Structure Stability and Optical Response of Lead Halide Hybrid Perovskite Photovoltaic Materials: A First-Principles Simulation Study

Siddharth Narendrakumar Rathod
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STRUCTURE STABILITY AND OPTICAL RESPONSE OF LEAD HALIDE HYBRID PEROVSKITE PHOTOVOLTAIC MATERIALS: A FIRST-PRINCIPLES SIMULATION STUDY

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Renewable and Clean Energy Engineering

By

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ABSTRACT


A third-generation of solar cell is based on organic-inorganic hybrid perovskite materials. These have reached up to 22.1% conversion efficiency through exponential growth just within the last decade, compared to much longer improvement times for other photovoltaic technologies. Lead halide perovskites are among the most commonly used materials in this context. Despite the relatively large number of available works on some of these materials, in particular CH₃NH₃PbI₃, others are less investigated. Here, we focused on CH₃NH₃PbCl₃, CH₃NH₃PbBr₃ and CH₃NH₃PbI₃ for assessing structure stability and optical response. Using quantum-mechanics-based first principles approaches, we calculated the optimized structures of these three materials in their cubic phase, followed by their optical response. Structure characteristics including geometrical features, energetics and phonon dispersions were presented and analyzed. Electronic structure calculations and resultant optical characteristics including real and imaginary dielectric constants, refractive index and absorption coefficient were calculated and discussed. Our results showed different stability characteristics for the three structures inferred from cohesive energy and phonon dispersion. The bromide and chloride materials showed narrower ranges of functional optical frequencies compared to iodide
one. However, the former two materials showed increased dielectric constant, refractive index and absorption at lower wavelength compared to those of the latter, indicating possibly better photovoltaic performance at those wavelengths. The results could be useful in feasibility assessments of lead halide hybrid perovskite photovoltaic materials.
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<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>VASP</td>
<td>Vienna ab initio Simulation Package</td>
</tr>
<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
</tr>
<tr>
<td>LDA</td>
<td>Local Density Approximation</td>
</tr>
<tr>
<td>LSDA</td>
<td>Local Spin Density Approximation</td>
</tr>
<tr>
<td>GGA</td>
<td>Generalized Gradient Approximation</td>
</tr>
<tr>
<td>PV</td>
<td>Photovoltaic</td>
</tr>
<tr>
<td>CIGS</td>
<td>Copper Indium Gallium Selenide</td>
</tr>
<tr>
<td>CdTe</td>
<td>Cadmium Telluride</td>
</tr>
<tr>
<td>CZTS</td>
<td>Copper Zinc Tin Sulfide</td>
</tr>
<tr>
<td>DSSC</td>
<td>Dye Sensitized Solar Cell</td>
</tr>
<tr>
<td>OPV</td>
<td>Organic Photovoltaic</td>
</tr>
<tr>
<td>QD</td>
<td>Quantum Dot</td>
</tr>
<tr>
<td>NREL</td>
<td>National Renewable Energy Lab</td>
</tr>
<tr>
<td>PCE</td>
<td>Power Conversion Efficiency</td>
</tr>
<tr>
<td>MA</td>
<td>Methyl-Ammonium</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium Tin Oxide</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
<tr>
<td>HTM</td>
<td>Hole Transport Material</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>FTO</td>
<td>Fluorine doped Tin Oxide</td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray Diffraction</td>
</tr>
<tr>
<td>UPS</td>
<td>Ultraviolet Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>IPES</td>
<td>Inverse Photoemission Spectroscopy</td>
</tr>
<tr>
<td>UV</td>
<td>Ultra Violet</td>
</tr>
<tr>
<td>LED</td>
<td>Light Emitting Diode</td>
</tr>
<tr>
<td>DOS</td>
<td>Density of states</td>
</tr>
<tr>
<td>VASP</td>
<td>Vienna Ab Initio Simulation Package</td>
</tr>
<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
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<tr>
<td>GGA</td>
<td>Generalized-Gradient Approximation</td>
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1. INTRODUCTION

In current scenario, fossil fuels are the primary sources of energy that cause maximum quantity of carbon dioxide and greenhouse gas emissions. Fossil fuels constitute ~85% of world’s energy supply [1]. Existing resources and reserves of fossil fuels are going to be depleted in the near future as predicted. If this happens, energy supply from fossil fuel will be depleted as well. Also, over the last few decades, the average temperature of Earth’s surface has risen by 1.4°F [2]. This small change in average temperature of the planet has led to many drastic changes in climate and weather.

Therefore, there is a real need of advanced clean energy technologies in order to face the global challenges of energy availability, climate change and sustainable energy development. Alternative energy sources will be in need such as solar energy, wind energy, geothermal energy, biogas power, etc. Among renewable energy sources wind and solar are the major contributors.

Solar energy has emerged as the fastest-growing resource of clean energy alternative to conventional energy resources [3]. Solar photovoltaic (PV) is a key technology that is predicted as an attractive alternate energy source in future. In the photovoltaic process, a material converts radiation energy into electrical energy. In most photovoltaic applications, the input is sunlight as radiation energy and the device is generally called a solar cell. Thus, a simple definition of solar cell is a device that produces electricity by using sunlight with the photovoltaic effect. The input features for a photovoltaic solar cell are light absorption, charge separation and carriers extraction to the output circuit. Solar cell technologies are generally categorized into three generations as shown in Figure 1.
First generation solar cells are mainly made up of crystalline silicon material (single and multi). They are typically produced with conversion efficiencies of 15-20%. The second-generation solar cells are based on amorphous silicon (a-Si), CIGS and CdTe thin film solar cells with typical efficiencies of 10-15%. Third generation solar cells use different organic materials such as nanoparticles and small molecules or polymers. Perovskite solar cells are of third-generation type and typically have high efficiency and stability similar to those of the organic solar cells [5].
Figure 2: Historical summary of best research-cell efficiencies for various PV technologies (1975-2016) [6], black oval highlights the efficiency improvement of perovskite solar cells.

The chart shown in Figure 2 published by National Renewable Energy Lab (NREL), shows research and developments in solar cell progress starting from 1975. Different solar cell technologies are considered here, e.g. crystalline and thin-film, single and multi-junction cells, organic cells, quantum dots, dye-sensitized and many more. The graph shows almost linear improvement in efficiency over time for all the different technologies. In just three years, perovskite solar cells have achieved efficiencies comparable to those of other solar technologies that required almost 40 years.

A perovskite solar cell is a compound with hybrid organic-inorganic lead halide (CH$_3$NH$_3$X$_3$, X= Cl, Br, I) material as photovoltaic material. Perovskite solar cell is a promising new technology for clean energy production, with maximum efficiencies
already increased from 3.8% in 2009 [7] to 22.1% in just six years [8]. In addition, they possess unique combination of low material cost, ease of assembly, and potential for further increase of efficiency [9].

1.1 LITERATURE REVIEW

Perovskite structures were named after Lev Perovski, founder of the Russian Geographical Society, and were first found in the Ural Mountains [10]. Lead-halide perovskites, CH$_3$NH$_3$PbX$_3$ (X = Cl, Br, I) are among the important materials for thin film solar cells. Lead-halide perovskite (CH$_3$NH$_3$Pb$_3$) solar cells were introduced first in 2009 and then reached up to 10.9% conversion efficiency in 2012. Further investigation into organic-inorganic hybrid solar cells has expanded vertically, leading to a highest power conversion efficiency (PCE) of 22.1% [8].

Perovskite solar cell materials have properties such as large diffusion, higher optical absorption coefficient, smaller values of effective masses, low fabrication temperature range and less grain boundaries which make them comparable to the current matured technologies such as single crystal silicon and CIGS thin film solar cells [11]. Interestingly, perovskite solar cells have emerged rapidly [12, 13] with very promising properties and efficiencies, similar to those of highly-efficient CIGS and CdTe solar cells.

Hybrid organic-inorganic perovskites can be represented by the general chemical formula ABX$_3$ shown in Figure 3, where A is a large organic cation (positively-charged), such as methyl-ammonium (CH$_3$NH$_3^+$ or MA) in the center of a cubic structure, and B is a metal cation (lead), and X is a halide anion at faces of the cubic structure with negative charge (e.g. Cl$, \text{Br}$, I$)$. Organic-inorganic lead halide structures’ stability is mostly depends on the size of molecule A [14].
Figure 3: A general perovskite crystal structure of the cubic form ABX₃ (solid lines represent crystal orientation) [10]

The cubic structures of perovskite solar cells so far have been generated with the following materials in the typical perovskite form ABX₃:

A = Organic cation – methyl ammonium (CH₃NH₃⁺)
B = Inorganic cation - lead (Pb²⁺)
X₃= Halogen anion - chloride (Cl⁻) or bromide (Br⁻) or iodide (I⁻)

*Figure 4* shows the general cubic crystal structure of lead-halide perovskite photovoltaic material using CH₃NH₃PbI₃. Here, it is clearly seen that organic and inorganic parts of the structure are separated (not connected by direct chemical bonds). The center of cube is made up of methyl-ammonium ion and all the corners contain lead which is connected to halogen ions (I⁻, in this case). Thus, the total volume of cube mostly depends on halogen ions (greater cell volume for I and lower cell volume for Cl) because all other atoms are the same for other lead-halide structures.
Figure 4: Unit cell of the most common perovskite solar cell: CH$_3$NH$_3$PbI$_3$ [15]

Although perovskite materials have different crystal structures, still they can be contained easily within a standard organic photovoltaic (OPV) cell. Until now, the best perovskite structures have been deposited in vacuums that provide uniformity in film qualities, but this procedure needs the evaporation of the organic component (methyl-ammonium) and simultaneously the inorganic component (lead halide). Therefore, specialized evaporation chambers are required for accurate evaporation of these materials and forming the perovskite solar cells. Such chambers are not available to many researchers. Therefore, many researchers currently use computational/simulation methods to accurately calculate properties of perovskite solar cells, to guide subsequent experiments toward promising outcomes.

The structure in Figure 5 represents the generic structure of a perovskite solar cell using a standard glass/ITO (Indium tin oxide) substrate with metal back contact. The glass is the layer which is used to protect the cell from external parameters. ITO is the contact layer which is a transparent material. Perovskite (ABX$_3$) is the main part of the
cell which generates electron-hole pairs collected at the electron- and hole-interface layers. The last part is the metal back contact layer that transfers electrons via cables.

![Generic structure of a standard perovskite solar cell with all layers.](image)

Figure 5: Generic structure of a standard perovskite solar cell with all layers. [10]

The selection of dual interface layers (for $e^-$ and $h^+$) is very important to form a good perovskite solar cell. There is a large collection of researchable materials for interface to be explored, and this field has shown potential for exponential growth during the last six years. Therefore, investigating these solar cells, their optimized structures and interactions of different materials, to find different properties at interfaces creates an opportunity in this area of research [10].

*Figure 6* shows the cross-section of CH$_3$NH$_3$PbI$_3$-sensitized solar cell. The scanning electron microscope (SEM) [16] is a device that generates a focused beam of high energy electrons to create various signals on solid specimens that provide information about the sample such as external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample. In this image, the bottom
layer is fluorine doped tin oxide (FTO) and the multi-junction is made up of CH$_3$NH$_3$PbI$_3$ + TiO$_2$ + hole transport material (HTM). Here, the metal back contact layer is created using Au. The active part thickness in this thin film solar cell is approximately 500 nm.

Figure 6: Scanning electron microscope (SEM) image of CH$_3$NH$_3$PbI$_3$- dye-sensitized solar cell (DSSC) cross section [17]

Crystal structures of MAPbX$_3$ are identified in different phases such as cubic, tetragonal ($a=b=c; \alpha=\beta=\gamma=90^\circ$), and orthorhombic ($a\neq b\neq c; \alpha=\beta=\gamma=90^\circ$) using the X-ray diffraction method (XRD) [18]. X-ray diffraction [19] is a technique used for solid crystal materials that provides information on crystal structure, transition of phases, and external morphology (texturing). CH$_3$NH$_3$PbI$_3$ phases are temperature-dependent: It exhibits phase transition from the orthorhombic ($<160$ K) to the tetragonal phase, and from the tetragonal ($160–330$ K) to the cubic phase ($>330$ K) as temperature rises [20]. Table 1 includes all the phase transitions with temperature for CH$_3$NH$_3$PbX$_3$ (X= Cl, Br, I) structures. Phases of all the structures change from orthorhombic phase to tetragonal
phase and from tetragonal phase to cubic phase upon increasing temperature. Transition temperature range in the case of CH$_3$NH$_3$PbCl$_3$ is short; as it changes phase from orthorhombic phase to tetragonal phase at 172 K and from tetragonal to cubic at 177 K. As for CH$_3$NH$_3$PbBr$_3$, the tetragonal phase is obtained between 149-154 K and transfers into cubic at 236 K. The CH$_3$NH$_3$PbI$_3$ phase transition temperatures are very well known and available in many publications. It changes from orthorhombic phase to tetragonal phase at 161 K and tetragonal phase to cubic phase at 330 K.

Table 1: Crystal systems and transition temperatures of CH$_3$NH$_3$PbX$_3$ (X= Cl, Br, I) [5]

<table>
<thead>
<tr>
<th>Perovskite Materials</th>
<th>CH$_3$NH$_3$PbCl$_3$</th>
<th>CH$_3$NH$_3$PbBr$_3$</th>
<th>CH$_3$NH$_3$PbI$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal Phase</td>
<td>Cubic</td>
<td>Cubic</td>
<td>Cubic</td>
</tr>
<tr>
<td>Transition Temperature (K)</td>
<td>177</td>
<td>236</td>
<td>330</td>
</tr>
<tr>
<td>Crystal Phase</td>
<td>Tetragonal</td>
<td>Tetragonal</td>
<td>Tetragonal</td>
</tr>
<tr>
<td>Transition Temperature (K)</td>
<td>172</td>
<td>149-154</td>
<td>161</td>
</tr>
<tr>
<td>Crystal Phase</td>
<td>Orthorhombic</td>
<td>Orthorhombic</td>
<td>Orthorhombic</td>
</tr>
</tbody>
</table>

MAPbI$_3$ structure parameters for tetragonal and cubic phases, according to X-ray diffraction experiments at different temperatures [21], are shown in Table 2. Close to 330 K, the tetragonal phase starts to diminish. This phase gradually disappear at higher temperatures. Cubic structure starts forming above 330 K. It has less atoms per unit cell
compared to the tetragonal phase. Thus, tetragonal structure requires more time to simulate.

Table 2: Lattice parameters of MAPbI₃ at different temperatures using X-ray diffraction experiments [21]

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>Tetragonal</th>
<th>Cubic</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a (Å)</td>
<td>c (Å)</td>
</tr>
<tr>
<td>298</td>
<td>8.851</td>
<td>12.444</td>
</tr>
<tr>
<td>308</td>
<td>8.855</td>
<td>12.446</td>
</tr>
<tr>
<td>318</td>
<td>8.861</td>
<td>12.460</td>
</tr>
<tr>
<td>328</td>
<td>8.864</td>
<td>12.497</td>
</tr>
<tr>
<td>338</td>
<td>8.865</td>
<td>12.518</td>
</tr>
<tr>
<td>348</td>
<td>8.875</td>
<td>12.525</td>
</tr>
<tr>
<td>358</td>
<td>8.877</td>
<td>12.526</td>
</tr>
</tbody>
</table>

*Figure 7* shows the phonon dispersion of CH₃NH₃PbI₃ [21], calculated using the harmonic approximation, calculation of force constants, density functional theory (DFT), and cubic phase using 2 × 2 × 2 supercell.
Figure 7: Phonon dispersion properties of the cubic phase of CH$_3$NH$_3$PbI$_3$ [21]

Here negative frequencies are found at the zone boundaries ($R$ and $M$) that show instability which are possibly shown for the perovskite structure. This shows a temporal characteristic of the hybrid perovskite structures [21, 56-58]. The temporal characteristic concerns orientation of the organic and inorganic parts of the unit cell.

Figure 8: Energy band gaps of various halide perovskite films (CH$_3$NH$_3$PbI$_3$, CH$_3$NH$_3$PbBr$_3$, and CH$_3$NH$_3$PbI$_3$) experimentally derived by ultraviolet photoelectron spectroscopy (UPS) and inverse photoemission spectroscopy (IPES). [26]
The electronic band structure of lead halide CH₃NH₃PbX₃ perovskite films are presented in Figure 8. In ultraviolet photoelectron spectroscopy (UPS), ultraviolet (UV) photons are used to probe the elemental distribution within a solid. UPS technique requires an ultrahigh vacuum to retain the quality of emitted photons, an electron detector and a UV photon source [23]. UPS is a very useful technique to determine the work function of the material being analyzed and is finding increasing application in characterization of organic and inorganic photovoltaics and organic Light Emitting Diodes (LEDs) [24]. Inverse photoemission spectroscopy (IPES) can be considered as the "time reversal" version of the photoemission process [25]. The material absorbs an electron, from electron gun, in an unoccupied band above the Fermi level, and emits a photon when the electron loses energy by going to lower energy (impurity) state above the valence band maximum. Interestingly, the halide substitution from I to Br and then to Cl will increase the gap energy \( E_g \) from 1.70 eV for CH₃NH₃PbI₃ to 2.32 eV for CH₃NH₃PbBr₃ and to 3.09 eV for CH₃NH₃PbCl₃.
Figure 9: Experimental Result of Absorption spectra of MAPbCl$_3$, MAPbBr$_3$, MAPbI$_3$, films [26]

Figure 9 shows the absorption spectra of CH$_3$NH$_3$PbX$_3$ perovskite, which shift to shorter wavelength by replacing the halide atom from I to Br to Cl. An absorption peak of CH$_3$NH$_3$PbI$_3$ is found at about 780 nm, while that of CH$_3$NH$_3$PbCl$_3$ appears at $\sim$410 nm. It is noted that the absorption peaks of CH$_3$NH$_3$PbX$_3$ perovskite films exhibit a trend similar to that of the gap energies observed in UPS/IPES-determined $E_g$ in Figure 8. Therefore, halide substitution provides an effective way to tune the absorption capability of CH$_3$NH$_3$PbX$_3$ perovskite films covering a broad region of thresholds from 410 to 780 nm.

1.2 THESIS OBJECTIVES

In this work, we focused on cubic phase of perovskite solar cells using different materials - CH$_3$NH$_3$PbCl$_3$, CH$_3$NH$_3$PbBr$_3$ and CH$_3$NH$_3$PbI$_3$ and presented the results of calculations for their structural, electronic and optical properties using first-principle computational methods.

For structural stability assessments, we initially use the structures which are reported in published literature [21]. As our optimization procedure was different, including e.g. van der Waals interactions, we optimized these structures by minimizing their energies. We calculated electron charge density, cohesive energy and phonon dispersion curve of each structure.
After getting optimized structures, we found electronic properties such as electronic band structure, bandgap and density of states (DOS) for halide structures. We plotted band structures and obtained bandgaps to compare with available published results.

Lastly, the aim was to get the optical responses of perovskite solar cells, e.g. real and imaginary parts of the dielectric constant, refractive index, absorption coefficient, and their implications towards photovoltaic application.

1.3 THESIS OUTLINE

Chapter 2 illustrates the methodology, i.e. brief introduction of first-principles electronic structure calculations using plane wave basis. It also includes a brief discussion of the density functional theory (DFT). The approximation methods involve in DFT are discussed briefly as well.

Chapter 3 includes our results and discussion. It begins with the structural properties of the cubic phase of CH$_3$NH$_3$PbCl$_3$, CH$_3$NH$_3$PbBr$_3$ and CH$_3$NH$_3$PbI$_3$. The electronic structure of the perovskite materials is investigated by DFT calculations, and the impacts on other properties are discussed. At the end, the results of optical properties are presented and analyzed.

Chapter 4 briefly describes the conclusions of this research work.

Chapter-5 includes all the references used in this research work.
2. METHODOLOGY

In this chapter, we explain basics of the simulation method implemented in the program Vienna Ab Initio Simulation Package (VASP) [27-30] used to obtain results reported in this thesis. VASP is a quantum-mechanics-based simulation tool for atomistic materials modelling such as calculations of electronic structures and quantum-mechanic simulation of molecular dynamics (MD), from first principles using plane wave basis. The Following section describes the first principles approach with explanations of necessary terms used for calculations.

2.1 FIRST-PRINCIPLES ELECTRONIC STRUCTURE CALCULATIONS USING PLANE WAVE BASIS

For first-principles materials modeling, the Schrödinger equation is expressed and solved in matrix form. This is achieved using a set of basis functions. A plane-wave basis is the basic method for a system with periodicity (in a system with periodic boundary conditions) and provides several benefits [31]. Two main benefits are: the basis is not related to the positions of atom and only wavelength (of the highest Fourier mode) is used in the calculation that needs to be changed to get proper convergence. In our calculations, we computed, using first principles, total system energy and forces on atoms, within density functional theory (DFT) as implemented in the code VASP. In most of the cases, DFT result shows agreement with the experimental result and the computational costs for DFT calculations are low when compared to other traditional methods [32]. This is the reason why DFT is widely used in recent years. So, let us now discuss DFT and its few approximations.
2.2 DENSITY FUNCTIONAL THEORY (DFT)

DFT is a quantum mechanical computational method used to determine the electronic structure of atoms or molecules [33, 34]. Electronic structure can be explained as the state of the electrons in a static electric field created by atomic nuclei. In general, the nucleus is heavy and assumed to be stable when compared to an atom’s electrons. On the other hand, electrons are light in weight with more pronounced quantum character. Hence, electronic structure is considered as a quantum mechanics problem. Here, we use functions of another function called functional to determine the properties of atoms or crystals.

Any quantum problem associated with matter or waves can in principle be solved using Schrödinger equations. So, let us understand some of the basics of Schrödinger equation. In general, we have time-dependent and time-independent Schrödinger equations, but first let us focus only on the time-independent equation [35, 36]. This equation is essential for predicting the wave functions as standing waves which are called stationary states. The general time independent Schrödinger equation is [35, 36]:

\[ \hat{H} \Psi = E \Psi \]  \hspace{1cm} (1)

Where \( \Psi \) is the wave function, \( E \) is the energy and \( \hat{H} \) is the Hamiltonian operator [36]. In the above equation, the Hamiltonian operator acts on the wave function \( \Psi \) and the result is directly proportional to wave function \( \Psi \). \( \Psi \) is called the stationary state and the corresponding \( E \) is the energy of the state \( \Psi \).

The Schrödinger wave equation for a single particle under the influence of external potential \( V \) (such as the one that causes an electric field) is [37]:

\[ \left[ \left( \frac{-\hbar^2}{2m} \right) \nabla^2 + V(r) \right] \Psi(r) = E \Psi(r) \]  \hspace{1cm} (2)
For many-body electronic structure calculations where nuclei are treated as fixed centers that create static potential $U$, the time independent Schrödinger equation is as follows:

$$\hat{H}\psi = [\hat{T} + \hat{U} + \hat{V}]\psi$$  \hspace{1cm} (3)

### 2.3 EXCHANGE CORRELATION APPROXIMATIONS

In a system of many interacting particles, the effects of exchange and correlation are crucial for an accurate description of its behavior. Exchange energy is the energy corresponding to exchange of two or more electrons in their positions with the same spin, and correlation energy is the difference between the total system energy and the sum of kinetic, potential, and exchange energies. These arise from the quantum-mechanical characteristics of electron wave function. To include these energies, there are a few approximations which can be used. The most widely used two approximations are local-density approximation (LDA) and generalized gradient approximation (GGA). Let us discuss a few points regarding these two approximations.

### 2.4 LOCAL DENSITY APPROXIMATION (LDA)

As most of the properties of solids depend on total energy calculations, it is essential to get accurate values of total energy. But the calculation of exchange-correlation energy is a difficult task. So, we have certain approximations which help us in estimating the exchange-correlation energy. According to the Hohenberg-Kohn theorem every energy term including exchange-energy is a function of electron density [38]. An approximate way of describing the exchange-correlation energies is local density approximation (LDA). This approximation is usually used for pseudopotential calculations. In the LDA
we assume that the exchange-correlation energy at position \( r \) in the system’s electron gas is equal to \([39]\),

\[
E_{xc}^{LDA} = \int \rho(r) \varepsilon_{xc}(\rho) dr,
\]

where \( \varepsilon_{xc}(\rho) \) is the exchange-correlation energy of a uniform electron gas of density \( \rho \).

The exchange-correlation potential is then given by \([40]\)

\[
v_{xc}^{LDA}[\rho(r)] = \frac{\delta E_{xc}^{LDA}}{\delta \rho(r)} = \varepsilon_{xc}(\rho) + \rho(r) \frac{\partial \varepsilon_{xc}(\rho)}{\partial \rho}
\]

One determines the exchange-correlation energy considering a uniform electron gas to use LDA in calculations. Usually, it is common to separate \( \varepsilon_{xc}(\rho) \) into exchange and correlation potentials: \( \varepsilon_{xc}(\rho) = \varepsilon_x(\rho) + \varepsilon_c(\rho) \). The exchange potential is given by \([41]\)

\[
\varepsilon_x[\rho(r)] = -\frac{3}{4} \left( \frac{3}{\pi} \right)^{1/3} [\rho(r)]^{1/3}
\]

Accurate values for \( \varepsilon_c(\rho) \) have been determined from Quantum Monte Carlo (QMC) calculations \([42]\). It is assumed that exchange-correlation energy is totally local in the LDA approximation. It also ignores the effect of nearby inhomogeneity in electron density on energy.

2.5 GENERALIZED GRADIENT APPROXIMATION (GGA)

GGA is also a local approximation but the difference is that it considers the gradient factor of electron density at the same location:

\[
E_{xc}^{GGA}[n_{\uparrow},n_{\downarrow}] = \int \varepsilon_{xc}(n_{\uparrow},n_{\downarrow},\nabla n_{\uparrow},\nabla n_{\downarrow}) n(r) d^3r
\]

Here the \( \nabla \) terms refer to the gradient terms of electron density. GGA accounts for inhomogeneity while LDA does not. Several functional are available for GGA. For example, this functional can be expressed as:
\[ E_{XC}^{GGA}[n] = -C_x \int n^{4/3} F(s) dr, \]  
(8)

\[ s = \frac{v_n}{2k_F n}. \]  
(9)

Here, \( s \) is the measure of inhomogeneity, \( k_F \) is the wave vector of homogenous electron gas with density \( n \). These are a few of the most commonly used approximations in DFT.

### 2.6 PSEUDOPOTENTIALS

Pseudopotentials represent core electrons and nuclei for calculating energies of outer-shell electrons. Pseudopotentials are a necessary element of all plane-wave methods. They can be used in methods with local-basis set to decrease the computational time. There are two methods used for generating pseudopotentials: ‘norm-conserving’ pseudopotentials [42] and “ultra-soft” pseudopotentials. The ultra-soft pseudopotentials applies to systems with first row elements (s- and p-) and for systems with d- or f-electrons.

In calculations involving pseudopotentials, if overlap between valence and core-electron densities is not negligible, one needs non-linear core corrections. This creates a problem in pseudopotential calculations. The projected-augmented wave method is an alternative to resolve this deficiency.

### 2.7 PROJECTOR-AUGMENTED WAVES

The projector-augmented wave (PAW) method was first introduced by Blöchl [43]. This is a method used to achieve higher efficiency in computations of the pseudopotential method and accurate result of the full-potential linearized augmented-plane wave
(FLAPW) method. This is generally known as the benchmark for DFT calculations on solids. Unlike the pseudopotential approach described in section-2.6, the PAW method causes orthogonality of the valence orbitals and core orbitals, which is crucial for correct quantum-mechanical calculations.

2.8 VAN DER WAALS DENSITY FUNCTIONALS

For systems including interacting parts without direct chemical bonds, such as interactions between the organic and inorganic parts in lead halide perovskites considered here, inclusion of van der Waals forces is necessary. The van der Waals density functional (vdW-DF) of Dion et al. [44] is a promising approach for including dispersion in approximate density functional theory exchange-correlation functional. Popular local and semi local density functionals are unable to describe correctly van der Waals interactions resulting from dynamical correlations between fluctuating charge distributions. A pragmatic method to work around this problem is to add a correction term to the conventional Kohn-Sham DFT energy,

$$E_{\text{DFT-disp}} = E_{\text{KS-DFT}} + E_{\text{disp}}. \quad (10)$$

The term $E_{\text{disp}}$ is computed using available approximate methods. By adding the vdW term to potential energy, forces between atoms, stress tensor, lattice parameters relaxations, molecular dynamics (MD), and analysis of vibrational properties, the result will all become more realistic when non-bonding interactions are present in the system.

2.9 PERDEW-BURKE-ERNZERHOF REVISED FOR SOLIDS (PBESOL)

PBESol is a GGA approach that improves simulations of solid materials and their surfaces by appropriately restoring the gradient expansion [51]. Standard GGA
approaches are better suited for free-atom calculations, not for solid systems. Restoring the gradient expansion improves the description for solid materials.

2.10 STRUCTURAL PROPERTIES CALCULATION SETUP

We performed optimization with relaxing atomic positions using the PBEsol semi local exchange-correlation functional. The projector-augmented wave (PAW) method was employed. All atomic forces were selected to reduce under a threshold value of 1 meV/Å. A plane wave cutoff of 500 eV is used throughout. Calculations of lead halide-organic-inorganic hybrid perovskite compounds with 12 atoms per cubic unit cell use a Γ-centered 4x4x4 k-point mesh. van der Waals interactions are included. Using these settings, we have optimized the structures of CH₃NH₃PbX₃.

2.11 VIBRATIONAL PROPERTIES

The phonon dispersion curve has implications in development of quantitative models for the generation, transport, and recombination of photo-generated pairs (e⁻ and h⁺) in hybrid perovskite solar cells. The phonon dispersion curve across the first Brillouin zone is reported already for the cubic phase of CH₃NH₃PbI₃ [21]. One challenge in calculating the phonons of hybrid perovskites is the soft nature and complicated potential-energy landscape of some of the restoring potentials, particularly those involving the organic cation. Negative values are found at the boundary of the Brillouin zone of the cubic phase which shows instabilities of structure. We have calculated phonon frequencies using finite difference method to obtain second derivatives of energy with respect to distance.
Phonon dispersion has been calculated using supercells and parameters identical to those which yielded the lowest energies for all the structures. The conversion factor of 1 THz = 33.4 cm\(^{-1}\) was applied. The default amplitude of atomic displacements of 0.01 Å was used. The calculations yielded phonon dispersion and form factors, phonon density of states and thermodynamic functions.

2.12 ELECTRONIC PROPERTIES

The energy band gap corresponds to the amount of energy needed from the source of light for conduction. During conduction, a hole is created where an electron was formerly bound. The energy level of below the band gap is valence band (with highest energy \(E_V\)) and the energy level where an electron is free above the band gap is conduction band (with lowest energy \(E_C\)). The energy difference between the lowest energy of the conduction band and the highest energy of the valence band is the bandgap.

Semiconductors can have direct band gap or indirect band gap. A direct band gap has the band edges aligned in \(k\)-mesh, so that with the emission of a photon, an electron can transit from the valence band to the conduction band without changing considerably its momentum. In the indirect band gap, the band edges do not occur at the same \(k\) so the electron transfer from valence band to the conduction band is accompanied by change in momentum.

The density of states (DOS) provides information of the number of states available for each energy level. A large value for the conduction band density of states represents a large number of states that can be occupied.
Using the optimized structures of CH$_3$NH$_3$PbX$_3$ we have calculated and compared their electronic band structure including band gap.

2.13 OPTICAL PROPERTIES

The optical properties (dielectric function, refractive index, and absorption coefficient) were obtained utilizing the calculation program VASP using a 4x4x4 Monkhorst-Pack $k$-point mesh along with electronic bands. The complex dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ (where $\varepsilon_1$ is the real part and $\varepsilon_2$ is the imaginary part) represents the main optical characteristics for a semiconductor material. The real part $\varepsilon_1$ of the dielectric function was obtained from the Kramers-Kronig transformation using the following equation [45-47]:

$$\varepsilon_1(\omega) = 1 + \frac{2}{\pi} P \int_0^\infty \frac{\varepsilon_2(\omega')\omega'}{\omega'^2 - \omega^2 + i\eta} d\omega'$$  \hspace{1cm} (11)

here $P$ is the principal value and $\eta$ is an infinitesimal number.

The imaginary part $\varepsilon_2$ of the dielectric function was calculated using the following equation [46, 47]:

$$\varepsilon_2(\omega) = \frac{4\pi^2e^2}{\Omega} \lim_{q \to 0} \frac{1}{q^2} \sum_{c,v,k} 2w_k \delta(E_{ck} - E_{vk} - \omega) \times \langle u_{ck+e_\alpha q} | u_{vk} \rangle \langle u_{ck+e_\beta q} | u_{vk} \rangle$$ \hspace{1cm} (12)

where $e$ is the charge of electron, $\Omega$ is the volume of primitive cell, $w_k$ is the weight of the $k$-points, and $e_\alpha$ and $e_\beta$ are the unit vectors for the X, Y and Z Cartesian directions. Here, $c$ and $v$ refers to the conduction band (CB) and valence band (VB) respectively. $E_{ck}$ and $E_{vk}$ are the energy state of single-electron at conduction band and valence band at wave vector $k$, and $u_{ck}$ and $u_{vk}$ are the periodic portion of the Bloch state corresponding to the eigenvalue $E_{ck}$ and $E_{vk}$.
The dielectric constants relate to energies of the VB\textsubscript{max} and CB\textsubscript{min}, i.e. relate to the energies close to the band-gap. Therefore, the calculated dielectric constants deliver further information in the analysis of the electronic structure of these materials, and vice versa. All the other optical properties such as absorption coefficient $a(\omega)$ and the refractive index $n(\omega)$ can be calculated using the values of $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ [48, 49].

The following equation shows the relationship between real dielectric constant, imaginary dielectric constant, refractive index, and reflectivity [50],

$$n = \frac{1}{\sqrt{2}} \sqrt{\varepsilon_1^2 + \varepsilon_2^2 + \varepsilon_1} \quad (13)$$

$$R = \frac{\sqrt{\varepsilon_1^2 \varepsilon_2^2 + 1} - \sqrt{2(\sqrt{\varepsilon_1^2 \varepsilon_2^2 + \varepsilon_1})}}{\sqrt{\varepsilon_1^2 \varepsilon_2^2 + 1} + \sqrt{2(\sqrt{\varepsilon_1^2 \varepsilon_2^2 + \varepsilon_1})}} \quad (14)$$

where, $\varepsilon_1$ is real part of dielectric constant, $\varepsilon_2$ is imaginary part of dielectric constant, $n$ is the refractive index, and $R$ is reflectivity. According to the definition of direct transition probability and Kramers-Kronig relations, we can deduce the reflectivity from following equation [50]:

$$R = \frac{(n-1)^2}{(n+1)^2} \quad (15)$$

The absorption coefficient $a(\omega)$ was obtained directly from the dielectric functions using the expression [46]:

$$a(\omega) = \left(\sqrt{2} \omega^2 / c\right) \left[\varepsilon_1(\omega)^2 + \varepsilon_2(\omega)^2 - \varepsilon_1(\omega)\right]^{1/2} \quad (16)$$

where $c$ is the speed of light.
3. RESULTS AND DISCUSSION

3.1 GEOMETRIC STRUCTURE AND OPTIMIZATION

Our initial step to obtain a stable structure is to optimize the atomic structure to its minimum energy. Thus, ab initio DFT calculations were performed using Vienna Ab Initio Simulation Package (VASP) to optimize CH$_3$NH$_3$PbCl$_3$, CH$_3$NH$_3$PbBr$_3$ and CH$_3$NH$_3$PbI$_3$ structures. We optimized electronic structures using DFT method with the exchange-correlation functional of Perdew, Burke, and Ernzerhof revised for solids (PBEsol) [55]. The Brillouin zone was sampled with Γ-centered $k$-point grids of 4×4×4 for all unit cells. The cutoff energy for plane-wave basis was set to 500 eV for the optimization calculations. The convergence threshold for residual forces exerted on the ions was $10^{-3}$ eV/Å. The van der Waals (vdW) interactions were also considered to model non-bonding interactions. All structures were obtained using 12 atoms per cubic unit cell; including one carbon atom, one nitrogen atom, six hydrogen atoms, one lead atom and three halogen atoms (Chlorine, Bromine and Iodine). The calculation was performed with fixed shape and volume of the unit cell that was obtained from previous published results [21]. Conjugate-gradient method was used for relaxing ions’ position by calculating forces including vdW interactions. Optimized unit cells of organic-inorganic halide structure are shown in Figure 10 (a), (b), (c).
Figure 10: Optimized Perovskite Structures (a) CH$_3$NH$_3$PbCl$_3$, (b) CH$_3$NH$_3$PbBr$_3$, (c) CH$_3$NH$_3$PbI$_3$
Total volume of CH$_3$NH$_3$PbCl$_3$ unit cell is 183.25 Å$^3$, CH$_3$NH$_3$PbBr$_3$ unit cell is 207.47 Å$^3$, and CH$_3$NH$_3$PbI$_3$ unit cell is 249.62 Å$^3$. The overall volume depends on the halogen atom in the structure. The distance Pb-Cl atom is 2.896 Å, Pb-Br is 2.966 Å and Pb-I atom is 3.127 Å. This shows that the replacement of the halogen has a strong influence on the crystallographic data.

The structural parameters for halide structures are listed in Table 3. The lattice parameters were 5.68 Å for CH$_3$NH$_3$PbCl$_3$, 5.92 Å for CH$_3$NH$_3$PbBr$_3$ and 6.29 Å for CH$_3$NH$_3$PbI$_3$, in accordance with the published source [21], and with the fact that radius of halogen elements increase with increasing atomic numbers that affect the lattice constants of CH$_3$NH$_3$PbX$_3$. The computational setup is summarized in Table 3; here Z represents the number of unit cell:

<table>
<thead>
<tr>
<th>Cubic Structure</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>Z</th>
<th>Cutoff (eV)</th>
<th>k points</th>
<th>Force Threshold (eV/Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$NH$_3$PbCl$_3$</td>
<td>5.68</td>
<td>5.68</td>
<td>5.68</td>
<td>1</td>
<td>500</td>
<td>4×4×4</td>
<td>1×10$^{-3}$</td>
</tr>
<tr>
<td>CH$_3$NH$_3$PbBr$_3$</td>
<td>5.92</td>
<td>5.92</td>
<td>5.92</td>
<td>1</td>
<td>500</td>
<td>4×4×4</td>
<td>1×10$^{-3}$</td>
</tr>
<tr>
<td>CH$_3$NH$_3$PbI$_3$</td>
<td>6.29</td>
<td>6.29</td>
<td>6.29</td>
<td>1</td>
<td>500</td>
<td>4×4×4</td>
<td>1×10$^{-3}$</td>
</tr>
</tbody>
</table>
3.2 ELECTRON CHARGE DENSITY

Electronic charge density maps were obtained from wave function and electronic density matrices that describe the density in an area. For visualization, the unit cell was expanded in the program VESTA [52]. *Figure 11* shows the electron charge density with the same threshold value for all the structures (*Table 4*).
Figure 11: Electron Charge Density with same threshold value for the structures (a) CH$_3$NH$_3$PbCl$_3$, (b) CH$_3$NH$_3$PbBr$_3$, and (c) CH$_3$NH$_3$PbI$_3$, (d) 3D-view of all structures
Changing from Cl to I, the saturation level reduces due to electronegativity of halogen atom being higher in Cl compared to I. Electronic density isolines around carbon and nitrogen atoms show the formation of dipoles between these atoms. For Cl, the isolines are overlapped with neighbor halide atom (Cl). For Br, the isolines are nearly touching the neighbor halide atom (Br) and for I, the isolines are separated from neighbor halide atom (I). The electron charge density threshold values calculated for halide structures are listed in Table 4.

Table 4: Calculated threshold values for charge density of mixed halide structures. All values are in electrons/bohr$^3$

<table>
<thead>
<tr>
<th></th>
<th>CH$_3$NH$_3$PbCl$_3$</th>
<th>CH$_3$NH$_3$PbBr$_3$</th>
<th>CH$_3$NH$_3$PbI$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Set Threshold Value</td>
<td>0.107</td>
<td>0.107</td>
<td>0.107</td>
</tr>
<tr>
<td>Min Saturation Level</td>
<td>0.001</td>
<td>-0.095</td>
<td>-0.100</td>
</tr>
<tr>
<td>Max Saturation Level</td>
<td>0.568</td>
<td>0.568</td>
<td>0.567</td>
</tr>
</tbody>
</table>

The visualization threshold value for all the structures stays the same (0.107 electrons/bohr$^3$). But, minimum and maximum saturation level vary from -0.100 to 0.568. The minimum saturation value varies from -0.100 for CH$_3$NH$_3$PbI$_3$ to 0.001 for CH$_3$NH$_3$PbCl$_3$, and maximum saturation value varies from 0.567 for CH$_3$NH$_3$PbI$_3$ to 0.568 for CH$_3$NH$_3$PbCl$_3$. Moving from I to Cl, the result shows maximum saturation level for Cl and minimum saturation level towards I which shows the electronegativity of the atoms affects the saturation level in the Figure 11.
Figure 12: Electron charge densities at planes with maximum interaction for CH$_3$NH$_3$PbI$_3$ and CH$_3$NH$_3$PbBr$_3$ using DFT calculations [53]

Comparing Figure 11 with results from literature [53] depicted in Figure 12, we can see results different from our charge density. In our results, there is charge isolation between Pb and I molecule that shows less ionic charge density on I in CH$_3$NH$_3$PbI$_3$ compared to the charge density on Br in CH$_3$NH$_3$PbBr$_3$. This is consistent with the increased electronegativity of Br compared to I. However, in the case shown in Figure 12, the charge density on I in CH$_3$NH$_3$PbI$_3$ appears to be higher (red color) compared to the charge density on Br in CH$_3$NH$_3$PbBr$_3$ (green color). This difference is attributed to the fact that we have used fixed charge density value for visualization on the same planes whereas Ref. [53] has used different planes (and orientations) corresponding to maximum interaction.

In addition to charge density, to estimate the structural stability, we analyzed the cohesive energy which is difference between the total energy of total MAPbX$_3$ and the sum of individual atom energies by the following formula [54]:
\[ E_{\text{cohe}} = E_{\text{MAPbX}_3} - \sum_{i=1}^{n} n_i E_i \]  

Here, \( E_{\text{cohe}} \) is Cohesive Energy, \( E_{\text{MAPbX}_3} \) is total energy of MAPbX\(_3\), \( i \) indicates different atoms and \( n \) indicates the number of atoms in a unit cell. The calculated cohesive energies for CH\(_3\)NH\(_3\)PbCl\(_3\), CH\(_3\)NH\(_3\)PbBr\(_3\) and CH\(_3\)NH\(_3\)PbI\(_3\) are shown in Table 5.

Table 5: Calculated Cohesive Energy for halide perovskite solar cells

<table>
<thead>
<tr>
<th>Structure</th>
<th>CH(_3)NH(_3)PbCl(_3)</th>
<th>CH(_3)NH(_3)PbBr(_3)</th>
<th>CH(_3)NH(_3)PbI(_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cohesive Energy</td>
<td>-40.541</td>
<td>-38.977</td>
<td>-36.831</td>
</tr>
</tbody>
</table>

We can see from Table 5, cohesive energies are -40.541, -38.977 and -36.831 for CH\(_3\)NH\(_3\)PbCl\(_3\), CH\(_3\)NH\(_3\)PbBr\(_3\) and CH\(_3\)NH\(_3\)PbI\(_3\), respectively. CH\(_3\)NH\(_3\)PbCl\(_3\) has the lowest cohesive energy, which indicates the most stable structure relative to the other structures. CH\(_3\)NH\(_3\)PbI\(_3\) has the highest cohesive energy, which indicates a less stable structure than other structures. Thus, the fabrication process of CH\(_3\)NH\(_3\)PbCl\(_3\) could be more feasible compared to the fabrication of a CH\(_3\)NH\(_3\)PbI\(_3\) perovskite solar cell.

3.3 PHONON DISPERSION

The phonon dispersion curves depict vibrational properties and can be used to assess stability of the structure. Furthermore, the phonon dispersion has implication for the generation, transport, and recombination of photo-generated pairs (e\(^-\) and h\(^+\)) in hybrid perovskite solar cells.
Figure 13: Phonon dispersion of (a) CH$_3$NH$_3$PbCl$_3$, (b) CH$_3$NH$_3$PbBr$_3$, (c) CH$_3$NH$_3$PbI$_3$
For our calculated phonon dispersions, the supercell cell contained 96 atoms as we took 2×2×2 supercell for all three materials, and used a 4×4×4 grid for \( k \)-point sampling. The phonon dispersion curves are calculated within the harmonic approximation, using the tool PHONOPY [55] to construct and evaluate the force constant matrix within DFT method. The phonon dispersions across the first Brillouin zone are shown for the cubic perovskite structures in *Figure 13*.

As is seen from *Figure 13*, phonon dispersions of CH\(_3\)NH\(_3\)PbCl\(_3\), CH\(_3\)NH\(_3\)PbBr\(_3\) and CH\(_3\)NH\(_3\)PbI\(_3\) have been plotted in the range of frequency values of -20 to 160 cm\(^{-1}\) and \( k \)-points along the high-symmetry directions in reciprocal lattice. The Brillouin zone directions for plotting the dispersion curves are selected as R-Γ-M-X. For CH\(_3\)NH\(_3\)PbI\(_3\), negative frequencies are found at R and M points in the reciprocal lattice with corresponding negative values approximately equal to ~ -12 cm\(^{-1}\). In the cases of CH\(_3\)NH\(_3\)PbCl\(_3\) and CH\(_3\)NH\(_3\)PbBr\(_3\), negative frequencies are found only at the point R with the same approximate value of ~ -15 cm\(^{-1}\). Also, we obtained maximum frequencies of 165 cm\(^{-1}\), 158 cm\(^{-1}\) and 143 cm\(^{-1}\) for CH\(_3\)NH\(_3\)PbCl\(_3\), CH\(_3\)NH\(_3\)PbBr\(_3\) and CH\(_3\)NH\(_3\)PbI\(_3\), respectively. It is noticed that changing from Cl to Br to I results mostly in decreased phonon dispersion peaks, which show lower frequency vibrations. This can be associated with increased atomic mass while changing from Cl to Br to I.

Comparing *Figure 7* in Chapter 1 that shows phonon dispersion for CH\(_3\)NH\(_3\)PbI\(_3\) from reference [21] with *Figure 13*, we can see a similar trend of phonon dispersion curves. The small deviations are expected due to different input settings in calculations: 2×2×2 super cell, 500 eV energy cut-off, 4×4×4 \( k \)-point mesh in our calculation compared to 3×3×3 super cell, 700 eV energy cut-off, 6×6×6 \( k \)-point mesh in the calculation of
reference [21]. But the most important difference is that we included van der Waals interactions which were absent in reference [21]. Van der Waals interactions are expected to play an important role in structure optimization and material characteristics as there is no direct bonding between the methyl-ammonium molecule and the inorganic cage. Negative frequency modes are found near R and M points for CH$_3$NH$_3$PbI$_3$ both in our results as well as those published in reference [21]. This refers to a temporal characteristic of the hybrid perovskite structures suggested in reference [21] and discussed in references [56-58]. The temporal variations in structure are associated with temporary methyl-ammonium orientation changes as well as temporary changes of the inorganic cage, as revealed by molecular dynamics simulation [56-58].

3.4 ELECTRONIC BAND STRUCTURE

According to experimental results of previous measurements from the 1990s and 2000s, the halide perovskites are semiconductor materials with band gaps ($E_g$) ranging between ~1.6–3.1 eV [59-62]. In Figure 14, our calculated band gap and band structures of three MAPbX$_3$ structures are shown. The band gap at the R point is indicated and is in good agreement with experiment [26].
Figure 14: Electronic band structure of MAPbX$_3$ where X=Cl (a), Br (b), I (c) in the cubic phase determined from a calculation using $4 \times 4 \times 4$ k-points.
Interestingly, the halide substitution from I to Br and then to Cl will increase the $E_g$ from 1.61 eV for MAPbI$_3$ to 2.09 eV for MAPbBr$_3$ and to 2.89 eV for MAPbCl$_3$. The increasing band gap of MAPbX$_3$ perovskite shifts the threshold of functional optical wavelength to smaller values by changing the halide from I to Br to Cl. Halide substitution therefore provides an effective way to tune the absorption capability of MAPbX$_3$ perovskite films covering threshold from 429 to 770 nm. The bandgap shows blue shift by changing I → Br → Cl in MAPbX$_3$ perovskite materials. More specifically the threshold wavelengths for MAPbCl$_3$, MAPbBr$_3$ and MAPbI$_3$ are 429 nm, 593 nm and 770 nm, respectively. These correspond to purple, green and red regions of the visible light. This variation provides the possibility of targeting different frequency regions of visible light for photovoltaic conversion.

We noticed that the calculated bandgaps and band structure for MAPbI$_3$ agree with the existing results in the literature. In particular, *Figure 8* in Chapter 1 shows the bandgaps for MAPbCl$_3$, MAPbBr$_3$ and MAPbI$_3$, as determined by ultraviolet photoemission spectroscopies (UPS) and inverse photoemission spectroscopy (IPES) spectra, to be 3.09, 2.32 and 1.70 eV, respectively [26]. The maximum relative deviation between these experimental results and our calculated values happens for MAPbBr$_3$ which shows 0.23 eV corresponding to 10% relative error with respect to the experimental values of Ref. [26]. This can be considered as acceptable given possible minor structure differences between the calculated and experimental systems. As for band structure of MAPbI$_3$, a previous study [64] predicted the following diagram:
Figure 15 Electronic band structure of MAPbI$_3$ in the cubic phase. [64]

Comparing Figure 15 with Figure 14 (c), we notice very good agreement. The slight differences are explained by slight difference in methodology (their force threshold is 0.05 eV/Å compared to our threshold which is 0.01 eV/Å, and their basis cut-off energy is 400 eV compared to our basis cut-off energy which is 500 eV).

Figure 16: Calculated Band-gap of MAPbX$_3$ in pusedo-cubic phase determined by Wannier interpolation [63]

Figure 16 shows the bandgap for halide perovskite structures calculated by Wannier interpolation in already published results [63]. This result shows bandgap values 3.07 eV, 2.34 eV, and 1.67 eV for MAPbCl$_3$, MAPbBr$_3$ and MAPbI$_3$, respectively. These values
show a maximum deviation of 0.25 eV for CH$_3$NH$_3$PbBr$_3$ compared to ours. This is due to selection of a different method and parameters in calculation such as 6x6x6 $k$-points used in their optical calculations, whereas we used 4x4x4 $k$-points in our optical calculations, and we included van der Waals interactions in our optimization calculations.

3.5 OPTICAL PROPERTIES

The optical response of perovskite solar cells can be understood by accurately calculating the optical constants such as dielectric constants, refractive index $n$ and absorption coefficient $\alpha$. Therefore, we analyze the optical properties (dielectric function, refractive index, and absorption coefficient) of CH$_3$NH$_3$PbCl$_3$, CH$_3$NH$_3$PbBr$_3$ and CH$_3$NH$_3$PbI$_3$.

The dielectric constant is a complex number that can be determined using, $\varepsilon = \varepsilon_1 + i\varepsilon_2$, where $\varepsilon_1$ is the real part, which corresponds to capacitance in a capacitor, and $\varepsilon_2$ is the imaginary part that corresponds to loss of electromagnetic energy within the material. The dielectric constant corresponds to the polarization of a material in a static electric field that shows why it depends on the value of frequency of that field.

The dielectric function (real and imaginary parts) describes the reaction of the material when the charge density is changed. Our calculated real and imaginary parts of dielectric function are shown in Figure 17 and Figure 18. We estimated the peak values of dielectric constants from the real part and imaginary part of the dielectric function.
Figure 17: Real Components of Dielectric constant ($\varepsilon_r$) of MAPbX$_3$ where, X=Cl (a), Br (b), I (c) in the cubic phase.
Figure 18: Imaginary Components of Dielectric constant ($\varepsilon_2$) of MAPbX$_3$ where, X=Cl (a), Br (b), I (c) in the cubic phase.
The real and imaginary dielectric constants were calculated within the range of 1 to 6 eV. Here, our results show the noticeable changes for every structure, e.g. peaks for real dielectric constants are at 3.15, 2.76 and 2.12 eV for CH$_3$NH$_3$PbCl$_3$, CH$_3$NH$_3$PbBr$_3$ and CH$_3$NH$_3$PbI$_3$, respectively. For imaginary components of dielectric constant, peaks are found at 3.6, 3.0 and 2.5 eV for CH$_3$NH$_3$PbCl$_3$, CH$_3$NH$_3$PbBr$_3$ and CH$_3$NH$_3$PbI$_3$, respectively. Also, the maximum values that we obtained for real dielectric constant are 5.8, 7.05, 9.28 for CH$_3$NH$_3$PbCl$_3$, CH$_3$NH$_3$PbBr$_3$ and CH$_3$NH$_3$PbI$_3$, respectively and 3.8, 4.76, 7.53 for corresponding imaginary components. Therefore, shifting from Cl to Br to I, higher value of dielectric constant is expected for both real and imaginary cases, and peaks can be expected to move toward lower values of energy. The real and imaginary dielectric constants of CH$_3$NH$_3$PbI$_3$ as derived experimentally from a previous study are shown here:

![Graph showing real ($\varepsilon_1$) and imaginary ($\varepsilon_2$) parts of dielectric constant of CH$_3$NH$_3$PbI$_3$ measured by experiments on CH$_3$NH$_3$PbI$_3$ thin films with different hydration ratios.](image)

Figure 19: Real ($\varepsilon_1$) and Imaginary ($\varepsilon_2$) parts of dielectric constant of CH$_3$NH$_3$PbI$_3$ measured by experiments on CH$_3$NH$_3$PbI$_3$ thin films with different hydration ratios. [65]
Figure 20: Experimental results for real ($\varepsilon_1$) and imaginary ($\varepsilon_2$) parts of dielectric constant of CH$_3$NH$_3$PbI$_3$. [66]

Figure 19 and Figure 20 show similar trend for real and imaginary dielectric constant compared to our calculation results for CH$_3$NH$_3$PbI$_3$. Figure 19 shows the real and imaginary dielectric constants with different hydration ratio of perovskite solar cells that have peak values around 6 at 2.5 eV for real part and peak value around 4.5 at 3.25 eV for imaginary part (for zero hydration). These are slightly different compared to our CH$_3$NH$_3$PbI$_3$ results that is expected due to difference of theoretical and experimental results. Figure 20 shows experimental results for PbI$_2$ and CH$_3$NH$_3$ solutions and CH$_3$NH$_3$PbI$_3$ thin film. It shows the peak value for real dielectric around 7 at 2.5 eV and peak value around 7 at 3.5 eV for imaginary part. These values are similar to Ref. [65] results and are basically consistent with current study.
Figure 21: Experimental results for real ($\varepsilon_1$) and imaginary ($\varepsilon_2$) parts of dielectric constant of CH$_3$NH$_3$PbI$_3$ thin films. [67]

Figure 21 shows another set of experimental results for dielectric constants of CH$_3$NH$_3$PbI$_3$ thin films versus wavelength [67] that show slightly different trend of real and imaginary dielectric constants compared to our results as well as those depicted in Figure 19 and Figure 20. It can be due to different method used to prepare thin films and parameters such as thickness of thin film, ratio of solvents in thin films, preparation time and temperature, etc.

c-Si and a-Si solar cells has higher values of dielectric constants (almost 40) [68] shown in Figure 22 which is 8-10 times higher than perovskite solar cells. The dielectric constant of CH$_3$NH$_3$PbX$_3$ ($X = \text{Cl, Br, I}$) perovskites is comparatively low because they are a mixed composition of a CH$_3$NH$_3^+$ cation and PbX$_3^-$ anion. This shows that the perovskites have low capacitance because of the proportionality between the capacitance and dielectric constant [69].
The CH$_3$NH$_3$PbX$_3$ (X = Br, I) perovskites will produce Wannier-type excitons [70], and therefore incident light will create charged carriers and weakly bounded excitons because the binding energies of excitons are on the same order as that of thermal energy. At low frequencies, the dielectric constant value is high because there is enough time to respond to the electric field. As the frequency increases the dielectric constant decreases as the molecules and ions are not able to follow the high frequency field due to the inertia of molecules and ions and corresponding relaxation times.
Figure 23: Refractive Index (n) of MAPbX$_3$ where X=Cl (a), Br (b), I (c) in the cubic phase.

We also computed the frequency dependent refractive index $n$ for CH$_3$NH$_3$PbCl$_3$, CH$_3$NH$_3$PbBr$_3$ and CH$_3$NH$_3$PbI$_3$. Results are presented in Figure 23, which shows close
match with the real part of the dielectric constant. The refractive index reaches its maximum value of \( \sim 2.5 \) for CH\(_3\)NH\(_3\)PbCl\(_3\) at \( \sim 380 \) nm, \( \sim 2.7 \) for CH\(_3\)NH\(_3\)PbBr\(_3\) at \( \sim 400 \) nm, and \( \sim 3.2 \) for CH\(_3\)NH\(_3\)PbI\(_3\) at \( \sim 550 \) nm, and thereafter decreases with increase in energy values.

![Figure 24](image1)

**Figure 24:** Refractive Index \( n \) of CH\(_3\)NH\(_3\)PbI\(_3\) measured by experiments on CH\(_3\)NH\(_3\)PbI\(_3\) thin films with different hydration ratios. [65]

![Figure 25](image2)

**Figure 25:** Experimental results of refractive index \( n \) for CH\(_3\)NH\(_3\)PbI\(_3\) thin films. [67]
Figure 24 and Figure 25 show the experimental results of refractive index for CH$_3$NH$_3$PbI$_3$ thin films. For Figure 24, the peak value of refractive index is 2.5 at 500 nm with a pattern that is similar to our results. But for Figure 25 the peak is very sharp at 350 nm and shows the maximum value of 3 with a pattern that is different from our refractive index. The curve of refractive index is smooth after maximum in our results while Figure 24 and Figure 25 show fluctuations after reaching maximum value. These changes could be because of difference in theoretical and experimental studies as some actual experimental conditions may be missing in theoretical studies.

In the higher frequency region, the energies of electrons are dissipated. Therefore, the refractive index shows decreasing nature at high energy values. It has been found that beyond 800 nm, $n$ reduces in a linear way that makes material opaque. It also results in the absorption of the photons with superluminal behavior. The real part of the refractive index $n$ for CH$_3$NH$_3$PbI$_3$ has a value of 2.61 at a wavelength of 633 nm, implying that CH$_3$NH$_3$PbI$_3$ is suited as an antireflective coating for silicon solar cells. To establish this argument for the CH$_3$NH$_3$PbBr$_3$ and CH$_3$NH$_3$PbCl$_3$ perovskite thin films, we noticed that the same trend existed but with lesser value of refractive index at lower wavelength. This discussion is consistent with bandgap effect presented in section 3.4.
Figure 26: Refractive index of c-Si, GaAs, CdTe, Ge, CGS, CIGS and CIS solar cells. [71]

The wavelength dependency of the refractive index for some common solar cell materials is shown in Figure 26. By comparing these wavelength dependent refractive indices, we can see c-Si has the highest refractive index (~6.5) which is twice value of perovskite solar cells. CdTe, CIGS, CIS solar cells are in the same range and following similar trend as perovskites.
Figure 27: Absorption coefficient $\alpha$ of MAPbX$_3$ where $X=$Cl (a), Br (b), I (c) in the cubic phase.
Our calculated absorption coefficients $\alpha$ of MAPbX$_3$ are depicted in Figure 27. In the case of CH$_3$NH$_3$PbI$_3$, for the range of 200-800 nm $\alpha$ are almost changing from of $\sim$5 × 10$^5$ cm$^{-1}$ to 1×10$^4$ cm$^{-1}$. For CH$_3$NH$_3$PbBr$_3$, for the range of 200-680 nm, $\alpha$ are almost changing from of $\sim$5 × 10$^5$ cm$^{-1}$ to 1×10$^4$ cm$^{-1}$ and for the range of 200-550 nm, $\alpha$ are almost changing from of $\sim$5 × 10$^5$ cm$^{-1}$ to 1×10$^4$ cm$^{-1}$ for CH$_3$NH$_3$PbCl$_3$. Despite general similarity of overall maximum values at low wavelengths, we notice that the maximum values of absorption coefficient increase by changing I to Br to Cl. Near 550 nm, a shoulder is found in the absorption coefficient curves of CH$_3$NH$_3$PbI$_3$. For, CH$_3$NH$_3$PbBr$_3$ and CH$_3$NH$_3$PbCl$_3$, the curves show shoulders near 440 nm and 350 nm, respectively. The peak values and the shoulders for different structures happen at different wavelengths with a trend similar to that of the bandgap values.

![Graph showing absorption coefficient spectra](image)

Figure 28: - Experimental results of absorption coefficient ($\alpha$) for CH$_3$NH$_3$PbI$_3$. [66]
Figure 29: Experimental results of absorption coefficient ($\alpha$) for different solar cells including CH$_3$NH$_3$PbI$_3$. [72]

Figure 30: Experimental results of absorption coefficient ($\alpha$) for CH$_3$NH$_3$PbI$_3$ thin films. [67]
Figure 28, Figure 29 and Figure 30 show the experimental data of absorption coefficient for CH$_3$NH$_3$PbI$_3$ thin films. For Figure 28, the local peak value of absorption coefficient is ~2×10$^5$ at 550 nm, which is similar to our results. The drop pattern of absorption coefficient curve after reaching maximum value in our results is similar to those in Figure 29 and Figure 30. Consistency between theoretical and experimental studies shows the reliability of theoretical simulations.

The absorption coefficient calculates how deep light will penetrate into a layer before it is absorbed. Light is rarely absorbed in a material with a low absorption coefficient, and if the material is not sufficiently thick, it will transparent to that prospective wavelength. The absorption coefficient depends on the thickness of material and on the wavelength range of incident light that is being absorbed. For a direct gap semiconductor absorption coefficient can reach high values. Absorption coefficients for CuInSe$_2$(CIS), CuInGaSe (CIGS) are shown in Figure 29 and show a wider range of wavelength compared to that of CH$_3$NH$_3$PbI$_3$.

If $\alpha$ is proportional to square root of energy $E=\hbar v$, then the material is a direct band gap material. On the other hand, if $\alpha$ is proportional to square of energy $E=\hbar v$, the material is an indirect band gap material, [73] represented, respectively, by

$$\alpha \propto (E - E_g)^2$$

and

$$\alpha \propto (E - E_g)^{1/2}.$$

Semiconductor materials with direct energy gap have features such as high absorption coefficient in the relevant energy range for photovoltaics. Most of the incident sunlight
on a material is absorbed within a small distance beneath the surface. This makes it possible to fabricate thin film solar cells.

Semiconductors with indirect energy gap generally need more thickness to harvest most of the energy of sunlight. Examples are Si, Ge, etc. for which thicker layers are needed; that means higher costs of material and increased demands on purity. In indirect bandgap semiconductors, the rise of absorption coefficient with the photon energy is slow. Short-wavelength photons have an energy more than required (>the bandgap), hence they are able to create e⁻ and h⁺ pairs and are easily absorbed by the crystalline silicon (c-Si) solar cells. However, large-wavelength photons cannot generate e⁻-h⁺ pairs and are not easily absorbed. Photons that are in the middle region are not easily absorbed, i.e. only can be absorbed after reaching deeper distance in the c-Si material [49].

What matters for absorption coefficient of material to make a good solar cell? The answer is high extinction coefficient, short absorption length (penetration depth), and high absorption coefficient.

\[ I = I_0 e^{-\alpha x} \]  

\( I_0 = \) Intensity of incoming light \\
\( x = \) distance to the surface \\

The wavelength-dependent \( \alpha \) determines how deep the incident light penetrates the semiconductor. In case of semiconductor, higher energy photons typically are absorbed more strongly, while low energy photons pass right through the semiconductor.

For CH₃NH₃PbI₃, at 700 nm, the absorption coefficient was \( 5 \times 10^5 \) cm⁻¹, that corresponds to a penetration depth 2 µm. Therefore, majority of incident light energy can
be absorbed by the perovskite solar cells within a micro layer (about 2 µm), which makes them highly efficient solar cells [74].

Figure 31: Electromagnetic Spectrum of visible lights within nm ranges of wavelength [75]

Comparing the onsets of increased in Figure 27 with Figure 31 above, these onset wavelengths correspond to purple, green and red regions of the visible light for Cl, Br, and I. In addition, published results presented in Figure 28 and Figure 29 show the same wavelength range between ~390-800 nm for CH$_3$NH$_3$PbI$_3$, which is comparable to CuInGaSe and CdTe semiconductors. Therefore, halide variation provides the possibility of targeting different frequency regions of visible light for photovoltaic conversion.
4. CONCLUSIONS

Organic-inorganic hybrid lead-halide perovskite materials are among the third generation of solar cell materials with promising potential for low-cost, easily producible applications. Investigating their characteristics and properties are of utmost importance toward mass production of affordable and efficient technology to utilize clean and abundant solar energy. Here we focus on structural and optical properties of hybrid lead halide perovskites to compare their stability and suitability for photovoltaic applications.

Organic-inorganic lead iodide (CH$_3$NH$_3$PbI$_3$) perovskite have been found in three different phases: orthorhombic (<160 K), tetragonal (160–330 K) and cubic (>330 K). We have chosen cubic phase of CH$_3$NH$_3$PbCl$_3$, CH$_3$NH$_3$PbBr$_3$ and CH$_3$NH$_3$PbI$_3$ in our calculations. We performed first principles density functional theory (DFT) calculations using Vienna Ab Initio Simulation Package (VASP) to calculate structural, electronics and optical properties.

We minimized the energy and obtained optimized structures with total volumes 183.25 Å$^3$, 207.47 Å$^3$, and 249.62 Å$^3$ of unit cell CH$_3$NH$_3$PbCl$_3$, CH$_3$NH$_3$PbBr$_3$ and CH$_3$NH$_3$PbI$_3$, respectively. The lattice parameters of the optimized structures were 5.68 Å for CH$_3$NH$_3$PbCl$_3$, 5.92 Å for CH$_3$NH$_3$PbBr$_3$ and 6.29 Å for CH$_3$NH$_3$PbI$_3$. In addition, we calculated cohesive energies, which were -40.541 eV, -38.977 eV and -36.831 eV for CH$_3$NH$_3$PbCl$_3$, CH$_3$NH$_3$PbBr$_3$ and CH$_3$NH$_3$PbI$_3$, respectively. We also found the phonon dispersion curves of all halide perovskite structures and noticed that changing from Cl to
Br to I mostly results in lower frequency vibrations that is associated with increased atomic mass. The cohesive energies and negative frequencies in phonon dispersions suggested reduced structure stability upon changing from Cl to Br to I.

Calculated electronic band gap of halide perovskite cells varies from 1.65 to 3.02 eV. The halide substitution from I to Br and then to Cl will increase the $E_g$ from 1.61 eV for MAPbI$_3$ to 2.09 eV for MAPbBr$_3$ and to 2.89 eV for MAPbCl$_3$. The resulting light absorption of MAPbX$_3$ cells can be changed in the visible region from 429 to 770 nm. Therefore, this variation provides the possibility of targeting different frequency regions of visible light for photovoltaic conversion.

We analyzed the optical properties, namely dielectric function, refractive index, and absorption coefficient of CH$_3$NH$_3$PbCl$_3$, CH$_3$NH$_3$PbBr$_3$ and CH$_3$NH$_3$PbI$_3$. We found peak values 5.8, 7.05, 9.28 for real dielectric constant and 3.8, 4.76, 7.53 for imaginary components, for CH$_3$NH$_3$PbCl$_3$, CH$_3$NH$_3$PbBr$_3$ and CH$_3$NH$_3$PbI$_3$, respectively. The frequency dependent refractive index $n$ was also computed for CH$_3$NH$_3$PbCl$_3$, CH$_3$NH$_3$PbBr$_3$ and CH$_3$NH$_3$PbI$_3$ which were 2.5 at 380 nm, 2.7 at 400 nm and 3.2 at 550 nm that is consistent with bandgap results. For chloride, bromide and iodide structures, the calculated optical absorption coefficient peaks occurred at 220 nm, 250 nm, and 350 nm, respectively. For all halide perovskite, an overall absorption coefficient plateau was found at $5 \times 10^5 \text{ cm}^{-1}$ that corresponds to a penetration depth 2 µm. Therefore, most of incident light from sunrays can be absorbed by the perovskite solar cells within a micro layer (about 2 µm), which makes them highly efficient solar cells. Bromide and especially chloride materials showed increased dielectric constant, refraction index, and absorption coefficients at lower wavelengths, compared to the iodide material. This
suggested the possibility of better photovoltaic performance of chloride and bromide materials at those wavelengths. Thus, halide perovskite solar cell using organic-inorganic materials can be potential competitor material with tunable light spectrum for photovoltaic application.
5. REFERENCES


