Quantum Theory and Basic Concepts for Electronic Properties in Molecular Structure

Zahraa Sadeq Kareem, Qassim Husian Sned and Zahraa Morus

Under the supervision of

Dr. Qusiy H. Al-Galiby

University of Al-Qadisiyah, College of education, Department of Physics,

Al Diwaniyah, Iraq

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Nothing we can do without the big support from our best supervisor **Dr. Qusiy Al-Galiby**. We would like to introduce our grateful feeling to him.

We would like to thank our father, mother and all our family members for helping and supporting us.

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Abstract

We present the important properties of electron propagation in molecular modelling, such as band structure, integrated density of state N(E) and density of state (DOS) using one-dimensional tight-binding model. The FORTRAN program have used to calculate these properties and to investigate the electron propagation on the one-dimensional crystal chain. We calculated the general band structure, number of eigenvalues less than E for small and large number of atoms and the DOS, we found that there was on line for the band structure attribute for one atom in the unit cell. In the N(E) calculation, the stairs line appeared when the system contains small number of atoms, whereas the line will be smooth at large number of atoms. These shows that the intensity of atoms in material play important role enhance the DOS. At the edges of band structure, the density of state goes to infinite and the DOS appeared with VAN-HOV singularity.

Introduction

Recent years have witnessed a significant increase in attention of studies, which related to electronic structure of materials and the need for the miniaturization of electronic devices. [1] These years of research in atoms have recently brought about the field of nanoscience, aiming at establishing control and making useful things at the atomic scale. [1-3] The modification of the electronic properties of such systems has applications such as the quantum interference effect transistor (QuLET) and development of molecular switch. [1-2] and [7] In this chapter, we introduce some models of molecular systems to study most important properties of electron propagation, such as energy bands, density of states.

Chapter 1

Electrical properties of molecular structure

We use the tight binding model to study the band structure for periodic structures and the density of state for the ordered system by using a numerical decimation.

Starting point to understand the electrical properties of a crystal is looking at its band structure. Here we start with very simple one-dimensional crystalline system as shown in Figure 1.1, and the band structure is shown in Figure 1.2.

Density of states is one of the electrical properties that we try to understand within these band structures that lead to be able to know the mechanism of transport in the materials.

1.1. The Tight Binding Model

Tight binding has existed for many years as a convenient and transparent model for the description of electronic structure in molecules and solids [1].

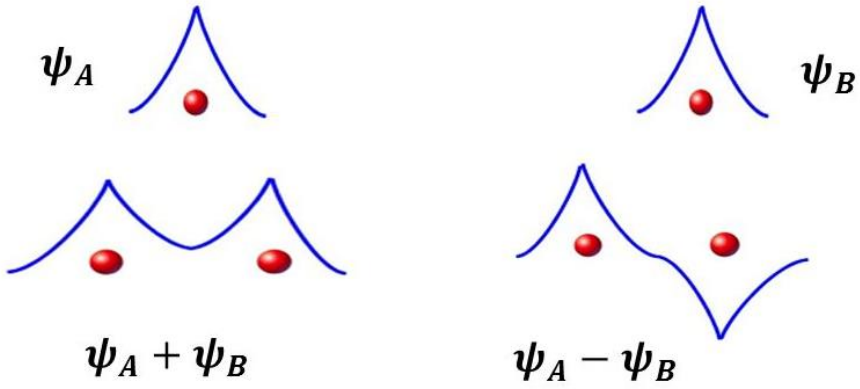

Figure 1.1 shows simply the tight-bind model and how the wave functions of atoms will interact as we consider the nearest neighbour atoms.

Figure 1.1 A model to describe the electronic structure in molecules and solids.The tight-binding model, we imagine how the wave functions of atoms will interact as we bring them together.

In our work, we use the tight binding model (TBM) (sometime referred to as the tight binding approximation). The TBM assumes that the electrons in a solid are sufficiently tightly bound that we need only consider nearest neighbours. This will be true in many physical problems when the wave functions at the individual atomic sites decay to zero before they reach the second nearest neighbour.

We know, as well, that in our one-dimensional model the spreading of the wave function will be blocked by the nearest neighbours and there are no other directions for interaction to take place in. The tight binding Hamiltonian (including only nearest neighbour interaction) for a chain as shown in Figure 1.2.

The behaviour of insulators and semiconductors has been described by using tight binding model and would be inappropriate for a metal (for which these assumptions would be incorrect as the electrons in a metal are highly mobile).

1.2. One dimensional (1-D) linear crystalline chain

We consider simple tight-binding approach to get qualitative understanding of electronic structure calculation in periodic systems, as shown in figure 1.2.

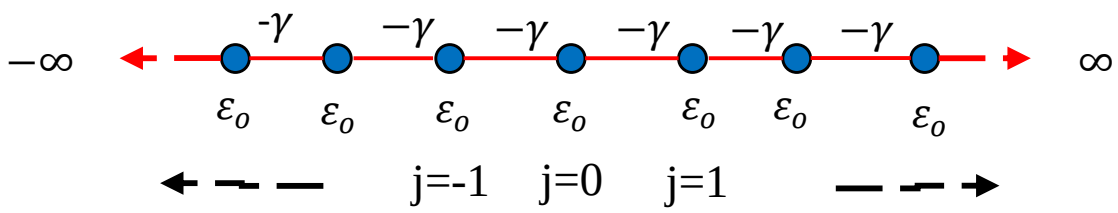

Figure 1.2: one dimension (1-D) linear crystalline chain [3]

In this system, ε_o and γ are the site and hopping energies respectively. According to the time independent Schrodinger equation:

$$H|\psi\rangle = E|\psi\rangle \tag{1.1}$$

$$\begin{pmatrix} -\infty & . & . & . & . & . & . & . & . \\ . & . & . & . & . & . & . & . & . \\ . & . & \varepsilon_o & -\gamma & 0 & 0 & 0 & . & . \\ . & . & -\gamma & \varepsilon_o & -\gamma & 0 & 0 & . & . \\ . & . & 0 & -\gamma & \varepsilon_o & -\gamma & 0 & . & . \\ . & . & 0 & 0 & -\gamma & \varepsilon_o & -\gamma & . & . \\ . & . & 0 & 0 & 0 & -\gamma & \varepsilon_o & . & . \\ . & . & . & . & . & . & . & . & . \\ . & . & . & . & . & . & . & . & +\infty \end{pmatrix} \begin{pmatrix} -\infty \\ \vdots \\ \psi_{j-2} \\ \psi_{j-1} \\ \psi_j \\ \psi_{j+1} \\ \psi_{j+2} \\ \vdots \\ \infty \end{pmatrix} = E \begin{pmatrix} -\infty \\ \vdots \\ \psi_{j-2} \\ \psi_{j-1} \\ \psi_j \\ \psi_{j+1} \\ \psi_{j+2} \\ \vdots \\ \infty \end{pmatrix}$$

The most general formula for infinite chain has given by:

$$\varepsilon_o \psi_j - \gamma \psi_{j-1} - \gamma \psi_{j+1} = E \psi_j \qquad (1.2)$$

The equation (3.2) is satisfied for all j go to $\pm\infty$, and we can write (3.2) as :

$$\psi_{j+1} = \left(\frac{\varepsilon_o - E}{\gamma}\right) \psi_j - \psi_{j-1} \qquad (1.3)$$

This is called Recurrent Relation.

Block's theorem has used to calculate the dispersion relation for this system by substituting $\psi_j = Ae^{ikj}$ into (1.2) eq. we get:

$$E(k) = \varepsilon_o - 2\gamma cosk \qquad (1.4)$$

The spectrum of an infinite system is continuous. Where *E* as a function of *k*, and the bandwidth is directly proportional to the hopping integral, where $BW = 4\gamma$, as shown in Figure 1.3.

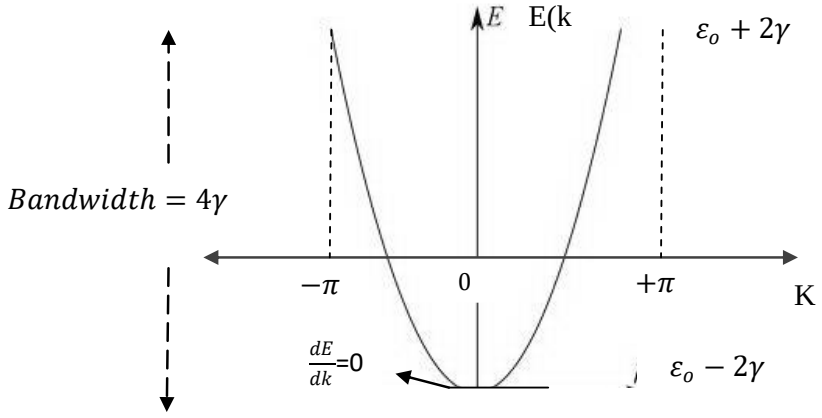

Figure 1.3: illustrates a simple band structure for (1-D) linear chain.

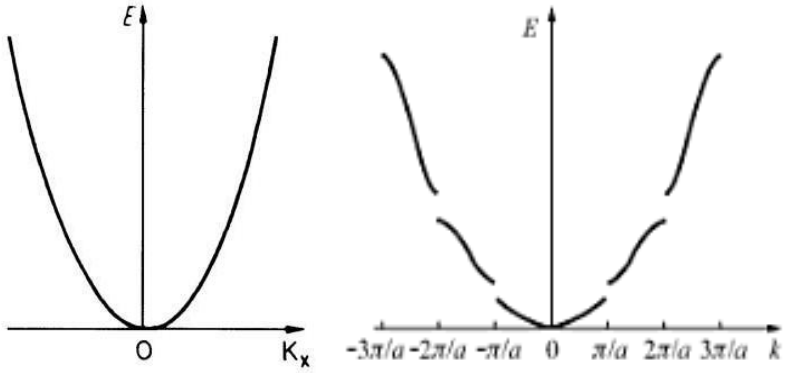

Figure 1.4. Energy gap and general band structure at free electron.

Figure 1.4 demonstrates (Left) the general band structure and (Right) the energy gap at free electron over a range of k points. We predict that the density of state lies within this range and outside it will be zero.

1.3. Density of state (DOS)

Density of state (DOS) is one of the physical quantities that is of great interest in Condensed Matter Physics [2, 5], that is described by analytical and numerical methods.

Using differential equations (1.4) with (k) and (n) respectively, we calculate the analytical Formula for DOS:

$$D(E) = \frac{dn}{dE} = \frac{dn}{dk} \cdot \frac{dk}{dE}$$

$$D(E) = \frac{dn}{dE} = \frac{(N+1)}{\pi} \frac{1}{\sqrt{4\gamma^2 - (\varepsilon_o - E)^2}} \qquad (1.5)$$

Where *dn* is the number of eigen values in an interval of k , *D(E)* is the density of state which is defined that the number of eigen values per unit energy, this is only correct if the energy lies within the energy band :

$$\varepsilon_o - 2\gamma < E < \varepsilon_o + 2\gamma$$

But when the energy lies outside these ranges then the energy band will be zero and then the DOS will be zero as well.

The density of state is proportional to the number of atoms, and also it is always going to proportional to $\frac{dk}{dE}$

$$D(E) = \frac{1}{\frac{dE}{dk}} \tag{1.6}$$

In Figure 1.2, the slope is $\frac{dE}{dk} = 0$, that means DOS goes to the infinite in the edges for energy band of crystals which are $E_{max} = \varepsilon_o + 2\gamma$ and $E_{min} = \varepsilon_o - 2\gamma$ this is called singularity DOS or Van Hove singularity-DOS, which is often referred to as critical points of the Brillouin zone [5]. As shown in Figure 1.5.

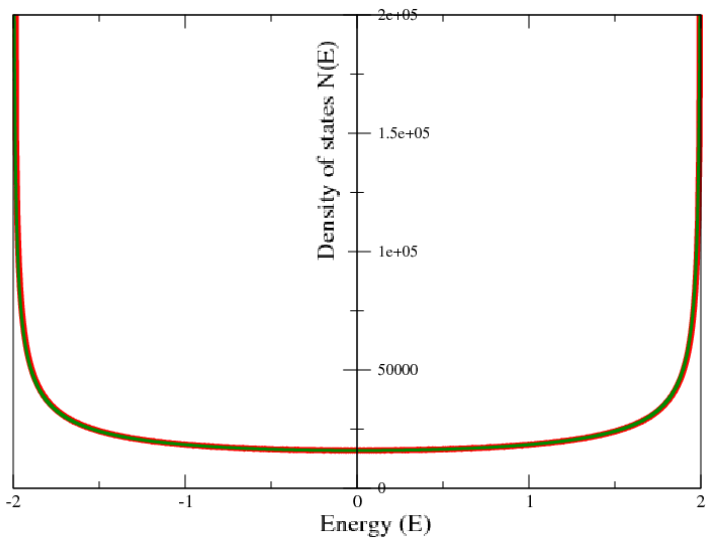

Figure 1.5. demonstrates the Van Hove singularity density of state (VH-DOS).

The density of state per atom is given by:

$$D(E)^{\wedge} = \left(\frac{N+1}{N}\right)\frac{1}{\pi}\frac{1}{\sqrt{4\gamma^2 - (\varepsilon_o - E)^2}} \qquad (1.7)$$

A Histogram and decimation are introduced as numerical methods to calculate the DOS numerically.

To create a Histogram of the eigen values as shown in Figure 1.6. it is important to know that these eigen values should put into box and the width of box is called ΔE , where $\Delta E = \frac{E_{max} - E_{min}}{N}$, then the DOS can be computed by:

$$D(E) = \frac{N(E)}{\Delta E} \qquad (1.8)$$

where $N(E)$ is the number of eigen values or sometime called integrated density of state, and by making ΔE small enough then we get a series delta function (δ) which is called the level spacing between E_{min} and E_{max} in this case the DOS can be described by:

$$D(E) = \sum_{n=1}^{N} \delta(E - E_n) \qquad (1.9)$$

and the level spacing is

$$\delta = \frac{E_{max} - Emin}{N} \tag{1.10}$$

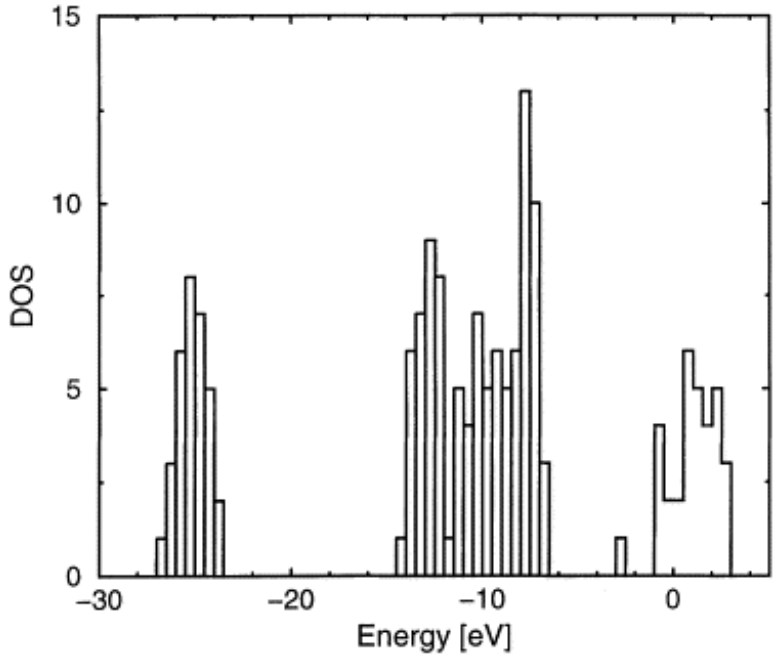

Figure 1.6. illustrates a histogram for DOS as a function of energy.

1.4. Decimation Method

A numerical decimation method is a powerful technique for the understanding of the electronic properties such as density of state and transport [3].

We deal with a large Hamiltonian to calculating the electronic properties like density of state DOS and transport TR.

$$H_{ij}^{\sim} = H_{ij} + \frac{H_{iN}H_{Nj}}{E - H_{NN}} \tag{1.11}$$

This is the general formula to decimate the finite system for N atoms, when $H_{ij}^{\sim}$ is a new Hamiltonian. It is important to know that the properties of lattice is preserved when we make a mathematical transformation.

Chapter 2

Results and discussion

FORTRAN_95 programs have written in this study to compute many electrical properties for our molecular model that is the one-dimensional crystal chain. The calculated properties are the band structure, integrated density of state N(E) and density of states (DOS). These calculations show how to create the Hamiltonian for simple or large system in nature and find the eigenvalues and eigenvectors when we demonstrate the one-dimensional infinite system and solving the Schrodinger equation in small-unit cell to calculate the band structure with periodic boundary condition. In this work, we will show that the tight-binding approximation get qualitative understanding of electronic structure calculations in

periodic structure. The results summarized in the following points:

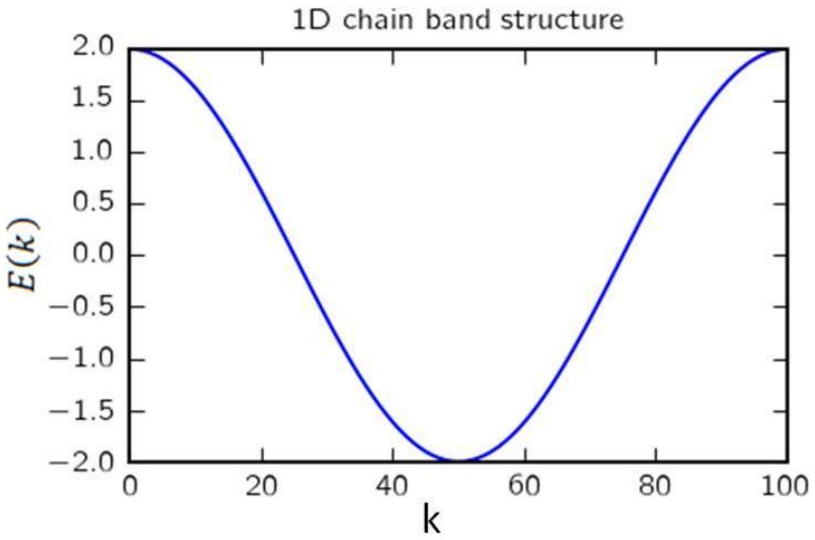

Figure 1.2. shows the calculation of band structure for single atom in unit cell for one-dimensional periodic chain over a range of k-points.

By evaluating the equation 1.4 in the FORTARN program, we calculated the band structure for single atom in the unit cell for one-dimensional periodic chain over a range of k-points. The calculation shows that the band structure (blue curve) lies between $k = \cos^{-1}\frac{E-\varepsilon_0}{2\gamma} = 0$ and $k = \cos^{-1}\frac{E-\varepsilon_0}{2\gamma} = 100$, as shown in Figure 1.2.

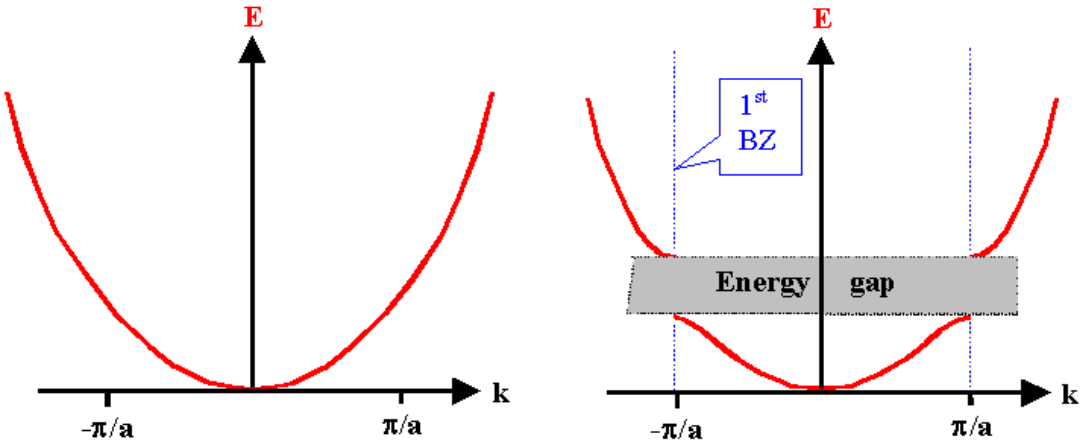

Figure 2.2. shows (Left) general band structure and (Right) energy gap at free electron, where **a** represents the lattice vector.

2.1. Calculation of integrated density of state N(E)

Using FORTRAN code, we calculated the number of eigenvalues less than E for small and large number of atoms. Figure 3.2 shows the plot of step function at small number of atoms (N=5), whereas Figure 4.2 shows plots at N=10. The calculations exhibit that there is stairs line when the system contains small number of atoms. Figure 5.2 shows the smooth plot at large number of atoms.

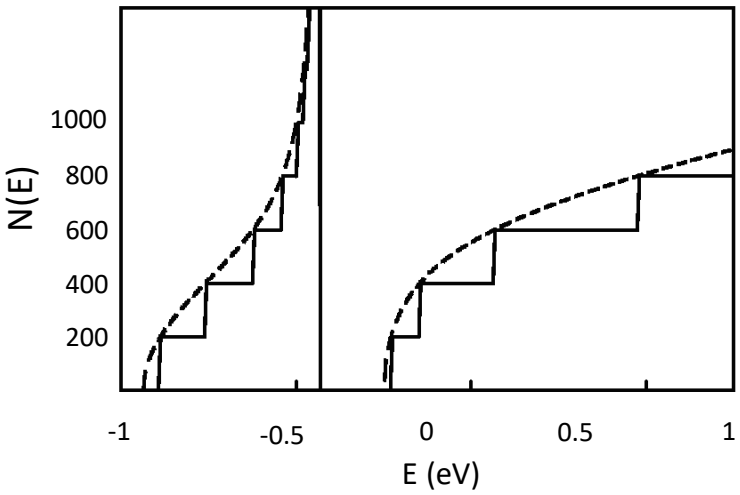

Figure 3.2. The calculation of integrated density of state N(E) versus E , by using the Decimation method (Fortran), N=5.

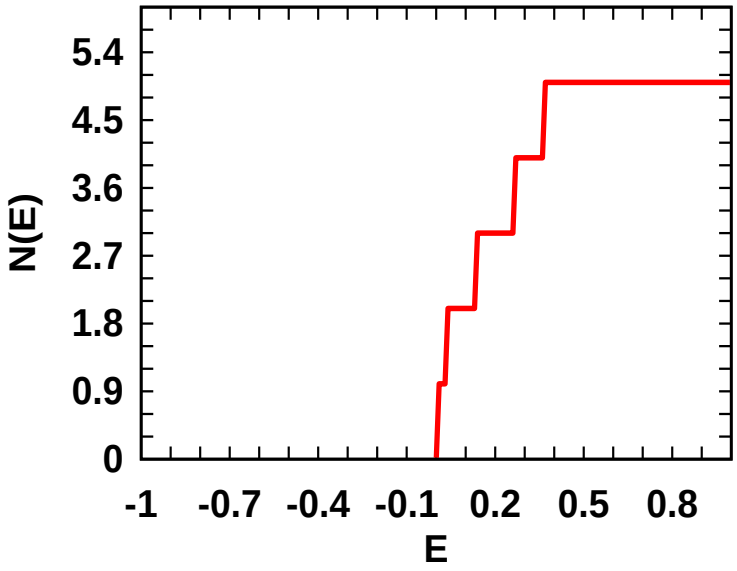

Figure 4.2. the calculation of integrated density of state N(E) versus E , by using the Decimation method (Fortran), N=10.

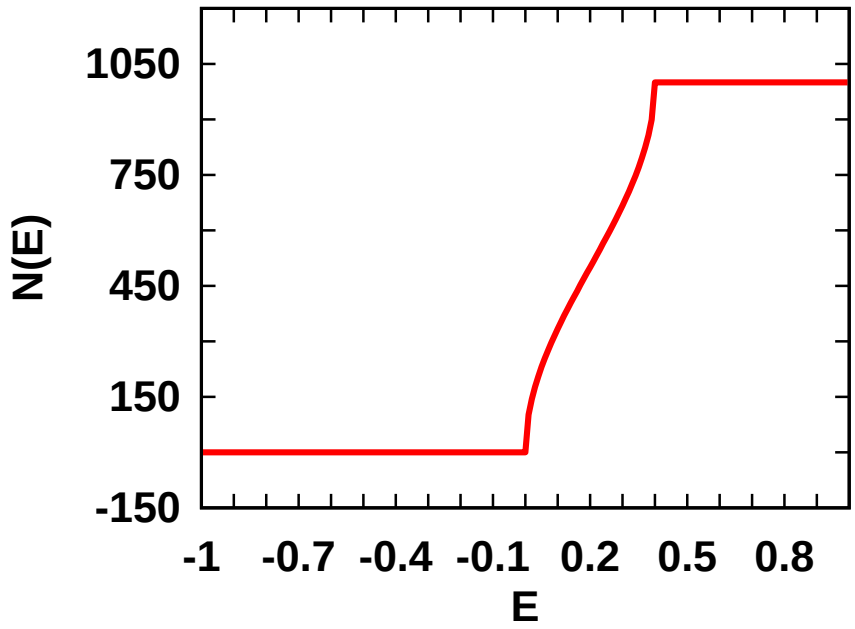

Figure 5.2. The calculation of integrated density of state N(E) versus E , by using the Decimation method (Fortran), N=500.

Using FRTRAN program, we calculated the density (DOS) of states over a range of energies. The calculation shows (blue curve) Van Hove singularity of DOS appeared when the edges of band structure $E_{max} = \varepsilon_o + 2\gamma = +2$ and $E_{min} = \varepsilon_o - 2\gamma = -2$, as shown in Figure 6.2.

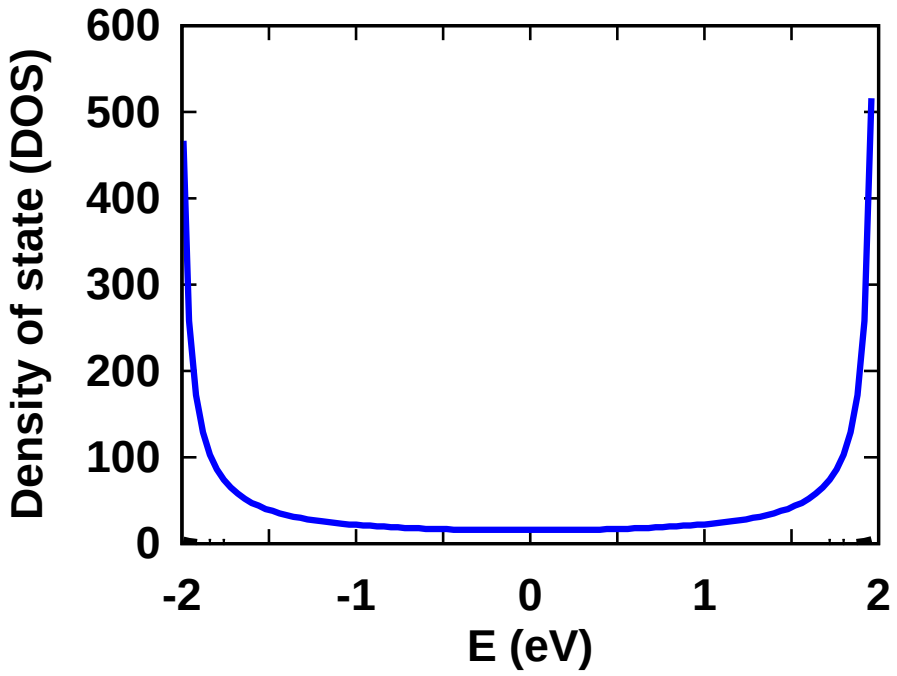

Figure 6.2. Analytical density of state (DOS), the plot shows Van Hove singularity of DOS appeared when the edges of band structure $E_{max} = \varepsilon_o + 2\gamma = +2$ and $E_{min} = \varepsilon_o - 2\gamma = -2$.

Chapter 3

An example of the realistic nanostructure materials

We present a brief review for an example of the realistic nanostructure materials, which recently have studied. These examples show the nature of crystalline in the materials and their physical properties.

Developing the performance of materials currently consider challenge for scientists [6,8,9,10]. Therefore, there are great efforts to study the electronic properties such as band structure and density of state (DOS)

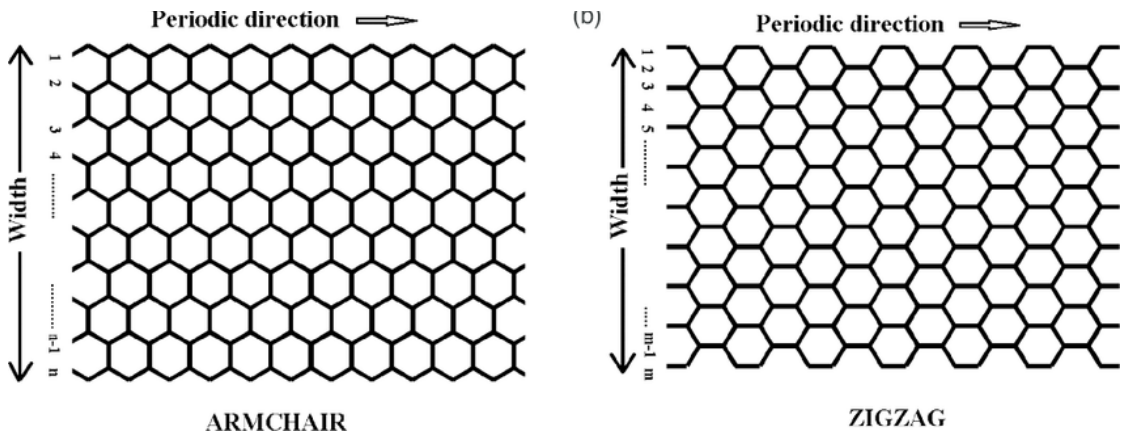

Figure 1.3. Crystal structure of graphene. The structures show the hexagonal lattice in two periodic directions: Zigzag and Armchair. The both states give us different behaviour of properties.

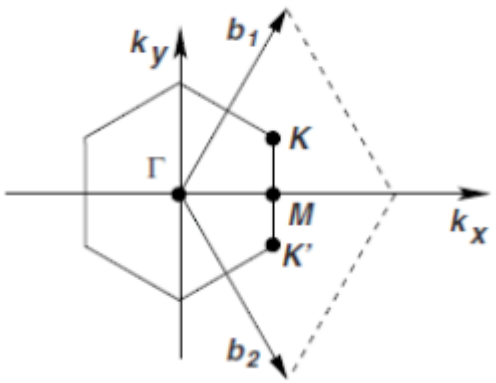

Figure 2.3. The Brillouin zone of graphene.

The graphene band structure has higher energy band (conduction band) and lower energy band (valence band). These two bands

intersect each other at Dirac points in the Brillouin zone contributing to the zero gap. The band structure of charge carriers in graphene is displayed in Figure 4. For graphene, the valence band is completely filled [4] that means the Fermi level of charge carriers in graphene is near the intersection of valence and conduction bands. Therefore, the electronic properties of graphene are determined by the energy band near the Dirac point or at low energy. At low energy, charge carriers in graphene are described by the Hamiltonian and eigen energy [5] where m/s is the Fermi velocity and are the Pauli matrices. This evidently indicates that charge carriers in graphene mimic the behaviors of massless relativistic particles described by Dirac equation. The E_k relation of charge carriers in graphene exhibits linear relation which differs from those in conventional metals and semiconductors where the energy spectrum are approximately parabolic relation [5].

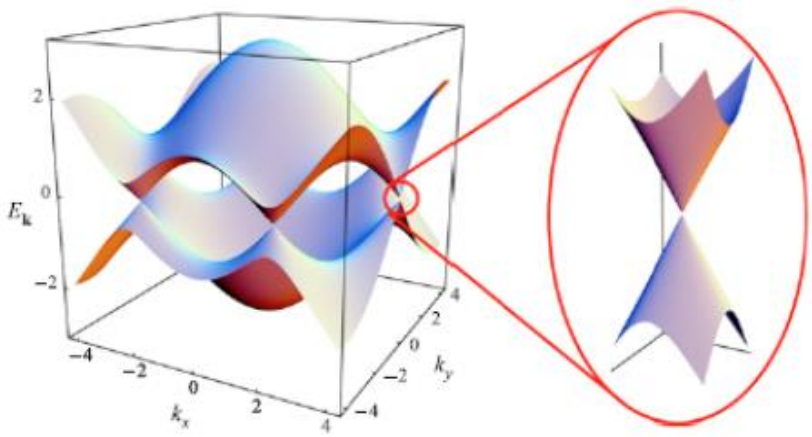

Figure 3.3. The band structure in graphene the energy bands close to a Dirac point [4].

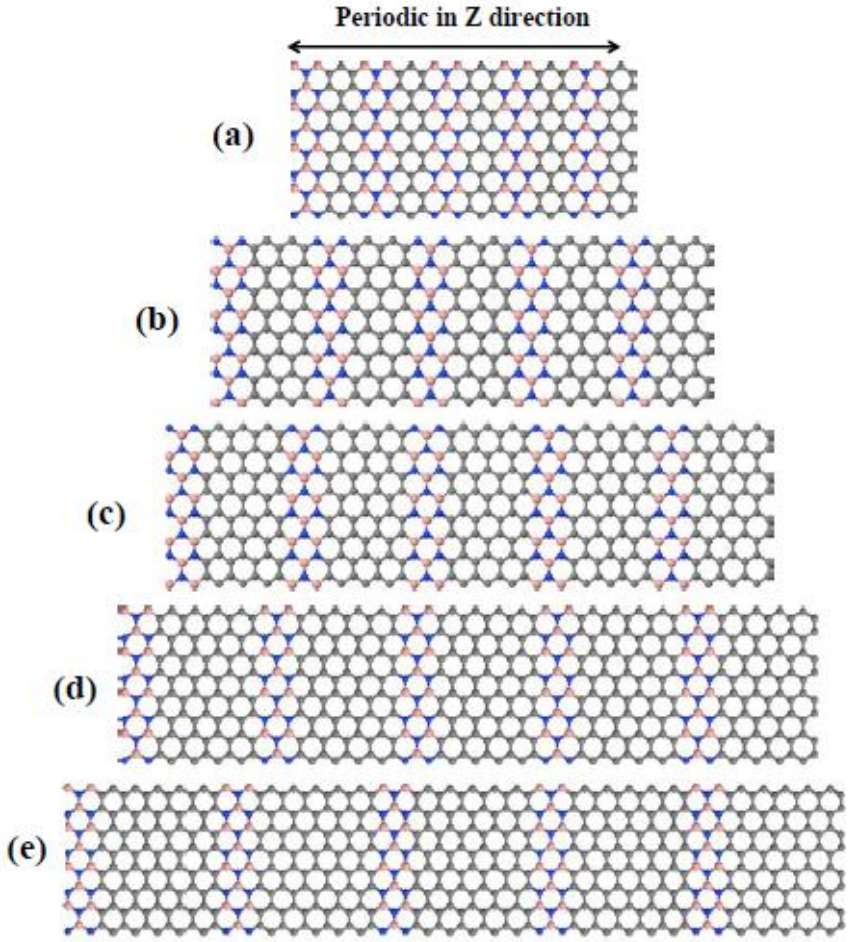

Figure 4.3. Different strips of relaxed structures for graphene/boron nitride hetero-ribbon [6]

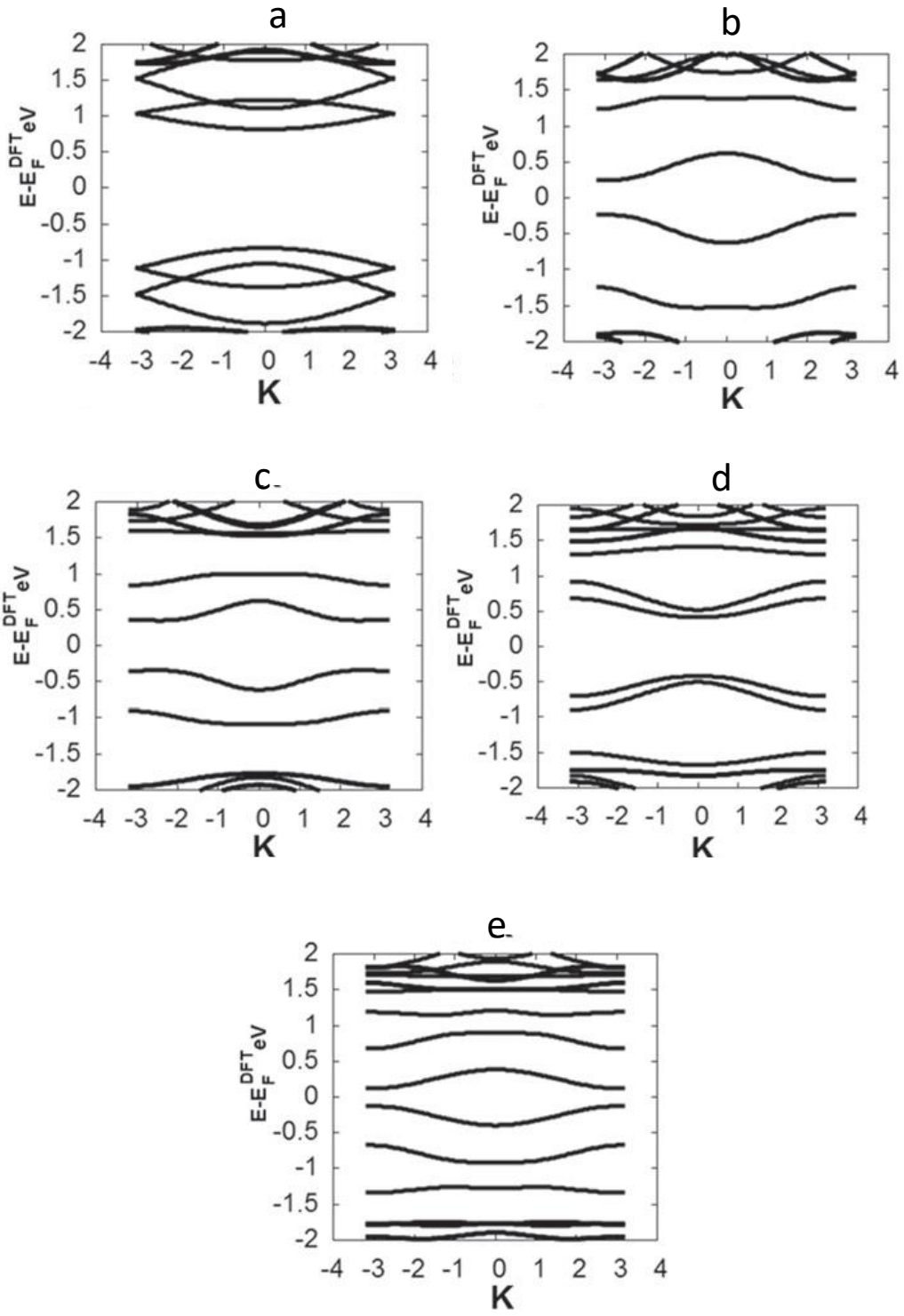

Figure 5.3. Band structures for all structures of length l = 1 (top) to l = 5 (bottom) hexagons. E_F^{DFT} is the DFT predicted value of the Fermi energy.[6]

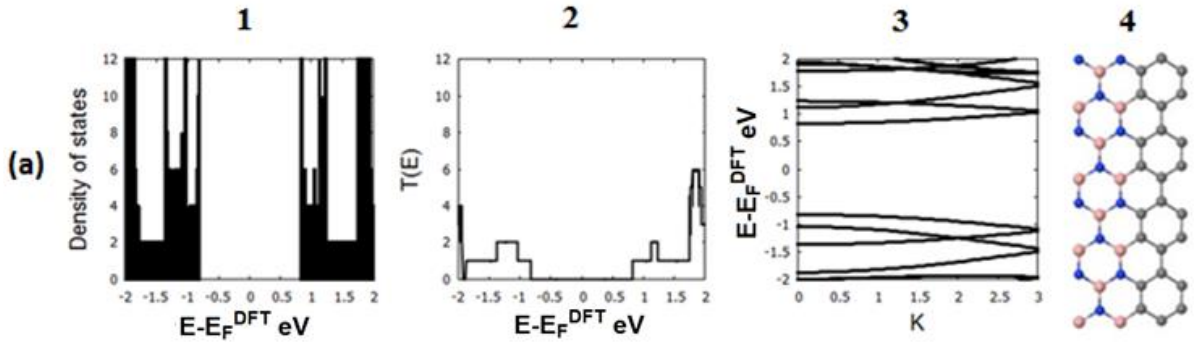

Figure 6.3. The density of states, number of open channels and band structures for, (a) the un-doped 1BN-1G, (b) the doped 1BN-1G by electron acceptor-TCNE, and (c) the doped 1BN-1G by electron donor-TTF.[6]

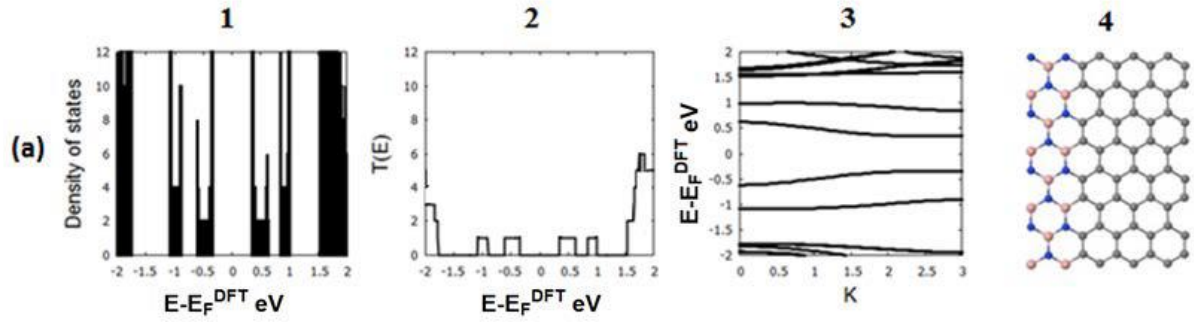

Figure 7.3. The density of states, number of open channels and band structures for, (a) the un-doped 1BN-3G, (b) the doped 1BN-3G by electron acceptor-TCNE, and (c) the doped 1BN-3G by electron donor-TTF.[6]

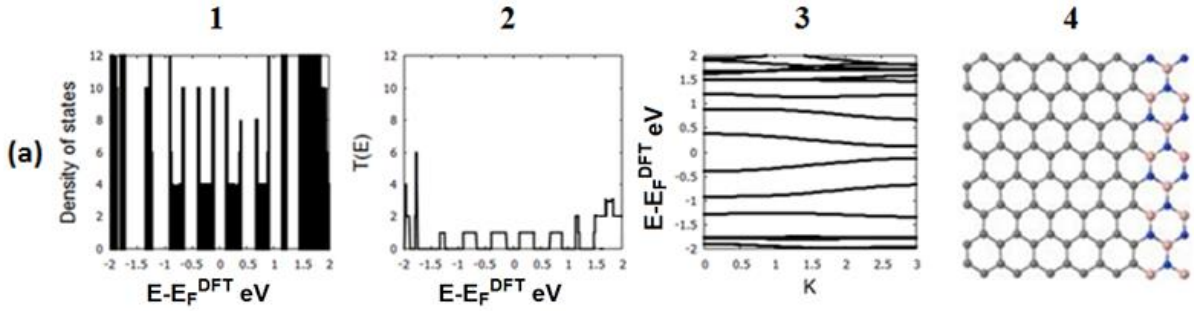

Figure 8.3. The density of states, number of open channels and band structures for, (a) the un-doped 1BN-5G, (b) the doped 1BN-5G by electron acceptor-TCNE, and (c) the doped 1BN-5G by electron donor-TTF.[6]

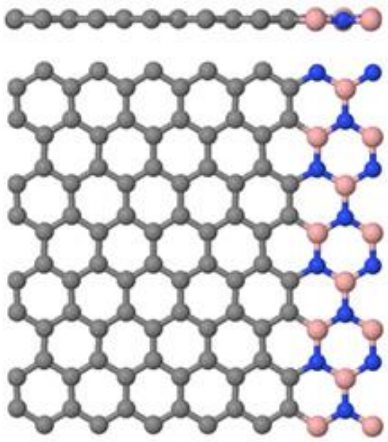

Figure 9.3. Optimized structure-(1BN-5G) for graphene-boron nitride: (A) without doping, (B) doped by electron acceptor-TCNE, and (C) doped by electron donor-TTF.[6]

Conclusions

We investigated the important properties of electron propagation in one-dimensional crystal chain. The FORTRAN program have used to calculate the simple band structure, integrated density of state N(E) and Density of state, and to investigate also the electron propagation in this model. We found that there was one line for the band structure attribute for one atom in the unit cell. In the N(E) calculation, the stairs line appeared when the system contains small number of atoms, whereas the line will be smooth at large number of atoms. These shows that the intensity of atoms in material play important role enhance the DOS. At the edges of band structure, the density of state goes to infinite and the DOS appeared with VAN-HOV singularity.

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