ELECTRONIC PROPERTIES OF GRAPHENE NANO STRUCTURES

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Abstract

Electronic Properties of Graphene Nanoribbons Using Extended Hückel Theory

The general objective of the research project is to study the electronic properties of graphene nanoribbons (GNRs). Graphene nanoribbons are an allotrope of carbon. These ribbons can be viewed as strips of graphene with infinite lengths and finite widths. These nanoribbons can be either metallic or semiconducting depending on their edge structures and widths. Based on the edge structure, GNRs are known as zigzag and armchair. These are robust materials with excellent electrical conductivity and the potential for device application.

Energy band structure, density of states, and conductance are calculated using a tight-binding (TB) model, Green’s function method, Landauer formula, and the Extended Hückel theory (EHT). The band structures and density of states are calculated using the EHT based TB model and the Green’s function method and the Landauer formula have been implemented for determining the transmission and conductance. Our interest is to compare the EHT results with the Hückel theory results where only Pz orbitals are included in the calculation. The EHT technique not only includes the π orbital interactions but also the stronger sigma orbitals. Therefore, one may expect additional insight into the physical properties of the ribbons when using the EHT compared to the simpler Huckel method. It is observed from this investigation that there is no fundamental difference in the electronic properties near the Fermi energy. The only difference between the two methods is observed at higher energies in the conduction and valence bands.
Chapter 1

Introduction

1.1 Overview

Graphene is a carbon based two-dimensional hexagonal material having a single atomic thickness, first isolated by Novoselov and others in 2004 [1]. There has always been interest in research on graphene [1]; this interest was enhanced after the successful isolation experimentally [1]. Graphene has the potential to be shaped into strips. These strips are known as graphene nanoribbons (GNRs). Figure 1 shows an example of a zigzag and an armchair nanoribbon nanostructure [2,3]. Each ribbon has finite width compared to a semi-infinite length. Since the discovery of graphene, lots of research has been done on graphene nanoribbons (GNRs) [4-12]. One of the reasons for the strong interest in studying GNRs is their unique electrical properties [13]. These electronic properties provide GNRs with the potential to become components for future nano-electronic devises and integrated circuits [4,9,12,14,].

![Figure 1: (a) Zig-zag graphene nanoribbon with N= 6 (total number of chains) (b) Armchair graphene nanoribbon with N= 10 (total number of dimers) [11].](image)
GNRs will have semiconducting or metallic properties that depend on the structure of their edges. The edge structure is used to classify the GNRs as either zigzag and armchair. It is known that all zigzag graphene nanoribbons (ZGNRs) are metallic on the other hand one third of the armchair graphene nanoribbons (AGNRs) are metallic and two thirds are semiconducting [2,3]. The metallic or semiconducting property of an AGNR depends on its widths. Much of the research done on the electronic properties focuses on the edge structure. The edge structure of the material can be changed by altering a number of factors, such as edge defects, edge termination with different elements and compounds, and doping with different materials [12,15,16,17,18,19]. Being able to control the defects and doping of a material is something that would be of great value for nano-electronic devices. This control would enhance the ability to ensure the desired semiconducting or metallic property.

Today, researchers are able to fabricate GNRs from bottom-up synthesis from molecular precursors [20,21]. Hydrogen plasma etching is then used to produce high-quality GNRs with well-defined edges [22].

The science involved in studying GNRs requires an understanding of solid state physics, condensed matter physics, quantum physics, and chemistry. Two of the theories used to study GNRs and their electrical properties are the tight-binding model and density functional theory [23,24,25]. The model used in this thesis follows the tight-binding approach using extended Huckel method [23,24]. The extended Huckel method is an expansion of the Huckel method. The Huckel method uses the weaker π bonds for calculations. In the case of GNRs the π bonds form from the interaction between Pz orbitals. The extended Huckel method uses all the outer
valence orbitals in the calculations. For the GNRs this includes the S, Px, and Py, thus increasing the number of calculations required by four [26,27].

In this project, electronic band structure, density of states, local density of states, and conductance are calculated. Two different types of graphene nanoribbons the armchair and zigzag have been studied. The electronic properties are investigated using a tight-binding model, Green’s function methodology, Landauer formalism, and the extended Huckel method [23,24,28]. The extended Huckel method results are compared with the Huckel method results. The organization of the thesis is described in the next section.

1.2 Thesis Map

In Chapter 2, the theoretical models used for calculation are discussed, these models are as follows, the tight-binding model, the Green’s function methodology, and the Extended Huckel method. The analyses of the Hamiltonian matrix will be shown for the calculation of band structure, density of state, and conductance.

Chapter 3 will present the results of energy band structure, density of states (DOS), conductance, and local density of states (LDOS) for armchair nanoribbons using the extended Huckel method. These band structure results are then compared with the results obtained using the Huckel method looking only at the Pz orbitals. In Chapter 4, results of energy band structure and the DOS are presented for zigzag nanoribbons. As in Chapter 3, the results obtained by the extended Huckel theory are compared with the simple Huckel method. Chapter 5 will provide the summary and conclusions, and include a plan for further investigation.
Chapter 2

Theory and Calculations

2.1 Introduction

The basic theoretical models used in this research project are the extended Hückel- tight-binding approach, Green’s function methodology, and the Landauer formalism. Electronic properties such as the band structure, density of state (DOS), local density of states (LDOS), and conductance of the graphene nanoribbons (GNRs) are calculated using these models. Briefly, these theories will be discussed in this chapter.

2.2 The Tight-binding Model

The tight-binding approach (TB) is a good approximation method for calculating the electronic properties of GNRs. In a TB model only the nearest-neighbor interactions of the atoms of the system are taken into account. The Hamiltonian matrix of a TB model is given by

\[ H = \sum_i \varepsilon_i a_i^\dagger a_i + \sum_{<i,j>} V_{ij} a_i^\dagger a_j. \]  

(2.1)

Here, \( \varepsilon_i \) is the on-site energy of the carbon orbital, \( a_i \) and \( a_i^\dagger \) represent the creation and annihilation operators of particles at sites \( i \) and \( j \), respectively. \( V_{ij} \) is the overlap interaction energy between nearest neighbor orbitals and the notation, \( <i,j> \) representing the restriction to nearest neighbor interactions. The matrix elements of the Hamiltonian are calculated from the relation [24]:
\[ V_{ijk} = \eta_{ijk} \frac{h^2}{md^2}. \]  

(2.2)

Here, \( m \) is the electron mass, \( d \) is the distance between neighboring nucleuses, and \( \eta_{ijk} \) is a constant used that depends on the type of orbital. For a graphene structure the value for \( d = 1.42 \text{ Å}^2 \) and the on-site energy \( \varepsilon_p = -8.97 \text{ eV} \) and \( \varepsilon_s = -17.52 \text{ eV} \). The \( i, j \) notations reflect the type of orbital and \( k \) relates to the type of bond either \( \sigma \) or \( \pi \). There are four \( \eta \) values and these include: \( pp\pi, pp\sigma, sp\sigma, \) and \( ss\sigma \) matrix elements. These are \( \eta_{ssa} = -1.40 \), \( \eta_{spa} = 1.84 \), \( \eta_{pp\sigma} = 3.24 \), and \( \eta_{pp\pi} = -0.81 \). These constants are obtained from the reference [24].

The band structures and the density of states (DOS) of the systems are obtained by diagonalizing the Hamiltonian matrix as a function wave vector \( k \). The density of the \( i \)th band is given by [10,11]

\[ DOS_i(E) = \frac{1}{2\pi} \int \delta [E_i(k) - E] dk. \]  

(2.3)

And the total density for all the bands can be calculated by summing each band

\[ DOS(E) = \sum_{i=1}^{N} \frac{1}{2\pi} \int \delta [E_i(k) - E] dk, \]  

(2.4)

where \( E_i \) is the \( i \)th band, the summation over all \( i = 1 \) to \( N \) bands shows the total DOS [11].

### 2.3 Green’s Function Formalism: Conductance and Local Density of States

In order to calculate the conductance and local density of states (LDOS) Green’s function formalism has been used for the GNRs. The conductance is obtained from the well-known Landauer formula [23]

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

(2.5)
Where $G$ is the conductance of the structure and $T$ is the transmission function. The transmission function is dependent on the total energy of the electron. The transmission function is calculated from the Green’s functions [4, 29, 30].

$$T(E) = \text{Trace}[\Gamma_1 \cdot G_m \cdot \Gamma_2 \cdot G_m^\dagger],$$

(2.6)

$\Gamma_1$ and $\Gamma_2$ are coupling functions, while $G_m$ and $G_m^\dagger$ are the total retarded Green’s function and total advanced Green’s function, respectively. The notations 1 and 2 are representing the left lead and the right lead, respectively. Next, the coupling functions (matrices) are expressed in terms of self-energy matrices [23]:

$$\Gamma_1 = \mathbb{1}[\Sigma_1 - \Sigma_1^\dagger]$$

$$\Gamma_2 = \mathbb{1}[\Sigma_2 - \Sigma_2^\dagger].$$

(2.7)

The self-energy matrices are calculated through the iteration process [4, 29]. The molecule and the leads are divided into sections in the iterating process. Therefore, there are three specific segments: the molecule, the left lead, and the right lead. The schematic structures of both zigzag and armchair structures are shown in Figure 1.1. The middle part marked with red color boundary is representing the molecule, and the leads are extended to the left and right, respectively.

The Green’s function ($G_m$) is calculated in terms of Hamiltonian matrix, total energy, and the self-energy matrices [23]:

$$G_m = [E \mathbb{1} - H_m - \Sigma_1 - \Sigma_2]^{-1}.$$
By finding the Green’s function, the local density of states can be calculated, and then a summation of the local density of states leads to the total density of states. Therefore, the local density of states of individual atoms is expressed from the Green’s function, $G_m$:

$$\text{LDOS}_i(E) = -\frac{1}{\pi} \text{Im}[G_m(i, i)]. \quad (2.9)$$

It should be noted that the total density of states (DOS) of all the atoms discussed above can also be obtained by summing the individual LDOS from the Green’s function. In this research project, the results are verified by both methods. The detailed analyses of the Green’s function calculations are illustrated in the references [4,11,12,29].

### 2.4 The Extended Huckel Method

The electronic configuration of the ground state of a single carbon atom is $1s^2 \ 2s^2 \ 2p_x^1 \ 2p_y$. On a hexagonal graphene structure the $2s$, $2p_x$, and $2p_y$ orbitals form $sp^2$ hybridized orbitals. These hybridized orbitals are at $120^0$ to each other and form $\sigma$ bonds on the 2-dimensional structures of graphene. Figure 2.1 illustrates a graphical presentation of the orbitals. Figure 2.1 (a) shows the $S$, $P_x$, and $P_y$ orbitals of the atoms. The $P_z$ orbitals are perpendicular to the plane and are not shown here. In addition, projections of the $P_x$ and $P_y$ orbitals of atom 1 on the $S$ orbital of atom 3 are shown in part (b). These $\pi$ bonds are relatively weaker compared to the $\sigma$ bonds and electrons can move from one atom to the other.
Figure 2.1: (a) shows a top down view of the unit cell with orbitals. Projections of the Px and Py orbitals of atom 1 on the S orbital of atom 3 are shown in part (b).

The electronic properties of these graphene structures are obtained by including only the p\textsubscript{z} orbitals for constructing the Hamiltonian of the structures. The basic Huckel method deals with only these 2p\textsubscript{z} orbitals in finding the electronic properties of structures of interests [24,31]. The extended Huckel method expands upon this calculation by not only using the π bonds from the 2p\textsubscript{z} orbitals, but includes the bonds from the 2s, 2p\textsubscript{x}, and 2p\textsubscript{y} [26]. Like the Huckel, the EHM only takes into account the nearest neighbor interactions between orbitals discussed above in the TB model.

In the case of a GNR the number of orbitals is directly dependent on the width of the ribbon in the unit cell. For an AGNR, with n being the number of dimers on the AGNR, the number of orbitals is obtained by taking n multiplied by 2 to get the total number of carbon atoms and
then scaling that number by the number of unique orbitals, in the case of carbon that is 4.

Figure 1.1 (b) represents an armchair GNR structure with n=10. For example, for the n= 10 dimer ribbon, the total number of carbon atoms would be 20 and the total number of orbitals will be 80. Thus, the size of the Hamiltonian matrix will be 80 by 80.

The next thing to consider is the edge bonds in the unit cell. With AGNRs there are two atoms at each edge of the periodic structure with dangling bonds. The zigzag and the armchair features at the top and bottom edges are clear in Figures (a) and (b). In this calculation a single hydrogen atom in the ground state is used to terminate each edge bonds. The hydrogen orbital is thus 1s. Since the size of the Hamiltonian matrix is determined by the total number of the orbitals, the addition of hydrogen atoms at the edges changes the size of the matrix. So, instead of simply being 2n*4 orbitals, the total number of orbitals becomes 2n*4+4, or 8n+4. The electronic properties such as the band structures and density of states of the system are obtained by diagonalizing the Hamiltonian matrix as a function of wave number k. The charge densities of individual atoms have been calculated by finding the eigenfunction of Hamiltonian matrix of each k.

Now, we discuss the calculation of an armchair graphene nanoribbons of single hexagon in thickness. Figure 2.2 shows the graphene ribbon structure.
Figure 2.2: A single hexagonal armchair graphene ribbon. The atoms are marked with numbers, the unit cell I is marked with lines and its neighbors are I+1 and I-1.

The unit cell along with its two nearest neighbors are represented by I, I-1, I+1 and the sites are marked 1 through 6. The Schrödinger equation (SE) for the structure is

\[
\hat{H} |\Psi\rangle = E |\Psi\rangle
\]  

(2.10)

and the Hamiltonian operator is given as

\[
\hat{H} = \frac{-\hbar^2}{2m} \nabla^2 + V(\vec{r})
\]  

(2.11)

and the wave function, |\Psi\rangle is given by

\[
|\Psi\rangle = \sum_{I=I,I+1,I-I} e^{ikR_I} |\Psi_I\rangle
\]  

(2.12)

where |\Psi_I\rangle is expressed by the four orbitals \( s, p_x, p_y \), and \( p_z \)

\[
|\Psi_I\rangle = \sum_{j=1} e^{ik\tau_j} [\alpha_1 |s_j\rangle + \beta_2 |P_x j\rangle + \gamma_3 |P_y j\rangle + \kappa_4 |P_z j\rangle]
\]  

(2.13)

In Eq. (2.12), \( R_I \) represents the location of the unit cell I, and \( \tau_j \) is the phase factor of the orbitals. Here, \( \alpha, \beta, \gamma, \kappa \) are the probability amplitudes. To construct the Hamiltonian matrix,
the following analytical steps are performed. First, scalar products of the individual orbitals are
taken with Eq. (2.10). Here an example is shown. Taking the scalar product of \( s_1 \) orbital one
finds

\[
\langle s_1 | \hat{H} | \sum_{j=1}^{6} e^{ik \tau j} [\alpha_j | s_j \rangle + \beta_j | Px_j \rangle + \gamma_j | Py_j \rangle + \kappa_j | Pz_j \rangle] = \\
\langle s_1 | E | \sum_{j=1}^{6} e^{ik \tau j} [\alpha_j | s_j \rangle + \beta_j | Px_j \rangle + \gamma_j | Py_j \rangle + \kappa_j | Pz_j \rangle]
\]

(2.14)

The left hand side of Equation (2.14) is expanded as:

\[
e^{ik \tau_1} \left[ \alpha_1 (s_1 | \hat{H} | s_1) + \beta_1 (s_1 | \hat{H} | Px_1) + \gamma_1 (s_1 | \hat{H} | Py_1) + \kappa_1 (s_1 | \hat{H} | Pz_1) \right] \\
+ e^{ik \tau_2} \left[ \alpha_2 (s_1 | \hat{H} | s_2) + \beta_2 (s_1 | \hat{H} | Px_2) + \gamma_2 (s_1 | \hat{H} | Py_2) + \kappa_2 (s_1 | \hat{H} | Pz_2) \right] \\
+ \ldots + e^{ik \tau_6} \left[ \alpha_6 (s_1 | \hat{H} | s_6) + \beta_6 (s_1 | \hat{H} | Px_6) + \gamma_6 (s_1 | \hat{H} | Py_6) + \kappa_6 (s_1 | \hat{H} | Pz_6) \right] \\
= e^{ik \tau_1} \alpha_1 (s_1 | \hat{H} | s_1) + e^{ik \tau_2} \left[ \alpha_2 (s_1 | \hat{H} | s_2) + \beta_2 (s_1 | \hat{H} | Px_2) \right] + \\
e^{ik \tau_3} \left[ \alpha_3 (s_1 | \hat{H} | s_3) + \beta_3 (s_1 | \hat{H} | Px_3) + \gamma_3 (s_1 | \hat{H} | Py_3) \right] \\
= e^{ik \tau_1} \alpha_1 (s_1 | \hat{H} | s_1) + e^{ik \tau_2} \left[ \alpha_2 (s_1 | \hat{H} | s_2) + \beta_2 (s_1 | \hat{H} | Px_2) \right] + \ldots \\
e^{ik \tau_6} \left[ \alpha_6 (s_1 | \hat{H} | s_6) + \beta_6 (s_1 | \hat{H} | Px_6) + \gamma_6 (s_1 | \hat{H} | Py_6) + \kappa_6 (s_1 | \hat{H} | Pz_6) \right] \\
= \alpha_1 e^{ik \tau_1} (s_1 | E | s_1) = \alpha_1 E e^{ik \tau_1}.
\]

(2.15)

In equation (2.15), all terms are zero except the nearest-neighbors. As shown in Figure 2.2, the
nearest-neighbors for atom 1 are atoms 2 and 3.

In a similar way the right hand side is expanded and it appears as:

\[
= e^{ik \tau_1} \left[ \alpha_1 (s_1 | E | s_1) + \beta_1 (s_1 | E | Px_1) + \gamma_1 (s_1 | E | Py_1) + \kappa_1 (s_1 | E | Pz_1) \right] \\
+ e^{ik \tau_2} \left[ \alpha_2 (s_1 | E | s_2) + \beta_2 (s_1 | E | Px_2) + \gamma_2 (s_1 | E | Py_2) + \kappa_2 (s_1 | E | Pz_2) \right] + \ldots \\
+ e^{ik \tau_6} \left[ \alpha_6 (s_1 | E | s_6) + \beta_6 (s_1 | E | Px_6) + \gamma_6 (s_1 | E | Py_6) + \kappa_6 (s_1 | E | Pz_6) \right] \\
= \alpha_1 e^{ik \tau_1} (s_1 | E | s_1) = \alpha_1 E e^{ik \tau_1}.
\]

(2.16)

In equation (2.16), only a single term is non-zero, because the \( S_1 \) orbital is orthogonal to all the
other orbitals except to itself.
Combining equations (2.15) and (2.16) the following expressions are obtained:

\[ \alpha_1 \langle s_1 | \hat{H} | s_1 \rangle + e^{i k \tau_2 - \tau_1} \left[ \alpha_2 \langle s_1 | \hat{H} | s_2 \rangle + \beta_2 \langle s_1 | \hat{H} | P x_2 \rangle \right] + \\
e^{i k \tau_3 - \tau_1} \left[ \alpha_3 \langle s_1 | \hat{H} | s_3 \rangle + \beta_3 \langle s_1 | \hat{H} | P x_3 \rangle + \gamma_3 \langle s_1 | \hat{H} | P y_3 \rangle \right] = \alpha_1 E. \]

(2.17)

The matrix elements in Equation (2.17) are then expressed in a simplified form as:

\[ \alpha_1 \varepsilon_s + e^{i k \tau_2 - \tau_1} \left[ \alpha_2 E_{ss} + \beta_2 E_{sx} \right] + \\
e^{i k \tau_3 - \tau_1} \left[ \alpha_3 E_{ss} + \beta_3 E_{sx} + \gamma_3 E_{sy} \right] = \alpha_1 E. \]

(2.18)

The matrix elements between atoms are defined by \( \varepsilon_s, E_{ss}, E_{sx}, \) and \( E_{sy} \). Here, \( \varepsilon_s \) is the on-site energy of the S-orbital and the later three elements are expressed in terms of overlap integrals, \( V_{i,j,k} \), defined in Equation (2.2). The complete expression of each element is shown in the Appendix 1. These elements represent the \( \sigma \) and \( \pi \) interactions between orbitals and are obtained from reference [24]. The phase factors are expressed in terms of lattice constant, \( a (=1.42 \text{Å}) \). It should be noted that there are 24 orbitals in a single unit cell. Here, we have shown complete analysis for a single orbital. Similarly, matrix element of the Hamiltonian is obtained from these scalar products of all the orbitals. The analysis is not shown for the rest of the orbitals here. Notice that each equation makes up a single row for the Hamiltonian matrix. I then sorted the Hamiltonian matrix with respect to each carbon atom and the 4 corresponding orbitals. This means every 4 rows are grouped in order by the corresponding S, P_x, P_y, and P_z. I can then combine each interaction between carbon atoms into their own sub groups, represented by \( H_{ij} \) with each group representing a 4 by 4 block. Table 2.1 shows the condensed Hamiltonian matrix using these \( H_{ij} \) Block elements, for visualization purposes \( C_{1-6} \) is set outside the Hamiltonian as a guide to help the reader cross reference terms and identify what each
block refers to. The phase factors, interaction parameters, and other terms are all contained in these sub groups and will be explained below.

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Table 2.1: The Hamiltonian matrix for a single graphene hexagon.

The Hamiltonian matrix elements in Table 2.1 are in the form of $H_{ij}$, with $i$ and $j$ terms going from 1 to 6 for the 6 carbon atoms in this hexagonal periodic structure. Note that each element $H_{ij}$ is a block matrix. These notations are used to show the Hamiltonian matrix in a compact form. The size of the Hamiltonian for this narrow $n=3$ dimer armchair ribbon is 24 by 24, but by condensing each section into 4 by 4 blocks it reduces the appearance of the Hamiltonian to a 6 by 6. This reduction of size although merely cosmetic in effect makes checking each element in the matrix much more manageable. Instead of checking the entire matrix at once, I am able to check each block at a time for accuracy and feel much more confident in the result. Examples of these block matrices are shown in Table 2.2
Table 2.2: Matrix elements $H_{11}$, $H_{12}$, and $H_{13}$ of Table 2.1 are shown in the blocks (a), (b), and (c). The phase factors of the corresponding elements are also shown on the top of each block.

The interaction matrix elements shown in Table 2.2 are described through schematic diagrams in Figure 2.1 and Figure 2.3. As discussed above, Figure 2.1 (a) shows the $S$, $P_x$, and $P_y$ orbitals of the atoms. The lobes of the $p$ orbitals are marked with positive and negative signs of atom 5.
Next, part (b), presents the orientations of the P\textsubscript{x} and P\textsubscript{y} orbitals toward the S orbital for atom 3. The left two configurations in part (b) represent the σ-bond between the S and P\textsubscript{x} and P\textsubscript{y} orbital requiring 240 and 150 degrees’ reorientation of the orbitals, respectively. While the two right configurations, represent the π-bond between the S and P\textsubscript{x} and P\textsubscript{y} orbital. Taking the Cosine of these angles will let you know what portion of the interaction term to take. For instance, the σ component for P\textsubscript{x1} interacting with S\textsubscript{3} will have Cos (240) = -1/2, and comparing this with Table 2.2(c) we see the term should be 1/2. But there is one major component one should take into account, the positive and negative sides of the lobes and how this effects the signs of the matrix elements. To address this issue, Figure 2.3 is introduced.

The matrix elements are illustrated in Figure 2.3. Six interaction parameters are shown through the schematic representation of the orientations of the orbitals. It should be mentioned that the interaction terms were defined in Equation (2.2) by \( V_{ijk} \), and for the case at hand \( i \) and \( j \) are either a s-orbital or p-orbital, and \( k \) is either be a sigma or pi bond. It should be mentioned that the filled (solid) lobes are positive and the empty ones are negative. Combing the results from Figure 2.1 (b), and implementing the sign rules of the lobes introduced in Figure 2.3, we get \((-1/2)(-V_{spo}) = 1/2(V_{spo})\). Following the same rules and techniques the other matrix elements for atom 1 and atom 3 are calculated and shown in Table 2.2 (c).

The phase factors appeared in Equation (2.17) can have one of the four possible values, \( \pm e^{ika} \) and \( \pm e^{-\frac{k\alpha}{2}} \), and two of them appear in parts (b) and (c) in Table 2.2.
The full Hamiltonian matrix is shown in the Appendix 1. A list of the matrix elements is also provided in the Appendix 1.

2.5 Summary

In this chapter, we have discussed and shown the theoretical models used in the present research project. First, the tight-binding model is discussed for the calculation of band structure and density of state. The associated interaction parameters and their values are presented. Next, the Green’s function formalism is discussed for the calculation of conductance and local density of states. In Section 2.4, the extended Huckel method is explained. A detailed analysis for a single Hamiltonian matrix element is shown. Finally, some schematic representation of the orientation of the orbitals is discussed to express the interaction parameters and phase factors for an AGNR.
Chapter 3

Armchair Graphene Nanoribbons

3.1 Introduction

In this chapter, we will present the results of electronic band structure, density of states (DOS), local density of states (LDOS), and conductance for armchair graphene nanoribbons (AGNRs). The band structure and density of states are calculated using the tight binding (TB) model discussed in chapter 2. Conductance and local density of states (LDOS) are calculated using Green’s functions methodology and the Landauer formula [4,23,29,30]. The extended Huckel method has been implemented in all these calculations [28].

First, a brief description of the structure used in this calculation will be presented. Next, the Band structure and Density of states will be shown, followed by a comparison with results obtained using the Huckel method. Lastly, the Conductance and LDOS results will be shown.

3.2 Band Structure and Density of States of Armchair Graphene Nanoribbons

As discussed earlier graphene nanoribbons are strips of graphene with finite widths and semi-infinite length along the axis of the strip. Figure 3.1 shows a GNR with an armchair shape at the edges. This armchair patterned GNR is known as AGNR. The AGNR is separated into unit cells, the Figure below shows several unit cells, we will focus on the center unit cell I. The number of dimers in Figure 3.1 is equal to 9. The width of an AGNR is given by \( \frac{\alpha \sqrt{3}}{2} n \), where \( \alpha \) is the the lattice constant, and \( n \) is the total number of dimers in the structure. Here \( \alpha = 1.42 \) Å, thereby
the width of the ribbon is 11.07\text{nm}. For a $n=9$ dimer AGNR, there are 18 atoms in the unit cell, and these are shown with numbers. In Figure 3.1, it is clear that the carbon atoms in the first and last dimer (at the top and bottom edges) are only connected to two other carbon atoms in the bulk of the structure; thus leaving a dangling bond at the edge. In order to terminate the dangling bond an atom can be added to the edge. In this study, the GNR edges are terminated with hydrogen. Band structures and DOS with and without edge terminated AGNRS are presented and discussed. The distinction between edge terminated bonds and non-terminated bonds and edges will be a major focus in the chapter.

![Figure 3.1: Armchair graphene nanoribbon, width n=9.](image)
In Figure 3.2 (a), the band structure of an armchair GNR with \( n = 3 \) is shown. The electronic band structures are plotted as a function of wave number \( k \), where \( k \) ranges over the first Brillouin zone boundary. When \( n = 3 \) there are 6 atoms in the unit cell. There is a total of 24 bands in the figure, proportional to the total number of orbitals. The Fermi level has been centered at 0 eV. The previous chapter stated that the number of orbitals in the unit cell was
obtained by taking the number of dimers \( n \) and multiplying by 8 (orbitals). The bands located above the Fermi level are known as the conduction bands while below the Fermi level the bands are the valence bands. An inspection of the bands reveals that not all valence and conduction bands are perfectly symmetric with respect to the Fermi level. One should also note that there are many flat valence bands below the Fermi energy. These flat bands are non-conducting and the group velocity of the mobile electrons is close to zero \([4,15]\). That means the effective mass of the electrons is infinite \([15]\). We predict these flat bands below the Fermi energy are from the \( \text{P}_x, \text{P}_y, \) and \( S \)-orbitals of the carbon atoms.

There is a distinct gap between highest valence band and the lowest conduction band. The gap in the Fermi level between the valence and conductance points to a material being semiconducting. This is what is expected for \( n = 3 \). The dimer rule to follow for AGNRs will be semiconducting when \( n=3p \) or \( n=3p+1 \) (with \( p \) being an integer). However, if \( n=3p+2 \), the AGNRs will be metallic \([2,3,15]\).

In Figure 3.2 (b) the density of states (DOS) are plotted as a function of electron energy. The DOS value shows the number of \( k \) points per energy value. Figure 3.2 (b) reveals that there are some sharp peaks and gaps in the DOS structure. As expected, there is a gap around Fermi energy. This gap in DOS corresponds to the band gap observed in Figure 3.2 (a).

From the theory, it is expected to find only the weakly held \( \pi \) bands around the Fermi level, mainly the 6 bands from the \( \text{P}_z \) interactions. In Figure 3.2 (a), there seems to be 4 extra bands located on the valence side close to the Fermi energy. The current calculation and results shown above do not account for the edge orbitals along the ribbon, as in they could be thought
of as dangling or non-bonding orbitals. These dangling edge atoms are C₁, C₂, C₅, and C₆ shown in Figure 2.2. To remedy this situation, the edges are terminated by adding hydrogen. The results with edge termination will be shown in Figure 3.4. Figure 3.3 shows the close up view around the Fermi level for n = 3. It is clear from this view that there are many flat bands in the valence band; subsequently there are many peaks observed in the DOS graph. The band gap at k = 0 is about 2.4 eV. This band gap indicates that n = 3 AGNR is a semiconducting structure.

Figure 3.3: (a) The band structure (b) the density of states near the Fermi energy of n= 3 dimer AGNR (without edge termination).
Next, we introduce the edge terminated results of the band structure and DOS in Figure 3.4.

Due to the addition of the hydrogen at the edges, the total number of bands should be 28. It is clear that due to the edge termination the qualitative features of the bands have changed. The bands are more symmetric about the Fermi energy. Also some flat bands observed in Figure 3.2 (a) moved at lower energy levels in the valence band region. We also see that around -20 there is a large increase in the number of bands compared to Figure 3.2 (a). From this observation,
one may suggest that the S-orbital of the hydrogen atom is hybridized with the other orbitals (Pₓ, Pᵧ, S) of the carbon atoms on the two-dimensional plane. From this observation, we conclude the bands at very low energy are tightly bound and are forming σ bonds. Those closer to the Fermi energy are forming π bonds and contribute to conduction. Figure 3.4 (b) also shows similar changes in DOS around the Fermi level. Instead of several distinct peaks below the Fermi level around -3 eV, we see only one peak. This relates with the one flat band in Figure 3.4 (a) at the same energy. Also more peaks are observed around -20 eV in the valence band region. A close up view of the bands and DOS are shown around the Fermi energy in Figure 3.5. As discussed above, the width of the band gap at k = 0 remains the same (≈2.4 eV).
Figure 3.5: (a) The band structure (b) the density of states near the Fermi energy of n= 3 dimer AGNR (edge terminated with hydrogen).
The next thing to study is the case of n=3p+2 dimer AGNR. In order to avoid the analytical and computational cost the lowest number of dimers in the relation n=3p+2 is considered in this calculation: n = 5. Figure 3.6 shows the band structure and the DOS. The electronic bands are plotted as a function of wave vector k and DOS are plotted as a function of energy. It should be mentioned that these results are without edge termination. One of the first things apparent in
Figure 3.6 (a) is the number of bands has increased significantly. Remembering that one band correlates to one orbital, there are 10 atoms for $n = 5$. Hence, there are 40 orbitals in total. Some of the bands overlap and appear close together. Looking at the highest valence band and the lowest conduction band it is seen that they meet at the Fermi level at $k=0$. This point of degeneracy between bands when $k = 0$ indicates that the structure is metallic. This follows the theory that the AGNR is metallic when $n=3p+2$. As discussed above about the flat bands and peaks in the DOS represent the non-conducting states and indicate infinite mass. The bands around the Fermi energy are linear, indicating the group velocity is nonzero and is measured to be about $10^6$ m/s $[1,4]$. The metallic property of the AGNR with $n=5$ is confirmed again by Figure 3.6 (b), which shows that the DOS is non-zero at the Fermi level. In conclusion, we see $n = 5$ AGNR is indeed metallic. Enhanced plots near the Fermi energy for the bands and DOS are displayed in Figure 3.7. The detailed characteristics of the bands and DOS are more visible here.
Figure 3.7: (a) The band structure (b) the density of states near the Fermi energy of n=5 dimer AGNR (without edge termination).
In Figure 3.8 the edge terminated results for n=5 AGNR are shown. The bands are shown in Figure 3.8 (a) and the DOS are in 3.8 (b). The addition of the hydrogen at the edges results in 44 bands. The general behavior of the bands moving away from the Fermi energy is similar, as observed in Figure 3.4 (a). The weakly bonded π orbitals are near the Fermi energy and the bands are symmetric about it. Due to hybridization of the orbitals on the plane with hydrogen,
the flat bands near the Fermi energy in Figure 3.6 (a) moved to very low energy region. The number of peaks observed in the energy range -2 eV to -6 eV in Figure 3.6 (b) has decreased to only one. This may suggest that they are hybridized with the other orbitals of the hydrogen atoms on the plane. Figure 3.9 shows the detailed features of the bands and DOS near the Fermi energy.

Figure 3.9: (a) The band structure (b) the density of states near the Fermi energy of n= 5 dimer AGNR (edge terminated with hydrogen).
For completeness, Figure 3.10 has been included to address the case for $n=3p+1$, and to confirm that it is semiconducting as expected. Figure 3.10 shows the band structure and the DOS for an $n=4$ AGNR with edge termination. The features will not be discussed in detail because they are similar to the $n=3$ AGNR case. Here, the main focus is to confirm the results of a semiconducting nature of the ribbon.

![Figure 3.10: (a) The band structure (b) the density of states of $n=4$ dimer AGNR (edge terminated with hydrogen).](image)
3.3 Comparison of Huckel and Extended Huckel Results of Armchair Graphene Nanoribbons

In this section, results will be discussed for comparison between the Huckel and extended Huckel methods different widths of armchair nanoribbons. Results from the extended Huckel method discussed in section 3.2 will be used for comparison. Only the band structure and the density of states will be compared. Since a detailed description for the extended Huckel method was presented in the previous section, only a short explanation will be given for the comparison.

Figures 3.11 and 3.5 present the band structure and density of states (DOS) for Huckel and extended Huckel method for n=3 dimer AGNRs, respectively. One may notice the bands and DOS are symmetric about the Fermi level for the Huckel method (Figure 3.11). On the other hand, both bands and DOS are not symmetric for the extended Huckel method. There are a few bands seen around 8.0eV in the conduction region. Consequently, the DOS is non-zero at this energy. As discussed in the previous section, the symmetric bands around the Fermi energy are due to the P₂-orbitals, therefore these bands around 8.0eV are from the other orbitals in the 2-D plane.
Figure 3.11: (a) The band structure (b) the density of states near the Fermi energy of n= 3 dimer AGNR (Huckel Method; edge terminated with hydrogen).

The band structures and DOS are compared for n=5 AGNR in Figures 3.12 and 3.9. Here due to the addition of dimers the number of bands increased. As seen above the bonding and anti-bonding orbitals are symmetric about the Fermi energy. The bands must be symmetric since the energy of all the Pz-orbitals is the same. There are some more bands and DOS observed
again around $E = 8.0\text{eV}$. In summary, the general characteristics of the bands and DOS are similar around the Fermi energy in both Huckel and extended Huckel method. The only difference observed $\sigma$ bands in the extended Huckel method and these are farther away from Fermi level.

![Figure 3.12](image)

Figure 3.12: (a) The band structure (b) the density of states near the Fermi energy of $n= 5$ dimer AGNR (Huckel Method; edge terminated with hydrogen).
3.4 Conductance of Armchair Graphene Nanoribbons

The conductance results of \( n = 3 \) and \( n = 5 \) AGNR will be discussed in this section. Figure 3.13 shows the conductance values as a function of energy.

![Conductance as a function of energy for (a) \( n = 3 \) AGNR (b) \( n = 5 \) AGNR (edge terminated with hydrogen).](image)

First, we will show and discuss the conductance results for the edge terminated cases. In Figure 3.13 (a) the conductance around the Fermi level is zero, the first quantized conductance value does not show up until \(-1.2 \text{ eV} \) and \(1.2 \text{ eV} \) respectively. This zero conductance nature is expected because \( n = 3 \) is a semiconductor type AGNR as seen in Figure 3.4. From the band structure, as well as DOS analysis discussed above the conductance should be zero within this energy range (shown in Figure 3.4(a) & (b)). This implies there is no propagating mode to contribute to the transport. From Figure 3.4 it is clear that the number of propagating states is zero within this range. From the Landauer formula, conductance is expressed by integer multiples of \((2e^2/h)\). Therefore, it is expected that the conductance will be quantized by \((2e^2/h)\).

In Figure 3.13 (a) the conductance between \(-3.2\text{ eV} \) to \(-1.2 \text{ eV} \) and \(3.2 \text{ eV} \) to \(1.2 \text{ eV} \) is equal to \((2e^2/h)\). This general behavior of quantization is expected for any semiconductor or metallic GNRs.
Next, we present the conductance for $n = 5$ AGNR. As stated earlier, $n = 5$ AGNR is metallic. The first quantized conduction band is between $-2.2\text{eV}$ to $2.2\text{eV}$ and the second quantized conduction band starts from $-2.2\text{eV}$ and $2.2\text{eV}$ with conductance value equal to 2 ($2e^2/h$). This corresponds to two possible allowed propagating states for transport.

In order to study the effects of edges on transport, the conductance results are produced without the edge termination. Figure 3.14 shows without edge terminated conductance for $n=3$ and $n=5$ dimer AGNRs. It is expected from the observations of band structures and DOS results shown in Figures 3.3 and 3.7 that the characteristics of the conductance curves will not be fully quantized and some different features will appear.

![Conductance as a function of energy for (a) n = 3 AGNR (b) n = 5 AGNR (without edge termination).](image)

For both $n=3$ and $n=5$ AGNRs, in Figure 3.14 (a) and (b) there is a sharp increment in conductance is observed in the valence band regions. It is predicted that these enhancements are due to the $\sigma$-bands observed in the without edge terminated structures in the valence bands below the Fermi level shown in Figures 3.3 and 3.7. The sharp spikes are at the same location as the energy bands. In conclusion, the edge termination is essential for clean quantized features in conductance curves. The dangling bonds at
the edges destroy the perfect quantized behavior expected from the Landauer formalism for perfect nanostructures.

### 3.5 Local Density of States of Armchair Graphene Nanoribbons

The local density of states (LDOS), shows the number of states per energy for each atom in the unit cell. Using the extended Huckel method each atom in the unit cell has four orbitals contributing to their particular LDOS. In this section, the LDOS results will be presented for the edge terminated AGNRs for \( n=3 \) and \( n=5 \).

![LDOS Graphs](image)

**Figure 3.15** LDOS for \( n=3 \) AGNR, (a) for carbon 1 atom, (b) for carbon 3 atom. Positions of the atoms are shown in Figure 2.2.

Figure 3.15(a) and (b) shows the LDOS for 2 of the atoms in the unit cell. The Figure shows carbon atom 1 and carbon atom 3 (refer to Figure 2.2(a)). Naturally this brings up the question of why only 2 of the 6 carbon atoms are shown. The reason has to do with the symmetry of the
unit cell and neighbors, because the general symmetric relationship between the matching atoms they have identical interactions between atoms, thus matching LDOS values. The general characteristics of LDOS for the edge atoms 1 and 2 are identical. Similarly, the features of LDOS for the middle atoms 3 and 4 are similar. It is also expected that the results of atoms 5 and 6 will be similar to atoms 1 and 2. Therefore, only the LDOS of two atoms will provide a general image of the characteristics of the electronic property. The graphs tend to show a lot of similarities. It is also noted the difference around the Fermi level between the two LDOS graphs. Figure 3.15(a) has several distinct peaks at different locations.

For the n=5 AGNR there are a total of ten LDOS graphs, but like the n=3 case many of the carbon atoms result in similar LDOS graphs. The matching carbon LDOS are as follows: 1, 2, 9, 10 make a set, 3, 4, 7, and 8 make a set, and 5, 6 make the final set. The atomic positions are shown in Figure 3.1.

Figure 3.16: two LDOS for a n=5 AGNR, (a) for the carbon 1 atom, (b) for the carbon 3 atom, (c) for the carbon 5 atom
Looking at Figure 3.16 (a) and (b) we can see that these are the carbon atoms where the electronic transport happens; it is shown by the nonzero LDOS at and around the Fermi energy. This becomes interesting when you note these are all the edge atoms. It is also noted for Figure 3.16 (c) there is 0 LDOS around the Fermi energy meaning no electronic transport. Being able to plot the LDOS becomes a very powerful tool when looking at the individual atoms and how they are affected by changes to the system as a whole. A good research topic for the future could follow an in-depth look at the LDOS, and how it changes with respect to anomalies and defects within the GNRs.

3.6 Summary

In this chapter, the electronic properties for several AGNR have been studied using the extended Huckel method. The band structure, DOS, conductance, and LDOS are calculated for several AGNRs. The number of dimers representing the width of the ribbons are chosen based upon the dimer rule: n=3p+2 is metallic, and n=3p and n=3p+1 are semiconducting. Here p is an integer. For n= 3, 4, and 5 AGNR have been investigated. As expected, n= 3 and 4 AGNR are semiconducting while n= 5 is metallic. From this investigation, we find that electron conduction mostly relies on the P_z orbitals. Results with and without edge termination are discussed for both cases. The addition of edge termination was required to successfully explain the results around the Fermi level.
Chapter 4

Zigzag Graphene Nanoribbons

4.1 Introduction

In this chapter, zigzag graphene nanoribbon (ZGNR) structure will be discussed and then it will be compared to the AGNR structures. Next, the results the band structure and DOS for two separate ZGNRs will be presented and discussed. Finally, the chapter will conclude with a comparison between the Huckel and extended Huckel results obtained for the ZGNR.

4.2 Band Structure and Density of States of Zigzag Graphene Nanoribbons

The name of a GNR comes from the zigzag pattern along the semi-infinite edge of the ribbon. In Figure 3.10 a ZGNR is displayed with the unit cell marked at the center. The unit cell is represented by I and its neighbors are shown by I +1 and I -1. There are 6 chains in the structure. The width of ZGNRs can determined by the number of chains (N) in the ribbon. The distance between two chains is $\frac{3a}{2}$. Therefore, the width of the chain with N=6 will be 12.78nm. The numbering scheme for the atoms in the unit cell is top down. Results for N=2 and N=6 will be presented here.

![Figure 4.1: Zigzag graphene nanoribbon, N= 6 chains.](image)
Figure 4.2: (a) The band structure (b) the density of states of N= 2 chain ZGNR (without edge termination).

Figure 4.2 displays the electronic band structure and the density of states for a N = 2 chain ZGNR. In Figure 4.2 (a) the electronic band structures are plotted as a function of wave vector k, where k ranges within the boundary of the first Brillouin zone. N = 2 is chosen because it is the smallest number of chains possible to make up a ZGNR. The same relation has been used to find the number of orbitals in a unit cell for the ZGNR as for the AGNR. For the case of N = 2 chain
ZGNR, the total number of orbitals is thus 16. The Fermi level energy has again been centered around 0 eV. It is observed that the highest valence band and the lowest conduction band meet at both ends of the Brillouin boundary indicating metallic properties [5,10,11]. This feature is explained by many researchers and these are due to the edge atoms. This metallic property is expected for all ZGNRs. It is also seen that the bands flatten out into each other as they meet on either edge. This is in stark contrast to the metallic AGNRs that meet at \( k = 0 \) and approached at a constant slope. These flat band’s characteristics indicate the group velocity of the electrons is zero and the bands are non-conducting. It is also noticed like the AGNR that the bands are not symmetric about the Fermi level in this dangling bond situation.

In Figure 4.2 (b) the density of states (DOS) are plotted as a function of electron energy. The DOS show the number of states per energy value. The DOS is non-zero at the Fermi energy confirms the result of metallic properties. Not only is it non-zero, but there is a peak at the Fermi energy which relates to the flattening of the bands as they meet. Figure 4.3 shows the close up view around the Fermi level, the flattening of the bands and the peak at the Fermi level are much more prominent.
As discussed in the last section with AGNRs, there was a problem with dangling edge-orbitals. This problem persists with the ZGNR. The solution is similar to the AGNR but instead of requiring two hydrogen atoms at each edge of the unit cell, ZGNR requires only one at each edge. The results with edge termination are shown in Figure 4.4 for a ZGNR with N = 2.
Figure 4.4: (a) The band structure (b) the density of states of N=2 chain ZGNR (edge terminated with hydrogen).

Figure 4.4 displays the bands and DOS for a ZGNR with N = 2 chain, where the dangling carbon orbitals are terminated with hydrogen. Due to the addition of the hydrogen at the edges the total number of bands is 18. It is clear that the edge termination has had an effect on several of the bands in Figure 4.4 (a). It is observed that the two bands located slightly below the Fermi
energy in Figure 4.4 (a) have both moved. This suggests that these two bands have now moved
to lower energy states with the forming sigma bonds now shared with the hydrogen. As
discussed for the AGNR, the orbitals that relate to the bands lying on the 2-D plane (S, P\textsubscript{x}, P\textsubscript{y}).
Therefore, the four bands about the Fermi energy are the contributions from the P\textsubscript{z} orbitals.
Recall that the bonding and anti-bonding orbitals are in the valence and conduction band about
the Fermi level, respectively. The picture around the Fermi level becomes clearer now that two
of the bands have gone. It is predicted that these two bands are from the dangling p- orbitals of
the edge atoms. Once the edges are terminated, the S-orbital of the hydrogen atom form sigma
bonds with the p-orbitals of the carbon atoms and move to the lower energy levels in the
valence band. The peak from the touching conduction and valence band at E = 0 eV is easily
discernible in Figure 4.4 (b). The increase in the DOS is produced by the flattening of the bands
as they approach the Fermi level. Figure 4.5 is used to display this same edge terminated ZGNR,
but with the energy ranging from -7 to 7 eV with respect to the Fermi level.
Figure 4.5: (a) The band structure (b) the density of states near the Fermi energy of N= 2 ZGNR (edge terminated with hydrogen).
Figure 4.6 displays the bands and the DOS for an $N = 6$ chain ZGNR. The number of bands in this case is 48. The edges are not terminated and hence the general characteristics of the bands as well as the DOS are alike, as found in $N = 2$ ZGNR shown in Figure 4.2. The valence bands form the bonding and the conduction bands form anti-bonding orbitals [26]. A difference between the two ZGNRs is shown with the flatter bands at the Fermi energy for the $N = 6$. As a result, the
DOS values at the Fermi energy are higher. In addition, the other $p_z$ orbitals degenerate at the boundary of the Brillouin zone at two different energy values (around -3 and 3 eV) [11]. As before, for clarity the bands in DOS around the Fermi level are displayed in Figure 4.7.

Figure 4.7: (a) The band structure (b) the density of state near the Fermi energy of N= 6 chain ZGNR (without edge terminated).
It is clear that there are additional bands mixed with the Pz-bands near the Fermi level in the valence band region. For the N=2 chain ZGNR, there are two bands observed of this nature shown in Figure 4.3. As discussed before, we consider that these bands formed from the dangling P-orbitals of the edge atoms. Apparently, it appears that there is a single band. One may consider it as a degenerate band. In order to avoid this confusion, the results for N= 3, 4, and 6 ZGNRs are plotted within a small window of energy shown in Figure 4.8. It is clear that bands are separated as seen in Figure 4.3.

Figure 4.8: The band structure of (a) N=3, (b) N=4, and (c) N=6 chain ZGNRs for a small energy range about the Fermi energy (without edge terminated).
Results of edge terminated bands and DOS for N = 6 ZGNR is presented in Figure 4.9. Because of the edge termination, the bands around the Fermi level are almost symmetric. Shifting of the non $P_z$ orbitals away from the Fermi level in the valence band region is consistent with previous results. This result is compared to the previously calculated result reported by others [11]. The electronic energy bands and DOS values are identical near the Fermi level. The only difference
appears away from the Fermi level in the conduction band region. In order to understand verify this discrepancy, it may require some further investigations in the future. For a better view around the Fermi region, Figure 4.9 is provided.

Figure 4.10: (a) The band structure (b) the density of state near the Fermi energy of N= 6 chain ZGNR (edge terminated with hydrogen).
4.3 Comparison of Huckel and Extended Huckel Results of Zigzag Graphene Nanoribbons

Here the band structure and DOS will be compared for the two different ZGNRs. Figures 4.11 and 4.5 show the results for a N=2 chain ZGNR using the Huckel and extended Huckel method, respectively. Like the AGNRs, the bands and DOS are symmetric about the Fermi level. These bonding and anti-bonding are from the $P_z$ orbitals. Therefore, one expects the asymmetric behavior to appear with the extended Huckel method at higher energy. Figure 4.5 reveals the features in the conduction band.
Next, for N=6 chain ZGNR results are displayed in Figures 4.12 and 4.9. Fundamentally, there are not much difference except there are many more bands. Overall, the general trend of the bands and DOS around the Fermi energy as well as away are similar for N=2 chain ZGNR discussed above. Therefore, with the extended Huckel technique one can extract the details of the electronic properties of the nanoribbons.
Figure 4.12: (a) The band structure (b) the density of states near the Fermi energy of N= 6 ZGNR (Huckel Method; edge terminated with hydrogen).

4.4 Summary

The band structure and the DOS calculations have been show for ZGNRs of two different widths. The addition of the Hydrogen to work with the dangling edge orbitals was required to move around some of the bands away from the Fermi level, leaving the extended Huckel method to match the Huckel method. As in AGNRs, the edges of ZGNRs are terminated with
hydrogen. The S-orbital of the hydrogen atom form bonds with the S- and P-orbitals of the edge atoms. There are two energy bands observed near the Fermi level in the valence band region. These are mixed with the Pz-bands and are predicted that these are due to the presence of dangling P-orbitals at the edges of the ribbons. Once the edges are terminated with hydrogen, these bands are pushed back at the lower energy levels. From this observation, we conclude these dangling P-orbitals are forming σ-bonds with the S-orbital of the hydrogen atom. If the edges are terminated with other element(s) then the investigation will be more interesting and conclusive.
Chapter 5

Summary and Conclusions

In this research project, two different graphene nanoribbons have been studied. These include the armchair and zigzag nanoribbons. Electronic properties are studied by using a tight-binding model, Green’s function methodology, Landauer formalism, and the extended Huckel method. The electronic properties investigated are the band structures, density of states, and conductance. The results obtained from the extended Huckel method are compared with the Huckel method.

In Chapter 2, the theoretical methods are presented. In addition to the well-known theories such as the TB model, the Green’s function model, examples of analytical and geometrical techniques used in the calculation of the Hamiltonian matrix elements are illustrated.

The electronic properties of AGNRs are presented in Chapter 3. The results of electronic band structures, DOS, conductance, and LDOS are shown for n = 3, 4, and 5 dimer AGNRs. The first two ribbons are semiconducting and the later one is metallic. These results are consistent with theory. Then these results are compared with the Huckel method. These results are produced with and without edge terminated structures. The edge atoms are terminated with hydrogen atom. The most interesting observation in this study is the effect of the dangling bonds at the edges of these nanoribbons. It is clear from this investigation, the edge termination is essential for quantized conductance as expected in perfect nanostructures.
Chapter 4 presents only electronic band structures and DOS results for N=2 and N=6 chain ZGNRs. These results are also compared with the results obtained by the Huckel method. As in AGNRs, the edge atoms are terminated with hydrogen. In the case of non-terminated edges, the most significant observation is the presence of two bands mixed with the Pz bands in the valence band region near the Fermi level. Once the edges are terminated, these bands are pulled into lower energy levels. From these analyses, we conclude that these bands are due to the contributions of the hanging P-orbitals of the edge atoms.

In summary, Extended Huckel method was significantly more challenging than the Huckel method. In the Huckel method, only Pz-orbitals are included in the Hamiltonian. On the other hand, the extended method uses all four (S, Px, Py, Pz) orbitals in the analyses. Specifically, the orientations of the orbitals of each atom have to take into account for calculation. Inclusion of only Pz-orbitals is good enough for a conclusive result near the Fermi energy. The detailed knowledge of the electronic properties at all energy level requires more involved theory such as the extended Huckel model or density functional theory (DFT). The results will be more exciting and interesting with the extended Huckel method if the edges are terminated with element(s) other than hydrogen. The addition of hydrogen element at the edges does not show any effect on the electronic properties in the Huckel theory because the S-orbital of the hydrogen atom is on the 2-D plane. The transport in GNRs near the Fermi energy is only due to pi orbitals formed by the Pz- orbitals. Our observation with the extended Huckel model demonstrates effects far away from the Fermi energy.
Therefore, I conclude that the research is not complete, meaning there are many different types of nanostructures that can be examined using the extended Huckel method, and that means there is still the possibility for the stronger σ-bonds to have an effect on the electrical properties. This leads to some real interesting possibilities of extension of this work. The first possibility would be to stay with GNRs and start introducing edge defects to the ribbon. This could be accomplished a few ways; my initial thought would be to vary one of two things. First, vary the types of atoms used in the edge termination. Second, vary the self-interaction on certain orbitals, or completely remove some orbitals from the unit cell completely. As noticed in Chapters 3 and 4, the results obtained without edge termination have very interesting changes to the band structure around the Fermi level. Another avenue for future research is to look at different materials that can be isolated into single layer ribbons. Whatever avenue is chosen has the possibility to discover some truly interesting physics, and that is always important and significant from the pedagogical point view as well as in applications.
### Appendix

1. Hamiltonian Matrix of an Armchair Graphene Nanoribbon with $n = 3$ Dimer

<table>
<thead>
<tr>
<th></th>
<th>$E_1$</th>
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</table>
The list of the matrix element of the Hamiltonian is defined here:

\[ E_{SS} = V_{ss\sigma} \quad E_{xx} = \frac{1}{4} V_{pp\sigma} + \frac{3}{4} V_{pp\pi}, \quad PE_{spx} = V_{sp\sigma} \]
\[ E_{spx} = \frac{1}{2} V_{sp\sigma} \quad E_{yy} = \frac{3}{4} V_{pp\sigma} + \frac{1}{4} V_{pp\pi} \quad PE_{xx} = V_{pp\sigma} \]
\[ E_{sp} = \frac{\sqrt{3}}{2} V_{sp\sigma} \quad E_{xy} = \frac{\sqrt{3}}{4} V_{pp\sigma} - \frac{\sqrt{3}}{4} V_{pp\pi} \quad PE_{yy} = V_{pp\pi} \]
\[ E_{zz} = V_{pp\pi} \]

The phase factors are defined as:

\[ g_1 = e^{ika} \quad g_2 = e^{i\frac{ka}{2}} \]
\[ g_1^* = e^{-ika} \quad g_2^* = e^{-i\frac{ka}{2}}. \]

2. Code for Calculating the Band Structure and Density of States for n= 3 AGNR

Author: Spencer Jones;
"Armchair with n=3 dimer:
Band Structure and Density of States, Size of the Hamiltonian matrix is 28x28
Note: Edge Terminated by Hydrogen.

n=3; "Number of dimers";
amp=8.05; "Changes Energy Scale of Plots";
a=1.42;
V=-0.81*7.62/a^2;
\(\epsilon\)=-8.97;

"Overlap Interaction Energy";
Vss\sigma=-1.40*7.61/a^2;
Vsp\sigma=1.84*7.61/a^2;
Vpp\sigma=3.24*7.61/a^2;
Vpp\pi=-0.81*7.61/a^2;

\(\epsilon\)=-8.97;
a=1.42;
bc=1/2 (2\pi)/(3a);
\[ \varepsilon_p = -8.97; \]
\[ \varepsilon_y = -8.97; \]
\[ \varepsilon_z = -8.97; \]
\[ \varepsilon_s = -17.52; \]

"Phase Factor;"
\[ g_1 = \exp[i \cdot k \cdot a]; \]
\[ g_{i1} = \exp[-i \cdot k \cdot a]; \]
\[ g_2 = \exp[i \cdot k \cdot a/2]; \]
\[ g_{i2} = \exp[-i \cdot k \cdot a/2]; \]

"Interaction Terms;"
\[ \varepsilon_{ss} = V_{ss}\sigma; \]
\[ \varepsilon_{sx} = V_{sp}\sigma/2; \]
\[ \varepsilon_{sy} = V_{sp}\sigma*\sqrt{3}/2; \]
\[ \varepsilon_{xx} = V_{pp}\sigma/4 + V_{pp}\pi*3/4; \]
\[ \varepsilon_{yy} = V_{pp}\sigma*3/4 + V_{pp}\pi/4; \]
\[ \varepsilon_{zz} = V_{pp}\pi; \]
\[ \varepsilon_{xy} = V_{pp}\sigma*\sqrt{3}/4 - V_{pp}\pi*\sqrt{3}/4; \]
\[ \varepsilon_{sx} = V_{sp}\sigma; \]
\[ \varepsilon_{xx} = V_{pp}\sigma; \]
\[ \varepsilon_{yy} = V_{pp}\pi; \]

"Hydrogen-Carbon Interaction Terms;"
\[ V_{Hss}\sigma = -1.40*7.61/b^2; \]
\[ V_{Hsp}\sigma = 1.84*7.61/b^2; \]
\[ b = 1.09; "Bond length between Carbon and Hydrogen;" \]
\[ \varepsilon_{Hss} = V_{Hss}\sigma; \]
\[ \varepsilon_{Hsx} = V_{Hsp}\sigma/2; \]
\[ \varepsilon_{Hsy} = V_{Hsp}\sigma*\sqrt{3}/2; \]
\[ \varepsilon_h = -13.6; \]

\[ \varepsilon_h = \text{Table}[0, \{x, 1, 8n+4\}, \{y, 1, 8n+4\}]; \]

"Diagonals \varepsilon_s AND \varepsilon_p;"
\[ \text{Do}[H[[4i-3]][[4i-3]] = \varepsilon_s; \{i, 1, 2*n\}]; \]
\[ \text{Do}[H[[4i-2]][[4i-2]] = \varepsilon_{px}; \{i, 1, 2*n\}]; \]
\[ \text{Do}[H[[4i-1]][[4i-1]] = \varepsilon_{py}; \{i, 1, 2*n\}]; \]
\[ \text{Do}[H[[4i]][[4i]] = \varepsilon_{pz}; \{i, 1, 2*n\}]; \]

"C_1 on C_2;"
"S1-S2, Px2;"
\[ \text{Do}[H[[16i-15]][[16i-11]] = g_1*\varepsilon_{ss}; \{i, 1, (n+1)/2\}]; \]
\[ \text{Do}[H[[16i-15]][[16i-10]] = g_1*\varepsilon_{sx}; \{i, 1, (n+1)/2\}]; \]
"Px1-S2, Px2;"
\[ \text{Do}[H[[16i-14]][[16i-11]] = g_1*\varepsilon_{sx}; \{i, 1, (n+1)/2\}]; \]
\[ \text{Do}[H[[16i-14]][[16i-10]] = g_1*\varepsilon_{sx}; \{i, 1, (n+1)/2\}]; \]
"Py1-Py2";
Do[H[[16i-13]][[16i-9]]==g1*PEyy;,\{i,1,\(\text{n+1}/2\)\}]
"Pz1-Pz2";
Do[H[[16i-12]][[16i-8]]==g1*Ezz;,\{i,1,\(\text{n+1}/2\)\}]

"C_1 on C_3";
"S1-S3, Px3, Py3";
Do[H[[16i-15]][[16i-7]]==gi2*Ess;,\{i,1,\(\text{n}/2\)\}]
Do[H[[16i-15]][[16i-6]]==gi2*(-Esx);,\{i,1,\(\text{n}/2\)\}]
Do[H[[16i-15]][[16i-5]]==gi2*(-Esy);,\{i,1,\(\text{n}/2\)\}]
"Px1-S3, Px3, Py3";
Do[H[[16i-14]][[16i-7]]==gi2*Esx;,\{i,1,\(\text{n}/2\)\}]
Do[H[[16i-14]][[16i-6]]==gi2*Exx;,\{i,1,\(\text{n}/2\)\}]
Do[H[[16i-14]][[16i-5]]==gi2*Exy;,\{i,1,\(\text{n}/2\)\}]
"Py1-S3, Pz3";
Do[H[[16i-13]][[16i-7]]==gi2*Esy;,\{i,1,\(\text{n}/2\)\}]
Do[H[[16i-13]][[16i-6]]==gi2*Exy;,\{i,1,\(\text{n}/2\)\}]
Do[H[[16i-13]][[16i-5]]==gi2*Eyy;,\{i,1,\(\text{n}/2\)\}]
"Pz1-Pz3";
Do[H[[16i-12]][[16i-4]]==gi2*Ezz;,\{i,1,\(\text{n}/2\)\}]

"C_2 on C_1";
"S2-S1, Px1";
Do[H[[16i-11]][[16i-15]]==gi1*Ess;,\{i,1,\(\text{n+1}/2\)\}]
Do[H[[16i-11]][[16i-14]]==gi1*(-PEsx);,\{i,1,\(\text{n+1}/2\)\}]
"Px2-S1, Px1";
Do[H[[16i-10]][[16i-15]]==gi1*PEsx;,\{i,1,\(\text{n+1}/2\)\}]
Do[H[[16i-10]][[16i-14]]==gi1*PExx;,\{i,1,\(\text{n+1}/2\)\}]
"Py2-Py1";
Do[H[[16i-9]][[16i-13]]==gi1*PEyy;,\{i,1,\(\text{n+1}/2\)\}]
"Pz2-Pz1";
Do[H[[16i-8]][[16i-12]]==gi1*Ezz;,\{i,1,\(\text{n+1}/2\)\}]

"C_2 on C_4";
"S2-S4, Px4, Py4";
Do[H[[16i-11]][[16i-3]]==g2*Ess;,\{i,1,\(\text{n}/2\)\}]
Do[H[[16i-11]][[16i-2]]==g2*Esx;,\{i,1,\(\text{n}/2\)\}]
Do[H[[16i-11]][[16i-1]]==g2*(-Esy);,\{i,1,\(\text{n}/2\)\}]
"Px2-S4, Px4, Py4";
Do[H[[16i-10]][[16i-3]]==g2*(-Esx);,\{i,1,\(\text{n}/2\)\}]
Do[H[[16i-10]][[16i-2]]==g2*Exx;,\{i,1,\(\text{n}/2\)\}]
Do[H[[16i-10]][[16i-1]]==g2*(-Exy);,\{i,1,\(\text{n}/2\)\}]
"Py2-S4, Pz4, Py4";
Do[H[[16i-9]][[16i-3]]==g2*Esy;,\{i,1,\(\text{n}/2\)\}]
Do[H[[16i-9]][[16i-2]]==g2*(-Exy);,\{i,1,\(\text{n}/2\)\}]
Do[H[[16i-9]][[16i-1]]==g2*Eyy;,\{i,1,\(\text{n}/2\)\}]
"Pz2-Pz4";
Do[H[[16i-8]][[16i]]==g2*Ezz;,{i,1,n/2}]

"C₃ on C₄";
Do[H[[16i-7]][[16i-3]]==g1*Ess;,{i,1,(n/2)}]
Do[H[[16i-7]][[16i-2]]==g1*(-PEsx);,{i,1,(n/2)}]
Do[H[[16i-6]][[16i-3]]==g1*PEsx;,{i,1,(n/2)}]
Do[H[[16i-6]][[16i-2]]==g1*PExx;,{i,1,(n/2)}]
Do[H[[16i-5]][[16i-1]]==g1*PEyy;,{i,1,(n/2)}]
Do[H[[16i-4]][[16i]]==g1*Ezz;,{i,1,(n/2)}]

"C₃ on C₅";
"S₃-S₁, Px₁, Py₁";
Do[H[[16i-7]][[16i-15]]==g2*Ess;,{i,1,n/2}]
Do[H[[16i-7]][[16i-14]]==g2*Esx;,{i,1,n/2}]
Do[H[[16i-7]][[16i-13]]==g2*Esy;,{i,1,n/2}]
"Px₃-S₁, Px₁, Py₁";
Do[H[[16i-6]][[16i-15]]==g2*(-Esx);,{i,1,n/2}]
Do[H[[16i-6]][[16i-14]]==g2*Exx;,{i,1,n/2}]
Do[H[[16i-6]][[16i-13]]==g2*Exy;,{i,1,n/2}]
"Py₃-S₁, Px₁, Py₁";
Do[H[[16i-5]][[16i-15]]==g2*(-Esy);,{i,1,n/2}]
Do[H[[16i-5]][[16i-14]]==g2*Exy;,{i,1,n/2}]
Do[H[[16i-5]][[16i-13]]==g2*Eyy;,{i,1,n/2}]
"Pz₃-Pz₁";
Do[H[[16i-4]][[16i-12]]==g2*Ezz;,{i,1,n/2}]

"C₄ on C₃";
"S₁-S₃, Px₃, Py₃";
Do[H[[16i-3]][[16i-7]]==g1*Ess;,{i,1,(n/2)}]
Do[H[[16i-3]][[16i-6]]==g1*PEsx;,{i,1,(n/2)}]
"Px₁-S₃, Px₃, Py₃";
Do[H[[16i-2]][[16i-7]]]=g1*(-PEsx);,{i,1,(n)/2}]
Do[H[[16i-2]][[16i-6]]]=g1*PExx;,{i,1,(n)/2}]
"Py1-S3,Px3,Py3";
Do[H[[16i-1]][[16i-5]]]=g1*PEyy;,{i,1,(n)/2}]
"Pz1-Pz3";
Do[H[[16i]][[16i-4]]]=g1*Ezz;,{i,1,(n)/2}]

"C4 on C2";
"S4-S2,Px2,Py2";
Do[H[[16i-3]][[16i-11]]]=gi2*Ess;,{i,1,n/2}]
Do[H[[16i-3]][[16i-10]]]=gi2*(-Esx);,{i,1,n/2}]
Do[H[[16i-3]][[16i-9]]]=gi2*Esy;,{i,1,n/2}]
"Px4-S2,Px2,Py2";
Do[H[[16i-2]][[16i-11]]]=gi2*Esx;,{i,1,n/2}]
Do[H[[16i-2]][[16i-10]]]=gi2*Exx;,{i,1,n/2}]
Do[H[[16i-2]][[16i-9]]]=gi2*(-Euy);,{i,1,n/2}]
"Py4-Py2";
Do[H[[16i]][[16i-8]]]=gi2*Ezz;,{i,1,n/2}]

"C4 on C6";
"S4-S6,Px6,Py6";
Do[H[[16i-3]][[16*(i+1)-11]]]=gi2*Ess;,{i,1,(n-1)/2}]
Do[H[[16i-3]][[16*(i+1)-10]]]=gi2*(-Esx);,{i,1,(n-1)/2}]
Do[H[[16i-3]][[16*(i+1)-9]]]=gi2*Esy;,{i,1,(n-1)/2}]
"Px4-S6,Px6,Py6";
Do[H[[16i-2]][[16*(i+1)-11]]]=gi2*Esx;,{i,1,(n-1)/2}]
Do[H[[16i-2]][[16*(i+1)-10]]]=gi2*Exx;,{i,1,(n-1)/2}]
Do[H[[16i-2]][[16*(i+1)-9]]]=gi2*(-Euy);,{i,1,(n-1)/2}]
"Py4-Py6";
Do[H[[16i]][[16*(i+1)-8]]]=gi2*Ezz;,{i,1,(n-1)/2}]

"C5 on C3";
"S5-S3,Px3,Py3";
Do[H[[16*(i+1)-15]][[16i-7]]]=gi2*Ess;,{i,1,(n-1)/2}]
Do[H[[16*(i+1)-15]][[16i-6]]]=gi2*(-Esx);,{i,1,(n-1)/2}]
Do[H[[16*(i+1)-15]][[16i-5]]]=gi2*Esy;,{i,1,(n-1)/2}]
"Px5-S3,Px3,Py3";
Do[H[[16*(i+1)-14]][[16i-7]]]=gi2*Esx;,{i,1,(n-1)/2}]
Do[H[[16*(i+1)-14]][[16i-6]]]=gi2*Exx;,{i,1,(n-1)/2}]

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Do[\[H\][16*(i+1)-14]][[16i-5]]=gi2*(-Exy);,{i,1,(n-1)/2}]
"Py5-S3,Px3,Py3";
Do[\[H\][16*(i+1)-13]][[16i-7]]=gi2*(-Esy);,{i,1,(n-1)/2}]
Do[\[H\][16*(i+1)-13]][[16i-6]]=gi2*(-Exy);,{i,1,(n-1)/2}]
Do[\[H\][16*(i+1)-13]][[16i-5]]=gi2*Eyy;,{i,1,(n-1)/2}]
"Pz5-Py3";
Do[\[H\][16*(i+1)-12]][[16i-4]]=gi2*Ezz;,{i,1,(n-1)/2}]

"C6 on C4";
"S6-S4,Px4,Py4";
Do[\[H\][16*(i+1)-11]][[16i-3]]=g2*Ess;,{i,1,(n-1)/2}]
Do[\[H\][16*(i+1)-11]][[16i-2]]=g2*Esx;,{i,1,(n-1)/2}]
Do[\[H\][16*(i+1)-11]][[16i-1]]=g2*Esy;,{i,1,(n-1)/2}]
"Px6-S4,Px4,Py4";
Do[\[H\][16*(i+1)-10]][[16i-3]]=g2*(-Esx);,{i,1,(n-1)/2}]
Do[\[H\][16*(i+1)-10]][[16i-2]]=g2*Exx;,{i,1,(n-1)/2}]
Do[\[H\][16*(i+1)-10]][[16i-1]]=g2*Exy;,{i,1,(n-1)/2}]
"Py6-S4,Px4,Py4";
Do[\[H\][16*(i+1)-9]][[16i-3]]=g2*(-Esy);,{i,1,(n-1)/2}]
Do[\[H\][16*(i+1)-9]][[16i-2]]=g2*Exy;,{i,1,(n-1)/2}]
Do[\[H\][16*(i+1)-9]][[16i-1]]=g2*Eyy;,{i,1,(n-1)/2}]
"Pz6-Py4";
Do[\[H\][16*(i+1)-8]][[16i]]=g2*Ezz;,{i,1,(n-1)/2}]

"Carbon and Hydrogen Elements";
"H1 on C1";

H[[1]][[8*n+1]]=gi2*EHss;
H[[8*n+1]][[1]]=g2*EHss;
H[[2]][[8*n+1]]=gi2*EHsx;
H[[8*n+1]][[2]]=g2*EHsx;
H[[3]][[8*n+1]]=g2*EHsy;
H[[8*n+1]][[3]]=g2*EHsy;

"H2 on C2";

H[[5]][[8*n+2]]=g2*EHss;
H[[8*n+2]][[5]]=gi2*EHss;
H[[6]][[8*n+2]]=g2*EHsx;
H[[8*n+2]][[6]]=g2*EHsx;
H[[7]][[8*n+2]]=g2*EHsy;
H[[8*n+2]][[7]]=g2*EHsy;

"H3 on C6";
If[OddQ[n]==True, 
H[[8*n-3]][[8*n+3]]=g2*EHss;
H[[8*n+3]][[8*n-3]]=gi2*EHss;
H[[8*n-2]][[8*n+3]]=g2*EHsx;
H[[8*n+3]][[8*n-2]]=gi2*EHsx;
\[ H[[8*n+3]][[8*n-2]]=\text{gi2*EHsx}; \]
\[ H[[8*n-1]][[8*n+3]]=\text{g2*EHsy}; \]
\[ H[[8*n+3]][[8*n-1]]=\text{gi2*EHsy}; \]

"H4 on C5";
\[ H[[8*n-7]][[8*n+4]]=\text{gi2*EHss}; \]
\[ H[[8*n+4]][[8*n-7]]=\text{g2*EHss}; \]
\[ H[[8*n-6]][[8*n+4]]=\text{gi2*EHsx}; \]
\[ H[[8*n+4]][[8*n-6]]=\text{g2*EHsx}; \]
\[ H[[8*n-5]][[8*n+4]]=\text{gi2*EHsy}; \]
\[ H[[8*n+4]][[8*n-5]]=\text{g2*EHsy}; \]

If[EvenQ[n]==True,
"H3 on C6";
\[ H[[8*n-3]][[8*n+3]]=\text{gi2*EHss}; \]
\[ H[[8*n+3]][[8*n-3]]=\text{g2*EHss}; \]
\[ H[[8*n-2]][[8*n+3]]=\text{gi2*EHsx}; \]
\[ H[[8*n+3]][[8*n-2]]=\text{g2*EHsx}; \]
\[ H[[8*n-1]][[8*n+3]]=\text{gi2*EHsy}; \]
\[ H[[8*n+3]][[8*n-1]]=\text{g2*EHsy}; \]

"H4 on C5";
\[ H[[8*n-7]][[8*n+4]]=\text{g2*EHss}; \]
\[ H[[8*n+4]][[8*n-7]]=\text{gi2*EHss}; \]
\[ H[[8*n-6]][[8*n+4]]=\text{g2*EHsx}; \]
\[ H[[8*n+4]][[8*n-6]]=\text{gi2*EHsx}; \]
\[ H[[8*n-5]][[8*n+4]]=\text{g2*EHsy}; \]
\[ H[[8*n+4]][[8*n-5]]=\text{gi2*EHsy}; \]

"Hydrogen Energy";
\[ H[[8*n+1]][[8*n+1]]=\mathcal{E}_h; \]
\[ H[[8*n+2]][[8*n+2]]=\mathcal{E}_h; \]
\[ H[[8*n+3]][[8*n+3]]=\mathcal{E}_h; \]
\[ H[[8*n+4]][[8*n+4]]=\mathcal{E}_h; \]

(*Numerical calculation, give "ks" higher value if needed*)
ks=500;
lh=Length[H];
ke=Table[0,{i,1,ks}];
ee=Table[Table[0,{i,1,ks}],[j,1,lh]];ed=Table[0,{l,1,ks}];
dos=Table[0,{l,1,ks}];
p=Table[0,{j,1,lh}];
Do[
ke[[i]]=(2*bc)/(ks-1) (i-ks)+bc;
eig=Sort[Eigenvalues[H/.k->ke[[i]]],Greater];
Do[...
ee[[j]][[i]] = eig[[j]];
, {j, 1, lh}
, {i, 1, ks}

Do[
  ed[[l]] = (2*amp*Abs[V])/(ks-1) (l-ks)+amp*Abs[V]+\epsilon;
dos[[l]] = Sum[1/ks*Sum[Exp[-(ee[[j]][[i]] -
ed[[l]])^2/0.01], {i, 1, ks}], {j, 1, lh}]
, {l, 1, ks}

(*Do the plots*)
Do[
  p[[j]] = ListLinePlot[Table[{ke[[i]], ee[[j]][[i]]-\epsilon}, {i, 1, ks}], Axes->False, Frame->True, PlotRange->{{-bc,bc}, {amp*V,-amp*V}}, FrameStyle->AbsoluteThickness[1.5], BaseStyle->"Helvetica", 15, Bold], PlotStyle->{Black, AbsoluteThickness[1.5]}, FrameLabel->"k (1/Å)","E (eV)"], AspectRatio->3/2, ImageSize->300, FrameTicks->{{Automatic, None}, {Automatic, None}};
  , {j, 1, lh}

  pd = ListLinePlot[Table[{dos[[l]], ed[[l]]-\epsilon}, {l, 1, ks}], Axes->False, Frame->True, FrameTicks->{{Automatic, None}, {Automatic, None}}, PlotRange->{{0, 1}, {amp*Vppn, -amp*Vppn}}, FrameStyle->AbsoluteThickness[1.5], BaseStyle->"Helvetica", 14, Bold],
  PlotStyle->Directive[Black, AbsoluteThickness[1.5]], FrameLabel->"DOS","E (eV)"], ImageSize->305, AspectRatio->3/2];

ped = GraphicsRow[{Show[p], pd}, Alignment->Top]
3. Code for Calculating the Conductance for n=3 AGNR

"GNR Armchair, Conductance All Orbitals with hydrogen on edge 6/26/2015 Spencer Jones"

n=3; "Number Of Diemers"
a=1.42;

amp = 1.05;
kB = 8.6173324 * 10^-5;
Troom = 22;
n = kB * Troom;

Vssσ = -1.40 * 7.61 / a^2;
Vspσ = 1.84 * 7.61 / a^2;
Vppσ = 3.24 * 7.61 / a^2;
Vppn = -0.81 * 7.61 / a^2;
ɛpx = -8.97;
ɛpy = -8.97;
ɛpz = -8.97;
ɛs = -17.52;
"Carbon-Carbon Interaction Terms";
Ess = Vssσ;
Espx = Vspσ / 2;
Espy = Vspσ * Sqrt[3] / 2;
Exx = Vppσ / 4 + Vppn * 3 / 4;
Eyy = Vppσ * 3 / 4 + Vppn / 4;
Ezz = Vppn;
PEspx = Vspσ;
PExx = Vppσ;
PExy = Vppn;
"Hydrogen-Carbon Interaction Terms";
VHssσ = -1.40 * 7.61 / b^2;
VHspσ = 1.84 * 7.61 / b^2;
b = 1.09;
EHss = VHssσ;
EHspx = VHspσ / 2;
EHspy = VHspσ * Sqrt[3] / 2;
ɛh = -13.6;

ks = 500;
ec = Table[0, {i, 1, ks}];
gc = Table[0, {i, 1, ks}];
ldostot = Table[0, {i, 1, ks}];
ldos = Table[Table[0, {i, 1, ks}], {j, 1, 8n + 4}];
pl = Table[0, {j, 1, 8n + 4}];

HM = H1 = H2 = HM1 = HM2 = Table[0, {x, 1, 8n + 4}, {y, 1, 8n + 4}]; "sets Matrix Size";
"Sets Diagonals $\mathcal{E}_s$ AND $\mathcal{E}_p$;"
Do[
  HM[[4i-3]][[4i-3]] = Es;,{i,1,2*n}]; "S Orbital";
Do[
  HM[[4i-2]][[4i-2]] = Ep;,{i,1,2*n}]; "Px Orbital";
Do[
  HM[[4i-1]][[4i-1]] = Ey;,{i,1,2*n}]; "Py Orbital";
Do[
  HM[[4i]][[4i]] = Ez;,{i,1,2*n}]; "Pz Orbital";

"C$_1$ on C$_2$;"
"S1=S2,Px2;"
Do[HM[[16i-15]][[16i-11]] = HM[[16i-11]][[16i-15]] = Es;,{i,1,(n+1)/2}]  
Do[HM[[16i-15]][[16i-10]] = HM[[16i-10]][[16i-15]] = Ep;,{i,1,(n+1)/2}]  
"Px1-Px2;"
Do[HM[[16i-14]][[16i-11]] = HM[[16i-11]][[16i-14]] = (-Ep).sax;,{i,1,(n+1)/2}]  
Do[HM[[16i-14]][[16i-10]] = HM[[16i-10]][[16i-14]] = Exx;,{i,1,(n+1)/2}]  
"Py1-Py2;"
Do[HM[[16i-13]][[16i-9]] = HM[[16i-9]][[16i-13]] = Eyy;,{i,1,(n+1)/2}]  
"Pz1-Pz2;"
Do[HM[[16i-12]][[16i-8]] = HM[[16i-8]][[16i-12]] = Ezz;,{i,1,(n+1)/2}]

"C$_1$ on C$_3$;"
"S1=S3,Px3,Py3;"
Do[HM[[16i-15]][[16i-7]] = HM[[16i-7]][[16i-15]] = Es;,{i,1,n/2}]  
Do[HM[[16i-15]][[16i-6]] = HM[[16i-6]][[16i-15]] = (-Ep)sax;,{i,1,n/2}]  
Do[HM[[16i-15]][[16i-5]] = HM[[16i-5]][[16i-15]] = (-Ep)ay;,{i,1,n/2}]  
"Px1-Px3,Py3;"
Do[HM[[16i-14]][[16i-7]] = HM[[16i-7]][[16i-14]] = Ep;,{i,1,n/2}]  
Do[HM[[16i-14]][[16i-6]] = HM[[16i-6]][[16i-14]] = Exx;,{i,1,n/2}]  
Do[HM[[16i-14]][[16i-5]] = HM[[16i-5]][[16i-14]] = Eyy;,{i,1,n/2}]  
"Py1-Py3;"
Do[HM[[16i-13]][[16i-7]] = HM[[16i-7]][[16i-13]] = Ep;,{i,1,n/2}]  
Do[HM[[16i-13]][[16i-6]] = HM[[16i-6]][[16i-13]] = Exx;,{i,1,n/2}]  
Do[HM[[16i-13]][[16i-5]] = HM[[16i-5]][[16i-13]] = Eyy;,{i,1,n/2}]  
"Pz1-Pz3;"
Do[HM[[16i-12]][[16i-4]] = HM[[16i-4]][[16i-12]] = Ez;,{i,1,n/2}]

"C$_2$ on C$_4$;"
"S2-S4,Px4,Py4;"
Do[HM[[16i-11]][[16i-3]] = HM[[16i-3]][[16i-11]] = Es;,{i,1,n/2}]  
Do[HM[[16i-11]][[16i-2]] = HM[[16i-2]][[16i-11]] = Ep;,{i,1,n/2}]  
Do[HM[[16i-11]][[16i-1]] = HM[[16i-1]][[16i-11]] = (-Ep)sax;,{i,1,n/2}]  
"Px2-Px4,Py4;"
Do[HM[[16i-10]][[16i-3]] = HM[[16i-3]][[16i-10]] = (-Ep)ax;,{i,1,n/2}]  
Do[HM[[16i-10]][[16i-2]] = HM[[16i-2]][[16i-10]] = Exx;,{i,1,n/2}]  
Do[HM[[16i-10]][[16i-1]] = HM[[16i-1]][[16i-10]] = (-Ex)ax;,{i,1,n/2}]  
"Py2-Py4;"
Do[HM[[16i-9]][[16i-3]] = HM[[16i-3]][[16i-9]] = Ep;,{i,1,n/2}]
Do[HM[[16i-9]][[16i-2]]==HM[[16i-2]][[16i-9]]==(-Exy);{i,1,n/2}]
Do[HM[[16i-9]][[16i-1]]==HM[[16i-1]][[16i-9]]==Eyy;{i,1,n/2}]
"Pz2-Pz4";
Do[HM[[16i-8]][[16i]]==HM[[16i]][[16i-8]]==Ezz;{i,1,n/2}]

"C_3 on C_5";
"S3-S5,Px5,Py5";
Do[HM[[16i-7]][[16*(i+1)-15]]==HM[[16*(i+1)-15]][[16i-7]]==Ess;{i,1,(n-1)/2}]
Do[HM[[16i-7]][[16*(i+1)-14]]==HM[[16*(i+1)-14]][[16i-7]]==Espy;{i,1,(n-1)/2}]
Do[HM[[16i-7]][[16*(i+1)-13]]==HM[[16*(i+1)-13]][[16i-7]]==(-Exy);{i,1,(n-1)/2}]
"Pz3-S5,Px5,Py5";
Do[HM[[16i-6]][[16*(i+1)-15]]==HM[[16*(i+1)-15]][[16i-6]]==(-Exy);{i,1,(n-1)/2}]
Do[HM[[16i-6]][[16*(i+1)-14]]==HM[[16*(i+1)-14]][[16i-6]]==Exx;{i,1,(n-1)/2}]
Do[HM[[16i-6]][[16*(i+1)-13]]==HM[[16*(i+1)-13]][[16i-6]]==(-Espy);{i,1,(n-1)/2}]

"C_6 on C_4";
"S6-S4,Px4,Py4";
Do[HM[[16*(i+1)-11]][[16i-3]]==HM[[16i-3]][[16*(i+1)-11]]==Ess;{i,1,(n-1)/2}]
Do[HM[[16*(i+1)-11]][[16i-2]]==HM[[16i-2]][[16*(i+1)-11]]==Espy;{i,1,(n-1)/2}]
Do[HM[[16*(i+1)-11]][[16i-1]]==HM[[16i-1]][[16*(i+1)-11]]==Exy;{i,1,(n-1)/2}]
"Px6-S4,Px4,Py4";
Do[HM[[16*(i+1)-10]][[16i-3]]==HM[[16i-3]][[16*(i+1)-10]]==(-Espx);{i,1,(n-1)/2}]
Do[HM[[16*(i+1)-10]][[16i-2]]==HM[[16i-2]][[16*(i+1)-10]]==Exx;{i,1,(n-1)/2}]
Do[HM[[16*(i+1)-10]][[16i-1]]==HM[[16i-1]][[16*(i+1)-10]]==Exy;{i,1,(n-1)/2}]
"Py6-S4,Px4,Py4";
Do[HM[[16*(i+1)-9]][[16i-3]]==HM[[16i-3]][[16*(i+1)-9]]==(-Espy);{i,1,(n-1)/2}]
Do[HM[[16*(i+1)-9]][[16i-2]]==HM[[16i-2]][[16*(i+1)-9]]==Exy;{i,1,(n-1)/2}]

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Do[HM[[16*(i+1)-9]][[16i-1]]=HM[[16i-1]][[16*(i+1)-9]]=Eyy;{i,1,(n-1)/2}]
"Pz6-Py4";
Do[HM[[16*(i+1)-8]][[16i]]=HM[[16i]][[16*(i+1)-8]]=Ezz;{i,1,(n-1)/2}]

"Edge Hydrogen In Conductor";
"Top Left Hydrogen - C1";
HM[[1]][[8*n+1]]=HM[[8*n+1]][[1]]=EHss;
HM[[2]][[8*n+1]]=HM[[8*n+1]][[2]]=EHspx;
HM[[3]][[8*n+1]]=HM[[8*n+1]][[3]]=-EHspy;

"Top Right Hydrogen - C2";
HM[[5]][[8*n+2]]=HM[[8*n+2]][[5]]=EHss;
HM[[6]][[8*n+2]]=HM[[8*n+2]][[6]]=-EHspx;
HM[[7]][[8*n+2]]=HM[[8*n+2]][[7]]=-EHspy;

If[OddQ[n]==True,
"Bottom Right - C(2*n)";
HM[[8*n-3]][[8*n+3]]=HM[[8*n+3]][[8*n-3]]=EHss;
HM[[8*n-2]][[8*n+3]]=HM[[8*n+3]][[8*n-2]]=-EHspx;
HM[[8*n-1]][[8*n+3]]=HM[[8*n+3]][[8*n-1]]=EHspy;

"Bottom Left - C(2*n-1)";
HM[[8*n-7]][[8*n+4]]=HM[[8*n+4]][[8*n-7]]=EHss;
HM[[8*n-6]][[8*n+4]]=HM[[8*n+4]][[8*n-6]]=EHspx;
HM[[8*n-5]][[8*n+4]]=HM[[8*n+4]][[8*n-5]]=EHspy;]

If[EvenQ[n]==True,
"Bottom Right - C(2*n)";
HM[[8*n-3]][[8*n+3]]=HM[[8*n+3]][[8*n-3]]=EHss;
HM[[8*n-2]][[8*n+3]]=HM[[8*n+3]][[8*n-2]]=EHspx;
HM[[8*n-1]][[8*n+3]]=HM[[8*n+3]][[8*n-1]]=EHspy;

"Bottom Left - C(2*n-1)";
HM[[8*n-7]][[8*n+4]]=HM[[8*n+4]][[8*n-7]]=EHss;
HM[[8*n-6]][[8*n+4]]=HM[[8*n+4]][[8*n-6]]=-EHspx;
HM[[8*n-5]][[8*n+4]]=HM[[8*n+4]][[8*n-5]]=EHspy;]

HM[[8*n+1]][[8*n+1]]=Eh;
HM[[8*n+2]][[8*n+2]]=Eh;
HM[[8*n+3]][[8*n+3]]=Eh;
HM[[8*n+4]][[8*n+4]]=Eh;

"Coupling Matrix between lead and conductor";
"C3 on C4";
"S=S4,Px4";
Do[HM1[[16i-7]][[16i-3]]=Ess;{i,1,(n/2)}]
Do[HM1[[16i-7]][[16i-2]]=(-PEspx);{i,1,(n/2)}]
"Pz3-S4,Px4";
Do[HM1[[16i-6]][[16i-3]]=PEspx;{i,1,(n/2)}]
Do[HM1[[16i-6]][[16i-2]]=PExx;{i,1,(n/2)}]

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Do[HM1[[16i-5]][[16i-1]]=PEyy;, {i,1,(n)/2}]

Do[HM1[[16i-4]][[16i]]=Ezz;, {i,1,(n)/2}]

H1=H2=HM;
HCL=HM2=HM1;
Iden=IdentityMatrix[8n+4];

iteration = 20;
ta=Table[0,{k,1,iteration}];
tb=Table[0,{k,1,iteration}];
ta[[1]]=Inverse[(ec[[i]]+I*η)*Iden-H2].ConjugateTranspose[HCL];
tb[[1]]=Inverse[(ec[[i]]+I*η)*Iden-H1].HCL;

Do[
  ta[[k+1]]=Inverse[Iden-ta[[k]].tb[[k]]-tb[[k]].ta[[k]].ta[[k]]],
  tb[[k+1]]=Inverse[Iden-ta[[k]].tb[[k]]-tb[[k]].ta[[k]].tb[[k]]],
  {k,1,iteration-1}];

Ta=ta[[1]]+Sum[(Apply[Dot,Table[tb[[k]],{k,1,l}]].ta[[l+1]]),
  {l,1,iteration-1}];
Tb=tb[[1]]+Sum[(Apply[Dot,Table[ta[[k]],{k,1,l}]].tb[[l+1]]),
  {l,1,iteration-1}];

Σ1=ConjugateTranspose[HM1].Inverse[(ec[[i]]+I*η)*Iden-H1-
  ConjugateTranspose[HM1].Ta].HM1;
Σ2=HM2.Inverse[(ec[[i]]+I*η)*Iden-H2-
  HM2.Tb].ConjugateTranspose[HM2];

GM=Inverse[(ec[[i]]+I*η)*Iden-HM-Σ1-Σ2];
Γ1=I(Σ1-ConjugateTranspose[Σ1]);
Γ2=I(Σ2-ConjugateTranspose[Σ2]);

GRM=GM;

GAM=ConjugateTranspose[GM];
gc[[i]]=Tr[Γ1.GRM.Γ2.GAM];
ldostot[[i]]=-1/π*Im[Tr[GM]]

Do[
  ldos[[j]][[i]]=1/π*Im[GM[[j]][[j]]],
  {j,1,8n+4},
  {i,1,ks}];

pc=ListLinePlot[Table[{ec[[i]]-Epz,Re[gc[[i]]]},{i,1,ks}],Axes->False,
  Frame->True,FrameTicks->Automatic,FrameLabel->"E (eV)","Conductance (2e²/h)";
  ImageSize->300,PlotLabel->"(a)"]
pltot=ListLinePlot[Table[{ec[[i]]-\[ScriptCapitalE]pz,ldostot[[i]]},{i,1,ks}],Axes->False,
    Frame->True,FrameTicks->{{Automatic,None},{Automatic,None}},
    PlotRange->{{amp*Vppπ, -amp*Vppπ},{0,3}},
    FrameStyle->AbsoluteThickness[1.5],BaseStyle->"Helvetica",14,Bold,
    PlotStyle->Directive[Black,AbsoluteThickness[1.5]],
    FrameLabel->"E (eV)","DOS"},ImageSize->300,PlotLabel->"(b)"]

Do[
  pl[[j]]=ListLinePlot[Table[{ec[[i]]-\[ScriptCapitalE]px,ldos[[j]][[i]]+ldos[[j+1]][[i]]+ldos[[j+2]][[i]]+ldos[[j+3]][[i]]}]
    ,[i,1,ks]],Axes->False,
    Frame->True,FrameTicks->{{Automatic,None},{Automatic,None}},
    FrameStyle->AbsoluteThickness[1.5],BaseStyle->"Helvetica",14,Bold,
    PlotStyle->Directive[Black,AbsoluteThickness[1.5]],
    FrameLabel->"E (eV)","LDOS of C" <> ToString[j],ImageSize->300,PlotLabel->"(c):"<>ToString[j]
    ,[j,1,8n+4,4]]

Do[Print[pl[[j]]],[j,1,8n,4]]
References


