An-Najah National University Faculty of Graduate Studies

# FP-LAPW Study of Structural, Electronic, Elastic and Optical Properties of Alkali Hydrides Compounds XH (X= Li, Na, K, Rb, Cs)

By

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# Dedication

To the Memory of my Mother.

To my father who was a constant inspiration to me.

To my wife who always encourages me to further my study.

To my brothers and sisters.

To my children: Qusay, Shaimae, Boraq, Ameen, Ahmed and Sham.

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## الاقرار

أنا الموقع أدناه مقدم الرسالة التي تحمل عنوان:

# FP-LAPW Study of Structural, Electronic, Elastic and Optical Properties of Alkali Hydrides Compounds XH (X= Li, Na, K, Rb, Cs)

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## Declaration

The work provided in this thesis, unless otherwise referenced, is the researcher's own work, and has not been submitted elsewhere for any other degree or qualification.

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### Abstract

Based on the density functional theory, the full-potential linearized augmented plane wave (FP-LAPW) method has been carried out to determine the structural stability of different crystallographic phases, the pressure-induced phase transition, the electronic properties, the elastic constants and their related properties, the mechanical properties, the thermodynamic properties as well as the optical properties of LiH, NaH, KH, RbH and CsH compounds. The rocksalt (RS), zincblende (ZB), cesium chloride (CsCl) and wurtzite (WZ) structures are considered. The Perdew, Burke and Ernzerhof Generalized Gradient Approximation (PBE-GGA) approach was used for the exchange-correlation potential to compute the equilibrium structural parameters, transition pressure, elastic constants and their related properties, the mechanical properties as well as the thermodynamic properties. The PBE-GGA and modified Becke-Johnson (mBJ-GGA) schemes have been used for the exchange-correlation potential to calculate the band structures and optical properties. The alkali hydrides lattice constant increases as going from Li to Cs in the periodic table, while bulk modulus decreases. The calculated band structures using the mBJ-GGA approach have an insulating nature for these compounds in all the considered structures, except the LiH and CsH in CsCl structure, which show a semi-conducting behavior. The calculated elastic constants for alkali hydrides in the four structures RS, CsCl, ZB and WZ at ambient

pressure are mechanically stable, except LiH and NaH in CsCl structure. The mBJ-GGA scheme is found to be more accurate than PBE-GGA in computing the energy-band gap and optical properties compared to the experimental results. The elastic constants (C11, C44, B) and their related properties in the RS structure are increasing with increasing pressure,  $C_{12}$ decreases as the pressure increases indicates that these compounds are unstable under high pressure, and the RS structure transforms to CsCl structure. Elastic constants, bulk modulus, Shear modulus (stiffness) and Debye temperatures of these compounds decrease as going from Li to Cs in the periodic table. These compounds in the RS structure are more mechanically stronger at ambient conditions. Alkali hydrides except the LiH and CsH in CsCl structure are suitable as dielectric compounds; they have a wide direct energy band gap. Alkali hydrides have a wide absorption region, on the other hand NaH and RbH absorption is very huge compared with LiH, KH and CsH absorption. NaH and RbH are excellent absorbent materials; maximum absorption regions are located in the middle ultraviolet (MUV) region and far ultraviolet (FUV) region. LiH, RbH and CsH compounds are also found to be a wide direct energy band gap; therefore, they could be suitable for the optoelectronic UV device applications. The absorption coefficient  $\alpha(w)$ , imaginary part of dielectric constant  $\varepsilon_2(w)$  and the extinction coefficient k(w) for alkali compounds vary in the same way. The calculated ground state parameters for these compounds in each structure are well compared with the available theoretical and experimental results, and most of them are in good agreement with other calculations and experimental measurements.

# Chapter One Introduction

Hydrogen is the lightest element in the periodic table, which is why alkali hydrides XH (X=Li, Na, K, Rb and Cs) have the simplest structures. These molecules attract researchers in various areas because they have the simplest electronic structure which enabling comparisons between different theoretical models. The alkali hydrides XH have been an important compounds due to their possible applications in nuclear and chemical industries [1]. They have many promising uses, such as hydrogen storage and obtaining high-energy fuels [1]. These compounds are, to some extent, soft solids: their bulk modulus gradually decreases from Li to Cs in the periodic table, while their lattice constants increases. These materials have been investigated both experimentally and theoretically for many years. The X-ray experimental study shows that XH compounds crystallize in the rocksalt (RS) structure at normal conditions [2, 3]. The structural phase transition of NaH, KH, RbH and CsH compounds from the low-pressure rocksalt structure to the high-pressure cesium chloride structure has been observed in diamond-anvil-cell high-pressure experiments [3, 4]. The transition pressure for these compounds ranges from 1.2 GPa for CsH to approximately 30 GPa for NaH [2-4], while the RS to CsCl phase transition in LiH has not yet been observed. The transition pressure for these alkali decreases as the alkali atomic mass increases. NaH has an enormous transition pressure compared to the others, which is approximately 30 GPa, and a volume fraction  $V/V_{\circ} = 0.61 \pm 0.01$ . The

KH, RbH and CsH transition pressures are 4.0, 2.2 and 1.2 GPa, respectively [2-5]. Hochheimer et al. [3] performed a high-pressure energydispersive X-ray study of the alkali hydrides NaH, KH, RbH, and CsH. The structural phase transition from RS to CsCl phase was observed for KH, RbH and CsH at high pressure, while this structural phase transition has not observed for NaH for a pressure up to 28.0 GPa. Hochheimer et al.[3] found that the transition pressure from the RS to CsCl phase structure decreases when increasing the alkali radii. This result has been suggested by Bashkin *et al.* [6], which depends on the assumption that the alkali hydrides and alkali halides show a similar behavior. There have been many theoretical predictions for LiH phase transition and the estimated transition pressure ranging from about 200 to 600 GPa. Sudha et al. [7] investigated the structural, electronic and elastic properties of alkali hydrides XH (X =Li, Na, K, Rb, Cs) by using the Vienna ab initio simulation package. The calculated transition pressure from the RS to CsCl phase is predicted to be 208.0, 37.0, 3.5, 3.0 and 2.1 GPa for LiH, NaH, KH, RbH and CsH, respectively, using the PBE-GGA approach [7]. These compounds were predicted to be semiconductors with the CsCl structure. Guangwei et al. [8] predicted that the structure of LiH will change from RS to CsCl at very high pressure, approximately at 660 GPa. Xiao-Wei et al. [9] used an ab initio plane-wave pseudo-potential density-functional theory method to investigate the RS to CsCl phase transition and bulk modulus of NaH; the transition pressure was predicted to be 32 GPa, and the bulk modulus was found to decrease as the temperature increases. Saitta et al. [10] carried out Density functional theory (DFT) calculations within the local-density approximation (LDA) and its gradient-corrected (GC) generalization using pseudo-potentials to calculate the transition pressure for CsH from the RS to CsCl; pressures of -0.8 and 1.5 GPa were obtained using the LDA and GC approaches, respectively. Rodriguez *et al.* [11] applied an improved linear muffin-tin orbital atomic-sphere approximation-energy approach to investigate the static structural properties and the pressure-induced phase transition from RS to CsCl for the NaH and KH compounds; the estimated transition pressures were found to be 30.7 and 2.0 GPa for NaH and KH, respectively. Ahuja *et al.* [12] used the full-potential linear-muffin-tin-orbital (FP-LMTO) method to investigate LiH, NaH, KH and RbH compounds. They predict that RbH and KH will transform to CsCl structure, while their calculations predict CrB crystal structures at high pressure for RbH and KH but not for the light Alkali compounds, NaH and LiH.

Sudha *et al.* [7] calculate theoretically the elastic constants and their related properties of alkali hydrides XH (X = Li, Na, K, Rb, Cs) in the Rock Salt and Cesium Chloride structures. Their calculations in the RS structure are in good agreement with experimental results. Gulebaglan *et al.* [13] used the method developed by Morteza Jamal integrated in WIEN2K code [14] to calculate the elastic properties and their related constants properties for RbH in RS structure and they found it to be stable at zero pressure and temperature. Xiao-Wei *et al.*[9] computed the elastic constants and their related properties for NaH in RS and CsCl structures, they found that NaH at zero temperature and pressure is stable in RS structure, while it is not

stable in CsCl structure ( $C_{44}<0$ ) which disagree with Sudha *et al.* [7]. Their results in CsCl structure were  $C_{11}=95.80$  GPa,  $C_{12}=-13.04$  GPa and  $C_{44}=-6.16$  GPa. Wen Yu *et al.* [15] have used plane wave pseudo-potential density functional and calculated the RS to CsCl phase transition and their thermodynamic properties of alkali hydrides LiH and NaH; they found from the phonon dispersion curves that the CsCl phase is unstable at low pressure.

From the above it is clear that there is considerable work on the considered compounds, involving both experimental and theoretical methods, but there are no reported studies on the ground state parameters, electronic structure, structural phase transition, elastic constants and optical properties for both the zincblende (ZB) and wurtzite (WZ) phases. The reasons mentioned above motivated us to perform such calculations on the structural, electronic and the structural phase transition for LiH, NaH, KH, RbH and CsH compounds in RS, CsCl, ZB and WZ phases, using the full-potential augmented plane wave method (FP-LAPW). This will provide reference data for the experimentalists and will serve as an additional data to the existing theoretical work on these compounds.

# Chapter 2 Density Functional Theory

### **2.1 Introduction**

Electromagnetic radiation can exhibit both particle and wave properties. De Broglie in his PhD thesis in 1924 has generalized the Einstein's postulate to matter by postulate the wave nature of electrons. De Broglie suggested the wave properties of matter, and in 1927, the wave-like behavior of matter was experimentally proved, and in 1929, he won the Nobel Prize.

De Broglie's postulate was a starting point for Schrödinger to construct his famous wave equation, which is known as Schrödinger equation. In 1926, Heitler and London solved Schrödinger equation for the simplest molecule, hydrogen molecule [16]. Heitler and London supposed a model known as Heitler and London model for the two electrons wave function in  $H_2$  and they have introduced an important concept of exchange energy for the two electrons. They have explained how the wave functions of the two hydrogen atoms are attached. Later, the challenge was to find a solution to the many body Schrödinger equation, this challenge motivate theorists to develop many methods to apply quantum physics to complex systems [17-22].

Thomas [17] and Fermi [18], in 1927 separately presented a semi-classical model, Thomas-Fermi theory, sometimes called the 'statistical theory', which is a quantum mechanical theory for the electronic structure of many body systems. Electrons in this model were considered as a free electron

gas distributed around the nuclei. This method for the first time uses the concept of electron density; it is based on the uncertainty principle and the Fermi distribution of electrons gas. Although it fails in explaining general features of the density, it has become a basis for more developed methods. Few years later, Hartree, Fock and Slater solved the many body Schrödinger equation. Hartree-Fock method [19] assumed that the electrons of N-body wave function of the system are independent from each other. The total wave function of the system then can be written as:

$$\psi(r_1, r_2, r_3, \dots, r_N) = \psi_1(r_1)\psi_2(r_2)\psi_3(r_3) \dots \psi_N(r_N)$$
(2.1)

The wave function of the system in Hartree-Fock method, which is sometimes called the self-consistent field method, is represented by the single particle orbital. Each particle in the Hartree–Fock equations considered as if it is subjected to the mean field, which is created by other system particles.

In 1964, another computational quantum mechanical method has been proposed and developed to solve the many particles Schrödinger equation by Hohenberg and Kohn [20]. This universal approach to quantum mechanical many-body problem method is called Density Functional Theory (DFT) [21]. One year after Hohenberg and Kohn published their theorem, a practical approach for DFT functional was published by Kohn and Sham in 1965 [22]. The Kohn-Sham theorem supposed that the ground state density of the supposed interacting electrons system is equivalent to the ground state density of a non-interacting particles system. Kohn and Sham equations by this assumption turn DFT into an efficient practical tool.

Many electrons systems as Hartree-Fock, Density Functional Theory and other methods require advanced computational modeling of material science. The development of computer hardware and increased computer power has led these quantum methods available for practical use. It uses the development of theoretical concepts to simulate the properties of material to understand and complement the experiments, a new branch of science called "Computational Materials Science" has been established to predict and validate different models.

### 2.2 Many-particles Schrödinger equation

In Computational Materials Science, one often starts with an ideal crystal to study some properties like (relative stability, chemical bonding, relaxation of atoms, electrical and elastic properties, phase transition, optical or magnetic behavior) on the atomic scale at zero temperature and zero pressure. The unit cell of the system contains several atoms at defined positions; the boundary conditions are periodic continues. For this, theorists came to face a many-body problem, it is a quantum many body problem; particles under study are so light compared with classical scale. To study the materials and their properties, theorist has to solve the many-particles time independent Schrödinger equation. Schrödinger equation can be written as:

$$\hat{H}\psi(R_1, R_2, \dots, R_N, r_1, r_2, \dots, r_N) = -i\hbar \frac{\partial}{\partial t}\psi(R_1, R_2, \dots, R_N, r_1, r_2, \dots, r_N)$$
(2.2)

where,  $\psi$  is the all participating particles wave function,  $R_i$  is the coordinates of the nuclei,  $r_j$  is the coordinates of electron and  $\hat{H}$  is the many-particles Hamiltonian for this system which can be written as:

$$\hat{H} = -\frac{\hbar^{2}}{2} \sum_{i} \frac{\nabla_{\vec{R}_{i}}^{2}}{M_{i}} - \frac{\hbar^{2}}{2} \sum_{i} \frac{\nabla_{\vec{r}_{j}}^{2}}{m_{e}} - \frac{1}{4\pi\epsilon_{0}} \sum_{i,j} \frac{e^{2}Z_{i}}{|\vec{R}_{i} - \vec{r}_{j}|} + \frac{1}{8\pi\epsilon_{0}} \sum_{i\neq j} \frac{e^{2}}{|\vec{R}_{i} - \vec{r}_{j}|} + \frac{1}{8\pi\epsilon_{0}} \sum_{i\neq j} \frac{e^{2}Z_{i}Z_{j}}{|\vec{R}_{i} - \vec{R}_{j}|}$$
(2.3)

where  $M_i$  is the mass of nucleus and  $m_i$  is the electron mass. The first term in equation (2.3) represents the kinetic energy operator for the nuclei ( $T_n$ ), while the second term represents the kinetic energy operator for the electrons ( $T_e$ ), the last three terms represent the Coulomb potential, and they are the electron-nuclear attraction ( $V_{en}$ ), electron-electron repulsion ( $V_{ee}$ ) and nucleus-nucleus repulsion ( $V_{nn}$ ), respectively.

It is a difficult task to have an exact solution for this kind of equations; it is a many body particle Schrödinger equation. The complexity is, the wave function  $\psi$  of the system depends on the coordinates of each particle in the system, and thus, the treatment of any system with more than a few numbers of particles is not feasible. Some approximations are needed to solve many body particles Schrödinger equation. The nucleus has a large mass compared with the electron mass; this fact enables us to use certain approximations. The nuclei to some extent can be considered as classical particles, which can be described by only their positions and velocities.

### 2.3 The Born-Oppenheimer approximation

Born-Oppenheimer approximation is one of the most important approximations [23]. The nucleus mass is about 1863 more massive than electrons mass, since the nuclei are more massive than electrons, nuclei are much slower than the electrons. They can be considered as static particles, with approximately zero kinetic energy. This approximation reduces the number of degree of freedom to  $3N_{el}$ , where  $N_{el}$  is the number of electrons in the system [24, 25].

This approximation treats the atomic nuclei classically; the operator represents the nuclei kinetic energy now can be neglected. Now the only effective players in the many particles Schrödinger equation (2.3) are electrons. Now the nuclei are reduced to a given source of positive charges; they become 'external' to the electron cloud, by this approximation the first term in equation (2.3) can be neglected while the last term is constant.

The problem now can be considered as a collection of interacting electrons, moving in the nuclei potential, external potential. The many particles problem now lifted with the kinetic energy of the electron gas ( $T_e$ ), electron-electron interaction potential energy ( $V_{ee}$ ) and the electrostatic

potential energy of the electrons in an external potential of the nuclei ( $V_{ext}$ ). The new Hamiltonian now can be written as:

$$\widehat{H} = \widehat{T}_e + \widehat{V}_{ee} + \widehat{V}_{ext} \tag{2.4}$$

Although the Born-Oppenheimer approximation simplifies the many particles problem, it is still difficult to solve. More simplifications are needed.

#### 2.4 Hartree and Hartree-Fock Approximation

Hartree-Fock theory can be considered as fundamental for many particles electronic structure theory. Independent particle assumption is the first step to solve the many-electron system problem. In Hartree approximation [19] the many-electron Schrödinger equation can be solved by assuming that each electron in the system moves in the average external potential, effective potential, of the surrounding electrons. They assumed that the electrons are independent from each other. According to this assumption, the total wave function for the system can be written as:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3..., \mathbf{r}_N) = \Psi_1(\mathbf{r}_1) \Psi_2(\mathbf{r}_2) \Psi_3(\mathbf{r}_3).... \Psi_N(\mathbf{r}_N)$$
(2.5)

where  $\Psi_N(r_N)$  is the single electron wave function. Now the time independent Schrödinger equation can be written as:

$$(T_s + V_{ext} + V_H)\psi(r) = E\psi(r)$$
(2.6)

where  $T_s$  is the single particle kinetic energy.  $V_H$  is given by

$$V_{H} = \frac{1}{8\pi\epsilon_{o}} \sum_{i,j} \frac{|\psi(r_{i})|^{2} |\psi(r_{j})|^{2} d^{3}r_{i} d^{3}r_{j}}{|\vec{r_{i}} - \vec{r_{j}}|}$$
(2.7)

where  $V_H$  is the Hartree potential.

Later, the problem was modified to include the electron spin 'Slater determinant' by the Hartree-Fock approximation [26], which is an extension of Hartree approximation. The many particles wave function now includes the permutation symmetry, which leads to the exchange interaction. The exchange interaction is due to the Pauli Exclusion Principle. Pauli Exclusion Principle is a quantum mechanical principle; it states that two or more identical particles cannot occupy the same quantum state, which means the total wave function must be anti-symmetric under particle exchange. Therefore, it is impossible for two electrons to have the same value of the four quantum numbers (n, l,  $m_l$  and  $m_s$ ); two electrons with the same spin cannot occupy the same state simultaneously. For two electrons problem, the anti-symmetry wave function is given by:

$$\psi(r_1, r_2) = \frac{1}{\sqrt{2}} [\chi_1(r_1)\chi_2(r_2) - \chi_2(r_1)\chi_1(r_2)$$
(2.8)

or in determinant form

$$\psi(r_1, r_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \chi_1(r_1) & \chi_2(r_1) \\ \chi_1(r_2) & \chi_2(r_2) \end{vmatrix}$$
(2.9)

The generalization to N electron is just

$$\psi(r_1, r_2 \dots r_N) = \frac{1}{\sqrt{N}} \begin{vmatrix} \chi_1(r_1) & \chi_2(r_1) & \dots & \chi_N(r_1) \\ \chi_1(r_2) & \chi_2(r_2) & \dots & \chi_N(r_2) \\ \ddots & \ddots & \dots & \ddots \\ \vdots & \ddots & \dots & \ddots \\ \chi_1(r_N) & \chi_2(r_N) & \dots & \chi_N(r_N) \end{vmatrix}$$
(2.10)

A determinant of spin orbitals is called a Slater determinant.

## **2.5 Density Functional Theory (DFT)**

Density Functional Theory (DFT) is a ground-state theorem based on the charge density  $\rho(r)$ , the charge density contains as much information as the wave function does [21, 27-30]. DFT is computationally simple and has proved that it is highly successful in describing structural, electronic, elastic, optical and other properties for different types of materials. For these reasons, DFT has become a common tool in the first-principles calculations, which aims to predict properties of many particles systems.

### 2.6 Hohenberg-Kohn theorem

Hohenberg and Kohn [20] proposed an idea to reduce the number of degrees of freedom of the system to just three. They replaced the many electrons wave function by electron density  $\rho$  (r), which depends only on 3 degrees of freedom and describes the charge density of all electrons in the system. This idea is theoretically possible in the non-interacting electrons system by describing the Coulomb repulsion between the electrons by the effective external potential. The charge density  $\rho$  (r) is defined as:

$$\rho(\mathbf{r}) = N \int |\psi(r_1, r_2 \dots r_N)|^2 dr_1 \dots dr_N$$
(2.11)

where  $|\psi(r_1, r_2 \dots r_N)|^2$  gives the probability density of measuring the first electron at the position  $r_1$ , the second electron at position  $r_2$  and the Nth electron at the position  $r_N$ , and N is the number of electrons in the atom.

Hohenberg and Kohn have proved that the energy corresponds to the ground state energy can be minimized by adding a universal potential  $F[\rho(r)]$  such that the minimum energy is given by the equation

$$E_{V_{ext}}(\rho) = \langle \psi | \hat{T} + \hat{V}_{ee} | \psi \rangle + \langle \psi | \hat{V}_{ext} | \psi \rangle$$
(2.12)

$$=F_{HK}\left[\rho(r)\right] + \int \rho(r)V_{ext}(r)dr \qquad (2.13)$$

These potentials, external potential  $V_{ext}(r)$  and Hohenberg-Kohn density functional  $F_{HK}$  [ $\rho$ ] are unique functional of the electron density  $\rho$  (r). The ground state density can be estimated by calculating the universal potential  $F_{HK}[\rho]$ . The universal potential  $F_{HK}[\rho]$  is given by the following equation [20, 21]:

$$F_{HK}[\rho(r)] = \langle \psi | \hat{T} + \hat{V}_{ee} | \psi \rangle$$
(2.14)

The ground state energy can be found by solving Thomas-Fermi-Hohenberg-Kohn equation [30]:

$$\frac{\delta E}{\delta \rho} = \frac{\delta F_{HK}[\rho]}{\delta \rho} + \frac{\delta V_{ne}}{\delta \rho} = \lambda$$
(2.15)

where  $V_{ne}$  is electron-nuclear attraction potential energy and  $\lambda$  is the Lagrange multiplier.

### 2.7 Kohn-Sham equations

Solving equation (2.15) in terms of the electron density is to some extent complicated. Instead of this, Kohn and Sham have proposed a simpler way. They introduced a method, which established on the Hohenberg-Kohn theorem, minimizing the total energy by varying the charge density, the normalization constraint is given by the following:

$$\int |\psi_i(r)|^2 = 1$$
 (2.16)

Kohn and Sham solved a set of one-electron Schrödinger equations for the non-interacting electrons "fictitious system", all quantities depend on the charge density, which is the same for the real system [20, 21]. These one-electron equations contain an unknown external potential V(r), which minimizes the electron-electron interaction of the real system, Kohn-Sham equation, is given by:

$$[T_{s} + V_{ext}(\rho(r)) + V_{H}(\rho(r)) + V_{xc}(\rho(r))]\phi_{i}(r) = \varepsilon_{i}\phi_{i}(r)$$
(2.17)

where,  $\varepsilon_i$  is the single particle energy and  $\phi_i$  is the electron wave function. The four operators represent the kinetic energy operator  $T_s$ , the Hartree potential  $V_H$ , the Coulomb potential  $V_{ext}$  and the exchange-correlation potential  $V_{XC}$ . The Hartree potential  $V_H$  can be written as:

$$V_{H} = \int \frac{\rho(r')}{|\vec{r} - \vec{r}'|} dr'$$
(2.18)

The new form of Schrödinger is:

$$\left(-\frac{\hbar^2}{2\mathrm{m}}\nabla^2 + V_{eff}(\vec{r})\right)\psi(\vec{r}) = E\psi(\vec{r})$$
(2.19)

where  $\psi(\vec{r})$  is the electrons total wave function,  $V_{eff}$  is the effective potential and E is the system total energy. Now by equation (2.19) instead of many particles problem we are dealing with one electron problem, an electron that is moving in an effective potential where  $V_{eff}$  is given by:

$$V_{eff}(\vec{r}) = V_{ext}(\vec{r}) + V_H(\vec{r}) + \frac{\delta E_{xc}(\rho)}{\delta \rho}$$
(2.20)

The third term in the equation represents the exchange-correlation potential  $V_{xc}$ . The exchange-correlation potential  $V_{xc}$  and Hartree potential  $V_{H}$  are both depending on the charge density  $\rho(\vec{r})$ ; on the other hand, the charge density  $\rho(\vec{r})$  depends on the electron wave function  $\varphi_i(\vec{r})$ , which is needed. The precise ground state density in Kohn-Sham theorem is given by:

$$\rho(\vec{r}) = \sum \varphi_i(\vec{r})\varphi_i(\vec{r})^*$$
(2.21)

The single particle wave function  $\varphi_i(\vec{r})$  is given by:

$$\varphi_n(\vec{r}) = \sum_i C_{ni} \varphi_i(\vec{r})$$
(2.22)

To express  $\varphi_n(\vec{r})$  (true single particle orbital), we need to find the coefficients  $C_{ni}$  in equation (2.22), the solution of the Kohn-Sham (KS) orbitals permits to determine the  $C_{ni}$  that minimize the total energy. Density functional calculation required  $C_{ni}$  optimization and the determination of the density. We are dealing with self-consistency problem as seen in Figure 2.1. The solution ( $\varphi_i$ ) determines the  $V_H$  and  $V_{xc}$  in  $H_{KS}$ . This can be done by starting with a guess charge density  $\rho_o$ , and a Hamiltonian  $H_{KS1}$  [31] is constructed with it. The eigen value problem is solved, and results in a set of  $\varphi_1$  from which a density  $\rho_1$  can be derived. Most probably,  $\rho_o$  will differ from  $\rho_1$ . Now  $\rho_1$  is used to construct  $H_{KS2}$ , which will yield a  $\rho_2$ , etc. The procedure can be set up in such a way that this series will converge to a final charge density  $\rho_f$ , which used to generate a final Kohn-Sham Hamiltonian  $H_{KSI}$ ; this final density is then consistent with the Hamiltonian.



Figure 2.1: Flow chart for the self-consistent density functional theory.

### 2.8: The local spin density approximation LSDA

The last term in equation (2.20) is due to exchange and correlation, exchange interaction between electrons with the same spin, while the correlation energy can be defined as the difference between Hartree-Fock energy and the exact energy. The electrons interact with each other and correlate their motion because they tend to avoid each other, an electron at r reduces the probability of finding another electron at r. Local-Spin Density Approximation (LSDA) (or simply Local Density Approximation (LDA) which is dealing only with nonmagnetic systems) [32] is an approximation which have been applied to DFT by Kohn-Sham method to calculate the unknown exchange-correlation energy  $E_{xc}$ , the only term in the effective potential of the Kohn-Sham equation which cannot be determined exactly. It divides the inhomogeneous system into a small set of regions containing homogeneous interacting electron gas with density  $\rho_{\sigma}$ , where ( $\sigma$ ) is the spin up or spin down, and the total density is

$$\rho(\vec{r}) = \rho_{\uparrow}(\vec{r}) + \rho_{\downarrow}(\vec{r}) \tag{2.23}$$

In each region, the exchange-correlation energy per particle of the homogeneous gas can be stated as:

$$\varepsilon_{xc}(\rho_{\uparrow},\rho_{\downarrow}) = \varepsilon_{x}(\rho_{\uparrow},\rho_{\downarrow}) + \varepsilon_{c}(\rho_{\uparrow},\rho_{\downarrow})$$
(2.24)

The analytic expression for the exchange energy  $\varepsilon_x(\rho\uparrow, \rho\downarrow)$  can be obtained from the Hartree-Fock approximation [26, 33, 34]. The total exchangecorrelation energy  $E_{xc}^{LDA}$  is the sum of the contribution of all regions [35], which is based on the quantum Monte-Carlo result of the ground-state energy for the homogenous electron gas [29]. The total exchange correlation energy is the sum of the contribution of all regions,  $E_{xc}^{LDA}$  is given by

$$E_{xc}^{LDA}(\rho_{\uparrow},\rho_{\downarrow}) = \int \rho(\vec{r}) \, \varepsilon_{xc}(\rho_{\uparrow},\rho_{\downarrow}) d^{3}\vec{r}$$
(2.25)

in addition, the exchange-correlation potential is calculated from

$$V_{xc}^{LDA}(X) = \frac{\delta E_{xc}}{\delta \rho(\vec{r})} = \varepsilon_{xc}(\rho_{\uparrow}, \rho_{\downarrow}) + \frac{\delta \varepsilon_{xc}(\rho_{\uparrow}, \rho_{\downarrow})}{\delta \rho(\vec{r})}(\rho_{\uparrow}(\vec{r}) + \rho_{\downarrow}(\vec{r}))$$
(2.26)

## 2.9 Generalized gradient approximation

Many modern theoretical codes that are using DFT have now more advantage approximations to improve accuracy for certain physical properties. The LDA uses the exchange-correlation energy for the uniform electron gas at every point in the system regardless of the homogeneity of the real charge density. For non-uniform charge densities the exchangecorrelation energy can deviate significantly from the uniform result, this deviation can be expressed in terms of the gradient and higher spatial derivatives of the total charge density. Generalized gradient approximation (GGA) came as a modification of (LDA), it inserts another parameter to the exchange-correlation energy  $E_{xc}$  [28, 36, 37];  $E_{xc}$  is now a functional of local electron density  $\rho(r)$  and their gradients of the local electron density or higher orders of density derivatives to correct this deviation,  $E_{xc}$  can be written as:

$$E_{xc}^{GGA}(\rho_{\uparrow},\rho_{\downarrow}) = \int \varepsilon_{xc}(\rho_{\uparrow},\rho_{\downarrow})\rho(\vec{r})\vec{\nabla}\rho(\vec{r})d^{3}\vec{r}$$
(2.27)

The (GGA) improves significantly ground state properties of light atoms, molecules and solids and generally tends to produce larger equilibrium lattice parameters with respect to the LDA.
# Chapter Three Methodology

# **3.1 Introduction**

In this chapter the basic concepts of (Full potential Linearized Augmented Plane Wave method (FP-LAPW) are presented. DFT equations are defined in terms of the functional; there are several techniques to solve these equations. The basis which are used in calculating one-electron functions are plane waves (PWs) corresponding to Bloch functions. However, these plane waves (PWs) are inefficient basis set and need modification for describing the rapidly varying wave functions close to the nuclei.

In order to overcome this problem, pseudo-potential calculations eliminate the oscillations, due to the presence of the core electrons, or one can augment the PW's basis set. An example of the second approach is the Linearized Augmented Plane Wave plus local orbitals (LAPW+lo) method that is one of the most accurate methods.

# **3.2 The Augmented Plane Wave method (APW)**

Slater introduced the APW method in 1937 as basis functions for solving Kohn-Sham equations [38, 39]. These basis functions are especially adapted to the problem, in the APW scheme the unit cell is partitioned into two types of regions as shown in Figure 3.1.

i) non-overlapping spheres centered at the atomic sites with radius  $R_{\alpha}$ , such a sphere is often called a muffin tin sphere.

ii) An interstitial region; the remaining space outside the spheres.

In this case, the wave functions are expanded into PWs each of which is augmented by atomic solutions in the form of partial waves, i.e. a radial function multiplied by spherical harmonics. Close to the nuclei, inside the atomic sphere where electrons behave quit as they were in a free atom, radial solutions of Schrödinger's equation are employed, in the remaining interstitial region; region far away from the nuclei; the electrons are more free, free electrons are described by plane waves.



**Figure 3.1:** Division of a unit cell in muffin tin regions and the interstitial region, for a case with two atoms.

The introduction of such basis set is due to the fact that between the atoms the potential and wave functions are smooth while close to the nuclei they are similar to those in an atom. The APWs consist of:

where  $\emptyset_{\vec{K}+\vec{G}}^{APW}$  is the wave function,  $\vec{r}$  is the position inside sphere with polar coordinates  $\vec{r}$ , V is the unit cell volume,  $\vec{G}$  is the reciprocal lattice vector,  $\vec{K}$  is a wave vector in the first Brillouin Zone,  $Y_{lm}$  are spherical harmonics,  $ulm(r,\varepsilon)$  is the regular solution to the radial part of the Schrödinger equation for a free atom at the energy  $\varepsilon$  and Alm, CG are expansion coefficients.

The Kohn-Sham (KS)  $\psi_i$  orbitals are expressed as a linear combination of APWs ( $\phi_i(\vec{r})$ ). Inside the Muffin Tin sphere, a KS's orbitals can only be described accurately if  $\varepsilon$  in the APW basis functions is equal to the eigenenergy  $\varepsilon$ . Therefore, a different energy dependent set of APW basis functions must be found for each eigen-energy. The ulm(r) satisfy the following equation:

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial u_{lm}(r)}{\partial r} \right) + \left[ \frac{2m}{\hbar^2} \left( E_l - V(r) \right) - \frac{l(l+1)}{r^2} \right] u_{lm}(r)$$

$$= 0$$
(3.2)

By these functions, Slater notes that in a constant potential, plane waves are the solution of the Schrödinger equation and in a spherical potential, radial functions are the solution. This potential approximation usually called "muffin-tin" (MT). The dual representation defined by equation (3.1) is not guaranteed to be continuous on the sphere boundary, as it must be for the kinetic energy to be well defined. Accordingly, it is necessary to impose this constraint. In the APW method, this is done by requiring that the augmented functions match (in value not in slope) the plane waves at the atomic sphere boundary, this is done in APW by defining the  $u_{lm}$  in terms of  $C_G$ .

$$u_{l,m} = \frac{4\pi i^l}{\sqrt{V}u_l(R)} \sum_G C_G j_l(|k+g|) Y_{l,m}^* \left(\vec{K} + \vec{G}\right)$$
(3.3)

where  $j_l(|k + g|)$  is the Bessel function of order *l*, the coefficients *l* and *m* are matched at the boundary of the sphere and the origin is taken at the center of the sphere.

There is no restriction on the derivative at the atomic sphere boundary. Therefore, the APW basis functions derivations are discontinuous at the boundary, in general they have a kink at  $r=R_{MT}$ . It must be mentioned that Linearized Augmented Plane Wave method (LAPW) is a more accurate method. In LAPW method, the basis functions and their derivatives are made continuous at the boundary by matching to a radial function at fixed  $E_l$  plus its derivative with respect to  $E_l$ . Linearized Augmented Plane Wave (LAPW) method (discussed in the next section) is more accurate in band structure calculation schemes, which use the basis functions and their derivatives.

#### **3.3 Linearized augmented plane wave method (LAPW):**

LAPW is the first successful improvements to solve the energy dependence of the basis set. Andersen introduced the Linearized Augmented Plane Wave method (LAPW) scheme [40]. In this scheme a linear combination of radial function times, spherical harmonics are used. LAPW method uses the basis functions and their first derivatives. The basis functions and their first derivatives made continuous at the boundary between core and interstitial region, so that it is more flexible and accurate method. The  $u_{lm}$ and its energy derivative satisfy the following equation:

$$\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2} + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2} + V(r) - E_l\right)r\dot{u}_{lm}(r) = ru_{lm}(r)$$
(3.4)

The original energy dependence of the radial basis function  $u_{lm}(r,\varepsilon)$ thereby replaced by the Taylor series:

$$u_{l}(r,\varepsilon) = u_{l}(r,\varepsilon_{l}) + (\varepsilon - \varepsilon_{l})\frac{\partial u_{l}}{\partial \varepsilon_{l}}|_{\varepsilon = \varepsilon_{l}} + O(\varepsilon - \varepsilon_{l})^{2}$$
(3.5)

In this way, the wave functions are affected by an error, which is quadratic in the deviation of the eigen-value  $\varepsilon$  from the energy parameter  $\varepsilon_l$ . Substituting the first two terms of the expansion in the APW for fixed  $\varepsilon_l$ gives the definition of the LAPW. This has a price; the energy difference  $(\varepsilon - \varepsilon_l)$  is yet unknown and hence undetermined  $B_{lm}$  must introduced:

At the sphere boundary, function inside the sphere matches the plane wave both in value and in slope in order to determine the coefficients  $A_{l,m}$  and  $B_{l,m}$ . The augmented wave functions  $ulm(r)Ylm(\theta, \varphi)$  and their derivatives are linearized to form the basis functions inside the spheres. Two radial functions are used in LAPWs instead of one in the APWs, so LAPW are more variation freedom inside the atomic spheres.

The linear compensation of  $ul_m(r)$  and its derivative is obtained by numerical integration of the radial Schrödinger equation on the radial mesh inside the sphere. Instead of one radial functions in APW there are two radial functions in inside spheres within LAPWs. Potential inside spheres can now be treated with no difficulties, on the other hand, there is a price to be paid for the additional radial function: the basis function must have continuous derivatives and consequently, higher plane wave cut-offs are required to achieve a given level of convergence. The solution of the KS equations expanded in this combined basis according to the linear variation method:

$$\psi_k = \sum_n C_n \varphi_{nk} \tag{3.7}$$

The coefficients Cn can be determined by the Rayleigh-Ritz variational

Principle. The convergence of this basis set can be controlled by a cut-off energy parameter  $R_{MT} \times K_{Max}$ , where  $R_{MT}$  is the smallest atomic sphere radius in the unit cell and  $K_{Max}$  is the largest Kn vector in equation (3.7).

# 3.4 The augmented plane wave plus local orbitals method (APW+lo):

APW+10 method was proposed by Sjöstedt *et al.* [41]. Some electrons are extremely bounded to nucleus and behave as if they are in a completely free atom but subject to the potential due to electrons of the valence states, it makes no sense to use LAPW to calculate the potential of these electrons. These states are called core states. The issue with core states is that they do not participate directly with other atoms in chemical bonding. They are contained entirely in the muffin tin sphere, while valence states leak out of the muffin tin sphere and participate in chemical bonds and treated by LAPW method. Electrons close to the nuclei can be treated as "core states" (e.g. 1s electrons) and add another different basis to LAPW for them, these basis are called local orbitals (LO) basis. Local orbitals exist inside the sphere of the particular atom and it is zero everywhere, so it is zero in the spheres of the other atoms and in the interstitial region. A local orbital (LO) is defined as:

$$\emptyset_{lm}^{\alpha,lo}(\vec{r}) = \begin{cases} \begin{bmatrix} A_{lm}^{\alpha,lo}u_{lm}^{\alpha}(r) + B_{lm}^{\alpha,lo}\frac{\partial u_{lm}^{\alpha}(r)}{\partial \varepsilon} \end{bmatrix} Y_{l,m}(\theta,\varphi), r \in II \\ 0, \qquad r \in I \end{cases}$$
(3.8)

The coefficients can be determined by assuming that local orbital should have zero value at the sphere boundary. High efficiency has been found for a mixed basis set, APW+lo are basis for low l-quantum numbers but the higher l is treated by LAPW. APW+lo is slightly increased computational time, this is a small price to be paid for high accuracy that local orbitals offer; therefore local orbitals are always used [42].

# **3.5** Full Potential Linearized Augmented Plane Wave Method (FP-LAPW)

The potential within atomic spheres of radius  $R_{\alpha}$  has been assumed spherically symmetric, and centered at atomic positions  $R_{\alpha}$  by APW and LAPW methods, while it is assumed constant in the interstitial region. In highly coordinated systems eg. close-packed metals this approximation works reasonably well, while for open structures, such as layered structures it might lead to serious discrepancies compared with experimental measurements. Therefore, for open systems, no shape of approximation is made for the system potential to understand and predict structural and electronic properties.

The full-potential LAPW method (FP-LAPW) is one of the most accurate schemes for solving the Kohn-Sham equations suggested by Andersen [41] on which WIEN2k code is based. Full potential LAPW method (FP-LAPW) combines the choice of the LAPW basis set with the treatment of the full-potential and charge density without any shape approximations in the interstitial region and inside muffin-tins. This generalization is achieved be relaxing the constant interstitial potential VI and the spherical muffin-tin approximation VMT(r) due to the inclusion of a warped interstitial  $\sum V_I^K e^{ikr}$ , where K are all reciprocal lattice vectors up to the largest value of KMax. The non-spherical terms inside the muffin-tin spheres:

$$V(\vec{r}) = \begin{cases} \sum_{K} V e^{i\vec{K}.\vec{r}}, & interstitial region\\ \sum_{lm} V_{lm}(r) Y_{lm}(\theta, \varphi), & muffin-tin region \end{cases}$$
(3.9)

FP-LAPW method becomes possible with the development of a technique for getting the coulomb potential for a general periodic charge density without shape-approximation and with including of the Hamiltonian matrix elements due to the warped interstitial and non-spherical terms of the potential.

#### **3.6 The modified Becke-Johnoson (mBJ)**

The Generalized Gradient Approximation (PBE-GGA) [28] has been used to calculate the structural properties. The modified Becke-Johoson (mBJ) formalism is also used to overcome the well-known underestimation of the band gap values by the GGA method [43, 44].

Ground state properties are well estimated by LDA and GGA approximations, on the other hand these approximations fail to deal with excited states properties. These approximations well reproduce the band structure of metallic or even complicated metallic systems, but in many semiconductors, wide band gap semiconductors and insulators the band gaps values are hardly underestimated. Improved band gaps values can be obtained by using the LDA+U method [45], but it can only be applied to localized and correlated electrons, e.g., 3d or 4f in rare-earth oxides. A successful but highly computational time costing method is GW method [46].

Electronic structure can be performed with the Kohn-Sham (KS) equations given by

$$\left(-\frac{1}{2}\nabla^2 + v_{eff,\sigma}^{KS}(r)\right)\psi_{i,\sigma}(r) = \epsilon_{i,\sigma}\psi_{i,\sigma}(r)$$
(3.10)

where  $\psi_{i,\sigma}$  is the one electron wave functions,  $\epsilon_{i,\sigma}$  is the electron energy and  $v_{eff,\sigma}^{KS}$  is the KS effective potential which includes the exchange correlation potential approximated by GGA and LDA approximations. A new exchange potential introduced by Becke and Johnson is modified by Tran and Blaha [47]. The modified Becke-Johnson (mBJ) potential is given by:

$$V_{x,\sigma}^{\rm mBJ}(r) = c V_{x,\sigma}^{BR}(r) + (3c-2)\frac{1}{\pi} \sqrt{\frac{5}{2}(2\tau_{\sigma}(r)/\rho_{\sigma}(r))}$$
(3.11)

where  $V_{x,\sigma}^{BR}$  is the Becke-Roussel exchange potential,  $\rho_{\sigma}(r)$  is the electron density,  $\tau_{\sigma}(r)$  is the kinetic energy.

$$c = A + B \sqrt{\frac{1}{V_{cell}} \int \frac{|\nabla \rho_{\sigma}(r')|}{\rho_{\sigma}(r')} d^3 r'}$$
(3.12)

where A and B are two parameters with values A= -0.012 and B= 1.023 a.u.<sup>1/2</sup> according to the best fit of the experimental results of the semiconductor band gaps [47] and V<sub>cell</sub> is the unit cell volume.

# Chapter Four Crystal structure

# 4.1 Rock-salt structure (RS)

The Rock-salt structure (RS) is called Fm3m (in Hermann–Mauguin notation) with number 225; it is a cubic crystal system and form a facecentered cubic (fcc) lattice type [50, 51]. The RS structure unit cell contains two kinds of atoms, one of the atoms at the lattice site itself (0, 0,0) and the other kind at (0.5, 0.5, 0.5)a as shown in figure 4.5, where a is the lattice constant. The primitive vectors that span the RS structure unit cell can be given by:

$$\vec{a}_1 = \frac{a}{2}\hat{y} + \frac{a}{2}\hat{z}$$
  $\vec{a}_2 = \frac{a}{2}\hat{x} + \frac{a}{2}\hat{z}$   $\vec{a}_3 = \frac{a}{2}\hat{x} + \frac{a}{2}\hat{y}$  (4.2)



Figure 4.1: Rock-salt structure (RS).

## **4.2** The zinc blende structure(ZB)

The zinc blende structure (ZB) is called F43\_m (in Hermann–Mauguin notation) with number 216; it is a cubic crystal system and forms a facecentered cubic (fcc) space lattice type as the RS structure. ZB unit cell has two kinds of atoms at the lattice site, one of the them positioned at the lattice site itself (0,0,0), while the other atom far from the lattice position by a/4 along all axes, its position is (0.25,0.25,0.25)a as shown in figure 4.6, where a is the lattice constant [49,50,51].



**Figure 4.2:** zinc blende structure(ZB)

# 4.3 Cesium Chloride structure (CsCl)

The Cesium Chloride structure (CsCl) also is a cubic crystal as the RS and ZB but with a (bcc) space lattice type instead of (fcc) for RS and ZB as shown in figure 4.7 CsCl has two kinds of atoms, an atom of one type positioned at the origin of the cube at (0, 0, 0), while at the corners of the

cube at (0.5, 0.5, 0.5)a. Each atom in the CsCl structure has eight nearest neighbors, the space group for CsCl structure is pm\_3m with number 221[49, 50, 51], the primitive vectors for CsCl structure can be given by:

$$\vec{a}_1 = a\hat{x} \qquad \vec{a}_2 = a\hat{y} \qquad \vec{a}_3 = a\hat{z} \tag{4.3}$$

# **4.4 The wurtzite structure(WZ)**

Various binary compounds like zinc sulfide crystallize in two different forms or more. Zinc sulfide can be found in the Wurtzite and Zincblende structures. In the wurtzite structure as shown in figure 4.8, the Zn atom positioned at (1/3, 2/3, 0)a and S positioned at (1/3, 2/3, u)a [49, 50, 51].



Figure 4.3: Cesium Chloride structure (CsCl).



Figure 4.4: Wurtzite structure (WZ).

The space group of wurtzite structure is P63-mc with number 186, the primitive vectors of the wurtzite structure are:

$$\vec{a}_1 = \frac{a}{2}\hat{x} + \frac{\sqrt{3}}{2}a\hat{y}$$
  $\vec{a}_2 = \frac{a}{2}\hat{x} + \frac{\sqrt{3}}{2}a\hat{y}$   $\vec{a}_3 = c\hat{z}$  (4.4)

# Chapter five Computational details

# **5.1 Introduction**

To study the region near the nucleus without introducing pseudo potential, the basis set must be efficient. Therefore, atomic space divided into the following two regions: the muffin-tin region and the interstitial region. The muffin-tin region is the space occupied by spheres of radius R<sub>MT</sub>, one around each atom; these spheres are often called muffin-tin (MT) spheres. The remaining space outside the spheres is called the interstitial region. Spherical harmonics expansion is used inside the muffin tin (MT) spheres, and the plane wave basis set is used in the interstitial part. The muffin tin radii (R<sub>MT</sub>) used in the present calculations for the H, Li, Na, K, Rb and Cs atoms are 1.25, 2.0, 2.56, 2.6, 2.67 and 2.76 atomic units (a.u.), respectively. The charge density was Fourier expanded up to  $G_{max}$  = 20 in RS, CsCl and ZB, while  $G_{max}$  = 14 in WZ structure. The plane wave cutoff was taken such as that the cutoff  $R_{MT}$ .  $K_{max} = 5$  (where  $K_{max}$  is the maximum value for the reciprocal lattice vector K). The basis functions, charge density and potential are expanded inside the muffin-tin spheres in combination with the spherical harmonic functions, with a cut-off  $l_{max} = 12$ for the WZ structure and  $l_{max} = 6$  for the cubic structures.

For energy convergence the full Brillouin zones (FBZ) were sampled with 1331 k-points for the three structures, RS, ZB and CsCl. In the irreducible Brillouin zone (IBZ), a grid size of  $11 \times 11 \times 11$  was used, which is

reduced to 56 special k-points. For the WZ structure, a grid size of  $18 \times 18 \times 18$  was used with 3700 k-points, which is then reduced to 222 special k-points in the (IBZ) [52]. The self-consistent calculation of the total energy of the unit cell gives convergence to less than  $10^{-5}$  Ry/unit cell.

# **5.2 Convergence Tests**

The accuracy of the Density functional theory (DFT) results as well as the calculations running time and calculations errors depend on some input computational parameters. In order to obtain accurate calculations and reducing the calculations time, one has to carry out some convergence tests to optimize the input computational parameters.

The parameters that have to be tested are the muffin tin radius  $R_{MT}$ , the  $R_{MT}$ . $K_{max}$ , number of k points in the Brillion zone (BZ) and the plane wave cutoff energy of the wave function.

The muffin tin radii  $R_{MT}$  have to be chosen in order to not allow an overlap. In order to reduce the computational time, the number of plane-waves required must be reduced, and this done by minimizing the interstitial region.  $R_{MT}$  must be chosen as large as possible to minimize the interstitial region [50, 51].

The number of k-points necessary needed for accurate self-consistent calculation results depends on the desired accuracy, the system type (metallic, semiconductor or insulator) and on the property under study, for example, optical properties need dense k-mesh.

#### **5.2.1 How to select R<sub>MT</sub> radii:**

The WIEN2k program can automatically set the muffin-tin-radius  $R_{MT}$  for the atomic spheres of the atoms under study. It is recommended to set  $R_{MT}$  by using some useful considerations.

To save computational time, choose the  $R_{MT}$  as large as possible but without overlapping. Choosing the smaller  $R_{MT}$  makes calculations more expensive but to more extent accurate, small  $R_{MT}$  means more plane waves (PW's) needed. The radii must not be too much different, but in present case, which contains Hydrogen atom,  $R_{MT}$  for Hydrogen must be approximately half Alkali  $R_{MT}$ . In case the core charge leaks out of the spheres, you must increase the  $R_{MT}$  of the atom.

# 5.2.3 Choosing R<sub>MT</sub>.K<sub>max</sub> and the number of K-points

In order to achieve the energy eigen value convergence, the interstitial region wave function expanded in terms of plane waves, with a cutoff of  $R_{MT}.K_{max}$ . Calculation of the bulk properties must be made after applying some tests. K-points and energy cutoff tests are very important procedures to get the best results in a reasonable time. Choosing  $R_{MT}.K_{max}$  in this test, we make a number of sessions with the same number of K- points, same  $R_{MT}$  for all sessions, the same  $l_{max}$  and the same lattice parameter. We make a run for every session and looking for the energy. Finally, we choose the  $R_{MT}.K_{max}$ , which minimizes the energy per unit cell, in other words we look for the  $R_{MT}.K_{max}$ , which makes the structure more stable. As an example,

Table 5.1 shows the best  $R_{MT}K_{max}$  for LiH compound in RS structure is  $R_{MT}K_{max}$ =5.

ture.					
	No.	<b>R</b> <sub>MT</sub> <b>K</b> <sub>max</sub>	Total energy E <sub>tot</sub> (Ry)		
	1	3	-16.21094328		
	2	4	-16.25141012		
	3	5	-16.27145976		
	4	6	-16.26941201		

-16.25135219

-16.24071573

-16.18013412

Table 5.1: Test to find the best  $R_{MT}K_{max}$  for LiH compound in RS structure.

To choose the best number of K-points, we must do the same steps for choosing the best  $R_{MT}K_{max}$ ; in this test, we must fix all parameters (lattice parameter,  $R_{MT}K_{max}$ ,  $l_{max}$  and the same  $R_{MT}$  except number of K-points. Table 5.2 shows the test results for LiH compound.

No.	K-points	K-reduced	Matrix	Total energy E <sub>tot</sub> (Ry)
1	512	40	8×8×8	-16.27020228
2	729	55	9×9×9	-16.27020566
3	1000	70	10×10×10	-16.27020705
4	1331	56	11×11×11	-16.27020903
5	1728	72	12×12×12	-16.27020816
6	2197	94	13×13×13	-16.27020279

# 5.3 Optimization

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The ground state properties for each structure obtained by calculating the total energy per unit cell at several volumes around the equilibrium volume, and fitting the calculated values to the Murnaghan's equation of state [53] equation (5.1).

$$E(V) = E_0 + \left\{ \frac{BV}{B'} \left( \frac{1}{B' - 1} \right) \left( \frac{V_0}{V} \right)^{B'} + 1 \right\} - \frac{BV_0}{B' - 1}$$
(5.1)

where  $E_0$  is the minimum energy at equilibrium volume  $V_0$ , E(V) is the energy at volume V,  $V_0$  is the equilibrium volume,  $B_0$  is the bulk modulus and

$$B_0' = d B_0/dP \tag{5.2}$$

To optimize a structure in WIEN2K, we usually start the calculations by building the struct.file with estimated parameters. After building the struct.file we must initialize the job by introducing number of k-points, R.K<sub>max</sub> and  $G_{max}$ . Then SCF cycle after choosing proper convergence parameters must be run. When the SCF cycle ends with good convergence (check convergence), we choose optimize job. Then "x-optimize" (a program which generates structures with different volumes), we choose the first option, vary volume with constants a, b and c to find the optimum lattice parameters for cubic structures, while we choose the second option; vary c/a with constant volume; with wurtzite structure to determine the optimum ratio of c/a. In the present calculations, we vary the volume by choosing the values (-9.-6,-3, 0, 3, 6, 9) % and run the optimized job and then we plot energy curve versus volume or c/a.

# **5.4 Phase transition**

The structural phase transition is determined by calculating the Gibbs free energy (G) for the two phases, which is given by the known relation  $G=E_0+PV+TS$ , where  $E_0$  is the equilibrium energy of the unit cell, P is the pressure, V is the unit cell volume and S is the system entropy. Since, the theoretical calculations are performed at T=0 K, Gibbs free energy becomes equal to the enthalpy, H=E\_0+PV. For a given pressure, a stable structure is one for which the enthalpy has its lowest value. Induce transition pressure can be estimated by using the usual condition of equal enthalpies for the two structures at the point of intersection.

# **5.5 Optical properties**

The optical properties of solids are very useful to calculate and estimate the energy band structure of solids, it is a useful tool to study impurity levels, magnetic excitations and lattice vibrations.

Some observable quantities can be measured by experimentalists, which provide up the way to determine the dielectric function  $\varepsilon(w)$  and optical conductivity  $\sigma(w)$ , which is related to the band structure such as optical reflectivity, transmission and refraction. Optical conductivity refers to the electrical conductivity in the presence of an electric field E(w) [54, 55, 56].

# 5.5.1 Kramers-Kronig Relations:

Experimentally, the imaginary part of the complex index of refraction cannot be measured directly; it can be estimated by the measurement of the absorption coefficient. The reflectivity also depends on both real and imaginary of the dielectric constant ( $\varepsilon_1$  and  $\varepsilon_2$ ). Thus we have insufficient information to determine  $\varepsilon_1$  and  $\varepsilon_2$  independently from measurements of absorption coefficient. However, if  $\varepsilon_1$  or  $\varepsilon_2$  is known over a wide frequency range, then Kramers-Kronig relations are useful relations to determine the unknown one. Kramers-Kronig relations are based on linear response theory and on causality, and can be given by the following two relations:[57, 58]

$$\varepsilon_{1(w)} = 1 + \frac{2}{\pi} p \int_{0}^{\infty} \frac{w' \varepsilon_{2}(w')}{w'^{2} - w^{2}} dw'$$
(5.3)

$$\varepsilon_2(w) = \frac{e^2\hbar}{\pi m^2 w^2} \sum_{\nu,c} \int_{BZ} |M_{c\nu}(k)|^2 \delta(w_{c\nu} - w) \, d^3k \tag{5.4}$$

where *p* is the principal part of the integral.

Kramers-Kronig relations connect both  $\varepsilon_1$  and  $\varepsilon_2$ , from these two relations if either  $\varepsilon_1$  or  $\varepsilon_2$  is known over a wide frequency range the other can be determined.

## **5.5.2 Optical calculations**

The analysis of optical spectroscopy is an important and useful tool to estimate and analyze the energy band structure of a given material. Complex dielectric function ( $\varepsilon_{Complex}$ ) depends on the energy band structure, so that it gives us more details about the electronic structure [54, 56]. The symmetries in the cubic structures; RS, CsCl and ZB; allow only one non-zero component of the dielectric tensor( $\varepsilon_{xx} = \varepsilon_{yy} = \varepsilon_{zz}$ ), these structures are optically isotropic. On the other hand symmetries in the WZ structure allow only ( $\varepsilon_{xx}$ ) and ( $\varepsilon_{zz}$ ) to be non-zero components of the dielectric tensor, these components are along the [100] and [001] polarizations directions, respectively. The imaginary part of the complex dielectric constant  $\varepsilon_2(w)$ ; which represents the optical absorption in the crystal; and real part  $\varepsilon_1(w)$  are given in equations (5.3) and (5.4), the other optical constants are related to real and imaginary dielectric constants[59-61]. Once we have calculated  $\varepsilon_1$  and  $\varepsilon_2$ , others like optical Reflectivity R(w), Refractive index n(w) in addition to the absorption coefficient I (w) can be calculated, they can be calculated from the following relations [59-61]:

$$R(w) = \left| \frac{\sqrt{\varepsilon(w)} - 1}{\sqrt{\varepsilon(w)} + 1} \right|$$
(5.5)

$$n(w) = \sqrt{\frac{1}{2\left(\sqrt{\varepsilon_1^2 + \varepsilon_2^2} + \varepsilon_1\right)}}$$
(5.6)

# **5.6 Calculation of elastic properties**

The basic elastic properties describe the homogeneous deformations (bulk modulus), while inhomogeneous deformations describe tensor of the elastic constants. These quantities can be derived from the change in the system total energy as a function of the change in the lattice cell volume as will be described below.

#### **5.6.1 Bulk modulus**

The bulk modulus describes the resistance of the solid to the uniform volume deformation; it is given by the following equation:

$$B = -V \frac{\partial P}{\partial V} \tag{5.7}$$

here V is a unit cell volume and P is the effected pressure. The bulk modulus can be estimated by calculating the total energy at different unit cell volumes and fitting the calculated E-V points to Murnaghan's equation EOS equation (5.1).[53] The accurate pressure corresponding to the desired volume can be calculated using the following relation:

$$P(V) = \frac{B}{B'} \left[ \left( \frac{V_{\circ}}{V} \right)^{B'} - 1 \right]$$
(5.8)

# **5.6.2 Elastic constants**

The optimized lattice constant  $(a_0)$  has been used to compute the elastic constants at ambient pressure by computing the stress generated by forcing a small strain to an optimized unit cell, calculations for strains in the range from -0.003 to 0.003 were carried out for each distortion. By following the system symmetry, the cubic crystal has three independent elastic constants namely (C<sub>11</sub>,C<sub>12</sub> and C<sub>44</sub>) and the hexagonal has five namely (C<sub>11</sub>, C<sub>12</sub>, C<sub>13</sub>, C<sub>33</sub> and C<sub>55</sub>). These elastic constants are crucial, in determining the material response to an applied macroscopic stress can be predicted. On the other hand elastic parameters are essential to derive useful mechanical properties such as brittleness/ductility, stiffness, hardness, shear's modulus (*S*), Young's modulus (Y), compressibility ( $\beta$ ), anisotropic ratio (A) and Poisson's ratio (v) for useful applications.

The following relations give the Born mechanical stability criteria for cubic structure [62]:  $C_{11} > 0$ ;  $C_{44} > 0$ ;  $C_{11} + 2C_{12} > 0$ ;  $C_{11} > B > C_{12}$ , where B is the bulk modulus, which can serve as an indicator of the resistance of the material to fracture. For hexagonal system (WZ), mechanical stability criteria [63] defined as  $C_{11} > |C_{12}|$ ,  $C_{55} > 0$ .

# **5.7 Mechanical properties**

To estimate the mechanical properties, two schemes of approximations are usually used (the Voigt (V) and Reuss (R) approximations [64, 65]). The Reuss and Voigt equations denote the lower and upper limits of the mechanical properties, elastic constants and their related parameters could be predicted by employing Voigt-Reuss-Hill (VRH) approximation, which signify the arithmetic mean of Voigt and Reuss [66]. The shear modulus describes the material's response to shear strain [64, 66]. Following Hill expressions, Hill shear modulus  $S_H$  is the arithmetic mean of Voigt and Reuss shear modulus given as:

$$S_H = \frac{1}{2}(S_v + S_R)$$
(5.9)

where the Voigt shear modulus  $S_v$  and the Reuss shear modulus  $S_R$  are given by the following equations:

$$S_{\nu} = \frac{1}{5} (C_{11} - C_{12} + 3C_{44}) \tag{5.10}$$

$$S_R = \frac{5C_{44}(C_{11}-C_{12})}{4C_{44}+3(C_{11}-C_{12})}$$
(5.11)

The Young's modulus (Y) is ratio of the stress to strain and gives further information about the stiffness of a material, the greater the value of (Y), the stiffer the material is[66], Y is given by:

$$Y = \frac{9S_H B}{(S_H + 3B)}$$
(5.12)

The following relations give the bulk modulus B:

$$B = \frac{1}{3}(C_{11} + 2C_{12})$$
, for cubic and structure (5.13)

$$B = \frac{1}{9} (2(C_{11} + C_{12}) + 4C_{13} + C_{33}) \text{, for hexagonal structure}$$
(5.14)

The elastic anisotropic factor (A) is a fundamental parameter characterizes the variation in atomic arrangement in different directions [25, 26]. The criterion of the anisotropy of the elastic wave velocity in a crystal is given by the following expression:

$$A = \frac{2C_{44}}{C_{11} - C_{12}} \text{ for the cubic systems}$$
(5.15)

$$A = \frac{4C_{44}}{C_{11} + C_{33} - 2C_{13}} \text{ for the hexagonal systems}$$
(5.16)

Material is completely isotropic when A = 1, deviation of A from the unity defines the anisotropy, the values smaller or larger than 1 measure the degree of elastic anisotropy [67, 68].

Poisson's ratio v is an indicator, which can be used to judge the brittleness and ductility of the solid compounds [69]. The critical value of v is 1/3, the compound has a ductile (brittle) nature when v > 1/3 (v < 1/3) [70, 71]. The Poisson's ratio (*v*) is given by:

$$\nu = \frac{3B - 2S_H}{2(3B + 2S_H)} \tag{5.17}$$

Pugh [72] has suggested a simple relationship, which is based on the ratio of the bulk modulus B to shear modulus S. B/S is used to estimate if the material is brittle or ductile in nature. The critical value, which separates ductile from brittle behavior, is around 1.75. The material has a ductile behavior if B/S > 1.75, otherwise the material has a brittle nature. Hardness, a macroscopic concept, which describes the material resistant against the volume changing, can be described by three essential concepts: (i) shear modulus; resistance against reversible deformations (ii) bulk modulus; the resistance to volume changes, and (iii) Vickers hardness. Hardness is better predicted by shear modulus as compared to bulk modulus [73]. In recent research, Chen and co workers have shown that the Vicker hardness approach demonstrates better hardness than shear modulus; Chen's model is given by [71]:

$$H_{\nu} = 2\left(\frac{S^3}{B^2}\right)^{0.585} - 3 \tag{5.18}$$

## **5.8 Thermal properties:**

With the help of the calculated elastic constants, bulk modulus (B), shear modulus (S<sub>H</sub>), Young's modulus (Y) and the Debye temperature ( $\theta_D$ ) are obtained by using the average sound velocity ( $v_m$ ).  $v_m$  has been approximated using a relation which involves transverse ( $v_t$ ) and longitudinal ( $v_l$ ) sound velocities. Debye temperature of material can be define as, the temperature of a crystal's highest normal mode of vibration, or in other words, the highest temperature that can be accomplished as a result of single normal of vibration. The Debye temperature ( $\theta_D$ ) is given by:

$$\theta_D \equiv \frac{h\vartheta_m}{k_B} = \frac{h}{k_B} \left[ \frac{3n}{4\pi} \left( \frac{N_A \rho}{M} \right) \right]^{1/3} v_m \tag{5.19}$$

where  $k_B$  is Boltzmann's constant, h is Plank's constant, n is the number of atoms per formula unit,  $N_A$  is Avogadro's number, M is the molecular weight,  $\rho$  is the mass density per unit volume,  $\vartheta_m$  is the Debye frequency and  $v_m$  is the average sound velocity. The average sound velocity  $v_m$ , longitudinal sound velocity  $v_l$  and transverse sound velocity  $v_t$  are given respectively by the following expressions [74-77].

$$v_m = \left[\frac{1}{3}\left(\frac{2}{V_t^3} + \frac{1}{V_l^3}\right)\right]^{-1/3}$$
(5.20)

$$v_t = \sqrt{\frac{S}{\rho}} \tag{5.21}$$

$$v_l = \sqrt{\frac{B+4S/3}{\rho}} \tag{5.22}$$

Computed values of the elastic constants have been used to calculate transverse, longitudinal and average velocity in addition to Debye temperature.

# Chapter six Results and discussions

# 6.1 LiH Compound

# **6.1.1 Structural properties**

The calculated structural parameters for LiH such as the lattice constant  $a_0$ , bulk modulus  $B_0$ , and the pressure derivative of the bulk modulus  $B'_0$  with RS, CsCl, ZB and WZ phases are obtained by calculating the total energy per unit-cell at several volumes around the equilibrium volume and fitting the calculated values to the Murnaghan's equation of state (ESO) [53]. Figure 6.1.1 shows the total energy as a function of the unit cell volume for LiH with RS, CsCl, ZB and WZ structures. Results for structures are listed in Tables 6.1.1 along with other experimental and theoretical works, while for WZ structure; results are listed in Table 6.1.2. The calculated structural parameters for LiH in RS structure are in agreement with the previous experimental results [4, 48, 78, 79] and other theoretical work [7, 80, 81, 82, 83]. There is an agreement between the predicted values of  $B_0$  and  $B'_0$ and the experimental results [4, 79].

Structure	Structural	Present	Experimental	Other theoretical
	parameters	calculation	results	results
RS	a( Å )	4.018	4.075 <sup>b</sup> , 4.084 <sup>c</sup>	4.0811 <sup>e</sup> , 3.92 <sup>f</sup> , 4.03 <sup>g</sup>
	Bo(GPa)	36.85	32.2 <sup>a</sup>	33 <sup>e</sup> , 34.1 <sup>h</sup> , 32.3 <sup>i</sup> , 31 <sup>g</sup>
	B'	4.02	3.95 <sup>d</sup>	$4.9^{\rm e}, 3.5^{\rm g}$
CsCl	a( Å )	2.510	==========	2.458 <sup>e</sup>
	Bo(GPa)	33.60	===========	30.16 <sup>e</sup>
	B'	4.01	=======	4.05 <sup>e</sup>
ZB	a( Å )	4.307	========	===========
	Bo(GPa)	27.17	=======	
	B'	3.94	=======	========
				=======================================

 Table 6.1.1: Structural parameters for LiH in RS, CsCl and ZB

 structures along with experimental and other theoretical results.

<sup>a</sup>Ref.[4], <sup>b</sup>Ref.[78], <sup>c</sup>Ref.[48], <sup>d</sup>Ref.[79], <sup>e</sup>Ref.[7], <sup>f</sup>Ref.[80], <sup>g</sup>Ref.[81], <sup>h</sup>Ref.[82], <sup>i</sup>Ref.[83]

For the CsCl structure, we have no experimental results to compare with. Structural parameters of LiH are closed to the results of Sudha *et al.*[7].

To the best of our knowledge, the structural parameters for LiH in ZB and WZ structures are not available experimentally and theoretically.

 Table 6.1.2: Structural parameters for LiH in WZ structure.

compound	a <sub>o</sub> (Å)	c/a	u(a.u.)	B(GPa)	В
LiH	3.115	1.4942	0.385	27.91	3.36



**Figure 6.1.1:** Calculated total energy per unit cell versus  $V/V_0$  for LiH in RS, CsCl, ZB and WZ structures

# **6.1.2 Phase transition**

The energy per unit cell as a function of volume is calculated by using PBE-GGA approach. The calculated total energy versus V/V<sub>0</sub>; where V is the unit cell volume and V<sub>0</sub> is the equilibrium unit cell volume; by using PBE-GGA for LiH is shown in Figure 6.1.1. It is clear from Figure 6.1.1that the RS structure, at ambient pressure (zero pressure and zero temperature), is the more stable ground state structure for LiH. Under compression, the calculations show that LiH will undergo a structural phase transition from RS to CsCl structures, while transition from RS to ZB or from RS to WZ undergoes under expansion. The enthalpy versus pressure curves for the both structures for LiH are displayed in Figure 6.1.2. The

calculated transition pressures from RS to CsCl structure for LiH compound is 211.8 GPa using PBE-GGA approach, which is in the range of the previous theoretical calculations [7, 8, 84], the difference between the theoretical calculations is related to variations in the approaches used. The transition from RS to CsCl is occurred at very high pressure with  $V/V_0$ =0.446, where  $V_0$  is the equilibrium volume of the RS unit cell and V is the transition volume, while the transition from RS to ZB or WZ needs volume expansion, the  $V/V_0$  fractions are listed in Table 6.1.3. The computed transition pressures as well as the previous theoretical data for LiH are given in Table 6.1.4.

Table 6.1.3: The V/V<sub>0</sub> fraction for LiH.

Compound	$RS \rightarrow CsCl$	$RS \rightarrow ZB$	$RS \rightarrow WZ$
$V/V_0$ for LiH	0.446	1.291	1.194

Table 6.1.4: Calculated transition pressure  $P_t$  as well the other theoretical data for LiH compound.

$RS \rightarrow CsCl P_t(0)$	GPa)	$RS \rightarrow ZB$	$RS \rightarrow WZ$
Present Work	Other theoretical works	P <sub>t</sub> (GPa)	P <sub>t</sub> (GPa)
211.8	208 <sup>a</sup> , 660 <sup>b</sup> , 329 <sup>c</sup>	-3.83	-2.4

<sup>a</sup>Ref.[7], <sup>b</sup>Ref.[8], <sup>c</sup>Ref.[84]



Figure 6.1.2: Enthalpy as a function of pressure for LiH using PBE-GGA approximation.

# 6.1.3 Electronic band structure

The calculated band structure along the high symmetry lines in Brillouin Zone of LiH in the RS, CsCl, ZB and WZ using PBE-GGA and mBJ-GGA approaches for the exchange-correlation potential are calculated and shown in Figure 6.1.3 The band structures are calculated using the computed equilibrium lattice constants in tables 6.1.1 and 6.1.2. Figure 6.1.3 shows that the LiH in the RS structure has a direct energy band gap with valence

and conduction bands both lying at X-point symmetry line, while the other structures have indirect energy band gap. The calculated energy band gaps are listed in Table 6.1.5, the calculated energy band gaps using mBJ-GGA is broader than that using PBE-GGA approach; the differences in minimum energy gap between PBE-GGA and mBJ-GGA are 2, 2.158, 1.462 and 1.623 eV with RS, CsCl, ZB and WZ structures. LiH compound in CsCl structure seems to be semiconductor when using PBE-GGA approach, while it is wideband gap semiconductor using mBJ-GGA approach. According to the above-mentioned approaches; PBE-GGA and mBJ-GGA; energy band gap E<sub>g</sub> using mBJ-GGA is proved to be more accurate compared to the experimental results. It is clear that LiH compound, using mBJ-GGA, is insulators in all structures except in CsCl structure; it is a wide energy band gap semiconductor. It is clear from Table 6.1.5 that the energy band gaps for LiH in RS structure, using PBE-GGA approximation is somewhat smaller than the experimental values and this is mainly due to the self-interaction problem. PBE-GGA approximation contains the selfinteraction error [15, 85], due to this unphysical problem (PBE-GGA shifts some states to incorrect high energy level), usually, the energy band gap is strongly underestimated and sometimes semiconductor or metallic state is obtained instead of an insulating one. This problem shifts the Li-2s state to incorrect high energy level and interacts with H-1s state; this interaction increases Coulomb repulsion that lowering the valence band and causes narrowing of energy band gap [85].

Table 6.1.5: Calculated energy band gap value  $E_g(eV)$  of LiH in RS,

Structure	Present work		Experimental	Other theoretical works
	GGA	mBJ	works	
RS	X→X: 3.190	5.200	4.4 <sup>a</sup>	$4.6723^{\rm b}, 4.94^{\rm c}, 5.37^{\rm d},$
	W→X: 3.250	5.400		4.92 <sup>e</sup>
CsCl	R→X: 0.740	2.940		
	M→M: 4.230	6.480		
ZB	W→L:4.340	6.150		1.5 <sup>b</sup>
	L→L: 5.240	6.950		
WZ	Λ→K: 3.800	5.730		
	K→K : 4.250	6.120		

CsCl, ZB and WZ structures.





Figure 6.1.3: Band structure of LiH in RS, CsCl, ZB and WZ in PBE-GGA and mBJ-GGA approaches.

Becke and Johnson proposed an exchange potential, which was designed to reproduce the exact exchange potential, the calculated energy band gaps by mBJ-GGA are in good agreement with the experimental value [86] and other theoretical values [7, 84, 87, 88]. Figure 6.1.4 shows the density of states for LiH compound using both GGA and mBJ-GGA approaches. For further understanding the nature of these electronic bands structure, the total and partial density of states for LiH compound at ambient pressure also have been calculated.

Density of state (DOS) of a system describes the number of states at each energy level that are available to be occupied. From the total and local partial DOS for LiH we can see that the energy below the Fermi energy (FE) indicated by a dotted horizontal line, comes mainly from H-s along with a small contribution from Li-s, Li-p. Above the (FE) it is mainly comes from Li-P and Li-s states with small contribution from H-s state. In case of LiH using PBE-GGA, the lowest lying bands above FE, bottom of the valence states, are around 0.74 eV along X-point, 4.3 eV along L-point and 3.65 eV along K-point for CsCl, ZB and WZ, while by using mBJ-GGA they are 2.9 eV along X-point, 5.75eV along L-point and 5.3eV along K-point. Figure 6.1.4 also shows that the density of states (states/eV), top of the peaks, by using mBJ-GGA are greater than that with PBE-GGA for all structures. It is clear from Figure 6.1.4, that the energy band gap using mBJ-GGA is broader than that with PBE-GGA approach.


Figure 6.1.4: Density of states of LiH in RS, CsCl, ZB and WZ structures.

# **6.1.4 Optical properties**

The dielectric function is complex function; it is an important optical parameter, which can be defined as the material response to electromagnetic radiation. Using the relations in section 5.5, optical constants can be determined and analyzed. The static real dielectric constants for LiH with the four studied structures (RS, CsCl, ZB and WZ) when photon energy is zero; namely  $\varepsilon_1(0)$  are 4.13, 3.92, 2.83 and 2.86eV, respectively using PBE-GGA approach and 2.46, 2.62, 2.0 and 2.0eV respectively using mBJ-GGA approach. It is clear that mBJ-GGA has a lower value of  $\varepsilon_1(0)$  and this is mainly relating to variation in electronic band structure as seen in section 6.1.3. In the high-energy region  $\varepsilon_1(w)$ value with the four structures is negative, which means LiH compound has a metallic behavior in the high-energy region. The calculated real and imaginary parts of the optical dielectric function for LiH compound with the RS, CsCl, ZB and WZ structures are displaying in Figure 6.1.5 and in Figure 6.1.6 as a function of the photon energy from 0.0 to 14.0eV. The maximum values of  $\varepsilon_1(w)$  with the four structures shifted toward the highenergy with decreasing intensity compared to PBE-GGA approach. The calculated values of dielectric constants indicate that the cubic structures of LiH is optically isotropic;  $\varepsilon_{xx} = \varepsilon_{zz}$ ; while the WZ structure is optically anisotropic;  $\varepsilon_{xx} \neq \varepsilon_{zz}$ . The imaginary part gives us information about absorption behavior of the studied compounds. From Figure 6.1.6,  $\varepsilon_2$ begins to have a considerable amount at about 3.0, 5.1, 6.0 and 5.0eV with PBE-GGA along [100] polarization and 6.1, 7.5, 7.8 and 9.0eV with mBJ-

GGA along [100] polarization. The imaginary part  $\varepsilon_2$  indicates that the LiH with RS, CsCl, ZB and WZ maximum absorption peak values are around 7.44, 6.49, 6.49 and 6.33eV, respectively using PBE-GGA and 9.6, 8.57, 8.44 and 8.43eV, respectively using mBJ-GGA method.



Figure 6.1.5: Real part of the dielectric constant of LiH in RS, CsCl, ZB and WZ structures.



Figure 6.1.6: Imaginary part of the dielectric constant of LiH in RS, CsCl, ZB and WZ structures.

Figure 6.1.7 shows the absorption spectrum which is related directly to the imaginary part of  $\varepsilon_2$ . It is clear that there are strong absorption peaks for LiH with RS, CsCl, ZB and WZ in the energy range from 3.0, 5.2, 6.1 and 5.8eV to 14eV, respectively using PBE-GGA and from 6.0, 7.2, 7.9 and 7.5eV to 14eV, respectively using mBJ-GGA, these peaks reflect some transitions between different orbits. From Figure 6.1.7, maximum absorption for LiH in RS, CsCl, ZB and WZ structures occurs at 7.54, 8.27, 6.59 and 6.31eV, respectively using PBE-GGA and 9.7, 9.64, 9.81 and 8.18eV, respectively using mBJ-GGA. Real conductivity, as shown in Figure 6.1.8, with the four structures has the same shape of absorption  $\alpha(\omega)$ , (Figure 6.1.7). The reflectivity coefficient R(w) for LiH with RS, CsCl, ZB and WZ are displayed in Figure 6.1.9, the zero-frequency or static reflectivity for RS, CsCl, ZB and WZ structures are 11.5%, 11.0%, 6.3% and 6.7%, respectively with PBE-GGA approach and 4.9%, 5.6, 2.6% and 3.0%, respectively with mBJ-GGA approach. With both PBE-GGA and GGA-mBJ approaches, R(w) increases as the photon energy increases with frequent peaks; these peaks originate from the inter-band transitions; as the photon energy reaches 14eV, R(w) goes to the maximum value. LiH compound has a high reflectivity against high-energy photons; it is a good coating material to avoid and prevent solar heating.



Figure 6.1.7: Absorption function of LiH in RS, CsCl, ZB, and WZ structures.



Figure 6.1.8: Real conductivity function of LiH in RS, CsCl, ZB, and WZ structures.

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Figure 6.1.10 is displaying the refractive index n(w). The static refractive index; when photons energy is zero; n(0) is found to be 2.02 in RS structure, 1.98 in CsCl structure, 1.68 in ZB structure and 1.69 in WZ structure, respectively using PBE-GGA approach and 1.55 in RS structure, 1.61 in CsCl structure, 1.4 in ZB structure and 1.41 in WZ structure, respectively using mBJ-GGA approach. The static refractive index n(0)value is equal the square root of the real part of dielectric function;  $n(0) = \sqrt{\varepsilon_1(0)}$ ; which is to some extent the same as that obtained from Figure 6.1.10. Figure 6.1.11 displaying the energy loss function L(w), L(w) is related to the energy loss of a fast electron in the material. Figure 6.1.11 shows that loss function maximum values for LiH in RS, CsCl, ZB and WZ structures are at 11.77, 13.0, 11.64 and 13.19 eV, respectively using GGA approach and 13.05, 13.0, 13.44 and 10.86 eV using mBJ approach, L(w) is usually large at the Plasmon energy [89]. The extinction coefficient k(w) is displayed in Figure 6.1.12; the curves of extinction coefficient  $k(\omega)$  are closed to the  $\varepsilon_2(\omega)$  and have similar features with the absorption coefficient  $\alpha(\omega)$ . k(w) of LiH in RS, CsCl, ZB and WZ structures starts from 2.1, 4.0, 3.8 and 4.8eV, respectively by using PBE-GGA approach and 5.7, 6.5, 6.0 and 6.9eV, respectively by using mBJ-GGA approach. k(w) of LiH in RS, CsCl, ZB and WZ structures has maximum value at energy equals 7.1, 5.68, 4.87 and 4.6eV, respectively using PBE-GGA approach and 12.7, 6.7, 8.13 and 8.32eV, respectively using mBJ-GGA approach.



Figure 6.1.9: Reflectivity coefficient R(w) of LiH in RS, CsCl, ZB, and WZ structures.



Figure 6.1.10: Refractive index n(w) of LiH in RS, CsCl, ZB, and WZ structures.

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Figure 6.1.11: Energy loss function L(w) of LiH in RS, CsCl, ZB, and WZ structures.



Figure 6.1.12: Extinction coefficient k(w) of LiH in RS, CsCl, ZB, and WZ structures.

#### **6.1.5 Elastic properties**

The calculated elastic constants and bulk moduli for LiH, together with the available experimental and theoretical results are displayed in Table 6.1.6 for the RS, CsCl and ZB structures, respectively [7, 80, 83, 90]. The computed elastic constants for LiH compound in the RS structure agree well with experimental and previous theoretical results [7, 80, 83, 90]. The variation in theoretical results is due to the variation in the potential approximations used.

Table 6.1.6: The calculated elastic constants C<sub>ij</sub> (GPa), Bulk modulus (B) in Voigt (V), Reuss (R) and Hill (H) approximations (in GPa) for LiH in cubic structures.

	RS Strue	cture		CsCl Structure		ZB
Elastic						Structure
Constant	Presen	Experimental	Other	Present	Other	Present
S	t work	work	theoretical	work	theoretical	work
			work		work	
C <sub>11</sub>	70.2	66.4 <sup>a</sup> , 74.1 <sup>b</sup>	78.01 <sup>°</sup> ,	175	66.5 <sup>e</sup>	35
C <sub>12</sub>	10.2	$15.6^{\rm a}, 14.2^{\rm b}$	82.7 <sup>d</sup>	-38	12 <sup>e</sup>	19.6
C <sub>44</sub>	50.4	$45.8^{\rm a}, 48.1^{\rm b}$	$10.5^{\rm e}, 10.7^{\rm d}$	-22	32 <sup>e</sup>	33.4
			43.3 <sup>e</sup> , 52.5 <sup>d</sup>			
B <sub>V</sub>	30.2		31.2 <sup>e</sup>	32	30 <sup>e</sup>	25
B <sub>R</sub>	30.2			32		25
B <sub>H</sub>	30.2			32		25

<sup>a</sup>Ref.[90], <sup>b</sup>Ref.[83], <sup>c</sup>Ref.[7], <sup>d</sup>Ref.[80]

It is clear from Table 6.1.6 that these elastic constants satisfy the Born– Huang criteria (defined in chapter 5) for the RS and CsCl structures; meaning that they are mechanically stable, while the CsCl structure does not satisfy the Born–Huang criteria. Similarly, for the hexagonal system (WZ) presented in Table 6.1.7, the criteria for mechanical stability is also satisfied.

Figure 6.1.13 shows the pressure dependence of the elastic constants and bulk moduli for LiH compound in RS structure. It is noticed that elastic constant  $C_{11}$  and bulk modulus increase with the applied pressure. It is also noticeable that elastic constant  $C_{11}$  is the most sensitive to pressure than  $C_{12}$ ,  $C_{44}$  and B. At high pressure,  $C_{44}$  approaches zero, indicating that these compounds are unstable under high pressure, and the RS structure transforms to CsCl structure.

Table 6.1.7: The calculated elastic constants C<sub>ij</sub> (GPa), Bulk modulus (B) in Voigt (V), Reuss (R) and Hill (H) approximations (in GPa) for LiH in WZ structure.



Figure 6.1.13: Variation of elastic constants and bulk moduli for LiH compound in RS structure.

#### **6.1.6** Mechanical properties

The bulk modulus for LiH compound is small, which means the weak resistance to the fracture of these materials. The CsCl phase is the hardest because it possess the most bulk modulus value, on the other hand the compressibility ( $\beta$ =1/B) of this phase structure is the least one, while WZ structure has the most compressibility. The value of the bulk modulus B computed from the elastic constants is to some extent agrees with the results obtained from Murnaghan's equation of state [53]. Table 6.4.7 displays the anisotropy factor (A) for LiH compound in the four structures; WZ structure is completely isotropic with A=1, while the other structures are anisotropic because A is far from unity.

Poisson's ratio v is an indicator, which can be used to judge the brittleness and ductility of the solid compounds. The critical value of v is 1/3, the compound has a ductile (brittle) nature when v > 1/3 (v < 1/3), Poisson's ratio for LiH compound as shown in table 6.1.8 is less than 1/3 in all structures, means they have a brittle nature.

Table 6.1.8: The calculated Young's modulus (Y), Shear modulus (S) (in GPa), compressibility ( $\beta$  in GPa<sup>-1</sup>), B/S ratio, Poisson's ratio ( $\upsilon$ ), Anisotropic ratio (A), Cauchy pressure C<sub>s</sub> and Vickers hardness (H<sub>v</sub>) for LiH compound in RS, CsCl, ZB and WZ structures in comparison with available theoretical data.

	Rs Structure		CsCl S	tructure	ZB	WZ
Constant					Structure	Structure
	Present	Other	Present	Other	Present	Present
	Calculations	theoretical	Calculations	theoretical	Calculations	Calculations
		Calculations		Calculations		
Y	86.5	83 <sup>a</sup>	68	68 <sup>a</sup>	53	68.2
S	42	39 <sup>a</sup>	29	30 <sup>a</sup>	23	32.4
B/S	0.72	$0.8^{\mathrm{a}}$	1.1	$1.0^{\mathrm{a}}$	1.08	0.8
$\upsilon_{\rm V}$	0.023	0.11 <sup>a</sup>	0.13	0.15 <sup>a</sup>	0.145	0.062
А	1.68	1.28 <sup>a</sup>	0.32	$1.17^{a}$	4.33	1.0
β	0.033	0.032	0.031	0.033	0.04	0.038
H <sub>v</sub>	23.19	19.1	9.77	11.6	8.35	16.6

<sup>a</sup>Ref.[7].

The material has a ductile behavior if B/S > 1.75, otherwise the material has a brittle nature. From Table 6.4.7, it is clear that LiH compound represents a brittle nature, which agrees with Poisson's ratio and the small value of the bulk modulus. Hardness is a macroscopic concept, which describes the material resistant against the volume changing. Chen's model for hardness is given by equation (6.12) in chapter 6.

Table 6.4.7 shows that the LiH in RS structure has the most value of Vicker's hardness ( $H_v$ ) (the most hardness), on the other hand, ZB structure has the least value of  $H_v$ , and Young's modulus (Y) value for LiH in RS structure is the highest value. Therefore, Y agrees with  $H_v$  that LiH in RS structure is the stiffer structure; the greater the value of Young's modulus (Y) is the stiffer the material. This means that RS structure is mechanically the strongest among all phases, which is consistent with the bulk modulus and  $H_v$  values, while ZB structure is the least strong mechanically.

# 6.1.7 Thermal properties

With the help of the calculated elastic constants, bulk modulus (B), shear modulus (S<sub>H</sub>), Young's modulus (Y) and the Debye temperature ( $\theta_D$ ) are obtained. Debye temperature and average wave velocity are displayed in Table 6.1.8. The RS structure has the least value of Debye temperature and average wave velocity, while WZ has the greater value of Debye temperature and ZB has the greatest value of the average velocity. To return to the previous shear modulus (S), bulk modulus (B) and sound velocity values, it is clear that mainly the sound velocity depends on the estimated values of the shear modulus (S) and bulk modulus (B). As the shear and bulk modulus increase, the sound velocity increases. Figure 6.1.14 shows the dependence of Debye temperature and average wave velocity on the pressure, Debye temperature increases as the pressure increases. The same view for the average wave velocity.

# Table 6.1.9: Average wave velocity ( $V_m$ in m/s) and Debye temperature ( $\Theta_D$ in K) for LiH compound in RS, ZB and WZ structures.

Constant		RS structure	CsCl	ZB structure	WZ structure
			structure		
	Present	Other	Present	Present	Present
	calculations	theoretical	calculations	calculations	calculations
		calculations			
$\Theta_{\rm D}$	1051	1131 <sup>a</sup>	784	820	1142
V <sub>m</sub>	7550	7748 <sup>a</sup>	4390	5931	7716

<sup>a</sup>Ref.[7].



Figure 6.1.14: Variation of average wave velocity for LiH compound in RS structure.



Figure 6.1.15: Variation of Debye temperature for LiH compound in RS structure.

# 6.2 NaH Compound

### **6.2.1 Structural properties**

The calculated structural parameters for NaH such as the lattice constant  $a_0$ , bulk modulus  $B_0$ , and the pressure derivative of the bulk modulus  $B'_0$  in RS, CsCl, ZB and WZ phases are obtained by calculating the total energy per unit-cell at several volumes and fitting the calculated values to the Murnaghan's equation of state (ESO) [53]. Figure 6.2.1 shows the total energy as a function of the unit cell volume for NaH with RS, CsCl, ZB and WZ structures. Results for RS, CsCl, and ZB structures are listed in Table 6.2.1, along with other experimental and theoretical works, while for WZ structure, results are listed in Table 6.2.2.

<b>C</b> 4	C41	<b>D</b> 4		
Structure	Structural	Present	Experimental	Other theoretical
	parameters	calculations	results	results
	a <sub>0</sub> (Å )	4.838	$4.880^{a}$	4.8511 <sup>d</sup> , 4.865 <sup>e</sup> , 4.921 <sup>f</sup>
RS	B <sub>0</sub> (GPa)	23.30	$14.3 \pm 1.5^{b}$ ,	4.775 <sup>g</sup>
	B'o	3.55	$19.4\pm2^{c}$	26 <sup> d</sup> , 22.90 <sup>e</sup> , 20 <sup>f</sup> , 27.4 <sup>h</sup> ,
			$7.7 \pm 1.0^{b}$ ,	29.6 <sup>g</sup>
			$4.40\pm0.5^{\circ}$	$3.62^{\rm d}, 4.1^{\rm f}, 3.78^{\rm e}$
CsCl	a <sub>0</sub> (Å )	2.965	3.094 <sup>c</sup>	3.010 <sup>d</sup> ,4.838 <sup>i</sup> , 4.955 <sup>j</sup> ,
	B <sub>0</sub> (GPa)	23.97	$28.30 \pm 3.0^{\circ}$	2.982 <sup>e</sup>
	B'o	3.83	4.30±0.40 <sup>c</sup>	$28^{\rm d}$ , $22.81^{\rm i}$ $23.5^{\rm k}$ ,
	, C			23.21 <sup>e</sup>
				$2.669^{d}$ , $3.75^{1}$ , $3.16^{k}$ ,
				3.75 <sup>e</sup>
ZB	a <sub>0</sub> (Å )	5.228	===========	==============
	B <sub>0</sub> (GPa)	17.49	=====================================	=============
	B'o	3.67	=====================================	=============

Table 6.2.1: Structural parameters for NaH with RS, CsCl and ZB structures along with experimental and other theoretical results.

<sup>a</sup>Ref[78], <sup>b</sup>Ref.[3], <sup>c</sup>Ref.[5], <sup>d</sup>Ref.[7], <sup>e</sup>Ref.[9], <sup>f</sup>Ref.[81], <sup>g</sup>Ref.[80], <sup>h</sup>Ref.[91], <sup>i</sup>Ref.[92], <sup>j</sup>[15], <sup>k</sup>[11], <sup>l</sup>[93].

 Table 6.2.2: Structural parameters for NaH with WZ structure.

Compound	a <sub>0</sub> (Å )	c/a <sub>0</sub>	u(a.u.)	B <sub>0</sub> (GPa)	B'o
NaH	3.748	1.5672	0.390	18.06	3.90

The calculated lattice constants for NaH in RS and CsCl structures are in agreement with the previous experimental results [3, 5, 78] and other theoretical work [7, 9, 11, 80, 81, 91, 93], while results of references [15, 92] for NaH in CsCl disagree with the present work and the experimental results. There is an agreement between the predicted values of  $B_0$  and  $B'_0$  and the experimental results in Ref.[5] and theatrical calculations [7, 9, 80, 81, 91], while  $B_0$  and  $B'_0$  values are far from results in Ref.[3].

The variation in theoretical results is due to the variation in the potential approximations used.

# **6.2.2 Phase transition**

The energy per unit cell as a function of volume is calculated by using PBE-GGA approach. The calculated total energy versus  $V/V_0$ , where V is the unit cell volume and  $V_0$  is the equilibrium unit cell volume, for NaH is shown in Figure 6.2.1. It is clear from Figure 6.2.1 that the RS structure, at ambient pressure (zero pressure), is thermodynamically stable structure (ground state structure), it has a minimum energy. Under compression, the calculations as shown in Table 6.2.4 show that the compound undergoes a structural phase transition from RS to CsCl structures (positive transition pressure), while transition from RS to ZB or from RS to WZ undergoes an expansion (negative transition pressure). The enthalpy versus pressure curves for the both structures for NaH are displayed in Figure 6.2.2. The calculated transition pressures from RS to CsCl structure for NaH compound is 34.26 GPa using PBE-GGA approach, which is in the range of the experimental [5] and other theoretical calculations [7, 8, 9, 12, 92]. The transition from RS to CsCl is occurred at very high pressure with  $V/V_0=0.565$ , where  $V_0$  is the equilibrium volume of the RS unit cell and V is the transition volume, while the transition.



**Figure 6.2.1:** calculated total energy per unit cell versus  $V/V_0$  for NaH in RS, CsCl, ZB and WZ structures.



Figure 6.2.2: Enthalpy as a function of pressure for NaH using PBE-GGA approximation.

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from RS to ZB or WZ needs volume expansion, the  $V/V_0$  fractions are listed in Table 6.2.3. The computed transition pressures as well as the previous theoretical data for NaH are given in Table 6.2.4.

# Table 6.2.3: The V/V<sub>0</sub> fraction for NaH.

$V/V_0$ for	$RS \rightarrow CsCl$	$RS \rightarrow ZB$	$RS \rightarrow WZ$
NaH	0.565	1.255	1.225

Table 6.2.4: Calculated transition pressure Pt as well the experimentaland other theoretical data for NaH compound.

Compound	$RS \rightarrow CsC$	Cl P <sub>t</sub> (GPa)	$RS \rightarrow ZB$	$RS \rightarrow WZ$	
	Present	Experiment	Other	P <sub>t</sub> (GPa)	P <sub>t</sub> (GPa)
	Work	al works	theoretical		
			works		
NaH	34.26	29.3±0.9 <sup>a</sup>	$37^{b, c, d}, 32^{e, f}$	-1.94	-1.57

<sup>a</sup>Ref.[5], <sup>b</sup>Ref.[12], <sup>c</sup>Ref.[7], <sup>d</sup>Ref[8], <sup>e</sup>Ref.[9], <sup>f</sup>Ref.[92]

# 6.2.3 Electronic band structure

The calculated band structure along the high symmetry lines in the Brillouin zone, for NaH in the RS, CsCl, ZB and WZ phases using PBE-GGA and mBJ-GGA approaches for the exchange-correlation potential, are shown in Figure 6.2.3. The band structures are calculated using the computed equilibrium lattice constants. Figure 6.2.3 shows that the NaH in the RS structure has a direct energy band gap with the valence and conduction bands that are situated at the X-point symmetry line, while the other phases have an indirect energy band gap. The calculated PBE-GGA and mBJ-GGA energy band gaps are listed in Table 6.2.5 along with other theoretical works [7, 82, 94]. It can be seen that the calculated energy band

gaps using mBJ-GGA are broader than those using PBE-GGA approach. The differences in the minimum energy gaps between GGA and mBJ-GGA are 2.88, 3.45, 2.75, and 2.80 eV in RS, CsCl, ZB and WZ structures, respectively. NaH in CsCl phase is semiconductors within the GGA approximation. By using the mBJ-GGA, the NaH is found to be an insulator. It is clear that these compounds, using mBJ-GGA, are insulators in all structures. Figure 6.2.4 shows the density of states for NaH compound, using both PBE-GGA and mBJ-GGA approaches. In order to understand the nature of these electronic bands structures further, the total and partial density of states for NaH compound at ambient pressure have also been calculated. Density of state (DOS) of a system describes the number of states at each energy level that are available to be occupied. From the total and partial DOS for NaH (Figure 6.2.4), one can see that the bands below the Fermi energy level (FE) - indicated by a dotted horizontal line - come mainly from the H-s states along with a small contribution from Na-s and Na-p states. Above the FE, the bands mainly come from Na-s and Na-p states, with a small contribution from H-s state.

Structure	Present work		Other theoretical works
	GGA	mBJ	
RS	W→L : 3.820	6.700	4.8560 <sup>a</sup> , 3.46 <sup>b</sup> , 5.68 <sup>c</sup>
	L→L : 4.630	7.130	
CsCl	R→X: 1.100	4.550	1.0 <sup>a</sup>
	X→X : 4.490	7.050	
ZB	W→L: 3.750	6.500	
	L→L : 4.380	6.900	
WZ	A→Γ: 3.800	6.600	
	M→M : 4.350	6.800	

Table 6.2.5: Calculated energy band gap value of NaH in RS, CsCl, ZB and WZ structures.

# <sup>a</sup>Ref.[7], <sup>b</sup>Ref.[82], <sup>c</sup>Ref.[94]

In the case of NaH compound using PBE-GGA, the lowest lying bands above FE are around 3.82eV along the L-symmetry point, 1.1 eV along the X-symmetry point, 3.75eV along the L-symmetry point and 3.8eV along the  $\Gamma$ -symmetry point for RS, CsCl, ZB and WZ structures, respectively. Lastly, by using the mBJ-GGA, the lowest lying bands above FE are around 6.7eV along the L-symmetry point, 4.55eV along the X-symmetry point, 6.50eV along the L-symmetry point and 6.6eV along the  $\Gamma$ symmetry point. Figure 6.2.4 also shows that the peaks of the density of states (states/eV) obtained by using mBJ-GGA approach are sharper and greater in magnitude compared to those obtained by using PBE-GGA approach. It is also clear from Figure 6.2.4 that the energy band gap using mBJ-GGA is broader than that using PBE-GGA method.



Figure 6.2.3: Band structure of NaH in RS, CsCl, ZB and WZ in PBE-GGA and mBJ-GGA approaches.



Figure 6.2.4: Density of states of NaH in RS, CsCl, ZB and WZ structures.

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#### **6.2.4 Optical properties**

The static real dielectric constants  $\varepsilon_1(0)$  (when photon energy is zero) for NaH with the four studied structures (RS, CsCl, ZB and WZ) are about 2.27, 2.9, 2.4 and 2.4eV, respectively using PBE-GGA approach and 1.7, 1.8, 1.5 and 1.5eV, respectively using mBJ-GGA approach. Because there are variations in the electronic band structure; band gap is broader with mBJ-GGA;  $\varepsilon_1(0)$  with mBJ-GGA has a lower value comparing to PBE-GGA approach. The calculated real and imaginary parts of the optical dielectric function for NaH compound with the RS, CsCl, ZB and WZ structures have been displayed in Figures 6.2.5 and 6.2.6 as a function of the photon energy from 0.0 to 14.0 eV.

The imaginary part gives us information about absorption behavior of the studied compounds. From Figure 6.2.6, the imaginary part of dielectric function  $\varepsilon_2$  onset of absorption around 4.5, 4.2, 4.1 and 4.1 eV with PBE-GGA and 7.20, 6.95, 6.9 and 6.5 eV with mBJ-GGA, which to some extent in accordance with the direct energy gap along L-symmetry point with RS and ZB structures, along X-symmetry point with CsCl and along M-symmetry point with WZ structure. The imaginary part  $\varepsilon_2$  indicates that the NaH with RS, CsCl, ZB and WZ maximum absorption peak values are around 6.44, 6.58, 6.33 and 5.86 eV, respectively using PBE-GGA and 9.0, 9.46, 8.8 and 8.31 eV, respectively using mBJ-GGA, respectively. From Figure 6.2.7 for the absorption spectrum  $\alpha(w)$  which is related directly to the imaginary part  $\varepsilon_2$ , it is clear that there are strong absorption peaks for NaH with RS, CsCl, ZB and WZ in the energy range from 6, 5.2, 5.2 and

5.0 eV to 14 eV, respectively using PBE-GGA and from 8.2, 8.0, 7.8 and 7.8 eV to 14 eV, respectively using mBJ-GGA, these peaks reflect some transitions between different orbits. From Figure 6.2.7, maximum absorption for NaH with RS, CsCl, ZB and WZ occurs at 5.9, 5.0, 4.8 and 4.6 eV, respectively using PBE-GGA and 8.0, 7.8, 7.75 and 7.3 eV respectively using mBJ-GGA. Absorption with mBJ-GGA is very large compared with that using PBE-GGA method.



**Figure 6.2.5:** Real dialectic constant  $\varepsilon_1(w)$  of NaH in RS, CsCl, ZB and WZ structures.



Figure 6.2.6: Imaginary dielectric constant  $\varepsilon_1(w)$  of NaH in RS, CsCl, ZB and WZ

The reflectivity coefficient R(w) for NaH in RS, CsCl, ZB and WZ structures are displayed in Figure 6.2.8, the zero-frequency reflectivity are 6%, 4.0%, 4.6% and 6.7%, respectively with PBE-GGA and 1.7%, 2.6, 1.1% and 1.1%, respectively with mBJ-GGA approach. It is clear that R(0) with RS structure using mBJ-GGA is greater than that using PBE-GGA approach. With the four structures and after R (w) reaches its maximum value, it begins to decreases until about 13 eV, again it increases with both PBE-GGA, and mBJ-GGA approaches. Along the spectrum from 0 eV to 14 eV, there are peaks; these peaks originate from the inter-band transitions. Figure 6.2.9 displays the energy loss function L(w), which is related to the energy loss of a fast electron in the material. Figure 6.2.9 shows that loss function for NaH in RS, CsCl, ZB and WZ structures begins at 5.48, 5.39, 4.84 and 4.45 eV, respectively using PBE-GGA

approach and 7.38, 8.0, 7.47 and 6.74 eV using mBJ-GGA approach, as seen L(w) increases as the photon energy increases.

Figure 6.2.10 displays the refractive index n(w). The static refractive index n(0) is found to have the values 1.64 with RS structure, 1.70 in CsCl structure, 1.55 in ZB structure and 1.54 in WZ structure, respectively using PBE-GGA approach and 1.34 in RS structure, 1.36 in CsCl structure, 1.24 in ZB structure and 1.24 in WZ structure, respectively, using mBJ-GGA approach.



**Figure 6.2.7**: Absorption spectrum α(w) of NaH in RS, CsCl, ZB and WZ structures.



Figure 6.2.8: Reflectivity coefficient R(w) for NaH in RS, CsCl, ZB and WZ structures.



Figure 6.2.9: Energy loss function L(w) for NaH in RS, CsCl, ZB and WZ structures.

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The static refractive index n(0) value is equal the square root of the real part of dielectric function;  $n(0) = \sqrt{\varepsilon_1(0)}$ ; which is to some extent the same as that obtained from Figure 6.2.10.

The extinction coefficient k(w) displays in Figure 6.2.11, K(w) of NaH starts to have a considerable value for NaH in RS, CsCl, ZB and WZ at 4.5, 4.3, 4.25 and 4.27eV, respectively using PBE-GGA and at 7.5, 7.4, 7.5 and 7.47eV respectively, using mBJ-GGA. From these figures, we can see that the cubic structures are optically isotropic but not the WZ structure.



Figure 6.2.10: Refractive index n(w) for NaH in RS, CsCl, ZB and WZ structures.



Figure 6.2.11: Extinction coefficient k(w) for NaH in RS, CsCl, ZB and WZ structures.

# **6.2.5 Elastic properties**

The calculated elastic constants and bulk moduli for NaH, together with the available experimental and other theoretical results are displayed in Table 6.2.6 in the RS, CsCl and ZB structures, respectively [7, 80, 83]. The computed elastic constants for NaH compound in the RS structure are to some extent in agreement with the experimental and previous theoretical results [7, 80, 83]. The Born mechanical stability criteria for cubic structure are given in chapter 5.

Table 6.2.6: The calculated elastic constants  $C_{ij}$  (GPa), Bulk modulus(B) in Voigt (V), Reuss (R) and Hill (H) approximations (in GPa) forNaH in cubic structures.

	RS Structu	ire		CsCl Structure		ZB
Elastic						Structure
Constants	Present	Experime	Other	Present	Other	Present
	work	ntal work	theoretical	work	theoretic	work
			work		al work	
C <sub>11</sub>	39.1	47.3 <sup>a</sup>	59.1 <sup>b</sup> , 53.2 <sup>c</sup>	95.2	73.02 <sup>b</sup>	19.5
C <sub>12</sub>	13.0	$2.5^{\rm a}$	$9.2^{\rm b}, 14.8^{\rm c}$	-14	11.9 <sup>b</sup>	13.7
$C_{44}$	24.1	22.5 <sup>a</sup>	22.02 <sup>b</sup> ,	-6.5	30.11 <sup>b</sup>	16.0
			22.7 <sup>c</sup>			
B <sub>V</sub>	21.7		26 <sup>b</sup>	32	26 <sup>b</sup>	15.7
B <sub>R</sub>	21.7			32		15.7
B <sub>H</sub>	21.7			32		15.7

<sup>a</sup>Ref.[83], <sup>b</sup>Ref.[7], <sup>c</sup>Ref.[80]

It is clear from Table 6.2.6 that these elastic constants satisfy the Born– Huang criteria for the RS and CsCl structures; meaning that they are mechanically stable, while the CsCl structure does not satisfy the Born– Huang criteria, NaH in the CsCl structure is not stable, it is reversible (when pressure is released it return to the RS structure). Elastic constants for the hexagonal system (WZ) presented in Table 6.2.7, they are satisfy the Born–Huang criteria for hexagonal (WZ) structure.

Figure 6.2.12 shows the pressure dependence of the elastic constants and bulk moduli for NaH compound in RS structure. It is noticed that elastic constant  $C_{11}$  and bulk modulus increase with the applied pressure. It is also noticeable that elastic constant  $C_{11}$  is the most sensitive to the pressure than  $C_{12}$ ,  $C_{44}$  and B. At high pressure,  $C_{44}$  approaches zero, indicating that these compounds are unstable under high pressure, and the RS structure transforms to CsCl structure.

Table 6.2.7: The calculated elastic constants C<sub>ij</sub> (GPa), Bulk modulus (B) in Voigt (V), Reuss (R) and Hill (H) approximations (in GPa) for NaH in WZ structure



Figure 6.2.12: Variation of elastic constants ( $C_{ij}$ ) and bulk modulus (B) for NaH compound with pressure in RS structure.

# **6.2.6** Mechanical properties

The bulk modulus for NaH compound is small, which means the weak resistance to the fracture of these materials. The CsCl phase is the hardest as in the LiH case, because it possesses the most bulk modulus value, on the other hand the compressibility ( $\beta$ =1/B) of this phase structure is the least one as shown in Table 6.2.8, while WZ structure has the most compressibility. The value of the bulk modulus B computed from the elastic constants is to some extent agrees with the results obtained from Murnaghan's equation of state [53]. Table 6.2.8 displays the anisotropy factor (A) for NaH compound in the four structures; WZ structure is completely isotropic with A=1, while the other structure are anisotropic because A is far from unity.

Table 6.2.8: The calculated Young's modulus (Y), Shear modulus (S) (in GPa), compressibility ( $\beta$  in GPa<sup>-1</sup>), B/S ratio, Poisson's ratio ( $\nu$ ), Anisotropic ratio (A), Cauchy pressure C<sub>s</sub> and Vickers hardness (H<sub>v</sub>) for NaH compound in RS, CsCl, ZB and WZ structures in comparison with available theoretical data.

	Rs Structure		CsCl Structure		ZB	WZ
Elastic					Structure	Structure
Constants						
	Present	Other	Present	Other	Present	Present
	Calculations	theoretical	Calculations	theoretical	Calculations	Calculations
		Calculations		Calculations		
Y	45.3	53 <sup>a</sup>	42	66 <sup>a</sup>	26	29.7
S	19.68	23 <sup>a</sup>	18	30.4 <sup>a</sup>	10	12.6
B/S	1.1	1.1 <sup>a</sup>	1.75	$0.85^{a}$	1.74	1.2
$\upsilon_{\rm V}$	0.152	0.13 <sup>a</sup>	0.178	0.14 <sup>a</sup>	0.218	0.174
А	1.84	$0.88^{a}$	0.16	$0.98^{\rm a}$	5.5	0.88
β	0.046	0.038 <sup>a</sup>	0.031	0.038 <sup>a</sup>	0.063	0.65
H <sub>v</sub>	7.19	7.8	2.5	14.6 <sup>a</sup>	1.53	4.0

<sup>a</sup>Ref.[7]

Poisson's ratio v is used to judge the brittleness and ductility of the solid compounds, as indicated in the previous section, Poisson's ratio for NaH compound as shown in table 6.2.8 is less than 1/3 in all structures, means has a brittle nature in these structures.

B/S is used to estimate if the material is brittle or ductile in nature. It is clear from Table 6.2.8 that NaH compound represents a brittle nature, which is in good agreement with Poisson's ratio. NaH in RS structure has the most value of Vickers hardness ( $H_v$ ) (the most hardness); on the other hand, ZB structure has the least value of  $H_v$ . This means that RS structure is the more mechanically strong among all phases. Young's modulus (Y) and the bulk modulus for NaH in RS structure have the greater value among the four structures; they are consistent with  $H_v$  that NaH in RS structure is the most mechanically stable, while ZB structure is the least strong mechanically.

# **6.2.7 Thermal properties**

Debye temperature and average wave velocity are displayed in Table 6.2.9. The RS structure has the greater value of Debye temperature, while WZ has the greater average wave velocity. Figure 6.1.13 and Figure 6.1.14 show the dependence of Debye temperature and average wave velocity on the pressure, Debye temperature increases as the pressure increases. The same view for the average wave velocity, it increases as the pressure increases.

Table 6.2.9: Average wave velocity (Vm in m/s) and Debye temperature ( $\Theta_D$  in K) for NaH compound in RS, ZB and WZ structures.

Constant	RS str	ucture	CsCl	ZB structure	WZ structure
			structure		
	Present	Other	Present	Present	Present
	calculations	theoretical	calculations	calculations	calculations
		calculations			
θ <sub>D</sub>	495.4	549 <sup>a</sup>	207	345	422
V <sub>m</sub>	3661	4475 <sup>a</sup>	1646	3033	3709

<sup>a</sup>Ref.[7].



Figure 6.2.13: Variation of Debye temperature vs pressure for NaH with RS structure.


Figure 6.2.14: Variation of average wave velocity versus pressure for NaH with RS structure.

## 6.3 KH Compound

## **6.3.1 Structural Properties**

The ground-state properties of KH compound in RS, CsCl, ZB and WZ structures have been estimated by calculating the total energy at different unit-cell volumes and fitting the calculated E-V points to Murnaghan's equation of state (EOS) [53], as shown in Figure 6.3.1. We can clearly see from these curves that the rock-salt structure has the lowest energy minimum at ambient pressure, which means that it is the most stable structure at ambient conditions (zero pressure and temperature). The calculated equilibrium lattice constant  $a_0$ , bulk modulus  $B_0$  and first-order pressure derivatives of the bulk modulus  $B'_0$  for KH in the RS, CsCl, ZB phases, along with the available experimental [2, 3, 6] and theoretical [7, 80, 95] results, are listed in Table 6.3.1, while they are listed in Table

6.3.2 for WZ structure. Structural parameters for KH in RS structure are in good agreement with experimental results [2, 3, 6].



**Figure 6.3.1**: Calculated total energy per unit cell versus cell volume for KH in RS, CsCl, ZB and WZ.

From Table 6.3.1, it is clear that the calculated structural parameters for KH in the CsCl structure are in good agreement with the results of Sudha *et al.*[7]. For the four structures RS, CsCl, ZB and WZ, if we make a comparison between LiH, NaH and KH we can see that the calculated lattice constant increases as the alkali radius increases, while the bulk modulus decreases. There are no experimental results for the lattice constant for KH in CsCl up to date. Present results of the structural parameters for KH compound in ZB and WZ structures are calculated for the first time.

ZB structures, along with experimental and other theoretical results.

Structure	Structural parameter s	Present work	Experimental work	Other theoretical work
RS	a <sub>0</sub> (Å)	5.70	5.70 <sup>a, c</sup>	$5.721^{d}, 5.701^{e}$
	B <sub>0</sub> (GPa)	13.41	$15.6 \pm 1.5^{b}$	16 <sup>d</sup> , 17.3 <sup>f</sup>
	Β'	3.9	$4.0\pm0.5^{ m b}$	2.955 <sup>d</sup>
CsCl	a <sub>0</sub> (Å)	3.41		3.520 <sup>d</sup>
	B <sub>0</sub> (GPa)	15.04	$28.5 \pm 1.5^{b}$	$20^{d}$
	Β'	4.00	$4.0 + 0.6^{b}$	3.007 <sup>d</sup>
ZB	a <sub>0</sub> (Å)	6.215		
	B <sub>0</sub> (GPa)	9.85		
	B'	3.40		

<sup>a</sup>Ref[2], <sup>b</sup>Ref[3], <sup>c</sup>Ref[6], <sup>d</sup>Ref[7], <sup>e</sup>Ref[80], <sup>f</sup>Ref[95]

# Table 6.3.2: Structural parameters for KH compound in WZstructure.

Compound	a <sub>0</sub> (Å)	c/a	u(a.u.)	B(GPa)	B
KH	4.492	1.514	0.393	10.12	3.62

## 6.3.2 Phase Transition

The energy per unit cell is calculated by using the PBE-GGA at different unit-cell volumes, and the results are fitted to the Murnaghan's equation of state [53], as shown in Figure 6.3.1. It is clearly shown that KH undergoes a structural phase transition from RS to the other structures. At the transition pressure, the enthalpies of the two consecutive phases are equal. Enthalpy-pressure curves for KH are displaced in Figure 6.3.2.



Figure 6.3.2: Enthalpy as a function of pressure for KH using PBE-GGA.

The estimated induced-transition pressures from RS to the other structures for KH are presented in Table 6.3.3. The computed transition pressure from RS to CsCl structure is found to be 5.11 GPa, which is in good agreement with the previous theoretical calculations and the experimental value [3]. Table 6.3.4 displays the V/V<sub>0</sub> fraction. The induced-transition pressures from RS to CsCl for KH occurred at V/V<sub>0</sub>= 0.693, which means that the RS to CsCl transition requires volume compression. The RS to ZB and RS to WZ phase transitions occur when V/V<sub>0</sub> is greater than one, meaning that these two transitions require volume expansion.

## Table 6.3.3: Calculated transition pressures as well as the experimental

and other theoretical data for KH compound.

	$RS \rightarrow CsCl P_t(GPa)$			$RS \rightarrow ZB$	$RS \rightarrow WZ$
Compound	Present	Experimental	Other	P <sub>t</sub> (GPa)	P <sub>t</sub> (GPa)
	Work	work	theoretical work		
KH	5.11	4 <sup>a</sup>	$3.5^{b, c}, 2^{d}$	-1.39	-1.25

<sup>a</sup>Ref.[3], <sup>b</sup>Ref[7], <sup>c</sup>Ref[10], <sup>d</sup>Ref[11]

## Table 6.3.4: The V/V<sub>0</sub> fractions for KH.

Compound	$RS \rightarrow CsCl$	$RS \rightarrow ZB$	$RS \rightarrow WZ$
$V/V_0$ for KH	0.693	1.571	1.513

There are small differences between the reported and experimental transition pressures, and one of the reasons for this phenomenon is that the experimental calculations are carried out at room temperature, while the theoretical calculations are performed at 0K, the induced transition pressure decreases as the temperature increases. In addition, the purity of the prepared compound affect the induced transition pressure, there is a presence of XOH (X=Li, Na, K, Rb, Cs) compounds which remain through the alkali transition. [5]

## **6.3.3 Electronic properties**

Atoms in a crystal interact with their neighbors and the energy levels of the electrons in an isolated atoms turn into bands. In fact, a material can be classified as a conductor, insulator or semiconductor by examining its band structure and the Fermi energy-level position. The self-consistent band structures of KH is calculated in cubic RS, CsCl and ZB structures and a hexagonal (WZ) structure using the computed equilibrium lattice constant

within PBE-GGA and mBJ-GGA for the exchange-correlation potential; the results are shown in Figure 6.3.3. We can clearly see that the Fermi level crosses the energy-band gap for all structures. The topologies of the energy-band structures for KH, LiH and NaH compounds are quite similar to one another. Using PBE-GGA and mBJ-GGA approaches, the minimum energy-band gap is direct along the L-point and M-point high symmetry lines for KH compound in RS and WZ structures, respectively. For the CsCl structure, the minimum energy-band gap is indirect. From Figure 6.3.3 and Figure 6.3.4 for the KH density of states, it is clear that the electronic energy bands are more vertically distributed in PBE-GGA; mBJ-GGA shifts them closer to one another. Differences in the width of the first valence band below the Fermi-energy between PBE-GGA and mBJ-GGA in RS, CsCl, ZB and WZ structures are 0.6, 1.1, 0.9 and 0.9 eV, respectively for KH compound. Table 6.3.5 reports the calculated energyband gaps using the two approaches, mBJ-GGA and PBE-GGA methods along with the available theoretical results [7, 80, 96, 97].

Table 6.3.5: Calculated energy band-gap values ((Eg (eV)) of KH inRS, CsCl, ZB and WZ structures.

Structure	Present work		Other theoretical works (Eg)
	PBE-GGA	mBJ-GGA	
RS	L→L: 3.428	L→L: 6.012	3.5992 <sup>a</sup> , 5.85 <sup>b</sup> , 3.203 <sup>c</sup> , 6.28 <sup>d</sup>
CsCl	R→X: 2.456	R→X: 4.971	2.0 <sup>a</sup>
ZB	W→L : 3.671	X→X : 6.801	
WZ	M→M : 3.655	M→M : 6.917	

<sup>a</sup>Ref.[7], <sup>b</sup>Ref.[80], <sup>c</sup>Ref.[96], <sup>d</sup>Ref.[97].



**Figure 6.3.3**: Band structure of KH in RS, CsCl, ZB and WZ in the PBE-GGA and mBJ-GGA approaches.

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**Figure 6.3.4**: Density of states of KH in RS, CsCl, ZB and WZ in the PBE-GGA and mBJ-GGA approaches.

The calculated energy-band gaps for KH in RS, CsCl, ZB and WZ structures are broader using mBJ-GGA than using PBE-GGA, by approximately 1.25eV to 3.4eV. The energy-band gap has been modified using mBJ-GGA approach, so the band gap calculated using mBJ-GGA are more accurate than those calculated using PBE-GGA approach compared to the experimental results. The band gap is used to classify the compound, KH in CsCl structure seems to be classified as semiconductors when using PBE-GGA, while it is classified as insulator when using mBJ-GGA method.

## **6.3.4 Optical properties**

Using the relations in section 5.5, optical constants can be determined and analyzed. The static real dielectric constants  $\varepsilon_1(0)$  for KH in the four studied structures (RS, CsCl, ZB and WZ) when photon energy is zero; are about 2.17, 2.47, 2.0 and 1.96eV, respectively using PBE-GGA approach and 1.51, 1.8, 1.36 and 1.4eV, respectively using mBJ-GGA approach. It is clear that mBJ-GGA has a lower value of  $\varepsilon_1(0)$  and this is mainly related to variation in electronic band structure as seen in section 6.3.3.  $\varepsilon_1(w)$  value is negative in some regions, which means KH compound has a metallic behavior in those regions. The calculated real and imaginary parts of the optical dielectric function for KH compound in the RS, CsCl, ZB and WZ structures are displayed in Figures 6.3.5 and 6.3.6 as a function of the photon energy from 0.0 to 14.0 eV. The cubic structures are optically isotropic, while the WZ structure is not isotropic because $\varepsilon_{xx} \neq \varepsilon_{zz}$ . From

Figure 6.3.6, the imaginary part of dielectric function  $\varepsilon_2$  in RS, CsCl, ZB and WZ structures onset of absorption around 3.43, 3.7, 4.1 and 3.95 eV, respectively within PBE-GGA and 6.68, 6.22, 7.5 and 7.5 eV, respectively within mBJ-GGA. They begin to have considerable values at 4.25, 4.59, 4.7 and 7.8 eV, respectively within PBE-GGA approach and 6.8, 6.49, 7.8 and 4.6 eV, respectively within mBJ-GGA approach. The mBJ-GGA approach is more accurate in predicting these optical constants , because these optical constants are strongly depend on energy gap, and mBJ-GGA is more accurate in predicting these energy gaps.



Figure 6.3.5: Real part of the dielectric constant of KH in RS, CsCl, ZB and WZ structures.



Figure 6.3.6: Imaginary part of the dielectric constant for KH in RS, CsCl, ZB and WZ structures.

The imaginary part  $\varepsilon_2$  indicates that the KH compound in RS, CsCl, ZB and WZ structures has maximum absorption peaks. These peaks are around 6.0, 7.0, 5.2 and 5.2 eV, respectively using PBE-GGA and 9.80, 8.72, 8.5 and 8.25 eV, respectively using mBJ-GGA. From Figure 6.3.7 for the absorption spectrum which is related directly to the imaginary part of  $\varepsilon_2$ . It is clear that there are strong absorption peaks for KH in RS, CsCl, ZB and WZ structures in the energy range from 4.3, 4.5, 4.8 and 4.6 eV to 14 eV, respectively using PBE-GGA and from 6.8, 6.5, 7.8 and 8.0 eV to 14 eV, respectively using mBJ-GGA.

From the same Figure 6.3.7, maximum absorption for KH in RS, CsCl and ZB occurs at 6.15, 7.2 and 5.4 eV, respectively using PBE-GGA and 9.8, 8.86 and 8.6 eV, respectively using mBJ-GGA, while in WZ structure,

maximum absorption occurs at 5.2 eV along [100] direction and at 5.45 eV along [001] direction using PBE-GGA approach and at 10.3 eV along [100] direction and at 8.53 eV along [001] direction using mBJ-GGA approach. Absorption spectrum approximately the same as imaginary dielectric function, they begin to have a considerable value approximately at the same point and reach maximum value at the same photon energy. Real conductivity, Figure 6.3.8 with the four structures, has the same shape of absorption function  $\alpha(\omega)$  as in Figure 6.3.7.

The reflectivity coefficient R(w) for KH in RS, CsCl, ZB and WZ structures are displayed in Figure 6.3.9, the zero-frequency reflectivity are 3.7%, 5.0%, 2.7% and 2.7%, respectively within PBE-GGA and 1.0%, 2.1%, 0.5% and 0.7%, respectively with mBJ-GGA approach. It is clear that R(0) within PBE-GGA is greater than that of mBJ-GGA approach. With the four structures and after R(w) reaches its maximum value, it begins to decrease and oscillates. Along the spectrum from 0 eV to 14 eV, there are peaks; these peaks originate from the inter-band transitions. With both PBE-GGA and mBJ-GGA approaches, R(w) in CsCl structure increases as the photon energy increases with different peaks. R(w) has a great value in the high-energy region, KH has a high reflectivity against high-energy photons; it is a good coating material to avoid and prevent solar heating. Since the mBJ-GGA is more accurate in predicting the energy gap and these constants are energy gap dependence, they are more accurate within mBJ-GGA method.



Figure 6.3.7: Absorption function of KH in RS, CsCl, ZB, and WZ structures.



Figure 6.3.8: Real conductivity function of KH in RS, CsCl, ZB, and WZ structures.

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Figure 6.3.9: Reflectivity coefficient R(w) of KH in RS, CsCl, ZB, and WZ structures.

Figure 6.3.10 displays the energy loss function L(w), which is related to the energy loss of a fast electron in the material. Figure 6.3.10 shows that loss function for KH in RS, CsCl, ZB and WZ structures begins at 4.49, 5.0, 4.68 and 4.0 eV, respectively using PBE-GGA approach and 7.19, 7.0, 7.72 and 7.5 eV using mBJ-GGA approach. L(w) oscillates but the peaks go to higher value as the photon energy increases. Figure 6.3.11 displays the refractive index n(w). The static refractive index n(0) is found to have the values 1.48 in RS structure, 1.57 in CsCl structure, 1.40 in ZB structure and 1.40 in WZ structure respectively using PBE-GGA approach and 1.22 in RS structure, 1.34 in CsCl structure, 1.16 in ZB structure and 1.18 in WZ structure, respectively using mBJ-GGA approach. The static refractive index n(0) value is equal to the square root of the real part of dielectric

function;  $n(0) = \sqrt{\varepsilon_1(0)}$ ; which are to some extent the same as that obtained from Figure 6.3.5.



Figure 6.3.10: Energy loss function L(w) for KH in RS, CsCl, ZB, and WZ structures.



Figure 6.3.11: Refractive index n(w) of KH in RS, CsCl, ZB, and WZ structures.

The extinction coefficient k(w) is displayed in Figure 6.3.12; the curves of extinction coefficient k( $\omega$ ) are closed to the  $\varepsilon_2(\omega)$  and have similar features with the coefficient  $\alpha(\omega)$ . K(w) starts to have a considerable value in RS, CsCl, ZB and WZ structures at 3.48, 4.56, 4.7 and 4.46 eV within PBE-GGA approach and 6.60, 6.13, 7.7 and 7.88 eV within mBJ-GGA approach. Variation in predicting the absorption and extinction coefficients between mBJ-GGA and PBE-GGA is related to the variation in energy gap prediction. From these figures, we can see that the cubic structures are optically isotropic while the WZ structure is not.



Figure 6.3.12: Extinction coefficient k(w) of KH in RS, CsCl, ZB, and WZ structures.

**6.3.5 Elastic properties** 

The calculated elastic constants and bulk moduli for KH, together with the available other theoretical results are displayed in Table 6.3.6 in the RS, CsCl and ZB structures, respectively [7, 80, 91, 96]. The computed elastic constants for KH compound in the RS structure are in a good agreement with the previous theoretical results. Although the calculated  $C_{12}$  value is negative for the KH compound in CsCl structure; as Xinyou *et al.*[96] result of KH compound; the results are to some extent are consistent with Sudha *et al.*[7] and Xinyou *et al.* [96]. It is clear from Table 6.3.6 that these elastic constants satisfy the Born–Huang criteria for the cubic structures as well as for WZ (hexagonal) structure (Table 6.3.7); meaning that they are mechanically stable.

Table 6.3.6: The calculated elastic constants C<sub>ij</sub> (GPa), Bulk modulus (B) in Voigt (V), Reuss (R) and Hill (H) approximations (in GPa) for KH in cubic structures.

	RS structure		CsCl structure		ZB
Compound					structure
	Present	Other theoretical	Present	Other	Present
	work	work	work	theoretical	work
				work	
C <sub>11</sub>	27.76	$31.10^{a}$ , $26.8^{b}$ ,	56.36	51 <sup>a</sup> , 56.66 <sup>d</sup>	13.41
C <sub>12</sub>	6.38	32.8 <sup>c</sup>	-4.67	$4.5^{\rm a}, -5.53^{\rm d}$	9.16
C <sub>44</sub>	13.73	$8.35^{\rm a}, 6.5^{\rm b}, 8.04^{\rm c}$	0.79	$20^{\rm a}, 4.54^{\rm d}$	11.27
		$14.47^{a}$ , $10.6^{b}$ ,			
		12.9 <sup>c</sup>			
B <sub>V</sub>	13.51	15.6 <sup>a</sup>	15.67	15.6 <sup>a</sup>	10.58
B <sub>R</sub>	13.51		15.67		10.58
B <sub>H</sub>	13.51		15.67		10.58

<sup>a</sup>Ref.[7], <sup>b</sup>Ref.[80], <sup>c</sup>Ref.[91], <sup>d</sup>Ref.[96].

Figure 6.3.13 shows the pressure dependence of the elastic constants and bulk moduli for KH compound in RS structure. It is noticed that elastic constant  $C_{11}$  and bulk modulus increase with the applied pressure. It is also noticeable that elastic constant  $C_{11}$  is the most sensitive to the pressure rather than  $C_{12}$ ,  $C_{44}$  and B.  $C_{12}$  almost constant during pressure increasing, it does not depend on pressure. At high pressure,  $C_{44}$  approaches zero, indicating that these compounds are unstable under high pressure, and the RS structure transforms to CsCl structure.





Figure 6.3.13: Variation of elastic constants and bulk moduli for KH compound in RS structure.

### **6.3.6** Mechanical properties

The bulk modulus for KH compound is small, which means the weak resistance to the fracture of these materials. The CsCl phase is the hardest phase as in the LiH and NaH cases, because it possesses the most bulk modulus value, on the other hand the compressibility ( $\beta$ =1/B) of this phase structure is the least one as shown in Table 6.3.8, while WZ structure has the most compressibility. The value of the bulk modulus B computed from the elastic constants is to some extent agrees with the results obtained from Murnaghan's equation of state [53]. Table 6.3.8 displays the anisotropy factor (A) for KH compound in the four structures; all structures are completely anisotropic with A far from unity.

Table 6.3.8: The calculated Young's modulus (Y), Shear modulus (S) (in GPa), compressibility ( $\beta$  in GPa<sup>-1</sup>), B/S ratio, Poisson's ratio ( $\upsilon$ ), Anisotropic ratio (A), Cauchy pressure C<sub>s</sub> and Vickers hardness (H<sub>V</sub>) for KH compound in RS, CsCl, ZB and WZ structures in comparison with available theoretical data.

	Rs structure		CsCl structure		ZB	WZ
Constant						structure
	Present	Other	Present	Other	Present	Present
	Calculations	theoretical	Calculations	theoretical	Calculations	Calculations
		Calculations		Calculations		
Y	28.69	31 <sup>a</sup>	29.9	18.40	18.40	11.30
S	12.5	13 <sup>a</sup>	12.68	7.60	7.60	4.20
β	0.0740		0.0638	0.0945	0.0945	2.7380
B/S	1.0808	1.2 <sup>a</sup>	1.014	1.3921	1.3921	0.0869
$\upsilon_V$	0.146	0.21 <sup>a</sup>	0.181,	0.209	0.209	0.336
Α	1.284	1.27 <sup>a</sup>	0.025	5.30	5.30	1.01
H <sub>v</sub>	5.00		3.89		1.44	-1.39

<sup>a</sup>Ref.[7].

Although both the calculated anisotropy factor (A) value and that calculated by Sudha *et al.* [7] for KH compound in CsCl structure indicate that KH compound is anisotropy (A is far from unity with both), there is a variation in A values. This variation is due to two main reasons: the used optimized lattice constant is different which tends to different estimated transition pressure. Poisson's ratio value Table 6.3.8 is lower than 1/3 in all structures, KH represents a brittle nature. B/S is used to estimate if the material is brittle or ductile in nature. It is clear from Table 6.3.8 that KH compound represents a brittle nature for the four structures, which agrees with Poisson's ratio. KH in RS structure has the most value of Hardness H<sub>v</sub> (the most hardness); on the other hand, WZ structure has the least value of H<sub>v</sub>. This means that RS structure is mechanically the strongest among all phases, which is consistence with the bulk modulus and H<sub>v</sub> values, while WZ structure is the least strong mechanically.

## **6.3.7** Thermal properties

Debye temperature and average wave velocity are displayed in Table 6.3.9. The RS structure has the greater value of Debye temperature and average wave velocity. The results are in agreement with Sudha *el al* [7] results. Figure 6.3.14 and Figure 6.3.15 show the dependence of Debye temperature and average wave velocity on the pressure, Debye temperature increases as the pressure increases until about 10 GPa, after that it starts to decrease. The same behavior for the average wave velocity. This behavior at enormous pressure may related to the structural transform from RS structure to the CsCl structure.

Table 6.3.9: Average wave velocity (Vm in m/s) and Debye temperature ( $\Theta_D$  in K) for KH compound in RS, ZB and WZ structures.

Const	tant	RS structure		CsCl	ZB	WZ structure
				structure	structure	
		Present	Other	Present	Present	Present
		calculations	theoretical	calculations	calculations	calculations
			calculations			
$\Theta_{\rm D}$		337.10	348 <sup>a</sup>	251.1	245.2	210
V <sub>m</sub>		3227	3347 <sup>a</sup>	2285	2557	2186

<sup>a</sup>Ref.[7].



Figure 6.3.14: Variation of Debye temperature vs pressure for KH with RS structure.



Figure 6.3.15: Variation of average wave velocity vs pressure for KH with RS structure.

## 6.4 RbH Compound

## **6.4.1 Structural Properties**

The ground-state properties of RbH compound in RS, CsCl, ZB and WZ structures have been estimated by calculating the total energy at different unit-cell volumes and fitting the calculated E-V points to Murnaghan's equation of state (EOS) [53], as shown in Figure 6.4.1. We can see clearly from these curves that the rock-salt structure has the lowest energy minimum at ambient pressure, which means that it is the most stable structure at ambient conditions.

The calculated equilibrium lattice constant  $a_0$ , bulk modulus  $B_0$  and firstorder pressure derivatives of the bulk modulus  $B'_0$  for RbH in the RS, CsCl and ZB phases, along with the available experimental [2, 3, 6] and theoretical [7, 13, 80, 95] results, are listed in Tables 6.4.1, respectively, while they are listed in Table 6.4.2 for WZ structure. Structural parameters for KH with RS structure are in good agreement in experimental results [2, 3, 6]. The bulk modulus  $B_0$  and  $B'_0$  for RbH in CsCl are experimentally measured, while the lattice constant has not yet been measured. From Table 6.4.1, it is clear that the calculated structural parameters for RbH in the CsCl structure are in good agreement with the results of Sudha *et al.*[7]. Table 6.4.2 displays the structural parameters for the RbH within the WZ structure. To the best of our knowledge, none of the structural parameters of RbH in ZB and WZ structures have yet been calculated experimentally and theoretically.



**Figure 6.4.1**: Calculated total energy per unit cell versus cell volume for RbH in RS, CsCl, ZB and WZ.

Table 6.4.1: Structural parameters for RbH compound in RS, CsCl and ZB structure, along with experimental and other theoretical results.

Structure	Structural parameter s	Present work	Experimental work	Other theoretical work
RS	a <sub>0</sub> (Å)	6.054	6.037 <sup>a</sup> , 6.048 <sup>b</sup>	5.992 <sup>d</sup> , 6.199 <sup>e</sup> , 6.064 <sup>f</sup>
	B <sub>0</sub> (GPa)	11.25	$10.0 \pm 1.0^{\rm c}$	14.1 <sup>d</sup> , 14.7 <sup>g</sup>
	B'	3.87	$3.9 \pm 0.5^{\circ}$	$2.840^{d}$
CsCl	a <sub>0</sub> (Å)	3.62		3.81 <sup>d</sup>
	B <sub>0</sub> (GPa)	13.64	$18.4 \pm 1.1^{c}$	14.9 <sup>d</sup>
	B'	4.21	$3.9 + 0.5^{\circ}$	2.866 <sup>d</sup>
ZB	a <sub>0</sub> (Å)	6.598		
	B <sub>0</sub> (GPa)	8.33		
	B'	3.25		

<sup>a</sup>Ref[2], <sup>b</sup>Ref[6], <sup>c</sup>Ref[3], <sup>d</sup>Ref[7], <sup>e</sup>Ref[80], <sup>f</sup>Ref[13], <sup>g</sup>Ref[95]

 Table 6.4.2: Structural parameters for RbH in WZ structure.

Compound	a <sub>0</sub> (Å)	c/a	u(a.u.)	B(GPa)	B
RbH	4.764	1.527	0.390	8.135	.06

## **6.4.2 Phase Transition**

The energy per unit cell is calculated by using the PBE-GGA at different unit-cell volumes, and the results are fitted to the Murnaghan's equation of state [53], as shown in Figure 6.4.2. It is clearly shown that RbH compound undergoes structural phase transition from RS to the other structures. At the transition pressure, the enthalpies of the two consecutive phases are equal. Enthalpy-pressure curves for RbH are displayed in Figure 6.4.2. The estimated induced-transition pressures from RS to the other structures for RbH compound is presented in Table 6.4.3. The computed transition pressure from RS to CsCl structures is found to be 3.5 GPa, which is in good agreement with the previous theoretical calculations and the highpressure experimental value of approximately 2.2 GPa [3].

 Table 6.4.3: Calculated transition pressures as well as the experimental and other theoretical data for RbH.

	$RS \rightarrow C$	sCl P <sub>t</sub> (GPa)	$RS \rightarrow ZB$	$RS \rightarrow WZ$	
Compound	Present	Experimental	Other theoretical	P <sub>t</sub> (GPa)	P <sub>t</sub> (GPa)
	Work	work	work		
RbH	3.50	$2.2 \rightarrow 3.1^{a}$	$3^{\rm b}, 1^{\rm c}$	-1.13	-1.05

<sup>a</sup>Ref.[3], <sup>b</sup>Ref[7], <sup>c</sup>Ref [12].



Figure 6.4.2: Enthalpy as a function of pressure for RbH using the PBE-GGA.

The induced-transition pressures from RS to CsCl for RbH occurred at  $V/V_0= 0.719$  which means that the RS to CsCl transition requires volume compression, While the RS to ZB and RS to WZ phase transitions occurred when  $V/V_0 = 1.546$  and 1.554 respectively, where V is the unit-cell volume at which the transition occurs and  $V_0$  is the unit-cell equilibrium volume of the RS structure.  $V/V_0$  greater than one for the transition from RS to ZB or from RS to WZ, this means these two transitions require volume expansion. There is small difference between the reported and experimental transition pressure, and one of the reasons for this phenomenon is that the experimental calculations are carried out at room temperature, while the theoretical calculations are performed at 0K.

## **6.4.3 Electronic properties**

In fact, a material can be classified as a conductor, insulator or semiconductor by examining its band structure and the Fermi energy-level position. The self-consistent band structures of RbH are calculated in cubic RS, CsCl and ZB structures and a hexagonal (WZ) structure using the computed equilibrium lattice constant within PBE-GGA and mBJ-GGA for the exchange-correlation potential; the results are shown in Figure 6.4.3. We can clearly see that the Fermi level crosses the energy-band gap for all structures. The minimum energy-band gap is direct along the L-point and X-point symmetry lines within the RS and ZB structures respectively for RbH compound, while for the CsCl structure, the minimum energy-band gap along the M-

point symmetry line within the WZ structure within PBE-GGA, but it is indirect within mBJ-GGA.

Table 6.4.4: Calculated energy band-gap values ((Eg (eV)) of RbH in RS, CsCl, ZB and WZ structures.

Structure	Present work		Other theoretical	Experimental
	PBE-GGA	mBJ-GGA	works (E <sub>g</sub> )	results
RS	L→L : 3.050	L→L : 5.633	3.0255 <sup>a</sup> , 2.960 <sup>b</sup> , 4.21 <sup>c</sup> ,	4.91 <sup>e</sup>
			6.97 <sup>d</sup>	
CsCl	R→X : 2.397	R→X : 4.474	2.1 <sup>a</sup>	
ZB	X→X : 3.379	X→X : 6.466		
WZ	M→M : 3.470	M→Σ : 6.907		

<sup>a</sup>Ref.[7], <sup>b</sup>Ref.[96], <sup>c</sup>Ref[100], <sup>d</sup>Ref[101], <sup>e</sup>Ref.[4].

Results are presented in Table 6.4.4; it is clearly shown from Figure 6.4.3 that PBE-GGA and mBJ-GGA approach gave us a different energy gap direction for RbH in WZ structure. From Figure 6.4.3, it is clear that the electronic energy bands are more vertically distributed within PBE-GGA; mBJ-GGA shifts them closer to one another. Differences in the width of the first valence band below the Fermi-energy between PBE-GGA and mBJ-GGA in RS, CsCl, ZB and WZ structures are 0.8, 0.82, 0.81 and 0.80 eV, respectively for RbH. Table 6.4.4 reports the energy-band gaps, calculated using the two approaches, mBJ-GGA and PBE-GGA along with the available theoretical [7, 96, 100, 101] and experimental [4] results. The calculated energy-band gaps for RbH in RS, CsCl, ZB and WZ structures are broader using mBJ-GGA approach than using PBE-GGA approach, by approximately 1.25eV to 3.4eV using mBJ-GGA. The energy-band gap has been modified using the mBJ-GGA approach, so the band gap calculated

using mBJ-GGA is more accurate than that calculated using the PBE-GGA approach and they are in good agreement with experimental results [4]. To our best knowledge, there is no previous study of the electronic properties of RbH in ZB and WZ structures. The present calculations using mBJ-GGA are greater than experimental results with about 0.72eV. This is mainly due to the greater temperature and pressure in the experiment, while theoretical calculations are carried out at zero temperature and ambient. In addition, the lattice constant used in the present work does not match the experimental one. The present calculations using mBJ-GGA are more accurate than the other represented theoretical calculations: there is a difference of approximately 1.88eV, 1.95eV and 2.06eV between the experimental results and the results of references 12, 42, respectively and of approximately 1.86 eV between the experimental results and present work using PBE-GGA. Due to the underestimated energy gap when using PBE-GGA for RbH in the CsCl structure, RbH in the CsCl seems to be classified as semiconductor, while it is classified as an insulator when using mBJ-GGA method. Although the ground state is well described by PBE-GGA, this approximation fails to account for excited-state properties. Due to a well-known non-physical problem in calculating the energy-band gap using PBE-GGA, which is the self-interaction error [69], differences in energy-band gap values between PBE-GGA on one hand and mBJ-GGA on the other hand arise. Within PBE-GGA, the energy-band gap is underestimated, and sometimes a semiconducting or metallic state may be obtained instead of an insulating one. Figure 6.4.4 displays the densities of states of RbH compound obtained using the PBE-GGA and mBJ-GGA approaches. The heights of the peaks vary from one phase structure to another, and depend on the phase structure and the method used to calculate the exchange potential. Total and partial densities of states for the RbH compound in the four structures (RS, CsCl, ZB and WZ) have been calculated for further understand the nature of electronic-band structures. It is clear that the energy bands below the Fermi energy (FE), indicated by a dotted horizontal line, arise mainly from H-s, along with small contributions from Rb-d. Above the FE, they mainly arise from Rb-d and with small contribution from Rb-p and H-s states.



**Figure 6.4.3**: Band structure of RbH in RS, CsCl, ZB and WZ within the PBE-GGA and mBJ-GGA approaches.



**Figure 6.4.4:** Density of states of RbH in RS, CsCl, ZB and WZ within the PBE-GGA and mBJ-GGA approaches.

## **6.4.4 Optical properties**

The calculated real dielectric constant for RbH in the four studied structures; RS, ZB CsCl and WZ; when photon energy is zero; namely  $\varepsilon_1(0)$  are 2.37, 2.63, 2.1 and 2.09, respectively within PBE-GGA approach and 1.59, 1.83, 1.4 and 1.38, respectively within mBJ-GGA approach. As we mentioned before,  $\varepsilon_1(0)$  within mBJ-GGA has a lower value than PBE-GGA approach because band gap within mBJ-GGA is broader than with PBE-GGA approach. The calculated real and imaginary parts of the optical dielectric function for RbH compound in the RS, CsCl, ZB and WZ structures have been displayed in Figures 6.4.5 and 6.4.6 as a function of the photon energy from 0.0 to 14.0 eV. The cubic structures are optically isotropic, while the WZ structure is anisotropic because  $\varepsilon_{xx} \neq \varepsilon_{zz}$ .  $\varepsilon_1(w)$  is negative in some regions.

From Figure 6.4.6, the imaginary part of dielectric function  $\varepsilon_2$  with RS, CsCl, ZB and WZ structures onset of absorption around 0.7, 1.71, 2 and 2.7 eV, respectively within PBE-GGA and 4.1, 5.68, 7.25 and 6.0 eV, respectively within mBJ-GGA. They begin to have considerable values at 2.6, 3.1, 3.25 and 3.34 eV, respectively with PBE-GGA approach and 5.7, 6.1, 7.53 and 6.7 eV, respectively within mBJ-GGA approach. The imaginary part  $\varepsilon_2$  indicates that the RbH in RS, CsCl and ZB has maximum absorption peak. These values are around 7.1, 5.2 and 4.0 eV, respectively using PBE-GGA and 8.0, 7.8 and 8.4 eV, respectively using mBJ-GGA.

3.9 eV in [100] direction and at 4.25 eV in [001] direction using PBE-GGA approach, while it is occurs at 7.36 eV and 7.28 eV, respectively along [100] and [001] directions using mBJ-GGA approach. In the case of mBJ-GGA, for  $\varepsilon_1$  and  $\varepsilon_2$  are shifted toward the high-energy region with weaker intensities.



Figure 6.4.5: Real Part of the dielectric constant of Rbh CsC1, ZB and Wz structures.



Figure 6.4.6: Imaginary part of the dielectric constant of RbH in RS, CsCl, ZB and WZ structures.

From Figure 6.4.7, the absorption spectrum is related directly to the imaginary part  $\varepsilon_2$ , it is clear that there are strong absorption peaks for RbH in RS, CsCl, ZB and WZ structures which onset at about 2.5, 3.57, 3.5 and 3.9 eV, respectively using PBE-GGA approach and 5.2, 5.0, 6.5 and 6.79 eV, respectively using mBJ-GGA approach. These peaks are shifted toward the high-energy region. From the same figure maximum absorption for KH in RS, CsCl and ZB structures occurs at 6.15, 7.2 and 5.4 eV, respectively using PBE-GGA and 9.8, 8.86 and 8.6 eV, respectively using mBJ-GGA, while in WZ structure, maximum absorption occurs at 5.2 eV along [100] direction and at 5.45 eV along [001] direction using PBE-GGA approach. Absorption spectrum approximately the same as imaginary dielectric function, they begin to have a considerable value approximately at the same point and reach maximum value at the same photon energy.

The reflectivity coefficient R(w) for RbH in RS, CsCl, ZB and WZ structures are displayed in Figure 6.4.8, the zero-frequency reflectivity are 4.5%, 5.6%, 3.3% and 3.4%, respectively with PBE-GGA and 1.3%, 1.79%, 0.79% and 0.7%, respectively with mBJ-GGA approach. It is clear that R(0) within PBE-GGA is greater than that of mBJ-GGA approach. With the four structures and after R(w) reaches its maximum value, it begins to decrease and oscillates. Along the spectrum from 0 eV to 14 eV, there are peaks; these peaks originate from the inter-band transitions.



Figure 6.4.7: Absorption spectrum of Rbh in Rs, Csc1, ZB and Wz structures.



Figure 6.4.8: Reflectivity coefficient R(w) for RbH in RS, CsCl, ZB and WZ structures.
Figure 6.4.9 displays the energy loss function L(w), which is related to the energy loss of a fast electron in the material. Figure 6.4.9 shows that loss function for KH in RS, CsCl, ZB and WZ structures begins at 4.49, 5.0, 4.68 and 4.0 eV, respectively using PBE-GGA approach and 7.19, 7.0, 7.72 and 7.5 eV, respectively using mBJ-GGA approach, as seen L(w) oscillates but the peaks go to higher value as the photon energy increases.



Figure 6.4.9: Energy loss function L(w)for RbH in RS, CsCl, ZB and WZ structures.

Figure 6.4.10 displays the refractive index n(w). The static refractive index n(0) is found to have the values 1.48 in RS structure, 1.57 in CsCl structure, 1.40 in ZB structure and 1.40 in WZ structure, respectively using PBE-GGA approach and 1.22 in RS structure, 1.34 in CsCl structure, 1.16 in ZB structure and 1.18 in WZ structure, respectively using mBJ-GGA approach.

The static refractive index n(0) value is equal the square root of the real part of dielectric function;  $n(0) = \sqrt{\varepsilon_1(0)}$ ; which is to some extent the same as that obtained from Figure 6.4.5.



Figure 6.4.10: Refractive index n(w) for RbH in RS, CsCl, ZB and WZ structures.



Figure 6.4.11: Extinction coefficient k(w) for RbH in RS, CsCl, ZB and WZ structures.

The extinction coefficient k(w) is displayed in Figure 6.4.10, K(w) starts to have a considerable value in RS, CsCl, ZB and WZ at 3.48, 4.56, 4.7and 4.46 eV with PBE-GGA approach and 6.60, 6.13, 7.7 and 7.88 eV in mBJ-GGA approach. From these figures, we can see that the cubic structures are optically isotropic while the WZ structure is not.

#### 6.4.5 Elastic properties

The calculated elastic constants and bulk moduli for RbH in the RS, CsCl and ZB structures, together with the available other theoretical results are displayed in Table 6.4.5 [7, 80, 91]. The computed elastic constants for RbH compound in the RS structure agree well with previous theoretical results [7, 80, 91], although the calculated  $C_{12}$  value is negative for the RbH compound in CsCl structure; as Xinyou *et al.*[98] result of KH compound; RbH compound still stable in the CsCl structure. The results are to some extent is consistent with Sudha *et al.* [7] and Xinyou *et al.* [98]. It is clear from Table 6.4.5 that these elastic constants satisfy the Born–Huang criteria for the cubic structures as well as for WZ (hexagonal) structure (Table 6.4.6); meaning that they are mechanically stable. Similarly, for the hexagonal system (WZ) presented in Table 6.4.7, are also satisfied. CsCl has the greater value of bulk modulus, while WZ in Table 6.4.6 has the lowest value of bulk modulus.

Table 6.4.5: The calculated elastic constants C<sub>ij</sub> (GPa), Bulk modulus (B) in Voigt (V), Reuss (R) and Hill (H) approximations (in GPa) for RbH in cubic structures.

	RS structure		CsCl structure		ZB structure
Compound	Present	Other theoretical	Present	Other	Present work
	work	work	work	theoretical	
				work	
C <sub>11</sub>	25.29	$26.46^{a}$ , $24.6^{b}$ ,	52.73	$42^{a}$	15.13
C <sub>12</sub>	5.07	28.2 <sup>c</sup>	-2.78	1.4 <sup>a</sup>	7.8
C <sub>44</sub>	8.44	$7.93^{\rm a}, 4.6^{\rm b}, 7.11^{\rm c}$	1.67	$12^{a}$	8.10
		$10.97^{\rm a}, 8.2^{\rm b},$			
		12.5 <sup>c</sup>			
B <sub>V</sub>	11.81	13.97 <sup>a</sup>	15.71	14.85 <sup>a</sup>	10.28
B <sub>R</sub>	11.81		15.71		10.28
B <sub>H</sub>	11.81		15.71		10.28

<sup>a</sup>Ref.[7], <sup>b</sup>Ref.[80], <sup>c</sup>Ref.[91].

Figure 6.4.13 shows the pressure dependence of the elastic constants and bulk modulus for RbH compound with RS structure. It is noticed that elastic constant  $C_{11}$  and bulk modulus increase in the applied pressure. It is also noticeable that elastic constant  $C_{11}$  is the most sensitive to the pressure rather than  $C_{12}$ ,  $C_{44}$  and B. At high pressure,  $C_{44}$  approaches zero, indicating that these compounds are unstable under high pressure, and the RS structure transforms to CsCl structure.

Table 6.4.6: The calculated elastic constants C<sub>ij</sub> (GPa), Bulk modulus (B) in Voigt (V), Reuss (R) and Hill (H) approximations (in GPa) for RbH in WZ structure.



Figure 6.4.12: Variation of elastic constants and bulk moduli for RbH compound in RS structure.

The bulk modulus for KH compound is small, which means the week resistance to the fracture of these materials. The CsCl phase is the hardest phase as in the case of previous compounds (LiH, NaH and KH), because it possesses the most bulk modulus value, on the other hand the compressibility ( $\beta$ =1/B) of this phase structure is the least one as shown in Table 6.4.7, while WZ structure has the most compressibility. The value of the bulk modulus B computed from the elastic constants is to some extent agrees with the results obtained from Murnaghan's equation of state [53]. Table 6.4.7 displays the anisotropy factor (A) for RbH compound in the four structures; WZ structure is completely isotropic with A=1, while the other structure are anisotropic because A is far from unity.

Table 6.4.7: The calculated Young's modulus (Y), Shear modulus (S) (in GPa), compressibility ( $\beta$  in GPa<sup>-1</sup>), B/S ratio, Poisson's ratio ( $\nu$ ), Anisotropic ratio (A), Cauchy pressure C<sub>s</sub> and Vickers hardness (H<sub>V</sub>) for RbH compound in RS, CsCl, ZB and WZ structures in comparison with available theoretical data.

	Rs structure		CsCl structure		ZB	WZ
Constant						structure
	Present	Other	Present	Other	Present	Present
	Calculations	theoretical	Calculations	theoretical	Calculations	Calculations
		Calculations		Calculations		
Y	21.73	25 <sup>a</sup>	28.9	34 <sup>a</sup>	15.70	12.60
S	9.10	10.2 <sup>a</sup>	12.1	15 <sup>a</sup>	6.30	4.97
β	0.0846		0.0636		0.0972	0.1123
B/S	1.2978	1.37 <sup>a</sup>	1.298	0.99 <sup>a</sup>	1.6317	1.7429
$\upsilon_V$	0.193	0.23 <sup>a</sup>	0.193	0.03 <sup>a</sup>	0.245	0.265
Α	0.834	$1.18^{a}$	0.060	0.95 <sup>a</sup>	2.21	0.97
H <sub>v</sub>	2.36		3.33		0.31	-0.479

<sup>a</sup>Ref.[7].

Poisson's ratio value and B/S value are displaying in Table 6.4.7, they indicate that RbH compound represents a brittle nature for all structures. RbH in CsCl structure has the most value of hardness  $H_v$  (the most hardness); on the other hand, WZ structure has the least value of  $H_v$ . This means that CsCl structure is mechanically the strongest among all phases, which is consistence with the bulk modulus and  $H_v$  values, while WZ structure is the least strong mechanically.

#### **6.4.7 Thermal properties**

Debye temperature and average wave velocity are displayed in Table 6.4.8. The RS structure has the greater value of Debye temperature and average wave velocity. The results are in agreement with Sudha *el al.*[7] results. Figure 6.4.14 and Figure 6.4.15 show the dependence of Debye temperature and average wave velocity on the pressure. Debye temperature increases as the pressure increases, while the average wave velocity is constant in the range from 12.5 GPa to about 50 GPa.

Table 6.4.8: Average wave velocity (Vm in m/s) and Debye temperature ( $\Theta_D$  in K) for RbH compound in RS, ZB and WZ structures.

Constant	RS structure		CsCl	ZB structure	WZ
			structure		structure
	Present Other		Present	Present	Present
	calculations	theoretical	calculations	calculations	calculations
		calculations			
$\Theta_{\rm D}$	203.15	215 <sup>a</sup>	180	171.8	157.8
V <sub>m</sub>	2065	2165 <sup>a</sup>	1745	1901	1746

<sup>a</sup>Ref.[7].



Figure 6.4.13: Variation of Debye temperature with pressure for RbH in RS structure.



Figure 6.4.14: Variation of average wave velocity with pressure for RbH in RS structure.

# 6.5 CsH Compound

### **6.5.1 Structural Properties**

The ground-state properties of CsH compound in RS, CsCl, ZB and WZ structures have been estimated by calculating the total energy at different unit-cell volumes and fitting the calculated E-V points to Murnaghan's

equation of state (EOS) [53], as shown in Figure 6.5.1. We can see clearly from these curves that the rock-salt structure has the lowest energy minimum at ambient pressure, which means that it is the most stable structure at ambient conditions.



**Figure 6.5.1**: Calculated total energy per unit cell versus cell volume for CsH in RS, CsCl, ZB and WZ.

The calculated equilibrium lattice constant  $a_0$ , bulk modulus  $B_0$  and firstorder pressure derivatives of the bulk modulus  $B'_0$  for CsH in the RS, CsCl and ZB phases, along with the available experimental [2, 3, 4, 6, 99] and theoretical [7, 80, 91, 95] results, are listed in Table 6.5.1. Table 6.5.1 shows that the calculated structural parameters for CsH in RS structures are in good agreement with experimental results and the calculated structural parameters in the CsCl structure are in good agreement with the results of Sudha *et al.*[7]. Table 6.5.2 displaying the structural parameters for CsH compound within the WZ structure.

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Structure	Structural parameters	Present work	Experimental work	Other theoretical work
RS	a <sub>0</sub> (Å)	6.446	6.387 <sup>a, b</sup> , 6.376 <sup>b</sup>	6.344 <sup>e</sup> , 6.407 <sup>f</sup>
	$B_0(GPa)$	8.9	$8.0\pm0.7^{\rm a}$ , $7.6\pm0.8^{\rm c}$	$12^{\rm e}, 11.9^{\rm g}, 8.8^{\rm h}$
	B'	3.26	$4.0^{\rm a}, 4 \pm 0.4^{\rm c}, 4.0^{\rm d}$	3.037 <sup>e</sup>
CsCl	a <sub>0</sub> (Å)	3.863		3.84 <sup>e</sup>
	$B_0(GPa)$	11.50	$14.2 \pm 1^{\rm a}, 22.3 \pm 1.5^{\rm c} \ 15.9^{\rm i}$	14 <sup>e</sup>
	B'	4.45	$4 \pm 0.2^{a}, 4.8 \pm 0.5^{c}$	4.675 <sup>e</sup>
ZB	a <sub>0</sub> (Å)		7.002	
	$B_0(GPa)$		6.47	
	B'		3.57	

Table 6.5.1: Structural parameters for CsH in the RS, CsCl and ZB structures, along with experimental and other theoretical results.

<sup>a</sup>Ref.[4], <sup>b</sup>Ref[2], <sup>c</sup>Ref[3], <sup>d</sup>Ref[99], <sup>e</sup>Ref[7], <sup>f</sup>Ref[80], <sup>g</sup>Ref[95], <sup>h</sup>Ref[91], <sup>i</sup>Ref [6].

 Table 6.5.2: Structural parameters for CsH in WZ structure.

a <sub>0</sub> (Å)	c/a	u(a.u.)	B(GPa)	B
5.037	1.548	0.389	6.374	3.71

# 6.5.2 Phase Transition

The energy per unit cell is calculated by using the PBE-GGA at different unit-cell volumes, and the results are fitted to the Murnaghan's equation of state [53], as shown in Figure 6.5.2. It is clearly shown that CsH compound undergoes a structural phase transition from RS to the other structures. At the transition pressure, the enthalpies of the two consecutive phases are equal. Enthalpy-pressure curves for CsH are displayed in Figure 6.5.2. The estimated induced-transition pressures from RS to the other structures for CsH compounds are presented in Table 6.5.3. The computed transition pressure from RS to CsCl structures is found to be equal to 2.45 GPa, which are in good agreement with the previous theoretical calculations and the high-pressure experimental values of approximately 1.2 GPa [3]. Table 6.5.4 displays the V/V<sub>0</sub> fraction, where V is the unit-cell volume at which the transition occurs and V<sub>0</sub> is the unit-cell equilibrium volume of the RS structure.



Figure 6.5.2: Enthalpy as a function of pressure for CsH using the PBE-GGA method.

# Table 6.5.3: Calculated transition pressures as well as the experimental and other theoretical data CsH compound.

	$RS \rightarrow CsC$	Cl P <sub>t</sub> (GPa)	$RS \rightarrow ZB$	$RS \rightarrow WZ$	
Compound	Present	Experimental	Other	P <sub>t</sub> (GPa)	P <sub>t</sub> (GPa)
	Work	work	theoretical		
			work		
CsH	2.45	1.2 <sup>a</sup>	$2.1^{\rm b}, 1.5^{\rm c}$	-0.81	-1.65

<sup>a</sup>Ref.[3], <sup>b</sup>Ref[7], <sup>c</sup>Ref [10].

Table 6.5.4: The V/V <sub>0</sub> fractions for Cs	H compound	
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Compound	$RS \rightarrow CsCl$	$RS \rightarrow ZB$	$RS \rightarrow WZ$
V/V <sub>0</sub> for CsH	0.736	1.511	2.373

The induced-transition pressures from RS to CsCl for CsH occurred at  $V/V_0= 0.736$ , which means that the RS to CsCl transition requires volume compression. The RS to ZB and RS to WZ phase transitions occur when  $V/V_0$  is greater than one, meaning that these two transitions require volume expansion. There is a small difference between the reported and experimental transition pressure, and one of the reasons for this phenomenon is that the experimental calculations are carried out at room temperature, while the theoretical calculations are performed at 0K, the induced transition pressure decreases as the temperature increases.

#### **6.5.3 Electronic properties**

Atoms in a crystal interact with their neighbors and the energy levels of the electrons in isolated atoms turn into bands. In fact, a material can be classified as a conductor, insulator or semiconductor by examining its band structure and the Fermi energy-level position. The self-consistent band structures of CsH is calculated in cubic RS, CsCl and ZB structures and a hexagonal (WZ) structure using the computed equilibrium lattice constant within PBE-GGA, mBJ-GGA for the exchange-correlation potential; the results are shown Figure 6.5.3. We can clearly see that the Fermi level crosses the energy-band gap for all structures. The energy-band structures scheme of KH, RbH and CsH compounds are quite similar to one another. The minimum energy-band gap is direct along the L-point symmetry and

X-point symmetry lines within the RS and ZB structures respectively for CsH compound. For the CsCl structure, the minimum energy-band gap is indirect within PBE-GGA approach, while it is direct along the R-point symmetry line within mBJ-GGA. CsH has a direct minimum energy-band gap along the M-point symmetry line in the WZ structure within mBJ-GGA, but it is indirect within PBE-GGA. From Figure 6.5.3, it is clear that the electronic energy bands are more vertically distributed within PBE-GGA; mBJ-GGA shifts them closer to one another.

Differences in the width of the first valence band below the Fermi-energy between PBE-GGA and mBJ-GGA in RS, CsCl, ZB and WZ structures are 0.60, 0.58, 0.64 and 0.60 eV, respectively for CsH. Table 6.5.5 reports the energy-band gaps, calculated using the two approaches mBJ-GGA and PBE-GGA along with the available theoretical [7, 93, 100, 101] and experimental results [102].



**Figure 6.5.3:** Band structure of CsH in RS, CsCl, ZB and WZ structures within the PBE-GGA and mBJ-GGA approaches.

Differences in the width of the first valence band below the Fermi-energy between PBE-GGA and mBJ-GGA in RS, CsCl, ZB and WZ structures are 0.60, 0.58, 0.64 and 0.60 eV, respectively for CsH compound.

Table 6.5.5: Calculated energy band-gap values ((Eg (eV)) of CsH inRS, CsCl, ZB and WZ structures.

Structure	Present work		Other theoretical works	Experimental
	PBE-GGA	mBJ-GGA		results
RS	L→L : 2.470	L→L : 4.650	$2.4472^{a}, 4.04^{b}, 6.67^{c}, 2.80^{d}$	4.4 <sup>e</sup>
CsCl	R→X :2.696	R→R: 3.950	2.5 <sup>a</sup>	
ZB	X→X : 2.894	X→X : 5.555		
WZ	$M \rightarrow \Sigma$ : 3.145	M→M : 5.974		

<sup>a</sup>Ref.[7], <sup>b</sup>Ref[100], <sup>c</sup>Ref[101], <sup>d</sup>Ref.[93], <sup>e</sup>Ref.[102].

The calculated energy-band gaps are broader using mBJ-GGA than using PBE-GGA, by approximately 1.25eV to 2.66eV, depending on which structure is used. The energy-band gap has been modified using the mBJ-GGA approach, so the band gap calculated using mBJ-GGA is more accurate than that calculated using the GGA approach and they are in good agreement with experimental results. The present calculations for RS structure on energy band gap using PBE-GGA approximation is smaller than experimental result of about 1.93eV, while using mBJ-GGA is greater than experimental results of about 0.25eV. This is mainly due to the greater temperature and pressure in the experiment, while theoretical calculations carried out at zero temperature and ambient pressure. In addition, the lattice constant used in this present work does not equal the experimental one. The present calculations using mBJ-GGA are more accurate than the other represented theoretical calculations: the energy band gap in references [7]

and [93] are smaller than the experimental result of approximately 1.95eV and 1.6eV respectively, while result of reference [101] greater by about 2.27eV. CsH is categorized as a semiconductor in the four structures using PBE-GGA and an insulator using mBJ-GGA method. Although the ground state is well described by PBE-GGA, this approximation fails to account for excited-state properties. Due to a well-known non-physical problem in calculating the energy-band gap using GGA, which is the self-interaction error [85], differences in energy-band gap values between GGA on one hand and mBJ-GGA on the other hand arise. With GGA, the energy-band gap is underestimated, and sometimes a semiconducting or metallic state may be obtained instead of an insulating one.

The density of states for the KH, RbH and CsH compounds are quite similar to one another. Figure 6.5.4 displays the densities of states of CsH compounds, obtained using the PBE-GGA and mBJ-GGA approaches. The heights of the peaks vary from one phase structure to another, and depend on the phase structure and the method used to calculate the exchange potential. By phase transition from RS to CsCl, the band gaps of these compounds decrease by about 0.7 to 1.2 eV. Total and partial densities of states CsH compound in the four structures (RS, CsCl, ZB and WZ) have been calculated to further understand the nature of electronic-band structures. It is clear that the energy bands below the Fermi energy (FE), indicated by a dotted horizontal line, arise mainly from H-s, along with small contributions from X-s and X-p. Above the FE, they mainly arise from X-P and X-s states, with a small contribution from the H-s state.

Table 6.5.5 and Figure 6.5.4 show that the energy-band gap calculated within mBJ-GGA is wider than that calculated within PBE-GGA, as mentioned before, and to some extent agree with the experimental results.



Figure 6.5.4: Density of states of CsH in RS, CsCl, ZB and WZ structures.

#### **6.5.4 Optical properties**

Using the relations in section 5.5 optical constants can be determined and analyzed. Figure 6.5.5 displaces the calculated real dielectric constant for CsH in the four studied structures. The static real dielectric constant for CsH in RS, CsCl, ZB and WZ structures are 2.37, 2.63, 2.1 and 2.09 respectively using PBE-GGA approach and 1.59, 1.83, 1.4 and 1.38, respectively using mBJ-GGA approach. It is clear that mBJ has a lower value of  $\varepsilon_1(0)$  comparing to PBE-GGA approach and this is relating to variation in electronic band structure as seen in section 6.5.3. The value of  $\varepsilon_1(w)$  within mBJ-GGA is almost positive in the whole spectrum, which means no metallic behavior exists, while within PBE-GGA there are small regions in which  $\varepsilon_1(w)$  has a negative values. The maximum value of  $\varepsilon_1(w)$  for RS, CsCl, ZB and WZ structures occurs at photons energy equals to 5.8, 3.98, 4.49 and 4.2 eV, respectively using GGA approach.

The maximum values of  $\varepsilon_1(w)$  for the four structures shifted toward the high energy with decreasing in the intensity compared to PBE-GGA approach. The calculated imaginary parts of the optical dielectric function for CsH compound in the RS, CsCl, ZB and WZ structures have been displayed in Figure 6.5.6 as a function of the photon energy from 0.0 to 14.0 eV. The calculated values of real and imaginary dielectric constants indicate that the cubic structures of CsH are optically isotropic;  $\varepsilon_{xx} = \varepsilon_{zz}$ , while the WZ structure is optically anisotropic;  $\varepsilon_{xx} \neq \varepsilon_{zz}$ . The imaginary part gives us information about absorption behavior of the studied compounds. From Figure 6.5.6,  $\varepsilon_2$  begins to have a considerable amount at about 2.83, 2.0, 2.1 and 3.3 eV within PBE-GGA along [100] polarization and 5.4, 4.0, 6.65 and 6.7 eV within mBJ-GGA along [100] polarization, which is to some extent close to the direct energy gap. The imaginary part  $\varepsilon_2$  indicates that the CsH in the RS, CsCl, ZB and WZ structures has maximum absorption peaks. These peaks at 5.9, 5.63, 4.8 and 4.25 eV, respectively using PBE-GGA and at 7.6, 6.6,-8.1 and 8.0 eV, respectively using mBJ-GGA.



Figure 6.5.5: Real part of the dielectric constant of CsH in RS, CsCl, ZB and WZ structures.



Figure 6.5.6: Imaginary part of the dielectric constant of CsH in RS, CsCl, ZB and WZ structures.

Figure 6.5.7 is displaying the absorption spectrum for CsH in the four structures. Absorption spectrum is related directly to the imaginary part of  $\varepsilon_2$ , it is clear that there are strong absorption peaks of CsH in RS, CsCl, ZB and WZ structures in the energy range from 3, 5.2, 5.0 and 5.8 eV to 14 eV, respectively using PBE-GGA and from 6, 7.2, 7.0 and 7.5 eV to 14 eV, respectively using mBJ-GGA, these peaks reflect some transitions between different orbits. From the same figure maximum absorption of CsH in RS, CsCl, ZB and WZ structures occurs at 7.54, 9.64, 6.59 and 6.31 eV, respectively using PBE-GGA and 9.7, 8.36, 9.8 and 8.18 eV, respectively using mBJ-GGA. The reflectivity coefficient R(w) of CsH in RS, CsCl, ZB and WZ structures are displayed in Figure 6.5.8. The zero-frequency reflectivity values are 4.5%, 5.6%, 3.3% and 3.4%, respectively within

PBE-GGA and 1.3%, 1.8, 0.79% and 0.7%, respectively within mBJ-GGA. Within both PBE-GGA and mBJ-GGA approaches, R(w) has a peaks; these peaks originate from the inter-band transitions; as the photon energy reaches 14 eV, R(w) within PBE-GGA goes to the maximum value. Figure 6.5.9 is displaying the energy loss function L(w), L(w) is related to the energy loss of a fast electron in the material.

Figure 6.5.9 shows that loss function for CsH in RS, CsCl, ZB and WZ structures using mBJ-GGA are shifted toward the higher energy and the peaks have greater value. Figure 6.5.10 displaces the refractive index n(w). The static refractive index; when photons energy is zero or w=0; n(0) is found to have the values 1.55 for RS structure, 2.63 for CsCl structure, 1.44 for ZB structure and 1.49 for WZ structure, respectively using PBE-GGA approach and 1.26 for RS structure, 1.35 for CsCl structure, 1.19 for ZB structure and 1.18 for WZ structure, respectively using mBJ-GGA approach. The static refractive index n(0) value is equal to the square root of the real part of dielectric function;  $n(0) = \sqrt{\varepsilon_1(0)}$ ; which is to some extent the same as those obtained from Figure 6.5.5.



Figure 6.5.7: Absorption function of CsH in RS, CsCl, ZB, and WZ structures.



Figure 6.5.8: Reflectivity coefficient R(w) of CsH in RS, CsCl, ZB, and WZ structures.

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Figure 6.5.9: Energy loss function L(w) of CsH in RS, CsCl, ZB, and WZ structures.

The extinction coefficient k(w) is displayed in Figure 6.5.11, the curves of extinction coefficient  $k(\omega)$  are closed to the  $\varepsilon_2(\omega)$  and have similar features with the absorption coefficient  $\alpha(\omega)$ , Figure 6.5.7. k(w) for RS, CsCl, ZB and WZ approaches starts from 3.0, 2.0, 3.0 and 3.17eV, respectively by using PBE-GGA approach and 5.67, 4.0, 6.5 and 6.39eV, respectively by using mBJ-GGA approach. Maximum value of k(w) for RS, CsCl, ZB and WZ structures occurs at energy equals to 7.1, 5.68, 4.87 and 4.6eV, respectively using PBE-GGA approach and 7.8, 6.7, 8.13 and 8.32eV, respectively using mBJ-GGA approach.



Figure 6.5.10: Refractive index n(w)(w) of CsH in Rs, CsC1,ZB, and WZ Structures.



Figure 6.5.11: Extinction coefficient k(w) of CsH in RS, CsCl, ZB, and WZ structures.

**6.5.5 Elastic properties** 

The calculated elastic constants and bulk modules of CsH, together with the available other theoretical results are displayed in Table 6.5.6 in the RS, CsCl and ZB structures, respectively [7, 80, 91]. The computed elastic constants for CsH compound in the RS structure agree well with the previous theoretical results, although the calculated  $C_{12}$  value is negative for the CsH compound in CsCl structure; it is stable; the results are to some extent is consistent with Sudha *et al.*[7]. It is clear from Table 6.5.6 that these elastic constants satisfy the Born–Huang criteria for the cubic structures as well as for WZ (hexagonal) structure (Table 6.5.7); meaning that they are mechanically stable. CsCl has the greater value of bulk modulus, while WZ in Table 6.5.7 has the lowest value of bulk modulus.

Table 6.5.6: The calculated elastic constants C<sub>ij</sub> (GPa), Bulk modulus (B) in Voigt (V), Reuss (R) and Hill (H) approximations (in GPa) for CsH in cubic structures.

		RS structure	CsCl struct	ZB structure	
Compound	Present Other theoretical		Present	Other	Present work
	work	work	work	theoretical	
				work	
C <sub>11</sub>	20.7	25.6 <sup>a</sup> , 22.4 <sup>b</sup> , 20.3 <sup>c</sup>	38.21	38 <sup>a</sup>	16.2
C <sub>12</sub>	3.17	$6.761^{a}, 3.2^{b}, 3.1^{c}$	-1.90	3.2 <sup>a</sup>	3.5
C <sub>44</sub>	8.0	$9.74^{a}, 5.8^{b}, 9.1^{c}$	4.30	6.5 <sup>a</sup>	6.1
B <sub>V</sub>	9.02	11.98 <sup>a</sup>	11.46	13.97 <sup>a</sup>	7.77
B <sub>R</sub>	9.02		11.46		7.77
$B_{H}$	9.02		11.46		7.77

<sup>a</sup>Ref.[7], <sup>b</sup>Ref.[80], <sup>c</sup>Ref.[91].

Figure 6.5.13 shows the pressure dependence of the elastic constants and bulk modulus for CsH compound in RS structure. It is noticed that elastic constant  $C_{11}$  and bulk modulus increase with the applied pressure. It is also noticeable that elastic constant  $C_{11}$  is the most sensitive to the pressure rather than  $C_{12}$ ,  $C_{44}$  and B. At high pressure,  $C_{44}$  approaches zero, indicating that these compounds are unstable under high pressure, and the RS structure transforms to CsCl structure.

Table 6.5.7: The calculated elastic constants C<sub>ij</sub> (GPa), Bulk modulus (B) in Voigt (V), Reuss (R) and Hill (H) approximations (in GPa) for CsH in WZ structure.

C <sub>11</sub>	C <sub>12</sub>	C <sub>13</sub>	C <sub>33</sub>	C <sub>55</sub>	B <sub>V</sub>	B <sub>R</sub>	B <sub>H</sub>
11.61	2.66	2.61	12.29	5.57	5.70	5.69	5.70



Figure 6.5.12: Variation of elastic constants and bulk modules for CsH compound in RS structure.

The bulk modulus for CsH compound is small, which means the week resistance to the fracture of these materials. The CsCl phase is the hardest phase as in the case of previous compounds (LiH, NaH, KH and RbH), because it possesses the most bulk modulus value, on the other hand the compressibility ( $\beta$ =1/B) of this phase structure is the least one as shown in Table 6.5.8, while WZ structure has the most compressibility. The value of the bulk modulus B computed from the elastic constants is some extent agrees with the results obtained from Murnaghan's equation. Table 6.5.8 displays the anisotropy factor (A) for CsH compound in the four structures; RS and ZB structures are some extent isotropic with A=0.912 and 0.96 respectively, while the CsCl and WZ structures are anisotropic because A is far from unity.

Table 6.5.8: The calculated Young's modulus (Y), Shear modulus (S) (in GPa), compressibility ( $\beta$  in GPa<sup>-1</sup>), B/S ratio, Poisson's ratio ( $\nu$ ), Anisotropic ratio (A), Cauchy pressure C<sub>s</sub> and Vickers hardness (H<sub>V</sub>) for CsH compound with RS, CsCl, ZB and WZ structures in comparison in available theoretical data.

	Rs structure		CsCl structure		ZB	WZ
Constant					structure	structure
	Present	Other	Present	Other	Present	Present
	Calculations	theoretical	Calculations	theoretical	Calculations	Calculations
		Calculations		Calculations		
Y	19.0	22 <sup>a</sup>	24.3	26 <sup>a</sup>	14.71	11.54
S	8.31	9.15 <sup>a</sup>	10.6	11 <sup>a</sup>	6.21	4.96
β	0.1108		0.0872		0.1287	0.1754
B/S	1.085	1.31 <sup>a</sup>	1.081	1.27 <sup>a</sup>	1.2512	1.14919
$\upsilon_V$	0.147	0.22 <sup>a</sup>	0.146	$0.07^{a}$	0.184	0.162
А	0.912	$1.18^{a}$	0.214	0.37 <sup>a</sup>	0.96	1.24
H <sub>V</sub>	3.27		4.26		1.47	1.33
Cs	-4.83	-2.97 <sup>a</sup>	-6.20	$-3.30^{a}$	-2.60	-2.91

<sup>a</sup>Ref.[7].

Poisson's ratio v and B/S value both are used to estimate if the material is brittle or ductile in nature. Table 6.4.8 shows that Poisson's ratio v value and B/S value in agree that CsH compound represents a brittle nature in the four structures. CsH in CsCl structure has the most value of  $H_v$  (the most hardness); on the other hand, WZ structure has the least value of  $H_v$ . This means that CsCl structure is mechanically the strongest among all phases, which is consistence with the bulk modulus and  $H_v$  values, while WZ structure is the least strong mechanically.

#### **6.5.7 Thermal properties**

Debye temperature and average wave velocity are displayed in Table 6.4.9. The RS structure has the greater value of Debye temperature and average wave velocity. The results agree well with Sudha *el al.* [7] results. Figure 6.4.14 and Figure 6.4.15 show the dependence of Debye temperature and average wave velocity on the pressure, both of Debye temperature and average wave velocity increase as the pressure increases.

Table 6.5.9: Average wave velocity (Vm in m/s) and Debye temperature ( $\Theta_D$  in K) for CsH compound in RS, ZB and WZ structures.

Constant	RS structure		CsCl	ZB structure	WZ
			structure		structure
	Present	Other	Present	Present	Present
	calculations	theoretical	calculations	calculations	calculations
		calculations			
$\Theta_{\rm D}$	160.37	167 <sup>a</sup>	158	145.2	128.9
V <sub>m</sub>	1735	1786 <sup>a</sup>	1634	1709	1513

<sup>a</sup>Ref.[7].



Figure 6.5.13: Variation of Debye temperature with pressure for CsH in RS structure.



Figure 6.5.14: Variation of average wave velocity with pressure for CsH in RS structure.

# Chapter seven Conclusion

#### 7.1 Conclusions

The structural, electronic properties, the structural phase transition, elastic and optical properties of the alkali hydrides XH (X=Li, Na, K, Rb and Cs) are calculated in the RS, ZB, CsCl and WZ structures. The FP-LAPW method was used, within the GGA and mBJ-GGA approaches, as implemented in WIEN2k code. A good agreement with the experimental results was obtained; by applying the mBJ-GGA approach, the energy band gap was modified and thus the CsCl structure was converted from a semiconductor to an insulator for LiH, KH and RbH compounds. The NaH and CsH compounds in CsCl structure were also converted from semiconductor to wide energy band gap semiconductor. The phase transitions predicted in this work are from RS to CsCl, RS to ZB, and RS to WZ. It is clear that XH (X= Li, Na, K, Rb and Cs), within the PBE-GGA approach, undergoes from RS to CsCl under high pressure of 211.8, 34.26, 5.00, 3.50 and 2.54 GPa for LiH, NaH, KH, RbH and CsH, respectively. Whereas, under low pressure the RS structure expands and transforms to WZ and ZB. It is noticed that the transition pressure needed for the transformation of RS phase to CsCl phase decreases as going from Li to Cs in the periodic table. In addition, it is observed that the present calculations are in agreement with other experimental and theoretical results. The optimized lattice constant (a<sub>0</sub>) has been used to compute the elastic constants and their related properties. Elastic constants for XH compounds decrease in going from Li to Cs in the periodic table, which means they become mechanically less stronger. The calculated elastic constants for the alkali hydrides satisfy the Born–Huang criteria except for LiH and NaH in CsCl structure. Satisfying the Born–Huang criteria means that they are mechanically stable. Elastic constant C<sub>11</sub> and bulk modulus for these compounds in the RS structure increase with the applied pressure, C<sub>11</sub> is more sensitive to pressure than  $C_{12}$ ,  $C_{44}$  and B. At high pressure,  $C_{44}$ becomes negative for KH and RbH compounds and goes to zero for the others, indicating that these compounds are unstable under high pressure, and the RS structure transforms to CsCl structure. LiH compound is the hardest among the studied compounds, hardness decreases as the Alkali radius increased. The Poisson's ratio v and Cauchy pressure ( $C_s=C_{12}-C_{44}$ ) for the alkali hydrides compounds are in the range from 0.145 to 0.245 with a negative Cauchy pressure C<sub>s</sub> for the cubic phases (RS, CsCl and ZB), they tend to form covalent bond in the RS, CsCl and ZB structures. Both KH and RbH are tending to form ionic bonds in WZ structure. From the value of B/S, these compounds represent a brittle nature, which agrees with the small value of the bulk modulus. LiH in RS structure has the most value of Vickers hardness  $(H_v)$  (the most hardness) and decreases as going from Li to Cs in the periodic table, on the other hand these compounds in the hexagonal system (WZ structure) have the least value of  $H_{v}$ .

The calculated Young's modulus, indicates that the stiffness of XH (X=Li, Na, K, Rb, Cs) compounds decreases as going from Li to Cs in the periodic table. The RS structure is the stiffest among all structures, while WZ

structure has the least value of stiffness. This means that RS structure of these compounds is the more mechanically stronger among all phases, which is consistent with the bulk modulus and  $H_v$  values. Debye temperature, transverse velocity, longitudinal velocity and average velocity decrease as going from Li to Cs in the periodic table with all the considered structures. RS structure has the large value of Debye temperature, transverse, longitudinal and average velocity. Debye temperature and average wave velocity increase as the pressure increases, but for KH the average wave velocity starts to decrease above 8 GPa.

Optical properties have been studied for XH compounds in RS, CsCl, ZB and WZ structures. For these compounds mBJ-GGA has a lower value of  $\varepsilon_1(0)$  and this is mainly related to variation in electronic band structure. The maximum values of  $\varepsilon_1(w)$  for the four structures shifted toward the high energy with decreasing in the intensity compared to PBE-GGA approach. The calculated dielectric constants indicate that the cubic structures of LiH are optically isotropic;  $\varepsilon_{xx} = \varepsilon_{zz}$ ; while the WZ structure is optically anisotropic;  $\varepsilon_{xx} \neq \varepsilon_{zz}$ . LiH compound has a high reflectivity against highenergy photons; it is a good coating material to avoid and prevent solar heating.

Our results are summarized in tables A, B, C and D in the appendix.

#### 7.2 Published papers

Four papers have been published from this work in an international journals with impact factors.

1-R. Jaradat, M. Abu-Jafar, I. Abdelraziq, R. Khenata, D. Varshney, S. Bin-Omran and S. Al-Qaisi, 2017. High-pressure structural phase transition and electronic properties of the alkali hydrides compounds XH (X = Li, Na). Phase Transitions 90:914. DOI: 10.1080/01411594.2017.1286488

2-R. Jaradat, M. Abu-Jafar, I. Abdelraziq, S. Bin-Omran, D. Dahliah, R. Khenata 2018. High-pressure structural phase transitions and electronic properties of the alkali hydride compounds XH (X=K, Rb and Cs) Materials Chemistry and Physics. 208: 132

3- R. Jaradat, M. S. Abu-Jafar, I. Abdelraziq, D. Dahliah and R. Khenata
2018. Elastic and thermodynamic properties of Alkali Hydrides XH (X= K,
Rb and Cs). Chinese Journal of Physics 56:830

3- R. Jaradat, M. S. Abu-Jafar, I. Abdelraziq, A. Mousa, T. Ouahrani, and R. Khenata, 2018 Insight into the structural, electronic, elastic and optical properties of the alkali hydride compounds, XH (X = Rb and Cs) AIP Advances 8, 045017; doi: 10.1063/1.5025002.

# **Future work**

1- The optical properties of LiH and NaH compounds in RS, CsCl, ZB and WZ Structures will be the next target.

2- The structural, electronic, elastic and optical properties of  $Al_xMn_{1-x}N$  alloys will be studied in different structures will be investigated.
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## 178 Appendix I

## Table A: Structural parameters for XH (X=Li, Na, K, Rb, Cs) in RS, CsCl, ZB and WZ structures.

Compound	Structural	RS	CsCl	ZB	WZ
	parameters	structure	structure	structure	structure
LiH	a <sub>0</sub> (Å)	4.018	2.510	4.307	3.115
	B <sub>0</sub> (GPa)	36.85	33.60	27.17	27.91
	Β'	4.02	4.01	3.94	3.36
NaH	a <sub>0</sub> (Å)	4.838	2.965	5.228	3.748
	B <sub>0</sub> (GPa)	23.30	23.97	17.49	18.06
	Β'	3.55	3.83	3.67	3.90
KH	a0( Å )	5.70	3.41	6.215	4.492
	B0(GPa)	13.41	15.04	9.85	10.12
	Β'	3.9	4.00	3.40	3.62
RbH	a <sub>0</sub> (Å)	6.054	3.62	6.598	4.764
	$B_0(GPa)$	11.25	13.64	8.33	8.135
	Β'	3.87	4.21	3.25	4.06
CsH	a <sub>0</sub> (Å)	6.446	3.863	7.002	5.037
	B <sub>0</sub> (GPa)	8.9	11.50	6.47	6.374
	Β'	3.26	4.45	3.57	3.71

Table	<b>B:</b>	Elastic	constants	for	XH	(X=Li,	Na,	K,	Rb,	Cs)	in	WZ
struct	are.											

Compound	C <sub>11</sub>	C <sub>12</sub>	C <sub>13</sub>	C <sub>33</sub>	C <sub>55</sub>
LiH	68.3	4.25	5.32	69.5	33.1
NaH	34.3	7.6	5.7	30.1	11.7
KH	16.2	7.7	9.3	19.0	4.3
RbH	15.3	5.8	5.1	17.9	4.6
CsH	11.61	2.66	2.61	12.29	5.57

Compound	Elastic	RS	CsCl	ZB
	constant	structure	structure	structure
LiH	C <sub>11</sub>	70.2	175	35
	C <sub>12</sub>	10.2	-38	19.6
	$C_{44}$	50.4	-22	33.4
NaH	C <sub>11</sub>	39.1	95.2	19.5
	$C_{12}$	13.0	-14	13.7 16.0
	$C_{44}$	24.1	-0.5	10.0
KH	C <sub>11</sub>	27.76	56.36	13.41
	C <sub>12</sub>	6.38	-4.67	9.16
	$C_{44}$	13.73	0.79	11.27
RbH	C <sub>11</sub>	25.29	52.73	15.13
	C <sub>12</sub>	5.07	-2.78	7.8
	$C_{44}$	8.44	1.67	8.10
CsH	C <sub>11</sub>	20.7	38.21	16.2
	C <sub>12</sub>	3.17	-1.90	3.5
	C <sub>44</sub>	8.0	4.30	6.1

Table C: Elastic constants for XH (X=Li, Na, K, Rb, Cs) in RS, CsCl and ZB structures.

Table D: Energy gap for XH (X=Li, Na, K, Rb, Cs) in RS, CsCl, ZB and WZ structures.

Compound		GGA	mBJ-GGA
LiH	RS	X→X 3.170	X→X 5.170
	CsCl	$R \rightarrow X 0.742$	R→X 2.900
	ZB	W→L 4.338	W→L 5.800
	WZ	Λ→K 3.697	Λ→K 5.320
NaH	RS	W→L 3.830	W→L 6.410
	CsCl	R→X 1.119	R→X 4.532
	ZB	W→L 3.751	W→L 6.222
	WZ	Л→Г 3.803	Л→Г 6.482
KH	RS	L→L 3.428	L→L 6.012
	CsCl	R→X 2.456	R→X 4.971
	ZB	W→L 3.671	X→X 6.801
	WS	M→M 3.655	M→M 6.917
RbH	RS	L→L 3.050	L→L 5.633
	CsCl	R→X 2.397	R→X 4.474
	ZB	X→X 3.379	X→X 6.466
	WS	M→M 3.470	M→Σ 6.907
CsH	RS	L→L 2.470	L→L 4.650
	CsCl	$R \rightarrow X 2.696$	R→R 3.950
	ZB	$X \rightarrow \overline{X 2.894}$	$X \rightarrow X 5.555$
	WS	$M \rightarrow \overline{\Sigma} 3.145$	M→M 5.974

كلية الدراسات العليا

## استخدام طريقة (FP-LAPW) لدراسة الخصائص التركيبية و الالكترونية والمرونية والضوئية لمركبات القلويات الهيدروجينية XH (X= Li, Na, K, Rb, Cs)

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قدمت هذه الأطروحة استكمالاً لمتطلبات الحصول على درجة الدكتوراه في الفيزياء، بكلية الدراسات العليا، في جامعة النجاح الوطنية، نابلس – فلسطين.

استخدام طريقة (FP-LAPW) لدراسة الخصائص التركيبية والالكترونية والمرونية والضوئية

لمركبات القلويات الهيدروجينية (X= Li, Na, K, Rb, Cs)

إعداد رائد توفيق عارف جرادات إشراف د. محمد سلامة أبو جعفر أ.د. عصام راشد الأشقر الملخص

تم استخدام المبادئ الأولية للحسابات و المبنية على نظرية الدالة الوظيفية للكثافة باستخدام طريقة الموجات المستوية المعدلة الخطية للجهد التام (FP-LAPW) لدراسة خصائص الاستقرار الهيكلي لحالات بلورية مختلفة والضغط المسبب للانتقال من حالة لأخرى والخصائص الالكترونية وثوابت المرونة والخصائص الميكانيكية وخصائص الديناميكا الحرارية وكذلك الخصائص الضوئية لمركبات قلويات الهيدروجين (LiH, NaH, KH, RbH, CsH).

وكذلك تم دراسة هذه المركبات في أربعة تراكيب بلورية هي rock-salt (RS) و rock-salt (RS) و surtzite (W). (ZB) و (ZB)

أما جهد الارتباط والتبادل(exchange correlation potential) تم التعامل معه بطريقتين وهما:

1- تقريب الميل الإتجاهي المعمم للجهد التبادلي ألارتباطي لبيرديو وبورك وإرنزهوف (PBE-GGA). وذلك لدراسة خصائص الاستقرار الهيكلي والضغط المسبب للانتقال والخصائص الالكترونية والخصائص الميكانيكية وخصائص الديناميكا الحرارية والخصائص الضوئية.

2- تقريب الميل الإتجاهي المعمم للجهد التبادلي ألارتباطي المعدل لبيكي وجونسون (mBJ-GGA). وذلك لدراسة مقدار فجوة الطاقة والخصائص الضوئية.

من هذه الدراسة استطعنا التوصل للنتائج التالية:

1- لوحظ أن ثابت الشبكة (a<sub>0</sub>) يزداد بالانتقال من ذرة الليثيوم (Li) إلى ذرة السيزيوم (Cs) في
 الجدول الدوري، بينما معامل الصلابة (B) يقل.

2− بنية أحزمة الطاقة لهذه المركبات هي بنية مواد شبه موصلة بطريقة (PBE-GGA) بينما بنيتها بنية مواد عازلة بطريقة (mBJ-GGA) في جميع الحالات البلورية، باستثناء المركبين LiH و CsCl في التركيب البلوري CsCl.

3- طريقة (mBJ-GGA) هي أكثر دقة من طريقة (PBE-GGA) واقرب إلى النتائج العملية في حساب مقدار فجوة الطاقة.

4- من حساب الثوابت المرونية تبين أن هذه المركبات مستقرة في جميع الحالات البلورية باستثناء المركبين LiH و NaH في التركيب البلوري CsCl.

5- أكثر الحالات البلورية استقرارا لقلويات الهيدروجين هي الحالة البلورية الملحية (RS).

6- الثوابت المرونية تتغير بتغير الضغط الواقع على هذه المركبات.

7- هذه المواد تعتبر مواد عازلة جيدة مع فجوة طاقة واسعة و مباشرة وتعتبر كذلك ممتصة جيدة للضوء وطيف الامتصاص لها واسع.

8- أقصى كمية امتصاص تقع في منطقة فوق البنفسجي المتوسط (MUV) وفوق البنفسجي المتوسط (MUV) وفوق البنفسجي البعيد (FUV).

ع وطيف  $\epsilon_2(w)$  وليف الامتصاص  $\alpha(w)$  والجزء الخيالي من ثابت العزل الكهربائي  $\epsilon_2(w)$  وطيف الطاقة المفقودة L(w) وكذلك طيف معامل الاضمحلال k(w)، لها أشكال متشابهة.

النتائج التي تم الحصول عليها في هذه الدراسة تتفق جيدا مع الدراسات التجريبية والدراسات النظرية الأخرى.