FIRST PRINCIPLE CALCULATIONS OF GALLIUM ARSENIDE USING DENSITY FUNCTIONAL THEORY

By

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To my father

Table of Contents

Abstract

Density functional theory (DFT) has had a rapidly growing impact not only on fundamental but also industrial research. The local density approximation (LDA) and the generalized gradient approximation (GGA) were used to compute the exchange correlation energy. The total minimum energy of GaAs is performed as a function of cutoff energy and Monk horst-pack grid size. The results show that, the total minimum energy of GaAs decreases with increasing cutoff energy due to variational principle. However, there is no systematic trend that can be predicted from just increasing the **k** point sampling. The total minimum force on GaAs is computed by displacing As atom in the z direction as a function of cutoff energy and **k** point grid size by 0.05 Bohr. Moreover, the total minimum force is converged at the cutoff 60 Rydberg and Monk horst-pack mesh of $14 \times 14 \times 14$ **k** points. In addition to this, the equilibrium lattice constant is calculated with different lattice constant.

Keywords: Gallium arsenide, Density functional theory, energy band gap, electronic structure, total energy, total force.

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List of Figures

List of Tables

Chapter 1

Introduction

1.1   General Background

Semiconductors are a group of materials having conductivities between metals and insulators [1]. Two general classifications of semiconductors are the elemental semiconductor materials, found in group IV of the periodic table and the compound semiconductor materials. Most of which are formed from special combinations of group III and group V elements [2, 3]. Gallium arsenide and related group III and V compounds were first investigated as semiconducting materials over thirty years ago [4]. The interatomic bonding is largely covalent [5]. GaAs is one of the most important material used in semiconductor physics. Its electronic properties such as a direct band gap and high electron mobility held the promise of new and unique devices such as high efficiency light emitters, light sensors and high speed switching devices fields where other similar materials don't compete. The reason behind these electronic and structural properties in gallium arsenide compound lies in the detailed nature of their electron energy band structures [6]. It has a direct energy band gap. That means the minimum in the $\epsilon(K)$ curve in the conduction band lies directly above the maximum in the valence band in $\mathbf{K}$ space. This allows direct interband

recombination of electrons and holes, with the emission of light energy of the appropriate wavelength to the band gap about 850 nm [7]. Hence, GaAs is said to be a good optoelectronic material that is used extensively in light-emitting diodes because of its high electron mobility [8], small dielectric constant and extensively utilized in high temperature resistance, ultrahigh frequency, low-power devices and circuits. It crystallizes in zinc-blende structure [9]. The zincblende lattice consists of a fcc Bravais point lattice, which contains two different atoms per lattice point. The distance b/n the two atoms equals one quarter of the body diagonal of the cube. The diamond lattice represents the crystal structure of zincblende. the difference is that in diamond structure there is only one type of atom where as in zincblende there are two types of atoms (the atoms in the basis are different). The face centered (fcc) cubic lattice contains 4 lattice points per cell. The nearest distance b/n lattice points is $a\frac{\sqrt{2}}{2}$ and the maximum packing density is $\Pi\frac{\sqrt{2}}{3}$.

1.2 Statement of the Problem

Density Functional Theory (DFT) is a many-body theory based on the idea of using only the density as the basic variable for describing many electron systems. Since, its introduction in the 1960s density functional theory has evolved into a powerful tool that is widely used in condensed matter theory and computational materials for the calculation of electronic, magnetic, and structural properties of solids. In recent years, there has been an upsurge of interest in structures and devices made from combinations of group III and V compounds and alloys [10]. Gallium arsenide is the most technologically important and studied compound semiconductor material. A systematic theoretical study of GaAs surface based on accurate, self consistent

total energy were investigated using density functional theory. Many band structure parameters for gallium arsenide are known with a greater precision than for any other compound semiconductors. Particularly the studies were focused on its direct band gap for photonic applications, nanotubes, its internal carrier transport and higher mobility for generating microwaves. This semiconducting material is truly many body system. Eventhough, there were many investigations; the electronic and structural properties of GaAs is not well studied computationally. So, the main target of this study is to investigate electronic and structural properties of GaAs with the help of density functional theory.

1.3 Objectives

1.3.1 General objective

The general objective of this study was to determine the electronic and structural properties of GaAs with respect to density functional theory.

1.3.2 Specific objective

The Specific objectives of this study were:

- To calculate the total minimum energy of GaAs per cell with respect to cutoff energy,

- To calculate the total minimum energy of GaAs per cell with respect to **k** points sampling,

- To calculate the total minimum force of GaAs per cell with respect to cutoff energy,

- To calculate the total minimum force of GaAs per cell with respect to **k** points sampling,

- To calculate the lattice constant of GaAs with respect to total energy.

1.4   Significance of the Study

This study would help to understand the electronic and structural properties of GaAs using a computational technique known as DFT. It also helps to practice new problem solving method.

1.5   Limitation of the Study

The scope of the study were limited to the calculations of electronic and structural properties of GaAs with the help of density functional theory. .

Chapter 2

Literature Review

2.1   Introduction

Gallium Arsenide compound were first investigated as semiconducting materials, it does not occur naturally, but may be found in zones of active or extinct volcanic activity. The interatomic bonding is largely covalent [11]. The direct band gap and high electron mobility of this material held the promise of new and unique devices such as high efficiency light emitters, light sensors and high speed switching devices [12]. It has a very high resistivity because of its wide band gap and also have high temperature performance. Its high electron mobility was the reason for much of the early research and development of GaAs field effect transistors. The driving force was to increase the operating frequency of transistor devices. Gallium arsenide exhibits the transferred electron (TE) effect. This is an electric field-induced transfer of electrons from one region of the energy band structure to another, which results in a negative resistance being observed at microwave frequencies. The applications of the effect are as microwave oscillators, amplifiers, and transferred electron devices (TEDs)[13]. There has been a great deal of research and development of GaAs devices. Utilizing the above features, results in the widespread commercial applications of

TEDs, GaAs FETs, ICs, LEDs and Lasers. The direct band gap of GaAs allows for emission of photons in LEDs and LASER devices. Transitions between the valance band and the conduction band require only a change in energy, but not change in momentum [13]. Semiconductor technology devices based on GaAs circuitry are a key element of many wireless and wi-fi consumer electronic products. GaAs is also used in specialized applications in which for example, high speed is required. GaAs-based solar cells also have many advantages, such as high photoelectric conversion efficiency, fine radiation resistance and good performance at high temperatures, etc. Doping other elements is one of the most commonly used methods, and is performed by replacing a small amount of anion species in GaAs with isovalent impurities, such as N, P, Sb.

2.1.1 Many Body Problems

Many body problems are very difficult to solve. That is the state of motion can not be solved analytically for systems in which three or more distinct masses interact. Atoms are made up of electrons and nuclei. In quantum mechanics, the electron is considered as wave functions rather than a classical particle. The solid or quantum system exhibits different electronic, electrical, transport and optical properties [15]. Schrödinger equation is used to solve the electronic structure of any time independent quantum system. The equation is given by

$$\hat{H}\Psi = E\Psi \tag{2.1.1}$$

where,

$$\hat{H} = -\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 - \sum_{(i,I)}\frac{Z_I e^2}{|r_i - R_I|} + \frac{1}{2}\sum_{(i\neq j)}\frac{e^2}{|r_i - r_j|} - \sum_I \frac{\hbar^2}{2M_I}\nabla_I^2 + \frac{1}{2}\sum_{(I\neq J)}\frac{Z_I Z_J e^2}{|R_I - R_J|} \tag{2.1.2}$$

Here, m_e and M_I represents the electron mass and nuclei mass respectively, r_i and R_I are positions of electron and nuclei. Z_I is charge of nuclei and e is charge of electron. The complex system is made-up of electrons and nuclei interacting each other due to coulomb force. The first and fourth terms represent the kinetic energy of electrons and nuclei respectively, the second term is the attractive interaction between the electron and nuclei, the third term is electron-electron repulsion term and the last term is nuclei-nuclei repulsion. Since, the real Hamiltonian of solids consists of electrons and nuclei of the order of 10^{23}, the problem is impossible to solve. So, we need new approximation to solve the many-body problem.

2.1.2   Born-Oppenheimer approximation

Born-Oppenheimer approximation is the early approximation used to solve the Hamiltonian by considering the fact that the nuclei can not move as much as electron due to its heavy mass [16]. Thus, the kinetic energy of nuclei term was omitted from the Hamiltonian equation and the new Hamiltonian is given by

$$\hat{H} = -\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 + \frac{1}{2}\sum_{(i\neq j)}\frac{e^2}{|r_i - r_j|} + V_{R\alpha}^{ext}(r_i) \qquad (2.1.3)$$

Even after omitting the nuclei terms in old Hamiltonian, still the electrons are in the order of 10^{23} making an exact solution impossible. Therefore, a new approximation is necessary, to solve the hamiltonian whereby considering number of independent particles (electrons) or by other variables as input [16, 17].

2.1.3   Density Functional Theory (DFT)

As the name density-functional theory (DFT) suggests, DFT is a many-body theory based on the idea of using only the density as the basic variable for describing many

electron systems [17, 18]. Since its introduction in the 1960s density functional theory has evolved into a powerful tool that is widely used in condensed matter theory and computational materials for the calculation of electronic, magnetic, and structural properties of solids. The method has been remarkably successful in predicting, reproducing, and/or explaining a wide variety of materials' phenomena. Density functional theory (DFT) is an extremely successful approach used to solve many body problems and to calculate the first principles of electronic structure. In 1964, Hohenberg and Kohn made conceptual roots to this theory [19]. It is a phenomenally successful approach to finding solutions to the fundamental equation for the quantum behavior of atoms and molecules, the Schrodinger equation, in settings of practical value, for the description of ground state properties of metals, semiconductors, and insulators. The success of density functional theory (DFT) not only encompasses standard bulk materials but also complex materials such as proteins and carbon nanotubes, it is the most successful method that forms the basis for advanced ab-inito (the fact that no experimental data is used and computations are based on quantum mechanics) calculations. By using DFT theory it is possible to calculate the properties of solids and molecules [20]. The DFT uses as a basic variable the electron density rather than considering many interacting and non-interacting electron wave functions in the external potential. DFT was formerly framed on two basic theorems.

2.1.4   The Hohenberg-Kohn Theorems

Theorem 1

The first Hohenberg-Kohn theorem states that if there are N interacting particles in a system and they are moving in an external field $V_{ext}(r)$, the $V_{ext}(r)$ is uniquely determined by the ground state particle density $n_o(r)$ up to a constant; that means

there are no two potentials existing to give rise to the same ground state. The ground state expectation value of any observable (Hamiltonaian) is a unique functional of the exact ground-state electron density $\rho_o(r)$ [21].

$$\langle \Psi | A | \Psi \rangle = A[\rho_o(r)] \tag{2.1.4}$$

Theorem 2

The second theorem of HK states that a universal functional for energy can be defined in terms of density, which is valid for any applied external potenial. The functional of the exact ground state energy of a system will have lowest energy only when the input density is the real ground density state [22].

$$E_o \leq E[\tilde{\rho}] = T[\tilde{\rho}] + E_{Ne}[\tilde{\rho}] + E_{ee}[\tilde{\rho}] \tag{2.1.5}$$

From the above first theorem one can conclude that if we know the ground state particle density, it is possible to reconstruct the new Hamiltonian. Schrödinger equation was used to solve the new many-body wave functions for new $\hat{H}$. They are independent of number of particles and purely dependent on electron density. The Second theorem states that the exact ground state is the global minimum value of the functional.

2.1.5 The Kohn-Sham Approximation

Kohn-Sham proposed new approach to solve many electron system based on the H-K theorems [23]. Total energy functional in an external potential $V_{ext}(\vec{r})$ can be

$$E[\rho(\vec{r})] = T[\rho(\vec{r})] + \int V_{ext}(\vec{r})d^3r + E_{ee}[\rho(\vec{r})] \tag{2.1.6}$$

$$E_{ee}[\rho(\vec{r})] = \int \int \frac{\rho(\vec{r})\rho(\acute{r})}{|r - \acute{r}|}d^3r d^3\acute{r} + \hat{E}_{xc}[\rho(\vec{r})] \tag{2.1.7}$$

11

The first term is the kinetic energy $T[\rho(\vec{r})]$, the second term is electron-electron potential and the last term contributes for both classical and non-classical exchange behind the mean field theory [24]. To solve the Kohn and Sham equations, it is assumed that for an interacting system describing the equation, there is a reference noninteracting system with ground state density same as interacting system [25]. The equation for the reference system can be written as

$$H_{eff}|\Psi_i\rangle = [-\sum_i \nabla_i^2 + V_{eff}[\rho(\vec{r})]|\Psi_i\rangle = \epsilon_i|\Psi_i\rangle \qquad (2.1.8)$$

Then, the kinetic energy of this system is

$$T_{eff}[\rho(\vec{r})] = \sum_i n_i\epsilon_i - V_{eff}[\rho(\vec{r})] \qquad (2.1.9)$$

The new pseudo kinetic energy in the form of exchange correlation energy functional $E_{xc}[\rho(\vec{r})]$ can be wirtten as

$$E_{xc}[\rho(\vec{r})] = T[\rho(\vec{r})] - T_{eff}[\rho(\vec{r})] + \hat{E}_{xc}[\rho(\vec{r})] \qquad (2.1.10)$$

Inserting the new exchange correlation functional into total energy system and deriving the new total energy of the non interacting system which is in potential with respect to $\rho(\vec{r})$, conserving the density,

$$\int \rho(\vec{r})dr = N \qquad (2.1.11)$$

where N is the total number of electrons. Solving the above 2 equations (2.1.8 and 2.1.9), we will obtain final Kohn-Sham equation. The one-electron Schrödinger like equation which is moving in a potential V_{eff} is

$$\epsilon_i\Psi_i(\vec{r}) = [-\nabla^2 + V_{eff}[\rho(\vec{r})]]\Psi_i(\vec{r}) \qquad (2.1.12)$$

and we get the final ground state energy given by

$$E_o = \sum_i n_i \epsilon_i - \int \int \frac{2\rho(\acute{r})}{|r - \acute{r}|} d^3\acute{r} - \int \frac{\rho E_{xc}[\rho]}{\delta \rho(\vec{r})} d^3r + E_{xc}[\rho(\vec{r})] \qquad (2.1.13)$$

where E_{xc} is the exchange-correlation potential which is unknown. So if we know the exact functional of E_{xc}, then, we know the exact solution of the many electron system.

2.1.6 Exchange-Correlation Functional approximations

No analytical solution has been made to solve the Kohn-Sham equations [26]. So we need more approximations to solve such a difficult and complicated equations. The new approximations such as Local Density Approximation (LDA) and Generalised Gradient Approximations are implemented analytically and solve many difficult of DFT.

Local Density Approximation (LDA)

The Local Density Approximation is an approximation for the exchange-correlation (xc), which can be defiend as

$$E_{xc}^{LDA} = \int d^3r \epsilon_{xc}(n_o)|n_o \to n(r) \qquad (2.1.14)$$

where $\epsilon_{xc}(n_o)|n_o \to n(r)$ is the exchange-correlation energy in a homogeneous electron gas with the density $n_o = n(r)$, i.e, replacing the local density n(r) of an inhomogeneous system at each point r by the constant density n_o of homogeneous electron gas [27].

Generalized Gradient Approximation (GGA)

LDA approximation fails to predict exact exchange energy when its density undergoes rapid (quick) changes in molecules. This problem can be solved by considering the

gradient of the electron density. The GGA approximation principally made by Perdew and co-workers [28]. The exchange-correlation energy is defined as,

$$E_{xc} = E_{xc}[\rho(r), \nabla\rho(r)] \tag{2.1.15}$$

Perdew-Burke-Ernzernhof (PBE)

PBE is a new version of GGA. The exchange energy of PBE approximation can be defined as an integral over the exchange density [29].

$$E_x^{PBE} = \int dr\rho(r)\epsilon_x^{PBE}(\rho(r)), s(r) \tag{2.1.16}$$

where

$$s = |\nabla|/(2k_F\rho) \tag{2.1.17}$$

is the reduced gradient with

$$k_F = (3\Pi^2\rho)^{\frac{1}{3}} \tag{2.1.18}$$

The PBE exchange energy density is the product of LDA exchange and enhancement factor, F_x^{PBE} which depends on s(r), which is defined in explicitly PBE functional.

$$\epsilon_x^{PBE}(\rho(r)), s(r)) = \epsilon_x^{LDA}(\rho(r)) \times F_x^{PBE}s(r)) \tag{2.1.19}$$

$$F_x^{PBE}s(r) = -\frac{8}{9}\int_0^\infty ydyJ^{PBE}(s, y) \tag{2.1.20}$$

Where, $J^{PBE}(s, y)$ is the PBE exchange hole.

2.1.7 Periodic Supper Cells

For solids the wave function of an electron placed in a periodic potential, i.e, the effective potential derived in a K-S equation has a periodicity of the crystalline lattice.

We can write K-S orbitals $\psi_k^n(r)$, as a product of a plane wave $e^{ik.r}$ and periodic function, $u_k^n(r)$ that has a periodicity of a lattice satisfying a fundamental property called 'Bloch's theorem'.

Bloch's Theorem

States that "in a periodic solid each electronic wave function can be written as the product of cell- periodic part and wave like part" [30-32].

$$\psi_k^i(r) = e^{i\vec{\mathbf{k}}.\vec{r}} u_k^n(r) \tag{2.1.21}$$

where $\mathbf{k}$ is vector in first Brillouin zone and n is a band index. Due to its periodicity $u_k^n(r)$ can be expanded as a set of plane waves,

$$\psi_k^n(r) = \frac{1}{\sqrt{\Omega_{cell}}} \sum_j c_j^n(k) e^{i(k+\mathbf{k}_j).r} \tag{2.1.22}$$

where k_j is the reciprocal lattice vector, Ω_{cell} cell is the volume of the primitive cell. Transferring the K-S orbitals to plane wave basis set, we obtained

$$\sum_{j\prime} Hjj'(k)c_{j\prime}^n(k) = \epsilon_n(k)c_j^n(k) \tag{2.1.23}$$

where

$$Hjj'(k) = \frac{\hbar^2}{2m}|k + K_j|\delta_{jj'} + V_{eff}(K_j - K_{j\prime}) \tag{2.1.24}$$

The above term is the matrix element of kinetic energy operator where the plane waves are orthonormalized once.

$$V_{eff}(K_j - K_{j\prime}) = \int_{\Omega_{cell}} V_{eff}(r) e^{i(k_j - k_{j\prime}).r} \tag{2.1.25}$$

where $\mathbf{k}$ and $\mathbf{K}$ are real space wave and reciprocal lattice vectors respectively. The above term is effective potential. By diagonalization of Hamiltonian, one can get

discrete set of eigenvalues and corresponding eigenfunctions for all n band index at each K point. The energy eigenvalue looks like,

$$\epsilon_n(k) = \epsilon_n(k + K) \tag{2.1.26}$$

We can choose cut-off vector in reciprocal space, K as

$$K \leq K_{max} \tag{2.1.27}$$

where K_{max} is the reciprocal space wave vector corresponding to the energy cut-off.

Energy cutoffs

Limit the number of plane wave componenets to those such that,

$$(\frac{G + K^2}{2}) \leq E_{cut} \tag{2.1.28}$$

This defines a length scale $\lambda = \frac{\Pi}{\sqrt{E_{cut}}}$. The discussion of **k** space began with Bloch's theorem, which tells us that solutions of the Schrödinger equation for a supercell have the form

$$\psi_k(r) = u_k(r)e^{i\vec{\mathbf{k}}.\vec{r}} \tag{2.1.29}$$

For $u_k(r)$ periodic in space with the same periodicity as a supercell, its periodicity can be expanded interms of a plane waves.

$$u_k(r) = \sum_{\mathbf{G}} c_i, Ge^{i\mathbf{G}r} \tag{2.1.30}$$

where the sumation is over all vecors given by

$$\overrightarrow{G} = n_1 \overrightarrow{b}_1 + n_2 \overrightarrow{b}_2 + n_3 \overrightarrow{b}_3 \tag{2.1.31}$$

with integer values for n_i, where $\overrightarrow{G}$ in a reciprocal lattice vector. For any real space lattice vector l_i, $G.l = 2\Pi n$, The two equations (2.1.28 and 2.1.29) combined to give

$$\psi_k(r) = \sum_G c_i, k + G e^{[i(k+G).r]} \tag{2.1.32}$$

Then the solutions with kinetic energy

$$E = \frac{\hbar^2}{2m}|k + G|^2 \tag{2.1.33}$$

The solutions with lower energies are more physically important than solutions with very high energies to define the length scale and the condnced matter easily. Therefore, it is obvious to shorten the infinite sum above to include only solutions with kinetic energies less than some value:

$$E_{cut} = \frac{\hbar^2}{2m}G_{cut}^2 \tag{2.1.34}$$

Then for the infinite sum it reduces to

$$\psi_k(r) = \sum_{|G+k|<G_{cut}} c_{G+k} e^{[i(K+G)r]} \tag{2.1.35}$$

The expression above slightly consists of different numbers of terms for different values of k. The discussion introduced one more parameter that must be defined whenever a DFT calculation is performed over cutoff energy, E_{cut}. In many ways, this parameter is easier to define than the **k** points.

K points sampling

The most widely used standard method (solution) was developed by Monkhorst and pack in 1976. Which is a regular grid in **k** space (an integration grid in the first BZ) [33, 34]. One can use these methods, and obtain an accurate approximation

for the electronic potential and the total energy of an insulator or semiconductor by calculating the electronic states at a very small number of **k** points. The electronic potential and total energy are more difficult to calculate if the system is metallic. The magnitude of any error in the total energy due to inadequacy of the **K** points sampling can always be reduced by using a denser set of **k** points. The computed total energy will converge as the density of **k** points increases, and the error due to the **k** point sampling approaches zero. In principle, a converged electronic potential and total energy can always be obtained provided that the computational time is available to calculate the electronic wave functions at sufficiently dense set of **k** points. The computational cost of performing a very dense sampling of **k** space can be significantly reduced by using the **k** points total energy method.

Plane wave basis sets

Bands represented on reciprocal space grid with in cut-off. Blochs theorem states that "the electronic wave functions at each **k** points can be expanded in terms of a discrete plane-wave basis sets". In principle, an infinite plane wave basis set is required to expand the electronic wave function. However, the coefficients $C_i, K + G$, for the plane waves with small kinetic energy, $\frac{\hbar^2}{2m}|K + G|^2$ are typically more important than those with large kinetic energy. Thus, the plane wave basis set can be shorten to include only plane waves that have kinetic energies less than some particular cutoff energy. If a continuum of plane wave basis states were required to expand each electronic wave function, the basis set would be infinitely large no matter how small the cutoff energy. Application of the Bloch theorem allows the electronic wave functions to be expanded in terms of a discrete set of plane waves. Introduction of any energy cutoff to discrete plane wave basis set produces a finite basis set.

2.1.8 Self-Consistent Kohn-Sham Equation

Here,we disscuss self-consistent Kohn-Sham algorithm to calcaulte ground state density and its energy from the Kohn-Sham non interacting system of equations. In first step, we assumed some initial electron density, calculate the effective potential energies and K-S equations to calculate new electron density. The diagonalization of Hamiltonian in K-S equations can be done by using different diagonolization methods. The new electron density from previous step is compared with old density. If the difference of two electron densities is zero, then, we stop the calculation otherwise put the new electron density into first step and repeat the above steps until converged solution is obtained. Converged electron density is used to calculate the eigenvalues, forces, energies and stresses [33].

Pseudopotentials

The fundamental idea of a pseudopotential is to replace one problem with another. The concept of a pseudopotential is related to replacing the effects of the core electrons with an effective balance electrons [33]. The pseudopotential generation procedure starts with the solution of the atomic problem using the Kohn-Sham approach. Once the KS orbitals are obtained, we make an arbitrary distinction between valence and core states. The core states are assumed to change very little due to changes in the environment so their effect is replaced by a model potential derived in the atomic configuration and it is assumed to be transferable. The valence states are seen to oscillate rapidly close to the core regions. With the introduction of the new potential, the valence states are made smoother. Let's now work out the pseudopotential transformation in its most general framework. Assume that we have a Hamiltonian

$\hat{H}$, core states $|x_n\rangle$ and core eigenvalues E_n. We are looking for a single valence state $|\Psi\rangle$. Let's replace the valence state by the smoother $|\Phi\rangle$ and expand the remaining portion in terms of core states[33].

$$|\Psi\rangle = |\Phi\rangle + \sum_n^{core} a_n|x_n\rangle \qquad (2.1.36)$$

Next, we take the inner product of the above equation with one of the core states. Because the valence state has to be orthogonal to the core states, we have

$$\langle x_n|\Psi\rangle = \langle x_n|\Phi\rangle + \sum_n^{core} a_n\langle x_m|x_n\rangle = 0 \qquad (2.1.37)$$

where $\sum_n^{core} a_n\langle x_m|x_n\rangle = 0$ is a_m the right-hand side of the above equation in terms of the pseudofunction,$|\Phi\rangle$

$$|\Psi\rangle = |\Phi\rangle - \sum_n \langle x_n|\Phi\rangle|x_n\rangle \qquad (2.1.38)$$

Applying the Hamiltonian on the expression above, we get

$$\hat{H}|\Phi\rangle + \sum_n^{core} (E - E_n)|x_n\rangle\langle x_n|\Phi\rangle = E|\Phi\rangle \qquad (2.1.39)$$

As a result, the smooth, pseudo wavefunction satisfies an effective equation with the same eigenenergy of the real valence wave function. In the case of isolated atoms, the indices n corresponds to the combined index $n_l m_l$ including the principal quantum number n, the angular momentum quantum number l and the magnetic quantum number m_l [34]. The above equation may then be written as an eigenvalue equation for the smooth pseudo wave function as

$$(\hat{H} + \hat{V}_{nl})|\Phi\rangle = E|\Phi\rangle \qquad (2.1.40)$$

where the extra potential $\hat{V}_{nl}$ depends on the angular momentum quantum number l due to spherical symmetry and its effect is localized to the core. Since $E > E_n$

20

by definition, it is a repulsive potential and it partially cancels the effect of the attractive Coulombic potential. The resulting potential is then a much weaker one than the original potential. This shows that the eigenstates of this new potential are smoother[35].

Chapter 3

Materials and Methodology

3.1 Materials

An intensive survey of literature from published articles, books, MSc. thesis and lecture note has been carried out on the project title.

3.2 Methodology

3.2.1 Computational methodology

The calculations would be based on density functional theory (DFT) with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional, Vanderbilt ultra soft pseudopotentials [36], and the plane wave basis set would be implemented in the Quantum-ESPRESSO program package [37]. Quantum ESPRESSO (Quantum opEn-Source Package for Research in Electronic Structure, Simulation, and Optimization), is an integrated suite of computer codes for electronic-structure calculations and materials modeling based on density-functional theory (DFT)[38], plane waves basis sets (PW) and pseudo potentials(PP)[39]. It is freely available and distributed as open-source software under the terms of the GNU (name of the free software foundation's project to develop a free UNIX-like operating systems, including the legal framework, such as

the source code and documentation) General Public License (GPL). The present applicability of quantum espresso ranges from simple electronic structure calculations to the most sophisticated theoretical spectroscopy such as nuclear magnetic resonance (nmr), Electron Paramagnetic Resonance (EPR), Raman and Scanning Tunneling Microscopy, etc. The most important input parameters in Quantum Espresso are the atomic geometries (number and types of atoms in the periodic cell, bravais-lattice index, crystallographic or lattice constants), the kinetic energy cutoff and the type of pseudopotentials [40].

Chapter 4

Results and discussions

Introduction

The structural and electronic properties of Gallium arsenide were calculated with respect to the density functional theory. One of the important aspects in studied GaAs was the total minimum energy. Results are mainly presented in Tables and Figures. The first results are the total minimum energy per cell and second results are force values for bulk Gallium arsenide. Then, the results for the equilibrium lattice constants with respect to total energy. The output files of the computations were used to deduce the Tables of energy cutoffs, $\mathbf{K}$ points and lattice constants against the total energies and graphs were plotted to obtain the optimized parameters for GaAs structure with in both LDA and GGA .

Table 4.1: The results of total minimum energy computed with energy cutoffs

Energy cutoffs(Ry)	Total minimum energy(Ry)
20	-190.69068564
30	-191.02127024
40	-191.02226521
50	-191.02425886
60	-191.02429954
70	-191.02451629
80	-191.02456173
90	-191.02458235
100	-191.02461137
110	-191.02462519
120	-191.02462904
130	-191.02463756
140	-191.02464318
150	-191.02464431

4.1 Total energy of GaAs per unit cell with respect to energy cutoffs

Here it has given an input $4 \times 4 \times 4$ **K** points mesh; some of these **K** points have nearly the same energy because of the symmetry of the crystal. The calculation was done using different values of energy cutoffs, starting from 20 to 150 Ry and lattice constant of 10.6827 Bohr.

4.1.1 Convergence test of total minimum energy of GaAs with respect to energy cutoffs

We see that, the total minimum energy of GaAs is calculated as a function of energy cutoff. The increasing value of energy cutoff for wave function is made until the convergence is achieved. We can see from Fig 4.1 that, the total minimum energy converge at 50 Ry plane wave cutoff energy and the total minimum energy had its minimum at -191.02425886 Ry. The total minimum energy is the sum of one electron contribution, hartree contribution, xc contribution and ewald contribution. Moreover, the total minimum energy decreases with increasing energy cutoffs for wave function.
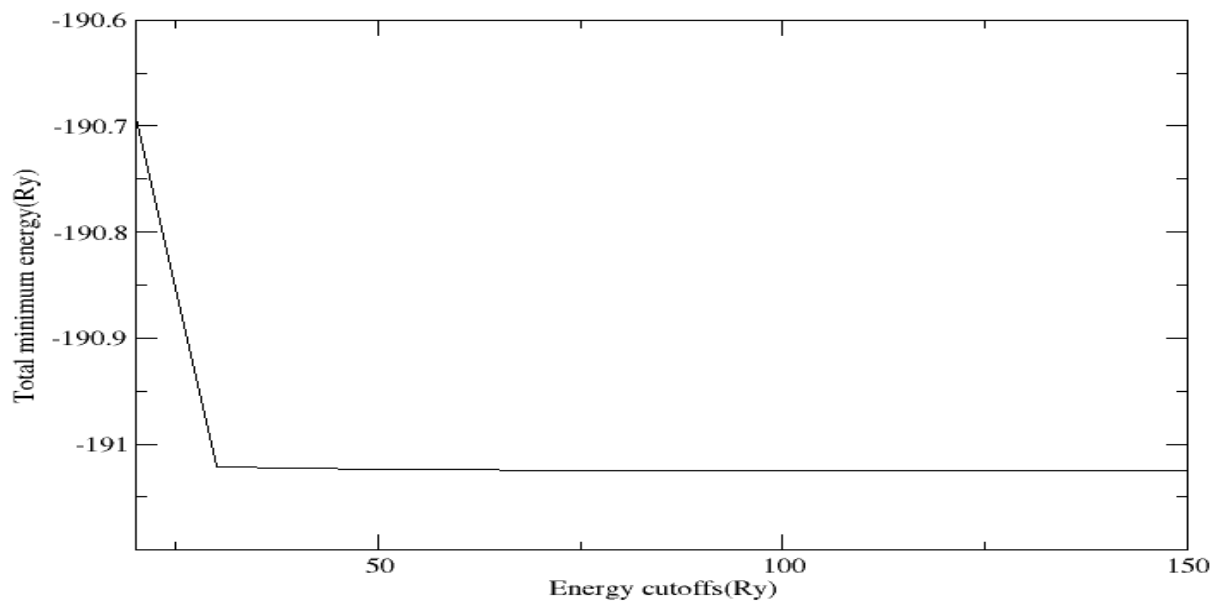
Figure 4.1:   *Total minimum energy of GaAs with respect to energy cutoffs*

Table 4.2: The results of the total minimum energy computed with **K** points grid size

kpoints grid	Total minimum energy(Ry)
4	-190.66288269
6	-190.66257510
8	-190.66010672
10	-190.66157751
12	-190.66174778
14	-190.66118085
16	-190.66069368
18	-190.66094901
20	-190.66108072

4.2 Total minimum energy of GaAs per unit cell with respect to K points grid size

In this case, the calculation was done using different **K** points value from $4 \times 4 \times 4$ to $20 \times 20 \times 20$ mesh with 2.0 points.

4.2.1 Convergence test of total energy of GaAs with respect to K points grid size

The total minimum energy of Gallium arsenide is calculated as a function of **K** points grid size using PWSCF code. For this calculation, the other variables (lattice constant, energy cutoff) are kept constant. The total energy of GaAs versus **K** points grid size is shown in Fig 4.2. It can be observed that the total minimum energy of Gallium arsenide converges at $8 \times 8 \times 8$ **K** points grid and the total ground state energy has its minimum at -190.66010672 Ry.

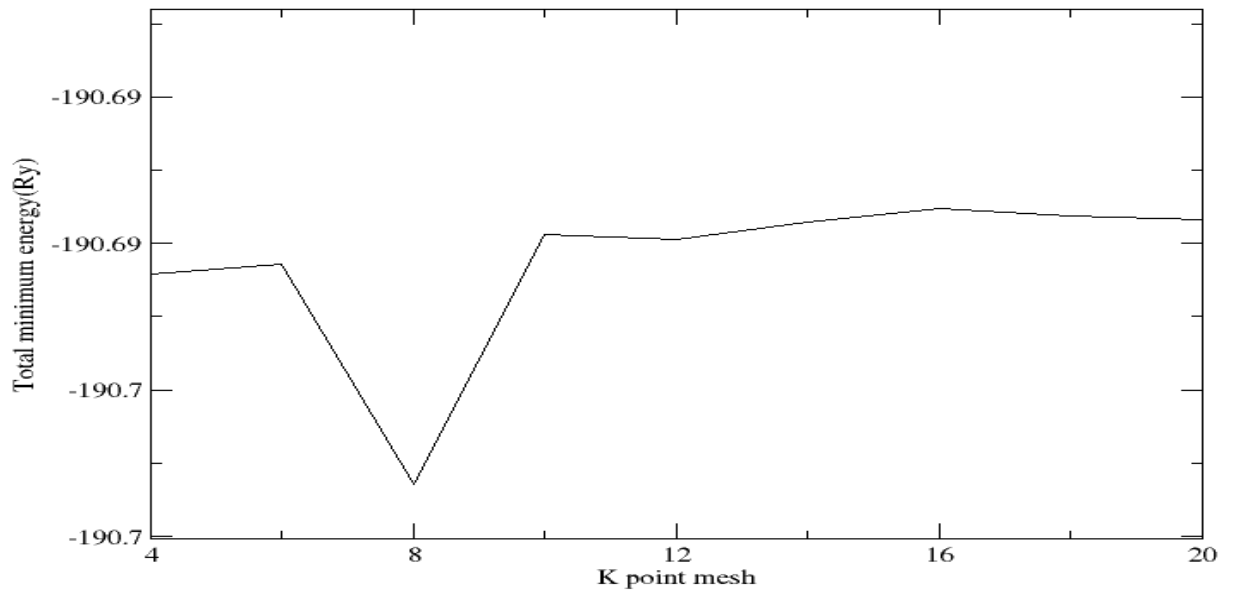Figure 4.2:   *Total minimum energy of GaAs with respect to **K** points mesh*

Table 4.3: The results of total minimum force of GaAs with respect to energy cutoffs

Energy cutoffs(Ry)	Total force(Ry/Bohr)
20	0.143301
30	0.140369
40	0.140311
50	0.140363
60	0.140394
70	0.140386
80	0.140383
90	0.140379
100	0.140378
110	0.140391
120	0.140399
130	0.140401
140	0.140420
150	0.140413

4.3 Total minimum force of GaAs with respect to energy cutoffs

4.3.1 Convergence test of total minimum force of GaAs with respect to energy cutoffs

It is possible to create forces by displacing Arsenic atom 0.05 Bohr in the z direction on GaAs compound. Here we calculated total force on GaAs as a function of plane wave cutoff energy by keeping other parameters fixed. For this calculation, we used the lattice constants a = 10.6827 Bohr and $4 \times 4 \times 4$ **K** points grid. In this simulation convergence is achieved when the energy cutoff is equal to 60 Ry. A total force value at this energy cutoff is 0.140394 Ry/Bohr.
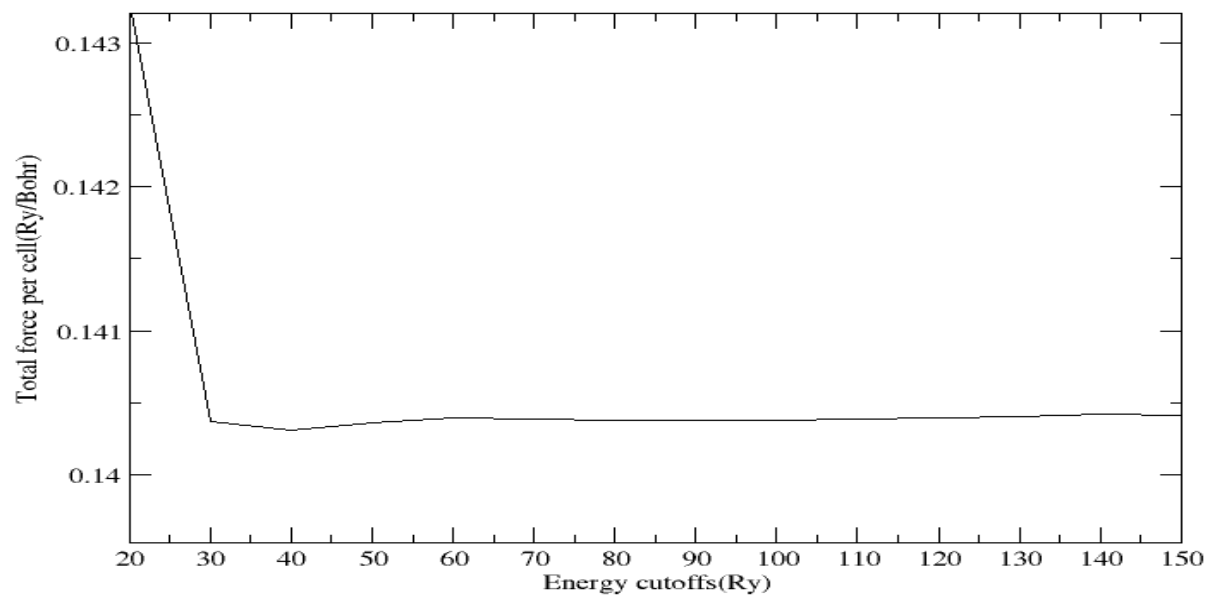
Figure 4.3:   *Total minimum force of GaAs with respect to energy cutoffs*

Table 4.4: The results of the total minimum force computed with **K** points grid size

kpoints grid	Total force(Ry/Bohr)
4	0.143317
6	0.143301
8	0.143251
10	0.143273
12	0.143251
14	0.143262
16	0.143261
18	0.143262
20	0.143258

4.4 Total minimum force of GaAs per unit cell with respect to K points sampling

4.4.1 Convergence test of total minimum force of GaAs with respect to K points sampling

We have calculated the force on 0.05 Bohr displaced As as a function of **K** points grid size, by keeping other parameters (lattice constant, energy cutoff) constant. The calculated force with respect to **K** points grid is shown in Table 4.4. Moreover, as it is observed in Fig 4.4 that, the total force converge at the grid size of $14\times14\times14$ **K** points mesh; and its value is 0.143262 Ry/Bohr. Generally, it is clear that different structural geometries will require different **K** points meshes in order to reach convergence.

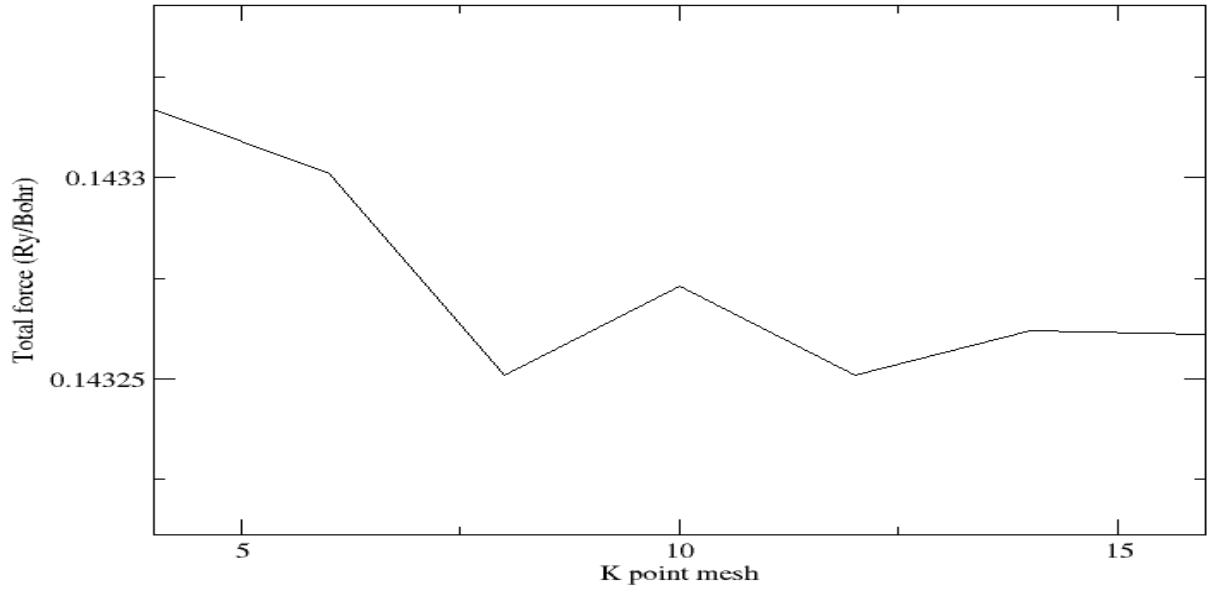Figure 4.4: *Total minimum force of GaAs with respect to **K** points sampling*

Table 4.5: The result of total energy of GaAs computed versus lattice constant

Lattice constant(Bohr)	Total energy(Ry)
10.1	-190.61174104
10.2	-190.62970838
10.3	-190.63773422
10.4	-190.64264967
10.5	-190.66189009
10.6	-190.65677732
10.7	-190.65977732
10.8	-190.66524938
10.9	-190.67136727
11.0	-190.67131668
11.1	-190.66541121

4.5 Total energy of GaAs computed with respect to lattice constant

4.5.1 Convergence test of total energy of GaAs computed versus lattice constant

The equilibrium lattice constant of GaAs were calculated by performing total energy calculation for a series of plausible parameters. In this case energy cutoff and the **K** points were kept constant. The computational calculation shows that the equilibrium lattice constant is 10.5565 Bohr. This result is approximately in good agreement with experimental value 10.6827 Bohr.
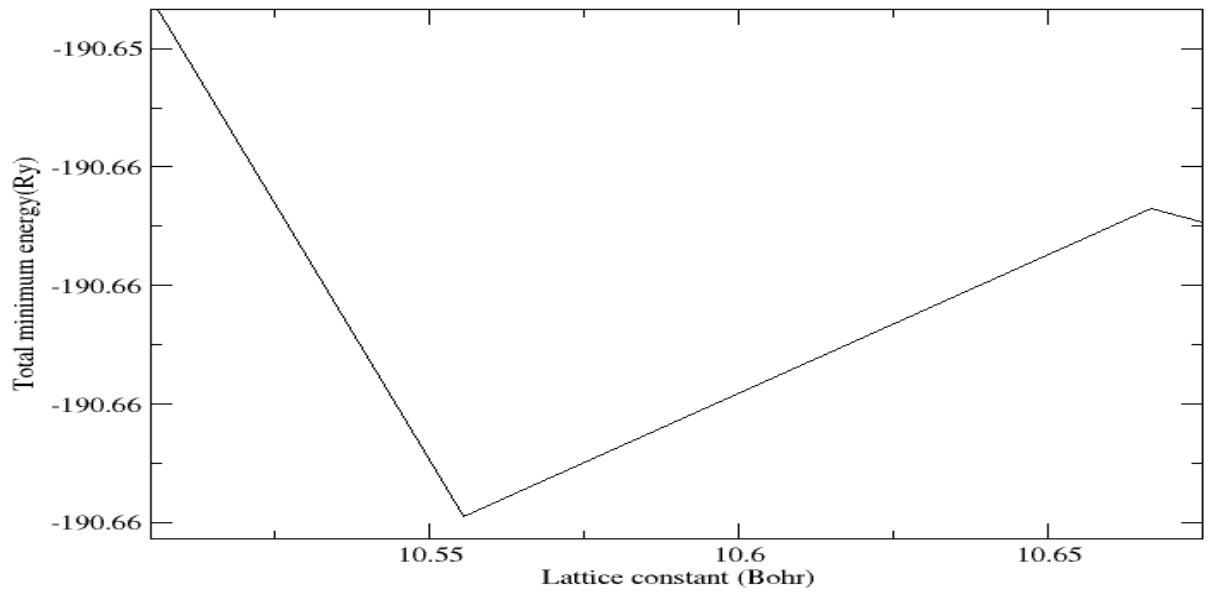
Figure 4.5:   *Total energy of GaAs versus lattice constant*

Chapter 5

Conclusion

The electronic and structural properties of Gallium arsenide (GaAs) were investigated within the frame work of the density functional theory, plane wave basis sets, and pseudo potentials (ultra-soft). All calculations have been done with the help of Quantum Espresso package (software). The total minimum energy calculated as a function of cutoff energy and Monkhorst pack-grid size, respectively keeping the other parameters constant. The total energy convergence test is achieved, at the energy cutoff 50 Ry for the first case and at $8 \times 8 \times 8$ **k**- points grid size for the second case. The total minimum energy is -191.02425886 Ry for the first case and -190.66010672 Ry for the second case. The total minimum force on GaAs as a function of cutoff energy and Monkhorst-Pack grid is calculated by displacing Arsenic atom by 0.05 Bohr in the z direction. Total force convergence test is achieved for the cutoff energy 60 Ry and for Monkhorst-Pack grid at $14 \times 14 \times 14$ **k**- points grid size. The numerical calculation shows that the equilibrium lattice constant is 10.5565 Bohr. This result is nearly in good agreement with experimental value 10.6827 Bohr.

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Course Code	Course Title	Cr. hr	Number Grade	Rank **	Remark
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**Ecellent, Very Good, Good, Satisfactory, Fail.

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