattice constants in three dimensions. Each of these variables contributes to the length of time it takes for the SCF cycle to complete and the accuracy of the final converged energy. The user must go through these four convergence tests individually before running a more practical calculation, i.e. to calculate band structure or DOS. It is important to keep in mind that false convergences can be achieved if such variables are not adequately tested for energy convergence themselves.

Sometimes these convergence tests can take an awfully long amount of time to complete and this partially depends on the amount of atoms in the primitive unit cell along with other parameters. Note that if a pseudopotential or XC functional doesn’t comfortably reflect the core/valence
potential or small fluctuations of electronic positions respectively to an acceptable degree, poor results can be obtained. For example, the largest system computed in ABINIT contained twelve atoms and completed the band structure and DOS calculation in sixteen hours. However, band structures and DOS for non-hydrogenated and hydrogenated ZBNNRs finished in fifty hours.

The data that will be shown in this chapter as part of the convergence testing entail DFT calculations on an infinite sheet of hexagonal boron nitride (hBN). Due to this material being of the same composition and its ability to be transformed into a nanoribbon, it is commonplace to use resulting parameters from these convergence studies on calculations involving BNNRs. The results on these studies for hBN will be presented first and it will be briefly mentioned which are used for the nanoribbons in the sections following. One should also note that Appendix C covers the names of the generic ABINIT input variables in conjunction with the convergence studies described in this chapter.

5.1.1 Choosing a Pseudopotential

There are a wide variety of pseudopotentials that one can use to model core electron interactions. Recall from Chapter 3 that a pseudopotential removes the core electron interactions and replaces them with fake core potential that doesn’t change the valence electron interactions. For the purposes of this thesis, the pseudopotentials used for DFT calculations are taken from ABINIT’s norm-conserving pseudopotential library. The library is a collection of optimized norm-conserving Vanderbilt pseudopotentials (ONCVPSP) which follow a strict norm-conservation requirement, among other conditions [46]. These pseudopotentials also serve as defaults for new users. Around two-thirds of elements in the periodic table have an ONCVPSP in ABINIT’s library.
Norm-conserved pseudopotentials are pseudopotentials where the core potential is replaced by a fake potential inside a cutoff radius that allows for normalization to be the same for both the wavefunction of the atom with a corresponding pseudopotential and the true wavefunction of an orbital outside the cutoff radius. Another common property for this class of pseudopotentials is that the eigenvalues of both wavefunctions need be the same. As a preference, the pseudopotential should be as smooth as possible. The ONCVPSP is the only pseudopotential scheme that utilizes both norm-conservation and smoothness [46]. More information on the technical details of pseudopotentials can be found in Hamann, Martin’s text and past theses [40-43, 46].

5.1.2 Choosing an Exchange-Correlation Functional

Like pseudopotentials, exchange-correlation (XC) functionals come in a huge variety. The purpose of the XC functional is to model the small fluctuations in electron positions due to the correlated electron-electron interaction and the quantum states of the electrons, as restricted by the Pauli Exclusion Principle. The XC energy term in Equation 3.7 is a correction for using the static charge density. Recall that the XC functional must be provided in order to solve the Kohn-Sham Equation (Equation 3.9) and calculate the ground state density.

Out of the many XC functionals that exist, the baseline standard is known as the Generalized Gradient Approximation (GGA) [55]. The GGA lowers energies of systems with fast, varying densities (like atoms and molecules) by carefully dealing with the XC energy of large density gradients [55]. Among the myriads of GGAs available, a common one for solid state calculations is the Perdew, Burke, and Ernzerhof GGA. For the purposes of this thesis, this specific XC functional that is used to generate results in Chapter 6. The GGA can be explained in greater detail by Watson and Nault [41, 43] and is not subject of detailed discussion for this work.
5.2 Cutoff Energy Convergence

Perhaps one of the most important components in testing a basis set when using ABINIT is the cutoff energy convergence. The cutoff energy is rather important for providing information about the basis set. Universally, the quality of the total energy calculation depends on this variable. A higher cutoff energy means better convergence in total energy. It is also usually one of the first convergence tests users should perform before going forth with other calculations. This input variable is called \textit{ecut} in ABINIT.

Whenever a basis set is constructed, ABINIT calculates the total energy by expanding plane-waves coupled with different reciprocal lattice vectors as explained in Section 3.3.2. Recall that the Bloch wavefunction for the system is described by Equation 3.12, where Equation 3.13 describes the plane-wave expansion for all reciprocal lattice vectors, \( \vec{G} \). The cutoff energy is introduced as a means to limit the computer from counting to infinity (due to periodicity) where \( G_{max} \) is the maximum G-vector in the 1st Brillouin Zone. As the cutoff energy increases, the amount of G-vectors increase and hence, the wavelength of the plane-waves decrease (see Equation 3.15). When the plane-waves have a short enough wavelength, they are able to probe the orbitals in an electronic system and inherently obtain more information than longer wavelengths. Thus in a sense, the cutoff energy also refers to the sharpness, size and shape of the orbitals.

Using a two atom basis set to generate an infinite sheet of hexagonal boron nitride (hBN), the cutoff energy was varied from 30 to 50 Hartrees to test for total energy convergence. The following cutoff energy values and their corresponding total energies are listed in Table 5.1.
Notice that after a cutoff energy of 45 Hartrees is reached, the total energy is constant to the third decimal place. Thus, the total energy is converged after 45 Hartrees. Intuitively, since hBN does possess inherent armchair and zigzag edges, the cutoff energy for modeling BNNRs can be taken from this data.

### 5.3 Vacuum Layer Convergence

Recall that two-dimensional (2D) infinite sheets of graphene and hexagonal boron nitride can be created by repeating a two-atom basis set to generate a lattice in the xy-plane. In ABINIT, the primitive unit cell containing the system is periodic for all three directions in real space, which is due to the use of plane-waves to describe the atomic orbitals. Knowing this, the z-direction cannot be ignored from the total energy calculation when modeling a 2D infinite sheet. Thus, by increasing the distance between periodic unit cells in the z-direction and filling it with vacuum, the total energy can be converged. The purpose for this is to ensure there is no interaction from neighboring cells when isolating a 2D infinite sheet (the importance of this will also be stressed in Chapter 6!). This input variable is called vacuum in ABINIT.
The goal of this study is to find a suitable vacuum buffer between layers associated with the ground state energy. For this study, a two-atom basis set – a boron nitride dimer – of hBN was used to model an infinite sheet. Table 5.2 below shows the total energy convergence for vacuum in the z-direction between layers of hBN.

<table>
<thead>
<tr>
<th>Vacuum Layer in z (Bohr)</th>
<th>Total Energy (Ha)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>-13.4240317</td>
</tr>
<tr>
<td>20</td>
<td>-13.4240537</td>
</tr>
<tr>
<td>25</td>
<td>-13.4240452</td>
</tr>
<tr>
<td>30</td>
<td>-13.4240508</td>
</tr>
<tr>
<td>35</td>
<td>-13.4240460</td>
</tr>
</tbody>
</table>

Table 5.2 – Vacuum layer convergence in z-direction between neighboring layers of hBN.

In Table 5.2, the amount of vacuum between layers is represented in units of Bohr (1 Bohr = 0.529 Å) and the total energy is in units of Hartrees (1 Ha = 27.2 eV). The vacuum layers tested ranged from 15 Bohr (7.935 Å) to 35 Bohr (18.52 Å) in the z-direction. Recall that the criterion for total energy convergence between consecutive SCF calculations is 1 mHa. All of the energies listed in Table 5.1 do indeed converge to the third decimal place. Thus, the total energy is converged for these five data sets. But much of the physics we want to understand depends upon the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies. Which of these results are suitable to converge the energies of the HOMO/LUMO orbitals?
It turns out that this same question was posed and answered by Blase, et al. This group of researchers found that a suitable vacuum at an interlayer distance of 13.5 Å (25.52 Bohr) [56]. Thus, an interlayer distance with vacuum of 25.0 Bohr was chosen for modeling hBN’s HOMO/LUMO states. This choice is also a good fit for modeling BNNRs in ABINIT since these systems are similar.

5.4 K-Point Grid Convergence

Another important component in testing a model with ABINIT is the k-point grid convergence. Recall that the Bloch wavefunction for an orbital of a crystal is described by Equation 3.12 for a given energy band \( n \) and crystal momentum \( k \). For an infinite crystal, there are an infinite number of such momentum states and an infinite number of orbitals to sum over. In order to obtain an electron density using Equation 3.6, which takes the probability amplitude of the wavefunction, an infinite, continuous set of wave vectors with an infinite crystal cannot be used.

Basic solid state theory says that all possible momentum states \( k \), occupiable by electrons, are inside the 1st Brillouin Zone [34]. For any energy band \( n \) and momentum state \( k \), this region is \(-\pi/a\) to \(\pi/a\) in one dimension (Note that this was the range of k-points used in Chapter 4 band structures!).

If a 2D material is used, the 1st Brillouin Zone will be in two dimensions in k-space. An example of the 2D hexagonal Brillouin Zone can be seen in Figure 5.1 with three special symmetry points: \( \Gamma \) (the center of the 1st Brillouin Zone), \( M \) (the center of a face), and \( K \) (the corner of a face). Note that the path from \( \Gamma \) to \( K \) to \( M \) to \( \Gamma \) represents a repeat unit that can be used to make
up the entire 1st Brillouin Zone. These are the high symmetry points used in the creation of energy band structures for 2D infinite hBN, as results in Chapter 6 will utilize.

Figure 5.1 - The 1st Brillouin Zone of a 2D hexagonal lattice with special symmetry points, \( \Gamma, K, \text{ and } M \) denoted.

Any k-point outside the 1st Brillouin Zone is a periodic duplicate of one inside it, as a result of Bragg scattering [34]. The k-points in this range are a continuum of points, but need to be discretized. When the k-points are discretized, this process creates a k-point grid. By adding in more k-points, the grid becomes so discretely fine that the electron density becomes converged and thus, a grid as such is minimized and produces the minimized ground state density. These
grids are called Monkhorst-Pack grids [57]. In ABINIT, the input variable describing the k-point grid is \( kptrlatt \).

Obviously, different lattices produce different arrangements of k-point grids. These grids are typically represented by a square matrix of three dimensions of reciprocal lattice vectors \( b_i' \) that span a superlattice composed of many primitive unit cells in the form of

\[
\begin{pmatrix}
    b_1' \\
    b_2' \\
    b_3'
\end{pmatrix} =
\begin{pmatrix}
    k_{11} & k_{12} & k_{13} \\
    k_{21} & k_{22} & k_{23} \\
    k_{31} & k_{32} & k_{33}
\end{pmatrix}
\begin{pmatrix}
    a_1' \\
    a_2' \\
    a_3'
\end{pmatrix},
\]

(5.1)

where \( k_{ij} \) is an integer and \( a_i' \) is a translational vector in real space. To check k-point grids for energy convergence, the integers \( k_{ij} \) are varied for a specific maximal plane-wavelength that is set by the user. Note that when the integers \( k_{ij} \) are very large, this corresponds to a very small wavelength, representing a finer grid. The final converged grid that was chosen for modeling 2D infinite hBN is \( \begin{pmatrix} 12 & 0 & 0 \\ -7 & 14 & 0 \\ 0 & 0 & 1 \end{pmatrix} \) and for modeling BNNRs, the final converged grid is \( \begin{pmatrix} 22 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \).

5.5 Cell Volume Optimization

The last important variable that will be discussed is the volume of the primitive unit cell, known as \( acell \) in ABINIT. The unit cell is housed in a volume which encompasses atoms of the user’s choosing and is adjustable in the three real space directions (x, y and z). Due to this cell volume being periodic, this variable is rather essential in order to obtain accurate total energies.
and other calculations. The cell volume can also be thought of as a real space volume composed of three lattice constants for each real space direction.

The two-atom basis for an infinite sheet of hBN is a single boron-nitrogen dimer. If the volume of the cell is not optimal, the influence of the neighboring cells on the primitive unit cell leads to a net force on this cell, and this causes an increase in the total energy. Thus, a convergence study is required to find which cell volume gives us a minimized total energy.

To gain a visual understanding of this concept, Figure 5.2 below shows the two-atom basis for 2D infinite hBN placed in a unit cell. This unit cell is periodic and thus, it generates a hexagonal lattice in the xy-plane.

![Figure 5.2](image)

**Figure 5.2** – The two-atom basis of 2D infinite hBN placed in a unit cell, as denoted by the dotted red lines. Repeating this structure creates a lattice in the xy-plane.

Since the z-direction has already been taken care of, the only lattice constants that need to be converged are those in the x and y-direction. Note that there was a special study for the z-direction which included vacuum between neighboring cells in Section 5.2. Thus, a lattice
constant in the z-direction can be obtained from that study for the purposes of modeling 2D infinite hBN, although the reader should understand that this is not the true lattice constant in the z-direction for bulk hBN. Increasing the size of the periodic unit cell in Figure 5.2 containing the two-atom basis is equivalent to stretching the lattice. Similarly, decreasing the size of the periodic unit cell is equivalent to compressing the lattice. This action surely affects the total energy calculation of the system.

Figure 5.3 shows the total energy as a function of the 2D cell size for the x and y directions. It is clear to see that the total energy is minimum and thus converged when the 2D cell size is near 4.75 Bohr (or 2.51 Å), indicating that this value will suffice for the 2D lattice constant.

**Figure 5.3 - Cell size convergence for sheet of hBN: total energy (Ha) vs. 2D lattice constant (Bohr).**
Other lattice constants of 2.511 Å and 2.506 Å from theory and experiment, respectively, agree very well with the choice of lattice constant picked in Figure 5.3 [58, 59, 67]. In the case of modeling BNNRs, this convergence study applies to the x-direction but not the y-direction since the ribbon width is able to extend in the y-direction. A preliminary study connected to results will be shown for this special case in Chapter 6.

5.6 Summary

This chapter emphasizes the importance of converging the total energy with respect to variables that are under the user’s control. The reason for this is due to the nature of the SCF cycle that is explained in Chapter 3. In an attempt to obtain accurate ground state energies, the user must test the efficiency of the model, the basis set, as well as the algorithm tolerance. A brief overview of the choice of pseudopotentials and XC functional were explained in regards to converging the total energy. The convergence studies included those in vacuum layer, cutoff energy, k-point grid, and the cell volume. These studies must be undertaken independently in order to ensure proper results are obtained for calculations like band structure and DOS. In addition to the explanation of the variables and their operations in ABINIT, the reader is encouraged to look at Appendix C for a list of input variables.
Chapter 6: Electronic Properties via Density Functional Theory

Here, I will present the electronic properties produced from DFT which include energy band structures, DOS, and LDOS with angular momentum projections for infinite hBN, a ZBNNR of N=4 chains and a special case of a hydrogenated ZBNNR where hydrogen atoms terminate the edge bonds. We are already familiar with the band structures and DOS, however the LDOS plots are able to tell us which states are more s-like, p-like, etc. In addition, visualizations of orbitals and electron densities will be shown. The purpose of these results is to compare DFT calculations to those of the TB Model, as shown in Chapter 4.

6.1 Electronic Properties and Structure of Hexagonal Boron Nitride

First, we will investigate the electronic properties and structure of infinite hBN. Typically, hBN in sheet form possesses a wide band gap nearing 5 eV [18, 29, 54] and is very much an insulator electronically. It has been studied in the past for its potential in applications to spintronics and band gap tuning through means of external electric field control, stress or strain, and edge modifications [19, 23, 28, 30, 48]. We know that BNNRs can be formed out of infinite hBN by cutting along edges to produce the distinct armchair and zigzag edges of which we are familiar with.

One could easily expect that using ABINIT to calculate DFT-based results such as band structure and DOS will provide more information than what was seen in the TB Model with Huckel
Theory since there is no restriction on valence orbitals and our ground state density is solved for self-consistently. Among those results are band structure, DOS and angular momentum projections on LDOS. The first two items we are familiar with and will be presented first. The last item in the list is similar to the LDOS explained in Chapter 4, yet it is a very powerful calculation that provides projections of angular momentum quantum states, $|l \ m\rangle$ on individual atoms. Thus, it can be observed which atoms have influence from s, p, d, f, and other orbitals. From the angular momentum projected (this phrase will be denoted as m-projected for short) LDOS, the LDOS which was shown in Chapter 4 with the TB Model can be compared.

6.1.1 Energy Band Structure and Density of States

Figure 6.1 shows the band structure and DOS for infinite hBN with a two-atom basis. The band structure in Figure 6.1(a) was plotted over the 1st Brillouin Zone as shown in Figure 5.1. It should be mentioned that similar band structures were found for infinite hBN through DFT calculations [29, 54]. Recall that the TB Model with Huckel Theory produced band structures showing only p$_z$ orbitals. Upon first glance, the 14 bands in the band structure in Figure 6.1(a) seems a bit less intuitive. However, recalling some simple facts gives plenty of insight on this band structure. Note that boron has three valence electrons with a ground state valence electron configuration of 2s$^2$ 2p$^1$ and nitrogen has five valence electrons with its ground state valence electron configuration being 2s$^2$ 2p$^3$. Thus, in the valence bands, some representation of s-orbitals and p-orbitals should be seen. However, sp$^3$ hybridization is possible for a single hBN dimer and is definitely utilized in the TB Model. This means evidence of this hybridization in the band structure should be seen as well.

The first valence band with an energy of -20 eV at the $\Gamma$-point has the lowest energy compared to other valence bands and therefore, it is a bound state. This band is identified to be an s-band. The
next valence band above the s-band (at the \( \Gamma \)-point) is the \( p_z \)-band. This is known to be true since the two closest bands from the Fermi energy (at 0 eV) are doubly degenerate at the \( \Gamma \)-point. This is due to the sp\(^2\) hybridization that the hBN dimer exhibits in general. Thus, these two degenerate bands make up the \( p_x \) and \( p_y \) orbitals, leaving the \( p_z \)-band obvious to point out. Note that ZBNNRs exhibit this \( p_z \) band as well (refer to Figure 4.4).

Figure 6.1 - (a) Band structure and (b) DOS of the two-atom basis of 2D infinite hBN.

Another similar feature is that the band gap is easily seen, yet the band gap in Figure 6.1(a) is not direct like what has been presented in Chapter 4. The band gap is indirect (from K to \( \Gamma \)) with a value of 4.615 eV, making infinite hBN an insulator. Band gaps for infinite hBN of 4.63 eV have
been reported in previous work [54]. It is important to mention that DFT does not predict band
gap calculations accurately and can be underestimated or overestimated accordingly [41, 68]. A
detailed investigation is provided by Watson and is not a subject of discussion for this work.

What is interesting is that the low s-band in Figure 6.1(a) has a parabolic feature and thus, the
DOS in Figure 6.1(b) has a constant shift at roughly -20 eV. A similar feature could also be seen
near the K-point for the p_z band and its corresponding DOS just below -2 eV. It is clear to see
that the DOS in Figure 6.1(b) corresponds to the band structure entirely, yet most of the available
states are not valence states. The majority of states exist in the conduction bands, but these
conduction bands are not easily identifiable in regards to being s-like or p-like. Recall that the
symmetry that was exhibited with the TB Model in the band structures does not hold here. Thus,
the DOS is not symmetric either. By looking at the K-point, the p_z valence band (HOMO)
appears as to reflectively mimic the conduction band (LUMO). As this conduction band
approaches Γ in k-space, band repulsion is evident and cause it to change shape. The
combination of these local band gaps fold into a p_z-like band suggest that there is some more
band hybridization occurring in the conduction bands than the valence bands.

6.1.2 Visualizing Electron Densities and Orbitals

In an attempt to confirm the identity of the bands and determine if they are s-like or p-
like, Visual Molecular Dynamics (VMD) is used to visualize the electronic system [61]. VMD
has the capability to show the orbital shape and structure as well as electron density. This is a
useful tool to visualize both simple and complicated systems. Thus, using this software gives an
advantage to understanding the not-so-obvious features that may pop up in band structures and
DOS.
Figure 6.2(a) shows the band structure from Figure 6.1 along with the visualizations of orbitals (b-g) for various bands at the Γ-point for infinite hBN.

![Figure 6.2](image)

**Figure 6.2** - (a) Band structure for infinite hBN and (b-g) multiple orbital visualizations with volume slices, corresponding to electron densities, at various bands at the Γ-point.

In Figure 6.2(b-g), each subfigure has a volume slice through the center of the atoms in the plane. The volume slices are color coded, indicating points of low or high electron density which ranges from blue to magenta, including other colors of the rainbow. Blue represents low electron
density and magenta represents high electron density and this pattern repeats several times. The colors are not tied to any actual electron density values as it is purely a symbolic representation. Note that the volume slices span through the middle of the plane of the infinite sheet. The pink colored atoms represent boron atoms and the blue colored atoms represent the nitrogen atoms. The grey “blobs” represent the isosurfaces. These isosurfaces are surfaces of constant charge per volume which correspond to orbital shapes. The isosurface values can vary depending upon what one wants to visualize with said orbitals. For Figure 6.2(b-g), the isosurface values are \( \sim 3.2 \) e/Bohr\(^3\). Note that the Γ-point can often be the easiest k-point to visualize these orbitals since it is the most intuitive high symmetry point. For clarity and completeness, other neighboring cells were included in these visualizations.

Recall from Section 6.1.1 that the valence bands were identifiable based off information about the bonding behavior and the valence orbitals contained in a two-atom hBN dimer. These predictions can be verified from Figure 6.2(b-e).

The first valence band is most definitely an s-band with the s-orbitals visible around the nitrogen atoms (Figure 6.2(b)). Yet, the s-orbitals appear elongated and as if they are touching the boron atoms so there must be a small bit of hybridization occurring (we will see how this is true in Section 6.1.5). From knowing trends in the periodic table, nitrogen atoms are more electronegative and hence, they will want to steal the electrons from the boron atoms. The second valence band is most definitely a p\(_x\)-band with a larger concentration of the orbital on the nitrogen atoms than the boron atoms (Figure 6.2(c)). This is due to the fact that nitrogen has a higher occupation of electrons than boron, thus, it will have a larger p-dominated orbital size. The third and fourth valence bands were predicted to be hybridized due to them being doubly degenerate at the Γ-point. Note that the highest valence band (in this case, there are two of them
at Γ which are degenerate) makes up the HOMO. From Figure 6.2(d, e), there is a mixing of pₓ and pᵧ orbitals in the plane of the infinite sheet. The prediction is confirmed from these visualizations.

The conduction band visualizations (Figure 6.2(f, g)) tell more interesting story. Notice that the first conduction band (or the LUMO) – corresponding to Figure 6.2(f) in the band structure is not s-like or p-like. The band is very much parabolic, indicating that the energy of the electron resembles that of a free particle. Yet, Figure 6.2(f) shows that this state is a state with no orbitals connected to the structure of the sheet itself. Instead, the electrons are residing in an interstitial area outside the infinite sheet (this will be denoted as the “surface state” for the remainder of this chapter). It makes sense that the state exists outside the structure is that of a free particle, but it doesn’t explain why this state occurs. Section 6.1.3 will elaborate on the significance of this surface state.

The topmost conduction band visualization in Figure 6.2(g) which shows the flat conduction band is also interesting. This conduction band is doubly degenerate, thus a pₓ/pᵧ state. Recall that “flat bands” represent non-conducting states. In Chapter 4, these bands were observed with ABNNRs in both the valence and conduction regions. In Figure 6.2(a), this band corresponds to an infinitely heavy effective mass, since the mass term in Equation 4.1 is what allows for the parabolic curvature of the E vs. k relationship in the band structure. It was also seen from Chapter 4 that ABNNRs had a combination of bands that created an entirely “flat band” as well (refer to Figure 4.2). It was proposed that these states were “stationary states” that resided above the structure in the z-direction since Huckel Theory allows us to produce band structures for pₓ orbitals only. Yet, the VMD visualization in Figure 6.2(g) shows pₓ-like orbitals in a doubly
degenerate p_x/p_y state. Looking closely, it is strange to see nitrogen atoms harboring a smaller distribution than boron atoms.

6.1.3 Confirming Vacuum Layer and Lattice Constants

It is important to check the accuracy of band structures and DOS when they are produced by comparing results as such to previous work. In general, if improper vacuum layer distances or lattice constants are used, band structures and DOS plots will most likely be inaccurate and insufficient for analysis. To illustrate this, two scenarios will be presented in this section to show the effect of such anomalies. The first scenario is the vacuum layer distance between neighboring cells in the z-direction in an attempt to isolate an infinite sheet of hBN. The second is a study on using improper 2D lattice constant that actually end up simulating stressed or strained infinite hBN.

Recall that vacuum layer convergence test in Section 5.2. The purpose of this convergence test was due to the fact that we were only interested in isolating a single layer of hBN that could form an infinite sheet. Having a vacuum layer between neighboring cells in the z-direction would serve this purpose, but a sufficient amount of vacuum that produces a convergence in the total energy had to be found. Blase, et al used DFT in the late 1990’s to model infinite hBN in the same manner that is shown in this section. This group of researchers found a charge presence between layers when trying to isolate an infinite sheet [56]. The interstitial charge presence was found at the LUMO (at the \(\Gamma\)-point) and the charge density between layers was nonzero as a result of there not being enough of a vacuum buffer. Figure 6.3 shows three different values of vacuum layer distance between neighboring cells in the z-direction.
Figure 6.3 – On edge visualizations of infinite hBN of the LUMO at the \( \Gamma \)-point with 8.5 Å (left), 10.6 Å (middle), and 13.2 Å (right) of vacuum layer in the z-direction with volume slices, respectively.

Figure 6.3 shows visualizations of infinite hBN with three different vacuum layers between neighboring cells in the z-direction composed of 8.5 Å, 10.6 Å, and 13.2 Å, respectively. The volume slices are in the z-direction and marked with a variety of colors. Between the rows of atoms, striped patterns of different colors are seen which represent the area between layers.

In order to check to see if the vacuum distance between layers in the z-direction is converged, a large blue colored region must be showing between the rows of atoms. Magenta color is seen
between the neighboring layers and this indicates moderate to high electron density in this region for both the 8.5 Å (Fig. 6.2 – left) and 10.6 Å (Fig. 6.3 – middle) cases. The blue color can be seen easily between the layers for the case of 13.2 Å (Fig. 6.3 – right), indicating low electron density in this region. This scenario visually indicates that the vacuum layer of 13.2 Å is appropriate and is suitable for isolating an infinite sheet of hBN. This result is in close agreement with Blase et al where a distance of 13.5 Å between hBN layers was deemed large enough to isolate an infinite sheet. Nonetheless, a visual representation coupled with real results show the importance of proper convergence tests.

One may suspect that changing the 2D lattice constant of infinite hBN would affect the band structure. This reasoning is correct since it relates back to the definition of the Brillouin Zone in k-space. The k-points represent momentum states of the crystal and each k-point has an affiliated eigenstate that gives the wavefunction for the system. By changing the lattice constant, the k-points change accordingly. If the lattice constant $a$ is increased, the spacing between successive k-points decreases. This results in the decrease in band width of energy levels. Similarly, if the lattice constant is decreased, the spacing between successive k-points increases and corresponds to an increase in band width of energy levels. One could even think about the infinite square well (a standard, introductory problem in quantum mechanics) and its ability for the energy levels to raise or lower if the width of the well is shortened or elongated, respectively. The same thinking applies to band structure as well. If the plane of the sheet of hBN undergoes some form of bi-axial strain, the bands will shift, resulting in change in band width.

Figure 6.4(a) shows the band structure for infinite hBN under compression and Figure 6.4(b) shows the band structure for infinite hBN under stretching. The dotted lines indicate shifted bands and the solid lines indicate the original band structure at the accepted 2D lattice constant.
of 2.51 Å. The 2D lattice constant was varied up to 5% (± 1.24 Å) from the accepted value. If the modified 2D lattice constant is smaller than 2.51 Å, this simulates compression in the plane of the sheet. Likewise, if the modified 2D lattice constant is larger than 2.51 Å, this simulates stretching in the plane of the sheet. Note that the lattice constant in the z-direction is not necessary for this study. It is also important to know that this simulation reflects a simple experiment where bi-axial strain is applied on a material, thus changing the lattice constant. Figure 6.4 is essentially measuring an actual physical effect.

Figure 6.4 – Modified band structures of infinite hBN under two forms of bi-axial strain up to 5% of the original 2D lattice constant: (a) compression and (b) stretching. Dotted lines indicate band width shifting and the solid lines indicate the original band structure at the accepted 2D lattice constant.
With the knowledge from understanding the behavior of the energy levels in an infinite square well with respect to the width of the well, we should expect the band structures in Figure 6.4 to change accordingly. Figure 6.4(a) shows the band structure for infinite hBN while the plane of the sheet undergoes compression. As a result, we can see the energy bands shift further apart from each other. Thus, the band width increases when compression is applied in the plane. However, Figure 6.4(b) shows the band structure for infinite hBN while the plane of the sheet undergoes stretching. This time, the energy bands shift closer to one another and thus, the band width decreases.

Note that if the incorrect choice of 2D lattice constant were used, it would yield these sorts of changes in the band structure for hBN. It can also yield incorrect band gap energies and details about the band gap. For example, the Γ-point in Figure 6.4(a) at its maximum case would end up being the LUMO if the hBN structure was compressed. Thus, it is crucial to compare theoretical predictions with experimental results after data like this is produced. This also reiterates the importance of performing the optimization study as outlined in Section 5.5 and confirms that our resulting band structure is indeed accurate and of the highest quality possible within the approximations of our physical model.

6.1.4 Preliminary Studies for Calculating Local Density of States

Recall that the LDOS gives the density of states for a single atomic site, as discussed in Chapter 4. The LDOS was also a product of Green’s Function theory. In order to obtain LDOS calculations using ABINIT, input based on the radii of the valence shells from the nucleus is required perform this calculation. Using these radii, ABINIT computes projections of different angular momentum states $|l \, m\rangle$ which are centered on a sphere around an atomic site with a defined radius. Note that $l$ is the angular momentum quantum number and $m$ is the magnetic spin.
quantum number. This implies that spherical harmonics are no longer ignored. However, these m-projections of LDOS will be able to tell us which states are s-like, p-like, etc.

First, the radii of the valence shells for the boron and nitrogen atom in the hBN dimer must be found. Off-hand, one would think the electron density on the bond axis of the dimer would suffice to help us find these radii. Figure 6.5 shows a plot of the electron density versus the position on the bond axis for the two-atom basis of infinite hBN.

![Figure 6.5 - Electron density (in atomic units) vs. the position along the bond axis (in Bohr) for the two-atom basis of infinite hBN. The nuclei of boron and nitrogen as well as the bonding region are pointed out in this plot.](image)

It is reasonable to consider the position along the bond axis since this interpolation will provide most of the electron density. Upon inspection of Figure 6.5, the boron nucleus and the nitrogen
nucleus are pointed out in the plot. Since the y-axis represents the electron density, this means we should see low density at the nuclei where no electrons are present. This is indicated by the sharp, inverted peaks in the plot. From periodic table trends, note that boron has a larger atomic radius than nitrogen. This is reflected in Figure 6.5 at the boron nucleus peak and the nitrogen nucleus peak, so it gives us some insight on the radius size compared to other valence shells. However, the valence shells overlap as part of the bonding process. Hence, it is not certain what the size of the radii between the nuclei and valence shells are for both atoms, as indicated by the bonding region in the figure.

A better quantity is available to analyze these valence shell radii. Instead, if the Laplacian of the density against the position on the bond axis is plotted, the radii can be found much easier than by observing Figure 6.5. Interestingly enough, this is due to the topology of the electron density where the Laplacian indicates charge concentration and depletion. More specifically, valence shell peaks can be identified where the Laplacian is a local minimum [62, 63]. Bond centers can also be represented as saddle points. Bader has also shown that if the Laplacian of an electron density is negative in the center of a bond, it is representative of covalent compounds rather than ionic compounds [62].

Figure 6.6 shows the Laplacian of the density versus the position on the bond axis for the two-atom basis of infinite hBN.
Figure 6.6 - Laplacian of the electron density (in atomic units) vs. the position along the bond axis (in Bohr) for the two-atom basis of infinite hBN. An inset is provided for a closer look at the bonding region, indicating valence shell peaks and the bond center.

Comparing Figure 6.6 to Figure 6.5, the bonding region is more transparent in Figure 6.6, as indicated by the dotted box. Since the Laplacian of the electron density has local minima in the bonding region, the nuclei are easily identifiable with large, upright peaks (2.7 Bohr for boron and 5.4 Bohr for nitrogen). Then, the valence shell peaks for both boron and nitrogen can also be identified. These boundaries are pointed out in the inset of Figure 6.6.

However, the center of the bond is a bit more difficult to decipher. To find this, it is easiest to approximate the bond center at the halfway point between the valence shell peaks. Thus, at 3.9 Bohr, between the two valence peaks, corresponds to the center of the bond. Knowing the
distances of the center of the bond to the valence shell peaks, radii for the LDOS calculations can be obtained. These radii are 1.2 Bohr for boron and 1.5 Bohr for nitrogen.

6.1.5 Local Density of States

The previous section was a preliminary study to calculate the LDOS. What makes this calculation different from what Green’s Function Theory produces in Chapter 2 is that when using ABINIT, we are able to make projections of angular momentum states $|l \, m\rangle$, centered on a sphere with a defined radius around an atom. This is to ensure the orbitals with certain angular momenta of a single atom can be captured in the projection. So, for example, the LDOS is able to reveal the amount of states that are $p_x$-like, $p_y$-like or $p_z$-like and also identifies which atom these states come from. Thus, we can further investigate the band structure of infinite hBN and learn more about which of these states are dominant. If one is interested in $p$-states, the angular momentum quantum number is $l=1$ which yields three different magnetic quantum numbers, $m=1, 0, -1$. Recall from quantum mechanics that the magnetic quantum number represents a rotation of the $z$-component of angular momentum.

Now, an analysis of the band structure for the two-atom basis of infinite hBN with these $m$-projections on the LDOS will be discussed. This also allows a comparison between the DFT results and TB results shown in Chapter 4.

Figure 6.7 shows the $m$-projections of the LDOS on the boron atom and nitrogen atom in the two-atom basis of hBN along with its band structure in Figure 6.7(a). Figure 6.7(b) is the LDOS for the boron atom and Figure 6.7(c) is the LDOS for the nitrogen atom. The legend indicates the different color curves of different $p$-states and the total DOS for Figures 6.7(b, c).
Figure 6.7 - (a) Band structure of the two-atom basis for infinite hBN with LDOS (b) for boron and (c) for nitrogen with angular momentum projections for all possible orientations of p-states and the total DOS, as shown in the legend.

Note that Figure 6.7(b) and (c) are denoted with a capital “B” and “N” in the lower right-hand corner of the plots to indicate which LDOS corresponds to which atom. Upon first glance of the LDOS plots, there is a lot of overlap between colors. Each color represents a specific angular
momentum state. For example, blue represents the \( (p_z) \) state \(|1 0\rangle\), green represents \((p_x/p_y)\) \(|1 − 1\rangle\), red represents \((p_x/p_y)\) \(|1 1\rangle\), black represents the combination of all three \(p\)-state projections \((p\ total)\), and purple without any color filling represents the total DOS.

In Chapter 4, we saw that the LDOS for BNNRs had similar features and shape as compared to the original DOS for those systems. The LDOS for the boron and nitrogen atoms in Figure 6.7(b, c) show some resemblance to the total DOS, outlined in purple on both plots. Recall that in Figure 6.1(a), we were able to confirm which valence bands corresponded to which orbitals, yet we did not know which atoms they originated from. From Figure 6.1(a) and by looking at Figure 6.7(b, c), the lowest valence band corresponds to mostly an \(s\)-state as there’s very little \(p\)-influence from the boron and nitrogen atom. Thus, about 95\% of this band is \(s\)-like since the total DOS (in purple) is much higher than the \(p\)-like states visible in red in both Figures 6.7(b, c), which culminate to around 5\%. When observing the degenerate \(p_x/p_y\) bands (at \(\Gamma\)), Figure 6.7(c) shows lots of \(p\)-states dominating the nitrogen atom, leaving very little contribution from the boron atom in Figure 6.7(b). Also, the majority of the \(p_x\) valence band appears to come from the nitrogen atom. This is most likely due to the extra two electrons that nitrogen has in the 2p shell as compared to boron. Note that the nitrogen \(p\)-bands section of the DOS in Figure 6.7(c) composes the majority of the total DOS in this region.

It was discussed earlier that the conduction bands were not as easily identifiable, but yet some similarities were seen between the HOMO and LUMO near the K-point as the first conduction band appeared to mimic the \(p_z\) valence band in a reflection. Near K, the nitrogen atom is mostly responsible for the HOMO, whereas the boron atom doesn’t seem to have much influence on the HOMO. An argument can’t be made as easily for the LUMO, since it is a combination of both boron conduction states and nitrogen conduction states. However, the conduction states shown, a
mixture of p-states, make up a minority of the total DOS. It is proposed that higher states like d or f states must be present in the conduction bands. These states could explain the interstitial state that was explained in Figure 6.2(f), though no orbital shape was clearly defined. Notice that the “flatter” conduction bands near the Γ-point are moreover p<sub>z</sub> states from the boron atom. The nitrogen atom only contributes a small amount of these infinitely heavy conducting states near the Γ-point. It is worth mentioning that the state |1 − 1⟩ in green is not very well visible in the boron LDOS as opposed to the nitrogen LDOS in the conduction region. This suggests that one orientation for orbital angular momentum is preferred with the nitrogen atom than it is with the boron atom.

The big takeaway from this study is that the m-projected LDOS gives a more detailed description of the conglomeration of states produced and which atoms they are more closely aligned with. In the case of the two-atom basis for infinite hBN, the conduction states remain relatively unknown since a minority of them are p-states so they must come from higher states like d or f states. It is expected that most of the s-states are present in the valence bands, not in the conduction bands. Also, the p<sub>z</sub> valence states predominantly come from the nitrogen atom whereas the p<sub>z</sub> conduction states are a mixture of both boron and nitrogen character.

6.2 Electronic Properties and Structure of ZBNNRs

In order to successfully model ZBNNRs, it is important to think about the structure of ZBNNRs. For this study, the electronic properties and structure of an N=4 chain ZBNNR consisting of eight atoms will be investigated. Note that in Chapter 5, it was discussed how the vacuum layer was important for the z-direction since the interest was in modeling an isolated, infinite sheet of hBN. Since nanoribbons have finite width in the transverse (y-) direction and
infinite length in the longitudinal (x) direction, the structure can be defined to lie in the xy-plane in real space with defined edges in the y-direction. Thus, vacuum layer must be included in the y-direction. Now the important question is, how much vacuum layer is enough to isolate the ZBNNR? Recall that we can confirm this from VMD simulations as well as total energy results (as discussed in Chapter 5).

6.2.1 Confirming Vacuum Layer

The method for confirming vacuum layer for ZBNNRs is the same as the procedure used in Section 5.2 with the exception of focusing the vacuum in the y-direction to create the zigzag edges for the nanoribbon. The z-direction has already been accounted for explained in Section 6.1.3. To save time, it is best to perform this convergence test on an N=2 chain ZBNNR. After the desired result for convergence is reached, this information can be used to model larger BNNRs.

One could think of a large vacuum layer as a replacement of atoms that make up larger width ZBNNRs, built off the N=2 chain case. Essentially, larger width ZBNNRs like N=4, N=6, N=8 or N=10 chains can be constructed and then, have two atom chains are removed until the bare 4 atom unit cell remains. Figure 6.8 shows the initial scenario of the ZBNNR with vacuum extending beyond the outside edges of the nanoribbon.
Figure 6.8 - Vacuum layer (in y-direction) outside an N=2 chain ZBNNR can be thought of as a larger width ZBNNR with every two atom chains removed until only one unit cell remains. The removed unit cells in red are replaced with vacuum.

Figure 6.8 above denotes the removed unit cells from a larger width ZBNNR in red. The arrows denote the extension of the vacuum in the y-direction. From geometry, the distance from the outer edge atom (an outside boron if on top or nitrogen if on bottom) to the edge of the unit cell increases by 4.05 Bohr for every two atoms that are removed. By knowing the distances of the edge atom boundary of the N=2 ZBNNR to the edge of the removed unit cells means a
convergence study can be performed to find the sufficient amount of vacuum layer in the y-direction to isolate the ZBNNR. After this, the band structure and DOS can be calculated accurately.

One way to check the accuracy of the vacuum layer in the y-direction is by a simple table comparing the total energy of the nanoribbon to the amount of vacuum extended in the y-direction. Table 6.1 below shows the convergence of the vacuum layer and the corresponding total energy of the N=2 ZBNNR.

<table>
<thead>
<tr>
<th>Vacuum Layer in Y- Direction From Both Edges of ZBNNR (Bohr)</th>
<th>Total Energy (Ha)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.4</td>
<td>-26.654966</td>
</tr>
<tr>
<td>9.45</td>
<td>-26.654482</td>
</tr>
<tr>
<td>13.5</td>
<td>-26.654224</td>
</tr>
<tr>
<td>17.55</td>
<td>-26.654093</td>
</tr>
</tbody>
</table>

**Table 6.1 - Vacuum layer convergence in y-direction for isolating an N=2 chain ZBNNR.**

Note that Table 6.1 shows a decrease in total energy as the vacuum layer from both edges of the ZBNNR becomes larger. However, the total energy is converged to 1 mHa, which is standard. Yet, the energy doesn’t appear to converge near the micro-Hartree scale. Thus, a second confirmation is in order.

Using VMD simulations to show the electron density in the y-direction will surely show us the proper layer of vacuum. Recall that we saw the same sort of visualizations in Section 6.1.3. This
also serves as a double check to ensure that mirroring images do not interact in the y-direction.

Figure 6.9 below shows the VMD visualization of the electron density for the four vacuum layers as listed in Table 6.1 in the plane of the ZBNNR. Recall that blue color represents low charge density and other colors represent varying densities. For a proper convergence in the y-direction, blue color must be visible in the y-direction.

Figure 6.9 – Volume slices of total charge density in y-direction of an N=2 chain ZBNNR with (a) 5.4 Bohr, (b) 9.45 Bohr, (c) 13.5 Bohr, and (d) 17.55 Bohr of vacuum surrounding both edges of the nanoribbon. Zero density is shown as blue and higher densities are shown by cycling through the color wheel.
Upon first glance of Figure 6.9, it is confirmed that the total energy values in Table 6.1 decrease due to the increasing distances from neighboring cells in the y-direction. Figure 6.9(a) shows evidence of interaction between the two mirroring images with green color. Thus, this vacuum layer distance is not suitable for modeling a ZBNNR. The rest of the images (Figure 6.9(b-d)) indicate that there is negligible charge density with all three of these vacuum layer distances. The vacuum layer distance in Figure 6.9(b) (9.45 Bohr) is chosen as the minimum vacuum layer required to isolate the ZBNNR. This value as such still converges to the milli-Hartree scale in total energy and also provides a wide enough buffer so the probability of interaction between neighboring cells is very low, as shown by Figure 6.9(b).

6.2.2 Energy Band Structure and Density of States

Now that the appropriate amount of vacuum to model a ZBNNR has been selected, the band structure and DOS for a ZBNNR of N=4 chains can be investigated. Recall that there are 2N atoms in the unit cell. Thus, the unit cell for this particular ZBNNR contains 8 atoms. Figure 6.10 shows the band structure and DOS for a ZBNNR of N=4 chains plotted over the 1\textsuperscript{st} Brillouin Zone in one dimension (Recall that $\Gamma$ is k=0 – the center of the 1\textsuperscript{st} Brillouin Zone – and $\pm \pi /a$ are the edges of the 1\textsuperscript{st} Brillouin Zone).

The first feature that is noticed in the band structure in Figure 6.10(a) is the presence of subbands. Subbands originate from the confinement of nanostructures, typically in quantum wells and nanotube structures [34]. Subbands occur when the number of atoms in a unit cell are increased (in the case of identical atoms, the subbands are usually very close in energy). Since atoms bring in their own electrons, the number of occupied bands increases (Note that the p\textsubscript{z} bands in band structures in Chapter 4 are examples of subbands). Therefore, if there are multiple atoms of the same species with the same amount of electrons, the eigenstates must exist at
varying but similar energies. For example, in the infinite hBN band structure (Figure 6.1(a)), only one s-type band was seen that represented both the boron atom and the nitrogen atom. Since there are four pairs of bonded boron and nitrogen atoms arranged into a nanoribbon, four s-type subbands will be seen in the band structure for the \( N=4 \) chain ZBNNR in Figure 6.12(a). However, notice that one of the s-type subbands exists at higher energy. This subband in particular runs from -13.8 eV to -15 eV in Figure 6.10(a). The same logic follows for the \( p_x/p_y \) bands as well as the \( p_z \) bands. Thus, there are a group of eight \( p_x/p_y \)-type subbands, with one of them shifted up near the Fermi energy, and a group of four \( p_z \)-type subbands. In total, there are sixteen valence bands.
Recall that the TB Model produced band structures for ZBNNRs that exhibited degeneracy at the edges of the 1st Brillouin Zone except for the highest valence band and lowest conduction band (Figure 4.4(a)). The subbands in Figure 6.10(a) do not exhibit this degeneracy. The conduction bands beyond 5 eV are all free-particle-like as they exhibit very shallow parabolas. The difference from the infinite hBN band structure is that of the conduction bands were definitively spread out and a number of them did not exhibit the same parabolic curvature. However, with the TB Model, Figure 4.4(a) showed that ZBNNRs produce bands that are symmetric across the
Fermi energy. The only symmetry that seems evident are the $p_z$ subbands in the valence region with those in the conduction region. The topmost valence band and the bottommost conduction band also appear to be symmetric everywhere except near the $\Gamma$-point. It can be seen that the LUMO is clearly not a subband of any sort as it is different from all the rest of the local band groups. Recall that this was not observed with infinite hBN.

It is also obvious to see that since the topmost valence band (the HOMO) and the bottommost conduction band (LUMO) both cross the Fermi energy, it is indicative that this ZBNNR in particular is metallic. This fact entirely contradicts the results of ZBNNRs from Chapter 4, since ZBNNRs had a clear and defined band gap. However, it has been reported that bare-edged ZBNNRs are metallic by some researchers [21, 29, 30]. These researchers claim that the result of a metallic ZBNNR is unexpected, yet the metallic property stems from the fact that the edges are not passivated and the dangling edge bonds are not terminated. The crossing between the HOMO and LUMO at the Fermi energy has been witnessed also by Terrones, et al [29]. In addition, others concluded that ZBNNRs can be metallic if terminated with oxygen or sulfur on the edge atoms [21, 22].

6.2.3 Edge States in ZBNNRs

The origin of the metallic behavior of the ZBNNR in the previous section stems from the localized edge states represented by flat bands in the band structure in Figure 6.10(a).

Researchers have shown that edge states are attributed to flat bands in ZBNNR band structures [54, 64]. The effect is primarily due to the excess electrons of edge atoms that are not bonded. Recall Figure 1.2(b) that shows a typical ZBNNR. There are $sp^2$ and $p_z$ dangling edge bonds present in this structure.
Recall that flat bands were a topic of interest in Chapter 4. Flat bands show little to no curvature and indicate effective electron masses that are infinitely heavy. Flat edge states make sense when the electrons are localized at the edge in such a way that they have no active role in bonding with other atoms in plane and act as if they are “stuck” in space. The reader should be reminded that a flat band does not always imply an edge state.

To take a closer look at the edge states, VMD visualizations are shown for the HOMO and LUMO in flat sections of the band structure in Figure 6.10(a). These flat sections are best observed at the center and edges of the 1st Brillouin Zone. Figure 6.11 shows the band structure of an N=4 chain ZBNNR with the HOMO and LUMO edge states at the center and edge of the 1st Brillouin Zone.
Figure 6.11 - (a) Band structure of an N=4 chain ZBNNR with the (b, c) HOMO and (d, e) LUMO edge states visible at the center and edge of the 1st Brillouin Zone, respectively.

It is particularly interesting to observe the edge states in Figure 6.11(b-e) since these four states show the localized behavior as mentioned. Figures 6.11(b, e) have isosurface values of 4.58 e/Bohr$^3$ and Figures 6.11(c, d) have isosurface values of 10.87 e/Bohr$^3$. In Figure 6.11(b) – which shows the HOMO at the Γ-point – the orbitals on the nitrogen edge are localized with most of the
charge on or around this edge of the ZBNNR. Yet, there’s a small charge presence indicated on
the opposite boron edge. All the orbitals orient in the xy-plane with nodes in the x-direction of
the ZBNNR and the bonding between neighboring boron atoms is particularly evident only at the
nitrogen edge. Note that this state could contribute to electron bonding and thus, charge
transport, since volume slice indicates nonzero density along the nitrogen edge. In Figure
6.11(c), the HOMO at the edge of the 1st Brillouin Zone is visible and shows entirely nitrogen-
dominated p\textsubscript{z} orbitals that orient perpendicular to the xy-plane of the nanoribbon. It is a
directional state and a pure atomic orbital, indicative of the dangling p\textsubscript{z} bonds in Figure 1.2(b).

Figure 6.11(d, e) show LUMO states for the center and edge of the 1st Brillouin Zone. The
LUMO at these two k-points presents similar behavior to the HOMO. In Figure 6.11(d), the
charge is only present in the y-direction on the boron atom so this state is directional as well.
This is indicative of dangling sp\textsuperscript{3} bonds in Figure 1.2(b). However, in the volume slice along the
xy-plane, the variation of colors show that the LUMO is localized on the boron side of the
ZBNNR and other charges can be distributed near the boron edge of the nanoribbon. In Figure
6.11(e), there are similar features to the LUMO at the \Gamma\text{-}point (Figure 6.11(b)) where bonding
occurs in the armchair (y-) direction and the localized orbitals on the boron edge compose the
majority of the charge in this state. However, it’s also interesting to see that the opposite nitrogen
edge also has charge oriented in the y-direction.

The HOMO and LUMO states at the \Gamma\text{-}point explain the metallic behavior of the ZBNNR
whereas the HOMO and LUMO states at the edge of the 1st Brillouin Zone reinforce the dangling
edge bonds at ZBNNR edges. Dangling edge bonds do play an important role in the electronic
classer of ZBNNRs and entirely contradict the results of Chapter 4 with ZBNNRs and
expectations thereafter.
6.2.4 Hydrogen Edge-Terminated Energy Band Structure and Density of States

The mechanism for the metallic behavior the ZBNNR has been explained by the presence of dangling edge bonds. These dangling edge bonds produce localized edge states. If bonding occurs to terminate these dangling edge bonds, there is a possibility of recovering the insulating character as the edge atoms will not induce localized edge effects. Researchers have claimed and shown that terminating the dangling edge bonds of ZBNNRs with hydrogen preserve its insulating character [21, 22, 29, 30, 54]. The same phenomenon has also been predicted with ABNNRs [19]. Others have also concluded that using hydrogen edge-terminated ZBNNRs accompanied by an external electric field can result in band gap tuning [64]. For this section, the band structure and DOS of the N=4 chain hydrogen edge-terminated ZBNNR will be discussed. Note that since the hydrogen atoms are located on the edges of the ZBNNR, the amount of vacuum layer in the y-direction should not be the same as what was used in Section 6.2.1. Therefore, a geometrical optimization algorithm developed by Schlegel was used to optimize the cell volume with vacuum in the y- and z-directions fixed by finding the configuration which gave the lowest ground state energy [65].

Figure 6.13 shows the band structure and DOS for a hydrogen edge-terminated ZBNNR of N=4 chains. The first noticeable feature is that the band gap is indeed preserved with the addition of hydrogen to the ZBNNR. The band gap is direct with a value of 4.106 eV and is clearly defined by the DOS in Figure 6.13(b) as well. Lopez-Bezanilla, et al have reported hydrogen edge-terminated ZBNNRs with a band gap of 3.81 eV [22].
Figure 6.12 - (a) Band structure and (b) DOS for an N=4 chain hydrogen edge-terminated ZBNNR.

Upon inspection, seventeen valence bands are seen in the band structure. Recall that without hydrogen edge-termination, there were sixteen valence bands present. The extra valence band appears in the $p_x/p_y$ group of subbands ranging from roughly -5 eV to -11 eV. Here, there are nine subbands. It is reasonable to consider the extra subband a product of the hydrogen being bonded in the xy-plane to the ZBNNR at the edges. Looking a bit more closely, the s-type subbands appear to tie together at the edges of the 1st Brillouin Zone. The hybridized $p_x/p_y$ subbands don’t exhibit this behavior, yet there are three $p_z$ subbands that tie together at the edges.
of the 1st Brillouin Zone and one subband does not. This feature is observed also in Chapter 4 with the TB Model with ZBNNRs (refer to Figure 4.4(a)). The general shape of the $p_z$ bands is also very similar to what was seen in Figure 4.4(a) where the bands were symmetric about the Fermi level. However, the $p_z$-type group of subbands (which are first four conduction bands from the edge of the 1st Brillouin Zone) in the conduction region appear as if they are trying to mimic the symmetry of the $p_z$-type valence subbands. It is also interesting to see that the conduction bands (from the Γ-point) at energies above 2 eV have parabolic features yet they happen to provide the highest DOS as shown in Figure 6.12(b). Recall that the ZBNNRs in Chapter 4 exhibited the highest DOS at the HOMO and LUMO near the edges of the 1st Brillouin Zone.

It is quite fascinating that the hydrogen edge-terminated ZBNNR brings more consistency and is closely-related to the TB Model’s predictions. The addition of hydrogen edge-termination does preserve the band gap, and thus, the hydrogen edge-terminated ZBNNR is an insulator.

6.2.5 Edge States in the Hydrogen Edge-Terminated ZBNNR

Since the HOMO and LUMO at the Γ-point were responsible for the metallic behavior of the bare edged ZBNNR, it is useful to take a quick look at these same bands and k-points for the hydrogen edge-terminated ZBNNR with VMD. This way, the changes in electronic structure can be investigated.

Figure 6.13 below shows the band structure of the N=4 chain hydrogen edge-terminated ZBNNR with the VMD visualizations of the HOMO and LUMO at the Γ-point. The white spheres on the outer edges of the nanoribbon represent hydrogen atoms.
Figure 6.13 - (a) Band structure for the N=4 chain hydrogen edge-terminated ZBNNR with VMD visualizations of the (b) HOMO and (c) LUMO at the Γ-point.

Note that the isosurface values for Figure 6.13(b, c) are both 4.58 e/Bohr$^3$. At the HOMO in Figure 6.13(b), the charge is mostly present on the nitrogen atoms in the hydrogen edge-terminated ZBNNR. The orbital shape resembles that of a $p_z$ orbital, yet the orbitals are forced to the inner sections of the nanoribbon due to the hydrogen atoms at the edge. The orbitals appear much larger in the middle of the nanoribbon than those near the edges. By terminating the edge
bonds with hydrogen, the electronic structure is reordered. This discrepancy can be easily seen when comparing Figure 6.11(b) to Figure 6.13(b).

Figure 6.13(c) shows a more interesting feature. Notice that the volume slice indicates lots of bonding activity in the armchair (y-) direction of the nanoribbon where nodes are also present. However, only charge presence is shown on the nitrogen edge of the nanoribbon, indicating a bond between the nitrogen atoms and the hydrogen atoms. The presence of hydrogen at the edges induces an extra bond and an extra band in the band structure to relinquish the metallic behavior of the bare edged ZBNNR.

6.3 Summary

In this chapter, the electronic properties and structure of infinite hBN, and ZBNNRs of both perfect and hydrogen edge-terminated structures using DFT have been explored. These results included band structure, DOS, and m-projected LDOS. Though the band structures for simple systems seem wildly different than what was observed in Chapter 4 with the TB Model, there are still plenty of comparisons that can be made between the two models. An additional tool to confirm the electronic states was by using VMD visualization software to visualize electron densities and orbitals of different bands and k-points.

When studying infinite hBN, the band structure and DOS revealed a great deal of information. The s-bands and p-bands were easily identifiable in the valence bands, yet the conduction bands were a bit more complicated. To help understand these states, VMD simulations of specific bands at the center of the 1st Brillouin Zone revealed the orbital structure. Strangely enough, a special surface state was found with VMD and the m-projected LDOS later confirmed was inherent of the boron atom. To produce m-projected LDOS on the two-atom basis, the Laplacian
of the electron density was studied to extract a proper valence shell radius with respect to the bond center. The LDOS revealed the identity of the energy bands and it was observed that p-states made up the minority of the LDOS in the hBN sheet. It is implied that higher states like d or f must be present in the conduction region. In addition to exploring these properties and attributes, bi-axial strain on infinite hBN was simulated and band structures were produced to show what happens under compression and stretching. Band width was found to change when bi-axial strain was applied. VMD helped confirm the choice of vacuum layer in the z-direction.

Moving onward to the N=4 chain ZBNNR, their electronic properties were found to be considerably different and contradictory to that of the TB Model. First, the vacuum layer convergence study from Chapter 5 was revisited and applied the y-direction since ZBNNRs have defined edges. After finding the proper amount of vacuum layer, band structure and DOS were produced with this new information. It was striking to see that the system was metallic and consisted of subbands, totally contradictory of what the TB Model predicts. The band structure showed a valence band crossing the Fermi energy, as part of the metallic behavior. Along with this, the dangling edge bonds (edge states) of the ZBNNR responsible for the metallic behavior. VMD was used to visualize the HOMO and LUMO at the center and edge of the 1st Brillouin Zone, which exhibited the metallic behavior.

After this, the band structure and DOS of a hydrogen edge-terminated ZBNNR of N=4 chains was studied. This nanostructure became a point of interest after noticing that the metallic behavior of the bare edged ZBNNR was characterized by the dangling edge bonds. Past work has shown that using hydrogen to terminate these dangling edge bonds preserves the band gap. This was confirmed again by investigating the band structure, where a band gap of 4.106 eV was visible. It is reasonable to see that this case brings more consistency and is more closely related
to the TB Model results as shown in Chapter 4. The \( p_z \) group of subbands in the hydrogen edge-terminated band structure were rather symmetric in both the valence and conduction regions. Like the bare edged ZBNNR, most of the available states were found in the conduction bands as indicated by the DOS. The HOMO and LUMO at the \( \Gamma \)-point were then visualized with VMD to investigate the changes in the electronic structure when hydrogen is added to the edges. Most of the charge was found to be redistributed due to the presence of hydrogen since bonds were formed. This passivation alone changes the metallic behavior once seen at the HOMO and LUMO at the \( \Gamma \)-point in the bare edged ZBNNR.
Chapter 7: Conclusions

7.1 Summary

In this thesis, the electronic properties of hexagonal boron nitride (BNNRs) and graphene nanoribbons (GNRs) have been studied. To study the electronic properties, a multitude of theories were used. The first theory used was the Tight-Binding (TB) Model with Huckel Theory, which allowed us to obtain Hamiltonian matrix elements in order to produce band structure and density of states (DOS). The second theory used was Green’s Function Theory, which allowed us to produce conductance and local density of states (LDOS) by modeling nanoribbons as ballistic conductors, composed of a conductor and left/right leads where scattering at the leads were not taken into account. The majority of the results fell under the first two theories mentioned, as pure structures and imperfect (perturbed) structures were investigated. When perturbations are applied to the edges of these nanoribbons, the electronic properties were found to be altered. The third theory used was Density Functional Theory (DFT), which allowed us to also produce band structure, DOS, and angular momentum projections of LDOS with the addition of using Visual Molecular Dynamics (VMD) simulations to visualize electronic structure and orbital characteristics of certain systems.

In Chapter 1, the nanostructures of graphene and hexagonal boron nitride were introduced. Both structures have an identical hexagonal lattice shape and geometry. Nanoribbons can be created by cutting out strips of an infinite sheet. Thus, nanoribbons can be constructed into different armchair and zigzag edges. The width of these nanoribbons can be characterized by N dimers (if armchair edge) and N chains (if zigzag edge). Both materials exhibit sp² hybridization which
allows for electrons to form bonds in the plane of the sheet/nanoribbon with $p_z$ orbitals perpendicular to the plane. The significance of these materials for current technology and research were also introduced as well.

In Chapter 2, the TB Model with Huckel Theory was explained. Huckel Theory allows us to consider the nearest neighbor interactions of only one specific set of atomic orbitals (in both cases, $p_z$ orbitals) in a periodic unit cell. These are the orbitals that characterize the electronic properties through the TB Model. The wavefunction for the system is composed of a linear combination of atomic orbitals (LCAO) and with the help of Bloch’s Theorem, can be substituted into the time-independent Schrodinger Equation. Solving the Schrodinger Equation is a matrix problem in which the determinant must be found. This process enables us to find the energy eigenvalues in the form of energy bands. When energy is plotted against the wave vector, a band structure is created. The DOS was also explains and characterizes the number of states per lattice length, per unit energy of the material.

In addition, Green’s Function Theory was introduced. To calculate conductance, the Landauer Formula is used and nanoribbons are modeled as conductors and left/right leads. Here, we assume ballistic transport such that no scattering of electrons occur at the lead-conductor junctions. The transmission is defined by retarded and advanced Green’s Functions. Also, the LDOS can be calculated from using the Green’s Functions. The LDOS is the DOS for a single atomic site.

In Chapter 3, DFT was introduced as a secondary technique to obtain ground state energies, which also leads to band structures and DOS. DFT operates on the Born-Oppenheimer Approximation and simplifies the many-body Hamiltonian. After this, the two famous Hohenberg-Kohn Theorems are utilized as the heart of DFT and allow us to find the ground state
energy in terms of an electron density. Also, the ground state density that minimizes the energy functional is the exact ground state density. The Kohn-Sham ansatz for the electron density is written as a sum over the probability amplitude of orbitals, thus replacing the many-body problem with a single-body problem. The total energy could be rewritten as a combination of five terms: the kinetic energy of the orbitals, the interaction between electrons and nuclei, the exchange-correlation (XC) energy, the static charge density (Hartree) energy, and the interaction between nuclei. Note that the XC energy is a correction to the Hartree energy since electrons are not stationary – this accounts for Coulomb repulsion and the Pauli Exclusion Principle. The Kohn-Sham Equation is a direct result of minimizing the energy functional with respect to the electron density.

Issues in implementing DFT were also discussed in this chapter. The Kohn-Sham Equation is used in a self-consistent field (SCF) cycle to converge the ground state energy. However, to solve the Kohn-Sham Equation, one must use a plane-wave basis set and a pseudopotential. ABINIT is the pseudopotential plane-wave expansion package used for this work. By solving the Kohn-Sham Equation, one can produce band structures and DOS.

In Chapter 4, the electronic properties from the TB Model were discussed for armchair boron nitride nanoribbons (ABNNRs) and zigzag boron nitride nanoribbons (ZBNNRs) of select widths. We found that N orbitals yields N bands in the band structures due to Huckel Theory. These BNNRs contained large band gaps and thus, they are classified as insulators. The DOS reveals characteristics of the BNNRs and indicates how many states are located at which energies. Band structures and DOS are symmetric about the Fermi level. The conductance and LDOS was studied in this chapter as well. Conductance of BNNRs is quantized and each band can be thought of as a mode of transport. It is noted that transport is highly dependent upon
degeneracy in the band structure. The LDOS showed the DOS for a single atomic site and the contribution to the total DOS. Valence bands are considered to be more nitrogen-rich and conduction bands are considered to be more boron-rich. The LDOS also revealed that the inner atoms of BNNRs have higher contributions to transport. Summing over all the LDOS yields and confirms the total DOS, which the TB Model and Green’s Function Theory both agree.

Next, small perturbations were applied to edge atoms of BNNRs. These small perturbations caused distortions in the band structure and DOS, depending on which atoms on which edges were perturbed. These alterations were achieved by changing the onsite energy of certain edge atoms in the range of ±3 eV. It was observed that delocalization occurs and bands will shift accordingly. Degeneracy also breaks in the band structure and both the band structure and DOS lose their symmetry about the Fermi level when these perturbations are applied. Since the bands in the band structure shifted, the band gap was also found to change. As a follow up, band gaps were studied under these sorts of perturbations. For ABNNRs, the band gap decreases at maximum to 27% from normal conditions (when there are no perturbations at the edges). For ZBNNRs, the band gap decreases at maximum to 63% from normal conditions. It was concluded that ZBNNRs have a higher probability of delocalizing from this data. Lastly, the conductance of BNNRs under small perturbations at the edges were studied. As a result, the modes of transport were altered or lost in ABNNRs, yet ZBNNRs preserved their modes of transport given that bands in the band structure shifted to different energies. It was that ZBNNRs are more suitable for transport and preserve the electronic behavior of the structure when subject to these edge perturbations.

Finally, the electronic properties of GNRs were compared to those of BNNRs. One third of armchair graphene nanoribbons (AGNRs) are considered to be metallic and the remaining two
thirds are considered to be semiconducting. All zigzag graphene nanoribbons (ZGNRs) are metallic regardless. AGNRs exhibit a linear dispersion near the Fermi level, which suggests that electrons have an effective mass of zero near the Fermi energy. This linear dispersion is also a signature feature of graphene and as a result, graphene can be metallic. The band structures, DOS, and conductance for select GNRs were compared to BNNRs in this chapter and agreed with previous work.

In Chapter 5, the SCF cycle was revisited in an attempt to explain the importance of converging the total energy for modeling hexagonal boron nitride (hBN) in sheet and nanoribbon form while using ABINIT computational software. To ensure calculation quality and that accurate ground state energies are produced, some important variables are under the user’s control. These variables include the vacuum between layers (in order to isolate the infinite hBN sheet), the cutoff energy, the k-point grid, and the volume of the primitive unit cell. Data tables were presented in this chapter, showing the convergence of total energy with respect to each of these variables. In this manner, one is able to test the efficiency of the model, the basis set, and the algorithm tolerance. In addition, these convergence tests also validate the accuracy of the results that were presented in Chapter 6.

In Chapter 6, the electronic properties from DFT were studied for an infinite sheet of hBN, a ZBNNR of N=4 chains, and a hydrogen edge-terminated ZBNNR. Results included band structures, DOS, angular momentum projected LDOS, and some of these systems were accompanied by VMD simulations. With the infinite hBN sheet, some interesting behavior was found in the band structure with some similarities to the TB Model’s predictions from Chapter 4. The valence bands were somewhat easy to identify, but the conduction bands were not as obvious. Consequently, VMD visualizations were produced to show electronic structure of
infinite hBN at the Γ-point. From one of these visualizations, a special surface state was found in infinite hBN which originated from both excited boron states and excited nitrogen states. In order to produce LDOS plots, the Laplacian of the electron density along the bond axis was investigated to find a suitable valence shell radius that could be centered around each atom to find angular momentum projections. The angular momentum projected LDOS later confirmed that s-states and p-states do exist in hBN, yet other higher states like d or f must also be present.

Second, the band structure and DOS for a ZBNNR of N=4 chains was shown. This band structure revealed lots of subbands as a result of more atomic species in the unit cell, all of which were at slightly different energies. No group of bands were degenerate, unlike what was seen in the TB Model in certain areas. Edge states were presented with VMD visualizations and it was found that the HOMO and LUMO at the edge of the 1st Brillouin Zone were directional states whereas the edge states at the HOMO and LUMO at the center of the 1st Brillouin Zone were very distinct. However, the most notable feature here is that the ZBNNR actually rendered metallic with no band gap. The metallic behavior was due to the dangling edge bonds. Totally contradictory to what was expected and what the TB Model predicts, hydrogen edge-termination was employed as a means to possibly preserve the insulating character. So, a hydrogen edge-terminated ZBNNR of the same width and its band structure and DOS were investigated. It was observed that the hydrogen edge-terminated ZBNNR had preserved the band gap with a value of 4.106 eV, which is very much an insulator. This special ZBNNR and its band structure is more closely related with the TB Model since the subbands appear to become degenerate and come together near the edge of the 1st Brillouin Zone. Since the HOMO and LUMO at the center of the 1st Brillouin Zone were responsible for the metallic behavior of the bare edged ZBNNR, VMD visualizations were shown at these two points for the hydrogen edge-terminated ZBNNR. The
VMD visualizations accompanied the band structure nicely and proved the insulating features of the nanoribbon were due to the presence of hydrogen edge-termination, as the electronic structure was reorganized and less charge overall was seen.

7.2 Suggestions for Further Investigation and Future Work

It can be assumed that science, in general, is never complete and is a continuing work in progress. However, there are a couple of routes this research can go in order to learn more about these special 2D materials. For the case of the TB Model, it may be wise to incorporate Extended Huckel Theory (EHT) into band structure and DOS calculations. This way, it will be easy to include other interactions and compare electronic properties of BNNRs produced with EHT to those with produced with DFT. One could also argue that the addition of edge terminated atoms like hydrogen, oxygen, sulfur, or fluorine could be useful. Since DFT predicted that hydrogen edge-terminated BNNRs are insulating with a wide band gap, perhaps EHT can also produce the same result.

The method of band gap tuning introduced in this work is quite simple but can be more carefully thought out. If one were to terminate edge atoms on BNNRs with those of oxygen, sulfur, or fluorine, the bond lengths between these edge atoms and edge-terminated atoms will also change. Experimental bond lengths can be used in this manner to best simulate these changes and results should be compared to experimental work.

For the case of Green’s Function Theory, the addition of edge-terminated atoms should also influence the conductance. It may be useful to observe these changes in transport and compare to what transport is like under normal conditions, without any edge-terminations. The LDOS would
also come in handy to look at when these edge-terminations are present in BNNRs. A method of weak scatter may also be investigated, as outlined by Li and Lu [9].

Perhaps the broadest avenue for research capability is utilizing DFT to model other edge-terminated BNNRs. Since it is a very popular method, it has been the first choice amongst many researchers who deal with electronic structure calculations. It would be interesting to see what DFT predicts as far as other edge atom terminations go with BNNRs and compare them to EHT and other previously published work to look for any major differences. Utilizing the LDOS to see which states are s-like, p-like, etc. is always a huge bonus and reveals a lot of information about the atomic character of bands in the band structure. Another route is to study the LDOS for the metallic ZBNNR as presented in Chapter 6. This special property is not seen with the TB Model at all and is completely contradictory. Thus, it is important to find out why this metallic behavior occurs and which atoms are responsible for it. Larger crystalline systems may be best investigated with other DFT-based codes, like SIESTA [66].
Appendix A

List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>GNRs</td>
<td>graphene nanoribbons</td>
</tr>
<tr>
<td>AGNRs</td>
<td>armchair graphene nanoribbons</td>
</tr>
<tr>
<td>ZGNRS</td>
<td>zigzag graphene nanoribbons</td>
</tr>
<tr>
<td>hBN</td>
<td>hexagonal boron nitride</td>
</tr>
<tr>
<td>BNNRs</td>
<td>boron nitride nanoribbons</td>
</tr>
<tr>
<td>ABNNRs</td>
<td>armchair boron nitride nanoribbons</td>
</tr>
<tr>
<td>ZBNNRs</td>
<td>zigzag boron nitride nanoribbons</td>
</tr>
<tr>
<td>TB</td>
<td>Tight-Binding</td>
</tr>
<tr>
<td>LCAO</td>
<td>linear combination of atomic orbitals</td>
</tr>
<tr>
<td>EHT</td>
<td>extended Hückel theory</td>
</tr>
<tr>
<td>DOS</td>
<td>density of states</td>
</tr>
<tr>
<td>LDOS</td>
<td>local density of states</td>
</tr>
<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
</tr>
<tr>
<td>LCPW</td>
<td>linear combination of plane-waves</td>
</tr>
<tr>
<td>KS</td>
<td>Kohn-Sham</td>
</tr>
<tr>
<td>XC</td>
<td>exchange-correlation</td>
</tr>
<tr>
<td>SCF</td>
<td>self-consistent field</td>
</tr>
<tr>
<td>ABINIT</td>
<td>pseudopotential plane-wave expansion package</td>
</tr>
<tr>
<td>ONCVPSP</td>
<td>optimized norm-conserving Vanderbilt pseudopotential</td>
</tr>
<tr>
<td>VMD</td>
<td>Visual Molecular Dynamics</td>
</tr>
<tr>
<td>HOMO</td>
<td>highest occupied molecular orbital</td>
</tr>
<tr>
<td>LUMO</td>
<td>lowest unoccupied molecular orbital</td>
</tr>
</tbody>
</table>
Appendix B

Sample Mathematica Codes

The following codes in this appendix are sample codes created for this thesis. The methodology is taken from Kan [5] and Mathematica is used for running these programs. The first code produces the band structure and DOS for an ABNNR. The second code produces the conductance and LDOS for an ABNNR. The third code produces the band gap versus the perturbation strength when edge perturbations are applied to an ABNNR. All sample codes will be in the standard Mathematica Notebook format, comments included with the characters (**).

Sample Code 1: Band Structure and DOS for an ABNNR

(*General parameters*)
n = 9; (*number of dimers*)
a = 1.43; (*bond length of BN from Oak Ridge paper*)
Vpp = -0.81*(7.62/a^2); (*Vpp\[Pi] bond overlap potential from Harrison*)
EB = -6.64; (*onsite energy for boron*)
EN = -11.47; (*onsite energy for nitrogen*)

(*Hamiltonian matrix*)
H = Table[0, {x, 1, 2 n}, {y, 1, 2 n}];

Do[H[[i, i]] = EB, {i, 1, 2 n, 4}]; (*assign borons down left side of unit cell*)
Do[H[[i, i]] = EN, {i, 2, 2 n, 4}];(*assign nitrogens down left side of unit cell*)
Do[H[[i, i]] = EB, {i, 4, 2 n, 4}]; (*assign borons down right side of unit cell*)
Do[H[[i, i]] = EN, {i, 3, 2 n, 4}]; (*assign nitrogens down right side of unit cell*)

Do[H[[i, i + 1]] = H[[i + 1, i]] = Vpp, {i, 1, 2 n, 2}]; (*assigns H12, H21, H34, H43, H56, H65, etc.*)
Do[H[[i, i + 2]] = H[[i + 2, i]] = Vpp, {i, 1, 2 n - 2}]; (*assigns H13, H31, H24, H42, etc.*)
Do[H[[i + 1, i]] = Vpp*Exp[I*k*(3 a)], {i, 3, 2 n, 4}]; (*assigns H43, H87 - coupling between neighboring cells to the right and overrides the first do loop above*)
Do[H[[i, i + 1]] = Vpp*Exp[-I*k*(3 a)], {i, 3, 2 n, 4}]; (*assigns H34, H78 - coupling between neighboring cells to the left and overrides the first do loop above*)
MatrixForm[H];

(*preliminary parameters*)
pbc = (1/2)*(2 \[Pi])/(3 a);(*periodic boundary condition*)
kstates = 800; (*number of k-states for plotting band structure and DOS - need this number to be >500 at least*)
kvals = Table[0, {i, 1, kstates}]; (*empty table to fill with k-states*)
ERange = Table[0, {l, 1, kstates}]; (*empty table to define an arbitrary energy range*)
EBands = Table[Table[0, {i, 1, kstates}], {j, 1, 2 n}]; (*empty table to define energy band values*)
EPlot = Table[0, {j, 1, 2 n}]; (*empty table to plot bands*)
DOS = Table[0, {l, 1, kstates}]; (*empty table to fill with DOS values*)

(*band structure calculation*)
Do[
kvals[[i]] = (2*pbc)/(kstates - 1)*(i - kstates) + pbc; (*generates k values across the first Brillouin zone, defined by how many kstates the user chooses*)
evals = Eigenvalues[H /. k -> kvals[[i]]]; (*replaces k in matrix with newly generated k values to calculate eigenvalues for different k*)
Do[
    EBands[[j]][[i]] = evals[[j]], {j, 1, 2 n}], {i, 1, kstates}]; (*throws newly calculated eigenvalues into a table for each band j*)
Do[EPlot[[j]] = ListPlot[Table[{kvals[[i]], EBands[[j]][[i]] - ((EB + EN)/2)}, {i, 1, kstates}],
    PlotRange -> {{{-pbc, pbc}, {-10, 10}}},
    Axes -> False,
    Frame -> True,
    FrameLabel -> {"k (1/Å)"", "Energy (eV)"},
    AspectRatio -> 2/1,
    PlotMarkers -> None,
    PlotLabel -> "(a)",
    LabelStyle -> {"Helvetica", 14, Black},
    FrameTicks -> {{Automatic, None}, {{-0.6, 0, 0.6}, None}},
    FrameStyle -> Directive[{Black, AbsoluteThickness[2]}],
    BaseStyle -> {"Helvetica", 14},
    PlotStyle -> Hue[0.2*Abs[j - 10]], {j, 1, 2 n}]; (*takes all the energies of each band for each k and puts it into another table*)
ab = Show[EPlot,
    ImageSize -> Medium] (*shows the band structure over the first Brillouin zone*)

(*DOS calculation*)
Do[
    ERange[[l]] = (10*Abs[Vpp])/(kstates - 1)*(l - kstates) + 5*Abs[Vpp] + (EB + EN)/2;
    (*defines an arbitrary energy range*)
    DOSplot = DOS[[l]] = 1/((Pi)*kstates)*Sum[Sum[0.01/((EBands[[j]][[i]] - ERange[[l]])^2 + 0.01^2), {i, 1, kstates}], {j, 1, 2 n}], {l, 1, kstates}]; (*calculates DOS using Zhe Kan's approximation*)
DOSimage = ListLinePlot[
    Table[{DOS[[l]], ERange[[l]] - ((EN + EB)/2)}, {l, 1, kstates}];
PlotRange -> {{0, 4}, {-10, 10}},
Axes -> False,
Frame -> True,
FrameLabel -> {"DOS", "Energy (eV)",
FrameTicks -> {{Automatic, None}, {{0, 1, 2, 3, 4}, None}},
PlotLabel -> "(b)",
LabelStyle -> {"Helvetica", 14, Black},
FrameStyle -> Directive[{Black, AbsoluteThickness[2]}],
AspectRatio -> 2/1,
BaseStyle -> {"Helvetica", 14}
(*plots the DOS vs. Energy*)

Sample Code 2: Conductance and LDOS for an ABNNR

(*---Input Parameters---*)
n = 8; (*number of dimers*)
EN = -11.47; (*onsite energy for nitrogen*)
EB = -6.64; (*onsite energy for boron*)
a = 1.43; (*bond length for BN*)
Vpp = -0.81*(7.62/a^2); (*Vpp\[Pi] bond overlap potential from Harrison*)
kB = 8.617*10^-5; (*Boltzmann constant in eV/K*)
T = 25; (*Temperature in Kelvin*)
\[Eta] = kB*T; (*constant needed for conductance calculation*)
kstates = 800; (*number of k values/states*)
IdM = IdentityMatrix[2 n]; (*Identity Matrix*)

(*---Hamiltonians---*)
(*Define Hamiltonians for conductor and leads*)
HM = Table[0, {x, 1, 2 n}, {y, 1, 2 n}];
H1 = Table[0, {x, 1, 2 n}, {y, 1, 2 n}];
H2 = Table[0, {x, 1, 2 n}, {y, 1, 2 n}];

(*Assign onsite energies and overlap potentials for conductor*)
Do[HM[[i, i]] = EB, {i, 1, 2 n, 4}];
Do[HM[[i, i]] = EB, {i, 4, 2 n, 4}];
Do[HM[[i, i]] = EN, {i, 3, 2 n, 4}];
Do[HM[[i, i]] = EN, {i, 2, 2 n, 4}];
Do[HM[[i, i + 2]] = HM[[i + 2, i]] = Vpp, {i, 1, 2 n - 2, 2}]
Do[HM[[i, i + 2]] = HM[[i + 2, i]] = Vpp, {i, 2, 2 n - 2, 2}]
Do[HM[[i, i + 1]] = HM[[i + 1, i]] = Vpp, {i, 1, 2 n, 4}]
H1 = H2 = HM;(*unit cells of molecule/conductor are the same unit cells for \ within the leads*)

(*Define Hamiltonians for coupling*)
H11 = Table[0, {x, 1, 2 n}, {y, 1, 2 n}];
H22 = Table[0, {x, 1, 2 n}, {y, 1, 2 n}];
H1M = Table[0, {x, 1, 2 n}, {y, 1, 2 n}];
HM2 = Table[0, {x, 1, 2 n}, {y, 1, 2 n}];

(*Coupling matrices between molecule and leads*)
Do [H1M[[i, i + 1]] = Vpp, {i, 3, 2 n - 1, 4}];
Do [HM2[[i, i - 1]] = Vpp, {i, 4, 2 n, 4}];
H11 = H22 = HM2 = H1M;

(*Check Hamiltonians*)
MatrixForm[HM];
MatrixForm[H1M];
MatrixForm[HM2];
MatrixForm[H1];
MatrixForm[H2];
MatrixForm[H11];
MatrixForm[H22];

(*---Conductance Calculation---*)
(*Define an energy range with total number of k values*)
ERange = Table[0, {i, 1, kstates}]; (*Empty matrix for a range of energies with x amount of k values*)
TransmissionFxn = Table[0, {i, 1, kstates}]; (*Empty matrix for the transmission function*)
dos = Table[0, {i, 1, kstates}]; (*Empty matrix for the DOS calculation*)
ldos = Table[Table[0, {i, 1, kstates}], {j, 1, 2 n}]; (*Empty table for LDOS calculation*)
LDOSplots = Table[0, {j, 1, 2 n}]; (*Empty table for LDOS plots*)

(*Start conductance calculation here*)
Do[ERange[[i]] = (10*Abs[Vpp])/(kstates - 1) (i - kstates) + 5*Abs[Vpp] + ((EN + EB)/2);
   iterations = 20;(*number of iterations for recursion method*)
   TransmissionFxn[[i]] = Inverse[(ERange[[i]] + I*[Eta])*IdM - H2].H11;
   TransmissionFxn[[i]] = Inverse[(ERange[[i]] + I*[Eta])*IdM - H1].H11;
   Do[
      t1[[k + 1]] = Inverse[IdM - t1[[k]].t2[[k]] - t2[[k]].t1[[k]]].t1[[k]];
      t2[[k + 1]] = Inverse[IdM - t1[[k]].t2[[k]] - t2[[k]].t1[[k]]].t2[[k]];
      , {k, 1, iterations - 1}
   ];
   (*Calculate the Transfer matrices*)
   \[CapitalLambda]1 = t1[[1]] +
      Sum[(Apply[Dot, Table[t2[[k]], {k, 1, l}]].t1[[l + 1]]), {l, 1, iterations - 1}];
   \[CapitalLambda]2 =
      t2[[1]] +
      Sum[(Apply[Dot, Table[t1[[k]], {k, 1, l}]].t2[[l + 1]]), {l, 1, iterations - 1}];
   (*Calculate the Self energy matrices*)
   \[CapitalSigma]1 =
      H1M[ConjugateTranspose].Inverse[(ERange[[i]] + I*[Eta])*IdM - H1 -
      H1M[ConjugateTranspose].\[CapitalLambda]2].H1M;

   (*Recursion formulas - set up empty matrices*)
   t1 = Table[0, {k, 1, iterations}];
   t2 = Table[0, {k, 1, iterations}];
   (*Calculate the first element of recursion formulas*)
   t1[[1]] = Inverse[(ERange[[i]] + I*[Eta])*IdM - H2].H11[ConjugateTranspose];
   t2[[1]] = Inverse[(ERange[[i]] + I*[Eta])*IdM - H1].H11;
   (*Recursion method to generate transfer matrices*)
   Do[
      t1[[k + 1]] = Inverse[IdM - t1[[k]].t2[[k]] - t2[[k]].t1[[k]]].t1[[k]].t1[[k]];
      t2[[k + 1]] = Inverse[IdM - t1[[k]].t2[[k]] - t2[[k]].t1[[k]]].t2[[k]].t2[[k]];
      , {k, 1, iterations - 1}];
   (*Calculate the Transfer matrices*)
   \[CapitalLambda]1 = t1[[1]] +
      Sum[(Apply[Dot, Table[t2[[k]], {k, 1, l}]].t1[[l + 1]]), {l, 1, iterations - 1}];
   \[CapitalLambda]2 =
      t2[[1]] +
      Sum[(Apply[Dot, Table[t1[[k]], {k, 1, l}]].t2[[l + 1]]), {l, 1, iterations - 1}];
   (*Calculate the Self energy matrices*)
   \[CapitalSigma]1 =
      H1M[ConjugateTranspose].Inverse[(ERange[[i]] + I*[Eta])*IdM - H1 -
      H1M[ConjugateTranspose].\[CapitalLambda]2].H1M;
\[\text{CapitalSigma}2 = \text{HM2.Inverse[(ERange[[i]] + I*[\text{Eta}])*\text{IdM} - \text{H2} - \text{HM2.[\text{CapitalLambda}1].HM2[ConjugateTranspose]};\]

(*Calculation of Green's function needed to describe conductance*)
GreensFxn = Inverse[(ERange[[i]] + I*[\text{Eta}])*\text{IdM} - \text{HM} - \text{CapitalSigma}1 - \text{CapitalSigma}2];

(*Calculate the Coupling matrices*)
\[\text{CapitalGamma}1 = I*(\text{CapitalSigma}1 - \text{CapitalSigma}1[\text{ConjugateTranspose}];\]
\[\text{CapitalGamma}2 = I*(\text{CapitalSigma}2 - \text{CapitalSigma}2[\text{ConjugateTranspose}];\]

(*Define an advanced and retarded Green's function for calculation*)
GRetFxn = GreensFxn;
GAdvFxn = GreensFxn[ConjugateTranspose];

(*Calculate the transmission function*)
TransmissionFxn[[i]] = Tr[\text{CapitalGamma}1.GRetFxn.\text{CapitalGamma}2.GAdvFxn];

(*Calculate the DOS and LDOS*)
dos[[i]] = (-1/Pi)*Im[Tr[GRetFxn]]; Do[ldos[[j]][[i]] = (-1/Pi)*Im[GRetFxn[[j]][[j]]], \{j, 1, 2 n\}, \{i, 1, kstates\}]

(*Plot conductance vs. energy*)
cplot = ListLinePlot[
  Table[{ERange[[i]] - ((EB + EN)/2), Re[TransmissionFxn[[i]]]}, \{i, 1, kstates\}],
  FrameLabel -> {"Energy (eV)", "G (2!\text{SuperscriptBox[\("(2)\)]/h)}"},
  Frame -> True,
  FrameTicks -> {{Automatic, None}, {Automatic, None}},
  PlotLabel -> "(a)",
  AspectRatio -> 1/2,
  Axes -> False,
  LabelStyle -> {"Helvetica", 14, Black},
  FrameStyle -> Directive[{Black, AbsoluteThickness[2]}],
  BaseStyle -> {"Helvetica", 14},
  ImageSize -> Medium]
abncimage=Show[cplot]

(*Plot DOS vs. energy*)
dosimage = ListLinePlot[
  Table[{ERange[[i]] - ((EB + EN)/2), dos[[i]]}, \{i, 1, kstates\}],
  FrameLabel -> {{"Energy (eV)", "DOS"}, {Automatic, None}},
  Frame -> True,
  FrameTicks -> {{Automatic, None}, {Automatic, None}},
  (*PlotLabel\[Rule]"(b)";*)
  AspectRatio -> 1/2,
  Axes -> False,
  LabelStyle -> {"Helvetica", 14, Black},
  ImageSize -> Medium]
Sample Code 3: Band gap versus perturbation strength for an ABNNR

(*---General parameters---*)

n = 9; (*number of dimers*)
a = 1.43; (*bond length of BN from Oak Ridge paper*)
Vpp = -0.81*(7.62/a^2); (*Vpp\[\pi\] bond overlap potential from Harrison*)
EB = -6.64; (*onsite energy for boron*)
EN = -11.47; (*onsite energy for nitrogen*)

(*---Hamiltonian matrix---*)

H = Table[0, {x, 1, 2 n}, {y, 1, 2 n}];

Do[H[[i, i]] = EB, {i, 1, 2 n, 4}]; (*assign borons down left side of unit cell*)
Do[H[[i, i]] = EN, {i, 2, 2 n, 4}]; (*assign nitrogens down left side of unit cell*)
Do[H[[i, i]] = EB, {i, 4, 2 n, 4}]; (*assign borons down right side of unit cell*)
Do[H[[i, i]] = EN, {i, 3, 2 n, 4}]; (*assign nitrogens down right side of unit cell*)

Do[H[[i, i + 1]] = H[[i + 1, i]] = Vpp, {i, 1, 2 n, 2}]; (*assigns H12, H21, H34, H43, H56, H65, etc.*)
Do[H[[i, i + 2]] = H[[i + 2, i]] = Vpp, {i, 1, 2 n - 2}]; (*assigns H13, H31, H24, H42, etc.*)
Do[H[[i + 1, i]] = Vpp*Exp[I*k*(3 a)], {i, 3, 2 n, 4}]; (*assigns H43, H87 - coupling between neighboring cells to the right and overrides the first do loop above*)
Do[H[[i, i + 1]] = Vpp*Exp[-I*k*(3 a)], {i, 3, 2 n, 4}]; (*assigns H34, H78 - coupling between neighboring cells to the left and overrides the first do loop above*)

(*---Band gap calculation, this is essentially a simple loop... SINGLE BORON ATOM---*)
k = 0; (*Use k=0 for \[CapitalGamma]-Point*)
p = 1; (*Defines which boron atom will be perturbed*)

(*Create range of \[Delta] to add/subtract to each onsite energy of the desired perturbed atom*)
\[Delta\]min = -3;
\[Delta\]max = 3;
\[Delta\]table = Table[0, {i, \[Delta\]min, \[Delta\]max}];
bandgaptab = Table[0, {i, 1, Length[\[Delta\]table]}];

Do[
  H[[p, p]] = EB + \[Delta];
  bandgap = Abs[Eigenvalues[H][[n + 1]] - Eigenvalues[H][[n]]];(*Mathematically calculate band gap*)
  \[Delta\]table[[i]] = \[Delta];(*Assign current perturbation strength to table*)
  bandgaptab[[i]] = bandgap;(*Assign current band gap calculation to table*)
  Print[{\[Delta\], bandgap}] // TableForm;(*Show \[Delta] and band gap in table form*)
  \[Delta\] = \[Delta\] + 1;(*Update \[Delta]*)

plotABtop = ListPlot[Table[{\[Delta\]table[[i]], bandgaptab[[i]]}, {i, \[Delta\]min, \[Delta\]max}],
  Axes -> False,
  Frame -> True,
  FrameLabel -> {"\!\(\*SubscriptBox[\(V\), \(B\)]\) (eV)",
                "\!\(\*SubscriptBox[\(E\), \(bg\)]\) (eV)"),
  FrameTicks -> Automatic, None},
  BaseStyle -> {FontWeight -> "Black", FontSize -> 14},
  PlotLabel -> "(a)",
  LabelStyle -> {"Helvetica", 14, Black},
  FrameStyle -> Directive[Black, AbsoluteThickness[2]],
  BaseStyle -> {"Helvetica", 14},
  ImageSize -> Large,
  PlotMarkers -> Automatic, Large,
  PlotStyle -> {Black, Dashed, Thick},
  Joined -> True],
  {i, \[Delta\]min, \[Delta\]max}];(*Create plot*)
Show[plotABtop](*Display plot*)
Appendix C

List of ABINIT Input Variables

Below is a list of variables that a user may see in ABINIT input files and a brief explanation for each variable is included. This appendix should not serve as the primary source of information for these variables. The author refers the reader to ABINIT’s documentation guide at www.abinit.org.

- ndset: number of data sets
- ecut: cutoff energy
- ixc: integer for exchange-correlation choice
- occopt: occupation option
- vacuum: vacuum identification
- acell: cell lattice vector scaling
- rprim: real space primitive translations
- ntypat: number of types of atoms
- znuc1: charge Z of the nucleus
- natom: number of atoms
- typat: type of atoms
- xred: vectors (X) of atom positions in reduced coordinates
- xcart: vectors (X) of atom positions in Cartesian coordinates
- kptopt: k-points option
- kptrans: k-points grid: real space lattice
- toldfe: tolerance on the difference of total energy
\( nband \)  number of bands
\( nstep \)  number of self-consistent field steps
\( ndivk \)  number of k-point divisions
\( kptbounds \)  k-point boundaries
\( tolwfr \)  tolerance on wavefunction squared residual
\( prtdos \)  print the density of states
\( prtdosm \)  print the density of states with m-decomposition
\( natsph \)  number of atomic spheres for the atom projected density of states
\( iatsph \)  index for the atomic spheres of the atom projected density of states
\( ratsph \)  radii of the atomic spheres
Appendix D

Sample ABINIT Input Files

In this appendix, sample ABINIT input files are shown. The first input file calculates the ground state energy using the SCF cycle, the band structure and DOS for an infinite sheet of hBN. The second input file calculates the ground state energy using the SCF cycle, the band structure, and the LDOS for a ZBNNR of N=2 chains. Again, the author refers the reader to ABINIT’s documentation guide online for more details on variables that are not listed in Appendix C. Input file comments are denoted with the character #.

Sample Input File 1: Total energy, band structure, and DOS for infinite hBN

# hBN bands/DOS calculation
ndtset 3  #number of data sets

#Definition of the planewave basis set
dcmt 35  #Maximal kinetic energy cut-off, in Hartree
dic 11  #Index indicating XC functional - the GGA by PBE

#Definition of electron occupation and vacuum
dcopt 7  #Gaussian smearing of electron occupation
dvacuum 0 0 1  #Expect vacuum along z- direction

#Definition of the unit cell
dacell 4.446 4.446 25.0  #x, y, z components of dimensions of box/lattice constant
drprim 1.0 0.0 0.0  #Translation vectors to build lattice, scaled by acell
  0.5 0.866 0.0
  0.0 0.0 1.0

#Definition of the atom types
ntypat 2  # Indicates two types of nuclei
znucl 5 7  # Indicates the charges of both nuclei

# Definition of the atoms
natom 2  # Indicates two atoms
typat 1 2  # Indicates two different types of atoms

xred
1/3 1/3 1/2  # reduced, crystallographic coordinates
2/3 2/3 1/2

# Dataset 1: SCF calculation
kptopt1 1  # Rely on kptrlatt and nshiftk, taking into account the symmetry
kptrlatt1 12 0 0  # Definition of the k-point grid
-7 14 0
0 0 1

nshiftk1 1  # Number of shifts in k-point grid
shiftk1 0 0 0  # Defines the shift of k-points
prtden1 1  # Print the density, for use by dataset 2
toldfe1 1.0d-7  # Tolerance for total energy convergence, for SCF cycle
nbands1 14  # Number of bands (also for band structure), 5N bands for N atoms
nstep1 70  # Maximum number of steps given for SCF cycle to converge

# Dataset 2: Compute the Band Structure
iscf2 -2  # Electron density will be read from previous dataset
getden2 -1  # Gets density from the previous dataset
kptopt2 -3  # Rely on kptbounds and ndivk to set up band structure: Value gives number of segments of the band structure (i.e. how many vectors in reciprocal space you're traveling)

nbands2 14
ndivk2 50 50 50  # Number of k-point divisions between each k-point bound
kptbounds2 0.5 0.0 0.0  # M point
0.0 0.0 0.0  # Gamma Point
2/3 1/3 0.0  # K Point
0.5 0.5 0.0  # M Point
tolwfr2 1.0d-12  # Tolerance in the wavefunction squared residual, for SCF cycle

### Dataset 3: Compute DOS
getden3 1
prtdos3 2  # Print the density of states

# Non-self-consistent calculation. Charge density comes from # DEN file with form of "abi_DENi"
iscf3 -3  # read in charge density, needed to get orbitals and eigenvalues for # DOS from an Abinit "i" file
tolwfr3 1.0d-12
kptopt3 1  # Rely on kptrlatt and nshiftk
  # taking into account the symmetry
kptrlatt3 24 0 0  # k-point grid components should be doubled or tripled when doing -14 28 0  # DOS calculations
0 0 1
nshiftk3 1
shiftk3 0 0 0
nbands3 14  # 5N bands for N atoms
Sample Input File 2: Total energy, band structure, and m-projected LDOS for a ZBNNR of N=2 chains

#ZBNNR N=2
#Total energy, band structure, and m-projected LDOS

ndtset 3

#Definition of the planewave basis set
ecut 45
ixc 11

#Definition of the SCF procedure
nstep 70
iprcel 45         #Preconditioning for Electron Response:
                  #A value of 45 instructs ABINIT to compute RPA dielectric
                  #matrix at the first step, and recompute it at a later step

#Definition of the unit cell
acell 4.68 24.3 25.0
rprim 1.0 0.0 0.0
      0.0 1.0 0.0
      0.0 0.0 1.0
chkprim 0  #check condition to allow ABINIT to proceed with translation vectors
           #which do not reflect the shape of lattice
occ2pt 7
vacuum 0 1 1   #vacuum in y and z directions
chksymbreak 0 #check condition to allow ABINIT to proceed if symmetry is broken

#Definition of the atom types
ntypat 2
znucl 5 7

#Definition of the atoms
natom 4
typat 1 2 1 2
xcart
  1.17 9.45 12.5  #Cartesian coordinates of atoms
  3.51 10.8 12.5
  3.51 13.5 12.5
  1.17 14.9 12.5

#Dataset 1: usual self-consistent calculation-----
kptopt 1
kptrlatt1 22 0 0
         0 1 0
         0 0 1
nshiftk1 1
shiftk1 0 0 0
prtden1 1
toldfe1 1.0d-7
#tolwfr1 1.0d-12
nbond1 20        #5N bands for N atoms

#Dataset 2: Compute the Band Structure
iscf2 -2          # Electron density will be read from previous dataset
getden2 -1        # Gets density from the previous dataset
kptopt2 -2
nband2 20
ndivk2 50 50
kptbounds2 -0.5 0.0 0.0    # left edge of 1st BZ
   0.0 0.0 0.0    # Gamma point
   0.5 0.0 0.0    # right edge of 1st BZ
tolwfr2 1.0d-12

# Dataset 3: Compute DOS
getden3 -1
prtdos3 3        # Tells ABINIT to do m-projected LDOS
prtdosm3 1       # Initiates m-projected LDOS
natsph3 4        # Number of spheres centered around atoms for LDOS
iatsph3 1 2 1 2  # Index of spheres centered around atoms
ratsph3 1.2 1.5 1.2 1.5      # Radii of spheres centered around atoms
iscf3 -3
tolwfr3 1.0d-12
kptopt3 1
kptrlatt3 66 0 0
   0 1 0
   0 0 1
nshiftk3 1
shiftk3 0 0 0
nband3 20        # 5N bands for N atoms
References


