Innovative: International Multi-disciplinary Journal of Applied Technology
(ISSN 2995-486X) VOLUME 02 ISSUE 05, 2024

Quantum Theory and Basic Concepts for Electronic Properties in Molecular Structure

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Abstract:

Using a one-dimensional tight-binding model, we show the key characteristics of electron propagation in molecular modelling, including band structure, integrated density of state N(E), and density of state (DOS). These characteristics have been computed and the electron propagation on the one-dimensional crystal chain has been studied using the FORTRAN programme. We computed the DOS, the number of eigenvalues smaller than E for both small and high numbers of atoms, and the general band structure. We discovered that the band structure attribute for a single atom in the unit cell was on line. When there are few atoms in the system, the N(E) computation shows a stair-line; when there are many atoms, the line is smooth. These demonstrate how the atoms' intensity within a material has a significant influence in enhancing DOS. The density of state approaches infinity near the band structure's boundaries, and the DOS manifests as a VAN-HOV singularity.

Introduction

Studies pertaining to the electronic structure of materials and the necessity of electronic device miniaturisation have received a great deal more attention in recent years. [1] The subject of nanoscience, which seeks to create usable objects at the atomic size and establish control, has emerged as a result of years of atom-focused research. [1-3] Applications for altering these systems' electrical characteristics include the creation of molecular switches and the quantum interference effect transistor (QuLET). [1-2] as well as [4] In order to examine the most crucial aspects of electron propagation, including energy bands and density of states, we present a few molecular system models in this chapter.

Electrical properties of molecular structure

Using a numerical decimation, we explore the density of state for the ordered system and the band structure for periodic structures using the tight binding concept. Examining a crystal's band structure can help you gain an understanding of its electrical characteristics. Here, Figure 1.1 depicts a very basic one-dimensional crystalline system, while Figure 1.2 shows the band structure. One of the electrical characteristics of these band structures that we attempt to comprehend in order to understand the transport mechanism in the materials is density of states. [5]

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].

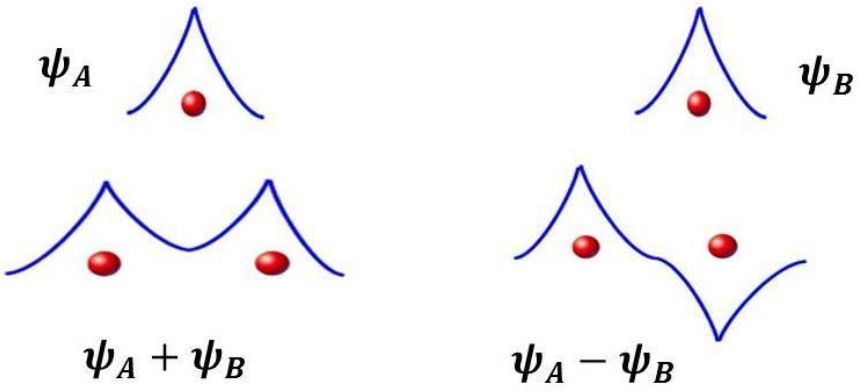

Figure 1.1 shows simply the tight-bind model and how the wave functions of atoms will interact as we consider the nearest neighbour atoms.

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.

We employ the tight binding model (TBM), also known as the tight binding approximation, in our work. According to TBM, we just need to take into account the electrons that are closest to us because they are sufficiently securely bonded together in a solid. When the wave functions at each particular atomic site decay to zero before they reach the second nearest neighbour, this will be true in many physical issues. We also know that in our one-dimensional model, there are no other directions in which interaction may occur and that the nearest neighbours will prevent the wave function from spreading. Figure 1.2 depicts the tight binding Hamiltonian for a chain, which solely includes the interaction with the nearest neighbour. Tight binding theory has been used to explain the behaviour of insulators and semiconductors; this model is inadequate for metals, as the electrons have high mobility, hence these assumptions are false. [6]

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.

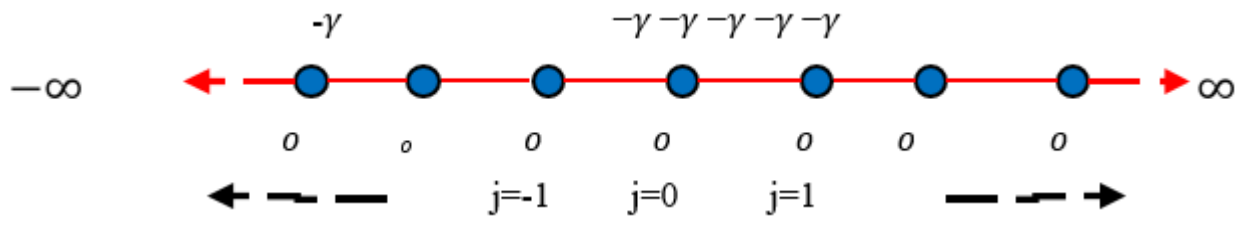

Figure 1: one dimension (1-D) linear crystalline chain [7]

In this system, $_o$ and γ are the site and hopping energies respectively. According to the time independent Schrodinger equation: The most general formula for infinite chain has given by:

$o\psi_j - \gamma\psi_{j-1} - \gamma\psi_{j+1} = E\psi_j$ (1.1)

The equation (1.2) is satisfied for all j go to $\pm\infty$, and we can write (1.3) as :

$\psi_{j+1} = (\varepsilon\_\_\_\_^{o}\gamma^{-E})\ \psi_j - \psi_{j-1}$ (1.2)

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:

$E(k) = _o - 2\gamma cosk$ (1.3)

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 2

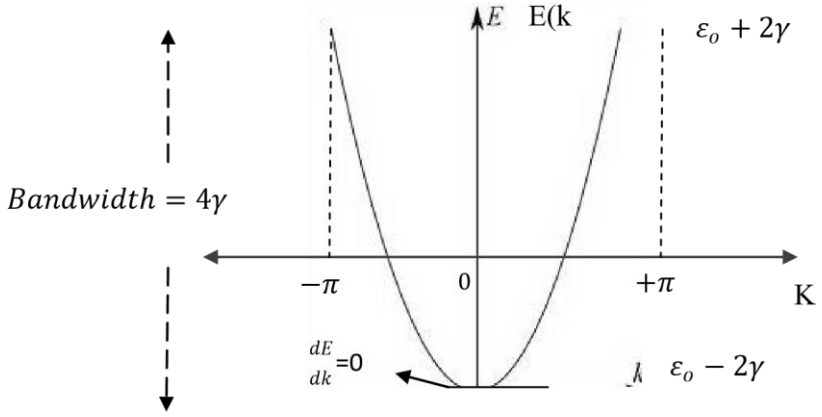

Figure 2: illustrates a simple band structure for (1-D) linear chain.

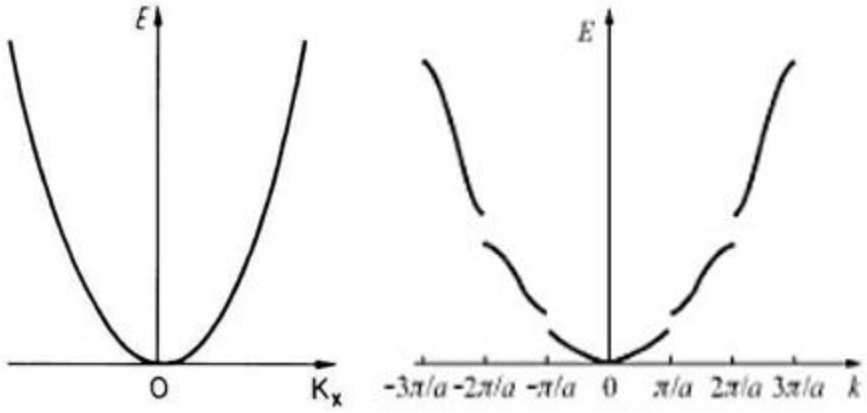

Figure 3. Energy gap and general band structure at free electron.

(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:

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

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

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 :

$o - 2\gamma < E <\ _o + 2\gamma$

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

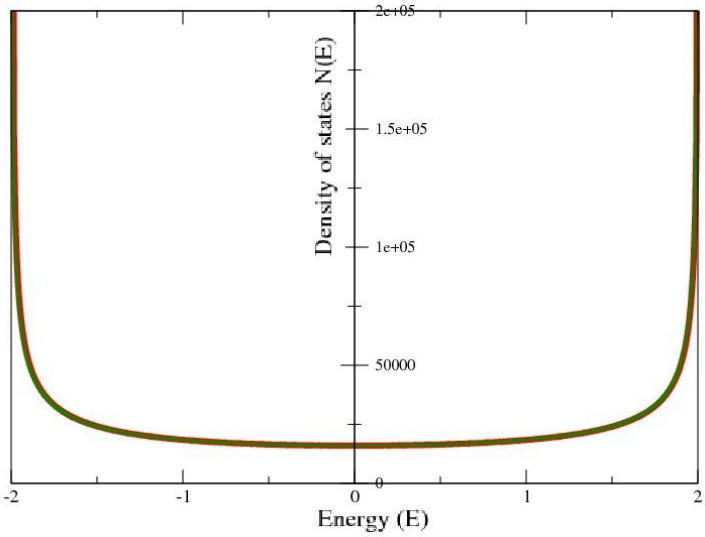

Figure 4. demonstrates the Van Hove singularity density of state (VH-DOS).

The density of state per atom is given by:

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

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 4. it is important to know that these eigen values should put into box and the width of box is called ΔE , where $\Delta E = {}^{Emax - Emin}$, then

N

the DOS can be computed by:

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

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:

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

and the level spacing is

$$\delta = \frac{E_{max} - Emin}{N} \quad (1.10)$$

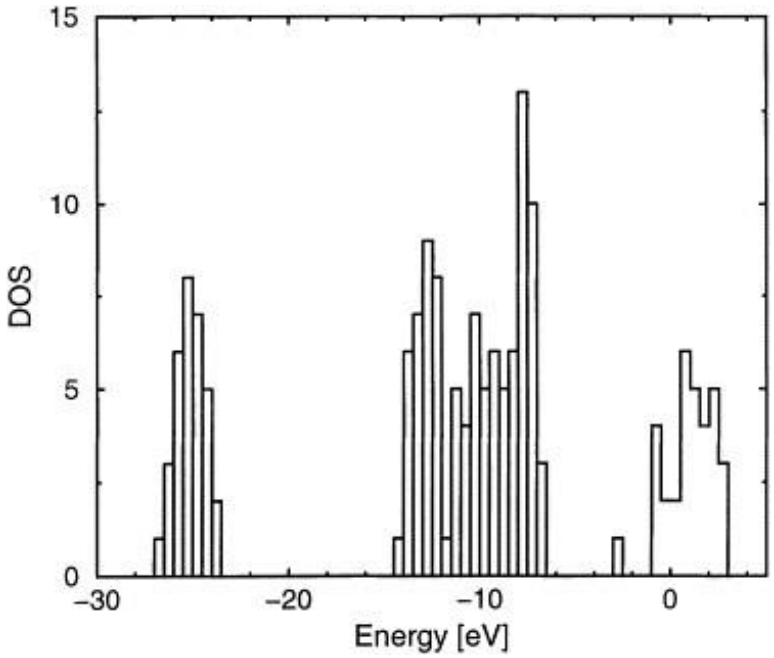

Figure 5. illustrates a histogram for DOS as a function of energy.

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.

$$\tilde{H} \qquad {}^{iN}H^{Nj}$$

$$H_{ij} = H_{ij} + E\frac{}{} - H_{NN} \quad (1.11)$$

This is the general formula to decimate the finite system for N atoms, when H_{ij}~ is a new Hamiltonian. It is important to know that the properties of lattice is preserved when we make a mathematical transformation[8].

Results and discussion

In this work, FORTRAN 95 programmes have been built to compute a variety of electrical properties for our one-dimensional crystal chain molecular model. The band structure, density of

states (DOS), and integrated density of state (N(E) are the computed properties. These computations illustrate how to solve the Schrodinger equation in a small-unit cell to compute the band structure with periodic boundary condition, as well as how to construct the Hamiltonian for large or simple systems in nature and determine the eigenvalues and eigenvectors. In this study, we will demonstrate how the tight-binding approximation provides a qualitative comprehension of periodic structure electronic structure computations.[10–9] The following points provide a summary of the findings:

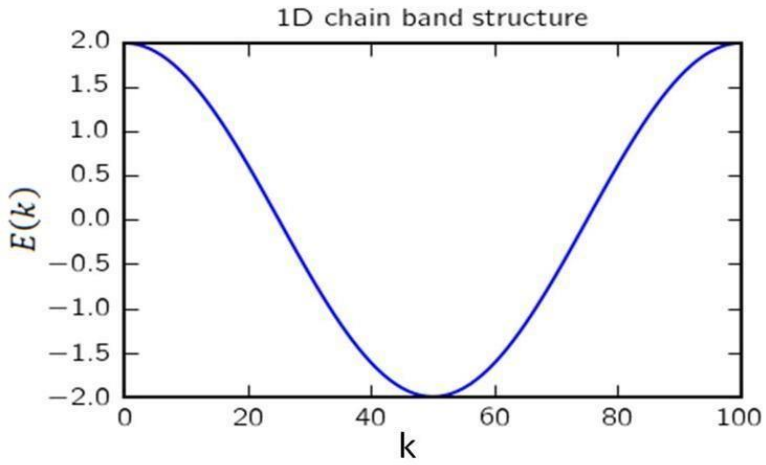

Figure 6. shows the calculation of band structure for single atom in unit cell for one-dimensional periodic chain over a range of k-points.

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 $k = \cos^{-1} \frac{E}{2\gamma} - \varepsilon 0 = 0$ and $k = \cos^{-1} \frac{E}{2\gamma} - \varepsilon 0 = 100$, as

shown in Figure 6.

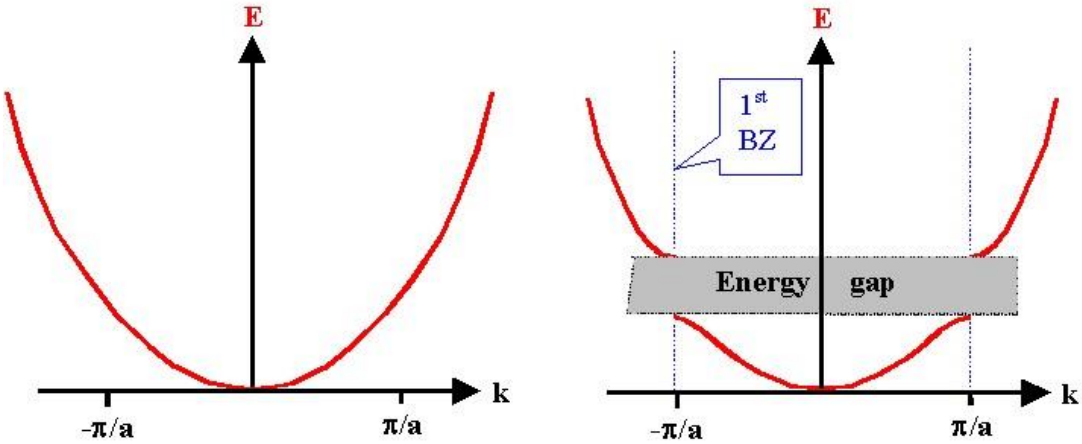

Figure 7. shows (Left) general band structure and (Right) energy gap at free electron, where a represents the lattice vector.

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.

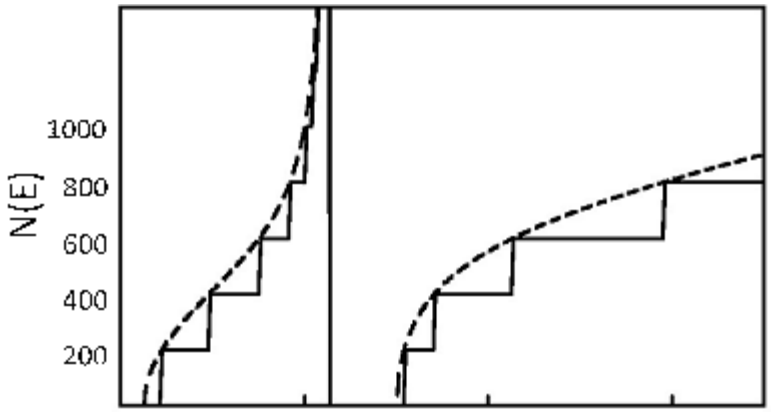

Figure 8. The calculation of integrated density of state N(E) versus E , by using the Decimation method (Fortran), N=5.

Figure 9. the calculation of integrated density of state N(E) versus E , by using the Decimation method (Fortran), N=10.

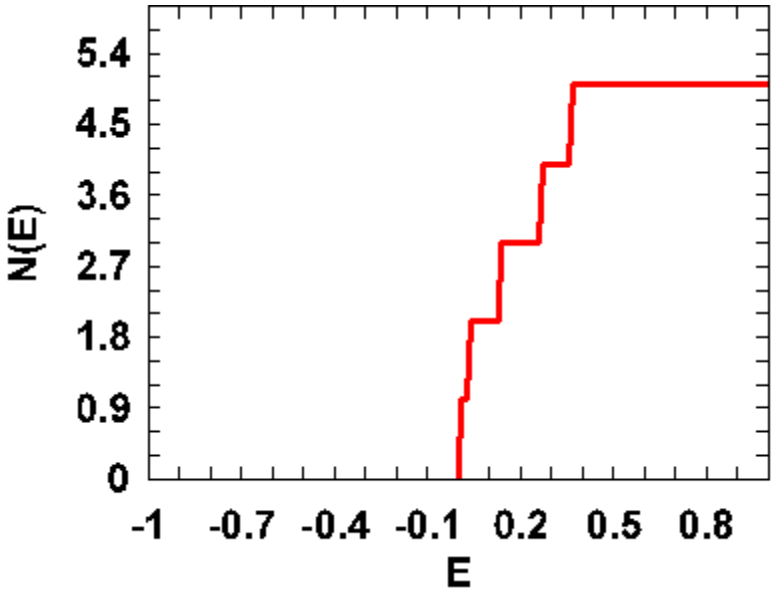

Figure 10. The calculation of integrated density of state N(E) versus E , by using the Decimation method (Fortran), N=500.

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 $E_{max} = {}_o + 2\gamma = +2$ and $E_{min} = {}_o - 2\gamma = -2$, as shown in Figure 6.2.

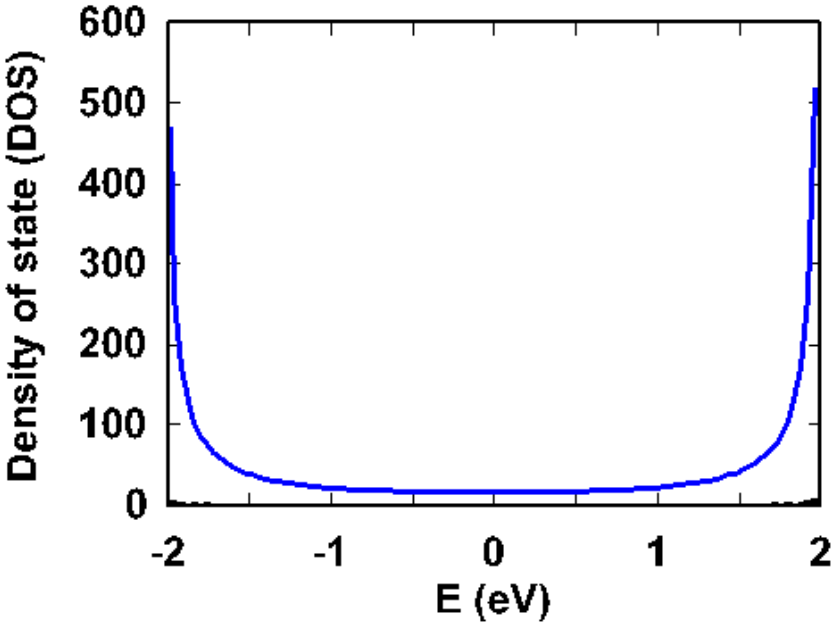

Figure 11. Analytical density of state (DOS), the plot shows Van Hove singularity of DOS appeared when the edges of band structure $E_{max} = {}_o + 2\gamma = +2$ and $E_{min} = {}_o - 2\gamma = -2$.

Conclusion

We studied the crucial characteristics of electron propagation in a chain of one-dimensional crystals. The integrated density of state N(E), density of state, and basic band structure were all computed using the FORTRAN programme, which was also utilised to look at the electron propagation in this model. We discovered that each atom in the unit cell has a single line representing its band structure property. When there are few atoms in the system, the N(E) computation shows a stair-line; when there are many atoms, the line is smooth. These demonstrate how the atoms' intensity within a material has a significant influence in enhancing DOS. The density of state approaches infinity near the band structure's boundaries, and the DOS manifests as a VAN-HOV singularity.

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