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

BY

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DEPARTMENT OF PHYSICS

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SUBMITTED TO

DEPARTMENT OF PHYSICS,

FACULTY OF PHYSICAL SCIENCES,

UNIVERSITY OF BENIN, BENIN CITY, NIGERIA.

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

FEBRUARY, 2025

CERTIFICATION

This is to certify that this project work was carried out by **AKPODONO OGHENEDORO EDAFE** with Matriculation Number **PSC2010357**, of the Department of Physics, Faculty of Physical Sciences, University of Benin, Benin City, Edo State, Nigeria.

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(Head of Department)	
_____	_____
External Examiner	**Date**

DEDICATION

My family has been my greatest source of strength because of their unwavering support, encouragement, and sacrifices, to whom I sincerely dedicate this endeavor. Their faith in my potential has motivated me to pursue greatness.

This work is also dedicated to God, my lecturers, mentors and friends whose advice and expertise have been invaluable to my academic career. My knowledge and development have been influenced by their tolerance and insight.

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CERTIFICATION OF DISSERTATION ON PLAGIARISM

ACKNOWLEDGEMENT

I want to thank Prof. B. E. Iyorzor, my project supervisor, whose advice, clarifications, tolerance, and encouragement were invaluable in helping me finish this study.

Additionally, I would like to thank Fred, Elijah, Dalu, Elizabeth, and Nath for their cooperation and friendship throughout this endeavor.

ABSTRACT

In this work, the structural, mechanical, and electronic properties of PbSe perovskite materials are investigated in detail ab initio using spin-polarized DFT, using the Ultra Soft Pseudopotential (USPP) method in the Quantum Espresso (QE) software package, the total energy was calculated and the lattice constants optimized using the Perdew-Burke-Ernzerhof (PBE) formulation of the Generalized Gradient Approximation (GGA).

In excellent agreement with previously published theoretical values, the study produced optimized equilibrium lattice parameters, band structures, elastic constants, and elastic moduli. Additionally, the Density of States (DOS) and band structures were analyzed in order to comprehensively study the electrical characteristics.

The findings support the efficacy of the computational techniques used and offer a thorough understanding of the structural, mechanical, and electrical properties of PbSe perovskites. These discoveries add to the growing corpus of information on

perovskite materials and provide insightful information for upcoming studies and technological uses.

CHAPTER 1

1.1 INTRODUCTION

The term "perovskite" refers to any material with the formula ABX3 that has a crystal structure similar to that of the mineral perovskite, which is made up of calcium titanium oxide (CaTiO3). The mineral was named after the Russian mineralogist L. A. Perovski (1792–1856) and was first found in the Ural mountains of Russia in 1839. The 'A' and 'B' are two positively charged ions (i.e., cations) that are typically of very different sizes, while X is a negatively charged ion (an anion, often oxide) that bonds to both cations. The atoms in the ideal cubic structure have the B cation in 6-fold coordination, surrounded by an octahedron of anions, and the A cation in 12-fold cuboctahedral coordination.

Perovskites are one of the most prevalent structural families and are present in a vast array of compounds with a wide range of properties, applications, and significance. Other perovskite forms may exist where both/either the A and B sites have a configuration of A1x-1A2x and/or B1y-1B2y, and the X may deviate from the ideal coordination configuration as ions within the A and B sites undergo changes in their oxidation states.

Perovskite, loparite, and the silicate perovskite bridgmanite are examples of natural substances that have this structure. Perovskite materials have attracted a lot of research interest with the 2009 discovery of perovskite solar cells, which incorporate halide perovskites (totally inorganic, like CsPbI3, or hybrid organic-inorganic, like MAPbI3).

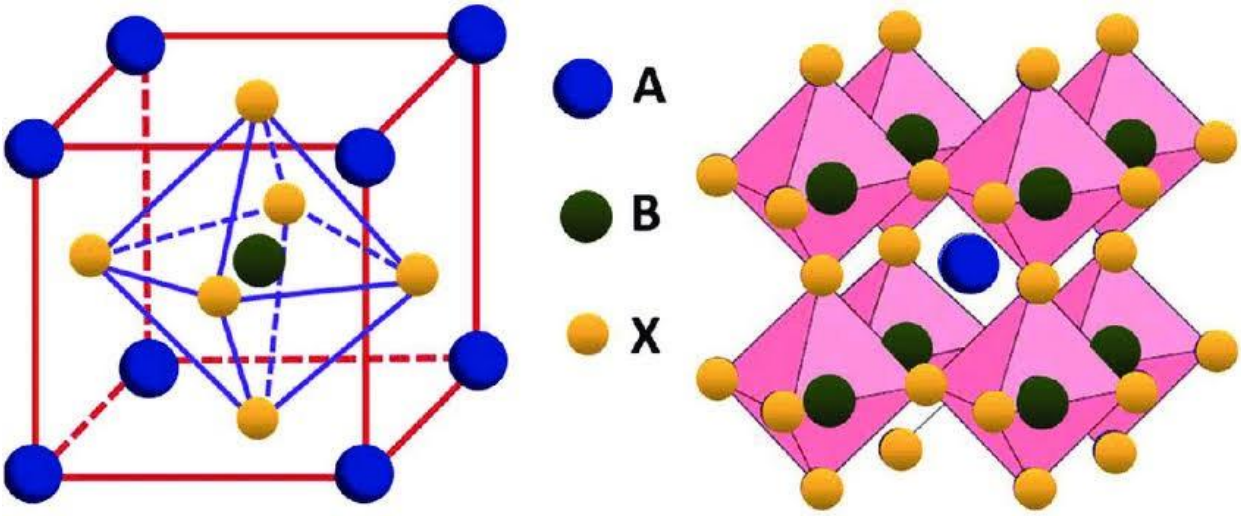

Figure 1.1: An ideal perovskite structure

As plate 1.3 illustrates, perovskites' structural flexibility enables the incorporation of a wide range of elements from the periodic table. The A-site, which is usually occupied by large cations, can accommodate elements from Groups 1, 2, or the lanthanide series, which fill the 12-coordinate holes created by the BX6 network. The B-site, which is located at the corners of the octahedra, is frequently occupied by smaller cations, often transition metals from Groups 3 to 12 or even main group elements like tin. Finally, the X-site can be occupied by the typical oxygen anion (O^{2-}) or heavier halide anions like chlorine (Cl^{-}) or bromine (Br^{-}).

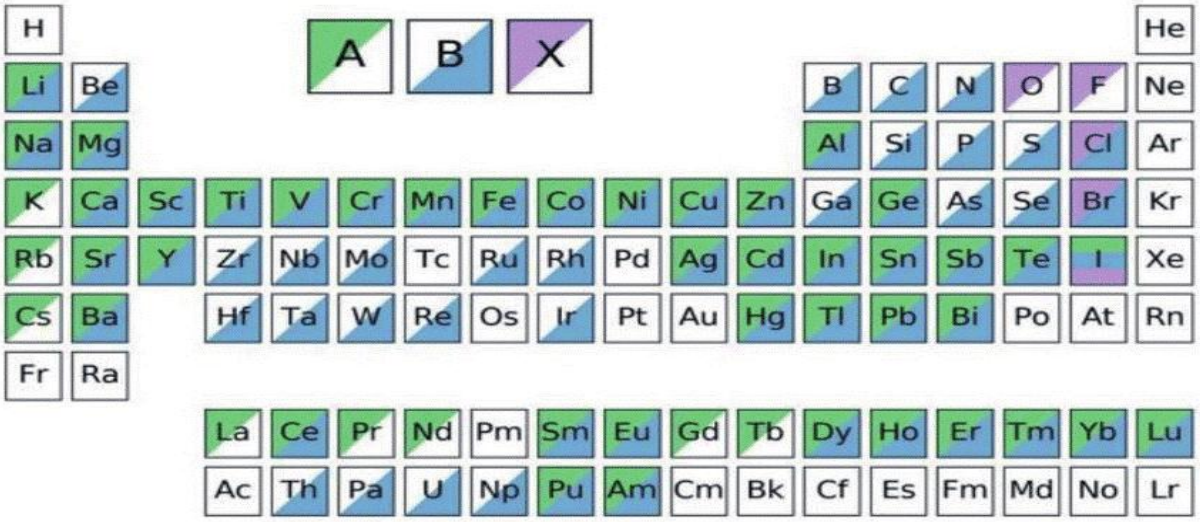

Figure 1.2: Regions of the periodic table where A, B and X are found.

The usual shape of perovskites is cubic, however some modifications can result in the production of orthorhombic, rhombohedral, hexagonal, and tetragonal shapes. Electroneutrality and ionic radius requirements are typically necessary to achieve perovskite formation (Shi and Jayatissa, 2018; Pandey et al., 2017). The emergence of spontaneous polarization in ferroelectric perovskites causes other kinds of deformations.

Some examples of Perovskite include;

- Strontium titanate ($SrTiO_3$)
- Methylammonium lead halide ($CH_3NH_3PbX_3$)
- Methylammonium tin halide ($CH_3NH_3SnX_3$)

- Lead scandium tantanate (PST)
- Rubidium Tantalate ($RbTaO_3$)

1.2 Properties of Perovskite

Since perovskite materials have a unique chemical structure and stoichiometry, they have a wide range of properties, some of which are listed here:

1.2.1 Optical Properties

With single domain crystals like BaTiO3 and SrTiO3 possessing constant refractive indices across temperatures and transmitting light in the infrared spectrum, perovskite materials have optical and photoluminescence characteristics. KTN and other perovskite oxides exhibit notable electro-optic properties, which makes them valuable for laser and optical communications applications. While ecologically friendly photoluminescent materials like BaZrO3 generate light in the visible range and have potential applications in scintillators, lighting, and display technologies, rare earth-doped perovskite oxides are stable and appropriate for a variety of display technologies. (Kim et al, 2005)

1.2.2 Multiferroicity

When materials exhibit many "ferroic" properties (such as ferroelectricity, ferromagnetism, and ferroelasticity) concurrently in the same phase, this is known

as multiferroicity. Often transition metal oxides with a perovskite crystal structure, such as ferrites and rare-earth manganites, are multiferroic materials that show multiferroicity even at ambient temperature. The rhombohedrally deformed perovskite bismuth ferrite is a prominent example, exhibiting both ferroelectric and antiferromagnetic ordering throughout a broad temperature range that is much higher than ambient temperature. In 2011, Singh et al. Applications in a variety of domains, including spintronics and multifunctional devices, are highly promising due to the special mix of features found in perovskite-based multiferroics.

1.2.3 Piezoelectricity

Some materials exhibit a phenomenon known as piezoelectricity, in which they produce an electrical charge in reaction to mechanical stress or deformation. On the other hand, when exposed to an external electric field, these materials can also undergo deformation or shape changes. Because piezoelectricity is bidirectional, it can be used in a number of ways.

Among the synthetic piezoelectric materials are piezoelectric ceramics with a perovskite crystal structure and the general formula $A^{2+}B^{4+}O^{2-}_3$ (Aksel et al. 2011). Moreover, tendon, rochelle salt, collagen, topaz, quartz, and cane sugar are examples of natural piezoelectric materials.

1.2.4 Catalytic activity

Because of their remarkable catalytic activity and great chemical stability, perovskites can be used to catalyze changed processes. They function as active site models and fall into one of two categories: oxidation or oxygen-activated catalysts. Roni (2018)

1.2.5 Superconductivity

When materials cool significantly, magnetic flux fields are released as their electrical resistance falls to zero, a phenomenon known as superconductivity. A good framework for obtaining superconductivity is provided by the crystal structure of perovskite oxides. Copper-containing perovskites hold great promise as high-temperature superconductors. La-Ba-Cu-O perovskite was the first example. In contrast to intermetallic compounds such as cesium tungsten bronzes, perovskite oxides have emerged as a more common source of superconductors. Cava (2008)

1.3 Applications of Perovskite

Because of its special qualities and adaptable architectures, perovskite materials are used in many different disciplines, such as Perovskite solar cells, Perovskite

Light-Emitting Diodes (PeLEDs), Perovskite-based photo detectors, Perovskite dielectric and ferroelectric devices, Perovskite catalysis and fuel cells, and more.

1.3.1 Perovskite Solar Cells (PSCs)

Materials like methylammonium lead iodide ($MAPbI_3$) are used in perovskite solar cells as the light-absorbing layer. By producing electron-hole pairs in response to light, these materials effectively transform sunlight into electrical power. These pairs are subsequently carried via charge-selective layers to produce current. Benefits include:

- High Power Conversion Efficiency (PCE): above 25%, in competition with solar cells made of silicon.
- Low-Cost Fabrication: Unlike silicon-based solar cells, this type of fabrication can be done at a lower cost because to solution processing. Both flexible and lightweight: It is appropriate for incorporation into portable and wearable electronics.
- Bandgap Tunability: By engineering perovskites to work in tandem with silicon in solar cells, efficiency can be increased.

1.3.2. Perovskite Light-Emitting Diodes (PeLEDs)

In order for perovskite LEDs to work, electrons and holes must be injected into the perovskite emissive layer, where they recombine to produce light. They hold promise for lighting and display technologies due to their narrow emission spectrum and great photoluminescence efficiency.

Advantages include:

- High Efficiency: On par with organic LEDs (OLEDs) and quantum dot LEDs (QLEDs).
- Tunable Emission: Emission may be adjusted from UV to near-infrared by changing the halide composition.
- High Color Purity: Vibrant colors are ensured by tight bandwidth.

1.3.3 Perovskite-Based Photodetectors

Perovskite photodetectors are employed in imaging and sensing applications because they can transform light into electrical signals. They provide effective photon detection over a wide range due to their high absorption coefficient and extended carrier diffusion length.

Advantages are:

- Broad Spectral Response: Detects light from ultraviolet to near-infrared wavelengths.

- High Sensitivity: Low noise and high responsivity are the results of efficient charge production
- Solution-Processability: Facilitates large-area, reasonably priced manufacturing.

1.3.4 Perovskite Dielectrics and Ferroelectric Devices

$BaTiO_3$ and $PbTiO_3$ are two examples of perovskites that show ferroelectric behavior and high dielectric constants. These characteristics are crucial for memory devices, capacitors, and adjustable microwave parts.

Advantages

- High Dielectric Constant: Allows capacitors to store energy.
- Ferroelectric Switching: Non-volatile memory (FeRAM) uses this technique. Communication equipment can benefit from the adjustable microwave properties.

1.3.5 Perovskite Catalysis and Fuel Cells

Perovskites, such as $La_{0.6}Sr_{0.4}MnO_3$, and $LaFeO_3$, are employed as electrodes in solid oxide fuel cells (SOFCs) and as catalysts for oxygen reduction/evolution processes (ORR/OER). They are perfect for energy conversion activities because

they can tolerate high temperatures and conduct oxygen ions.

Advantages:

- High conductivity of oxygen ions: improves electrochemical processes.
- An Affordable Substitute for Noble Metals: The need of costly platinum-based catalysts is lessened by perovskite catalysts.
- High-Temperature Stability: Long-term use in fuel cells is possible.

1.4 Aim and Objectives

AIM

The aim of this study is to examine PbSe's ground state energy and physical properties.

OBJECTIVES

The objectives of this research are to;

1. Calculate the structural properties (lattice constant, bulk constant, modulus, pressure derivatives)
2. Calculate the electronic properties of the compound (band structure, DOS, material type)
3. Calculate the mechanical properties of the compound (elastic constant, shear modulus, Young’s modulus, etc.)

CHAPTER 2

2.1 Literature Review

Because of its many uses, perovskite compounds have attracted a lot of attention in a variety of industries, including electronics and catalysis. RbTaO3 has become a strong contender among these perovskites because of its distinct structural, electrical, and functional properties.

Analysis of Structure:

Although lead selenide (PbSe), more frequently crystallizes in the rock-salt (NaCl-type) cubic form at room temperature, it can occasionally take on a perovskite-like structure.

- Structure of Perovskite-like PbSe:

  The Crystal System Pm-3m is the cubic space group (like oxide perovskites).
- Lattice Constant: Usually approximately 6 Å, although can vary based on the synthesis conditions.
- Bonding: Strong spin-orbit coupling (SOC) from heavy Pb atoms contributes to the mostly ionic-covalent Pb–Se bonding.

  Stability and Distortion: Under pressure or doped with other elements such as Sr, Sn, or halides, it may display octahedral distortion.

Under specific circumstances, a tolerance factor (t) near 1 indicates good perovskite stability.

Electronic Specifications:

PbSe is renowned for its intriguing electrical characteristics and small bandgap:

- The bandgap:

  At ambient temperature, PbSe's indirect bandgap in bulk is roughly 0.27 eV.

  The bandgap in nanostructured PbSe can be greatly increased by quantum confinement (up to 1 eV for extremely small nanoparticles).

- Mobility of Carrier and Effective Mass:

  PbSe has great mobility due to its comparatively low effective mass of charge carriers.

  Band dispersion is influenced by optical and transport features when there is a high spin-orbit interaction.

- Behavior of Topological Insulators:

  Due of significant SOC effects, PbSe can display topological insulator-like properties under specific doping circumstances.

  Because of its capacity to maintain high Seebeck coefficients, it has been investigated for possible thermoelectric uses.

Dielectric and Ferroelectric Characteristics:

Although PbSe is not typically a ferroelectric material, its dielectric properties and potential for phase transitions under strain or doping make it an intriguing candidate for some applications.

- Ferroelectric Behavior: PbSe does not exhibit intrinsic ferroelectricity, but perovskite-like PbSe structures (particularly when alloyed with PbTe or PbS) can exhibit polar distortions leading to pseudo-ferroelectric behavior. Under strain engineering, PbSe can transition into a ferroelectric-like phase, making it a promising material for next-generation memory devices.

Photocatalytic and Catalytic potential:

Particularly in solar-driven processes, PbSe is becoming more and more significant in catalysis and photocatalysis.

- Photocatalysis:

  Near-infrared (NIR) photocatalysis can benefit from PbSe's narrow bandgap, which allows it to absorb infrared (IR) radiation effectively.

  H2 Evolution: The hydrogen evolution reactions (HER) caused by PbSe quantum dots under solar radiation have been studied.

  CO2 Reduction: Possible uses in the production of valuable fuels through

photocatalysis.

Uses of Catalysis:

Batteries and fuel cells are two examples of energy storage devices that can use PbSe-based materials as electrocatalysts.

It is more active when combined with metallic co-catalysts (such as Pt, Ag, or MoS2).

Mechanical and Heating Characteristics:

Because of its intriguing mechanical and thermal characteristics, PbSe is a good choice for thermoelectric and infrared application. Resistance to mechanical stress and hardness are moderate.

With a Young's modulus of 40–50 GPa, the structure is reasonably rigid.

Phase changes reliant on strain: Under external pressure, it is possible for its structure to change, improving its dielectric and piezoelectric qualities.

Future Prospects: PbSe has enormous potential in a number of fields due to its unique properties:

- Energy Harvesting & Thermoelectrics: PbSe is a strong candidate for waste heat recovery systems due to its high thermoelectric figure of merit (ZT);

- PbSe quantum dots show promise for infrared photodetectors, night vision cameras, and solar cells; and tunable bandgap engineering through strain or doping can enhance its role in next-generation optoelectronic devices. Future studies on nano-engineered PbSe composites could result in breakthroughs in energy conversion.

CHAPTER 3

3.1. Methodology

3.1.1. Density Functional Theory (DFT)

One of the most popular and effective quantum mechanical theories for describing matter in physics and chemistry is density functional theory (DFT), which is used to determine among other things the band structure of materials and the binding energy of molecules. DFT has been used to investigate a variety of phenomena, such as relativistic effects in heavy elements and atomic nuclei, superconductivity, atoms under intense laser pulses, classical liquids, and magnetic properties of alloys.

In quantum mechanics, the wave function of a system contains all the possible information about the system, which depends on the electronic coordinates; the wave function is computed without taking relativity into account using the Schrodinger equation, which computes the wave function of a single electron moving with a potential. This fact accounts for the versatility of DFT, which is based on the universality of its fundamental concepts and the flexibility with which they can be applied.

Ab initio Without the need for higher-order factors like basic material properties, DFT calculations in computational material science allow the computation and prediction of material behavior based on quantum mechanical

principles. Current DFT techniques assess the electronic structure of a system by using a potential acting on its electrons. The effective potential, Veff, which denotes inter-electronic interactions, and the external potentials, Vext, which are determined only by the structure and elemental makeup of the system, add up to the total potential, V.

DFT provides a more flexible solution to the many-body problem by studying a set of non-interacting electron Schrodinger equations, also known as Kohn-Sham equations, for a representative supercell of a material with n electrons. The electron density, n(r), is the key variable in DFT and is determined by the square of the wave function for a normalized wave function.

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

After decades of struggle, several successful methods have been developed to solve Schrodinger's equation, such as diagrammatic perturbation theory in physics, which is based on Feynman diagrams and Green's functions, and configuration interaction (CI) methods in chemistry, which involve systematic expansion in Slater determinants. Although there are many specialized methods available, these methods are computationally intensive and may not be feasible for large, complex

systems. DFT provides a suitable alternative, which may be less precise but is more flexible. The density-functional approach can be summed up as follows:

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

3.1.2 Generalized Gradient Approximation (GGA)

In ab initio total energy calculations for exchange-correlation energy in density-functional theory, the generalized gradient approximation, or GGA, is currently gaining popularity as a less complicated substitute for the local density approximation (LDA) (Jones et al., 1898). In atomic and molecular physics, where experimental data is more easily accessible and LDA overestimates by 20% or more, it is not as accurate as it is in condensed matter systems.

Gradient corrections are introduced to address the issue of underestimation of bond lengths caused by cohesive energies and bond strength in molecules and solids. By writing the exchange-correlation functional as a function of both the local density and the local gradient of the density, the non-homogeneity of the electron density can be accounted for. This represents a logical step beyond LDA, which only considers the density at a given point.

3.1.3. Local Density Approximation (LDA)

The exchange-correlation (XC) energy functional in density functional theory (DFT) is estimated using the local density approximation (LDA), a collection of approximations that only use the electronic density information from the Kohn-Sham orbitals. Local approximations of the XC energy can be produced using a variety of methods; the homogeneous electron gas (HEG) model offers many useful local approximations. Functionals based on the HEG approximation are frequently used interchangeably with LDA when applied to real systems, such as molecules and solids. A local-density approximation for the XC energy in unpolarized systems is commonly written as follows:

$$E_{XC}^{LDA}[\rho] = \int \rho\,(r)\varepsilon_{XC}\big(\rho(r)\big)dr \qquad (3.3)$$

The electronic density n and the exchange-correlation energy per particle of a homogeneous electron plasma with charge density ρ are used to describe the exchange-correlation energy Exc per particle, which is linearly divided into exchange and correlation components.

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

The exchange term assumes a simple analytical form of HEG. Solid state physicists commonly employ GGAs in ab-initio DFT studies to interpret electronic

and magnetic interactions in semiconductor materials, such as semiconductor oxides and spintronics, but the precise correlation density limiting expressions are the only ones known, leading to a variety of approximations for Ec. The significance of these computational studies comes from the complexity of the system, which makes it extremely sensitive to synthesis parameters and requires first-principles based analysis. LDA in conjunction with simulated packages is frequently used to estimate the Fermi level and structure in perovskites. On the other hand, an underestimating of band gap values, which is frequently linked to LDA and GGA approximations, can result in inaccurate estimates of impurity effects, conductivity influenced by carriers, and magnetism mediated by carriers in these systems. Since 1998, the Rayleigh theorem for eigenvalues has been applied using LDA potentials, yielding generally accurate band gap predictions for materials. The context of the two DFT theorems' assertions in the study of density functional theory clarifies a widespread misunderstanding about the second DFT theorem.

3.1.3.1 Khon Shan Equation

For a hypothetical system of non-interacting particles, usually electrons, the Khon-Sham equation is a one-electron Schrodinger equation that produces the same electron density as a specific system of interacting particles. A local effective

potential, commonly represented as V(r) or Veff(r), defines this equation by functioning as a false external potential on the non-interacting particles. A set of orbitals that are the lowest-energy solutions to the Khon-Sham equation are used to generate the single Slater determinant that is the Khon-Sham wave function. (Walter Kohn and Lu Jeu Sham, 1965)

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

One common way to represent the Khon-Sham equation is as an eigenvalue equation itself. The density for an N-particle system is determined by the sum of the squares of the absolute values of the Khon-Sham orbitals, and this equation includes the orbital energy (E1) of the corresponding Khon-Sham orbital.

$$\rho(r) = \sum_i^N / \varphi_i(r) \; / \qquad (3.6)$$

3.1.4. Pseudopotentials and Applications

This chapter examines both ab-initio and empirical pseudopotentials, as well as their various applications. The concept of the pseudopotential, also referred to as the standard model for condensed phases, has greatly advanced our understanding

of semiconductor electrical structure. The first applications of empirical pseudopotentials were to describe the optical and dielectric properties of tetrahedral semiconductors, and it was later demonstrated that the resulting image of a one-electron band structure was valid. These band structures were developed more than 30 years ago, but they are still largely accurate. Current concepts for understanding the chemical bond in solids rely on the combination of density functional theory and pseudopotentials, which have been used to accurately predict the compressibility, vibration modes, phase stability, and structural properties of semiconductors in multiple states.

The intrinsic energy and spatial separation of valence and core electrons provide the basis of the pseudopotential idea. Gaussian type functions are commonly used to fit pseudo potentials in traditional quantum expresso computing systems. Within the framework of density functional theory (DFT), pseudopotentials can be created in a number of ways, such as by employing parameterized analytical pseudopotentials or by constructing pseudo potentials using pseudo orbitals obtained from atomic calculations. Since the matrix elements of an effective Hamiltonian can be computed directly using either analytical or numerical basis sets (or a mixed one), the discrete variation method (DVM), a specific implementation of numerical integration for solving the DFT one electron equations, does not require the fitting of pseudo orbitals to any analytical functions.

The simplicity of controlling the precision of a plane wave basis is one of its benefits, but a major disadvantage is that the size of the basis set needed for a particular system is frequently far greater than what would be required with a localized basis set. This is due to the fact that orbitals in condensed matter systems have a tendency to oscillate more quickly near atomic nuclei and more gradually in other areas. Since most of the space in the cells does not include rapidly oscillating orbitals, a high cut-off energy is required to include plane waves with short wavelengths in order to represent this rapid oscillation. However, the majority of the processing expenses related to these plane waves are wasted. This issue can be considerably lessened by using pseudopotential in combination with plane waves. Pseudopotential allows for more effective computations of the electronic structure of the system by substituting a smoother, easier-to-manage potential that has the same effect on the valence electrons as the genuine potential for the fast oscillating core electrons. We take note of the following information regarding orbitals in the condensed matter system in order to comprehend what pseudopotentials are:

- Electrons that are firmly attached to an atom's nucleus and inhabit lower energy orbitals are known as core electrons. They have a high degree of localization around the nucleus and are typically unaffected by the atom's chemical surroundings.

- Because they must be orthogonal to the core electrons, many of the fast oscillations in the orbitals of non-core electrons close to atomic nuclei can be ignored. This implies that the orbitals of the non-core electrons must be built differently from those of the core electrons, which will suppress some oscillations.

The nuclear charge is effectively represented by pseudopotential theory, which substitutes a false potential for the core electrons and guarantees that the behavior of the valence electrons stays constant after a specific distance from the nucleus. As long as the radius does not overlap with areas engaged in chemical bonding, the pseudopotential approximation should not substantially change the behavior of condensed matter, which is determined by interatomic interactions. There are four ways that employing pseudopotential lowers the computing cost of computations:

- The number of Kohn-Sham orbitals is reduced by removing core electrons from the calculations, which also reduces the amount of memory required to store the orbitals and the amount of time required to orthogonalize a collection of orbitals.
- The corresponding orbitals close to the nucleus oscillate less when there are no core electrons for the valence electrons to be orthogonal to. This makes it

possible to represent orbitals with a lower cut-off energy, which speeds up calculations and uses less memory. Efficiency can be greatly increased by lowering the cut-off energy, which frequently leads to orders of magnitude gains in computational performance.

- Because the pseudopotential's form is modifiable rather than fixed for a particular element, optimization to obtain the lowest cut-off energy is possible. This enhancement increases calculation efficiency by reducing memory usage and speeding up processing.
- Because the pseudopotential's form is modifiable rather than fixed for a particular element, optimization to obtain the lowest cut-off energy is possible. This enhancement increases calculation efficiency by reducing memory usage and speeding up processing.

3.1.4.1. Ultra Soft Pseudopotentials (USPP)

Ultrasoft pseudopotentials relax the norm-conserving criterion to further reduce the required size of the basis set, however this results in a generalized eigenvalue problem. David Vanderbilt, April 1990

3.1.4.2. Quantum Espresso (QE)

Released under the GNU General Public License, Quantum ESPRESSO is a publicly available package of quantum chemistry methods for electronic structure computations and materials modeling. It is based on norm-conserving and ultrasoft pseudopotentials, plane wave basis sets, and Density Functional Theory. The CNR-IOM DEMOCRITOS National Simulation Center in Trieste, Italy, is the leader of the open-source package, called ESPRESSO, in partnership with other international research institutions like MIT, Princeton University, the University of Minnesota, and the Ecole Polytechnique Federal de Lausanne. (Giannozzi, Paolo, and others, 2009). Essential plane wave DFT procedures are provided by the package's core programs, which are primarily written in Fortran-90 with some parts in C or Fortran 77. These key programs include pwsef, which solves the self-consistent Kohn and Sham equations in a periodic solid, Post Proc, which analyzes and charts data, and CP, which deals with Car-Parrinello molecular dynamics. Other packages include Atomic for generating pseudopotentials, NEB for calculating reaction routes and energy barriers, and Phonon for computing second and third order derivatives of the energy with regard to atomic displacement using Density-Functional Perturbation Theory.

The foundation of Quantum ESPRESSO is the Plane-Self-Consistent Field (PWSCF) component of the Open-Source Package for Research in Electronic

Structure, Simulation, and Optimization, or ESPRESSO, which was first made available on June 15, 2001, and has since been continuously developed and improved by the international consortium of research centers and organizations that oversee the project.

```
control
  calculation = 'scf',
  prefix= 'PbSe'
  pseudo_dir = '/home/ben/PSEUDOPOTENTIALS/',
  outdir = './',
 /
&system
  Ibrav=1,
  celldm(1)= 11.7564
  nat=2, ntyp=2, occupations= 'smearing', smearing= 'mv', degauss=0.01
  ecutwfc=90,
 /
&electrons
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ATOMIC_SPECIES

Pb 207.20000 Pb.pbe-dn-kjpaw_psl.0.2.2.UPF

Se 78.96000 Se.pbe-n-kjpaw_psl.0.2.UPF

ATOMIC_POSITIONS {crystal}

Pb 0.00000000 0.00000000 0.00000000

Se 0.50000000 0.50000000 0.50000000

K_POINTS (automatic)

8 8 8 0 0 0

3.1.4.3. Post Processing

The software for post-processing computations was originally built by Stefano Baroni, Stefano de Gironcoli, Andrea Dal Corso (from SISSA), and Paolo Giannozzi (from the University of Udine), together with several other authors. (www.quantum-espresso.org) Plotting bands and computing the density of states (DOS) are two further small calculations we perform after finishing the self-consistent calculation. The following are the main post-processing programs that carry out further computations and retrieve the required data/files from the PWSCF calculations:

1. pw.x: We use this command 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.
2. bands.x: In order to prepare the data for processing, this pulls the files from the PWSCF computations and logs 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. plotband.x: Auxiliary codes plotband.x read the output files from bands.x directly and transform them to a plottable format. The values of the k-points must be placed in the proper order; otherwise, if the k-points are not arranged along lines or if two consecutive points are the same, surprising plots may emerge. As a result, selecting the k-point sequence correctly is crucial.
4. dos.x: It helps to calculate the electronic density of states at different k-points.
5. thermo_pw.x: It is a Fortran driver that leverages Quantum ESPRESSO (QE) routines as the underlying engine for the parallel and/or automatic computation of material properties. It generates postscript figures of some material properties after reading the same input as the QE PW.x code. (github.io)

3.1.4.4. Band Structure

As the basis of most crystal properties, the band structure of a solid can be used to determine various electrical properties. The electronic band structure is a commonly used analytical technique in the first-principles electronic structure calculation of crystals, especially within the Kohn-Sham framework of density functional theory. It provides the electronic levels in (perfect) crystal formations, which are identified by a band index (n) and a Bloch vector (K), an element of reciprocal space, measured in length units, and typically limited to the first Brillouin Zone. (Andreas Wacker, 2010). The close packing of atoms in a solid causes their interaction to disturb the initial atomic levels when a large number of atoms are brought together. Since no two electrons can occupy the same energy state, all of the electrons in the orbitals are filled up according to Pauli's Exclusion Principle.

The electrons in the inner shell of a band are least affected by interatomic interactions, whereas the electrons in the valence band, which are nearest to adjacent ions, are most affected. This leads to the establishment of an energy continuum in which separate levels created by individual atoms cannot be recognized. A single, sharp level splits when two atoms are close to one another. A solid's band structure can be utilized to identify its different electrical and optical

properties. According to band theory, the measurement of the band gap identifies the type of solid. The pseudopotential and plane wave basis set approaches are used in density functional theory (DFT) to calculate the band structures. The Generalized Gradient Approximation (GGA) is used to treat the exchange correlation functional as the Predew Berke-Erzndof (PBE) functional.

3.1.4.5. Density of State (DOS)

The number of states that particles within a specific energy range can occupy per unit energy is known as the "Density of States" (DOS) (Walter, 1989). It is defined as the number of quantum states per unit of energy range and, in other words, is a measure of the concentration of quantum states in a system. In solid state and condensed matter physics, the density of states is important because it may be used to calculate a number of parameters that provide information about a wide range of electronic, magnetic, and transport properties.

3.1.5. Computational Details

3.1.5.1 Convergence Test (Optimization)

The self-consistent field (SCF) calculations were performed to ascertain fundamental parameters, specifically:

1. The kinetic energy cut-off for the k-points grid and plane wave basis, and
2. The lattice parameters, which were obtained through energy minimization.

These parameters were evaluated by examining the convergence of the total energy with respect to each of these parameters individually.

3.1.5.2. Kinetic Energy cut-off (ecutwfc)

The kinetic energy cut-off, ecutwfc, measured in Ry, determines the dimension of the plane-wave (PW) basis sets used to expand the wave function (Kohn-Sham orbitals). The closeness of the interactions determines the size of the kinetic energy cut-off in a periodic system. A more accurate result can be obtained by include long-range interactions by raising the cut-off energy. Nevertheless, doing so necessitates using greater processing power. A modest energy cut-off could lead to inaccurate results even though the computations are reasonably priced. Determining the ideal cut-off energy value is so crucial.

CELL DIMENSION (LATTICE PARAMETER)

The orderly arrangement of atoms in three dimensions, or the crystal lattice, is described by the lattice constant, whether or not it is an atomic attribute. It is normally measured in angstroms (Å), and for most crystals, its value is a few

angstroms. The length of the lattice's repeat unit is essentially represented by the lattice constant.

K-POINTS GRID

A dense enough grid of k-points is needed to capture periodicity, and a large number of grid points is essential for discretely representing interactions in the Brillouin zone, but because of practical computational resource constraints, the number of k-points must often be optimized using a rectangular grid of points with dimensions k x k x k, evenly distributed throughout the Brillouin zone, called 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 all

   scf.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 edit

scf.in

nscf.in

dos.in

pdos.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

3.1.6. POST PROCESSING

Auxiliary codes are available for performing small-scale calculations such as density of states (DOS) and band charting. The following are the main post-processing algorithms that do further calculations and retrieve particular data or files from PWSCF calculations:

- 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 energy at every k-points. Also it is used to calculate electronic structure, structural optimization, molecular dynamics
- ph.x: This command is used to calculate the phonon frequencies and displacement patterns, dielectric tensors, effective charges (using data produced by pw.x)
- q2r.x. This code calculates the Inter-Atomic Force Constants(IFC) in real space from dynamical matrices produced by ph.x on a regular q-grid.
- matdyn.x. This codes helps in producing phonon frequencies at a generic wave vector wing the IFC file calculated by q2rx; which may also calculate phonon DOS.
- pp.x: The extracts the specified data form files produced by pw.x prepared data for plotting 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 different k-points with corresponding energies values ready for further process mg. 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 structure for Post Script plots.
- dos.x: This command is used to calculate the electronic Density of State (DOS) at different k-points.

CHAPTER 4

4.1 Results and Discussion

4.1.1 Structural and Mechanical Properties

To reduce its overall energy with regard to changes in the lattice parameters, the PbSe perovskite complex was subjected to a structural optimization procedure. A thorough examination of the structural characteristics related to the Pbse perovskite's ground state configuration was made possible by this optimization. Plate 4.1 below displays the PbSe crystal structure. A basic cubic perovskite is PbSe.

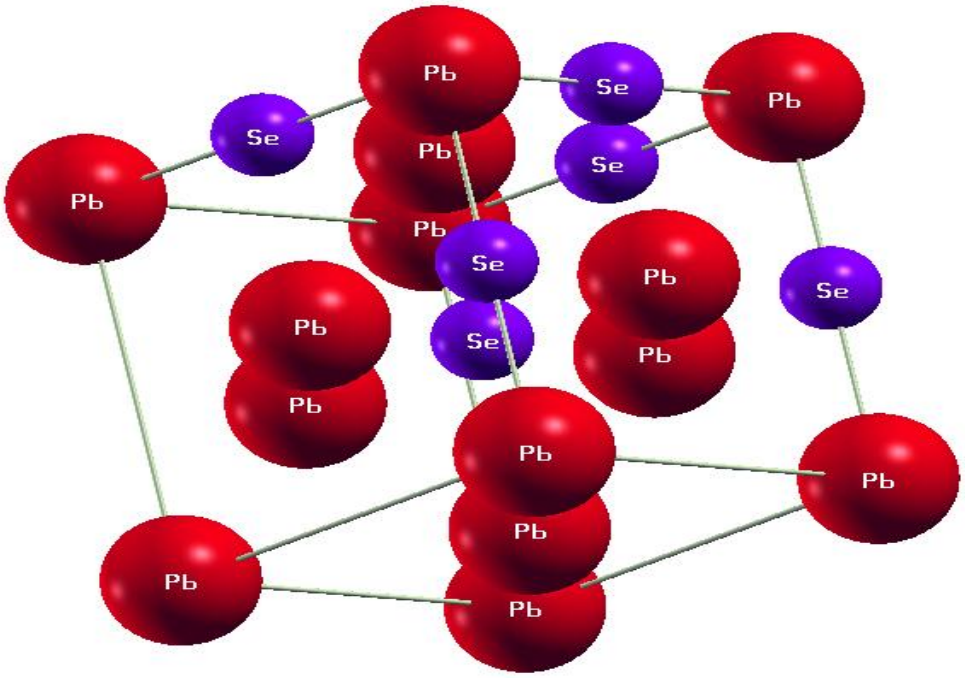

Figure 4.1: Crystallographic structure of PbSe Perovskite compound

The lattice parameters, a (Å), which show the separation between neighboring atoms and the bulk modulus, B (GPa), are displayed in Table 4.1 below.

Table 4.1: Factors that contribute to the structural properties of the PbSe:

S/N	Perovskite compound	PbSe

I	a (Å)	46.99
Ii	B(Gpa)	6.2178

A series of self-consistent computations (SCF) carried out throughout the optimization procedure described in Chapter 3 produced the results shown in Table 4.1. A material's resistance to compressibility is indicated by its bulk modulus, and its reaction to minute changes in pressure is measured by its pressure derivative.

Deformation resistance is the capacity of a material to tolerate the application of a compressive force. The mechanical characteristics that measure this resistance include the caunchy pressure (Cp = C12-C44), the elastic constants (C11, C12, and C44), the bulk modulus (B, measured in GPa), the young modulus (E, also measured in GPa), and the shear modulus (G, also measured in GPa). Table 4.2 displays these parameters.

Table 4.2: Factors that contribute to the mechanical properties PbSe Perovskite compound

S/N	Mechanical Property	PbSe
I	E (GPa)	68.04
Ii	G (GPa)	27.11
Iii	B/G	0.25471

Iv	N	1.7333
V	C_{11} (GPa)	115.9
Vi	C_{12} (GPa)	12.6
Vii	C_{44} (GPa)	17.1
Viii	C_{12} (GPa) - C_{44} (GPa)	-4.5

A perovskite material's Poisson ratio gives information about its elasticity and deformation characteristics; a positive Poisson ratio indicates steady tensile deformation, while a negative Poisson ratio indicates compressive deformation. The Poisson ratio of PbSe indicates that it possesses steady tensile deformation. Elastic constants are crucial for evaluating the stability of solid materials, along with other structural attributes (Wu Z., 2007). In cubic phases, stability is evaluated using the criteria outlined in equations (4.1), (4.2), and (4.3) (Smirnow N.A., 2002).

$C_{11} > 0$ (4.1)

$C_{44} > 0$ (4.2)

$C_{11} + 2C_{12} > 0$ (4.3)

Table 4.2 contains the data on elastic constants needed for these equations. The findings demonstrate that RbTaO3 is stable since it satisfies the required criterion.

The type of bonding in a material can be described by the Cauchy pressure. Covalently bound solids have a high resistance to bond bending, which is shown by a negative Cauchy pressure. On the other hand, a positive Cauchy pressure is seen in materials that have metallic bonding. This characteristic is important for comprehending how materials behave mechanically and react to outside forces. Equation (4.4) illustrates how to compute this pressure using a cubic material's crystal elastic constants. According to table 4.2, the material's Cauchy pressure of 280.88 suggests that it is mettalic.

$$C_p = C_{12} - C_{44} \qquad (4.4)$$

Pugh's ratio is also used to analyze the material's brittle or ductile characteristics. In 1954, Pugh found that the ratio of a compound's bulk modulus to shear modulus indicated whether it was brittle or ductile (S. F. Pugh, 1954). According to pubs.rsc.org, a crucial value of 1.75 for the B/G ratio is deemed significant: a $B/G > 1.75$ value implies ductility, whilst a $B/G < 1.75$ value shows brittleness. This ratio is a useful measure of a material's mechanical characteristics and propensity to fracture or deform plastically under stress. With a Pugh's ratio of 1.7333, the PbSe perovskite compound is brittle by nature.

4.1.2 Electronic and Magnetic Properties

In the analysis of the ab initio calculation of the electronic properties of PbSe perovskite material, the electronic band structures and density of states of the material are presented in figures 4.2, 4.3, and 4.4 below.

In the both the upward spin and downward spin of the PbSe, there is a narrow band gap between the conduction bands and the valence bands which portrays semiconductor properties.

For semiconductors to be suitable for photovoltaic and photochemistry applications, they should possess an appropriate band gap that falls within the range of 1.4 to 3.0 eV. (Iyorzor B. E., Babalola M. I. and Ebuwa S.O. (2022)). The PbSe Perovskite compound is considered a good candidate for photovoltaic and photochemistry applications.

The PDOS plot aims to illuminate the bonding nature between orbitals and the impact of individual orbitals on the Density of States (DOS). Within the conduction band the major contribution is from Pb-2p and the least from Se-2p. While in the valence band the major contribution is from Se-2p and the least from Pb-2p.

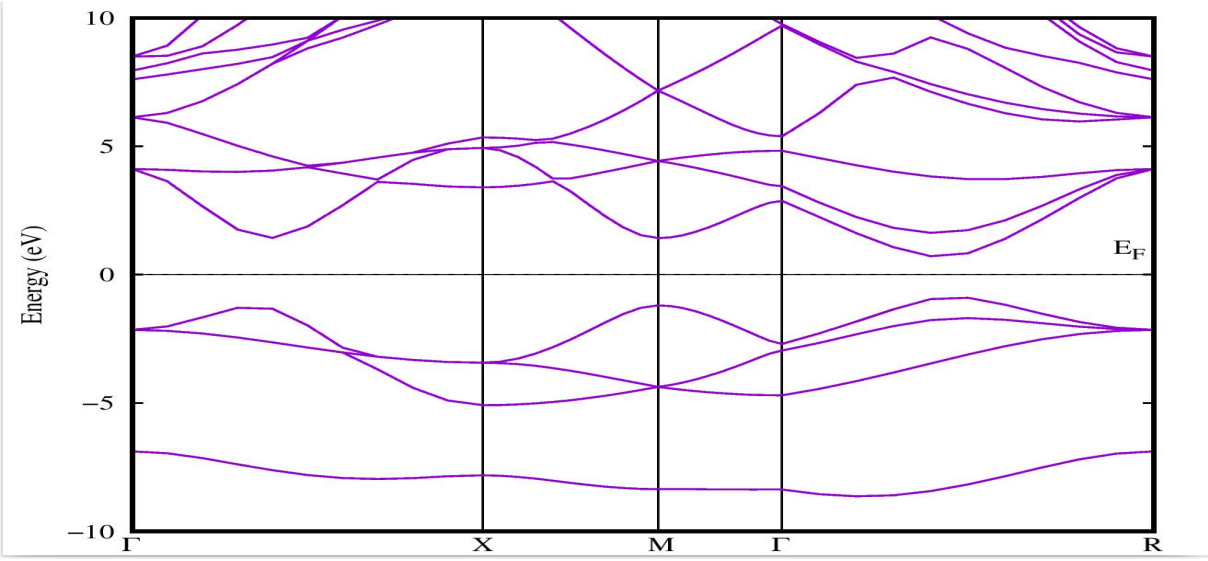

Figure 4.2: Up band spin for Pbse Perovskite compound

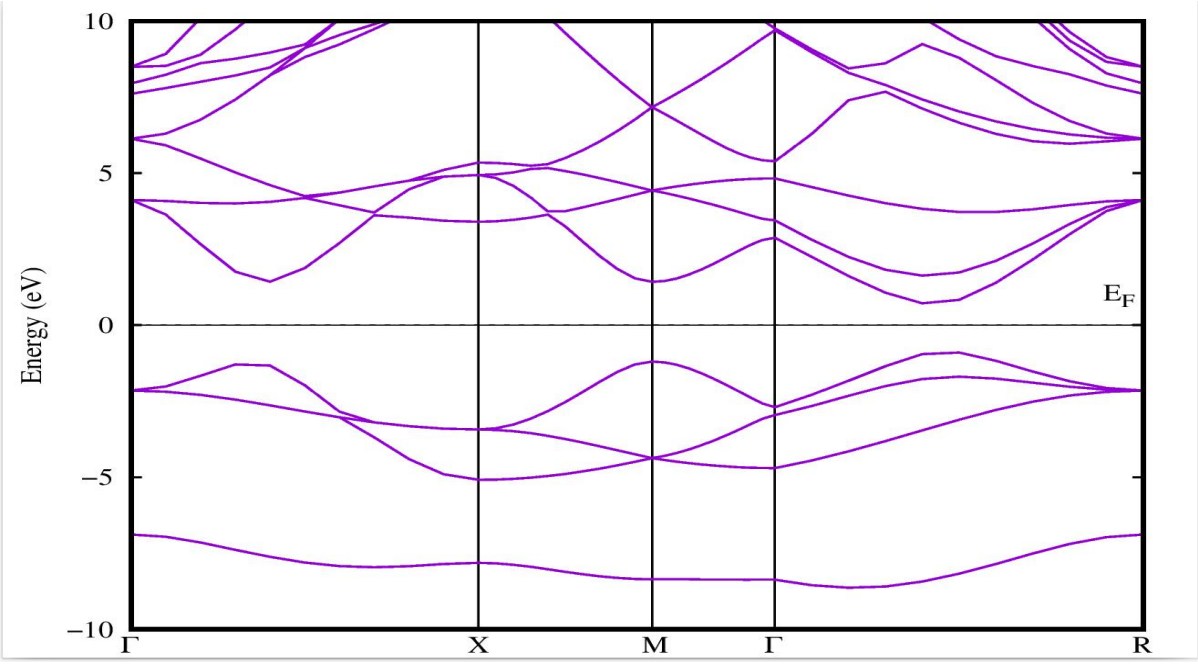

Figure 4.3: Down band spin for PbSe Perovskite compound

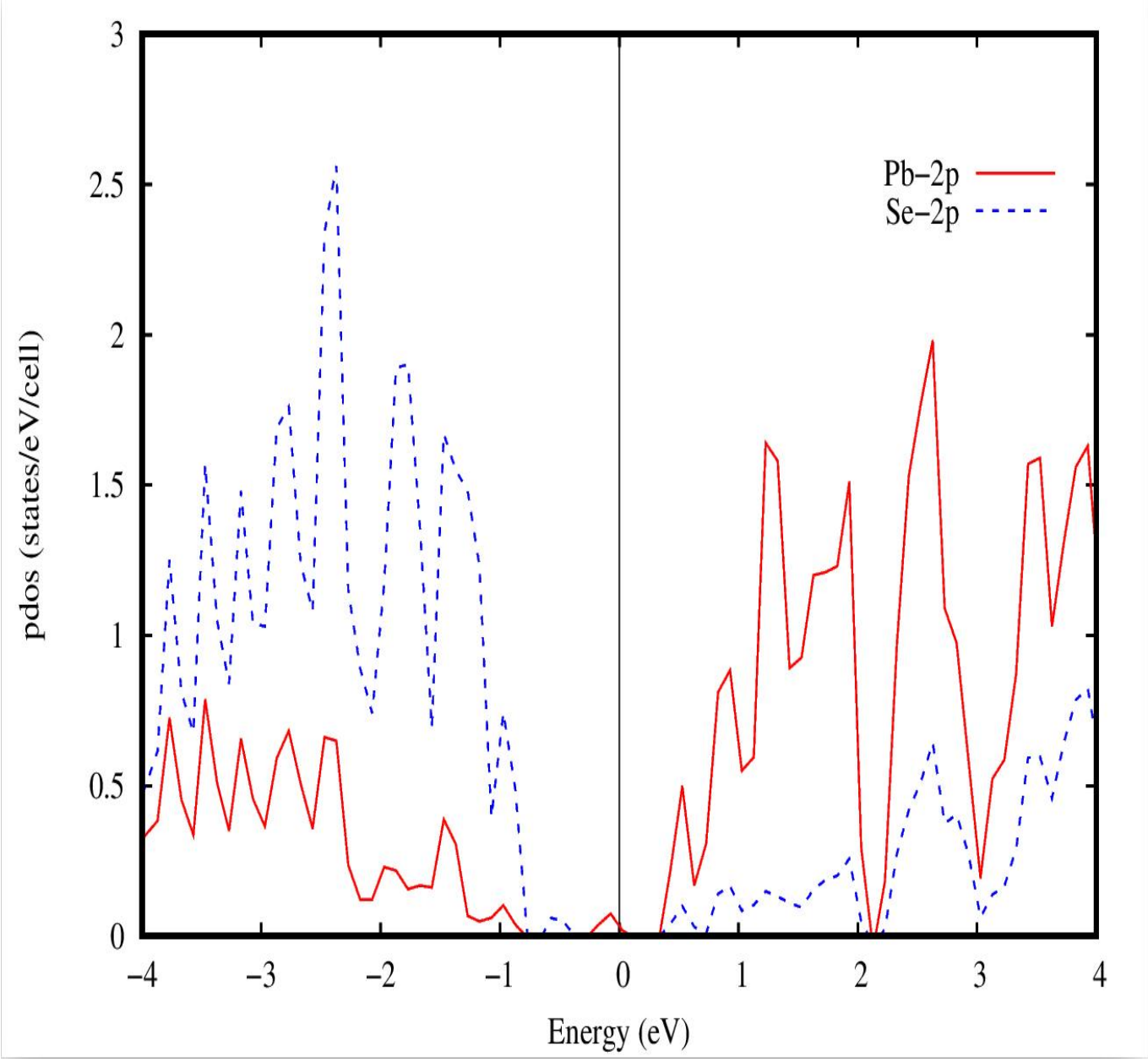

Plate 4.4: Density of state of the PbSe Perovskite compound

CHAPTER 5

5.1 Findings and Conclusion

The optimization, mechanical properties, electronic band structure, and density of states (DOS) of the perovskite material PbSe were examined through first principle calculations using the quantum espresso program. The computations led to the following findings.

1. The physical properties of PbSe have been studied using first principle calculation.
2. From Pugh's ratio (B/G), it shows that the compound is brittle.
3. From the plotted band structure graph, the perovskite compound is a semiconductor

From the calculations, the PbSe Perovskite compound is stable.

5.2 Suggestions for Further Studies

The density of states (DOS), electronic band structure, and mechanical characteristics of the perovskite compound PbSe were calculated from first principles. It is recommended that efforts be made to enhance the utilization of PbSe perovskite compound in photochemistry and photovoltaic applications.

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