A FIRST PRINCIPLE CALCULATION ON THE STRUCTURAL, OPTICAL, MECHANICAL AND ELECTRONIC PROPERTIES OF PbS PEROVSKITE MATERIAL

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FACULTY OF PHYSICAL SCIENCES

UNIVERSITY OF BENIN

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SUBMITTED TO

DEPARTMENT OF PHYSICS,

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IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE AWARD OF BACHELOR OF SCIENCE (B. Sc.) IN PHYSICS

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CERTIFICATION

This is to certify that this project work was carried out by **UBAH CHUKWUDALU FRANCIS** with Matriculation Number **PSC2003875**, of the Department of Physics, Faculty of Physical Sciences, University of Benin, Benin City, Edo State, Nigeria.

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PROF C.O. AIGBOGUN **(Head of Department)**	**Date**
______________________	______________________
External Examiner	**Date**

DEDICATION

I dedicate this project to God, whose by his infinite mercy has kept me alive and healthy to this moment. I also dedicate it to my families, my mum: Ogechukwu Ubah my dad: Chidi Ubah my uncles: Chibuike Okeke, Anthony Akaeme, Izuchukwu Akaeme my aunties: Chibugo Okekeonyeagba, Amara Ubah, my lovely siblings especially my elder sister: Somtochukwu Ubah, Chiemerie Ubah, Ikedinaekpere Ubah, Chiezigomu Ubah, Idinmachukwu Ubah and my friends: Ogbomo Precious, Ibebuike Chizoba, Ojima Ozioma, Egedi Collins, Alabi Gabriel whose by their constant support made it possible for me to complete this work.

CERTIFICATION OF DISSERTATION ON PLAGIARISM

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I would like to express my gratitude to my Project Supervisor, Prof. B. E. Iyorzor, whose guidance, explanations, patience and support greatly aided the completion of this project.

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ABSTRACT

The prospective use of lead(II) sulfide (PbS) perovskite in thermometric, optoelectronics, and photovoltaic have attracted a lot of interest. However, a number of issues, such as inadequate optical absorption, mechanical softness, suboptimal electrical characteristics, and structural instability, make practical use of it difficult. In this work, we thoroughly examine the structural, mechanical, electrical, and optical characteristics of PbS perovskite using first-principles density functional theory (DFT) computations. Our study reveals the fundamental stability requirements by analyzing formation energies and elastic constants. By analyzing the material's mechanical characteristics, including bulk modulus, shear modulus, and Poisson's ratio, the mechanical resilience of the material is evaluated. In order to maximize light-harvesting capabilities, optical characteristics such as the dielectric function and absorption coefficient are also investigated. We suggest doping, strain engineering, and defect passivation techniques to improve PbS's stability, mechanical strength, and optoelectronic efficiency in order to get beyond current restrictions. Our research provides important information for improving PbS-based materials for upcoming electrical and energy applications.

Chapter 1

1 Introduction

Perovskite is generally a material with a crystal structure following the formula ABX_3. Perovskite is originally a calcium titanium oxide (calcium titanium-chemical formula, $CaTiO_3$). (Wenk; Bulakh, 2004) The original perovskite was first discovered by the German mineralogist, Professor Gustavus Rose in 1839 in the Ural Mountains of Russia and named after the Russian nobleman and mineralogist, Count Lev Aleskseyevich von Perovski (1792-1856). The notable perovskite crystal structure was first described by Norwegian mineralogist Victor Moritz Goldschmidt in 1926 in his work on tolerance factors. The original perovskite crystal structure was later published in 1945 from x-ray diffraction data on barium titanate by Irish crystallographer, Helen Dick Megaw. From the chemical formula ABX_3, atoms 'A' and 'B' are two cations that are often of very different sizes with the 'A' atoms larger than the 'B' atoms. At the same time, 'X' is an anion that generally can be an oxide, a chalcogenide, a halide, and a nitride etc, that bonds to both cations. (Wikipedia.org).

As shown in figure 1.1, the ideal cubic perovskite structure has the A cation in 12-

folds cuboctahedron coordination and the B cation in 6-folds coordination, surrounded by an octahedron of anions. In real perovskite structures though, additional forms do exist where all the A, B and the X deviate from the ideal ionic coordination configuration as ions within the A and B sites undergo changes in their oxidation states. (N, Orlovskaya, N. Browning, ed., 2003). The ideal perovskite lattice arrangement may also be described as a large atomic or molecular cubic structure having a type A cation in the center of a cube. The edges of the cube are been occupied by B atoms which are also cations and the faces of the cube are occupied by smaller atoms X which are anions. (Perovskite-info).

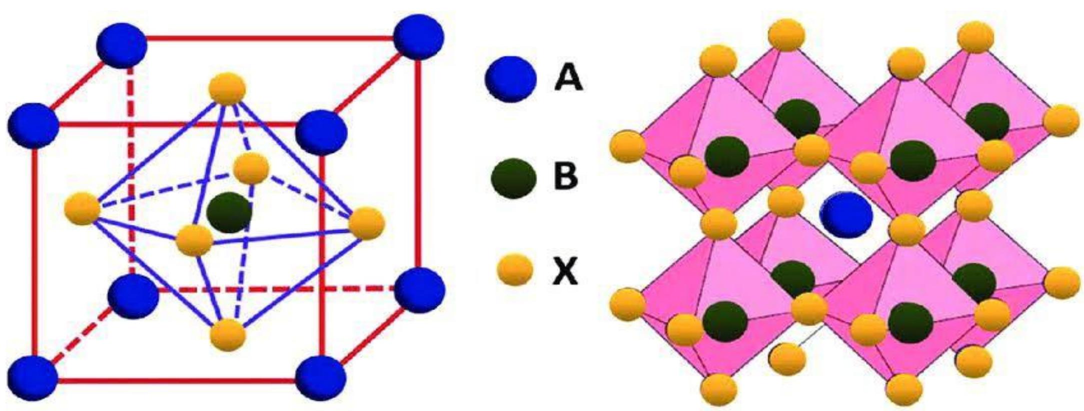

FIGURE 1.1: An ideal perovskite structure with general chemical formula ABX_3. The blue spheres are the A atom (positively charged cation), the black spheres are B atom (also positively charged cation), and the yellow spheres are the X atom (negatively charge anion).

Depending on the atom/molecules used in the structure, perovskites can have a spectacular range of captivating properties including “colossal magnetoresistance” their electrical resistance changes when they are put in a magnetic field (which can be useful for microelectronics). Some perovskites are superconductors, which means they can conduct electricity with no resistance at all. Perovskite materials exhibit many captivating and exciting properties. ferroelectricity, charge ordering, spin dependent transport, high thermopower and the interplay of structural, magnetic and transport properties are commonly observed features in this family. Perovskites therefore holds interesting opportunities for phycists, chemists and material scientists.

The A-site, which is typically occupied by large cations, can accommodate elements from Groups 1, 2, or the lanthanide series. These cations fill the 12-coordinate holes created by the BX6 network. The B-site, located at the corners of the octahedral, is often occupied by smaller cations, frequently transition metals from Groups 3 to 12 or even main group elements like tin. And the X-site, can be occupied by the usual oxygen anion (O^{2-}) or heavier halide anions like chlorine (Cl^{-}) or bromine (Br^{-}).

In the past decade the lead (Pb)-based HOIP have attracted a great deal of interest for applications in high performance optoelectronics and efficient photovoltaics due their ability to tune optical band-gaps from violet to near infrared as well as their highest absorption coefficients and potential for long-range electrons and hole transport . Furthermore, it is widely understood that perovskites exhibit a plethora of functionality such as dielectric, ferroelectric, magnetoresistance, electro-optics, thermoelectric, semiconducting, super conduction, and conducting.

Some literal examples of perovskites include:

- **Calcium titanate ($CaTiO_3$)**
- **Lead titanate ($PbTiO_3$)**
- **Barium tin oxide**
- **Lanthanum ytterbium oxide**
- **Silicate perovskite**
- **Rubidium ($RbTaO_3$) and others.**

1.2 Properties of Perovskite

Perovskite materials possess a large range of properties as a result of their unique chemical structure and stoichiometry. Some of these properties are highlighted as follows:

1.2.1 Dielectric Properties

Dielectric materials are insulators with a strong resistance to the flow of electric current and the ability to sustain an electric field for extended periods of time. To improve performance, capacitors employ them. A permanent electric dipole that maybe directed by an electric field is a feature of ferroelectric materials, a class of dielectric. Their low dielectric loss and high dielectricconstant make them ideal for use dynamic random access memory (DRAM) and tunable microwave device applications. Depending on the configuration of the B-site cations and octahedral tilting or distortion. These compounds have better dielectric qualities and a higher Curie temperature (TC). Ferroelectric, dielectric, and piezoelectric characteristics are displayed by nitride perovskites, which also have significant static dielectric constants along certain directions and polarization values that are close to those of normal (Eman et al., 2019).

1.2.2 Optical Properties

Lead sulfide (PbS) perovskites exhibit prominent optical properties including a narrow bandgap, strong light absorption across the near infrared spectrum, high absorption coefficient, and tunable emission wavelength depending on the size of the nanocrystals, making them attractive for applications like solar cells and infrared detectors; the key feature is their ability to efficiently absorb light within the near infrared region due to their small bandgap, which can be further manipulated by controlling the size of the PbS nanoparticles.

1.2.3 Superconductivity

Perovskite materials can exhibit superconductivity, meaning they can conduct electricity with zero resistance below a critical temperature, due to their unique crystal structure which allows for the manipulation of electronic properties by altering the composition of the constituent atoms, enabling the creation of materials with high transition temperature (Tc) for superconductivity; notable examples includes the copper oxide based perovskite like La2CuO4 where doping with element like strontium can induce superconductivity at relatively high temperatures compared to traditional superconductors.

1.2.4 Ferroelectricity

Ferroelectric materials are both pyroelectric and piezoelectric and they produce a large amount of current interest because their electric dipoles can be modified by the application of an electric field. However it losses it’s inherent polar properties above their Curie temperature (Tc) changing into a non-polar state known as the para electric phase.

1.2.5 Catalytic activity

They are considered as potential substitutes for noble metal catalysts, which are expensive. Perovskite catalysts combine low cost, thermo-chemical stability at high operating temperature and satisfactory catalytic activity.

Perovskite exhibit an array of interesting characteristics, including thermal/chemical stability, super magnetic, photocatalytic, thermos-electric and dielectric properties, as well as electronic conductivity and oxide ion mobility within their crystal lattice.

1.2.6 Piezoelectricity

Piezoelectricity is a phenomenon observed in certain materials where they generate an electrical charge in response to mechanical stress or deformation. Conversely, these materials can also be deform or change shape when subjected to an external electric field. This bidirectional nature of piezoelectricity makes it useful in various applications.

Piezoelectric ceramics with a perovskite crystal structure and a general formula of A2+B4+O2-3 are among the synthetic piezoelectric materials (Aksel et al. 2011) Additionally there are piezoelectric materials that are found such as tendon, collagen, topaz, quartz, and cane sugar.

1.3 Applications

Perovskites have a very large range of applications in various fields because of their unique properties and structures which are: uses in sensors catalyst electrodes, certain types of solar cells, lasers, memory devices, and spintronic applications etc. (Eman 2019).

1.3.1 Solar Cells

Solar energy is a renewable energy and environmentally friendly energy source that can replace fossil fuels. It can be converted into electricity using photovoltaic solar cells, which are naturally built on silicon. However, the high cost of electricity produced by silicon-based solar cells necessitates the development of low-cost alternatives. (Wang et al, 2012, Li et al, 2016) The availability of the perovskite-based solar cells raw materials and the reduced cost of its product compared to that of the traditional silicon solar cells makes it more desirable. They possess desirable properties for photovoltaic applications, such as a suitable band gap, excellent stability, long hole-electron diffusion length, high absorption coefficient, high carrier mobility and transport, low processing temperature, charge carriers with small effective mass, and easy processing steps. These advantages make perovskite-based solar cells a promising alternative to traditional silicon solar cells. (Jin et al., 2013, Bao et al., 2015).

1.3.2 Gas Sensors

Certain requirement must be met in gas sensing devices, such as hydrothermal stability, compatibility with target gases, appropriate electronic structure, resistance to poisoning and also adaptability to existing technologies (Christen and Eres, 2008).

Perovskite oxides, like LaFeO3 and SrTiO3, are used as gas sensors due to their ideal band gap, thermal stability, and size difference between the cations of B- and A-sites. Perovskites containing cobaltates, titanates, and ferrites have been employed as gas sensors for detecting CO, NO2, methanol, ethanol, and hydrocarbons (Taylor et al., 2019).

1.3.3 Solid Oxide Fuel Cells

Fuel cells are an alternative to internal combustion engines, offering environmental benefits through their ability to reduce pollution. They convert chemical energy into electrical energy, similar to batteries, and are preferred for their efficiency, wide applicability, quiet operation, low emissions, and potential role in hydrogen fuel economy. Solid oxide fuel cells (SOFCs) are a common type of fuel cell, and perovskites are often used as an active component due to their electrical conductivity, which is comparable to metals and exhibits high ionic and electronic conductivity. (Eman, 2019).

1.4 Aim and objectives

AIM

The aim of this work is to deduce from first principle calculation, the ground stateenergy, the structural, mechanical, optical, electronic properties of PbS perovskite materials.

OBJECTIVES

The objectives of this work are to:

- Determine the electronic properties of the compound (band structure, DOS, materialtype)
- Determine the mechanical properties of the compound (elastic constant, shear modulus,Young's modulus, etc.)

- Determine the optical properties of the material
- Determine the structural properties of the compound (lattice constant, bulk constant,modulus, pressure derivatives)
- Deduce from the first-principle, the mechanical stability of the perovskite compound.

CHAPTER 2

2.0 Literature Review

2.1 PbS

The lead chalcogenide materials, such as PbS, have been significantly applied for solar cells such as the quantum dot solar cells. The PbS quantum dots serve as light harvesting materials and undergo charge transfer process to nearby semiconductor substrates, i.e. TiO_2 and halide perovskites. In current research superior solar cell and light emitting performance have been formed to be offered by the novel structures of PbS/perovskite composites, the dot-in-matrix structures with the PbS quantum dots immersed in halide perovskite material matrix.

It is necessary to classify the PbS perovskite heterostructure to atomistically understand the system. PbS materials are being engineered by frequently applying the organic molecules and ligand to the surface/interface. The PbS nanocrystals in the synthetic stage/ are being stabilized by the organic ligand, with the ligand bearing anchoring moieties as the terminal group of the ligand molecule. The organic molecules (such as those forming halogen bond and Lewis acid-base adducts) are immensely applied to neutralize the surfaces/interfaces of the halide perovskite materials in solar cells, since their surfaces and interfaces are rich under-coordinated species that could act as potential charge traps. In addition, organic cross linking agents have been applied to subsequently couple nearby halide perovskite crystals, resulting in improved film quality and enhanced solar cell performance. Therefore, it would be interesting to research on the effects of interfacial organic modifiers for the PbS perovskites heterostructure.

Applying the first principle calculations to explore PbS heterostructure with the interfacial organic modifiers and the impacts of the molecular engineering method on the properties of the heterostructure.

The PbS surfaces interact simultaneously with the interfacial organic molecules, altering the nanoscopic structure of the heterostructure. In application of the molecular engineering method, the electronic and optical properties of PbS heterostructures are effectively manipulated. Lead sulphide (PbS) perovskite heterostructures have been mixed to improve the performance of halide perovskite based optoelectronic devices. Molecular ligand coordination and molecular passivation methods are being used in preparation of halide perovskite and PbS.

We focus on the interfacial bifunctional molecules bearing Lewis base moieties and halogen bond. The bifunctional molecules include 4-chloropyridine, 4-flouropyridine, 4-bromopyridine, 4-iodopyridine, pyridine-4-amine, pyrazine and 4,4-bipyridine, which either contains a pyridine moiety or a halogen species in the terminal group, the pyridine moiety or a halogen atoms have been experimentally approved to be applicably additives for perovskite solar cells. The first principle calculation analyses the nanoscopic structures, charger transfer properties and optical properties that are being obtained in details. In order to modify the interfacial structure and properties of the lead chalcogenide/perovskite interfaces, the interfacial molecular engineering methods are effectively applied.

CHAPTER 3

3.0 Methodology

3.1 Density Functional Theory (DFT)

Density Functional Theory is one of the most used successful quantum mechanical theories for explaining matter. It is routinely applied in calculating, for example, the binding energy of molecules in chemistry and the band structure (Klause Capella, 2006) of solids in physics. DFT has been applied to study a wide range of phenomena, including relativistic effects in heavy elements and atomic nuclei, superconductivity, atoms under intense laser pulses, classical liquids, and magnetic characteristics of alloys. First applications relevant for fields traditionally considered more distant from quantum mechanics, such as biology and mineralogy are beginning to appear. Superconductivity, atoms in the focus of strong laser pulses, relativistic effect in heavy elements and in atomic nuclei, classical liquids, and magnetic properties of alloy have all been studied with DFT.

DFT's versatility is due to the universality of its core concepts and the flexibility with which they can be applied. Despite its broad scope, DFT is based on a solid conceptual foundation that requires an understanding of basic quantum physics. In quantum mechanics, the wave function of a system contains all the possible information about the system, which is dependent on the electronic coordinates.

Non-relativistic, the wave function is calculated from Schrodinger's equation, which is for a single electron moving with a potential $V_{(r).}$

Ab initio DFT computations in computational material science enable the computation and prediction of material behavior based on quantum mechanical principles, without requiring higher-order parameters like fundamental material properties. Modern DFT methods use a potential acting on a system's electrons to evaluate the electronic structure. The total potential, V, is the sum of external potentials, Vext, based solely on the system's structure and elemental composition, and the effective potential, Veff, which represents inter-electronic interactions.

By examining a set of non-interacting electron Schrodinger equations, or Kohn-Sham equations, for a representative supercell of a material with n electrons, DFT offers a more flexible alternative to the many-body problem. The key variable in DFT is the electron density, n(r), which is given by the square of the wave function for a normalized wave function.

$$(r) = N \int d^3r_2 \ldots \int d^3r_N \psi^x (r_1, r_2, \ldots, r_N)\psi(r_1, r_2, \ldots, r_N) \qquad (3.1)$$

During decades of struggling, various effective strategies have been developed to solve Schrodinger's equation, including configuration interaction

(CI) methods in chemistry, which involve systematic expansion in Slater determinants, and diagrammatic perturbation theory in physics, which is based on Feynman diagrams and Green's functions. There are also numerous specialized methods available. However, these approaches are computationally intensive and may not be practical for large, complex systems. DFT offers a suitable alternative, which may be less precise but is more flexible. The density-functional approach can be summarized as follows:

$$n(r) = (r_1, \ldots\ldots, r_N) = V(r) \qquad (3.2)$$

That is: knowledge of n(r) implies knowledge of the wave function and the potential and henceof all other observable.

3.1.2 The Generalized Gradient Approximation (GGA)

The generalized gradient approximation (GGA), is currently receiving growing interest as a simple alternative to the local density approximation (LDA) in ab initio total energy calculations for exchange-correlation energy in density-functional theory (Jones et al., 1898). The accuracy of LDA is considered more accurate in condensed matter systems, but it failed in atomic and molecular physics, where experimental data are available and LDA overestimates by 20% and more. The introduction of gradient corrections help approach the issue of underestimation of cohesive energies and bond strength in molecules and solids.

The exchange-correlation functional is written as a function of both the local density and the local gradient of the density. Also, as the LDA approximates the energy of the initial density by the energy of a local constant density, it falls short in the situation where the density undergoes rapid changes such as in molecules. To account for the non-homogeneity of the electron density, the first logical step to go beyond LDA is the use of the information about the density of the electron, n(r) at a given point r, and also to supplement the density with information about the gradient of density. These are two sets of functional forms widely used in exchange correlation- energy, introduced by Pardew and Wang in 1992 and Perdew-Burke-Ernzerhof in 1996(PBE).

3.1.3. Local Density Approximation (LDA)

The local density approximation (LDA) is a set of approximation that solely rely on the value of the electronic density or the Khan-Shan orbitals and it is being used to estimate the exchange- correlation (XC) energy functional in density functional theory (DFT). There are different techniques in which the local approximations of the XC energy, with the homogeneous electron gas (HEG) model providing numerous effective local approximation can be generated.

When applied to real systems like molecules and solids, functional based on the HEG approximation are commonly used interchangeably with LDA. For unpolarized systems, a local- density approximation for the XC energy is typically expressed as:

$$[\rho] = \int \rho\ (r)\varepsilon_{XC}(\rho(r))dr \qquad (3.3)$$

Where ρ is the electronic density and E_{xc} is the exchange-correlation energy per particle of a homogeneous electron gas of change density ρ. The exchange-correlation energy is divided into exchange and correlation components linearly,

$$E_{xc} = E_x + E_c \qquad (3.4)$$

In order words different expression for E_x and E_c are obtained. The exchange term takes a simple analytic form of HEG. GGAs are employed by solid state physicist in ab initio DFT studies to interpret electronic and magnetic interactions in semiconducting materials including semiconductor oxides and spintronic. However the limiting expressions for correlation density are known, resulting to different approximations of Ec. The importance of these computational studies stems from the systems complexities which brings about high sensitivity to synthesis parameters and necessitates first-principles based analysis. The band structure and fermi level in perovskites are being predicted using LDA combined with simulated packages. Conversely, incorrect predictions of impurity effects, conductivity influenced by carriers, and magnetism mediated by carriers in these systems can stem from an underestimation of band gap values, often associated with LDA and GGA approximations. Employing LDA potentials, the Rayleigh theorem for eigenvalues has been utilized since 1998, producing band gap predictions for materials that are typically precise. A misunderstanding of the second theorem of DFT appears to explain most of the underestimation of band gap by LDA and GGA calculations, as explained in the description of density functional theory, in connection with the statements of the two theorems of DFT.

3.1.4 Khon-Sham Equation

The Khon-Sham equation is a one-electron Schrodinger equation for a hypothetical system of non-interacting particles, typically electrons, that generates the same electron density as a particular system of interacting particles. The Khon-Sham equation is defined by a local effective external potential in which the non-interacting particles move, often denoted as V(r) or Veff(r), called the Khon-Sham wave equation is a single slater determinant constructed from a set of orbitals that are the lowest-energy solutions to the Khon-Sham equation. (Kohn, Walter; Sham,Lu Jeu (1965))

$$\left(-\left(\frac{\hbar^2}{2m}\right)\nabla^2 + v_{eff}(r)\right)\varphi_i = \varepsilon_i \varphi_i(r) \tag{3.5}$$

The Khon-Sham equation can be expressed as an eigenvalue equation, which is a standard representation. This equation features the orbital energy (E1) of the corresponding Khon-Sham orbital, and the density for an N-particle system is given by the sum of the squares of the absolute values of the Khon-Sham orbitals.

$$(r) = \sum^{N} | \ (r) \ |^{2} \qquad (3.6)$$

3.2 Pseudopotentials and Applications

The pseudopotential concept, has significantly impact on our understanding of the electronic structure of semiconductors and also known as the standard model for condensed phases. This chapter reviews both empirical and ab initio pseudopotential concepts along with their various applications. Empirical pseudopotentials were first used to describe the optical and dielectric properties of tetrahedral semiconductors, in which the validity of one-electron band structure image was established. These band structure still stand basically accurate, although it was first developed over 30 years ago. Modern theories for understanding the chemical bond in solid depends on the element of pseudopotentials have been used to accurately predict the structural properties, vibration modes, phase stability, and compressibility of semiconductors in the liquid, amorphous, and solid states. (Stewart Clark, 2012)

The pseudopotential concept is based on the elementary energy and spatial separation of core and valence electrons. The atomic pseudo orbitals and pseudopotentials are generally suitable with Gaussian type functions in order to be used in standard program of quantum expresso calculations. Several advance for generation of pseudopotential were made within the density functional theory (DFT), including the use of parameterized analytical pseudopotentials and the creation of pseudo potentials using pseudo orbitals derived from atomic computations. The discrete variation method (DVM), a particular implementation of numerical integration for solving the DFT one electron equations, does not require the fitting of pseudo orbitals to any analytical functions, as the matrix elements of an effective Hamiltonian can be computed directly with either analytical or numerical basis sets (or a mixed one). (Stewart Clark, 2012).

One main advantages of using a plane wave basis set is that its accuracy can be contained with ease, a major setback is the size of the basis set needed for a given system is often much larger than what is needed with a localized basis set. This is because in condensed matter systems, the orbitals tend to oscillate very swiftly in the atomic nuclei region, and very smoothly in some other region. To describe this swiftly oscillation, a high cut-off energy is set to include plane wave with very short wavelengths. Most of the computing expenses associated with all these plane wave are wasted since most of the space in the cells does not contain swiftly oscillating orbitals. The use of pseudopotential in conjunction with plane waves can extremely reduce the magnitude of this problem. To understand what pseudopotentials does we note the following facts about orbitals in condensed matter system:

1. The orbitals of non-core electron orbitals oscillate very swiftly in region of atomic nuclei,but most of its oscillation can be disregarded because they must be orthogonal to the core electron.

2. Core electrons are often considered to be represented by lower energy orbitals. These electrons have a high degree of localization around an atomic nucleus and its properties do not change significantly with the atom's chemical environment.

In pseudopotential theory, a fictitious potential is initiated to replace the core electrons, which ensures that the valence electrons' behavior remains unchanged beyond a certain distance from the nucleus, effectively representing the nuclear charge. The behavior of condensed matter is governed by interatomic interactions, and the pseudopotential approximation should not significantly alter this behavior as long as the radius does not overlap with regions involved in chemical bonding.

By using pseudopotential, the computational cost of calculations is reduced in four ways:

i. We can optimize the shape the shape of the potential to give as low a needed cut-off energy, because the pseudopotential is not uniquely defined for a particular element. This reduces memory and increase speed.

ii. By effectively removing core electrons from the calculations, the number of Kohn-Sham orbitals is reduced. This reduces memory needed to store the orbitals, the time required to ortho normalize a set of orbitals.

iii. The absence of core electrons for valence electrons to be orthogonal to leads to reduced oscillations of the corresponding orbitals near the nucleus. This allows for the representation of orbitals with a lower cut-off energy, leading to quicker computations and reduced memory requirements. This reduction in cut-off energy can significantly enhance efficiency, often resulting in orders of magnitude improvements in computational performance.

iv. We tend to think of the system as being made of electrons and ions rather than electrons and nuclei, because we only express the valence electrons in a calculation when using pseudopotentials.

3.2.1 Ultra Soft Pseudopotentials (USPP)

The ultra-soft pseudopotentials repose the norm-conserving condition to reduce the necessary basis set size at the expense of generating a generalized eigenvalue problem. (Vanderbilt David, April 1990)

3.2.2 Quantum ESPRESSO, QE

Quantum ESPRESSO (Quantum open source package for research in electronic structure, simulation, optimization; QE) is a suite for first-principle electronic structure calculations and materials modelling, distributed for free and as a free software under the (GNU) General Public License. It is based on Density Functional Theory (DFT), Plane wave basis sets, and pseudopotentials (both norm-conserving and ultra-soft).

The core plane wave (DFT) function of QE are provided by the PWscf component (PWscf). Previously existed as an independent project). PWscf (plane wave-self consistent field) is a set of program for electronic structure calculation within DFT and Density Functional Perturbation theory, using plane wave basis sets and pseudopotentials.

Quantum ESPRESSO is an open initiative, of the CNR-IOM DEMOCRITOS National simulation center in Trieste (Italy) and its partners, in collaboration with different centers worldwide such as MIT, Princeton University, the University of Minnesota and the Ecolepolytechnique Federal de Lausanne. (Paolo Giannozzi et al., 2009).

The program is written in mainly Fotran-90 with some parts in C or in Fortran-77. It is composedof a set of core component, a set of plug-ins for advance tasks, and a set of third party packages. The basis packages include PWscf, which solves the self-consistence Kohn-Sham equations,obtained for a periodic solid, CP to carry out Car-Parrinellon molecular dynamics, and PostProc,which allows that analysis and plotting, noteworthy additional packages include atomic for pseudopotential generation, PHONON for density-functional perturbation theory (DFPT) and thecalculation of the second and third order derivatives of the energy with respect to atomicdisplacement and (NEB) nudged elastic band for the calculation of reaction pathways and energybarriers.

& CONTROL

Calculation =

‘scf’Prefix =

‘PbS’

Pseudo_dir =

‘/home/ben/PSEUDOPOTENTIALS/’,

outdir = ‘./’,

/

& SYSTEM

ibrav= 2,

celldm (1) = 11.8369

nat=2, ntyp=2, occupations= ‘smearing’, smearing= ‘mv’,

degauss=0.01ecutwfc=80,

/

& electrons

mixing_beta = 0.7, conv_thr = 1.0d-8

/

ATOMIC_SPECIES

Pb 118.71 Pb.pbe-dn-kjpaw_psl.0.2.2.UPF

S 32.065 S.pbe-n-kjpaw_psl.0.1.UPF

ATOMIC_POSITIONS {crystal}

Pb 0.00000000 0.00000000 0.00000000

S 0.50000000 0.50000000 0.50000000

K_POINTS (automatic)8 8 8 0 0 0

3.2.3 Post Processing

Post processing is an integral aspect of engineering simulation studies. It involves manipulating, or 'processing' the result we get from our preliminary analysis to draw meaningful result.

The package for post processing calculations was originally created by Stefano Baroni, Stefano de Gironocoli, Andrea Dal Corso (from SISSA), and Paolo Giannozi (from the University of Udine), along with several other contributors.(www.quantum-espresso.org). After the self-consistent calculation has been completed, we perform additional minor calculations such as plotting of bands and calculating the density of states (DOS). The major post processing codes that extract the required data/files from the PWSCF calculations and execute further calculations are as follows;

3.2.2.1 pw.x: This command is used to run input files of scf and nscf calculations of energy and wave functions at each and every point. \>hichextrs.c:s :i- :e output files for the energy calculation at every k-point.

3.2.2.2 bands.x: In order to prepare the data for processing, this extract the files from the PWSCF calculations and stores the eigenvalues at various k-points along with the associated energy values. The symmetry analysis of the band structure is likewise carried out using the codes bands.x.

3.2.2.3 plotband.x: Auxiliary codes plotband.x read the output files of bands.x directly and trans- form them to a plottable format. The values of the k-points must be accurately put in sequence; otherwise, if the k-points are not arranged along lines or if two consecutive points are the same, surprising plots may result. Therefore, proper selection of sequence of k points is necessary.

3.2.2.4 dos.x: It helps to calculate the electronic density of states at different k-points.

3.2.2.5 thermo_pw.x: It is a FORTRAN driver for the parallel and/or automatic computation of material properties that uses Quantum ESPRESSO (QE) pattern as the underlying engine. It generates postscript figures of some material properties after reading the same input as the QE Pw.x code. (github.io)

3.2.4 Band Structure

In the first-principles electronic structure calculation of crystals, the electronic band structure is auniversally used analytical technique within the Kohn-Sham framework of density functional theory. It provides the electronic levels in (perfect) crystal structure, which are characterized by aband index (n) and a Bloch vector (K). The Bloch vector is an element of reciprocal space, measured in length units, and is routinely restrained to the first

Brillouin Zone. (Andreas Wacker (2010)) The band structure of a solid can be used to determine various electrical properties of solid, as it consist of the basic ingredients of most crystal properties. When a large number of atoms are brought together, their interaction interrupt the initial atomic levels due to the close packing of atoms in a solid. Pauli's Exclusion Principle states that no two electrons can occupy the same energy state, meaning that all of the electrons in the orbitals are filled up.

The electrons in the inner shell of a band are least affected by interatomic interactions, while the electrons in the valence band, which are closest to neighboring ions, are most affected. This leads to the creation of an energy continuum in which several levels due to individual atomscannot be identified. The effect of putting one atom closer to another is to split a single, sharp level. The band structure of a solid can be used to determine its different optical and electrical properties of solid. The measurement of band gap, according to band theory helps determine the types of solid. Within density functional theory (DFT), the band structures are calculated using the pseudopotential and plane wave basis set method. The exchange correlation functional is treated with the Generalized Gradient Approximation (GGA) in the form of the Predew Berke- Erzndof (PBE) functional.

3.2.5 Density of States (DOS)

The density of states (DOS) of a system refers to the number of allowed modes or states per unit energy range that can be occupied by particles (Walter, 1989). In other words, it measures the concentration of quantum states in a system and is defined as the number of quantum states per energy range unit.

The density of states is of very importance as it can be used to calculate the various parameters that offers insights into different electronic, magnetic, and transport properties in solid state and condense matter physics. The density of states provides various information on the states that areavailable at each energy level. The value of zero density of states indicates that there are no available states for occupation in an energetic level.

3.3 Computational Details

3.3.1 Convergence Test (Optimization)

The self-consistent field (SCF) calculations were carried out to determine fundamentalparameters, specifically:

- The kinetic energy cut-off for the plane wave basis and k-point grid by testing theconvergence of total energy with these parameters individually.
- The lattice parameters, which are obtained by energy minimization.

3.3.2 Kinetic Energy cut-off (ecutwfc)

The kinetic cut-off, ecutwfc (in Ry) determines the size of the plane wave (PW) basis set uses to expand wave function (Kohn- Sham orbitals). According to the periodic system, the value of the kinetic energy cut-off corresponds to the neighboring interaction. By taking large cut-off energy, long range interactions and results seems to be more accurate, however this result in the consumption of more computing resources. But if we attempt a small cut-off energy, the result could be inaccurate though computationally cheap. Therefore, it is necessary to take the optimumvalue of this cut-off energy value.

CELL DIMENSION (LATTICE PARAMETER)

Lattice constant is a property of crystal lattice i.e. the periodic arrangement of atoms in three di- mension whether it is a property of atom or not. Initially the lattice constant is the length of peri- odicity of the lattice repeat itself, for most crystals the lattice constants are a few angstroms (Å).

K-POINTS GRID

In order to account for periodicity, a sufficiently dense grid of k-point is required. Obtaining a large number of grid points is important for discretely representing interactions within the Brillouin zone. But in practice, we optimize the number of k-points grids due to restriction of computational resources. By calculating total energy versus k-point grids. The rectangular grid of point of dimension k x k x k, spaced evenly throughout the Brillouin zone, known as the k-points grid.

BAND STRUCTURE

Procedures:

1. Open a new folder and name it band.
2. Copy the following files into the folder

and edit allscf.in

nscf.in

bands.in

3. Open

terminal/cd…

cd/element/Bands

start with

scf.in

nscf.in

bands.in

Code to compute band structure calculation

$~/qe-6.4.1/bin/pw.x<scf.in>scf.out

$~/qe-6.4.1/bin/pw.x<nscf.in>nscf.out

$~/qe-6.4.1/bin/pw.x<band.in>band.out

To plot graph:

$~/qe-6.4.1/bin/plotband.x(press

return)Input

file:>ba.bands.dat(press enter)

Range:-0.000 413.150ev Emin Emax 0.0, 413

(press enter)Output file (xmgr) > ba.xmgr (press

enter)

Output file(ps)>ba.ps(press

enter)Fermi>0.00 (press

enter)

Delta Fe, reference E (for ties) 50,0

DENSITY OF STATES (DOS)

How to calculate for DOS:

1. Open a new folder, name it 'DOS'
2. Copy the following files into the folder

and editscf.in

nscf.

in

dos.

in

pdo

s.in

note: all files were edited with respect to material name and scf.in

3. Open terminal/cd...

Cd[space]/element/Dos

Start with

1. scf.in pw.x<rbtao3.scf.in>rbtaao3.scf.out
2. scf.in pw.x<rbtao3.nscf.in>rbtao3.nscf.out

3. dos.in dos.x<rbtao3.dos.in>rbtao3.dos.out my
4. pdos projwfc.x<rbtao3.pdos.in>rbtao3.pdos.out

3.4 POST PROCESSING

There are numbers of auxiliary codes performing minor computations like band plotting and density of states (DOS) etc. The main post-processing codes that extract specific data/files from PWSCF calculations and perform further calculations are as follows:

- **pw.x:** we use this command to run the input files of scf and nscf calculations of energy and wave functions at each and every k-points, which extracts the output files for the en- ergy at every k-points. Which is also used to calculate electronic structure, structural op- timization, molecular dynamics.
- **ph.x**: This command is used to calculate the phonon frequencies and displacement pat- terns, dielectric tensors, effective charges (using data produced by pw.x).
- **q2r.x**. This code calculates the Interatomic Force Constants(IFC) in real space from dy- namical matrices produced by ph.x on a regular q-grid.
- **matdyn**.**x.** This codes helps in producing phonon frequencies at a generic

wave vector using the IFC file calculated by q2r.x; which may also calculate phonon DOS.

- **pp.x:** This extracts the specified data form files produced by pw.x, prepared data for plot-ting by writing them into formats that can be read by several plotting programs.
- **bands.x**: This extracts the files from PWscf calculation and records its eigenvalues at dif-ferent k-points with corresponding energies values ready for further processing. The code bands.x also performs the symmetry analysis of the band structure.
- **plotband.x**: This codes reads the output files of bands.x, and then produces band struc- ture for Post Script plots.
- **dos.x**: This command is used to calculate the electronic Density of State (DOS) at differ- ent k-points.
- **Projwfc.x**: This code helps in calculating the projections of wave function over atomic orbitals s,p,d,f.

CHAPTER 4

4.1 Results and Discussion

4.1.1 Structural and Mechanical Properties

Investigation of the structural properties of the ground state configuration of PbS perovskite was carried out by firstly, optimizing the compounds structurally by minimizing the total energy of the compounds as regards to the variation of the lattice parameters. The crystal structure of PbS is presented in Figure (4.1) below. PbS is a simple cubic Perovskite.

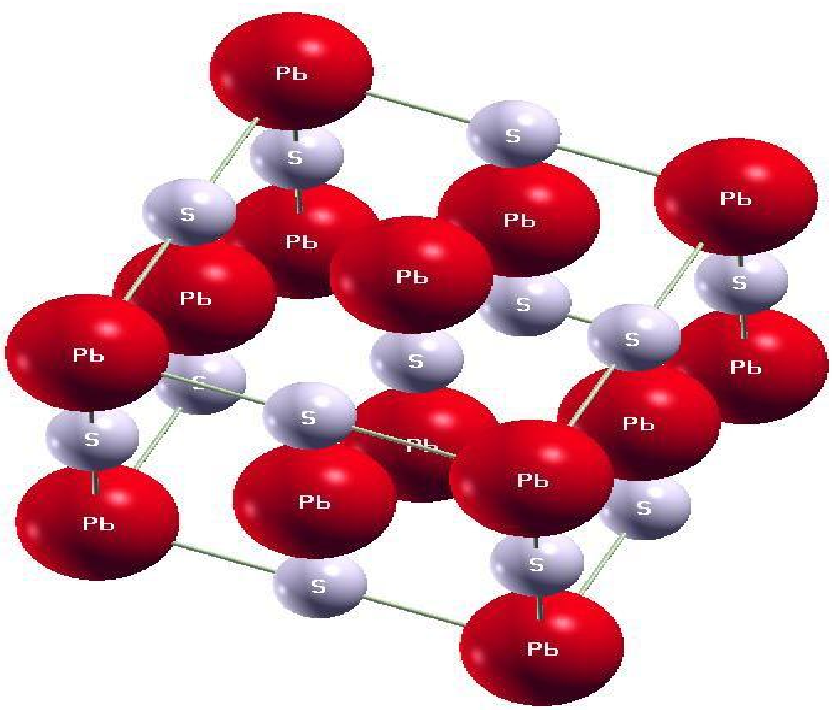

FIGURE 4.1: The data presented in Table 4.1 below displays the parameters, a(Å),

which indicate the distance between adjacent atoms and the bulk modulus, B (GPa).

Table 4.1: Factors that contribute to the structural properties of the PbS Perovskite material.

S/N	Perovskite compound	PbS
I	a (Å),	5.9025
Ii	B(GPa)	51.43

The values from Table 4.1 were obtained by conducting a series of self-consistent calculations (SCF), following the optimization process initiated in Chapter 3. The bulk modulus measures a material resistance to compressibility, it also measures its response to slight increase in pressure.

Deformation resistance is the ability of a material to withstand the application of a compressive force. The mechanical properties of solids that qualify the deformation resistance are as follows; the Bulk Modulus B(GPa), Young Modulus E (GPa), and the Shear Modulus G (GPa), Elastic Constants (C11, C12, C44), and Cauchy pressure (Cp = C12 -C44). These parameters are shown in Table 4.2.

Table 4.2: Factors that contributes to the mechanical properties PbS perovskite material

S/N	Mechanical property	PbS
I.	E (GPa)	74.5
II.	G (GPa)	29.64
III.	N	0.25640
IV	C_{11} (GPa)	120.7
V	C_{12} (GPa)	16.8
VI	C_{44} (GPa)	20.0
VII	C_{12} (GPa) - C_{44} (GPa)	-3.2
VIII	B/G	1.73
IX	C_{11} (GPa) + $2C_{12}$ (GPa)	154.3

The Poisson ratio and elastic constants are calculated to verify the mechanical stability of the compound against shear stress. The poison ratio, n is the nature of the bonding forces in materi- als. The value range is as follows;

$$0<n>0.5 \qquad (4.1)$$

A positive Poisson ratio implies a steady tensile deformation, while a negative Poisson ratio im- plies a compressibility deformation. The Poisson ratio of PbS shows that it possesses a steady tensile deformation.

Elastic constants, C_{11} (GPa) and some other structural characteristics play vital roles in determin- ing the mechanical stability of solids materials. (WU Z., 2007). In cubic phases, stability is ob- tained using the criteria shown in equations (4.2), (4.3), (4.4) (Smirnow N.A., 2002)

$$C_{11} > 0 \tag{4.2}$$

$$C_{44} > 0 \tag{4.3}$$

$$C_{11} + 2C_{12} > 0 \tag{4.4}$$

The data values of the equations (4.2) to (4.4) is shown in Table 4.2 above. The results signify that PbS compound satisfies the necessary condition hence it is mechanically stable.

The Cauchy pressure can be used to describe the nature of bonding in a material. A negative Cauchy pressure signifies a high resistance to bond bending, which is characteristic of covalently bonded solids, i.e. C44 > C12. Conversely, materials with metallic bonding exhibit a positive Cauchy pressure. This property is significant for understanding the mechanical behavior of mate- rials and their response to external forces. This pressure is calculated using the crystal elastic constants of a cubic material, as shown in equation (4.5). The Cauchy pressure, -3.2, as seen in table 4.2, indicates that the material is a covalently bonding solid.

$$C_p = C_{12} - C_{44} \tag{4.5}$$

The material ductility or brittle behaviour is also investigated using Pugh's ratio. In 1954, Pugh summed up a crucial conclusion that the ductile-brittle transition was related to the ratio between Bulk Modulus B (GPa), Shear Modulus G (GPa). (S. F. Pugh, 1954). The critical value of the ratio B/G is 1.75 is considered significant: when $B/G > 1.75$ it indicates that the material is duc- tile, while $B/G < 1.75$ it indicates that the material is brittle. (pubs.rsc.org). Table 4.2 shows that the perovskite compound material is brittle.

This ratio serves as a valuable indicator of a material's mechanical properties and its tendency to deform plastically or fracture under stress. PbS Perovskite compound have a Pugh's ratio of 1.73,hence it is brittle in nature.

4.2 Electronic and Magnetic Properties

According to the findings of the ab initio calculation of the electronic properties of PbS perov- skite material, the electronic band structures and density of states of the material are shown in figure, 4.2, 4.3, and 4.4 below

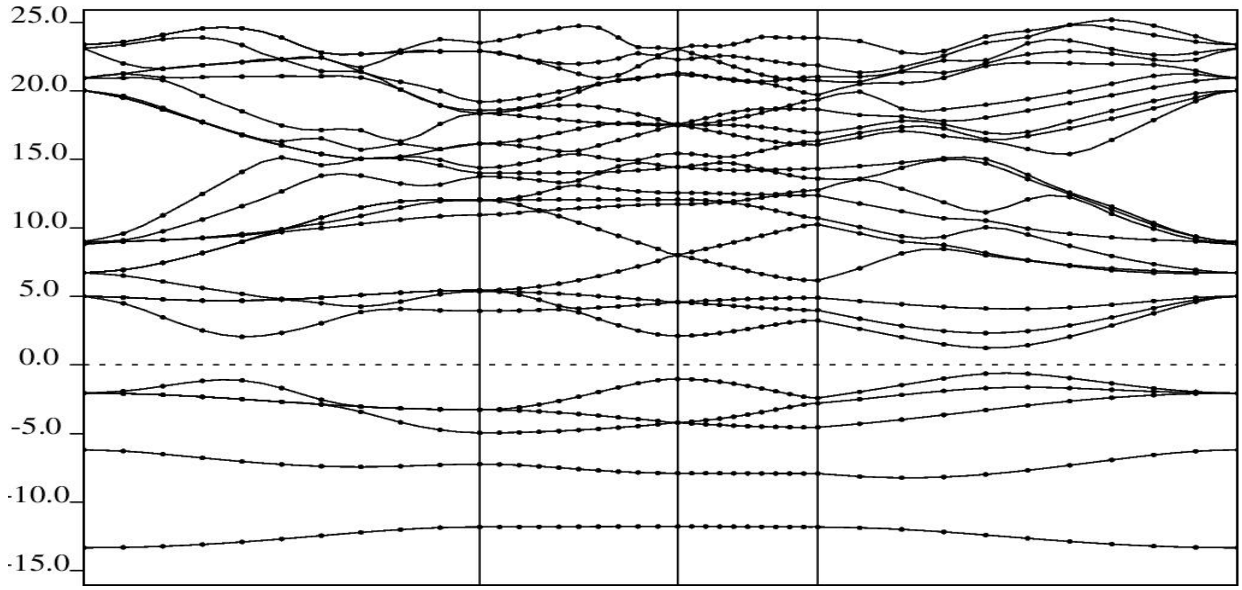

Fig. 4.2: Band structure for PbS (band up) Perovskite material.

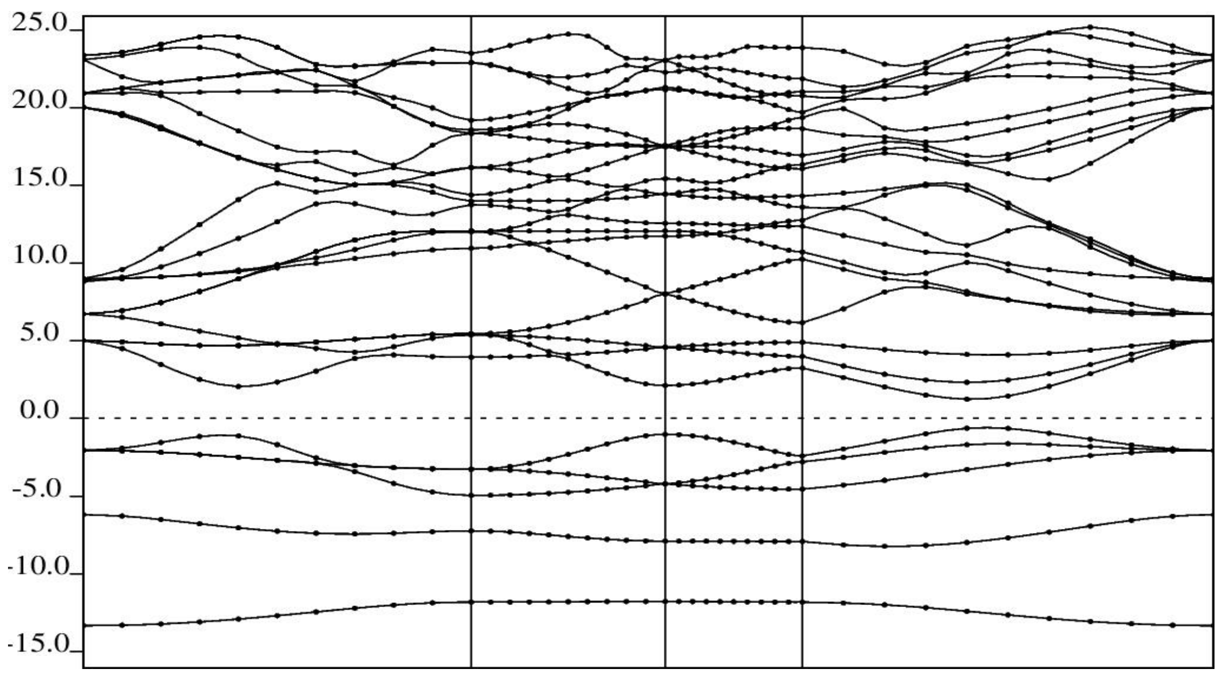

Fig. 4.3: Band structure for PbS (band down) Perovskite material.

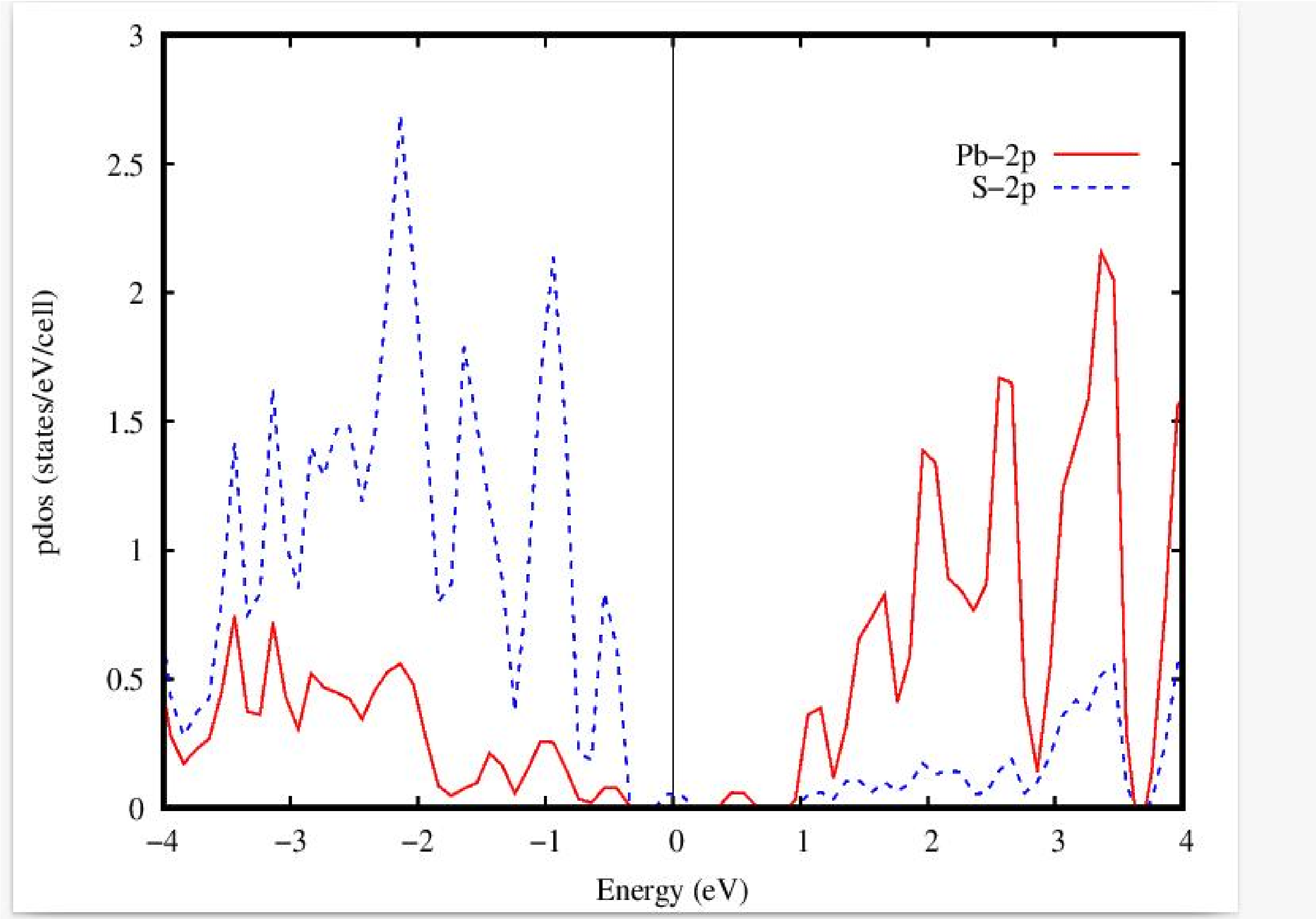

Figure 4.4: Density of state of the PbS Perovskite compound

4.3 Optical properties

The optical properties of the PbS compound under hydro-static pressure in the 0–9eV range are presented in the Figures 4.5-4.11 below . The optical characteristics are calculated using thecomplex dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$, where $\varepsilon(\omega)$ represents the interaction ofincoming radiation with matter. The complex dielectric function describes the linear response of a system to external electromagnetic radiation. The momentum matrix elements between the occupied andunoccupied wave functions are used to calculate the dispersion of the imaginary part of the complex dielectric function $\varepsilon_2(\omega)$, and the real part of the dielectric function $\varepsilon_1(\omega)$ is calculated using the Kramer's–Kronig transformation. The real part of the dielectric constant, which is the electronic part of thestatic dielectric constant, is an important quantity in the zero frequency limits. The static dielectric constants is 5.6 GPa. The maximum peak in the imaginary part of the dielectricfunction $\varepsilon_2(\omega)$ spectra of the compound at 0GPa occur at 5.8eV.

We can calculate the essential optical functions such as refractive index $n(\omega)$, absorption coefficient spectrum $\alpha(\omega)$, reflectivity $R(\omega)$, electron energy-loss spectrum $L(\omega)$, the extinction coefficient $k(\omega)$ and optical conductivity by understanding the real and imaginary parts of the dielectricfunction.

The absorption coefficient is a key component since it informs us about the best solar energy conversion efficiency and reveals how much light of a specific energy or frequency may pass through a material before it is absorbed. The absorption coefficient describes the intensity attenuation of the light passing through a material. It can be understood as the sum of the absorption cross-sections per unit volume of a material for an optical process.

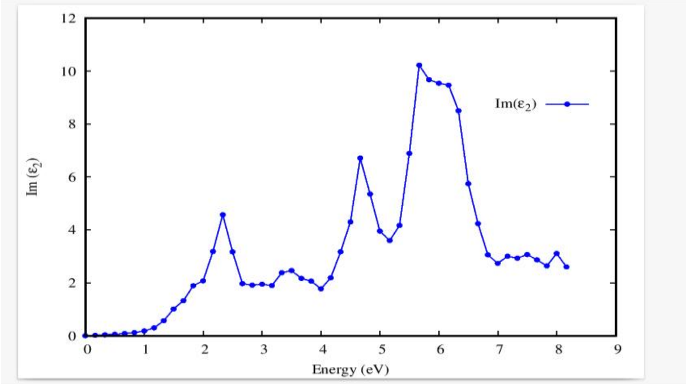

FIGURE 4.6

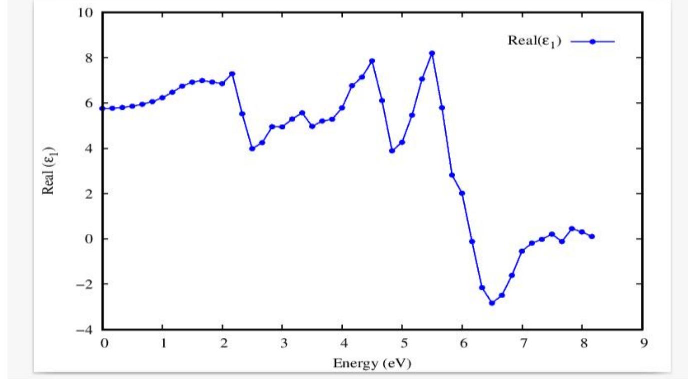

FIGURE 4.5

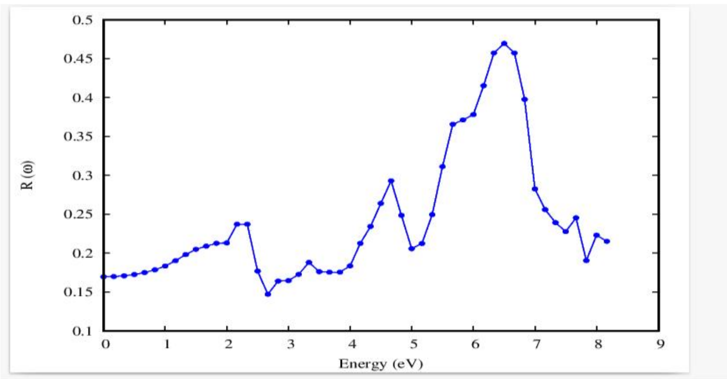

FIGURE 4.7

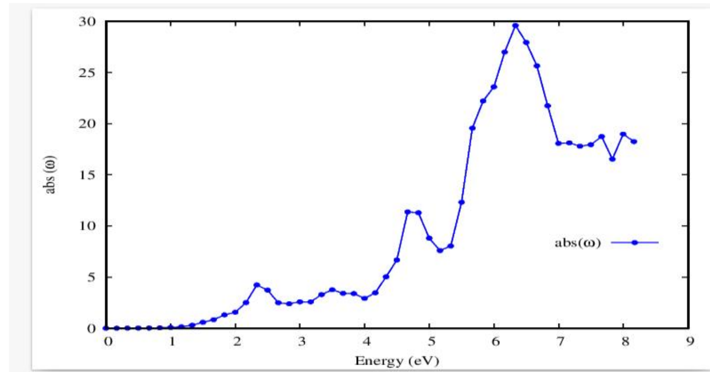

FIGURE 4.8

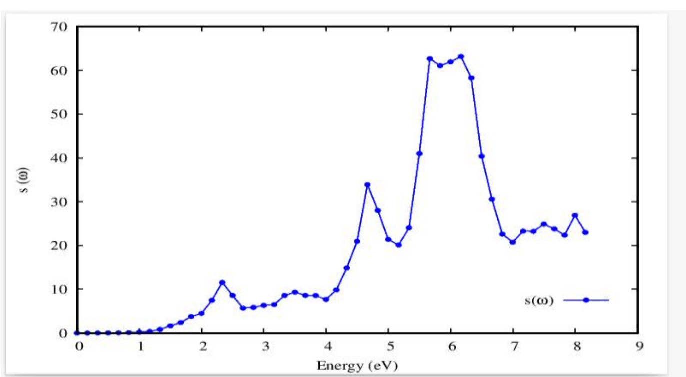

FIGURE 4.9

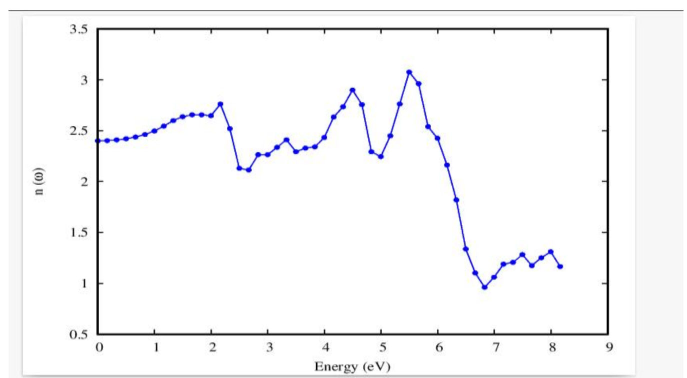

FIGURE 4.10

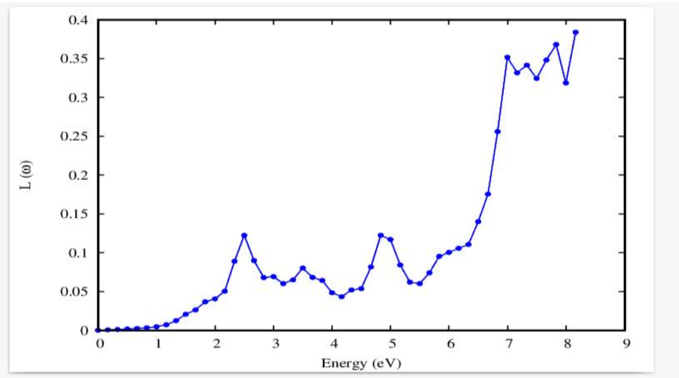

FIGURE 4.11

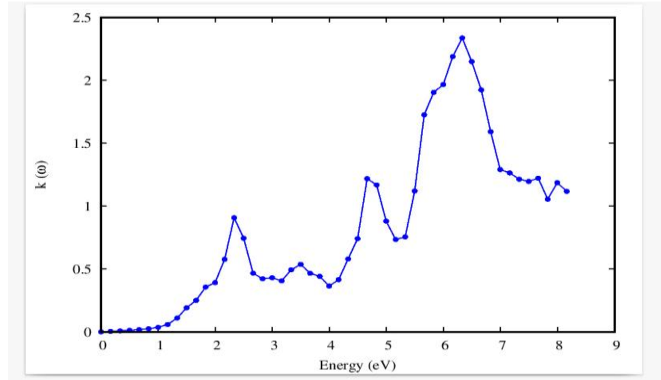

FIGURE 4.12

The Figure (4.5-4.12): (4.5) Real part of the dielectric function ε1(ω), (4.6) Imaginary part of the complex dielectric function ε2 (ω), (4.7) reflectivity R(ω), (4.8) absorption coefficient spectrumα (ω), (4.9) conductivity S (w), (4.11) electron energy-loss spectrum L (ω), (4.10) refractive index n (ω), (4.12) the extinction coefficient k (ω) The PbS seems to have a good absorption coefficient since it has a wide range of about 1.5eV-6.3eV and occurring at low energy region. Figure 4.7 shows the computed reflectivity R(ω) of the investigated compound in the energy range of 0.17 to 7.8 eV. The calculated refractive index n (ω) from the complex dielectric function is presented in Figure 4.11. The electron energy loss function, L (ω) is a critical optical characteristic that indicates the potential for rapid electron interactions inside a material. These interactions are responsible for intra-band transitions, phonon excitation, inner shell ionizations, and Plasmon excitations in addition to interband transitions. The calculated extinction coefficientk (ω) for PbS at

0GPa is displayed in Figure 4.12.

The following are formulas used in calculating the above quantities:

- Refractive Index n(w) = $\sqrt{\frac{1}{2}({\varepsilon_1}^2 + {\varepsilon_2}^2)^{\frac{1}{2}} + \varepsilon_1}$
- Extinction coefficient k(w) = $\sqrt{\frac{1}{2}({\varepsilon_1}^2 + {\varepsilon_2}^2)^{\frac{1}{2}} - \varepsilon_1}$
- Absorption coefficient $(\alpha) = \sqrt{2W}\sqrt{{\varepsilon_1}^2(w) + {\varepsilon_2}^2(w)^{\frac{1}{2}} - \varepsilon_1(w)}$
- Energy Loss L(w) = $\frac{\varepsilon_2(w)}{{\varepsilon_1}^2(w)+{\varepsilon_2}^2(w)}$
- Reflectivity R(w) = $\frac{(n-1)^2+K^2}{(n+1)^2+K^2}$
- Optical Conductivity $\sigma = \frac{\omega\varepsilon_2}{4\pi}$

CHAPTER 5

5.0Findings, Conclusion and Suggestion for Further Studies

5.1 Findings and Conclusion

The first-principle calculation was carried-out using quantum espresso program to determine the mechanical properties, electronic band structure, optimization, and density of states (DOS).

The following findings were produced from the calculation:

3.1.1 The physical properties of PbS have been studied using first principle calculation.

3.1.2 From Pugh's ratio (B/G), it shows that the compound is brittle.

3.1.3 From the plotted band structure graph, the perovskite compound is a semiconductor

3.1.4 From the calculations, the PbS Perovskite compound is stable.

3.1.5 From the Cauchy ratio B/G proves that the perovskite compound PbS is brittle.

3.2 Suggestions for Further Studies

The first principle calculation of mechanical properties, electronic band structure, and density of states (DOS) for the perovskite compound PbS was performed. As a suggestion, effort should be made to obtain the following properties:

3.2.1 Phonon- properties

3.2.2 vibrational properties

3.2.3 Thermodynamic properties

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