Electronic structure of 2D-gallium arsenide as studied using First principles density functional theory (DFT)

By

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Table of Contents

List of Tables

List of Figures

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Abbreviations

LCAO :linear combinations of atomic orbitals
GVB : generalized valence bond
CI : configuration interaction
HF : Hartree-Fock
BO : Born Oppenheimer
CP : Car-Parrinello
DFT : Density Functional Theory
DFPT : Density Functional Perturbation Theory
CPMD : Car-Parrinello Molecular Dynamics
DOS : Density of State
PDOS : Partial Density of State
FPMD : First Principle Molecular Dynamics
GGA : Generalized Gradient Approximation
HEG : Homogeneous Electron Gas
HK : Hohenberg-Kohn
KS : Kohn-Sham
LDA : Local Density Approximation
NSCF : Non Self Consistent Field
PBE : Perdew, Burke and Ernzerhof
PW : Plane Wave
PP : Pseudo Potential
QE : Quantum Espresso
MBE : Molecular Beam Epitaxy
XC : EXchange Correlation

Abstract

In this thesis we have calculated electronic structure of 2D-GaAs within the first principles using Quantum ESPRESSO pacakage. We optimized lattice constant and identified the nature and values of band gap of Zinc Blende structure gallium aresnide (GaAs). Norm-conserving pseudopotential is used for the self-consistent calculation, and the Generalized Gradient Approximation (GGA) for the exchange correlation. An optimum lattice constant of 7.4Å, 6.1Å, and 5.7Å, respectively, is obtained for 1D, 2D, and 3D, and in close agreement with the experimental value 5.65Å. 2-D GaAs is known to have a gap of 1.8 eV which is in close agreement with previous observations [45], but has 25.9 % error to the experimental value 1.43 eV [42]. This work clearly explains that lattice constant increases with decrease in crystal size. Moreover, we could identify the charge transfer between the Ga and As atoms. Generally we could make calculations and compare with its 1-D and 3-D structures results.

CHAPTER 1

Literature reviews of semiconductors and the system of interest

1.1 Semiconductors Theory

Semiconductors are materials whose electronic properties are intermediate between those of metals and insulators. The conductivity of a semiconductor material can be varied under an external electric field. Devises made from semiconductor materials are the foundation of modern electronics, including computer, radio, telephones and many other. In a metallic conductor, current is carried by the flow of electrons. In semiconductors, current can be carried by either flow of electrons or flow of holes or both. Germanium and Silicon are the best examples for semiconductor materials. Both are tetravalent (i.e. four valence electrons) and both have diamond crystal structure. At T=0K, the semiconductor acts as insulator.

The electronic and optical properties of crystals are determined by the chemical properties of the different atomic constituents, the crystal structure (i.e., the relative positions of the different atoms), and the distance over which a basic unit of the crystal structure is repeated. The property of semiconductors which is most useful for making electronic devices is that their conductivity may easily be modified by introducing impurities into their crystal lattice [1].

In classic crystalline semiconductors, the electrons can have energies only within certain bands (i.e. ranges of levels of energy). Energetically, these bands are located between the energy of the ground state, corresponding to electrons tightly bound to the atomic nuclei of the material, and the free electron energy. The latter is the energy required for an electron to escape entirely from the material [2]. Each energy band corresponds to a large number of discrete quantum states of the electrons. The interactions between different atoms in the crystal result in grouping these states into bands of allowed energies, with successive bands being separated from each other by forbidden energy gaps [3]. Most of the states with low energy (closer to the nucleus) are full, up to a particular band called the valence band. Semiconductors and insulators are distinguished from metals because the valence band in the semiconductor materials is nearly filled under usual operating conditions, thus causing more electrons to be available in the conduction band, the band immediately above the valence band, as shown in Fig.1.1.

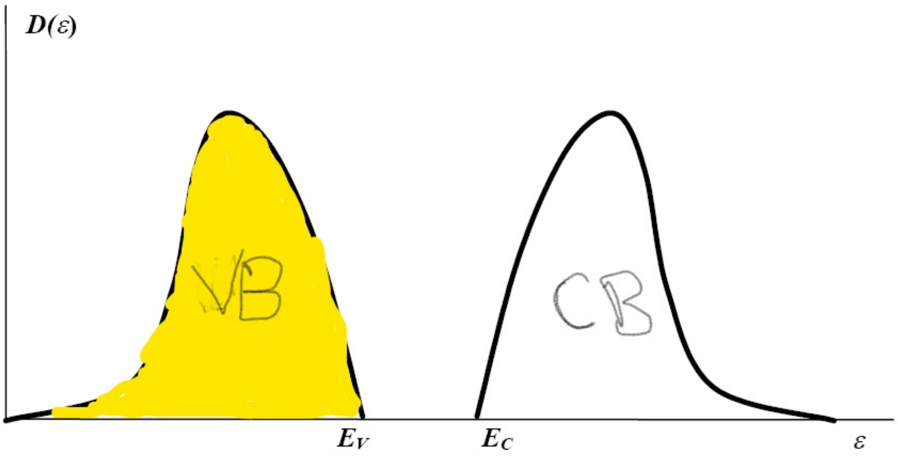


Figure 1.1: The plot of energy gap between conduction and valance band of GaA [4]

The ease with which electrons in a semiconductor can be excited from the valence band to the conduction band depends on the bandgap between the bands. The size of the energy bandgap serves as an arbitrary dividing line (roughly 4 eV) between semiconductors and insulators [5].

1.1.1 Elemental semiconductor

Semiconductors may be broadly divided into two distinct groups, namely elemental or compound semiconductors [6]. As the name suggests, elemental semiconductors are formed from single chemical elements, and important members of this family include Si and Ge. The crystal structure of Si and Ge is the same as that of diamond and α-tin (a zero gap semiconductor also known as *grey* tin). In this structure each atom is surrounded by four nearest neighbour atoms (each atom is said to be four-fold coordinated), forming a tetrahedron. These tetrahedral bonded semiconductors form the mainstay of the electronics industry and the cornerstone of modern technology. Some elements from the groups V and VI of the periodical table, such as phosphorus (P), sulfur(S), selenium (Se) and tellurium (Te), are also semiconductors. The atoms in these crystals can be three-fold (P), two-fold (S, Se, Te) or four-fold coordinated (lead sulphide (PbS). Hence these elements exist in different crystal structures and they are also good glass-formers.

1.1.2 Compound semiconductor

Compound semiconductors represent the largest group and are formed as a result of the chemical reaction between two or more different elements. Examples are gallium arsenide (GaAs), indium arsenide (InAs), indium phosphide (InP), and gallium nitride (GaN). Compounds formed from elements of the groups III and V of the periodic table (such as GaAs) have properties similar to their group IV counterparts. In going from the group IV elements to the group III-V compounds, the bonding becomes partly ionic due to transfer of electronic charge from the group III atom to the group V atom.

The compound semiconductors formed by combining group II and group VI elements, such as CdS and ZnO, are called II-VI compounds. The bonding in these compounds is a mixture of covalent and ionic types and the average number of valence electrons per atom remains four. The band gap in this case is even larger than the band gap in III-V compound semiconductors.

The another group of compound semiconductors that has attracted attention in recent times is IV-IV compounds, also known as narrow gap semiconductors. Examples of such compounds are SiC, SiGe etc. The bonding in these compounds is mainly ionic along with some covalent contribution. They crystallise in simple cubic NaCl structure.

1.1.3 Alloy semiconductors

Alloying of two materials is one of the oldest techniques to modify the properties of materials, not only in semiconductors, but also in metals and insulators as well. The desire to form alloys in semiconductors is motivated by two objectives:

1. achieving a desired band gap which essentially determines the energy of the

light emitted and absorbed.

2. creating a material with a proper lattice constant to match or mismatch with an available substrate.

When two semiconductors A and B are mixed by an appropriate growth technique, for the same lattice structure materials, the lattice constant obeys the Vegard's law for the alloy A_xB_{1-x} as

$$a_{alloy} = xa_A + (1-x)a_B \tag{1.1}$$

where $'a'_A$ and $'a'_B$ are the lattice constants of A and B.

by virtual crystal approximation, the band gap [7] is given by

$$E_g^{alloy} = xE_g^A + (1-x)E_g^B \tag{1.2}$$

Ternary semiconductors are formed by the addition of a small quantity of a third element to the mixture, for example the alloy gallium aluminium arsenide $(Al_xGa_{1-x}As)$. The subscript x refers to the alloy content of the material, or the proportion of the material that is replaced by the alloy material. The addition of alloys (i.e., the alloy contents as x, y) to semiconductors can be extended to include quaternary materials such as the alloys gallium indium arsenic phosphide$(Ga_xIn_{1-x}As_yP_{1-y})$ or gallium indium nitrogen arsenide $(GaInNAs)$ and even quinternary materials such as gallium indium nitrogen arsenic antimonide $(GaInNAsSb)$.

Alloying semiconductors in this way allow the energy gap and lattice spacing of the crystal to suit the applications [8]

1.1.4 Direct and Indirect bandgap semiconductors

In semiconductor physics, the bandgap of a semiconductor is either of the two types namely, a direct bandgap or an indirect bandgap as shown in Fig.1.2 [9]. The minimal energy state in the conduction band and the maximal energy state in the valence band are each characterized by a certain k-vector in the Brillouin zone. If the k-vectors are the same, it is called a direct gap. Thus an electron making a smallest energy transition from the conduction band to the valence band, can do it without a change in k value or without a momentum change and gives off the energy change as photon of light.

If the k-values are different, it is called an indirect gap. Then for a transition from the minimum point in the conduction band to the maximum point of the valence band, requires some change in k. Thus an indirect transition involves a momentum change. In these transitions both a phonon and a photon are involved. The energy is generally given up as heat to the lattice rather than an emitted photon.

Direct gap semiconductors have many unique properties which are advantageous for optical and electronic applications, especially for detectors and emitters of infrared radiation associated with interband optical transitions. GaAs based structures have principally been used in the near infrared region, and are called narrow gap semiconductors in the mid-infrared (MIR) spectral regions [10].

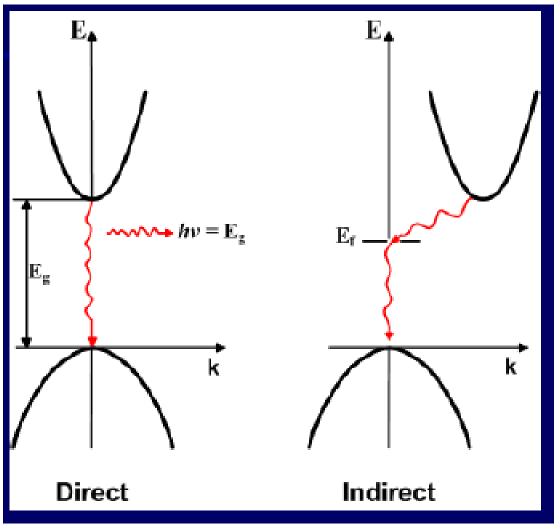


Figure 1.2: Energy level diagram of LHS Direct and RHS Indirect band gab semiconductors.[11]

1.1.5 Intrinsic and Extrinsic semiconductors

An intrinsic semiconductor material is chemically very pure and possesses poor conductivity. It has equal numbers of negative carriers (electrons) and positive carriers (holes). Semiconductor crystals are different from an insulator because at any temperature above absolute zero, there is a finite probability that an electron in the lattice will be knocked and loose from its position, leaving behind an electron deficiency called a "hole".

This hole can travel from one atom to the adjacent atom by accepting an electron from later one. This process involves formation of new covalent bond and breaking an existing bond by filling up the hole and creating a new hole. In this way, the holes travel from one atom to the adjacent atoms in crystal lattice

If a voltage is applied, then both the electron and the hole can contribute to a small current flow.

Extrinsic semiconductor is an improved intrinsic semiconductor with a small amount of impurities added by a process, known as doping, which alters the electrical properties of the semiconductor and alter its conductivity.

Introducing impurities into the semiconductor materials (doping process) can control their conductivity. This process produces two groups of semiconductors: the negative charge conductor (n-type) and the positive charge conductor (p-type).

Si and Ge both have a crystalline structure called the diamond lattice. That is, each atom has its four nearest neighbours at the corners of a regular tetrahedron with the atom itself being at the centre. In addition to the pure element semiconductors, many alloys and compounds are semiconductors. The advantage of compound semiconductor is that they provide the device engineer with a wide range of energy gaps and mobilities, so that materials are available with properties that meet specific requirements. The band gap of semiconductors range from 0.1 eV to 2.0 eV, and that of GaAs in between 1.52 eV and 1.43 eV at 0 K and 300 K, respectively.

1.2 Literature Review of early studies

1.2.1 Gallium Arsenide

GaAs is also the III-V compound semiconductor composed of the element gallium (Ga) from column III and the element arsenic (As) from column V of the periodic table of the elements. Gallium Arsenide has molecular formula as GaAs which is very dark red in appearance. The molecular mass of GaAs is 144.645 gm/mole having density $5.23 gm/cm^3$ [12]. The coefficient of thermal expansion is 5.8^{-6} /K

[12]. Bulk resistivity can range from $10^{-4}\Omega m$ to about $10^{24}\Omega m$, with the practical range being $10^{-1}\Omega m$ to $10^{-6}\Omega m$ [12]. GaAs was first discovered by Goldschmidt and reported in 1929 [12], but the first reported electronic properties of III-V compounds as semiconductors did not appear until 1952 [13]. Mobility is an important parameter for carrier transport because it describes how strongly the motion of an electron is influenced by an applied electric field.

Although the peak mobility of GaAs in the linear region can be as much as six times greater than that of silicon (Si) at typical field strengths, the advantage of GaAs may be only as much as a factor of two [14].

GaAs has caused wide spread concern as a semiconductor saturable absorber for its advantages of photochemical and good thermal conductivity [15]. GaAs-based devices hold the world record for the highest efficiency single junction solar cells [16]. Such solar cells also have many advantages, like high photoelectric conversion efficiency, fine radiation resistance and good performance at high temperatures [17, 18]. GaAs is used in the manufacture of device such as microwave frequency circuits, laser diodes, optical windows and infrared LEDs [19]. It has been used to produce near-infra red laser diodes since 1962 [20].

1.2.2 Crystalline properties

GaAs is a III-V compound semiconductor composed of the element gallium (Ga) from column III and the element arsenic (As) from column V of the periodic table of the elements. Group III-V compounds crystallize in the zinc-blende structure. The lattice of this compound consists of two interpenetrating, face-centred cubic (fcc) lattices, displaced from one another by one fourth of the cube main diagonal as shown in Fig. 2.3. The zinc blende lattice is not a Bravais lattice because the elementary cell contains two atoms, one located at the origin and the other at $(\frac{a}{4}, \frac{a}{4}, \frac{a}{4})$ where a is the cube side.

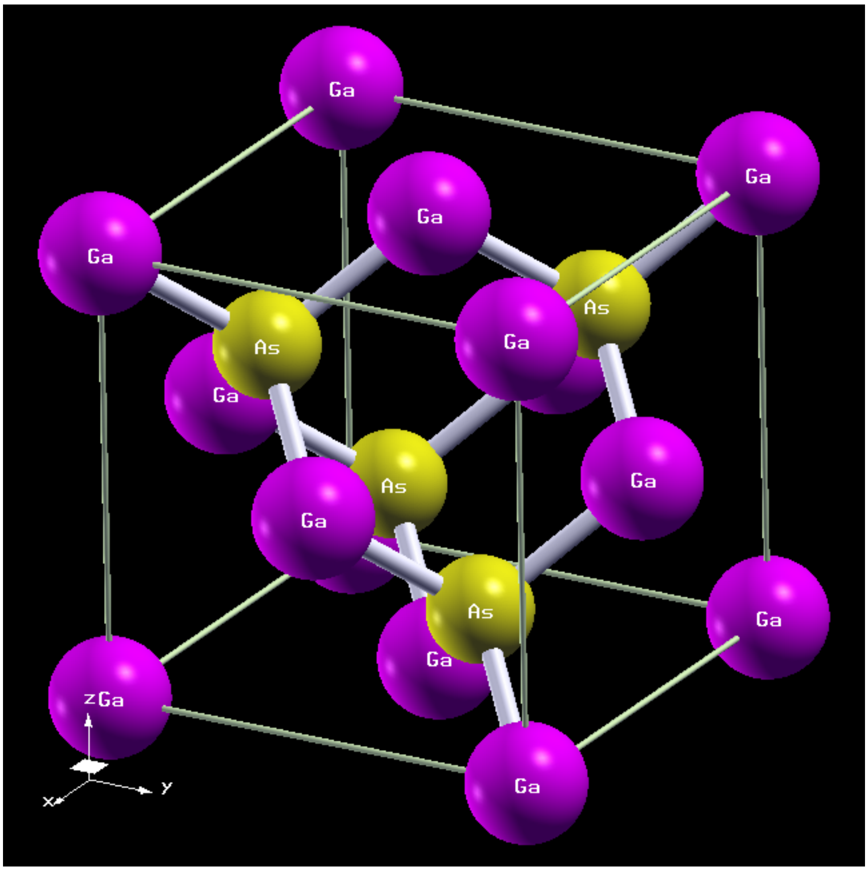


Figure 1.3: Conventional unit cell of GaAs in Zinc Blende structure. The experimental lattice constant is a = 5.65 Å

1.3 Objectives of the Study

1.3.1 General objective

The general objective of this reasearch work is to study electronic structure of 2D-GaAs using density functional theory (DFT).

1.3.2 Specific objective

The clear specfic objectives of the study are as follows:

- To calculate the lattice parameter of 2D-GaAs and corresponding minimum energy; and compaire with that of 1D and 3D structures.
- To calculate and compare the total and partial density of states of 2D-GaAs crystal.
- To analyze the band structure and charge Density in 2D-GaAs.

1.4 Organization of the thesis

The first chapter gives a brief reveiw of properties of semiconductor theory and objectives of the thesis work. The second chapter contains background information on electronic structure calculations. In the third chapter, the Quantum ESPRESSO Package used in this work is introduced in which codes are briefly explained. In the forth chapter data and data analysis is given starting with convergence testes, and finally a brief discussion and conclusion is given in the fifth chapter. References are included at the end of the writing.

CHAPTER 2

Introduction to theoretical background

In order to describe the physical properties of an atomic system, we have to solve Schrodinger wave equation. we can write Schrodinger equation as:

$$\hat{H}\Psi(\vec{r}_i, \vec{R}_A) = E\Psi(\vec{r}_i, \vec{R}_A), \tag{2.1}$$

where $\hat{H}$ is the Hamiltonian operator with the total energy E as Eigenvalue and many wave functions $\Psi(\vec{r}_i, \vec{R}_A)$ as Eigenfunction with $\vec{r}_i$ electron spatial coordinates and $\vec{R}_A$ nuclei spatial coordinates [21]. The Hamiltonian operator with N electrons and M nuclei in atomic unit. ($m_e = \epsilon = \frac{1}{4\pi\epsilon_o} = \hbar = 1$) is given by

$$\begin{aligned} \hat{H} = &-\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 + \frac{1}{2}\sum_{A=1}^{M}\sum_{J=1}^{M}\frac{Z_A Z_J e^2}{|\vec{R}_A - \vec{R}_J|} - \frac{1}{2}\sum_{A=1}^{M}\frac{1}{m_A}\nabla_A^2 \\ &-\sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A e^2}{|\vec{r}_i - \vec{R}_A|} + \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\frac{e^2}{|\vec{r}_i - \vec{r}_j|}. \end{aligned} \tag{2.2}$$

The indices i and j run over N electrons while A and B over the M nuclei.∇^2 is the Laplacian operator acting on particles, m_A is the mass of nuclei A and Z_A is its nucleus charge; r_{ij} is the distance between the particle i and j which is equal to $|\vec{r}_i - \vec{r}_j|$, and the same to r_{iA} is the distance between i^{th} electron and A^{th} nucleus. The first term in equation (2.2) is the operator for the kinetic energy of the electrons; the second term represents mutual repulsion between nuclei; the third term is the operator for kinetic energy of the nuclei; fourth term represents the coulomb attraction between electron and nuclei and the last term represents the mutual repulsion of the electrons. The wave function ψ is a function of (3N + 3M) spatial coordinate for a system containing N electrons and M nuclei. This is very complicated problem that is impossible to be solved exactly. The first step in simplifying this problem is the Born- Oppenheimer Approximation. Since the nuclei are much heavier than electrons, they move more slowly. Hence, a good approximation can be made by considering the electrons in a molecule to be moving in the field of fixed nuclei [22]. As a result, the second term of equation (2.2) can be neglected and the last term can be considered to be a constant which has no effect on the operator eigen functions. We can add a constant term to the eigen value, the remaining terms are called the electronic Hamiltonian.

$$\hat{H} = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 + \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\frac{e^2}{|\vec{r}_i - \vec{r}_j|} - \sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A e^2}{|\vec{r}_i - \vec{R}_A|}. \tag{2.3}$$

The schrodinger equation was simplified with the Born-Oppenheimer approximation. However, the electron-electron interaction still very complicated to be solved exactly for systems with more than a few electrons and further approximation must be introduced. One fundamental approach is the Hartree-Fock (HF) scheme. In HF the principle approximation is called the central field approximation which means the coulomb electron-electron repulsion is not specifically taken into account. Only its net effect is included in the calculation. In HF, each molecular orbital is expanded in terms of a set of basis functions which are normally centered on the atoms in the molecule, as given by LCAO equation. The basis functions collectively are the basis set. As a result of the central field approximation, the energies from HF calculation are always greater than the exact energy and tend to the limiting value called the Hartree-Fock limit.

Post, Hartree-Fock methods which are used by many calculation, begin with a Hartree- Fock calculation and subsequently correct for electron-electron repulsion, refereed to also as electronic correlation. Some of these methods are Miller-Plesset perterperation theory (MPn, where n is the order of correction), the generalized valence bond (GVB) method, Multi-configuration self consistent Field (MCSCF), configuration interaction (CI), other important formalisms which treats the correlation energy is Density Functional Theory (DFT). In this method, energy is expressed as a function of total electron density. DFT is selected as the method of electronic structure in this research. Another method of ab-intio (first principle) is Quantum Monte Carlo (QMC) which avoids making the HF mistakes in the first place. QMC methods work with an explicitly correlated wave function and accurate methods known today. As these methods are pushed to the limit, they approach the exact solution of the non-relativistic Schrodinger wave equation. Relativistic and spin-orbit term should be included to obtain exact agreement with experiment. In conclusion, ab-intio methods aim for high accuracy, by solving the Schrodinger wave equation to a high degree of precision, but this involves a high cost interms of computational effort.

2.1 Hartree and Hartree - Fock methods

The forerunners of modern electronic structure calculations are the approximation. The starting point for the Hartree and Hartree-Fock methods, is the general, non-relativistic Schrodinger wave equation for a system of N elements in the presence of nuclei at fixed positions,

$$-\frac{\hbar^2}{2m}\sum_{i=1}^{N}(\frac{\partial^2\Psi}{\partial x^2}+\frac{\partial^2\Psi}{\partial y^2}+\frac{\partial^2\Psi}{\partial z^2})+V_{ee}\Psi+V_{en}=E\Psi, \tag{2.4}$$

where $\Psi=\Psi(r_1,\zeta_1,r_2,\zeta_2,.........r_n,\zeta_n,R_1,R_2,R_{Nn})$
where V_{en} is the potential energy due to the electron-nuclei interaction and V_{ee} is the coulomb potential energy due to the electron- electron interactions and r_i, and ζ_i are the space and spin coordinates of i^{th} electron and $\vec{R}_j$ is the fixed coordinate of the j^{th} nucleus at absolute zero. E.q (2.5) is the overall wave function, depending on the spatial and spin coordinates of all electrons. Taking the Hamiltonian for the system and applying the variational principle, the total energy of the system is minimized if the wave function is converted to a product form.

$$\Psi=\Psi_1(r_1)\chi(\zeta_1)\psi_2(r_2)\chi(\zeta_2).........\psi_N(r_N)\chi(\zeta_N) \tag{2.5}$$

and the product terms, the individual electron spital wave function, satisfy the following individual electron wave equations.

$$-\frac{\hbar^2}{2m}\nabla^2\psi_i+V_{Hi}(r_i)\psi_i=\varepsilon_i\psi_i, i=1,2,........N \tag{2.6}$$

For all valence electrons, where the potential energy function is given by

$$V_{Hi}(r_i)=-e^2\sum_{\alpha=1^{N\alpha}}\frac{Z\alpha}{|r_{i-R_i}|}+(-e^2)\sum_{j\neq 1}^{N}\frac{|\psi_j(r_1')|^2}{|r_i-r_j|} \tag{2.7}$$

The first term in (2.7) is the potential energy of the electron in the field of nuclei and the second term is the potential energy of the electron in the field of other electrons. This is the so-called Hartree approximation single-electron wave equation [23]. In the Hartree-Fock method, a Slater determinant is used to create anti-symmetric wave function which satisfy the exclusion principle, as well as in corporating spin factors in the wave functions. This again leads to a set of coupled, single-electrons wave equations, but with an additional exchange integrals term present in the potential energy of the electrons, so that the potential energy term $V_H(r_i)$ is the single electron wave equation, and is replaced by

$$V_{HF}(r_i) = V_{Hi}(r_i) + (-e)^2 \sum_{j \neq 1}^{N} \int \frac{\psi_j \psi_i}{|r_i - r_j^{'}|} dr_j \psi_j \delta \chi_i \chi_j. \tag{2.8}$$

Both the Hartree and Hartree-Fock method use a time averaged electron density to estimate the electron-electron repulsion coulomb energy. The Hartree-Fock method includes the additional exchange integrals, which represents the influence of the exclusion principle, causing electrons with parallel spin to avoid each other. However, both these methods ignore the change to the wave functions and electron densities caused by the coulomb electron-electron repulsion, which also causes electrons to avoid each other. This coulomb-based repulsion, or coulomb correlation, contributes a second correction to the electrons potential energy, the so-called correlation energy. A very successful modern method which allows both exchange and correlation energies to be estimated in Density Functional Theory.

2.2 Density Functional Theory

Density Functional Theory (DFT) is among the most popular and versatile methods in condensed matter physics or computational physics as well as computational chemistry. It is a quantum mechanical method that is widely used to investigate the electronic structure of many body system, particularly molecules and condensed phases. The contribution of DFT was recognized with the award of the 1998 Nobel prize in chemistry to Walter Kohn and John Pople. DFT has been applied successfully to systems of electrons like atoms, molecules, clusters, homogenous solids, surface and interface, quantum wells, quantum wirs, quantum dots, and others [24]. It provides a way for the exchange and correlation contributions the electrons potential energy to be calculated. The main objective of density functional theory is to replace the many-body electronic wave function with the electronic density as the basic quantity. The many-body Schrodinger equation is similar to equation (2.1) and can be simply written as.

$$\hat{H}\Psi(\vec{r}_1,\vec{r}_2,......,\vec{r}_N) = E\Psi(\vec{r}_1,\vec{r}_2,......\vec{r}_N) \tag{2.9}$$

The particle density which is the key variable in DFT is given by

$$n(\vec{r}_1) = N\int d^3r_2\int d^3r_3....\int d^3r_N\psi^*(\vec{r}_1,\vec{r}_2,....\vec{r}_N)\psi(\vec{r}_1,r_2,...\vec{r}_N) \tag{2.10}$$

This is the probability per unit volume of finding any of the N electrons in the system at $\vec{r}_1$. The electron density only depends on 3N spatial coordinates, but implicitly contains all the information needed to determine the Hamiltonian; for example number of electrons N, the coordinates of nuclei $\vec{R}_I$ and the charge of nuclei Z_I. This is the advantage of electron density compared to wave function. The total number of electrons in the system N is simply given by the integral over $n(r)$:

$$\int n(r)d^3r = N \tag{2.11}$$

2.3 Development of Density Functional Theory

The very first attempt to use electron density $n(\vec{r})$ to calculate its total energy is done by Thomas-Fermi Theory formulated by Thomas and Fermi in 1927 [25, 26].They calculated the energy of an atom by representing its kinetic energy as a functional of the electron density, combining this with the classical expression for the nuclear-electron and electron-electron interactions. Thus, Thomas-Fermi model is predecessor to density functional theory, however, Thomas-Fermi model is not very accurate since there are no exchange or correlation terms included, and also the Thomas-Fermi kinetic energy functional is only a crude approximation to the actual kinetic energy.

In 1964 Hohenberg-Kohn justified the use of electron density as basic variable is determining total energy. They gave a firm theoretical footing to DFT with two remarkable and powerful theorems. The first Hohenberg-Kohn theorem proved that the relation expressed in equation (2.11) can be reversed in which the ground state wave function $\psi_o(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N)$ can be calculated by a given ground state density $n_o(\vec{r})$ with a unique functional as shown below

$$\psi_o = \psi_o[n_o]. \tag{2.12}$$

This equation shows that there exists the one - to - one mapping between ground state electron densities and external potential. Therefore, ground state energy is given by

$$E_o = E[n_o] =< \psi_o[n_o]|H_{ele}|\psi_o[n_o] > . \tag{2.13}$$

The original N-electron Hamiltonian H_{ele} is given by equation (2.3) when the form of this is modified to correspond to the DFT wave function $\psi_o[n_o]$, the energy expectation value as a function of $n(\vec{r})$ is obtained

$$E[n(\vec{r})] = \int n(\vec{r})V_{ext}d^3r + (T_e[n(\vec{r})]) + u_{ee}[n(\vec{r})], \tag{2.14}$$

where V_{ext} gives the interaction of the electrons with the nuclei and the second term of equation (2.3) is given by

$$V_{ext} = -\sum_A \frac{z_A}{r - R_A}. \tag{2.15}$$

The other two terms of the energy functional, $T_e[n]$ and $V_{ee}[n]$ represents the contributions to the energy from the electrons kinetic energy and the electron-electron density coulomb interaction respectively. These are written as functionals of the electron density $n[\vec{r}]$. The two terms taken together are known as the universal Hohenberg-Kohn functional,

$$F_{HK}[n] = T_e[n] + V_{ee}[n] \tag{2.16}$$

The minimization of the energy functional shown in equation (2.14) will yield ground state density and thus all other ground state observable. The exact form of F_{HK} has not been found and thus approximations must be used for the variational principle that was introduced in the second Hohenberg-Kohn theorem. The variational of minimizing the energy functional $E[n]$ can be solved by applying the Lagrangian method of under determined multipliers, which was done by Kohn-Sham.

2.4 Kohn-Sham Theory

In 1965, the year after the Hohenberg-Kohn theorem was published, Kohn and Shame proposed a method to obtain an exact single particle like description of many-body system by an approximation of the universal Hohenberg-Kohn functional F_{HK}. Kohn and Shame separated $F_{HK}[n]$ in to three parts.

$$F_{HK}[n] = T_e[n] + J[n] + E_{XC}[n] \tag{2.17}$$

where $T_e[n]$ is the kinetic energy of the electrons, as before, $J[n]$ is the Hartree potential and $E_{XC}[n]$ is the exchange-correlation term. with, this, the total energy functional $E[N_{\vec{r}}]$ becomes

$$E[n_{\vec{r}}] = T_e[n(\vec{r})] + \frac{1}{2}\int\int \frac{n(\vec{r})n(\vec{r'})}{|r-r'|}d^3rd^3r' + E_{XC}[n(\vec{r})] + \int n(\vec{r})V_{ect}(\vec{r})d^3r, \tag{2.18}$$

where $T_e[n(r)]$ is the kinetic energy of the non-interacting electron gas with density $n(\vec{r})$, the second term is the Hartree potential which describes coulomb interaction between electrons, $E_{XC}[n(\vec{r})]$ is the new exchange-correlation energy. $T_e[n]$ is calculated in terms of the (DFT) electron wave function, $\phi(r)$,

$$T_e[n(\vec{r})] = \sum_i \int \phi_i^*(r)(-\frac{1}{2}\nabla^2)\phi_i(\vec{r})d^3r. \tag{2.19}$$

Though $T_e[n]$ is not the exact kinetic energy; it is well defined and is treated exactly in this method.

The Kohn-Sham equation for the system of electrons are obtained by applying the variational principle to the total energy functional equation (2.17), by considering variations in the electron density.

$$\frac{\delta E[n]}{\delta n} = \frac{\delta T_0[n]}{\delta n} + V_{ext}(r) + V_H(\vec{r}) + V_{XC} = \mu, \tag{2.20}$$

where $V_{XC} = \frac{\delta E_{XC}}{\delta n}$,

$$V_H(r) = \frac{1}{2}\int \frac{n(\vec{r'})}{|r-r'|}d^3r', \tag{2.21}$$

and μ is the lagrange multiplier related to the conservation of N. Minimizing the energy functional in this way leads to the Kohn-Sham equations for the single electron wave function $\Phi_i\vec{r}$.

$$(-\frac{\nabla^2}{2} + V_{eff}(\vec{r}))\phi_i(\vec{r}) = \varepsilon_i\phi_i(\vec{r}), \tag{2.22}$$

where $V_{eff}(\vec{r}) = V_{ext}(\vec{r}) + V_H(\vec{r}) + V_{XC}$
and the density is constructed from a set of one-electron orbital's or called Kohn-Sham orbital's (non-interacting reference system);

$$n(\vec{r}) = \sum_i |\phi_i(\vec{r})|^2. \tag{2.23}$$

These equation are solved in a self -consistent way similar to the HF equation, to obtain the single-electron wave function $\phi(\vec{r})$ and the energy eigne values ε_i.
The total energy functional of the system can be expressed in terms of these energy eigenvalues as follows.
The sum of the energy eigne values gives when $V_{eff(\vec{r})}$ is substitute for using equation and the terms are arranged, the following equation is obtained for the total energy functional $E[n(\vec{r})]$. What remains is to define the equations for the exchange-correlation term. This is the subject of the following section.
Equation (2.17) and (2.21) allow for the formulation and implementaion of self-consistance field methods using approximate Exchange-corrilation functionals. The self-consistance field method (SCF) follow the flow scheme that can be seen in Fig.2.1.

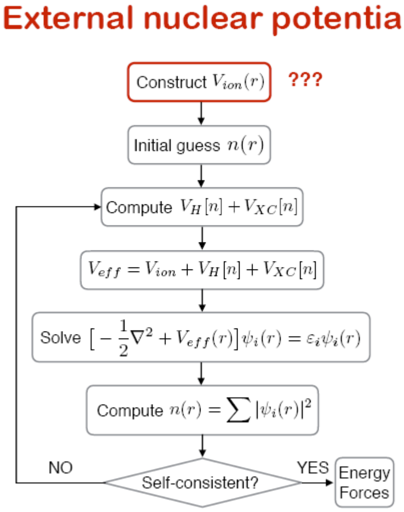


Figure 2.1: Flowchart that describes an SCF implementation of DFT [27].

2.5 The Exchange-Correlation

In the previous section we introduced the Kohn-Sham formalism which allows all the contributions to the electronic energy of an atomic or molecular system to be estimated, and gives a set of equation for single-electron wave-functions that can be solved in a self-consistent way, similar to the Hartree-Fock method.

The major advantage of the Kohn-Sham formalism over the Hartree-Fock is that it allows the exchange and correlation energies of the electrons to be estimated these are represented by the exchange-correlation functional $E_{XC}[n]$. This term includes the non-classical portion of the electron-electron interaction (the exchange term) along with the correlation for the self-interaction of the electron charge density (the correlation term). Crucial to the success of the Kohn-Sham Scheme for solving the many-electron Schrodinger equation is the availability of explicit approximations to this functional. The quality of the density functional approach hinges solely on the accuracy of the chosen approximation to E_{XC}. In fact there is no systematic way for developing accurate functional, this in fact represents one of the major drawbacks associated with this approach. In the following section we introduce the simple concepts of the local density approximation based on the uniform electron gas, which represents the bedrock of almost all current functional. Even though this physical model performs better than anticipated, it is not accurate enough for much application in molecular chemistry and physics. Because of this, we also introduce the more sophisticated generalized gradient approximation, which can be considered as a development of the local density approximation.

2.5.1 Local Density Approximation

Local Density Approximation are a class of approximation to the exchange correlation, energy functional in density functional theory (DFT) that depends solely up on the value of the electronic density at each point in space (and not, for example, derivatives of the densitiy or the Kohn-Sham orbital's). Many approaches can yield local approximation to the exchange energy [28]. In general, for a spin-unpolarized system, a local density approximation for the exchange-correlation energy is written as

$$E_{XC}[n] = \int n(r)\varepsilon_{xc}[n]dr, \tag{2.24}$$

where $n(r)$ is the electron density and ε_{xc} is the exchange correlation energy per particles of homogeneous electron gas of charge density. The exchange-correlation energy is decomposed in to exchange and correlation terms linearly [29].

$$E_{XC} = E_X + E_C \tag{2.25}$$

The exchange term and (Ex) takes on a simple analytic form the homogenous electron gas. Only limiting expressions for the correlation density are known exactly, leading to numerous different approximations for ε_c. Local Density Approximation are important in the construction of more sophisticated approximation to the exchange-correlation energy, such as generalized gradient approximation or hybrid functional, as a desirable properly of any approximation the exchange-correlation functional is that it reproduce the exact results of the HEG for non-varying densities. As such, LDAs are often an explicit component of such functional.

2.5.2 The Generalized Gradient Approximation

The accuracy of LDA is often considered satisfactory in condensed-matter systems, but it is much less so in atomic and molecular physics, for which highly accurate experimental data are available. Also, LDA overestimates (~ 20) and more cohesive energies and bond strengths in molecules and solids, and as a consequence bond lengths are often underestimated. Such problems are mostly corrected by the introduction of gradient corrections. The exchange-correlation functional is written as a function of the local density and of the local gradient of the density. Also, as the LDA approximates the energy of true density by the energy of a local constant density, it fails in the situation where the density undergoes rapid changes such as in molecules. The first logical step to go beyond LDA is the use of not only the information about the density of electron, $n(r)$ at a point r, but also to supplement the density with information about the gradient of density, (r) in order to account for the non-homogeneity of the true electron density. This approximation is called generalized gradient approximation (GGA). Symbolically this can be written as,

$$E_{XC}^{GGA} = E_{XC}[n(r), (r)]; \tag{2.26}$$

which can be also written as:

$$E_{XC}^{GGA}[n] = \int n(r)e_{XC}[\nabla n(r), n(r)]dr. \tag{2.27}$$

There are two sets of functional forms widely used in exchange correlation energy, introduced respectively by Perdew and Wang in 1992 (pw91) [30] and Perdew, Burke, and Ernzerhof in 1996 (PBE) [31]. It is observed that GGA in PBE form give rather accurate results for most of the periodic systems. Both LDA and GGA perform badly in materials where the electrons tend to be localized and strongly correlated such as transition metal oxides and rare-earth elements and compounds. This drawback leads to approximations beyond LDA and GGA.

2.6 Planewaves

In electronic structure calculation, two alternative approaches for synthesizing electron wave function are:
linear combinations of atomic orbitals (LCAO) and linear combinations of plane waves (plane waves bases set) (LCPWb).
VASP uses linear combinations of plane waves for the active electrons, because the behavior of those electrons in the region between atoms can be thought of as approaching free electrons behavior, the more complex, oscillatory behavior of the wave function close to the atoms cores, is effectively eliminated by the use of pseudopotential, in place of the full nuclear potential energy term, in the region of the atom cores this is explained in the following sub-section. In practice, the set of plane waves is restricted to a sphere in reciprocal space most conveniently represented interms of a cutoff energy, such that for all values of G. Ecut(r) used in the expansion is given by

$$\frac{\hbar^2|K+g|^2}{2m} \leq E_{cut} \tag{2.28}$$

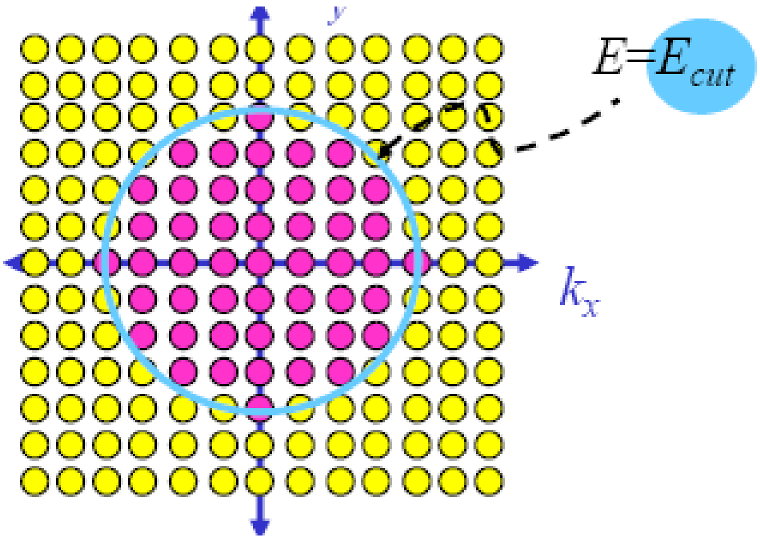


Figure 2.2: planewaves expansion represented as a grid in k-space [32].

2.7 PseudoPotentials

The coulomb interaction is inversely proportional to the radial distance $\vec{r}$. Because of this in the core region of the atom, potential becomes too large when electron is too close to core. The wave functions of valance and core electrons have to be orthogonal. So that plane waves of these valance electrons are oscillating too much. To avoid this we can define a pseudo potential.

Instead of considering the potential of all core electrons, we can define a single pseudopotential which can describe the system with a good approximation.

Figure 2.3. showes this behavior

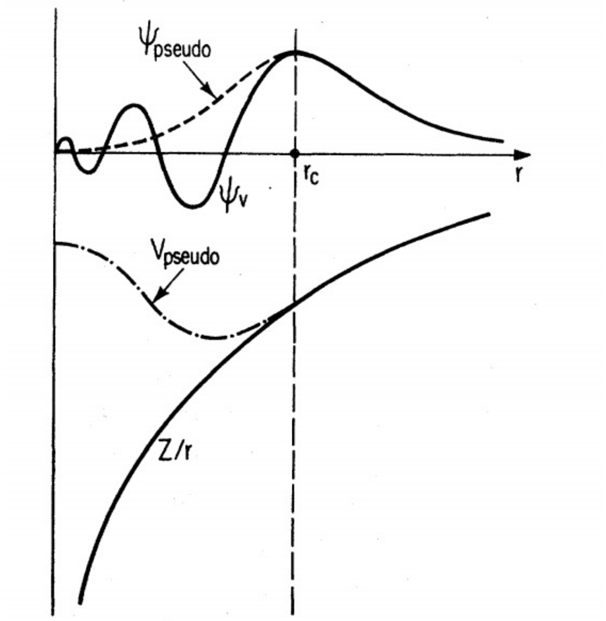


Figure 2.3: Figure 2.3: Illustration of all-electron (solid lines) and pseudoelectron (dashed lines) potentials and their corresponding wave functions. The radius at which all electron and pseudo electron values match is designated r_c(Reproduced from [33])

CHAPTER 3

Methodology

3.1 General Consideration

In this chapter, we discuss details about our present work with the first principles density functional calculations using pseudopotential based on norm-conserving approach and within the implemetation of Quantum ESPRESSO (QE) code. Some practicable commands along with their functions are well detailed here.

3.2 Quantum Espresso Program

Quantum ESPRESSO- an abbreviation for Quantum op**E**n-**S**ource **P**ackage for **R**esearch in **E**lectronic **S**tructure, **S**imulation, and **O**ptimization program is a multi-purpose and multi-platform computer coding program for electronic-structure calculations and materials modeling [34]. This package is mainly used in the ab-initio calculations of condensed matter systems. In condensed matter physics, it's normal application in the ab-initio calculations like-structural optimizations (both at zero and finite temperature), linear response calculations (Phonons, elastic constants, dielectric and many more) etc. extends to high temperature molecular dynamics. The major ingredient of the package included in the software are

- Plane Wave self-consistent field (PWscf).
- First-Principles Molecular Dynamics (FPMD).

QE, based on DFT, implements a variety of methods and algorithms for a chemically realistic modeling of materials from the nano-scale upwards.This package uses a plane waves (PWs) basis set for the expansion of electronic wave function, a pseudo potentials (PPs) to represent electron-ion interactions and DFT for the description of electron-electron interaction [35]. Some basic simulations that can performed by this package include:

- Calculations of the Kohn-Sham (KS) orbitals and energies for isolated and extended systems, and of their ground state energies.
- Structural modeling (equilibrium structures of molecules, crystals, surfaces).
- Atomic forces and stresses.
- Ground state studies of magnetic or spin-polarized systems.
- Dynamical modeling (first-principles molecular dynamics) either on the electronic ground state (Born-Oppenheimer) or with fictitious electronic kinetic energy (Car-Parrinello).

Density-Functional Perturbation Theory (DFPT) used in the package to calculate the energy derivatives and related quantites. QE package are used as our first-principles code.QE is a full ab-intio package implementing electronic structure and energy calculation, linear response method (to calculate dielectric constants, Born effective charge and phonon dispersion curves) and third order an-harmonic perturbation theory. It also contains two molecular-dynamics codes, CPMD (Car-Parrinello Molecular Dynamics) and FPMD (First-Principles Molecular Dynamics). Among them, to perform total energy calculations, PWscf code is used, both norm-conserving pseudo potential (PP) and Ultra soft Pseudo-potentials (US-PP) within DFT are used. In our case, we use Quantum ESPRESSO integrated module of codes, based on DFT by using plane basis set for expansion of wave function and pseudo potential with required content in first-principle method of calculation to calculate total energies and optimized geometries of compound semiconductors GaAs. Also, by using this package, band structure is calculated and partial density of states (PDOS) is used to study the nature of material.

3.2.1 pw.x executable and inputs

PWscf stands for Plane Wave self-consistent field, developed by S. Baroni et a [36, 37]. PWscf implements an iterative approach for self-consistency, in the framework of the plane-wave pseudo potential method. This package uses the well-established

LDA and GGA exchange-correlation functionals, including spin-polarizations. The main feature of PWscf calculation is the self-consistency calculations, structural relaxation, electronic structure calculations, variable cell molecular dynamics calculation etc, performed by invoking executable file called pw.x. The structural optimization is performed using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm [38]. Some of the most important parameters in the input file of the Quantum espresso are as indicated below.

- **ibrav =2** , this keyword generates face centered cubic (fcc) structure.
- **celldm (1)**, specifies the lattice constant of the crystal and are usually given in atomic unit.
- **ecutwfc** , this keyword determines the value of kinetic energy cutoff in Ry or eV unit (1Ry=13.6 eV).
- **nat** , gives the number of atoms in the simulating cell.
- **ntyp** , represents the number of different types of the atomic species used in the unit cell.
- **nbnd**, represents the number of electronic stated (bands) to be calculated.
- **Atomic Species**, it specifies the symbols of the atoms, their corresponding masses (in amu)and the name of the files containing the pseudo-potentials.
- **Atomic Positions** , specifies the atomic co-ordinates of the atoms which are defined for the proper structure.
- **k-points**, represents the rectangular grid of points of dimensions k_x,k_y ,k_z, spaced evenly throughout the Brillouin zone and this keyword requires appropriate unit.

3.2.2 Other analysis tools

The package called Postprocessing was Originally developed by Stefano Baroni, Stefano de Gironcoli, Andrea Dal Corso(SISSA), Paolo Giannozzi (Univ. Udine), and many others [36, 37]. After the Self Consistent calculation has been converged, we use many small calculations such as plotting of band, density of states (DOS) etc. The main post processing codes which extract the specified data/files from the PWscf calculations and perform further calculations are as follows;

- **pw.x;** We use this command to the input files of scf and nscf calculations of energy and wave functions at each and every k-points, which extracts the output files for the energy calculation at every k-points.
- **bands.x;** This extracts the files from PWscf calculation and records its eigenvalues at different K-points with corresponding energies values ready for further processing. The code bands.x also performs the band structure.
- **plotband.x:** The output file of bands.x is directly read and converted to plottable format by auxiliary code plotband.x. The value of k-points must be correctly put in a sequence, otherwise unpredictable plots may results if k-points are not in sequence along lines or if two consecutive points are same. Thus proper choice of sequence of k-points is important.
- **dos.x:** This code helps us to calculate the electronic density of states at different k-points.
- **projwfc.x:** This code calculates projections of wave functions over atomic orbital. It gives the contributions of the atomic orbital **s, p, d, f.**

3.3 Density of states

We now review the way the density of stats (DOS) is calculated for one compound of GaAs: The DOS of a compound describes the number of states per interval of energy at each energy levels that are available to be occupied. The usual definition of the density of stats (DOS) is the number of states in the range E to E + dE. Define N as the total number of states and also define

$$G = \frac{totalnumberofstates}{unitofvolum} = \frac{N}{V} \tag{3.1}$$

and let g denote the DOS, defined as

$$g = \frac{dG}{dE} \tag{3.2}$$

which is the number of states per unit volume in the range E to E + dE. Note that per unit volum refers to the space between intervals or points, and thus may be a length or area in lower dimensions.

3.4 Modelling of 3D SYSTEM

Here, there are no quantum confinement effects, the electrons wave vector k has three components which very continuously, k_X, k_Y, k_Z,

- Density of states N(E) is given by;

$$N(E) \sim (E - v_o)^{\frac{1}{2}} \tag{3.3}$$

3.5 Modelling of 2D SYSTEM

Here, there are quantum confinement effects in one of the three dimensions, so that of the electrons wave vector k has three components, two very continuously, k_X, k_Y, but one is limited to discrete values, k_Z.

- For two dimentional system we have no energy dependence.

3.6 Modelling of 1D SYSTEM

- Quantum confinement effects in two dimenstions.
- k_y, only varies continuously,
- k_x, k_z, limited to discrete values
- Density of states N(E) is given by;

$$N(E) \sim (E - v_o)^{\frac{-1}{2}} \tag{3.4}$$

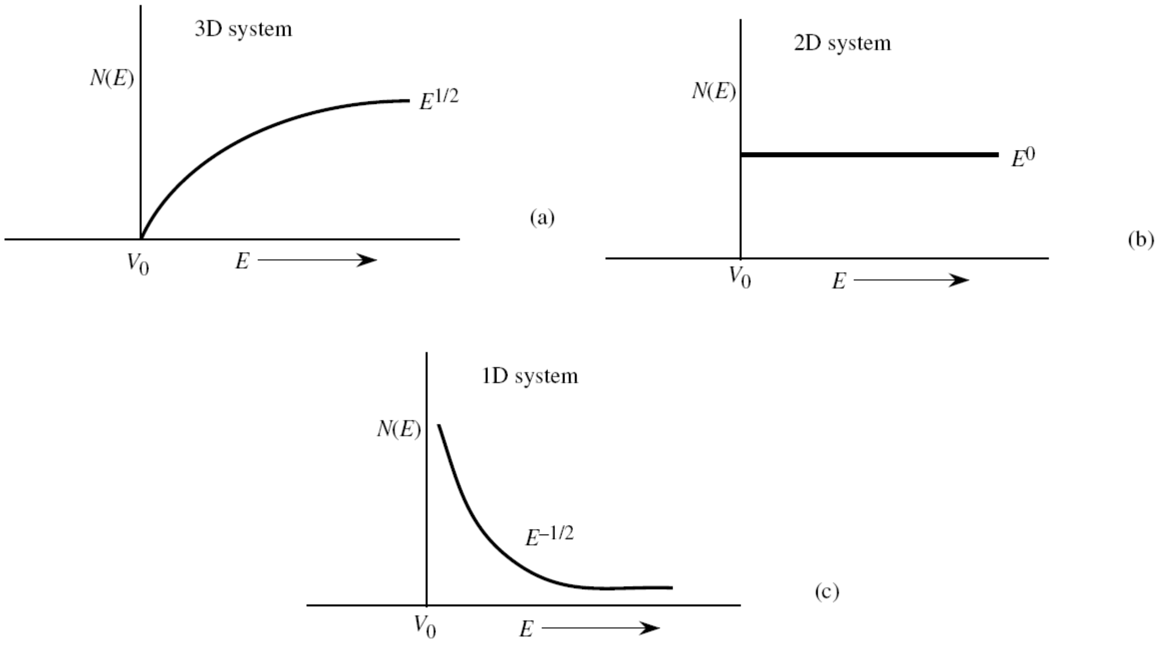


Figure 3.1: Energy dependence of the density of states in (a) 3D, (b) 2D, and (c) 1D systems [39].

CHAPTER 4

Results and discussion

4.1 General Technical process

This thesis has describes the study of compound semiconductors GaAs in two dimension. One of the main challenges in first principle calculation is the geometric optimization of structures. We have taken out the energy minimization of GaAs followed by the study of electronic band structures and density of states. The calculation has been carried out using density functional theory [36, 37], using generalized gradient approximation. At first, in GGA method, energy minimization is done with respect to lattice parameter then the same lattice parameter corresponding to the minimum energy state are used to carry out further calculations. In band structure calculations, we plott the graph of energy versus the high symmetry k-points, and then analyz properties of the substance on the basis of band lines and band gap. To view the individual contribution of different orbital electrons, we study the conduction band edge and valance band edge. Likewise, Density of states (DOS) perform to get the information about nature of the band gap and Partial Density of states (PDOS) gives information about origin of bands. In all these self consistent field (scf) calculations, we use the convergence criteria as the difference between energy. in this chapter, we discuss about;

- calculation of lattice parameter, band structure, and.
- Density of states (DOS) as well as Partial Density of States (PDOS).

We started with a series of convergence tests and energy minimization.

4.1.1 Convergence Tests

The self-consistent field (scf) calculations are performed to determine basic parameters: kinetic energy cut-off for the plane wave basis and k-points grid by testing the convergence of total energy and calculation of lattice parameter by energy minimization.

4.1.2 (Convergence tests in cut off energy)

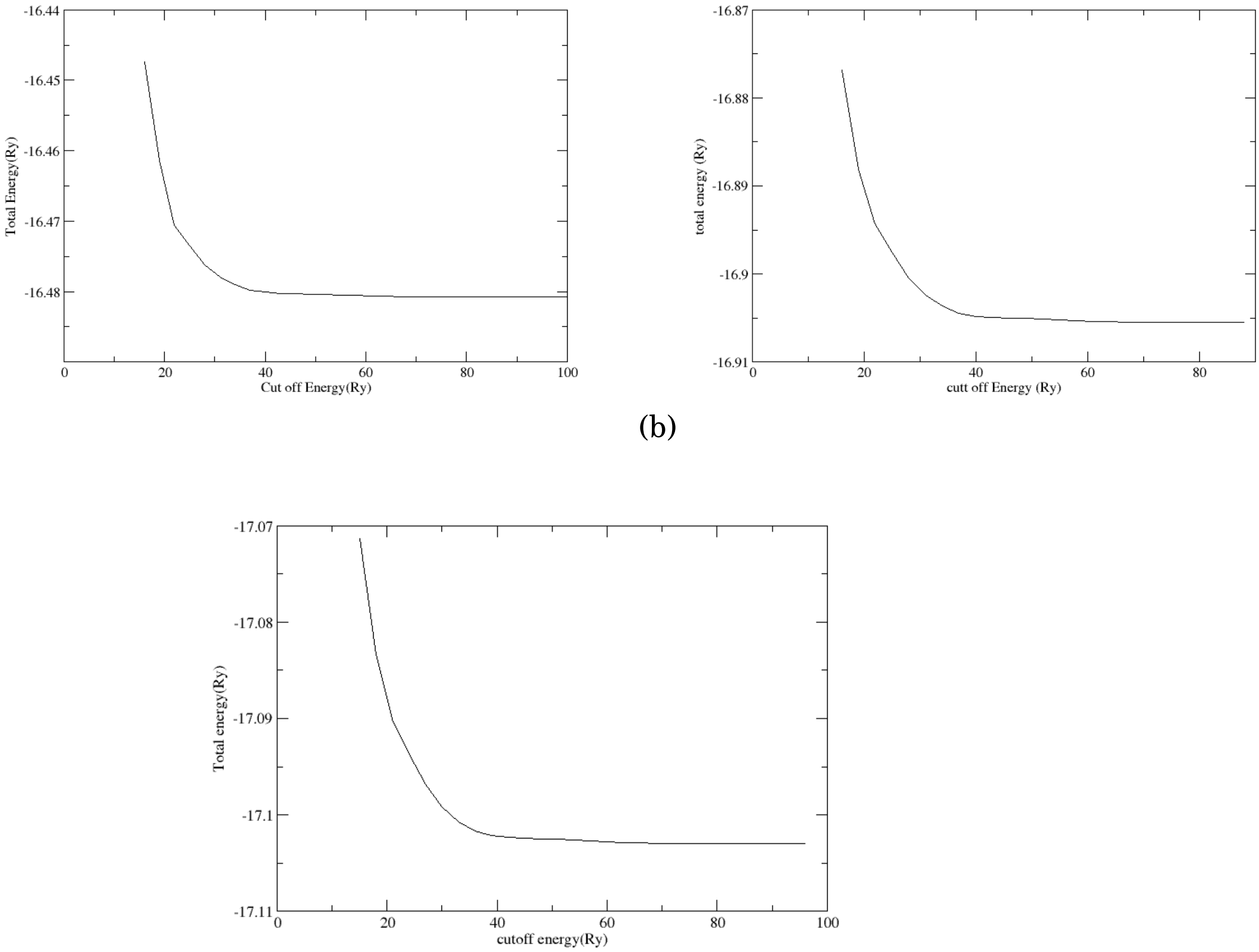
The plane wave scf code implemented in the Quantum Espresso [34]. Expands the electron wave-function in terms of the infinite basis function that is plane waves. The value of the kinetic energy cut-off corresponds to the neighboring interactions in the periodic system. If we take this cut-off energy large, we include long range interactions and the results will be more accurate, but this takes more computing resources. If we take this energy small, the results could be inaccurate though computationally cheap. Therefore, we have to take optimum (the best possible result) value of this cut-off energy. It is expressed in unit of the energy Ry. The plane wave expansion in the reciprocal space is

$$\Psi_K(r) = \frac{1}{\Omega}\sum c_{K.G}e^{(K+G).r}, \tag{4.1}$$

where Ω is the volume of the box, G are the reciprocal lattice vectors defined by $G.l = 2\pi m$ for all l, where l is a lattice vector of the crystal and m an integer, $C_{K.G}$ are the coefficients for the plane waves and k represent the reciprocal space vectors within the first Brillion zone of the periodic cell [42]. In principle, we need infinite numbers of plane waves but in order to reduce the computational cost we have to truncate the plane wave expansion from some acceptable value. To make the plane wave expansion infinite, we truncated according to the condition.

$$\frac{|K+G|^2}{2m} \leq E_{cut}. \tag{4.2}$$

We performed the scf calculations using the experimental value of the lattice parameter (a= 5.65 A^o) and some arbitrary k-point mesh in the scf input file. The scf calculations were performed for different values of the ecutwfc ranging from 16 R_y to 100 R_y. At these different values of cut-off energy, we found different values of total scf energy. Then we plot the graph between the scf total energy versus kinetic energy cut-off value and the appropriate value of kinetic energy cut-off is chosen from which the convergence of total energy starts to occur. In different dimension for one dimension (1D), two dimension (2D) and three dimension (3D), we obtained different values of cut-off energy 67 Ry, 73 Ry, and 67 Ry respectively. As seen from Fig. 4.1 it shows that at 67 Ry, 73 Ry, and 67 Ry in 1D, 2D, and 3D, respectively, is a sufficient cutoff energy for GaAs.



(a)

(b)

(c)

Figure 4.1: The total energy versus cutoff energy of GaAs. The figure in the left side of the upper panels is (a) 1D (b) 2D (c) 3D.

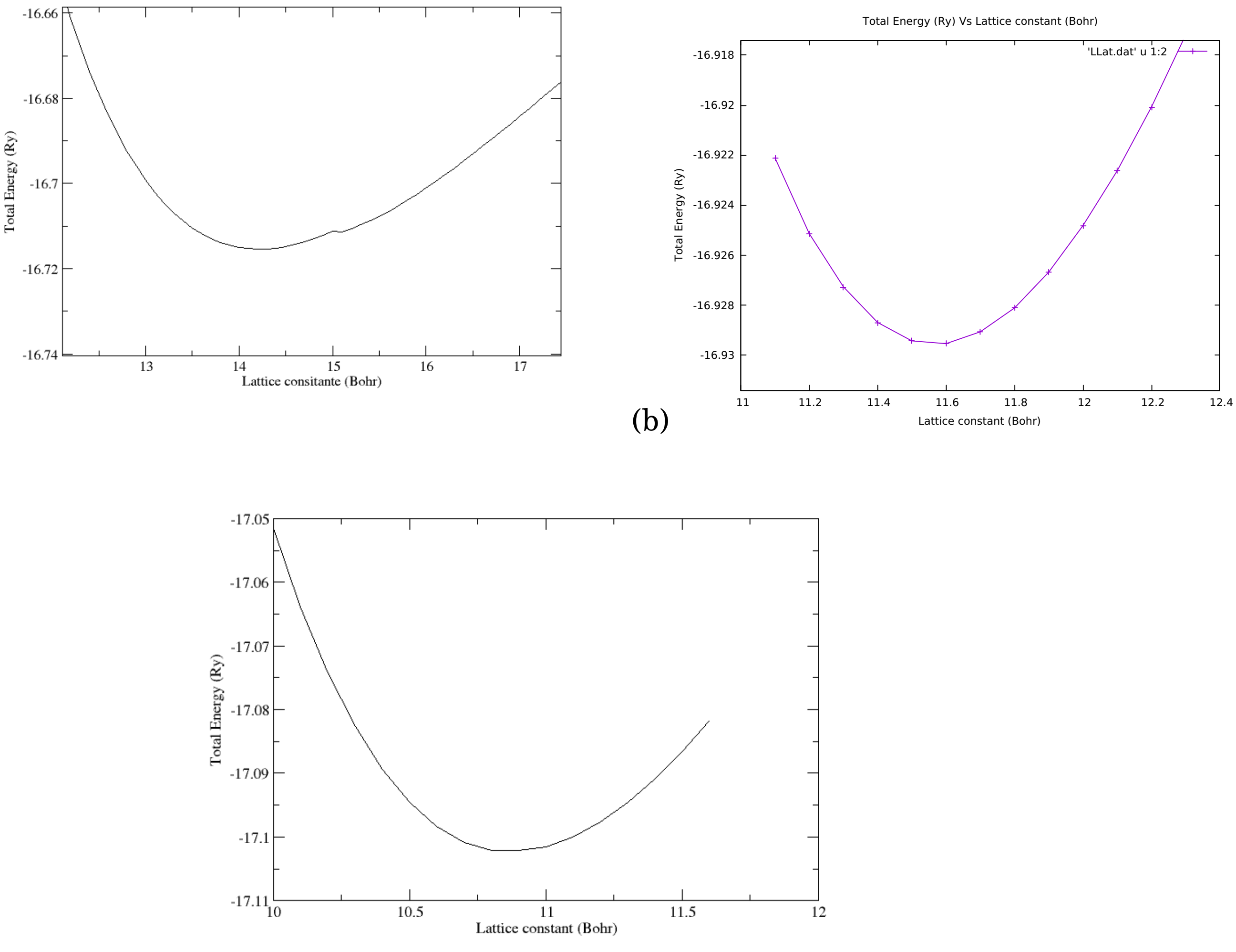
4.1.3 (Convergence tests in lattice conestant)

Lattice constant is a property of crystal lattice i.e periodic arrangement of atoms in three dimensions whether it is not a property of atoms. Basically, the lattice constant is the length of periodicity of the lattice repeats itself, for most crystals the lattice constant are few angstroms. After the calculation and value of ecutwfc and k-point, performed a convergence test for lattice parameter by using the converged value of ecutwfc and k-point mesh GaAs. GaAs we performed the scf calculations for total scf energy with different value of lattice parameters ranging from 10.0 to 20.4 Bohrs for 1D, ranging from 10.0 to 14.5 Bohrs for 2D and for 3D the ranging from 10.0 to 13.8 Bohrs. Then we plot a graph between total energy with lattice parameter as shown in Figure 4.2, then we obtained the suitable value of parameters for the input file at which the energy is minimum.

From Fig 4.2, the minimum total energy is at 14.0 Bohr (7.4Å) in 1D, 11.5 Bohr (6.1Å) in 2D, and 10.8Bohr (5.7Å) in 3D which is near with experimental value (5.63 Å) [41] and same as the previous work performed by Tahini by using PBE [42]. From the avaliable data, our value increased by 31.4 % in 1D, 7.9 % in 2D, and 1.4 % in 3D [41] and it is in satisfactory agreement.

4.1.4 (Convergence tests in k points)

In order to perform the Brillouin zone interaction in discrete scheme, it is essential to have a large number of grid points. But in practice, due to limitations of computational resources, we optimize the number of k-points grids. By calculating total energy versus k-point grids. The rectangular grid of points of dimensions $k_x \times \mathrm{k}_y \times \mathrm{k}_z$ spaced evenly throughout the Brillouin zone is called k-points grid. More the number of the grid points sampling will be more precession and accurate but computationally expensive. Here, the size of grid required depends on the system under study. We can estimate appropriate size by means of total energy calculation. Our approach of k-point sampling is as suggested by Monkhrost and Pack [45]. At first,we performed the scf calculations of GaAs for total scf energy with different values of k-points grid starting from $1\ \times 1 \times 1 to 10 \times 10 \times 10$ increasis in increment of $1 \times 1 \times 1$.

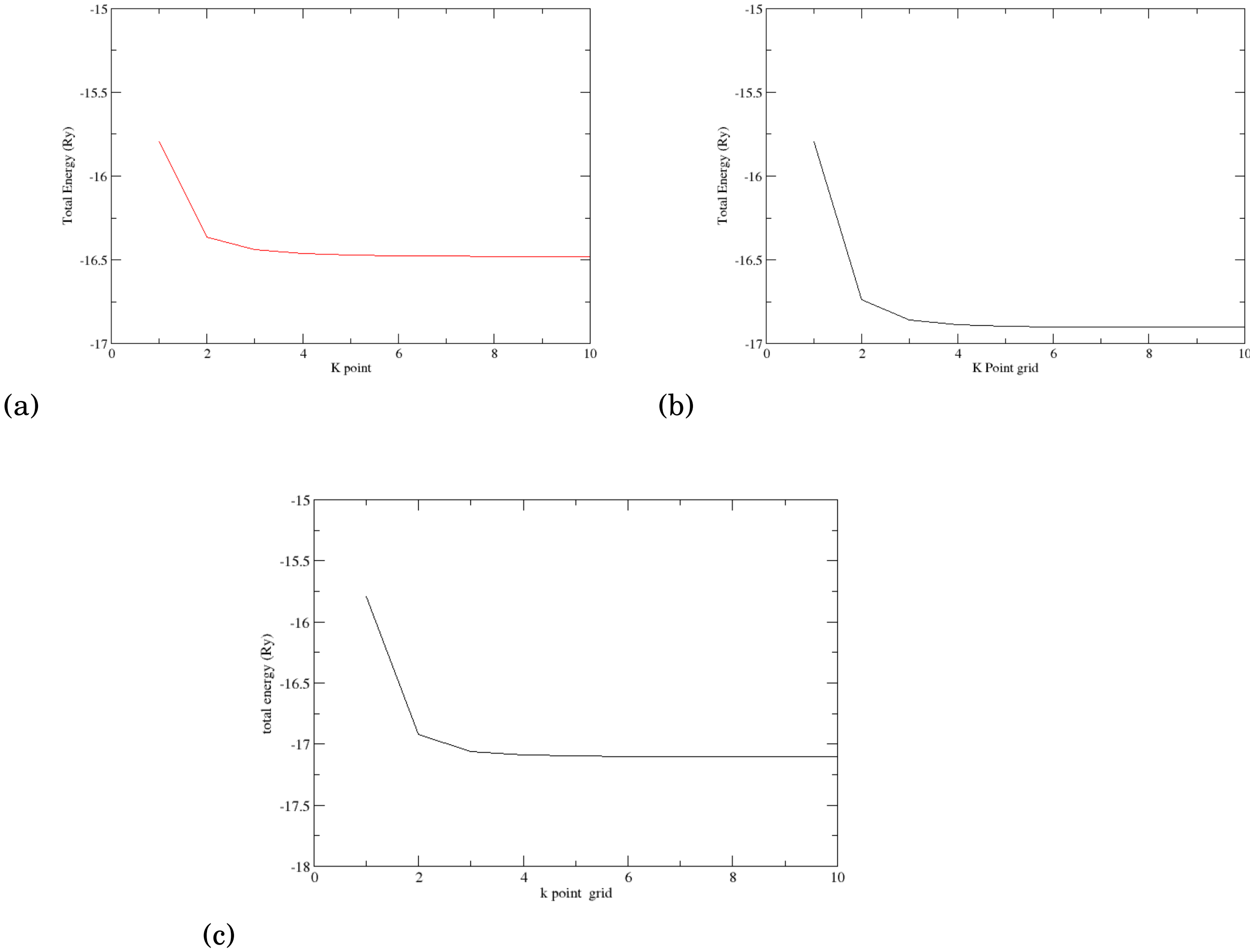


(a)

(b)

(c)

Figure 4.2: Total energy versus lattice constant for GaAs. (a) 1D (b) 2D (c) 3D system.



(a)

(b)

(c)

Figure 4.3: Total energy versus k points for GaAs. (a) 1D (b) 2D (c) 3D system.

As seen from Fig. 4.3 we have used a Monkhrost and Pack of $5\times1\times1$ for 1D, for 2D system $6\times6\times1$ and 3D system we have taken Monkhrost and Pack mesh of $7\times7\times7$. We have also calculated the band structure of Compound Semiconductor GaAs. For bands calculations of GaAs, we took $6\times6\times1$, k-points along specific direction of irreducible Brillouin zone in order to obtain the band structure which is performed by executable pw.x. Then, we performed post processing calculations with executable plotband.x in order to obtain band structure of Gallium Arsenide (GaAs.) Further, we have calculated the DOS and PDOS for both GaAs. Finally we performed scf calculation and then nscf calculation, we used more denser k-point mesh in order to obtain smooth partial density of states curve. These calculations were performed using the executable pw.x. Then, we performed PDOS calculation using executables projwfc.x command.

In this proceeding sections, we discuss the results of the first principles calculations carried out to obtain

- Band structure,
- Density of states and
- Partial Density of states of GaAs structure.

4.2 Electronic structure and analysis

4.2.1 Band structure 2D-GaAs

In the first principles electronic structure calculation of crystals, the electronic band structure is one of the most widely applied analytical tools especially with in the Kohn-sham framework of density functional theory. The band structure of solid are helpful to determine different electronic properties of solid.It contains the basic ingredients to almost all the crystal properties. Since the atoms in a solid are closely packed the interaction between them perturbed the initial atomic levels when a large number of atoms are brought together. Electrons in the orbital are filled up according to Paulis exclusion principle i.e. no two electron can occupy the same energy state. Bands constitute a sort of energy continuum, in which separate level due to individual atoms cannot be identified. In the process of inter atomic interaction, the inner shell electron stated are the least affected. Where as the valence electron, which are closest to neighboring ions, are the most affected. The effect of bringing one atom closer to the other is to split a single sharp levels. The bands structure of solids are helpful in determining different electronic and optical properties of the solid. According to Band theory [44], the measure of band gap determines the types of the solid.

The band structure are calculated by pseudopotential and planewave basis set method within the Density functional theory (DFT), treating exchange-correlation functional with generalized gradient approximation (GGA) in the form of Predew Berke- Ernzerhof (PBE) functional [43].

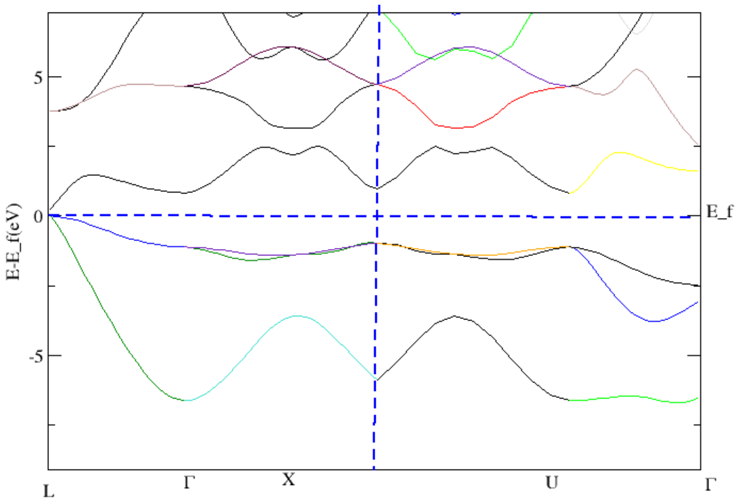


Figure 4.4: The plot of energy gap between conduction and valance band of GaAs in 2D

Figure 4.4 shows a band gap between the valence and the conduction band has an energy band gap approximetely band gap is 1.8 eV and has a direct band gap. Hence we can say that this material shows semiconductor behavior.

4.2.2 Density of States

The density of states (DOS) is defined as the number of states per unit energy range available for the particles to be occupied. In other words, the density of states refers to the number of quantum states per unit energy range and it indicates how density packed quantum states in a particular system.

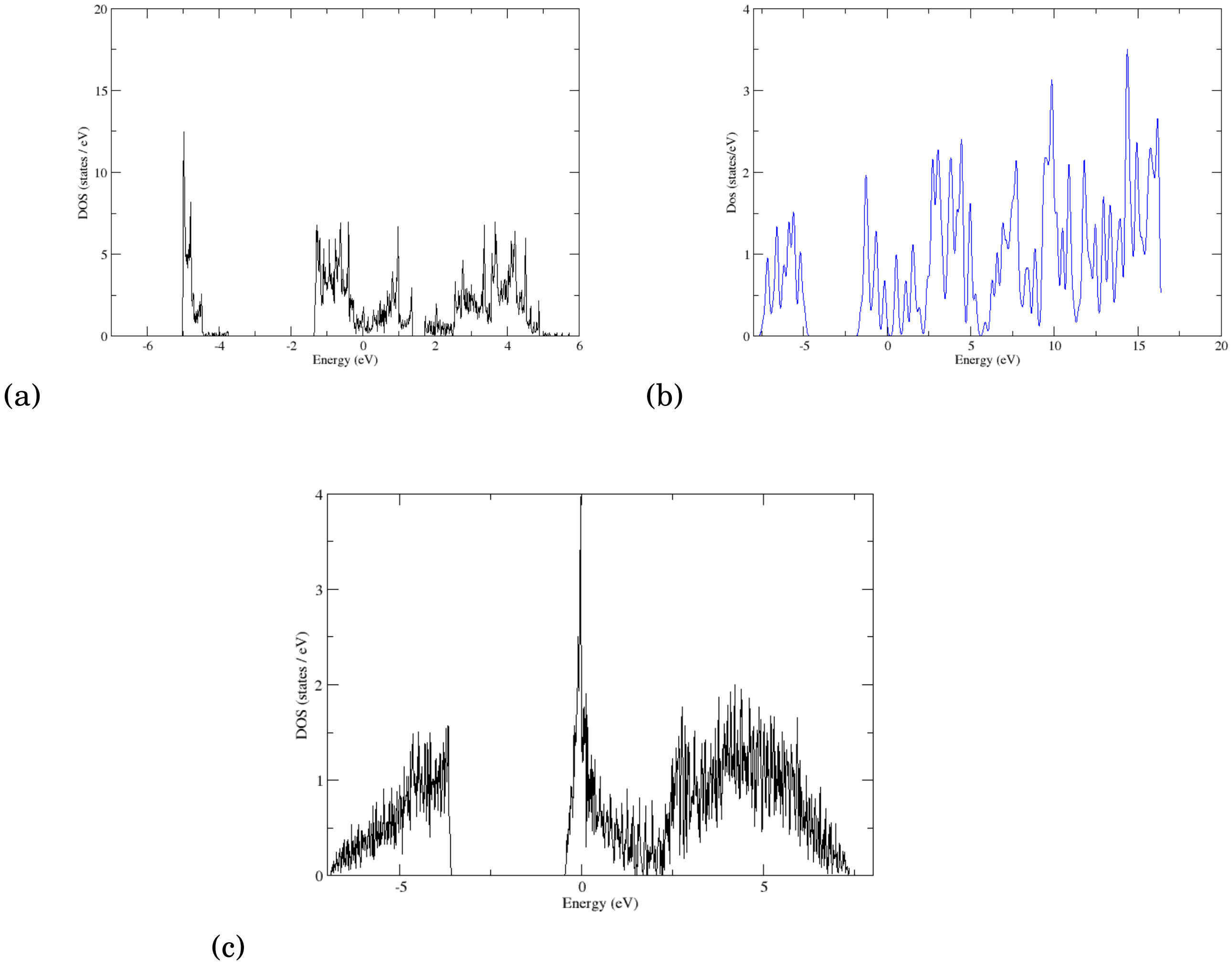
The density of states provides numerical information on the states that are available at each energy level. The value of zero density of states indicates that there are no available states for occupation in an energetic level [44]. The density of sates are calculated by pseudopotential and planewave basis set method within the Density functional theory (DFT), treating exchange-correlation functional with generalized gradient approximation (GGA) in the form of Predew Berke- Ernzerhof (PBE) functional [45]. All pseudopotential used in the calculations were norm- conserving scalar relativistic and full relativistic pseudo potentials. All calculation were performed within the Quantum-ESPRESSO package, plane wave kinetic energy cut-off were set at 67 R_y for GaAs.

The results of density of states of GaAs help to furthere elaborate the nature of the band gap as shown in Fig.4.5, where density of states Delta=0.01, shows the respective states of crystal which clarify the nature of the compound and as a compound semiconductores which is similar to the previous work performed by Tahini [47].

4.2.3 Partial Density of State

The projected or partial density of state (pdos) is the relative contribution of a particular atom or orbital to the total dos.

The results of partial densities of states (PDOS) GaAs help to further elaborate the nature of band gap as shown in Fig. 4.6. The partial density of states gives information about the origin of bands. In Fig. 4.6, left side from zero energy point indicates valance band whereas right side of zero indicates conduction band. In case of 1D GaAs the valence band is formed by 1s- orbital of Ga with smaller contribution of 2p- orbital of As whereas the conduction band is formed by 2p- orbital of As with a smaller contribution from 2p- orbital of Ga which is similar to previous results [42]. Similarlly GaAs in 2D, we observed the valence band is composed mainly from 1s- orbital of As and a smaller contribution of 2p- orbital of Ga. Where as the conduction band is formed



(a)

(b)

(c)

Figure 4.5: Dos curve of GaAs with energy at Delta = 0.01eV. (a) 1D (b) 2D (c) 3D system.

2p- orbital of As with a small contribution from 2p-orbital of Ga. Similarlly GaAs in 3D, the valence band is formed by 1s- orbital of As with smaller contribution of 2p- orbital of Ga. whereas the conduction band is formed by 2s- orbital of As smaller contribution 2p- orbital of Ga, which is similar to previous results. [47].when a graph was plotted for the relationship between pdos (arb.unit) along Y-axis versus energy (eV) along X-axis of GaAs in 1D, 2D, and 3D, respectivelly the following graph was obtained.

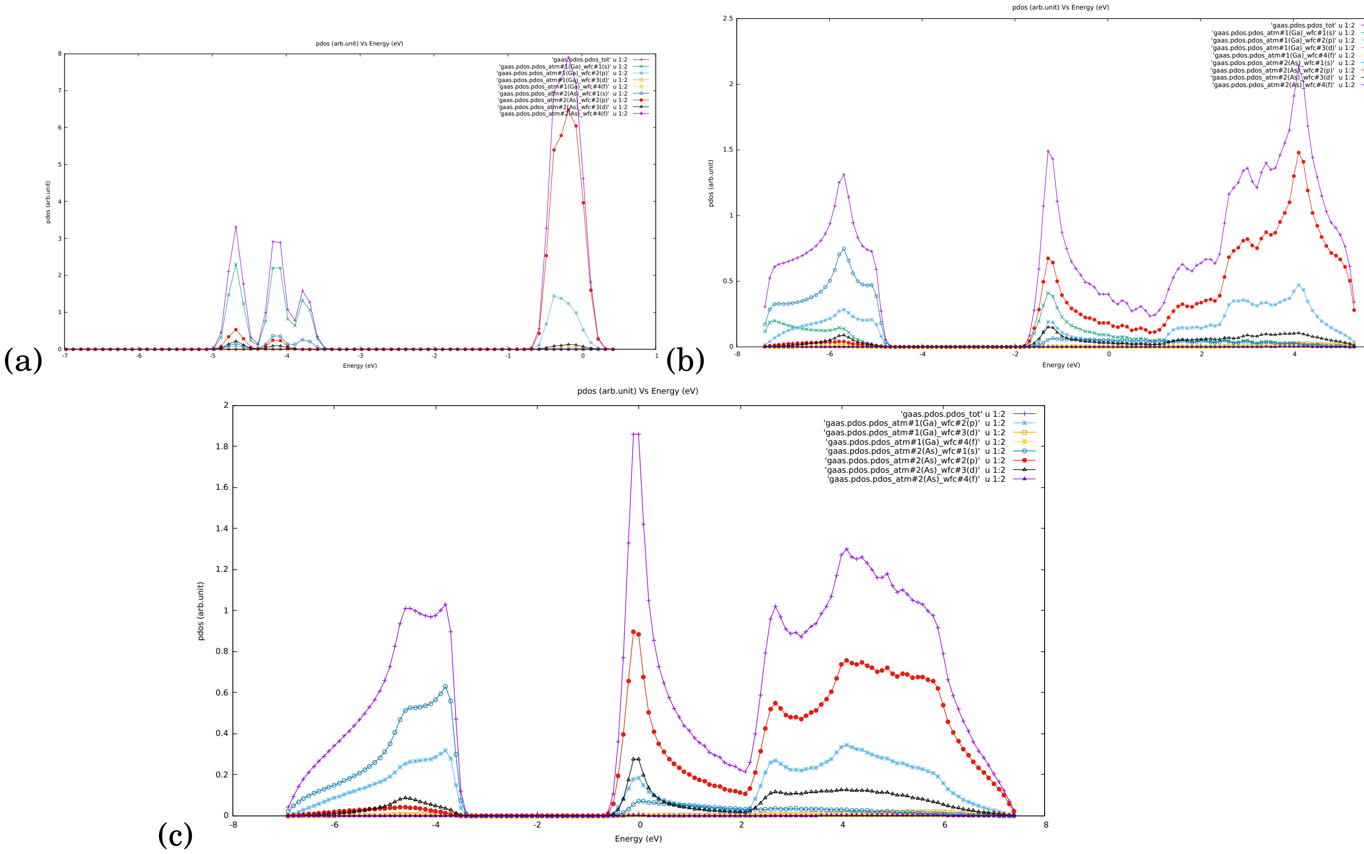


Figure 4.6: pDos curve of GaAs with energy at Delta=0.01eV. (a) 1D (b) 2D (c) 3D systems.

4.2.4 Analysis of Charge Density

Figure 4.7 shows the differiential charge density of pure GaAs and the yellow region indicates the increase in the charge density (As), and blue region indicate the decrease charge density (Ga) atom. The distribution of the differential charge density around the As atom appears directionality, and this is becouse of that the coupling of the 4p orbit of Ga atom and 4p orbit of As; the Ga atom and As atom form a semiconductor by hybrid mode, and the isolated electrons of Ga atom enter the hybrid orbit to form the coordination bond, which strengthens the combination of Ga atom and As atom. The gain and loss of electron between Ga atom and As atom are more compact, therefore, the distribution of the differintial charge density appears directionality. From the differintial charge density of pure GaAs, it can be seen that surrounding the Ga atom slightly losses electrons, and surrounding the As atom gain electrons, indicating that between Ga atom and As atom are mainly ionic bonds with a certain covalent bond.

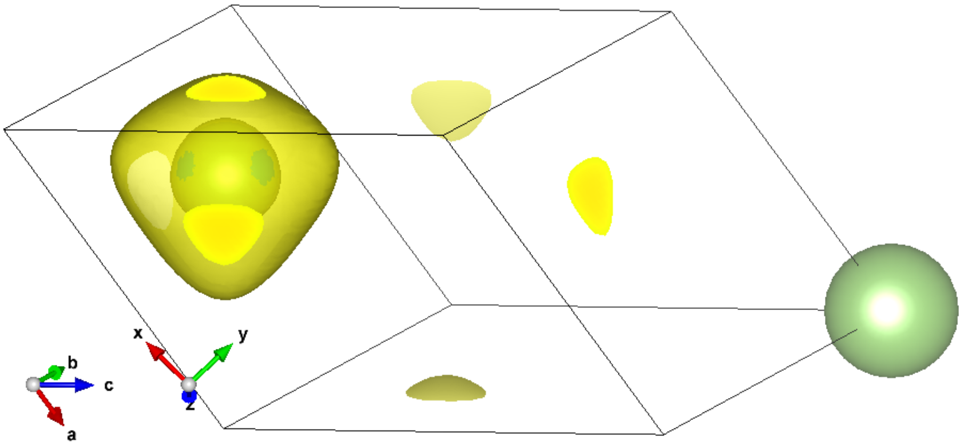


Figure 4.7: The charge density of pure GaAs.

CHAPTER 5

Conclusion

This thesis has performed first principle calculation to explore the structural and electronic properties of compound semiconductors GaAs. Moreover, with the help of DFT, GGA implemented with Quantum ESPRESSO code, to perform the first principle calculation. Firstly, we obtained optimized structure of unit cell of cubical (Zinc Blende) structure of GaAs.

The lattice parameter is found to be 7.4 Å, 6.1 Å, and 5.71 Å, in (1D), (2D) and (3D) for which is very near with experimental results as well as previous calculated data. From the available experimental data, our results increased by 31.4 % in 1(D), 7.9 % in 2(D) and 1.4 % in 3(D) [45], and similar to the previous work done by Tahini [46] and is in satisfactory agreement.

Then we calulated the band structure of GaAs. The calculated band structure of GaAs has a direct band gap with energy band gap of 1.8 eV which is in agreement to the previous work done by Tahini [41] and nearly about 45 % error with the experimental value [44].

Next we calculated Density of States (DOS) along with Partial Density of States (PDOS) of GaAs which clarify the nature of compound semiconductor [44], and finally the results from charge density of pure GaAs, show Ga atom losses electrons, and the As atom gain electrons, indicating that between Ga atom and As atom are mainly ionic bonds with a certain covalent bond.

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DECLARATION

ADDIS ABABA UNIVERSITY
COLLEGE OF NATURAL AND COMPUTATIONAL SCIENCES
DEPARTMENT OF PHYSICS

MSc Thesis

Electronic structure of 2D-gallium arsenide as studied using First principles density functional theory (DFT)

Name of Candidate: Andinet Amare

I the under signed declare that the thesis is my original work and no part of it can be claimed as an intellectual property of anybody else except me and my advisors.

Signature: ________________________