# Density Functional Theory Calculations of Photovoltaic Materials

**Tushar Hasamnis** 





### Density Functional Theory Calculations of Photovoltaic Materials

by

#### **Tushar Hasamnis**

in partial fulfilment of the requirements for the degree of

Master of Science in Sustainable Energy Technology

at the Delft University of Technology, to be defended publicly on Monday August 8, 2021 at 09:30 AM

 Student number:
 5121558

 Project duration:
 September 2020 – August 2022

 Thesis committee:
 Dr. R. Santbergen
 TU Delft, ESE-PVMD

 Dr. P. A. Procel Moya
 TU Delft, ESE-PVMD

 Dr. L. Mazzarella
 TU Delft, ESE-PVMD

 Prof. Dr. F.C. Grozema
 TU Delft, CE-TNW

An electronic version of this thesis is available at http://repository.tudelft.nl/.



## Abstract

Photovoltaic (PV) materials are gaining rapid popularity for their use in commercial solar cell applications. Due to the growing need for high efficiency solar cells, new materials such as perovskites are being researched. While the conventional experimental methods are still used to test new PV materials, PV modelling is gaining importance as an efficient and cheap alternative to physically synthesizing and testing each new material. In the PVMD group at TU Delft, multiple stages of modelling PV materials to study their efficiency have been researched, however, an ab initio method to obtain fundamental optical and electrical properties of new materials is currently absent. While these properties are currently studied using experimentation, this thesis aims to provide a reliable simulation procedure to calculate the optical and electrical properties of PV materials using Density Functional Theory (DFT) software and verify its accuracy.

The fundamentals of DFT and its implementation in DFT software are first studied to better understand the Vienna Ab Initio Simulation Package (VASP) software, on which simulations are performed during this thesis. The VASP software is a plane wave classical DFT software that employs the Projector Augmented Wave (PAW) method for electron structure calculations and has a wide range of electron density functionals available in its library making it a perfect fit to study optical and electrical properties of materials using DFT.

Based on their success in previous computational research on material properties, the PBE and HSE06 electron density functionals are used in this thesis for simulations. A step-by-step procedure is then developed for simulations on the VASP software using both the PBE and HSE06 functionals detailing every step involved in the simulation, the inputs required at each step and the configuration of the input files at every step in order to obtain the density of states, band structure, band gap and complex refractive index for PV materials. Monocrystalline Silicon, a well-studied PV material is then used as a case study to examine the accuracy of the developed procedure.

The procedure is then employed to study new and promising solar cell materials such as inorganic halide perovskites and inorganic perovskites with mixed halides. Multiple simulations are performed to study the variation in the band gap and complex refractive index of inorganic perovskites as the composition of the halides is changed. Finally, the trends visible in the properties of the different perovskites are analyzed to better understand the usefulness of the VASP simulations. Finally, recommendations are provided for future research into the study of PV material properties using DFT software such as VASP.

# Acknowledgements

Tushar Hasamnis Delft, August 2022

With the completion of this thesis, my journey in TU Delft reaches its finale. My degree in MSc Sustainable Energy Technology taught me a lot of things, not just about sustainable energy but also life lessons and skills that will stay with me for life. I look forward to taking forward the knowledge, teaching and experiences I gained from this course to future pursuits in my life.

Working on this thesis has been quite a journey for me and I would like to extend a heartfelt thanks to my supervisor Dr. Rudi Santbergen for always being encouraging and supportive even through all the tough obstacles I faced during this pandemic period. I found him very approachable and he always provided valuable insight on how I should proceed further whenever I felt stuck during my research.

The work in this thesis largely relied on simulations on the VASP software for which I also like to thank Dr. Jouke Heringa and Antoon Frehe who helped not just with the installation of the software but also later on when I was working on VASP. Antoon was very quick to help out whenever I had issues accessing VASP and Dr. Jouke was kind enough to provide insight as well as recommendations on some of my simulations that yielded unsatisfactory results. I would also like to thank Alba Alcañiz Moya and Max van Duffelen, who both also worked on the VASP software in the PVMD group at TU Delft. Their work provided me a good introduction to VASP and led me to references in literature that were very handy during this thesis.

I would also like to thank Dr. Paul Procel Moya, who provided me insight on the direction and objectives this thesis could follow and suggested some resources that would be useful for me while performing simulations on VASP. Finally, I also wish to thank Paul, Dr. Luana Mazzarella and Prof. Dr. Ferdinand Grozema for being a part of my thesis committee.

The completion of my thesis as well as the rest of my MSc degree would be absolutely impossible without the invaluable support of my parents, grandparents and family. They always had faith that I would achieve success in the things I chose to pursue and their motivation and kindness played a big role in helping me overcome any hurdles I faced to complete my degree.

# Contents

At	ostrac	ct in the second se	i
A	knov	vledgements	iii
Li	st of I	Figures	vii
Lie	st of <sup>-</sup>	Tables	viii
N	omen	clature	IX
1	Intro	oduction	1
	1.1	Photovoltaic modelling	1
	1.2	Density Functional Theory	2
	1.3	Research objectives of the thesis	3
	1.4		3
2	Den	sity Functional Theory and its application	5
	2.1	Density Functional Theory	5
	2.2	Overview of DFT software	6
		2.2.1 Time-Dependent DFT software	6
	<b>•</b> • •	2.2.2 Classical DFT software fundamentals	7
	2.5	2.3.1 Solving the Kohn Sham equations	7
		2.3.2 Electron structure calculations	, 8
		2.3.3 Electron density functionals	10
	2.4	Vienna Ab Initio Simulation Package (VASP)	11
	2.5	Conclusions	11
3	DFT	Simulations with VASP	13
	3.1	Introduction to VASP simulations	13
		3.1.1 Simulation process	14
	3.2	Inputs for VASP simulations	15
		3.2.1 POSCAR	15
		3.2.2 POTCAR	15
		3.2.3 INCAR	16
		3.2.4 KPOINTS	17
		3.2.5 CHGCAR	17
	22	3.2.0 WAVECAR	10
	5.5	3.3.1 Creating POSCAR and POTCAR files for the material	10
		3.3.2 Structural relaxation	18
		3.3.3 Self-Consistency Field calculation	19
		3.3.4 Density of states calculation	19
		3.3.5 Band structure calculation	20
		3.3.6 Complex refractive index calculation	20
	3.4	Post-processing methods	20
		3.4.1 Correction of band gap obtained using the PBE functional	21
		3.4.2 Correction of dielectric parameters obtained using PBE simulations	21
	3.5	Conclusions	21

4	Case study: DFT simulations for monocrystalline Silicon	24
	4.1 Monocrystalline Silicon	24
	4.2 Simulation inputs	26
	4.3 Results	26
	4.3.1 Density of states	26
	4.3.2 Band structure	27
	4.3.3 Complex refractive index	28
	4.4 Conclusions	29
5	DFT simulations for perovskite materials	32
	5.1 Perovskite materials	32
	5.2 Simulation inputs	32
	5.3 Results	33
	5.3.1 Band gap	33
	5.3.2 Complex refractive index	36
	5.3.3 Discussion	38
	5.4 Conclusions	39
6	Conclusion	41
	6.1 Recommendations	42
Bi	bliography	45
Α	Appendix A - VASP simulation tutorial for PVMD group simulations	51
в	Appendix B - Additional simulation results	54

# List of Figures

2.1 2.2	Iterative process to solve Kohn-Sham equations [1].	7 10
3.1 3.2 3.3	Flowchart explaining the inputs at each step of the simulation. Lattice structure for $CsPbI_3$ visualized using the VESTA software. Absorption spectrum for GaAs calculated using PHS, HSE06 and experimental data [3].	14 18 21
4.1 4.2 4.3 4.4 4.5 4.6 4.7	Unit cell of monocrystalline Silicon. Density of states and band structure for Silicon reported in literature [4]. Complex refractive index reported in literature for Silicon [5]. Density of states calculated for Silicon. Band structure calculated for Silicon. Complex refractive index of Silicon simulated for different k-points meshes. Comparison of complex refractive index for Silicon between simulation and experiment.	24 25 25 26 27 28 29
5.1 5.2 5.3 5.4 5.5 5.6 5.7 5.8 5.9 5.10	Perovskite structures visualized using the VESTA software. Density of states calculations for perovskites of the form $CsPbX_3$ with $X = I$ , Br or Cl. Band structure calculations for perovskites of the form $CsPbX_3$ with $X = I$ , Br or Cl. Band gap variation as I is changed to Br. Density of states using HSE06 for $CsPbI_3$ . Simulated band gap variation with halide change. Variation of complex refractive index as I is changed to Br. Variation of complex refractive index as Br is changed to Cl. Band gaps for all the simulated perovskites.	33 34 34 35 36 37 37 38 38
B.1 B.2 B.3 B.4 B.5 B.6 B.7	Density of states and band structure for $CsPbI_2Br$ . Density of states and band structure for $CsPbIBr_2$ . Density of states and band structure for $CsPbBr_2Cl$ . Density of states and band structure for $CsPbBrCl_2$ . Density of states and band structure for $CsPbI_2Cl$ .	54 55 56 56 57 57

# **List of Tables**

1.1	Required optical and electrical properties.	2
4.1	Silicon band gap obtained using simulation and from literature (in eV).	27
5.1	Band gaps obtained using PBE in this work and in literature (all values in eV).	35

## Nomenclature

#### Greek symbols

- $\epsilon$  Dielectric function
- $\epsilon_i$  Orbital energy
- $\rho$  Electrical charge density
- Φ Wave function
- $\Psi$  Electronic wave function

#### Latin symbols

- As Arsenic
- Br Bromine
- C Carbon
- Cl Chlorine
- Cs Caesium
- e Euler's number
- *E<sub>cut</sub>* Cut-off energy
- Ga Gallium
- H Hydrogen
- *Ĥ* Hamiltonian operator
- *ħ* Reduced Planck constant
- I Iodine
- k Imaginary part of complex refractive index
- $\vec{k}$  Wave vector
- m Mass
- N Nitrogen
- n Real part of complex refractive index
- $n(\vec{r})$  Electron charge density
- Pb Lead
- Si Silicon
- Sn Tin
- $v_{eff}$  Kohn-Sham potential
- $v_{ext}$  External potential
- $v_H$  Hartree potential
- *v<sub>XC</sub>* Exchange-correlation potential

#### Abbreviations

AMS DFT DOS EPR EQE GAMESS GGA GTO HK HSE06 LAPW LDA MTO NCPP PAW PBE PHS PV PZ QHA RG SCF STO TDDFT	Amsterdam Modeling Suite Density Functional Theory Density of States Electron Paramagnetic Resonance External Quantum Efficiency General Atomic and Molecular Electronic Structure System Generalized Gradient Approximation Gaussian-Type Orbital Hohenberg-Kohn Heyd, Scuseria and Ernzerhof functional Linearized Augmented Plane-Wave Local-Density Approximation Muffin-Type Orbital Norm-Conserving Pseudopotentials Projector Augmented Wave Perdew, Burke and Ernzerhof functional PBE + HSE06 + Sum rule Photovoltaic Perdew and Zunger functional Quasi-Harmonic Approximation Runge-Gross Self-Consistency Field Slater-Type Orbital Time-Dependent Density Functional Theory
TDDFT VASP VESTA	Time-Dependent Density Functional Theory Vienna Ab initio Simulation Package
VESIA	visualization for Electronic and Structural Analysis

# Introduction

#### 1.1. Photovoltaic modelling

With the growing need for renewable energy across the world, photovoltaic technologies are proving to be the most promising choice. IEA suggests an increase of more than 700% in the use of solar PV from 2020-2040 as compared to the previous 20 years, higher than any other source of energy [6]. However, a major limitation of PV technologies is their relatively low efficiency. A record laboratory efficiency of 47.1% was achieved by NREL in 2019 for a solar cell with expensive technology for extraterrestrial applications, however most commercial solar cells have an efficiency between 15-20% [7]. Thus, a major challenge in photovoltaic energy research for commercial, terrestrial use, is to achieve higher efficiencies in solar cells. New materials and designs, such as perovskite-Silicon tandem solar cells, are being researched for this reason [8]. In this regard, an efficient and cheap alternative to physically synthesizing and testing new solar cell designs is to use modelling approaches to predict their performance.

The goal in PV modelling is to be able to predict the energy yield of a PV system composed of PV cells having new materials or a novel composition. The yield of the PV system can be determined from solar cell parameters such as the absorptance, EQE and J-V curve, as well as information about the location of the system [9]. The solar cell parameters in turn depend on the optical and electrical properties of the solar cell material and the composition of the solar cell. Ultimately, the optical and electrical properties of the material depend on the composition and lattice structure of the material. External properties like the location information are easy to obtain and the weather data can also be sourced from available databases such as Meteonorm [10]. A complete method to obtain energy yield from solar cell parameters is available [9] and there exist dedicated software to perform optical and electrical simulations to obtain solar cell parameters such as the GenPro4 [11] and ASA software [12]. However, a comprehensive method for ab initio calculations of the optical and electrical properties of the solar cell parameters.

The optical and electrical properties of materials are usually determined experimentally using spectroscopic ellipsometry or spectrophotometry [13]. However, to have a holistic modelling approach, a suitable method to determine fundamental material properties such as density of states, electronic band gap and complex refractive index needs to be outlined. Being able to calculate these properties theoretically will mean that the cost of synthesis and testing new PV materials that accompanies experimentation can be cut down. The time and energy spent in repeated experimentation to find a suitable material will also thereby be reduced. The PVMD group at TU Delft in particular is interested in formulating a method to simulate material properties theoretically to thereby create a complete PV modelling procedure, from the choice of material for the solar cell all the way to the yield of the PV system.

In recent times, some degree of success to theoretically determine material properties has been achieved with the help of software utilising the Density Functional Theory (DFT). Several DFT software such as VASP, Quantum ESPRESSO, Amsterdam Modelling Suite etc. have been utilised to obtain material

properties using first principles [3, 14, 15, 16, 17, 18]. Thus, it is of interest, especially to the PVMD group at TU Delft, to develop a reliable method to obtain the desired opto-electrical properties required for PV simulations using DFT software for a multitude of PV materials. The primary goal of this thesis is to help establish a method to do so for some well-known and promising PV materials.

It is evident that the required optical and electrical properties need to first be specifically identified. With the goal of PV device modelling in mind, the outputs required can be defined by checking the required inputs for the GenPro4 and ASA software [12]. A comprehensive list of required properties that DFT could potentially explain is compiled in table 1.1.

Complex Refractive Index	Relative Permittivity	
Band Gap	Doping Concentration	
Electron Affinity	Electron and Hole Mobility	
Density of States	Carrier Lifetime (Crystalline Materials)/	
Density of States	DoS Parameters (Amorphous Materials)	

Table 1.1: Required optical and electrical properties	Table 1.1:	: Required	optical and	electrical	properties.
---	------------	------------	-------------	------------	-------------

While there are quite a few properties of interest, for the scope of this thesis only three main parameters will be studied:

- · Density of states
- Band gap
- Complex refractive index

Further, it is important to clarify that for the purpose of this thesis, only the absorber layer of the solar cell will be studied. In section 1.3, the objectives for the thesis are presented to give a more specific idea about the role of this thesis and the scope of its study.

#### **1.2.** Density Functional Theory

As mentioned in section 1.1, DFT has been used to calculate some optical and electrical material properties of certain materials theoretically in some existing literature. These calculations are often computationally expensive with a trade-off between accuracy and calculation time. Thus, efforts have been made to find methods that are reasonably accurate and computationally feasible, for example in ref. 14. In some cases, post-processing methods are utilised to correct the error generated by using a simpler method, for instance in ref. 3. With these sort of corrections, a reasonable degree of accuracy was obtained in the said research. For the purpose of this thesis, while developing a method to determine PV material properties, it is thereby vital to keep in mind that running highly accurate simulations is not always feasible and post-processing methods can sometimes be the preferred option instead.

The calculation of these properties are performed mainly using DFT software such as VASP, Quantum Espresso or AMS. Chapter 2 details upon these different software in more detail. For the purpose of this thesis, the VASP software will be utilised. To obtain accurate outputs using VASP, it is highly important not just to understand the fundamentals of DFT or the overall simulation procedure, but also to have a deep understanding of what inputs need to be specified and what role each input and each tag plays in each step of the simulation. Multiple choices such as the choice of functional, the k-point density, the cut-off energy and so on need to be made depending on the purpose of the simulation and degree of accuracy of the output. Chapter 3 will discuss in-depth these inputs and the simulation procedure, giving a deeper understanding of how to assign values to these inputs depending on the degree of accuracy desired from the simulation. This is primarily of interest for future research in DFT simulations at the PVMD group.

In the PVMD group at TU Delft, the use of DFT software such as VASP to determine optical and electrical properties for absorber materials in photovoltaic cells is a new concept. The possibility of achieving this as well as the accuracy that can be obtained with this procedure are yet unknown. Thus, establishing a procedure to obtain these properties is of interest to the photovoltaic modelling research in the group. While there is some literature available on obtaining some material properties using DFT, doing so in the context of relevant photovoltaic materials, and more specifically photovoltaic device modelling, is the primary concern of this thesis.

#### 1.3. Research objectives of the thesis

The ultimate goal of this project in the PVMD group is to simulate optical and electrical properties required for photovoltaic device modelling using DFT software, in particular the VASP software. However, that is quite a vast topic with a lot of possibilities and issues to tackle. Keeping the scope of this project in mind, the specific objectives for this thesis are as follows:

- Understand the fundamentals of DFT software and the benefits of using the VASP software.
- Develop a simulation procedure for use in the TU Delft PVMD group to obtain the density of states, band structure and complex refractive index for absorber materials in photovoltaic cells using the VASP software.
- Ascertain the accuracy of this procedure for a well-studied photovoltaic absorber material such as monocrystalline Silicon.
- Apply the developed procedure to examine the variation in the band gap and complex refractive index of inorganic perovskites with different halides.

#### 1.4. Skeleton of the thesis

While a general introduction to the topic has been provided in Chapter 1, the remaining chapters will be utilized to achieve the objectives laid forth in section 1.3. Chapter 2 introduces the relevant theoretical framework for density functional theory, the application of this theory in DFT software as well as an introduction to common DFT software and the benefit of using the VASP software. To obtain the desired opto-electrical properties, chapter 3 focuses on the inputs and simulation procedure for the VASP software, provides a detailed understanding of these inputs, a procedure to systematically obtain the desired outputs as well as certain post-processing methods to improve the accuracy of the results. In chapter 4, the aforementioned procedure is applied to monocrystalline Silicon and the results are compared with literature simulation and experimental values. Chapter 5 applies the developed simulation procedure to promising new PV materials, namely perovskites, and studies the variation in the band gap and complex refractive index for inorganic halide perovskites as the composition of the halides is changed. Lastly, chapter 6 summarizes the conclusions drawn from the results of the previous chapters and makes recommendations for future research in this subject.

# 2

# Density Functional Theory and its application

This chapter aims to answer the first research objective outlined in section 1.3, which is to understand the fundamentals of DFT software and the benefits of using the VASP software. To do so, the chapter first introduces some key concepts in DFT that are relevant to the scope of this thesis in section 2.1. Section 2.2 provides an overview of the applications in which commercially available DFT software are utilized and their classification. Section 2.3 focuses on classical DFT software and the basic principles on which they operate and section 2.4 talks specifically about the VASP software which is utilized in this thesis and the advantages of using it. Section 2.5 lastly highlights the conclusions that are drawn from this chapter.

#### 2.1. Density Functional Theory

At a quantum level, the information of a system is contained in its wave function  $\Psi$ , which is described by the Schrödinger equation. In a practical scenario of trying to find the properties of a material, the many-body time-independent Schrödinger equation is of interest, shown below in equation 2.1 [1]. The solution to this equation yields the wave function that contains the information about the system.

$$i\frac{\partial}{\partial t}\phi = \hat{H}\phi \tag{2.1}$$

However, it is not possible to obtain the exact solution for this equation and determine the wave function. What can be done instead is to achieve an approximate solution that can deliver a high level of accuracy. The density functional theory is an approach that reduces a many electron Schrödinger equation effectively to a single-electron Schrödinger-like equation which can be approximately solved [19].

Over time, multiple approximations were developed within DFT, however, the most popular one that is still used to this day, was proposed by Walter Kohn and Lu Jeu Sham in 1965 in the form of the Kohn-Sham equations. The Kohn-Sham equations are based on the Born-Oppenheimer approximation and Hohenberg-Kohn theorems which are explained fairly well in literature such as ref. 1, 19, 20. Now used as the basis for most DFT software, the Kohn-Sham equations simplified the problem of having a system of multiple interacting electrons to a system of non-interacting electrons that would generate the same electron density [21]. This was done by introducing a Kohn-Sham potential  $v_{eff}(r)$  as described in equation 2.2.

$$(-\frac{\hbar^2}{2m} + v_{eff}(r))\Psi_i(r) = \epsilon_i \Psi_i(r)$$
(2.2)

The unknown in this equation, the Kohn-Sham potential, can further be broken into three components: the external potential  $v_{ext}(r)$ , the Hartree potential  $v_H(r)$  and the exchange-correlation potential  $v_{xc}(r)$ , shown in equation 2.3 [21].

$$v_{eff}(r) = v_{ext}(r) + v_H(r) + v_{XC}(r)$$
(2.3)

Here, the Hartree potential and exchange-correlation potential represent the potentials indicated in equations 2.4 and 2.5 respectively.

$$v_H(r) = e^2 \int \frac{\rho(r')}{|r - r'|} dr'$$
(2.4)

$$v_{XC}(r) = \frac{\partial E_{XC}[\rho]}{\partial \rho(r)}$$
(2.5)

A popular method to deal with the external potential and Hartree potential employed in most DFT software these days is the Projector Augmented Wave (PAW) method. The PAW approach effectively combines pseudopotentials and linear augmented-plane-wave methods to transform rapidly oscillating valence wavefunctions at ion cores to smooth, computationally cheap wavefunctions [22]. That leaves the exchange-correlation potential to be the only unknown, which is tackled using various electron density functionals. These topics will be detailed upon further in sections 2.3.2 and 2.3.3.

#### **2.2.** Overview of DFT software

Section 2.1 has mainly discussed the theory of DFT applicable to time-independent periodic structures, to be referred to here as classical DFT, which is useful in the case of this thesis among other applications. However, the natural question that then arises is regarding DFT applicable to non-periodic or time-dependent systems.

DFT software are built for a wide variety of uses in the fields of computational quantum chemistry as well as solid state physics. These include optimizing geometries of structures, studying reaction mechanisms and transition state structures during reactions, calculation of vibrational frequencies, calculation of optical spectra, EPR spectroscopy, molecular dynamics, calculation of material properties and more [23].

Considering the diversity of applications, it is pretty evident that certain applications need to be studied based on time-dependent systems while some applications can be studied with time-independent systems. Thus, different DFT software are created to cater to different needs. At the highest level, these can be distinguished based on two major criteria:

- Time-Dependent DFT software
- Classical DFT software

Section 2.2.1 provides a brief insight into Time-Dependent DFT software after which section 2.2.2 focuses on classical DFT, which is of importance to study optical and electrical properties of PV materials among other things.

#### 2.2.1. Time-Dependent DFT software

As opposed to the classical theory presented in section 2.1, for time-dependent, non-periodic applications, Time-Dependent DFT (TDDFT) is utilised. TDDFT fundamentally relies on the Runge-Gross (RG) theorem, which is the time-dependent analogue of the Hohenberg-Kohn (HK) theorem that modern-day classical DFT relies upon [24]. While all modern day DFT software utilise Kohn-Sham DFT, described in section 2.1, time-dependent and non-periodic systems utilise time-dependent Kohn-Sham approaches where the Kohn-Sham potential  $v_{eff}(r,t)$  is also a function of time. In practice, non-periodic dynamics simulations are less common than static calculations, however, with methods such as TDDFT being implemented into powerful DFT codes, their usage is likely to grow with time. DFT software such as GAMESS, ORCA and TeraChem cater to the needs of non-periodic systems [25, 26, 27]. However, as TDDFT is not required for the purpose of this project, this thesis will only focus on the understanding and application of classical DFT software in the context of opto-electrical properties of PV materials.

#### 2.2.2. Classical DFT software

The DFT theory applied in classical DFT software is generally outlined in section 2.1. However, there are multiple classical DFT software available such as VASP, Quantum ESPRESSO, AMS and so on [28, 29, 30]. Although they are generally required for similar applications and provide fairly good results, there are some differences behind the working of some of these. Section 2.3 will provide a better understanding of the fundamentals behind classical DFT software and outline certain differences that might exist between some of them.

#### 2.3. Classical DFT software fundamentals

As mentioned in section 2.1, most classical DFT software rely on Kohn-Sham equations to approximately solve the Schrödinger equation. Thus, to understand the fundamentals of how classical DFT software operate, it is important to understand how they solve the Kohn-Sham equations. DFT software make use of an iterative process to solve the Kohn-Sham equations. This process is described in section 2.3.1. Section 2.1 also mentioned that the unknown Kohn-Sham potential in the Kohn-Sham equation can be divided into the external potential, the Hartree potential and the exchange-correlation potential. Different methods utilized to approach the first two are mentioned in section 2.3.2 including the aforementioned PAW method, and the different functionals used to tackle the exchange-correlation potential are described in depth in section 2.3.3.

#### 2.3.1. Solving the Kohn-Sham equations

Iteratively solving the Kohn-Sham equations is the basis for most classical DFT software and there are not really many differences between software when it comes to this. To solve the system, an initial guess of the electron charge density  $n(\vec{r})$  is made by overlapping atomic charge densities [31]. The iterative process followed is summed up very well in figure 2.1.

Figure 2.1: Iterative process to solve Kohn-Sham equations [1].

The initial guess is represented by k = 1 in figure 2.1. Using this, the effective Kohn-Sham potential  $v_{eff}(r)$  can be evaluated and in turn the Kohn-Sham equation, represented in the second equation

in the image above, can be solved to yield the wave function. This wave function is then utilized in the third equation in figure 2.1 to yield the actual charge density. The actual density is then compared with the initial density and if their difference is found to be less than a certain threshold  $\delta$ , the required properties are evaluated. However, if the difference is larger than the threshold, the whole procedure is repeated for k+1, k+2 and so on until a small enough difference is obtained. Self-consistency is achieved once the difference is smaller than the threshold.

#### 2.3.2. Electron structure calculations

The differences between different classical DFT software can be observed beginning with this topic. To evaluate the Kohn-Sham potential, its three components need to be tackled. There are multiple approaches utilised to calculate the external and Hartree potential of a system, and different software have been created with different approaches used as their basis. It is important to understand here that the Hartree potential is representative of the Coulomb potential arising from the system of electrons [19]. Thus, the goal here is to calculate the electronic structure for a system containing many electrons, some of which are in their core states (strongly bound to nuclei), while some are in their valence states [32].

Generally speaking, there are three main methods utilised for electronic structure calculations [32]. Note that all methods are in agreement with each other theoretically, however, their implementation and usage in software can lead to differences in simulation time and complexity [33]. The three methods are as follows:

- Plane waves
- Localized orbitals
- Augmented methods

#### Plane waves

For periodic solids, Bloch's theorem prescribes that the wavefunction must be composed of a phase factor and a periodic term as shown in equation 2.6 [34]. Here, the periodic part has the same periodicity as the lattice; so  $u_n(r + R) = u_n(r)$  where *R* is a lattice vector.

$$\psi_n(r) = u_n(r)e^{ik\cdot r} \tag{2.6}$$

Here, *k* represents the wave vector of the plane wave part confined to the first Brillouin zone. With a Fourier series expansion, the wave function can be written as a sum of infinite plane waves as seen in equation 2.7, where  $c_{n,G}$  and *G* are reciprocal lattice vectors [34, 35].

$$\psi_n(r) = \sum_G c_{n,k+G} e^{i(k+G) \cdot r}$$
(2.7)

In practice, only a sample of k-points needs to be chosen and a region of k-space can be represented by the wavefunction at a single k-point. Schemes such as the Monkhorst and Pack are utilized for k-point sampling in some DFT software such as VASP [33]. This will be further discussed in section 3.2.4. Another thing to note is the sum in equation 2.7 is performed to infinity to fully describe the wavefunction. However, this is not possible practically, and thus a cut-off energy is used where the coefficients  $c_{n,k+G}$  become small for large values of |k + G| [34, 36]. The cut-off energy is indicated in equation 2.8.

$$E_{cut} \ge \frac{1}{2} |k+G|^2$$
 (2.8)

Plane wave basis sets have a lot of advantages and are widely used in solid-state calculations [35]. The use of Fast Fourier Transform makes it easy to change from a real-space representation to a

momentum-space, the total energies can be monitored as a function of the cut-off energy, they are computationally simple, model all space with equal accuracy and are independent of atomic positions [33]. However, they also have some drawbacks such as the basis set size scaling with simulation volume, the inability to focus on specific regions as the space is modelled with equal accuracy and the need for some kind of pseudopotential to describe the core electron interaction for the convergence of the plane wave expansion as the potential has singularities at atomic nuclei [33]. The accuracy and transferability of these pseudopotentials is then a matter of concern. Among others, Quantum ESPRESSO, a widely used DFT software, utilises a plane wave basis set and pseudopotentials while also offering additional packages for specialized calculations [29].

#### Localized orbitals

Localized orbital methods make use of atom-centering and use different methods such as Gaussian-Type Orbitals (GTOs), Slater-Type Orbitals (STOs) which also are atom-centered but use eigenfunctions of atomic orbitals and Muffin-Type Orbitals (MTOs) which are also atom-centered but use eigenfunctions in spherically-symmetric, truncated potentials [35]. Localized orbitals are typically used in molecular calculations.

Localized orbital software are based off of different methods such as the Boys-Foster method and the Pipek-Mezey method, for which more information can be read in literature such as ref. **37**. Since they are centered on atoms, localized basis sets offer their fair share of advantages by allowing the space to be modelled with variable accuracy - improving it in regions of interest and reducing it in uninteresting regions. The basis set size does not scale with the simulation volume and pseudopotentials can also be used to reduce computational effort [**33**]. However, localized basis sets are disadvantageous in a lot of scenarios, such as modelling solid systems with defects for example. Even though in theory they can also yield identical results to plane wave methods, they are often computationally more complicated and expensive as was observed in literature such as ref. **38**, **39**. That said, a lot of DFT software such as the Amsterdam Modeling Suite (AMS), GAMESS, Gaussian, ORCA, Q-chem and more implement this theory due to the advantages it possesses, especially in quantum chemistry [**25**, **26**, **37**].

#### Augmented methods

Dubbed as the "best of both worlds" [32], augmented methods make use of augmented plane waves, which are essentially plane waves in an interstitial region centered around atoms [35]. The most general form of this approach is the Linearized Augmented Plane-Wave (LAPW) method, known to be one of the most accurate methods for electronic structure calculations, which is explained in more detail in ref. 40. The key point to note here is that LAPW methods do not utilise pseudopotentials to approximate the singularities at atoms but instead make use of a sophisticated basis set for the potential, which is computationally intensive. However, to improve the efficiency of the LAPW method, an additional local orbital (lo) can be used. The LAPW +lo method has seen use in popular DFT software such as WIEN2k [40].

The major drawback of using LAPW methods is the high computational complexity and expense associated with them. Attempts have been made to improve the efficiency [41], however, alternate methods with similar accuracy have also been developed for this purpose. The most popular one being the Projector Augmented Wave (PAW) method, which has shown remarkably identical accuracy to the LAPW simulations [42, 43].

The PAW method attempts to simultaneously achieve the accuracy of the LAPW method and the computational efficiency of the plane wave psuedopotential method [33]. The PAW method basically combines partial wave functions from the isolated atom with pseudo partial waves through projector functions constructed to match the all electron solution. The PAW method can be understood further in literature such as ref. 22.

Having combined the best parts of the methods described previously, the PAW method allows accurate calculations with better computational efficiency, and is thus implemented in popular DFT software such as VASP [28]. PAW pseudopotentials are well tested and computationally efficient compared to other pseudopotentials such as norm-conserving pseudopotentials (NCPPs) that can be used in other plane-wave DFT software such as Quantum ESPRESSO.

#### 2.3.3. Electron density functionals

Electron density functionals are used to approximate the exchange-correlation potential of a system in the Kohn-Sham equations. A plethora of functionals, dubbed a "functional zoo" [44], are currently available, each having their own method to describe the potential. Some such as GGA and LDA rely on quantum mechanical formalism, while some hybrid functionals also make use of empirical fitting of data to obtain more accurate results [2]. Based on the complexity and accuracy of the functionals, they are separated into different rungs on Jacob's ladder, which provides an insight into which functional might be useful for what application, as illustrated in figure 2.2.



Figure 2.2: Jacob's ladder of hierarchy for functionals [2].

Different functionals have varying success for different applications. Attempts have been made in existing literature to calculate the optical and electrical properties for semiconductor materials using DFT, which is of relevance to this thesis, and the LDA-PZ, GGA-PBE and hybrid-GGA - HSE06 functionals have found great success in doing so [3, 14, 16, 18]. The choice of the functional is one of the most crucial inputs in DFT simulations. For the purpose of this thesis, the PBE and HSE06 functionals will be utilized in future chapters thanks to the success they have seen in past research.

The Perdew-Burke-Ernzerhof (PBE) functional is a non-empirical functional that provides a good degree of accuracy for a variety of systems. PBE is a Generalized Gradient Approximation (GGA) type functional, which essentially introduces a dependence of the exchange-correlation functional on the local gradient of the electron density [45]. While PBE generally provides a good degree of accuracy for simulations, a well-known issue with its usage is the underestimation of the band gap [14]. On the contrary, HSE06 is known to produce remarkably accurate results at the cost of being computationally intensive [3]. A hybrid exchange correlation functional developed by Heyd, Scuseria and Ernzerhof, HSE06 makes use of a screened Coulomb potential to circumvent the computationally expensive task of calculating the exact Hartree-Fock exchange [46].

#### 2.4. Vienna Ab Initio Simulation Package (VASP)

As mentioned in section 1.2, for the purpose of this thesis, the Vienna ab initio Simulation Package (VASP) is utilised. The aim of this project is to calculate the density of states, band gap and complex refractive index for PV materials using the PBE and HSE06 functionals. Keeping this in mind, VASP seems to be the perfect choice for this task. Having understood the fundamentals of DFT software previously in this chapter, the benefits of using VASP to meet the objectives of this project can be stated as follows:

- VASP is developed based on classical DFT as opposed to TDDFT, which is favourable to study material properties of solids [28].
- The most prominent advantage of using VASP is that it utilizes PAW pseudopotentials for electron structure calculations. As discussed in section 2.3.2, PAW pseudopotentials are well tested and provide a high degree of accuracy while also being computationally feasible.
- VASP also has a wide library of functionals available to use [28] and is also able to perform simulations using the HSE06 functional in a fairly low amount of time compared to some of its counterparts [47].

#### 2.5. Conclusions

As outlined in section 1.3, the first research objective of understanding the fundamentals of DFT software and the advantages of using the VASP software was addressed in this chapter. To understand the working of DFT software, it was important to first understand the basic relevant principles of DFT, such as the multi-body time-independent Schrödinger equation, the Kohn-Sham equations and potential, and the components of the Kohn-Sham potential such as the Hartree potential and exchange-correlation potential.

The difference between TDDFT and classical DFT was first clarified to understand the significance of using software relying on classical DFT. The working of these software was then made clear by understanding how the software solve the Kohn-Sham equations, which are the basis for all DFT software. The Kohn-Sham equations are solved iteratively by the software until self-consistency is achieved. Electron structure calculations need to be performed to take care of the external and Hartree potential and different software utilize different electron structure calculation methods to do so. The popular methods being plane waves with pseudopotentials, localized orbital methods such as STOs and augmented methods such as the PAW method. The final unknown, the exchange-correlation potential, is handled with the use of functionals. A variety of functionals are available based on the application, but the significant ones for the purpose of this thesis, namely PBE and HSE06 were discussed during this chapter.

Finally, the VASP software, which is utilized for the simulations in this project, was discussed. VASP is a very useful software for periodic DFT calculations which makes use of the PAW method allowing it to perform simulations accurately and efficiently. VASP offers a wide variety of functionals and provides good efficiency for hybrid functionals such as HSE06, making it a suitable choice for this project.

# 3

### **DFT Simulations with VASP**

One important objective for this thesis, mentioned in section 1.3, is to develop a simulation procedure to obtain the density of states, band gap and complex refractive index for absorber materials in photovoltaic cells using the VASP software. This objective is addressed in this chapter. In section 3.1, a general overview of the simulation procedure adopted and the inputs required for the simulations are described. Sections 3.2 and 3.3 are mainly only of interest to readers who are doing VASP simulations to obtain opto-electrical material properties, particularly within the TU Delft PVMD group. Section 3.2 discusses the inputs required for each simulation step in depth and section 3.3 explains the detailed simulation procedure to obtain the desired results in VASP. Section 3.4 might be interesting to all readers as it discusses some well-known limitations of the adopted procedure and post-processing methods that could be used to improve accuracy. Lastly, section 3.5 summarizes the conclusions drawn from this chapter.

#### **3.1.** Introduction to VASP simulations

As discussed in section 2.3.3, the PBE and HSE06 functionals will be used for VASP simulations in this thesis. Simulations are first performed using the PBE functional to obtain the band gap and density of states for the material. Simulations for these parameters are then also performed using the HSE06 functional due to its expected higher accuracy. For the complex refractive index, simulations are performed only using the PBE functional since HSE06 simulations are computationally intensive.

There are multiple simulation steps involved in the simulation of a single parameter, for instance the density of states, using a particular functional. There are a few major input files required for any VASP simulation, and these need to be correctly configured for each simulation step in order to obtain the correct final output. The major input files for VASP include:

- POSCAR
- POTCAR
- INCAR
- KPOINTS
- CHGCAR
- WAVECAR

In order to perform simulations for density of states, band structure and complex refractive index, it is first important to understand the different simulation steps, which input files are required for each step and what are the relevant outputs of interest. This is explained in section 3.1.1. A better understanding of the input files and their configuration for each simulation step is provided in later chapters.

#### 3.1.1. Simulation process

As discussed above, simulations are performed for each material first using the PBE functional and then using the HSE06 functional to obtain the density of states and band structure, and then a PBE simulation is performed to obtain the complex refractive index. In order to do so, the following steps are performed, also visualized in figure 3.1:

- · Create the POSCAR and POTCAR files for the material.
- Structural relaxation
- · Self-Consistency Field (SCF) calculation using PBE and then HSE06
- Density of states calculation using PBE and then HSE06
- Band structure calculation using PBE and then HSE06
- Dielectric function calculation using PBE



Figure 3.1: Flowchart explaining the inputs at each step of the simulation.

The POSCAR file defines the lattice structure of the material and the POTCAR file contains the relevant pseudopotentials for the atomic species involved. However, their creation does not involve a proper VASP simulation and can thus be viewed as a preparatory step. Each of the remaining steps however involve a full VASP simulation.

The first step is structural relaxation, which is done to minimize the bond energy of the atoms in the structure. On running this simulation, the output file of interest is the CONTCAR file which contains the relaxed structure in it. The CONTCAR file is renamed as the POSCAR file and is used as the POSCAR file for all further simulation steps.

The outputs of interest in the second step, the SCF calculation, are the CHGCAR and WAVECAR files, which provide the charge density and initial wave functions for future simulations respectively. The CHGCAR and WAVECAR files should be used as inputs for the DOS, band structure and dielectric function simulations later. Specifically for band structure calculations using HSE06, the IBZKPT output file of the SCF simulation is also required to generate the KPOINTS file, and should thus also be saved for later. The use of the IBZKPT file is detailed upon further in section 3.2.4. It is important to note here that a separate SCF calculations is done using PBE for all the PBE calculations and a separate HSE06 one for all HSE06 calculations.

The third step can be viewed to be either the calculation of the DOS, band structure or complex refractive index depending on the desired output, and the results of this simulation can be exported outside VASP for further use. The POTCAR, relaxed POSCAR, CHGCAR and WAVECAR files are now used in this step. The major difference in these three simulations exists within the INCAR and KPOINTS files, which is discussed more in section 3.3.

#### 3.2. Inputs for VASP simulations

As discussed in section 3.1, the main input files of interest are the POSCAR, POTCAR, INCAR, KPOINTS, CHGCAR and WAVECAR. These are discussed in depth here.

#### 3.2.1. POSCAR

Every time a simulation is to be run for a material, creating the POSCAR file is the first step. The POSCAR file defines the geometry and structure for the material. It contains information about the lattice vectors, number of atoms for each atomic species and the atomic positions, often supplied in Cartesian coordinates [28]. It is important to ensure that the order in which the atoms appear in the POSCAR file is the same as the order in the POTCAR file.

There are multiple methods to create the POSCAR file for a material. For some common materials, the POSCAR file might be readily available on resources such as the VASP wiki or Materials Project [28, 48]. It is also possible to create POSCAR files using basic structure files in the cif format that can be found on major online databases such as the Crystallography Open Database [49].

3D visualization programs such as VESTA are incredibly useful in the creation of POSCAR files [50]. VESTA is utilized for the simulations in this thesis to create POSCAR files for pervoskite materials. It is possible to convert cif files into POSCAR files using VESTA, and it is also possible to use VESTA for the creation of newer materials. If a POSCAR file is available for a material, it is also quite simple to change the atomic species of an element within the material by simply replacing the element name in the POSCAR file, as the lattice vectors or atomic positions do not change in that case.

The POSCAR file created in this way must be used in the structural relaxation step. The relaxed structure must then be used for future steps as clarified earlier.

#### 3.2.2. POTCAR

The POTCAR file contains information about all the atomic species in the material being simulated. The pseudopotentials are particularly important here, as they are required in the PAW method employed by VASP, as explained in section 2.3.2. Another important parameter in the POTCAR file is the ENMAX tag which helps specify the cut-off energy, which was described in section 2.3.2 as well. The cut-off energy ENCUT is specified in the INCAR file, but is recommended to be set to around 1x to 1.3x the value of the highest ENMAX in the POTCAR file.

When a material contains more than one atomic species, the POTCAR file is essentially a concatenation of the POTCARs of all the individual atoms involved. It is important to ensure that the atoms are concatenated in the same order as they appear in the POSCAR file. Specific information about accessing individual atom POTCARs and concatenating them, particularly for the PVMD group at TU Delft, can be found in appendix A.

The PAW PBE potentials are used for this thesis. The pseudopotential library contains a variety of PAW potentials for most elements. The basic potentials have been utilized in this thesis, however, it could be of interest to explore the effect of using other versions such as the hard potential denoted by an h. More information about the different potentials can be found on the VASP wiki [28].

Once the POTCAR file is created for the material, the same file is used throughout all the further simulation steps. Nothing needs to be altered in the file for any particular simulation step.

#### 3.2.3. INCAR

The INCAR file is the central input file which tells VASP exactly what needs to be done. Through the use of multiple tags, the INCAR file instructs the system about what calculation needs to be performed and how it should be executed. There are a plethora of INCAR tags available, however, only a select few need to be used for each simulation depending on the desired output. As discussed in section 3.1.1, the steps to be performed for the purpose of this thesis include structural relaxation, SCF calculation, DOS calculation, band structure calculation and dielectric function calculation. Thus, only the INCAR tags relevant to these simulations will be discussed here.

The INCAR tags can be grouped together based on what instruction they provide to VASP as follows:

#### Initialization

- **ISTART** Tells the system to start a job and clarifies whether it should start from scratch or if it is a continuation job.
- · ICHARG Tells the system about the initial charge density.

#### **Electronic optimization**

- ENCUT Specifies the cut-off energy for the system in eV.
- **ISMEAR** Defines the smearing method to determine partial occupancies for each orbital.
- **SIGMA** Defines the width of the smearing.

#### Structural relaxation

- **IBRION** Indicates how the ions are moved.
- ISIF Specifies which degrees of freedom are allowed to change.
- NSW Specifies the maximum number of ionic steps.
- EDIFFG Tells the system when to break the ionic relaxation loop.

#### Self-Consistency Loop

• EDIFF - Tells the system when to break the self-consistency loop.

#### Density of states

- LORBIT Indicates the system to output the DOSCAR file which contains the density of states alongside other files such as the PROCAR file.
- **NEDOS** Specifies the number of grid points on which the DOS is evaluated.

The EMIN, EMAX and NBANDS tags together can also be used in place of the NEDOS tag. However, the use of NEDOS is sufficient for this thesis.

#### Hybrid functionals

- LHFCALC Indicates to the system whether hybrid functional calculations are to be performed.
- **HFSCREEN** Specifies the hybrid functional to be used.
- ALGO Selects the algorithm used to optimize the orbital.
- **TIME** Specifies the time step for ALGO.

#### **Dielectric function**

- LOPTICS Tells the system whether it should calculate the frequency dependent dielectric matrix.
- CSHIFT Sets the complex shift in the Kramers-Kronig transformation.
- NBANDS Specifies the total number of Kohn-Sham orbitals.

Although there are a lot more INCAR tags available for use, the aforementioned tags are the only relevant ones for the calculation of DOS, band structure and complex refractive index. For all simulations, the initialization and electronic optimization tags must be set in the INCAR. Further, based on the simulation step being performed, the relevant tags for that step must be defined. The values to be used for these tags are better explained in section 3.3.

It is thus essential to remember that the INCAR file needs to be modified for every single simulation step, as each step has a different objective.

#### **3.2.4. KPOINTS**

The reciprocal lattice is used to visualize the Fourier transform of a lattice such as the Bravais lattice. The first Brillouin zone is defined as a primitive cell in the reciprocal lattice. It contains points of high symmetry known as critical points such as  $\Gamma$  which indicates the center of the Brillouin zone and *X*, *M*, *R* etc. which indicate geometric center or corner points in the lattice structure of the material. More information about this can be found in literature [51, 52].

The k-points mesh is a mesh containing a finite number of points in the Brillouin Zone. The KPOINTS input file in VASP specifies the k-points used to sample the Brillouin Zone. The higher the k-points density, the higher the accuracy of the calculation. However, high k-points also result in longer simulation times, and thus a balance needs to be struck.

Outside of band structure simulations, the automatic Monkhorst-Pack can be utilized to create the KPOINTS files for every other simulation step. Using the Monkhorst-Pack, the grid density, for example 11 11 11, is the only specification in the KPOINTS file that needs to be modified for each step. It is preferable to use a denser KPOINTS grid for DOS calculations compared to structural relaxation or SCF simulations in order to get a better estimate of the DOS.

For band structure simulations, a high-symmetry critical point path is desired to determine the band structure. To generate the KPOINTS file for PBE band structure simulations, the SeeK-path tool can be utilized [53]. The relaxed POSCAR file can be used as an input and the SeeK-path tool provides a suitable KPOINTS file in return. For HSE06 band structure simulations, the SeeK-path tool can also be utilized. However, it is important to note that the data in the IBZKPT file must also be added on to the KPOINTS file generated by the SeeK-path tool in this case.

#### 3.2.5. CHGCAR

The CHGCAR is obtained as an output of the SCF simulation and encodes the charge density. Further DOS, band structure and dielectric function calculations can then use this as an input so that the simulation has an initial charge density to work with. Although CHGCAR is technically used as an input file, no modifications are required to be made to it, and thus there is no configuration involved for this file.

#### 3.2.6. WAVECAR

Similar to the CHGCAR, the WAVECAR file is also an output of the SCF simulation that encodes the wave function which can be used in the initiation of future simulation steps. There are also no modifications to be made to the WAVECAR, it is simply supposed to be included as an input for further simulations.

#### 3.3. Detailed simulation procedure

Having laid the foundations by discussing the general outline for the simulations in section 3.1 and the input files and their meaning in section 3.2, sections 3.3.1 - 3.3.6 will now focus on the detailed simulation procedure developed to address the objective presented in section 1.3.

#### 3.3.1. Creating POSCAR and POTCAR files for the material

The first preparatory step is to create the POSCAR and POTCAR files once a material is selected. As suggested in section 3.2.1, there are online databases available to access the structure files for common materials which can be used to create the POSCAR file. The use of 3D visualization software such as VESTA also make it possible to create POSCAR files for a variety of materials. Figure 3.2 below shows an example of the structure of the perovskite material *CsPb1*<sub>3</sub> visualized using VESTA.



Figure 3.2: Lattice structure for CsPbI<sub>3</sub> visualized using the VESTA software.

The POTCAR file library for individual elements comes along with the VASP license. Once the POT-CARs for the individual elements involved in the material are selected, they can be concatenated into one within VASP. Instructions on accessing the library within the PVMD group at TU Delft and concatenating the files can be found in appendix A. It is vital to ensure that they element files are concatenated in the same order as they appear in the POSCAR file.

#### 3.3.2. Structural relaxation

The input files for this step include the POSCAR and POTCAR file generated in section 3.3.1 alongside the KPOINTS and INCAR file. A suitable KPOINTS mesh can be selected for this step such as 11x11x11, or a smaller one in case of larger, complex materials.

The INCAR file should contain the initialization tags of ISTART = 0 and ICHARG = 2. ISTART = 0 indicates to the system that a new calculation is to be started without the presence of a WAVECAR input file. The cut-off energy ENCUT should be set slightly above the ENMAX value found in the POTCAR file for the material. If the material contains multiple elements, the highest ENMAX of all the elements is considered. As the POTCAR does not change during any simulation step, the same ENCUT value can be used for further simulation steps as well. ISMEAR = 0 and SIGMA = 0.01 can

be set to utilize Gaussian smearing. IBRION = 2 is used to indicate to the system that the structure is to undergo ionic relaxation using the conjugate gradient algorithm and ISIF = 3 is used to indicate that both the atoms as well as the cell is to be relaxed. Lastly, a negative value such as -0.02 can be set for EDIFFG to utilize the forces as a convergence criteria instead of total energy. NSW depends on how many ionic steps are desired, and a value of 100 was used in this thesis for relaxation.

The output CONTCAR file is the only one of interest here, which contains the relaxed structure and is to be renamed and used as the POSCAR file for all further steps.

#### 3.3.3. Self-Consistency Field calculation

The input files here are the POSCAR obtained from the previous step, alongside the POTCAR, KPOINTS and INCAR files. The same KPOINTS file can be used here as the previous step. For HSE06, it is important to note that the SCF simulation takes a significantly long amount of time and thus the KPOINTS density might be set lower than it would for PBE.

For the INCAR file, ISTART = 0 and ICHARG = 2 is used again as there is no input CHGCAR or WAVECAR file at this stage. IBRION = -1 and NSW = 0 is also set as there is no relaxation to be performed here. As mentioned earlier, the values for ENCUT alongside ISMEAR and SIGMA are also kept the same as during structural relaxation. The main change here is to use EDIFF instead of EDIFFG. A value of EDIFF = 1E-6 is required to obtain precise results.

When simulating with HSE06, additional hybrid functional tags also need to be used in the INCAR. LHFCALC = .TRUE. indicates that hybrid functional calculations are to be performed and HFSCREEN = 0.2 indicates that the HSE06 functional is to be utilized. The default HFSCREEN value of 0 will make use of the hybrid PBE0 functional. The default TIME=0.4 can be used here.

The outputs of interest here are the CHGCAR and WAVECAR files which are used for every future step, and in case of HSE06 band structure calculations, the IBZKPT file is also of use.

#### 3.3.4. Density of states calculation

The input files at this stage are the same POSCAR and POTCAR as the previous step, the newly obtained CHGCAR and WAVECAR from the SCF calculation, as well as the KPOINTS and INCAR files. A denser KPOINTS grid is preferred for this step compared to the SCF calculation, but it is once again important to keep in mind that a high density grid could result in very long simulation times when using hybrid functionals such as HSE06.

For the INCAR file, this time ISTART = 1 is used as we are using the WAVECAR from the previous step and not starting from scratch. ICHARG = 11 is set to obtain DOS and band structure eigenvalues based on the charge density that can be read from the CHGCAR. ENCUT is again the same for this step, but ISMEAR = -5 is used to make use of the tetrahedron method with Blöchl corrections for smearing, which is recommended for DOS calculations. LORBIT can be set to either 10 or 11. Having LORBIT = 11 allows partial DOS to also be studied and is thus recommended. NEDOS will define the number of points on which the DOS is calculated, the more points the longer the simulation takes. A NEDOS value between 1000 to 3000 is usually sufficient.

When simulating with HSE06, the PBE INCAR file is modified with the same hybrid functional tags that were used in the SCF step, while also specifying ALGO = D. It might be preferable to reduce the NEDOS points here due to how computationally intensive the HSE06 simulation is.

The density of states output obtained can be visualised using p4Vasp [54], however, it is preferable to export the data from p4Vasp and plot it using an external software such as MATLAB. Instructions on how data can be exported to MATLAB can be found in appendix A.

#### 3.3.5. Band structure calculation

The same POSCAR, POTCAR, CHGCAR and WAVECAR files that were used as inputs for the DOS simulation are used as inputs in band structure calculations. In the INCAR file, the NEDOS need not be specified and ISMEAR = 0 and SIGMA = 0.01 are set again for Gaussian smearinng, but the rest of the INCAR file is the same as the one in the DOS simulation. The major change in this step lies in the KPOINTS file.

As mentioned in section 3.2.4, the KPOINTS file needs to be along a high-symmetry critical points path. The SeeK-path tool is a very useful tool to achieve this and in case of HSE06 simulations, it is also important to include the IBZKPT file generated in the SCF step into the generated KPOINTS file.

Similar to the DOS simulation, the results can be visualized using p4Vasp and can be exported and plotted externally.

#### 3.3.6. Complex refractive index calculation

The dielectric function can be simulated with the help of VASP. For this, the CHGCAR and WAVECAR files generated from the SCF simulation are used alongside the POSCAR and POTCAR files. A simple Monkhorst-Pack KPOINTS file is also used.

In the INCAR file, ISTART = 1 and ICHARG = 11 should be set as the CHGCAR and WAVECAR files are provided. The same ENCUT, ISMEAR and SIGMA is used as the SCF step. However, optics tags need to be used to indicate the simulation of the dielectric function. This is done by setting LOPTICS = .TRUE. and CSHIFT = 0.1. NBANDS is set at 64 and ALGO = Exact for the purpose of this simulation.

The output can be plotted using p4Vasp which visualises the real and imaginary part of the dielectric function. The procedure to extract these values and plot them externally is slightly different, as detailed upon in appendix A. The n and k values of the complex refractive index can then be plotted by calculating them using the dielectric function values using equations 3.1 and 3.2 shown below.

$$n = \sqrt{\frac{e + e_r}{2}} \tag{3.1}$$

$$k = \sqrt{\frac{e - e_r}{2}} \tag{3.2}$$

Here,  $e_r$  and  $e_i$  are the real and imaginary parts of the dielectric function respectively and e is obtained using equation 3.3.

$$e = \sqrt{e_r^2 + e_i^2} \tag{3.3}$$

#### **3.4.** Post-processing methods

The procedure to be followed in order to obtain the DOS, band structure and complex refractive index using VASP has been discussed thus far. However, for simulations using the PBE functional, there are some well known limitations with the calculation results. These occur due to the natural inaccuracy of the PBE functional, and thus certain post-processing methods are suggested in literature to improve the accuracy of the results. In the context of the band gap and complex refractive index, two interesting methods are discussed in sections 3.4.1 and 3.4.2. These methods have not been implemented for the simulations done in this project but are good recommendations for future DFT projects on PV materials.
#### 3.4.1. Correction of band gap obtained using the PBE functional

While the hybrid HSE06 functional is very popular to obtain quite accurate results, use of simpler GGA or LDA functionals is preferred due to their smaller computational requirements. A common problem of using a simple GGA functional such as PBE is the underestimation of the band gap of the material, known as the "band gap problem" [14]. An efficient method to tackle this is suggested in ref. 14 by the use of the so-called " $\Delta$ -sol method". The  $\Delta$ -sol method defines the band gap to be the energy required to create an unbound electron-hole pair in the system, and calculates its value for different number of electrons in the system. Ultimately, an error reduction of 70% for various materials is obtained using this method [14].

#### 3.4.2. Correction of dielectric parameters obtained using PBE simulations

As mentioned in section 3.1, the simulations for the complex refractive index are only performed using the PBE functional in this project, as HSE06 is computationally intensive. However, due to the band gap problem that accompanies the PBE simulation, there are also inaccuracies in the dielectric function generated. To correct for this error, the "PHS method" is proposed in ref. 3 which yields more accurate results. Instead of using the accurate HSE06 functional for calculating the absorption spectra, the PHS method only utilizes HSE06 to correct the value of the band gap obtained by the PBE functional. The  $\epsilon$ 2 spectrum obtained using PBE is blue-shifted by the band gap correction value obtained using PBE and HSE06 earlier. The amplitude of the  $\epsilon$ 2 spectrum is then corrected using the sum rule and  $\epsilon$ 1 is calculated thereafter using Kramers-Kronig integration [55]. A remarkable accuracy is then observed in the absorption spectrum thus obtained, as visible in figure 3.3.



Figure 3.3: Absorption spectrum for GaAs calculated using PHS, HSE06 and experimental data [3].

#### 3.5. Conclusions

In section 1.3, an important objective to develop a simulation method to obtain the density of states, band structure and complex refractive index for PV absorber materials using VASP was set forth. In order to achieve this, a general procedure and introduction was first provided. To obtain any singular output, it was clarified that multiple simulation steps are involved.

With this context in mind, the different input files required by VASP were then explained. Each simulation step requires different input files and some input files need to be modified for each step. General guidelines and explanations on how to configure input files were thus also detailed upon. Finally, with the detailed knowledge about the inputs as well as an overview of the whole process now known, the elaborate simulation procedure that was developed was put forth. In this, the inputs required for the different simulation steps, the values to be assigned to them and the outputs and their processing was explained. Lastly, the known limitations of using PBE as a functional for the simulations were acknowledged and post-processing methods suggested in literature to improve the accuracy of the results were discussed.

# 4

## Case study: DFT simulations for monocrystalline Silicon

In this chapter, monocrystalline Silicon, a simple but widely used and well-studied material for solar cells, is used as a case study to verify the accuracy of the procedure developed in chapter 3. Section 4.1 provides a general introduction to monocrystalline Silicon and its relevant optical and electrical properties studied in literature. Section 4.2 then provides a brief summary of how the procedure developed in chapter 3 is applied to the specific case of Silicon. In section 4.3, the results obtained from the simulations are provided and their accuracy and limitations are discussed. Lastly, section 4.4 summarizes the conclusions that can be drawn from this chapter.

#### 4.1. Monocrystalline Silicon

The global cumulative PV capacity has jumped from 306.5 GW in 2016 to 942 GW in 2021, which is an increase of over 200% in a span of five years [56]. In this rapidly growing PV market, a rough estimate of 90% of all commercially used solar cells are made using crystalline Silicon [57]. These can be either in the form of monocrystalline or polycrystalline Silicon. For the purpose of this case study, the simple monocrystalline form of Silicon is studied.

Monocrystalline Silicon has a lattice with long-range order and symmetry which makes it easier to study its optical and electrical properties using DFT [9]. Crystalline Silicon is observed to have a diamond cubic lattice structure which has been visualized with the help of the VESTA software in figure 4.1.



Figure 4.1: Unit cell of monocrystalline Silicon.

Since crystalline Silicon is such a widely used material, it has been studied thoroughly in theory and experiment. Figure 4.2 shows the density of states and band structure reported in literature for Silicon [4].



Figure 4.2: Density of states and band structure for Silicon reported in literature [4].

The experimentally obtained band gap for Silicon reported in literature is 1.12 eV [9]. This can also be inferred from figure 4.2. Further, the complex refractive index reported in literature can be observed in figure 4.3 [5].



Figure 4.3: Complex refractive index reported in literature for Silicon [5].

The density of states, band structure, band gap and complex refractive index are the only properties of interest for the purpose of this thesis. Using the procedure defined in chapter 3, DFT simulations are

performed on Silicon to gauge how accurate the results are as compared to literature in the following sections.

#### 4.2. Simulation inputs

Since Silicon is a basic and widely studied material, the POSCAR and POTCAR files for it are readily available. A KPOINTS mesh of 11x11x11 is used for the relaxation and SCF calculations while a 21x21x21 mesh is used for the DOS calculation. Multiple KPOINTS meshes are implemented for complex refractive index calculations, discussed further in section 4.3.3. The KPOINTS files for band structure simulations are generated using the SeeK-path tool mentioned in section 3.2.4.

As can be observed from section 3.3, most of the tags in the INCAR file are used to instruct the system on what is to be done and the only real material-dependent tag for any simulation step is the ENCUT which defines the cut-off energy. A cut-off energy of 250 eV is used for the simulations on Silicon.

Using these values and the procedure defined in section 3.3, DFT calculations are performed on Silicon using VASP. An important takeaway from this section is that using the developed procedure, for any new material to be simulated, the only parts that must be changed are the POTCAR and POSCAR files, the KPOINTS mesh density and the cut-off energy.

#### 4.3. Results

Density of states calculations are first performed on Silicon using the PBE and HSE06 functionals. The results for this are discussed in section 4.3.1. The same functionals are then used to study the band structure, the results of which are presented in section 4.3.2. As HSE06 simulations for complex refractive index are too computationally expensive, only PBE simulations are performed for the same. The results for these simulations are lastly studied in section 4.3.3.

#### 4.3.1. Density of states

The density of states is studied using the PBE functional, and the reportedly more accurate hybrid HSE06 functional. Figures 4.4a and 4.4b show the density of states calculated using the PBE and HSE06 functionals respectively.



Figure 4.4: Density of states calculated for Silicon.

It can be observed that the graph obtained using both functionals shows very similar trends and they also match the trend observed in figure 4.2 from literature. The major difference between the PBE and

HSE06 simulations however is the band gap obtained. The band gap is the range where the density of states stays at a value of 0, and can thus be determined from the density of states plots in figure 4.4. While the PBE simulation takes significantly lesser time than HSE06 which requires around a day, it also results in a highly underestimated band gap compared to the experimental value. The band gap values for Silicon from experiment, simulations in existing literature as well as the simulations performed in this work are summarized in table 4.1 [9, 58].

	Experiment	PBE	HSE06
This work	-	0.59	1.19
Literature	1.12	0.56	1.14

Table 4.1: Silicon band gap obtained using simulation and from literature (in eV).

From the table, it is clear that the band gap obtained using PBE in literature is much lower than the accurate experimental value while that obtained using HSE06 is fairly close to the experimental value. This band gap underestimation using PBE is a well-known phenomenon and a suggestion to improve its accuracy using post-processing has already been made in section 3.4.1. However, the accuracy of the simulations performed in this project are of more interest here.

It can be observed that the PBE simulation shows a deviation of about 7% and the HSE06 simulation shows a deviation of 4% from the band gap values reported in literature. Although it is hard to ascertain the exact reason behind this deviation, different sources in literature also mention slightly different values for the band gap, for instance in ref. 59 and ref. 60. Keeping this in mind, it is safe to say that the results obtained from this simulation portray a reasonable degree of accuracy, which validates the simulation procedure developed in section 3.3.4.

To summarize, the density of states graphs obtained using both PBE and HSE06 functionals show a nearly identical trend to the one reported in literature, and the band gap deduced using PBE is an underestimation of the experimental value while the band gap obtained using HSE06 is fairly close to the actual experimental value.

#### 4.3.2. Band structure

The band structure is also simulated using both PBE and HSE06, and similar to the density of states simulations, HSE06 takes considerably longer to simulate as compared to PBE. Figures 4.5a and 4.5b show the band structure obtained using PBE and HSE06 respectively.



Figure 4.5: Band structure calculated for Silicon.

The PBE simulation band structure shows a very good trend, nearly identical to the one portrayed in literature in figure 4.2. The band gap can be deduced by taking the difference between the lowest positive and the highest negative value present in the band structure. The major difference is again the band gap which was already addressed in the previous section. The procedure developed in section 3.3.5 for PBE band gap simulations can thus be considered to portray a high degree of accuracy as well.

For HSE06, it can be observed that the simulation result is quite inaccurate. The reason behind the failure in the HSE06 simulation is most likely due to insufficient accuracy. Since it is already computationally expensive to perform HSE06 simulations, increasing the accuracy on them would require days or even a week to finish the simulation. An alternative could be to try the same simulation using another hybrid functional such as PBE0. The accuracy of the procedure set up for HSE06 band structure calculations cannot be fully ascertained until these suggestions are tested.

Due to the unsatisfactory results obtained using HSE06 band structure simulations, further band structure simulations in this project are performed only using the PBE functional. It is important to keep in mind that the PBE results are very useful to gauge the band structure shape for the material but not to extract its exact band gap itself.

#### 4.3.3. Complex refractive index

As mentioned earlier, only PBE simulations are performed for the complex refractive index due to the high computational requirement for HSE06. VASP makes it possible to simulate the dielectric function which can then be used to obtain the complex refractive index using equations 3.1 and 3.2.

For Silicon, complex refractive index simulations are first done using a k-points mesh of 21x21x21, the same as what was used in the density of states simulation step. However, another simulation was performed with a mesh of 30x30x30 to observe the difference. Figures 4.6a and 4.6b show the *n* and *k* values obtained using both these k-points meshes.



Figure 4.6: Complex refractive index of Silicon simulated for different k-points meshes.

It is evident from figure 4.6 that a similar trend is observed in both cases but a much smoother graph is obtained as a result of a higher k-points mesh. Thus, the 30x30x30 mesh is used to compare the results with experimental data. A simulation with a higher k-points mesh than 30x30x30 is not performed due to the current simulation already requiring multiple hours. The *n* and *k* values obtained for Silicon from this simulation are compared against the *n* and *k* values obtained from experiment in figure 4.7 [61].



Figure 4.7: Comparison of complex refractive index for Silicon between simulation and experiment.

The general trend followed by the n and k values as the wavelength increases follows a similar pattern as that found experimentally. However, it is easy to notice that the graphs do not show a perfect match, as the experimental result shows a higher peak of nearly 7 for n and above 5 for k along with a slightly misaligned trend in the nature of the graphs. Based on figures 4.7a and 4.7b, the deviation between simulation and experiment is calculated at every point and the average deviation from experimental values is found to be 13.4% for n and 17.4% for k.

While a deviation of 13.4% and 17.4% looks substantial, this is not a surprising result due to the wellknown limitation of using the PBE functional. As suggested in section 3.4.2, the PHS method can be used to obtain a much more accurate result. The study in literature depicted in figure 3.3 also indicated a substantial deviation from experimental value for the GW (PBE) simulation which is in agreement with the observations in figure 4.7. Thus, the procedure developed in section 3.3.6 to determine the complex refractive index can be considered accurate enough to gauge the trend of the variation in the nand k values of the material, however, it is not suitable to use the outputs obtained as inputs for future PV modelling simulations. Keeping this in mind, further complex refractive index simulations in this thesis are performed mainly to study the variation in the trend of the n and k values for the material.

#### 4.4. Conclusions

The third objective presented in section 1.3 was to ascertain the accuracy of the procedure developed in chapter 3 by testing it on a well-studied material such as Silicon. Thus, simulations were performed on Silicon as a case study and the accuracy of the procedure was evaluated in this chapter. The density of states and band structure were evaluated using the PBE and HSE06 functionals, while the complex refractive index was evaluated only using the PBE functional.

The density of states showed a striking similarity to the graph presented in literature using both the PBE and HSE06 functionals. The HSE06 band gap was much closer to the experimental value as compared to the PBE band gap which was an underestimation of the actual value. These results are in agreement with DFT simulations on Silicon in literature and thus the procedure developed in chapter 3 is verified to be correct for the density of states calculations.

The band structure generated using the PBE functional showed very close resemblance to the band structure presented in literature, with the only notable inaccuracy being the band gap, which is known to be underestimated using PBE. With HSE06, the result obtained was quite unsatisfactory due to insufficient accuracy of the simulation. Thus, the procedure developed in chapter 3 for band structure simulations can be verified to be accurate for PBE, however to ascertain the accuracy for HSE06, a

computationally expensive simulation with many more simulation points will be required. Alternately, another hybrid functional such as PBE0 could be implemented to check its accuracy.

Finally, the complex refractive index was observed to show a much smoother graph with a high k-points mesh, and the resulting n and k values for Silicon showed a very similar trend to the experimental results. However, a deviation of 13.4% for the n value and 17.4% for the k value from experiment was obtained which is primarily due to the known limitation of using the PBE functional. Thus, the procedure developed in chapter 3 can be considered accurate enough to gauge the trend in the nature of the complex refractive index, but cannot be utilised as accurate output values that can be used for further PV modelling. To improve the accuracy, the PHS method suggested in section 3.4.2 should be implemented or simulations using hybrid functionals such as PBE0 or HSE06 should be performed.

# 5

## DFT simulations for perovskite materials

The accuracy of the procedure developed in chapter 3 was verified in chapter 4. The procedure can thus be used to study promising new solar cell materials, namely perovskites. In this chapter, the variation in the band gap and complex refractive index as the composition of halides in inorganic perovskites is varied is studied. Section 5.1 introduces pervoskite materials and their use in solar cells. Section 5.2 then discusses the parameters used as inputs for the perovskite VASP simulations. The results of the simulations are discussed in section 5.3 and section 5.4 finally concludes the chapter.

#### 5.1. Perovskite materials

Perovskite materials are materials with the  $ABX_3$  crystal structure where A and B are cations and X is an anion. Perovskites gained attention as promising solar cell materials as they showed the possibility of producing high-efficiency solar cells at low monetary and energy costs [62]. Metal halide perovskites particularly have risen to popularity due to the ease of processing them and their opto-electronic properties being suitable for use as absorber materials in solar cells [63]. All-inorganic perovskites where the A cation is usually Cs, the B cation is either Pb or Sn and the X anion is a halogen such as I, Br or CI have found popularity for use in solar cells alongside hybrid perovskite materials where the Acation is usually methylammonium or formaldinium [63]. Further, high efficiency has been observed for perovskites with mixed cations at the A position as well as mixed halides at the X position [8].

As mentioned in section 1.3, inorganic perovskites are studied in the scope of this thesis. The perovskite materials for which VASP simulations are performed are of the form  $C_SPbX_3$  where X is a halogen such as I, Br or CI and perovskites of the form  $C_SPbX_2Y$  or  $C_SPbXY_2$  where X and Y can be any two of the three halogens mentioned earlier, namely I, Br or CI. Of these materials, the most well-studied in literature are the ones using either I, Br or a combination of both [64]. These are thus used to validate the perovskite simulations first and the procedure developed in chapter 3 is then utilized further to study remaining halogen combinations possible involving CI.

#### **5.2.** Simulation inputs

As mentioned in section 4.2, the only inputs that need to be defined for each new material to be simulated are the POSCAR and POTCAR files, the KPOINTS mesh density and the ENCUT value in the INCAR file. The POTCAR files for all the aforementioned materials were generated by concatenating individual atomic POTCAR files, as described in section 3.2.2. All the aforementioned materials to be simulated can be grouped into four different lattice structures, each of which needs a separate POSCAR file. These include structures of the type  $C_{SPbX_3}$ ,  $C_{SPbX_2}Y$ ,  $C_{SPbXY_2}$  where X and Y can be any two of the three halides of I, Br or CI followed by a final simulation on the material  $C_{SPbIBrCl}$ . The structures of the type  $C_{SPbX_3}$  have been visualized already in figure 3.2. Figure 5.1 shows the remaining structures also visualized using the VESTA software [50].



Figure 5.1: Perovskite structures visualized using the VESTA software.

In this figure, the cyan central atom represents Cs, the grey atoms on the corners of the cube represent Pb and the remaining atoms represent the halogens. In figures 5.1a and 5.1b, the purple atoms represent X and the brown atoms represent Y. In figure 5.1c for the halogens, the purple atoms represent I, the brown atoms represent Br and the green atoms represent Cl. Once these four structures are generated using VESTA, it is simple to replace the halogen in the POSCAR file for different X and Y as described in section 3.2.1.

An 11x11x11 k-points grid is used yet again for relaxation and SCF steps while a 21x21x21 grid is used for density of states calculations. The KPOINTS file for band structure simulations is calculated again using the SeeK-path tool [53], this time only for PBE simulations. For complex refractive index, due to the higher simulation time required for perovskite materials, a k-points grid of 11x11x11 is used for all simulations.

Based on the ENMAX values for the atomic species involved, a cut-off energy of 270 eV is used for every simulation involving the Chlorine atom whereas a cut-off energy of 230 eV is used for all the other simulations.

#### 5.3. Results

The band gap is calculated by performing density of states and band structure simulations. The results of these are presented in section 5.3.1. The complex refractive index results are then presented in 5.3.2. Finally, the results are discussed and analyzed in section 5.3.3.

#### 5.3.1. Band gap

The procedure developed in chapter 3 is employed to perform density of states calculations for perovskite materials. The materials of the type  $CsPbX_3$  are studied first. The density of states obtained using the PBE functional for  $CsPbI_3$ ,  $CsPbBr_3$  and  $CsPbCl_3$  is indicated in figure 5.2.



Figure 5.2: Density of states calculations for perovskites of the form  $CsPbX_3$  with X = I, Br or Cl.

It can be observed from this figure that the graphs follow a similar trend to each other with the main variation being in the band gap and height of the peaks. However, since the primary purpose of performing density of states and band structure simulations is to evaluate the band gap in this section, only the trend in the band gap is of relevance to the thesis. Band structure simulations using the PBE functional also portray a similar result and their graphs are shown in figure 5.3.



Figure 5.3: Band structure calculations for perovskites of the form  $CsPbX_3$  with X = I, Br or CI.

Since the trend in the band gaps is the focus of this section, the density of states and band structure graphs for the remaining materials can be found in appendix B.

As indicated in section 5.1,  $CsPbI_3$ ,  $CsPbI_2Br$ ,  $CsPbIBr_2$  and  $CsPbBr_3$  are well studied materials and are thus suitable to gauge the accuracy of the perovskite simulations done in this project. Figure 5.4 shows a comparison between the experimental band gap values [65, 66, 67] and the band gaps determined from the simulations in this project.



Figure 5.4: Band gap variation as I is changed to Br.

It can be observed that the band gap increases as each lodine atom is replaced by Bromine, in both the experimental as well as the simulated case. The band gaps obtained from simulation are an underestimation of their corresponding experimental values, which is once again a well-known result of using the PBE simulation, as described in section 3.4. However, it can also be observed that the band

gaps obtained as a result of simulation do not exhibit the same slope of increase as the experimental band gaps. In both cases, the band gap increases linearly from  $CsPBI_3$  to  $CsPbI_2Br$  and  $CsPbIBr_2$ , but the slope of increase is much steeper in the experimental case. A similar steeper increase can be observed from  $CsPbIBr_2$  to  $CsPbBr_3$  in the experimental case.

While the cause behind this differing slope is unknown, the results obtained from PBE simulations in this work show a remarkable accuracy when compared to the PBE simulation results available in literature for these four materials. Table 5.1 shows a comparison between the PBE band gap values available in literature [68, 69, 70, 71] and those obtained in this work.

Material	CsPbI <sub>3</sub>	CsPbI <sub>2</sub> Br	CsPbIBr <sub>2</sub>	CsPbBr <sub>3</sub>
This work	1.5	1.54	1.57	1.79
Literature	1.49	1.49	1.54	1.76
Deviation	0.67%	3.36%	1.95%	1.70%

Table 5.1: Band gaps obtained using PBE in this work and in literature (all values in eV).

While there is a deviation observed seems to vary for the different materials, it is most likely due to the fact that the literature band gaps are sourced from multiple different papers. However, the more important take away from this comparison is the deviation value itself from the actual band gap values reported in literature. The perovskite PBE band gaps seem to be in very close agreement with literature, as the highest deviation observed is that of 3.36%, while the rest are within 2%. This is a clear indication of the accuracy of these results and thus provides motivation to study the properties of even more materials using the aforementioned simulation procedure. It is important to note that the even though the PBE results are accurate to literature, the band gap values of the PBE simulations themselves are an underestimation of the experimental values, and thus the trend in the band gaps is the more useful result than the value of the band gap itself.

In section 4.3.1 it was observed that the HSE06 functional yielded a band gap value that was much closer to the experimental value for Silicon as compared to the PBE functional. Thus, a density of states calculation was also performed on  $CsPbI_3$  using HSE06, the graph of which is shown in figure 5.5.



Figure 5.5: Density of states using HSE06 for CsPbI<sub>3</sub>.

A band gap of 2.7 eV was obtained from the HSE06 simulation, which is an extreme overestimation of the experimental value of 1.74 eV, indicating a fair amount of inaccuracy in the simulation result. While the reason behind this overestimation is unknown, potential solutions to obtain better results might be the use of a much higher k-points mesh and a high value of NEDOS or the use of the PBE0 hybrid functional in place of HSE06. The HSE06 perovskite simulation time stretched over multiple days, and in combination with the inaccurate result obtained for  $CsPbI_3$ , it was decided to not perform further simulations for other perovskites using HSE06 in this project.

Having confirmed the high accuracy of the PBE simulation and the inaccuracy of the HSE06 simulation by studying the band gaps of  $CsPbX_3$  for I and Br halides, other halide combinations involving CI are then simulated only using PBE. Since these variations are not studied much in literature, there is no experimental or simulation data to compare these results against. However, considering the accuracy of the PBE simulations for the band gap variation from  $CsPbI_3$  to  $CsPbBr_3$ , it is assumed that a similar level of accuracy is generated by the further simulations involving CI.



Figure 5.6: Simulated band gap variation with halide change.

Figure 5.6a shows the band gap variation as Br is changed to Cl and figure 5.6b shows the variation as I is changed to Cl. In both cases, an increasing trend in the band gap can be observed. Similar to the variation observed from I to Br, the first three band gaps are nearly collinear and then a sudden increase is observed at the end.

A band gap of 1.62 eV is also obtained from the simulation for CsPbIBrCl, the graphs for which are also provided in appendix B. This trend behind these band gaps is further analyzed in section 5.3.3.

#### 5.3.2. Complex refractive index

As observed in section 4.3.3, the complex refractive index simulations showed a deviation of 13-18% from experimental values for Silicon, but portrayed a similar trend to the experimental values. While the deviation is mainly due to the inaccuracy of the PBE functional, the trend in the n and k values is still useful to gauge the optical properties of the materials. Due to the lack of experimental or simulation data available in literature for the perovskite materials being studied, the accuracy of the perovskite simulations is considered to be in a similar range to that of Silicon, and the trends in their properties instead are of the highest interest.

The trend in the complex refractive index for varying halide compositions in the aforementioned perovskite materials is studied by plotting the *n* and *k* graphs for  $CsPbI_xBr_{3-x}$ ,  $CsPbBr_xCl_{3-x}$  and  $CsPbI_xCl_{3-x}$ respectively for x = 0 to 3. These trends are further analyzed in section 5.3.3. Figure 5.7a shows the variation in the value of *n* and figure 5.7b shows the variation in the value of *k* for materials  $CsPbI_xBr_{3-x}$ 



Figure 5.7: Variation of complex refractive index as I is changed to Br.

It can be observed from the figure that the n and k values for all the materials show a similar trend. The n value increases gradually from about 250 nm to 450 nm and then slightly decreases and stabilizes after 800 nm. The k value also increases from about 200 nm to 300 nm and then gradually declines until about 800 nm after which it approaches zero. The main difference that is observed is that the value for both n and k uniformly decreases as I is changed to Br in the material. It can also be observed that the peak for n and k for the materials happens at shorter wavelengths as I is changed to Br.

Figure 5.8 shows the n and k graphs as the halide is gradually changed from Br to Cl. Similar to the shift observed in the change from I to Br, a uniform decrease is observed for both the n and k values as Br is changed to Cl and the peaks for the materials also seem to move towards shorter wavelengths as Br changes to Cl.



Figure 5.8: Variation of complex refractive index as Br is changed to Cl.

Finally, the variation in the *n* and *k* values for materials  $CsPbI_xCl_{3-x}$  can be observed in figure 5.9. Similar to the previous two cases, the values of *n* and *k* as well as the peaks in *n* and *k* reduce and get shifted to shorter wavelengths as I is changed to CI.



Figure 5.9: Variation of complex refractive index as I is changed to CI.

The graphs obtained from this discussion thus show a consistent trend of declining n and k values as well as a shift in the peaks of the n and k values as the atomic number of the halogen reduces. This is further discussed in section 5.3.3.

#### 5.3.3. Discussion

The trend observed in the band gap as the halides were varied in all three cases, namely  $CsPbI_xBr_{3-x}$ ,  $CsPbBr_xCl_{3-x}$  and  $CsPbI_xCl_{3-x}$ , was a slow increase from the halogen having the higher atomic number to the mixed halides and then a steep increase to the halogen having the lower atomic number. Thus, all the band gaps have been plotted against the total atomic number of all the atoms involved in the material in figure 5.10.



Figure 5.10: Band gaps for all the simulated perovskites.

It can be noticed that although the band gap does increase with a decrease in the atomic number of the halogens involved, it is not purely dependent on their atomic number. For instance, the total atomic number for  $CsPbBr_3$  and CsPbIBrCl is the same but their band gaps are quite different. Thus, no empirical relationship between the atomic number of the halides and the band gap of the inorganic

perovskite can be established. The only trend that can be verified is that the band gap of an inorganic halide perovskite is higher for a lower atomic number halogen as compared to a higher atomic number halogen. Further, for mixed halides, the band gap increases as the total atomic number of the mixed halides decreases in a non-linear manner.

The band gaps and complex refractive index results obtained are all based on the PBE simulations, and thus their values are not accurate to the experimental values. Methods to improve the accuracy of these values have been detailed upon in section 3.4 in addition to the potential use of hybrid functionals to obtain accurate results. While HSE06 failed to yield an accurate band gap in this thesis, the cause for it is not certain and there is potential to implement other hybrid functionals such as PBE0 instead.

However, what is more interesting from these PBE simulations is the trend in the results obtained as opposed to the actual value of the results themselves. Figure 5.4 was a good indication that although the output values of the simulation are not accurate due to the use of the PBE functional, the trend followed by the results matches the trends observed in experiment. The trends seen in the complex refractive index have already been discussed in section 5.3.2. Since their values are not accurate, the important takeaway from the simulation is that similar to the case of the band gap, the values of n and k for the inorganic halide perovskite reduce as the atomic number of the halide decreases. The peak values for n and k also shift towards lower wavelengths as the atomic number of the halide decreases. This can help provide insight on which materials are useful to absorb light for a given wavelength range in solar cells.

#### 5.4. Conclusions

In section 1.3 the final objective presented was to apply the procedure developed in chapter 3 to examine the variation in the band gap and complex refractive index of inorganic perovskites with different halides. This objective has been addressed in this chapter.

The band gap and complex refractive index simulations were only performed using the PBE functional. This is because it was observed that HSE06 provided an inaccurate band gap for  $CsPbI_3$  in combination with the fact that HSE06 simulations require multiple days if not over a week to perform simulations on perovskites depending on the desired accuracy. As the PBE functional is known to have a degree of inaccuracy, the trends in the band gap and complex refractive index were the important takeaway from these simulations, and the actual values obtained are not useful for further PV modelling calculations.

The accuracy of PBE simulations for the trends in the *n* and *k* values of the complex refractive index was already established in section 4.3.3. The accuracy of the PBE simulations for band gap calculations was verified for perovskite materials of the type  $CsPbI_xBr_{3-x}$  where x = 0 to 3 by comparing the results with PBE simulation results available in literature. A remarkable accuracy was observed for these simulations, with the highest observed deviation from literature being merely 3.36%.

For the band gap, it was observed that the band gap of the perovskite material increased as the total atomic number of the halides used decreased. For mixed halides, it was observed that the band gap for the mixed halides increased from the halide having the higher atomic number to the halide having the lower atomic number in a non-linear manner. The n and k values of the complex refractive index decreased as the total atomic number of the halides decreased and the peaks in the n and k values also shifted towards shorter wavelengths as the total atomic number of the halides decreased.

It can thus be concluded that PBE simulations using the procedure provided in chapter 3 can be used to help notice trends in opto-electrical properties of solar cell materials, compare the trends in the properties of different solar cell materials and gauge which materials can be suitable for use in different solar cells. The calculation results can not however be utilized as direct inputs for further PV modelling simulations unless post-processing correction methods or hybrid functionals are correctly employed.

## 6 Conclusion

In chapter 1, four research objectives were defined to be studied in this thesis. Chapters 2 - 5 addressed these objectives and the conclusions drawn from these are summarized in this chapter.

#### 1. Understand the fundamentals of DFT software and the benefits of using the VASP software.

In chapter 2, the basic relevant principles of DFT, such as the multi-body time-independent Schrödinger equation, the Kohn-Sham equations and potential, and the components of the Kohn-Sham potential such as the Hartree potential and exchange-correlation potential were first introduced to help gain an understanding of the basics of DFT software. Chapter 2 also described how classical DFT is required for the purposes of this thesis and that it works by iteratively solving Kohn-Sham equations until self-consistency is achieved. While the exchange-correlation potential is handled by the software using different functionals, the Hartree potential is obtained using different electron structure calculation methods such as plane waves with pseudopotentials, STOs and the PAW method. While many functionals are available in most DFT software, only the PBE and HSE06 functionals are used in this thesis.

Among many available DFT software, VASP is a very useful software for periodic DFT calculations which makes use of the PAW method allowing it to perform simulations accurately and efficiently. VASP offers a wide variety of functionals and provides good efficiency for hybrid functionals such as HSE06, making it a suitable choice for this thesis.

## 2. Develop a simulation procedure for use in the TU Delft PVMD group to obtain the density of states, band structure and complex refractive index for absorber materials in photovoltaic cells using the VASP software.

VASP requires multiple input files for each simulation. Further, to simulate the density of states, band structure or complex refractive index, multiple simulation steps are involved, each of which requires different input files and some input files need to be modified for each step. A detailed step-by-step procedure indicating each step required for each desired output, the inputs required at every step of the process, and the configuration of each input file for each simulation step was provided in chapter 3. Further, the known limitations of using PBE as a functional for the simulations were acknowledged and recommendations made in literature to improve the accuracy of the results were also discussed.

### 3. Ascertain the accuracy of this procedure for a well-studied photovoltaic absorber material such as monocrystalline Silicon.

For Silicon, the density of states and band structure were evaluated using the PBE and HSE06 functionals, while the complex refractive index was evaluated only using the PBE functional. The density of states showed a striking similarity to the graph presented in literature using both the PBE and HSE06 functionals. The HSE06 band gap was much closer to the experimental value as compared to the PBE band gap which was an underestimation of the actual value. These results were in agreement with DFT simulations on Silicon in literature and thus the procedure developed in chapter 3 was verified to be correct for the density of states calculations.

The band structure generated using the PBE functional showed very close resemblance to the band structure presented in literature, with the only notable inaccuracy being the band gap, which is known to be underestimated using PBE. With HSE06, the result obtained was quite unsatisfactory due to insufficient accuracy of the simulation. Thus, the procedure developed in chapter 3 for band structure simulations was verified to be accurate for PBE, however the accuracy of the procedure for HSE06 simulations could not be verified as the cause for inaccuracy in the results was not certain.

Finally, the complex refractive index was observed to show a much smoother graph with a high k-points mesh, and the resulting n and k values for Silicon showed a very similar trend to the experimental results. However, the exact nature of the graph was not the same which is also a known limitation of using the PBE functional. Thus, the procedure developed in chapter 3 was considered accurate enough to gauge the trend in the nature of the complex refractive index, but unsuitable to calculate accurate output values that can be used for further PV modelling.

### 4. Apply the developed procedure to examine the variation in the band gap and complex refractive index of inorganic perovskites with different halides.

The band gap and complex refractive index simulations were only performed using the PBE functional. This is because it was observed that HSE06 provided an inaccurate band gap for  $CsPbI_3$  in combination with the fact that HSE06 simulations require multiple days if not over a week to perform simulations on perovskites depending on the desired accuracy.

The accuracy of the PBE simulations for band gap calculations was verified for perovskite materials of the type  $CsPbI_xBr_{3-x}$  where x = 0 to 3 by comparing the results with PBE simulation results available in literature and a remarkable accuracy was observed for these simulations, with the highest observed deviation from literature being merely 3.36%. It was observed that the band gap of the perovskite material increased as the total atomic number of the halides used decreased. For mixed halides, it was observed that the band gap for the mixed halides increased from the halide having the higher atomic number to the halide having the lower atomic number in a non-linear manner.

For the complex refractive index, the *n* and *k* values decreased as the total atomic number of the halides decreased and the peaks in the *n* and *k* values also shifted towards shorter wavelengths as the total atomic number of the halides decreased. As PBE simulations are known to have a degree of inaccuracy, it was concluded that these PBE simulations can be used to help notice trends in optoelectrical properties of solar cell materials, compare the trends in the properties of different solar cell materials and gauge which materials can be suitable for use in different solar cells. The calculation results can not however be utilized as direct inputs for further PV modelling simulations unless post-processing correction methods or hybrid functionals are correctly employed.

#### 6.1. Recommendations

Although this thesis managed to successfully define a procedure for opto-electrical simulations on VASP, there is still plenty of scope for further research into this topic. Some recommendations for further research are presented here.

#### Implementing post-processing methods to improve result accuracy.

In section 3.4, some post-processing methods are presented to improve the accuracy of PBE simulations done on VASP. These could be implemented to investigate the accuracy improvement in the result. Further, it might also be of interest to investigate or develop even more post-processing methods that can be easily integrated with the simulation procedure developed in chapter 3.

#### Use of hybrid functionals instead of PBE.

Although hybrid functionals were explored in this thesis, only some of their results yielded good accuracy. While it seems like it might be possible to improve the accuracy of the Silicon HSE06 band structure simulation from section 4.3.2 by running a longer simulation which lasts perhaps over a week, the reason behind the inaccuracy of the density of states simulation for  $CsPbI_3$  in section 5.3.1 is unclear. Potentially using PBE0 instead of HSE06, or running high accuracy simulations using HSE06 itself which may last over a week could be interesting as hybrid functionals are reported to have very good accuracy in literature [3, 16] and have also demonstrated good accuracy for density of states simulations for Silicon in this work in chapter 4. High accuracy results using hybrid functionals would eliminate the need of implementing post-processing methods, but would naturally be more time consuming.

#### Use of VASP on the DelftBlue supercomputer in TU Delft.

For research in TU Delft, especially within the PVMD group, the use of VASP on the DelftBlue supercomputer is interesting. VASP is available on the DelftBlue supercomputer which has extremely high simulation capabilities which may open up possibilities for many more simulations that were currently too time consuming. High accuracy density of states and band structure simulations for perovskite, or even more complex materials, might be feasible using hybrid functionals on DelftBlue. Further, it might also be possible to try dielectric function simulations using hybrid functionals on this supercomputer.

#### Simulations of more complex solar cell materials using VASP

In this thesis, the most complicated materials studied were mixed halide inorganic perovskites such as  $CsPbI_2Br$ . However, there is also potential to study perovskites with more complex structures such as  $CH_3NH_3PbI_3$  and even try mixed halide combinations on these methylammonium perovskites such as  $CH_3NH_3PbI_2Br$ .

It could also be interesting to try simulations on amorphous PV materials such as amorphous Silicon [72]. The procedure developed in chapter 3 is likely not applicable to amorphous materials due to the absence of symmetry in their structures. The procedure to simulate amorphous materials is not clear yet and could be of value to study in the future.

#### Investigating temperature-dependent band gap simulations using VASP

The ISMEAR tag described in section 3.2.3 that is used in the INCAR file is used by VASP to determine partial occupancies for the orbitals which can be indicative of the temperature. It is perhaps possible to introduce a degree of temperature-dependent variation by altering the ISMEAR file, however the accuracy of this may not be too accurate [28]. To perform proper temperature-dependent simulations on VASP, the Quasi-Harmonic Approximation (QHA) method is required to determine the effect of temperature on lattice parameters [73]. It is suggested in literature that a package known as Phonopy can be used interfaced with VASP to implement QHA calculations [74]. However, the intricacy of this has not been assessed during this thesis and thus actually performing temperature-dependent calculations using VASP could be quite a tall task.

### Bibliography

- [1] P. Erhart, "A very short introduction to density functional theory (dft)," 2016.
- [2] Q. Peng, F. Duarte, and R. S. Paton, "Computing organic stereoselectivity from concepts to quantitative calculations and predictions," *Chem. Soc. Rev.*, vol. 45, pp. 6093–6107, 2016. [Online]. Available: http://dx.doi.org/10.1039/C6CS00573J
- [3] M. Nishiwaki and H. Fujiwara, "Highly accurate prediction of material optical properties based on density functional theory," *Computational Materials Science*, vol. 172, p. 109315, 2020.
- [4] M. Greiner, "Electronic structure of solids," 2017.
- [5] E. D. Palik, Handbook of optical constants of solids. Academic press, 1998, vol. 3.
- [6] P. IEA, "lea, change in global electricity generation by source in the stated policies scenario, 2000-2040." [Online]. Available: https://www.iea.org/data-and-statistics/charts/ change-in-global-electricity-generation-by-source-in-the-stated-policies-scenario-2000-2040
- [7] J. F. Geisz, M. A. Steiner, N. Jain, K. L. Schulte, R. M. France, W. E. McMahon, E. E. Perl, and D. J. Friedman, "Building a six-junction inverted metamorphic concentrator solar cell," *IEEE Journal of Photovoltaics*, vol. 8, no. 2, pp. 626–632, 2018.
- [8] K. A. Bush, A. F. Palmstrom, J. Y. Zhengshan, M. Boccard, R. Cheacharoen, J. P. Mailoa, D. P. McMeekin, R. L. Hoye, C. D. Bailie, T. Leijtens *et al.*, "23.6%-efficient monolithic perovskite/silicon tandem solar cells with improved stability," *Nature Energy*, vol. 2, no. 4, pp. 1–7, 2017.
- [9] A. Smets, K. Jäger, O. Isabella, R. Van Swaaij, and M. Zeman, Solar Energy The physics and engineering of photovoltaic conversion, technologies and systems, 02 2016.
- [10] Meteotest, Meteonorm Handbook part I: Software, version 7 ed. Meteotest, 2020.
- [11] R. Santbergen, T. Meguro, T. Suezaki, G. Koizumi, K. Yamamoto, and M. Zeman, "Genpro4 optical model for solar cell simulation and its application to multijunction solar cells," *IEEE Journal of Photovoltaics*, vol. 7, no. 3, pp. 919–926, 2017.
- [12] M. Zeman, J. v. d. Heuvel, M. Kroon, J. Willemen, B. Pieters, J. Krč, and S. Solntsev, Advanced Semiconductor Analysis User's Manual, version 6.0 ed.
- [13] J. Koh, H. Fujiwara, Y. Lu, C. Wronski, and R. Collins, "Real time spectroscopic ellipsometry for characterization and optimization of amorphous silicon-based solar cell structures," *Thin solid films*, vol. 313, pp. 469–473, 1998.
- [14] M. Chan and G. Ceder, "Efficient band gap prediction for solids," *Physical review letters*, vol. 105, no. 19, p. 196403, 2010.
- [15] A. Reshak and S. A. Khan, "Density of electronic states and dispersion of optical functions of defect chalcopyrite cdga2x4 (x= s, se): Dft study," *Materials Research Bulletin*, vol. 48, no. 11, pp. 4555–4564, 2013.
- [16] P. Pitriana, T. D. K. Wungu, R. Hidayat *et al.*, "The characteristics of band structures and crystal binding in all-inorganic perovskite apbbr3 studied by the first principle calculations using the density functional theory (dft) method," *Results in Physics*, vol. 15, p. 102592, 2019.
- [17] J.-J. Zhou and M. Bernardi, "Ab initio electron mobility and polar phonon scattering in gaas," *Physical Review B*, vol. 94, no. 20, p. 201201, 2016.

- [18] V. L. Shaposhnikov, A. V. Krivosheeva, V. E. Borisenko, J.-L. Lazzari, and F. A. d'Avitaya, "Ab initio modeling of the structural, electronic, and optical properties of a<sup>ii</sup>b<sup>iv</sup>c<sup>v</sup><sub>2</sub> semiconductors," *Phys. Rev. B*, vol. 85, p. 205201, May 2012. [Online]. Available: https://link.aps.org/doi/10.1103/ PhysRevB.85.205201
- [19] D. Sholl and J. A. Steckel, Density functional theory: a practical introduction. John Wiley & Sons, 2011.
- [20] J.-M. Combes, P. Duclos, and R. Seiler, "The born-oppenheimer approximation," in *Rigorous atomic and molecular physics*. Springer, 1981, pp. 185–213.
- [21] W. Kohn and L. J. Sham, "Self-consistent equations including exchange and correlation effects," *Phys. Rev.*, vol. 140, pp. A1133–A1138, Nov 1965. [Online]. Available: https: //link.aps.org/doi/10.1103/PhysRev.140.A1133
- [22] C. Rostgaard, "The projector augmented-wave method," 2009.
- [23] M. Orio, D. A. Pantazis, and F. Neese, "Density functional theory," *Photosynthesis research*, vol. 102, no. 2, pp. 443–453, 2009.
- [24] E. Runge and E. K. Gross, "Density-functional theory for time-dependent systems," *Physical Review Letters*, vol. 52, no. 12, p. 997, 1984.
- [25] G. M. J. Barca, C. Bertoni, L. Carrington, D. Datta, N. De Silva, J. E. Deustua, D. G. Fedorov, J. R. Gour, A. O. Gunina, E. Guidez, T. Harville, S. Irle, J. Ivanic, K. Kowalski, S. S. Leang, H. Li, W. Li, J. J. Lutz, I. Magoulas, J. Mato, V. Mironov, H. Nakata, B. Q. Pham, P. Piecuch, D. Poole, S. R. Pruitt, A. P. Rendell, L. B. Roskop, K. Ruedenberg, T. Sattasathuchana, M. W. Schmidt, J. Shen, L. Slipchenko, M. Sosonkina, V. Sundriyal, A. Tiwari, J. L. Galvez Vallejo, B. Westheimer, M. Wloch, P. Xu, F. Zahariev, and M. S. Gordon, "Recent developments in the general atomic and molecular electronic structure system," *The Journal of Chemical Physics*, vol. 152, no. 15, p. 154102, Apr. 2020. [Online]. Available: http://aip.scitation.org/doi/10.1063/5.0005188
- [26] F. Neese, "The orca program system," WIREs Computational Molecular Science, vol. 2, no. 1, pp. 73–78, 2012. [Online]. Available: https://wires.onlinelibrary.wiley.com/doi/abs/10.1002/wcms.81
- [27] I. S. Ufimtsev and T. J. Martinez, "Quantum chemistry on graphical processing units. 3. analytical energy gradients, geometry optimization, and first principles molecular dynamics," *Journal of Chemical Theory and Computation*, vol. 5, no. 10, pp. 2619–2628, 2009.
- [28] "The vasp manual." [Online]. Available: https://www.vasp.at/wiki/index.php/The\_VASP\_Manual
- [29] "Quantum espresso user's guide." [Online]. Available: https://www.quantum-espresso.org/Doc/ pw\_user\_guide/
- [30] SCM, "Band manual amsterdam modelling suite 2022.1," 2022.
- [31] A. A. Moya, "Numerical simulation of c-si solar cells based on transition metal oxide as carrier selective contact," 2020.
- [32] R. M. Martin, "Bridging time and length scales in materials science and biophysics," 2005.
- [33] J. Hafner, "Ab-initio simulations of materials using vasp: Density-functional theory and beyond," Journal of computational chemistry, vol. 29, no. 13, pp. 2044–2078, 2008.
- [34] S. Clark, "Plane waves as a basis," 2012.
- [35] K. Refson, "Introduction to dft and the plane-wave pseudopotential method," 2014.
- [36] R. M. Martin, *Electronic structure: basic theory and practical methods*. Cambridge university press, 2020.
- [37] SCM, "Adf manual amsterdam modelling suite 2022.1," 2022.

- [38] K. Adhikari, A. Chakrabarty, O. Bouhali, N. Mousseau, C. S. Becquart, and F. El-Mellouhi, "Benchmarking the performance of plane-wave vs. localized orbital basis set methods in dft modeling of metal surface: a case study for fe-(110)," *Journal of computational science*, vol. 29, pp. 163–167, 2018.
- [39] J. Paier, R. Hirschl, M. Marsman, and G. Kresse, "The perdew-burke-ernzerhof exchangecorrelation functional applied to the g2-1 test set using a plane-wave basis set," *The Journal of chemical physics*, vol. 122, no. 23, p. 234102, 2005.
- [40] P. Blaha, K. Schwarz, F. Tran, R. Laskowski, G. K. Madsen, and L. D. Marks, "Wien2k: An apw+ lo program for calculating the properties of solids," *The Journal of Chemical Physics*, vol. 152, no. 7, p. 074101, 2020.
- [41] M. Petersen, F. Wagner, L. Hufnagel, M. Scheffler, P. Blaha, and K. Schwarz, "Improving the efficiency of fp-lapw calculations," *Computer Physics Communications*, vol. 126, no. 3, pp. 294– 309, 2000.
- [42] G. I. Csonka, J. P. Perdew, A. Ruzsinszky, P. H. Philipsen, S. Lebègue, J. Paier, O. A. Vydrov, and J. G. Ángyán, "Assessing the performance of recent density functionals for bulk solids," *Physical Review B*, vol. 79, no. 15, p. 155107, 2009.
- [43] N. Holzwarth, G. Matthews, R. Dunning, A. Tackett, and Y. Zeng, "Comparison of the projector augmented-wave, pseudopotential, and linearized augmented-plane-wave formalisms for densityfunctional calculations of solids," *Physical Review B*, vol. 55, no. 4, p. 2005, 1997.
- [44] J. P. Perdew, A. Ruzsinszky, L. A. Constantin, J. Sun, and G. I. Csonka, "Some fundamental issues in ground-state density functional theory: A guide for the perplexed," *Journal of chemical theory* and computation, vol. 5, no. 4, pp. 902–908, 2009.
- [45] J. P. Perdew, K. Burke, and M. Ernzerhof, "Generalized gradient approximation made simple," *Physical review letters*, vol. 77, no. 18, p. 3865, 1996.
- [46] J. Heyd, G. E. Scuseria, and M. Ernzerhof, "Hybrid functionals based on a screened coulomb potential," *The Journal of chemical physics*, vol. 118, no. 18, pp. 8207–8215, 2003.
- [47] X. (https://mattermodeling.stackexchange.com/users/683/xivi76), "Quantum espresso vs vasp," Matter Modeling Stack Exchange, uRL:https://mattermodeling.stackexchange.com/q/952 (version: 2020-05-21). [Online]. Available: https://mattermodeling.stackexchange.com/q/952
- [48] M. de Jong, W. Chen, T. Angsten, A. Jain, R. Notestine, A. Gamst, M. Sluiter, C. Krishna Ande, S. van der Zwaag, J. J. Plata, C. Toher, S. Curtarolo, G. Ceder, K. A. Persson, and M. Asta, "Charting the complete elastic properties of inorganic crystalline compounds," *Scientific Data*, vol. 2, 03 2015. [Online]. Available: http://perssongroup.lbl.gov/papers/sdata2015-elasticprops. pdf
- [49] S. Gražulis, D. Chateigner, R. T. Downs, A. Yokochi, M. Quirós, L. Lutterotti, E. Manakova, J. Butkus, P. Moeck, and A. Le Bail, "Crystallography open database–an open-access collection of crystal structures," *Journal of applied crystallography*, vol. 42, no. 4, pp. 726–729, 2009.
- [50] K. Momma and F. Izumi, "Vesta: a three-dimensional visualization system for electronic and structural analysis," *Journal of Applied crystallography*, vol. 41, no. 3, pp. 653–658, 2008.
- [51] D. J. Chadi and M. L. Cohen, "Special points in the brillouin zone," *Physical Review B*, vol. 8, no. 12, p. 5747, 1973.
- [52] P. E. Blöchl, O. Jepsen, and O. K. Andersen, "Improved tetrahedron method for brillouin-zone integrations," *Physical Review B*, vol. 49, no. 23, p. 16223, 1994.
- [53] Y. Hinuma, G. Pizzi, Y. Kumagai, F. Oba, and I. Tanaka, "Band structure diagram paths based on crystallography," *Computational Materials Science*, vol. 128, pp. 140–184, 2017.

- [54] A. M. Ganose, A. J. Jackson, and D. O. Scanlon, "sumo: Command-line tools for plotting and analysis of periodic\* ab initio\* calculations," *Journal of Open Source Software*, vol. 3, no. 28, p. 717, 2018.
- [55] M. P. Marder, Condensed matter physics. John Wiley & Sons, 2010.
- [56] I. PVPS, "Snapshot of global pv markets 2021," *International Energy Agency (IEA): Paris, France*, 2020.
- [57] A. Allouhi, S. Rehman, M. S. Buker, and Z. Said, "Up-to-date literature review on solar pv systems: Technology progress, market status and r&d," *Journal of Cleaner Production*, p. 132339, 2022.
- [58] P. Das, M. Mohammadi, and T. Bazhirov, "Accessible computational materials design with high fidelity and high throughput," *arXiv preprint arXiv:1807.05623*, 2018.
- [59] M. Jain, J. R. Chelikowsky, and S. G. Louie, "Reliability of hybrid functionals in predicting band gaps," *Physical review letters*, vol. 107, no. 21, p. 216806, 2011.
- [60] Y. Zhao and D. G. Truhlar, "Calculation of semiconductor band gaps with the m06-I density functional," *The Journal of chemical physics*, vol. 130, no. 7, p. 074103, 2009.
- [61] E. Palik and G. Ghosh, "Handbook of optical constants of solids (new york: Academic)," 1985.
- [62] C. Zuo, H. J. Bolink, H. Han, J. Huang, D. Cahen, and L. Ding, "Advances in perovskite solar cells," Advanced Science, vol. 3, no. 7, p. 1500324, 2016.
- [63] H. J. Snaith, "Present status and future prospects of perovskite photovoltaics," *Nature materials*, vol. 17, no. 5, pp. 372–376, 2018.
- [64] I. M. Maafa, "All-inorganic perovskite solar cells: Recent advancements and challenges," Nanomaterials, vol. 12, no. 10, p. 1651, 2022.
- [65] M. Ahmad, G. Rehman, L. Ali, M. Shafiq, R. Iqbal, R. Ahmad, T. Khan, S. Jalali-Asadabadi, M. Maqbool, and I. Ahmad, "Structural, electronic and optical properties of cspbx3 (x= cl, br, i) for energy storage and hybrid solar cell applications," *Journal of Alloys and Compounds*, vol. 705, pp. 828–839, 2017.
- [66] H. W. Qiao, M. Chen, Z. Zhou, Q. Cheng, Y. Hou, and H. G. Yang, "Improved photovoltaic performance of cspbi2br perovskite films via bivalent metal chloride doping," *Frontiers in Energy Research*, vol. 9, p. 692059, 2021.
- [67] Y. Guo, X. Yin, J. Liu, S. Wen, Y. Wu, and W. Que, "Inorganic cspbibr2-based perovskite solar cells: fabrication technique modification and efficiency improvement," *Solar RRL*, vol. 3, no. 9, p. 1900135, 2019.
- [68] C. Grote and R. F. Berger, "Strain tuning of tin–halide and lead–halide perovskites: a first-principles atomic and electronic structure study," *The Journal of Physical Chemistry C*, vol. 119, no. 40, pp. 22 832–22 837, 2015.
- [69] Y. Yuan, R. Xu, H.-T. Xu, F. Hong, F. Xu, and L.-J. Wang, "Nature of the band gap of halide perovskites abx3 (a= ch3nh3, cs; b= sn, pb; x= cl, br, i): First-principles calculations," *Chinese Physics B*, vol. 24, no. 11, p. 116302, 2015.
- [70] D. Saikia, A. Betal, J. Bera, and S. Sahu, "First principles study on structural and electronic properties of cspbi3-xbrx (x= 1, 2) under strain."
- [71] Y. Chen, T. Shi, P. Liu, W. Xie, K. Chen, X. Xu, L. Shui, C. Shang, Z. Chen, H.-L. Yip *et al.*, "The distinctive phase stability and defect physics in cspbi 2 br perovskite," *Journal of Materials Chemistry A*, vol. 7, no. 35, pp. 20201–20207, 2019.
- [72] K. Jarolimek, R. De Groot, G. De Wijs, and M. Zeman, "First-principles study of hydrogenated amorphous silicon," *Physical Review B*, vol. 79, no. 15, p. 155206, 2009.

- [73] P. Nath, J. J. Plata, D. Usanmaz, R. A. R. Al Orabi, M. Fornari, M. B. Nardelli, C. Toher, and S. Curtarolo, "High-throughput prediction of finite-temperature properties using the quasi-harmonic approximation," *Computational Materials Science*, vol. 125, pp. 82–91, 2016.
- [74] A. Togo, "phonopy manual," 2013.

## A

## Appendix A - VASP simulation tutorial for PVMD group simulations

While the procedure to do simulations on VASP has been detailed in chapter 3, this section provides a tutorial on the practicality of running a VASP simulation specifically within the PVMD group and exporting the results to plot graphs. The procedure is defined in the following steps.

- Login to your PC and access MobaXterm. If MobaXterm is not installed on your PC you can get it
  installed with the help of the service desk. You also need access to the eseserv2 server in order
  to access VASP.
- Once you have access to MobaXterm and eseserv2, in MobaXterm go to "create a session" and select SSH. At "remote host", enter eseserv2.ewi.tudelft.nl.
- Tick the "specify username" box and fill in your NetID credentials using the button next to it.
- Go to "Network settings" and press the "SSH gateway (jump host)" button.
- At "Gateway host", fill in srv229.tudelft.net and your NetID at the username section.
- Click "OK" on both the open windows and you should be connected to eseserv2.
- To run a simulation, go to the STDB folder within MobaXterm and create a new folder within it which will contain your input files for your simulation.
- Once the input files have been uploaded to the folder, in the command line type "module load vasp/6.1.2".
- To specify the directory, type "cd STDB/(yourfoldername)" and you can type "Is" to check the files present in the folder to confirm it is the correct folder.
- If you wish to access the pseudopotential library to obtain the POTCAR file for a certain element, you can type "cd /opt/POTCARs" and access the relevant POTCAR through this directory. You can type "ls" to check which files are available within the directory.
- To concatenate the POTCARs for 2 or more elements, you can simply use the command "cat POTCAR\_A POTCAR\_B > POTCAR" and the combined POTCAR will be created in the folder in which you are concatenating them.
- Once all the inputs are ready, you can run the simulation by typing "mpirun -np 1 vasp\_std". The 1 represents that the simulation is running on 1 node. This can be increased for larger simulations.
- Once the simulation is complete, you can see the output files by refreshing the folder containing your input files within MobaXterm, which you can download or move if you wish to use them for future simulations.

- To visualize your results for density of states and band structure simulations, type "p4v" in the command line once the simulations is complete. In the window that opens, go to "Electronic", select "DOS + Bands", press "Show" and select the output you wish to visualize.
- It is usually preferable to export the data of the visualized graph and plot it in an external tool such as MATLAB, and thus the data can be exported from p4v by clicking "Graph" and selecting "Export". When exporting the data file, make sure to add ".dat" to the file name you provide.
- To find the data file, you can refresh the folder containing the files within MobaXterm. Then transfer the data into an excel sheet which can be used to create a suitable graph using your external software.
- To export data from a notepad to an excel sheet, you can open an excel workbook and open the notepad file into it. This should open a text import wizard where you can select "Delimited" and both "Tab" and "Space" on the next page which should arrange the data into the excel properly.
- Finally, you need to write a code on MATLAB or whichever software you choose to use in order to visualize your graph nicely.
- For the dielectric function, I had trouble exporting the data from p4v itself, and had to instead manually export data from the "vasprun.xml" file which contains the data used by p4v.

# B

## Appendix B - Additional simulation results

While the most relevant results for the perovskite simulations have been presented in chapter 5, this appendix contains the graphs for the density of states and band structure for the mixed halide perovskites that were not included in chapter 5.

The density of states and band structure for  $CsPbI_2Br$  is shown in figure B.1. The band gap obtained is 1.5416 eV.



Figure B.1: Density of states and band structure for CsPbI2Br.

The density of states and band structure for  $CsPbIBr_2$  is shown in figure B.2. The band gap obtained is 1.5744 eV.



Figure B.2: Density of states and band structure for *CsPbIBr*<sub>2</sub>.

The density of states and band structure for  $CsPbBr_2Cl$  is shown in figure B.3. The band gap obtained is 1.8338 eV.



Figure B.3: Density of states and band structure for CsPbBr<sub>2</sub>Cl.



The density of states and band structure for  $CsPbBrCl_2$  is shown in figure B.4. The band gap obtained is 1.8919 eV.

Figure B.4: Density of states and band structure for CsPbBrCl<sub>2</sub>.

The density of states and band structure for  $CsPbI_2Cl$  is shown in figure B.5. The band gap obtained is 1.5633 eV.



Figure B.5: Density of states and band structure for CsPbI<sub>2</sub>Cl.
The density of states and band structure for  $CsPbICl_2$  is shown in figure B.6. The band gap obtained is 1.6786 eV.



Figure B.6: Density of states and band structure for CsPbICl<sub>2</sub>.

The density of states and band structure for *CsPbIBrCl* is shown in figure B.7. The band gap obtained is 1.619 eV.



Figure B.7: Density of states and band structure for CsPbIBrCl.