M.Sc. Thesis



A theoretical study of effective mass of electrons in the Iron-doped CsPbBr₃ perovskite using VASP

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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled A *theoretical* study of effective mass of electrons in the Iron-doped CsPbBr₃ perovskite using VASP in the partial fulfillment of the requirements for the award of the degree of MASTER OF SCIENCE and submitted in the DISCIPLINE OF PHYSICS, Indian Institute of Technology Indore, is an authentic record of my own work carried out during the time period from July 2021 to May 2022 under the supervision of Dr. Srimanta Pakhira, Assistant Professor, DISCIPLINE OF PHYSICS.

The matter presented in this thesis has not been submitted by me for the award of any other degree at this or any other institute.

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Signature of the student with date (Adhyayan Boora)

This is to certify that the above statement made by the candidate is correct to the best of my Dr. Srimanta Pakhira, Ph. D. knowledge.

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Abstract

Over the last few decades, computational based quantum-mechanical illustration of the interaction between electrons and ions has advance in impacting the material science significantly – not only in extensive understanding but also in developing the new material design for future technologies. The development is based on two considerable factors: first is improvement in illustration of electronic many bodies problem within the frameworks of Density Functional Theory (DFT) methods and second one is other new functional and technique to solve many bodies with highly efficient, stable, and computer codes which unlocks the potential of modern-day architectures.

The Vienna *Ab Initio* Simulation Package (VASP) is a simulation package which is used for atomic scale material modeling to study the electronic structure calculations with the properties like band structure, density of state, wave function, charge density etc. for different material. VASP code is just the implementation of the DFT approach for the calculation of electronic structure of material represented by wave function of the electron in the plane wave basis sets and the interaction between electron and ion are represented by PAW model that are ultra-soft pseudo potentials considering valence electron interaction and use the frozen core approximation. This approximation is the inner electron are strongly bound to the nucleus. The VASP code uses iterative technique for the DFT Hamiltonian diagonalization and allows performing the energy calculation and optimization structure for the large crystal system even containing thousands of atoms and ions. These computational methods have many applications in many different areas like magnetism, nanostructure, optimization, mechanical and dynamical properties, semiconductor, interface, and catalysis.

Over the last decade, there is re-emergence of halide perovskite caught the attention due to its versatile merits as photovoltaic materials exhibiting high absorption coefficient, bandgap tenability, and low-cost processing. To study the conductivity of the material, we use the concept of the effective mass which comes from the band theory of solids. Effective mass is one of the main factors to estimate the curvature of the electronic band by one-band approximation. Here, we have studied Cesium lead tribromide and Cesium lead other halides (CsPbX₃) perovskites.

Chapter 1 : Introduction

Due to the rapid growth of industrialization, we are using fossil fuels at much higher rate which results in pollution. As the burning of fossil fuels are the primary source of energy that produces harmful gases. Major emissions of greenhouse gases are due to the burning of fossil fuels. CO₂ is a greenhouse gas responsible for global warming which leads to hazardous changes to the environment that is the melting of glaciers, climate change, global warming, change of weather,



etc. the So, replacement of the fossil fuels from the current source of energy supply is essential for sustainable development.

85% world energy supply demand is fulfilled by only the fossil fuel. Fossil is non-renewable source of energy and it takes millions of years to reform in Earth's crust again. If we use these resources continuously, eventually we will run out of these nonrenewable resources within 50 years. Also, burning of coal and gas releases CO₂, Sulphur dioxide (SO₂), and many other harmful gases which cause breathing problems. SO₂ is major cause of acid rain. These gases are destroying the living environment and making it incompatible for living organism.

So, need of renewable source of energy is very high to meet the future energy demand, and also considering the concern toward environment, we need to find alternative energy sources of green energy. Green energy refers to clean energy, which doesn't affect the wellbeing of environment and is more sustainable. Main advantage of green energy is no carbon emission & inexhaustible energy source. There are several sources of green energy like solar energy, wind energy, hydroelectric energy, geothermal energy, bioenergy etc. Among the renewable resource of green energy, solar and wind energy are the major contributors in energy demand. From decades, we are using solar cells made up of crystalline silicon. Silicon solar cells are the most efficient but the commercialization of these is not possible because they are too much expensive to afford by the common man. Solar cell has its own challenges like performance of solar cell, manufacturability, reliability, and location.

In recent decade, Perovskites solar cells^{1–3} shows great development in solar cell efficiency. Perovskite might be the key to make the commercialization of the solar cell. But still perovskite solar cells have its own drawback related to the stability of perovskite solar cell. Also due to weatherization front, exposure to moisture, oxygen and other environmental factor cause degradation of solar cell made of layered perovskites & no carbon emission. In search of material that is cheap, stable, and has suitable band gap for solar cell, research is still ongoing.

Chapter 2: Perovskite

Perovskites⁴ are the material having the general formula ABX₃ like calcium titanium oxide (CaTiO₃). This mineral was first discovered by German mineralogist Gustav Rose in 1839 and was named in honor of the Russian mineralogist Lev Perovski (1792–1856).



Fig 2.1 Structure of the perovskite having general formula ABX₃

Generally, perovskite follow cubic symmetry, but it seems to have a structure like FCC as atoms are placed at 8 B-atoms at corners, 6 X-atoms at face-center & one atom of A is at body center of the cube. A and B are generally cations and X is an anion that is bonded to both cations.

Perovskite exhibits excellent physical and chemical characteristics such as band gap tuneability⁵, electrical conductivity, stability, high absorption coefficient, high carrier mobility, etc. Also, some perovskites behave like superconductor, photocatalysts, photodetector^{6–8} and thermo-catalysts. Due to these various interesting properties, perovskites have caught a tremendous attention of the researchers in recent decades. Due to band gap tunability property, they are the promising material in making of solar cell. They can also be used as a catalyst in oxidation-reduction reactions.



Fig. 2.2 Electronic and chemical structure of perovskites. (Center right) ABO_3 perovskite crystal structure. (Center left) The electronic DOS contributions from the oxygen (O 2p) and metal (B 3d) states, which make up perovskite electronic structure. (Outer) Applications for catalytic processes, bulk ion diffusion for gas sensors and fuel cells, solid-state ferroelectric devices, and superconducting properties⁹.

Chapter 3: Density Functional Theory



Fig 3.1 Different approaches related to time & length scale

Wave-function in Quantum mechanics contains all the information about the system. For the case of 2D square potential or even a hydrogen atom, we can solve the Schrödinger wave equation exactly to get the wave function of the system. Unfortunately, it's very hard to solve the Schrödinger wave equation for an N-body system.

$$\left[\sum_{i}^{N}\left(-\frac{\hbar^{2}\nabla_{i}^{2}}{2m}+\nu(r_{i})\right)+\sum_{i< j}U(r_{i}r_{j})\right]\psi(r_{1}r_{2}\ldots,r_{N})=E\psi(r_{1}r_{2}\ldots,r_{N})$$

Where N is the number of electrons in the system

As for $U(r_i r_j)$, which is the potential energy due to interaction between electron-electron. For a coulomb interaction it is given by

$$\widehat{U} = \frac{1}{4\pi\varepsilon} \sum_{i < j} \frac{q^2}{|r_i - r_j|}$$

And for the potential $v(r_i)$

$$\hat{V} = \sum_{i} v(r_i) = \sum_{i} \frac{Qq}{|r_i - R|'}$$

Density Functional Theory (DFT)^{10,11} provides an approximate solution to the Schrödinger wave equation of a many body system. Computational codes based on DFT are used in practice to investigate the structural, magnetic, and electronic properties of the materials. The bridge from many body problems to one body problem is DFT.

1.1 Born-Oppenheimer Approximation

The Born-Oppenheimer Approximation is the assumption that the electronic motion and the nuclear motion in molecules can be separated. It tells that nuclei are big, heavy and slow & electrons are small and fast. This approximation is reasonable since the mass of a typical nucleus is thousands times greater than that of an electron. The nuclei move very slowly with respect to the electrons, and the electrons react essentially instantaneously to changes in nuclear position. Thus, the electron distribution within a molecular system depends on the positions of the nuclei, and not on their velocities. Put another way, the nuclei look fixed to the electrons, and electronic motion can be described as occurring in a field of fixed nuclei.

Using these assumptions made by Bohr, we can decouple the wave function of both electron and nuclei.

$$\Psi(r,R) = \Psi(r) * \Psi(R)$$

We decoupled the wavefunction of electron and nuclei (r represent electron and R represents nuclei).

$$\left[\sum_{i}^{N}\left(-\frac{\hbar^{2}\nabla_{i}^{2}}{2m}+v(r_{i})\right)+\sum_{i< j}U(r_{i}r_{j})\right]\Psi_{e}(r_{1}r_{2}\ldots,r_{N})=E\psi_{e}(r_{1}r_{2}\ldots,r_{N})$$

1.2 Hartree product

Hartree product gives the wavefunction of system of many particles as a combination of wavefunction of the individual particle. Hartree product is the simple method of combining the wavefunction of the individual electron is known as Hartree product.

$$\Psi(x_1, x_2, x_3 \dots \dots , x_n) = \Psi_{\alpha}(x_1) \cdot \Psi_{\beta}(x_2) \cdot \Psi_{\gamma}(x_3) \dots \dots \Psi_{\pi}(x_n)$$

1.3 Slater Determinant and Pauli exclusion principle

Consider two electrons occupying the spin orbitals and put one electron in χ_i and second electron in χ_j orbital we have

$$\Psi_{12}^{HP}(X_1, X_2) = \chi_i(X_1)\chi_i(X_2)$$

If we switch the position of the electrons, then we have

$$\Psi_{21}^{HP}(X_1, X_2) = \chi_i(X_2)\chi_j(X_1)$$

Each of these Hartree product clearly distinguishes between electrons. Linear combination of two Hartree product as follows to obtain the wavefunction

$$\Psi(X_1, X_2) = 2^{-\frac{1}{2}} (\chi_i(X_1)\chi_j(X_2) - \chi_i(X_2)\chi_j(X_1))$$

If both electrons occupy the same spin orbital (if a = j) then the wave function will vanish. Thus, the anti-symmetry requirement leads to statement of the Pauli exclusion principle that no more than one electron occupies a spin orbital.

$$\Psi(X_1, X_2) = -\Psi(X_2, X_1)$$

The antisymmetric wavefunction can be written as Slater determinant as follow:

$$\Psi(X_1, X_2) = 2^{-\frac{1}{2}} \begin{vmatrix} \chi_i(X_1) & \chi_j(X_1) \\ \chi_i(X_2) & \chi_j(X_2) \end{vmatrix}$$

The Slater determinant meets the requirement of the anti-symmetry principle.

1.4 Kohn-Sham Equation

Kohn-Sham proposed to work with a system of non-interacting electron. The wave function of the non-interacting electrons is different from that of the interacting ones and so is the density. However, Kohn-Sham assumed that a system is created that has no interaction, but it has same electron density as that of interacting system.¹²

This is many body problem equation and the Schrodinger equation is given below.

$$\left[\sum_{i}^{N}\left(-\frac{\hbar^{2}\nabla_{i}^{2}}{2m}+v(r_{i})\right)+\sum_{i< j}U(r_{i}r_{j})\right]\Psi_{e}(r_{1}r_{2}\ldots,r_{N})=E\psi_{e}(r_{1}r_{2}\ldots,r_{N})$$

Now, due to assumption of non-interactive system we need to add some term to this equation to counter that assumption.



Hence Kohn-Sham (KS) equation can be written as follows



1.5 Exchange Co-relations Energy functions

In LDA^{13,14} approximation, we assume that the exchange-correlational energy of electron at distance r in the electron gas $o_x(n(r))$, is equal to the exchange-correlation energy in homogeneous electron gas as that has same density as the electron gas at distance r.

$$E_{xc}^{LDA}[n] = \int n(\vec{r}) \, \varepsilon_{xc}^{uniform}(n(\vec{r})) d^{3}\vec{r}$$
$$\varepsilon_{xc} = \varepsilon_{xc}^{hom}[n(r)]$$

It assumes the exchange energy is local. It ignores the in-homogeneities in electron density on energy.

LDA is modified to gradient-expansion approximation (GEA). One way of deriving the GEA is to start from the uniform electron gas, introduce a weak and slowly varying potential, and expand the exchange-correlation energy in terms of the gradient of the density. At second order:

$$E_{xc}^{GEA}[n] = \int d^3 \vec{r} \ \varepsilon_{xc}^{LDA}[n] \ n(\vec{r}) \left[1 + C \left(\frac{\vec{\nabla} n(\vec{r})}{2k_f(\vec{r})n(\vec{r})} \right)^2 \right]$$

For real system, GEA turn out to be worse than LDA. The source of GEA was found to be caused by the violation of the sum rules.

$$\int n_c(\vec{r}, \vec{r'}) d^3 \vec{r'} = 0 \quad \text{And}$$
$$n_x(\vec{r}, \vec{r'}) = 0$$

The failure of the GEA leads to the development of generalized-gradient approximation of the generic form:

$$E_{xc}^{GGA}[n] = \int f\left(n(\vec{r}), \vec{\nabla}n(\vec{r})\right) d^{3}\vec{r}$$

That preserves the desired sum rules. GGA^{15,16} are built with real-space cutoffs of GEAs to include only that contribution from the GEA exchange hole that are negative and truncate the resulting hole at the first distance which satisfies the sum rule. Therefore, even though simply throwing away positive contribution to GEA the exchange hole looks very ugly in real space, and the important quantity is its average. The most used implementation is Perdew-Burke-Ernzerhof¹⁷ (PBE) GGA:

$$E_{xc} = E_x + E_c$$

$$E_x^{GGA} = \int d^3 \vec{r} \ n(\vec{r}) \varepsilon_x^{uniform}(n) F_x(s)$$

$$F_x = l + 0.804 - \frac{0.804}{\left(1 + \frac{0.21951}{0.804} s^2\right)} \text{ And}$$

$$S = \frac{\left|\vec{\nabla}n\right|}{2k_f n}$$

And the correlation function is as below

$$E_c^{GGA} = \int d^3 \vec{r} \ n(\vec{r}) \left[\varepsilon_x^{uniform}(n) + H(r_s, t) \right]$$
$$H^{PBE}(r_s, t) = \frac{\beta^2}{2\alpha} \ Ln \left[1 + \frac{2\alpha}{\beta} \ \frac{t^2 + At^4}{1 + At^2 + At^4} \right]$$

With

$$A = \frac{2\alpha}{\left(\beta \exp\left(\frac{-2\alpha\varepsilon_c^{uni}(n)}{\beta^2} - \right) - 1\right)}$$

$$\alpha = 0.0716, \qquad \beta = 0.066725, \qquad t = \frac{\left|\vec{\nabla}n\right|}{2k_s n}, \qquad K_s = \left(\frac{4k_f}{\pi}\right)^{\frac{1}{2}}$$

1.6 Hohenberg-Kohn-Sham theorem

- 1. The ground-state energy of a many-body system is a unique functional of the particle density $E_0 = E$ [(r)]. Energy is the function of electron density. We only need to know electron density to know about the ground state of the system.
- 2. The function E [(r)] has its minimum relative to variation δn (r) of the particle density at the equilibrium density $n_o(r)$.¹⁸

$$\frac{\delta E(n(r))}{\delta \varepsilon(r)}|_{n(r)=n_0(r)}=0$$

1.7 Effective mass

Inside various crystal or conductor, these electron does not remain completely free. Usually, they are under the influence of periodic forces due to crystalline structure, and we can thus define an effective mass of the electron. Effective mass of the electron is nothing but the total force acting on an electron inside the crystal. An interesting crystal system is graphene in which the effective mass of these electrons is zero. The effective mass is a constant quantity for each material depending on different condition. Also, the value of the effective mass varies on many factors. One of the remarkable properties of the effective is that it can also become negative, when band curves downward away from the maxima.

$$m^* = \frac{\hbar^2}{\frac{d^2 E}{dk^2}}$$

Where \hbar is the Planck is constant and E is the energy.

1.8 Parabolic Approximation of Bands

We use effective mass study as it is the most common parameterizing feature of a band structure calculation. We use the approximation for the non-parabolic curvature of the bands. For these non-parabolic bands m* is not constant and the local slope and curvature of E-k relationship must be used to obtain the velocity and the acceleration of the particle with energy E.

The Shape of the conduction band and valence band can approximate by the parabolas which results in the constant effective masses.

$$E \cong E_c + \frac{\hbar^2 k^2}{2m_e^*}$$
$$E \cong E_v - \frac{\hbar^2 k^2}{2m_h^*}$$



Chapter 4: Introduction to VASP

Vienna *ab initio* stimulation package (VASP) developed by Kresse and his co-workers and on applications this code in key areas of modern-solid physics and chemistry. VASP¹⁸ is a complex package for performing ab-initio quantum-mechanical simulations based on density functional theory (DFT) using pseudo potentials or the projector-augmented wave method and a plane wave basis set used for atomic scale materials modeling. VASP implements the concepts of DFT and uses them to analyze the electronic and optical properties of the material. The VASP solves a variety of problem including electronic structure calculation and quantum mechanical molecular dynamics.

- VASP is software that is based on concepts of DFT.
- Uses periodic boundary conditions.
- Uses pseudo potential method with a plane wave basis set
- Can model systems with maximum no. of atoms in the range of 100-200. [9]

2.1 VASP Input files

There are 4 input files for VASP program that contain the information about the specimen of the systems

- 1. INCAR: The INCAR file is responsible for "What to do and how to do". We talk about the information about cutoff energy and convergence of the energy calculation.
- 2. POSCAR: The POSCAR file contains the geometry information. It includes the lattice geometry and the ionic positions.
- 3. POTCAR: POTCAR file contains the atomic masses, valence, and the cut-off energy for each species and among other features. POTCAR file contains the information about the pseudo potential.
- 4. K-Points: The KPOINTS file contains all the information regarding the K-point coordinates and weights for creating k-point's grid.

2.1.1 INCAR file

The INCAR file is responsible for "What to do and how to do ". We talk about the information about cutoff energy, convergence of the energy calculation.

1.) The ENCUT (E_{cut}) tag specifies the plane-wave basis cutoff energy in eV. The basis set only allows those plane-waves whose kinetic energy is less than E_{cut} . The mathematical expression is shown as

$$|G + K| < G_{cut}$$

We set it always to ENMAX in the POTCAR file.

Concept of Cutoff energy:

Bloch Theorem: A theorem relating to the quantum mechanics of crystals stating that the wave function ψ for an electron in a periodic potential has the form $\psi(\mathbf{r}) = e^{-(i \vec{k} \cdot \vec{r})} U(\mathbf{r})$, where k is the wave vector, r is a position vector, and U(r) is a periodic potential function which satisfies U(r+R) = U(r), for all vectors R of the Bravais lattice

The form of Bloch theorem is:

$$\psi_{nk}(r) = U_{nk}(r) * \exp(iK.r)$$

Using Fourier transformation

$$\psi_{nk}(r) = \exp(iK.r) * \sum_{k=1}^{k=\infty} C_k * \exp(iG.r) = Sum of plane waves$$

Each plane wave in the sum of $K.E. = \frac{\hbar}{2m} |\vec{K} + \vec{G}|^2$. We must define the cutoff energy for the expression. E_{cuttoff} should be selected in accordance with convergence of the loop. There are infinite number of planes, so we need to define the cutoff energy.^{19,20}

2.) EDIFF - This is the value of the threshold difference between total energy of the consecutive runs of the iterations. This simple specifies the SCF tolerance, which is the allowed error in the energy of the system. The tag specifies the break condition for electronic calculation loop. The default value set to 10^{-4} .

3.) EDIFFG - This is the value of threshold force. The EDIFFG simply means the break condition for the ionic relaxation loop. Relaxation loop will be terminated if the two successive ionic step difference is less than EDIFFG.

2.1.2 POSCAR

The POSCAR file contains the geometry information. It includes the lattice contents and the ionic positions.

2.1.3 POTCAR



Fig 4.1 Pseudopotential pictorial representation.

This file contains the required datasets for all atomic species specified in the POSCAR. POTCAR file contains the atomic masses, valence, and the cut-off energy for each species and among other features. The energy tag should be left as default in INCAR file.

Also, POTCAR file contains the information about the pseudopotential which we are used to calculate the energy of the given system. Transferability is the main benefit of the pseudo potential technique over all electron DFT implementations. Following point help to understand pseudo potential^{15,20–22}:

- Chemical bonding and the other characteristics of the material are defined mainly by the valence electron of the atom
- > Pseudopotentials replace electron from a chosen set core electron with smooth density.
- It uses the frozen core approximation means the inner core electrons are neglected as they are in system with strong positive potential of the nuclei.

2.1.4 K-Points

The KPOINTS file contains all the information regarding the K-points coordinates and weights for creating k-point's grid. We use automatic k-mesh generation method. The method only requires the input of division of the Brillouin zone in every direction and the origin of the k-mesh. An illustration is shown below

Automatic mesh

0

Monkhorst pack

444

000



Fig 4.2 Representation of real to reciprocal space

It should be noted that as the unit cell increases in size, the size of Brillouin zone, or reciprocal lattice unit cell decreases in size. Therefore, in real space, larger cells require fewer k points to sample the smaller reciprocal space.

2.2 VASP Output files

The list of output files are as follows:

- 1. CHGCAR: contains charge density, lattice vectors and atomic coordinates.
- 2. CONTCAR: contains the updated version of the POSCAR after each calculation, whether ionic movement was performed or not.
- 3. DOSCAR: contains the information about the density of states and integrated density of states.
- 4. EIGENVAL: For each k-points there is corresponding energy eigenvalues.
- 5. OSZICAR : contains the information about each electronic and ionic SCF step.
- 6. OUTCAR : It is the main output file. It contains the information about the fermi level, energies and about the eigenvalues.
- 7. WAVECAR : contains derivatives of wave function coefficients, eigenvalues, Fermi weights.
- 8. BAND.dat : contains the information about the eigenvalue and the k points and used to plot the band structure using the GNU plot.

We present a study on the effective mass of the electron using the first principles-based DFT calculation implemented in Vienna Ab initio Simulation Package (VASP). VASP is a versatile package used for structure optimization, relaxation of structure, calculation of band structure and density of states (DOS). The code uses the method of diagonalization of DFT Hamiltonian using iterative methods and it allows the code to compute the structure optimization and total-energy calculations of the systems containing large number of atoms. For practical calculation, we use the exchange co-relation function energy as a function of density as approximation. We generally use local density approximation (LDA) as the exchange co-relation function for the atomic structure, elasticity, and vibrational properties calculation for a variety of system. LDA does lead to the accurate result in some of the system like calculation of binding energy in chemical reaction and in solid system also. As there are many molecular system or bulk crystal where LDA calculated the wrong energy order.^{23,24} Generalize gradient approximation (GGA) has overcome many shortcomings of LDA up to some extent. GGA calculates more realistic and accurate results for the adsorption of hydrogen upon metal and semi-conductor^{25,26}. GGA-PBE is more preferred than LDA for the calculation of band gap, structure optimization and density of states. So, we use GGA-PBE (Perdew-Burke-Ernzerhof) exchange potential for the calculation of perovskite material cesium lead halides perovskite. Modern electronic calculation falls in two broad classes of choice of basis sets for the expansion of the valence orbital, charge density, and potential: plane-wave method and localized basis function like gaussian basis sets. As VASP uses plane wave basis sets for the calculation of total energy calculation and structure optimizations. Plane wave basis set has its own advantages over localized basis sets that are: (i) easy to convert from real space to reciprocal space via Fast Fourier Transform to momentum space where kinetic energy T is diagonal; (ii) for convergence, the highest kinetic energy of plane wave basis to be choose within the basis set; (iii) also, basis sets superposition error can be avoided. Recently, investigating the performance of plane-wave (VASP) and local-basis sets method (Using GAUSSIAN and SEISTA) in structural studies of small clusters has been presented by Gruber et al.²⁷ Both the basis sets give good agreement between biding energy calculations, while plane structure found to have somewhat reduced stability in local-basis sets (gaussian basis sets). Ultrasoft pseudo potential are used to

describe the interaction of valence electron and uses frozen approximation (i.e., inner core electron interaction is neglected as they are strongly bound by the nucleus). The ultrasoft pseudo potential have a merit to make calculation for the *d*- and *f*- orbital electron. But, the major drawback of pseudo potential is the of non-linearity of the exchange interaction between valence and core electron, elaborate the non-linear core correction are required for the system in which the core and valence electron density overlap and has a significant value which can't be neglected. That why we use PAW pseudopotential (projector-augmented waves) for electronic calculation of the systems. The projector-augmented waves method (PAW) is originally introduced by Bloch²² to achieve the computational efficiency of the pseudo potential method as well as the accuracy of the full-potential linearized augmented plane wave (FLAPW). The projector augmented wave method (PAW) is a technique used in *ab initio* electronic structure calculations. It is a generalization of the pseudopotential and linear augmented-plane-wave methods, and allows for density functional theory calculations to be performed with greater computational efficiency. In PAW approach, all-electron (AE) valence wave function is reconstructed from pseudo (PS) wave function via linear transformation.^{20,22}

$$|\Psi_{n}^{AE}\rangle = |\Psi_{n}^{PS}\rangle + \sum_{i} \left(|\Psi_{i}^{AE}\rangle - |\Psi_{i}^{PS}\rangle \right) \langle \Psi_{i}^{PS} |\Psi_{i}^{PS}\rangle$$

Perovskite CsPbBr₃^{5,28} has crystal cubic structure with symmetry space group *Pnma* but after doping of the iron (Fe) CsFe_{0.25}Pb_{0.75}Br₃, the symmetry has been changed to P1 symmetry. The PAW pseudopotential with an energy cutoff of 250 eV using plain wave basis has been used in the computations. We employed gamma center grid of dimension 4x4x4 to obtain the converged results for geometry optimization. We substitute the Pb atom at face center with iron (Fe) and the crystal lattice CsFe_{0.25}Pb_{0.75}Br₃ follows P1 symmetry. For CsFe_{0.25}Pb_{0.75}Br₃ model, we use a denser gamma K-point grid of dimension $12 \times 12 \times 12$. We have used the same correlation function^{13,17,29} PBE (Perdew-Burke-Ernzerhof) and the same procedure for the rest of the calculations. Brillouin zone is sampled using automatic generated Monk horst-pack like $4 \times 4 \times 4$. GGA-SOC (Spin-orbit coupling) calculation have been performed on perovskite to calculate the band structure. We have used high symmetry k-point for the band structure calculations. We also studied the band structure of cesium lead halides (CsPbX₃, X=Cl and I). For CsPbCl₃ & CsPbI₃, we use $6 \times 6 \times 6$ and 8×8

x 8 gamma centric K-points, respectively. Both CsPbCl₃ & CsPbI₃²⁸ follows *Pm-3m* symmetry. For both the cesium lead halides, we can use a maximum cutoff energy 450 eV.

Chapter 6: Results

We have analyzed the structure of the cesium lead halide (CsPbX₃, X=Cl, Br, I). We find out the optimized geometry, band structure and density of states of all inorganic cesium lead halide (CsPbX₃, X=Cl, Br, I) perovskite nanocrystal. We also find out the band gap of all in-organic lead halides which are suitable in applications like LED (light emitting diode), solar cells, photodetector³⁰, laser and photocatalysis³¹. The calculated electronic band structure²² shows excellent agreement with the literature. Cesium lead halides³² (CsPbX₃, X=Cl, I) follow the symmetry *Pm-3m* and the electronic band structure of these perovskite are measure along the K-path Γ -X-S- Γ -R-S. The band gap is measured between the conduction band and the valence band at high symmetry point Γ -R. CsPbBr₃ follow *Pnma* symmetry and CsFe_{0.25}Pb_{0.75}Br₃ follow P1 symmetry. Electronic band structure is measured along the k-path Γ -X-S- Γ -Z-U for both pure and doped cesium lead bromide. The band gap is measured between the conduction and valence band at high symmetry point Y- Γ . The effective mass of electron is important parameter for in describing transport properties and the electrical properties of the material. We study the electronic band curvature using the parameter i.e., effective mass of the electron along the path Γ -X-S We use the vaspkit module for the calculation of effective mass of the electron



Fig 6.1 (a) Crystal structure (b) Band structure of perovskite CsPbI₃

 $(\bullet Cs, \bullet Pb, \bullet I)$





Fig 6.3 (a) Crystal structure (b) Band structure of perovskite CsPbBr₃

 $(\bullet Cs, \bullet Pb, \bullet Br)$



Fig 6.4 (a) Crystal structure (b) Band structure of perovskite CsFe_{0.25}Pb_{0.75}Br₃

 $(\bullet Cs, \bullet Pb, \bullet Br, \bullet Fe)$

Table 6.1 Lattice parameters of optimized geometry of Cesium Lead Halides ($CsPbX_3$, X = Cl, Br, I) parameters

Perovskite	a (Å)	b (Å)	c (Å)	α°	β°	γ°
CsPbI ₃	6.414	6.414	6.414	90.00	90.00	90.00
CsPbCl ₃	5.733	5.733	5.733	90.00	90.00	90.00
CsPbBr ₃	8.425	12.011	8.370	90.00	90.00	90.00
CsFe _{0.25} Pb _{0.75} Br ₃	8.425	12.011	8.370	90.00	90.00	90.00

To obtain the optimized geometry and electronic band structure, we use the PBE-GGA method and plane wave basis sets¹⁹ in VASP which shows good agreement with the theoretical data. For solar cell, the optimum range of band gap is to be 1.4 - 1.7 eV. We also study the electronic band properties of these lead halides perovskites using ab initio calculation³⁵. These lead halides are the promising candidates for the solar cell's material.

Table 6.2 Band gap of Cesium Lead Halides ($CsPbX_3$, X = Cl, Br, I)

Perovskite	Band Gap (eV)
CsPbI ₃	1.459
CsPbCl ₃	2.214
CsPbBr ₃	2.122
CsFe _{0.25} Pb _{0.75} Br ₃	1.868

We use the effective mass of electron as a parameter to study the electronic band structure curvature of cesium lead bromide¹⁰ (CsPbBr₃).

Number of states (N) =
$$2 * \frac{k_f^2}{6\pi^2} L^2$$

 $\frac{dN}{dk} = \left(\frac{L}{\pi}\right)^3 \pi k^2 \frac{dk}{dE}$
 $E = \frac{h^2 k^2}{2m^*}$, providing $\frac{dk}{dE} = \frac{m^*}{h^2 k}$

$$g(E) = \frac{dn}{dE} = \frac{dn}{dk}\frac{dk}{dE} = \frac{1}{2\pi^2} \left(\frac{2m^*}{\hbar^2}\right)^{\frac{3}{2}} (E - E_0)^{\frac{1}{2}}$$

This is the clear indication that we can use the effective mass^{36,37} as a parameter to study about the electronic band structure curvature. From above equation, we can predict about the curvature of band like lighter the effective mass of the particle steeper the curve will be and heavier the effective mass³⁸ the curvature will be shallow.³⁹

We use the module vaspkit and VASP⁴⁰ to find the effective mass (m_e^*) of the electron along the Γ -*X*-*S* k-path. We reported the effective mass of pure and iron (Fe) doped in the following Table 6.3.

Table 6.3 Effective mass of electron in cesium lead bromide

	CsPbBr ₃	$CsFe_{0.25}Pb_{0.75}Br_3$
K-Path	Γ-Χ-Տ	Г-Х-Ѕ
Effective mass (m_e^*)	1.261	0.297

Since the derivation in above equation refers to "curvature" of the dispersion relation, the bands with large curvature correspond to small effective masses (light "quasiparticles") while the bands with small curvature are heavier quasiparticles. The effective mass is decreased after doping refers to the increase in the curvature of band along the path Γ -X-S. Also relating the parameter effective mass of electron with the conductivity and mobility of the charge carrier in the perovskite. From Ohm law:

$$\sigma = \frac{ne^2\tau}{m_e^*}$$
$$\mu_d = \frac{e\tau}{m^*}$$

As we reported, after doping of CsFe_{0.25}Pb_{0.75}Br₃ the effective mass of the electron decreases from 1.261 to 0.297. From the above equation, the conductivity and drift mobility of the material is inversely proportional to the effective mass of the electron⁴¹. The conductivity and the drift mobility of CsFe_{0.25}Pb_{0.75}Br₃ are more than the pure perovskite CsPbBr₃ which can be explained based on decrease in effective mass of the electron. Also, the band gap of CsFe_{0.25}Pb_{0.75}Br₃ is less than its pure crystal form. The decreased value of effective mass implies that electron became

lighter than its weight and hence the mobility of electron to move inside the crystal increase. The DFT-D provides more accurate geometries and structures with properties for the crystal and 2D materaisl.⁴²⁻⁵²

Chapter 7: Conclusions

The stability issues with the organic-inorganic hybrid perovskite appear to hinder the commercialization of solar cell. Although the cesium lead halides are highly efficient material, and their low stability condition is noticed by researcher in the early days of research. The main task for the researcher is the interplay between the band gap and the phase stability of the inorganic perovskite solar cells. As the band gap of the pristine CsPbI₃ is less in all cesium lead halides but the larger the ionic radius of I as compared to Br affects the stability and hinders the fabrication of photovoltaic device under suitable environment. Enhance the Br content, stability can be improved significantly. Although material with band gap less the 2.0 eV offers an ideal material for highly efficient devices but due to restriction of stability their performed is limited. Also, there are literature survey, and it was found out that iodine-rich nano composition has less band gap but unstable in nature, while the CsPbBr3 perovskite exhibits excellent stability & suitable for superior devices. Its show stability in ambient conditions without any changes in its color and shape. Thus, it can be utilized as the promising light harvesting material. We studied the electronic properties of all cesium lead halides using the first principle and reported the band gap of all lead halides. As CsPbI₃ has the lowest band gap, but due to the larger ionic radius of iodine ion hinder the stability of material. Also, we have studied the iron doped cesium lead bromide in which the band gap is reduced, and curvature of the band flattened. 25% doping of iron reduce the band gap up to 1.8 eV. As the band gap tuneeability property of these perovskite help us to find the suitable doped perovskite material for the commercialization of the solar cell which in turn help humans to strive toward the green energy. These perovskite shows excellent potential to become the key changing in the field of energy generation. Also, they show the excellent catalytic properties in redox

reaction which help in fuel cell and ultimately contribute toward the new method of green energy generation.

Chapter 8: Procedure for Band Structure

For band structure we do in three step process as follow:

- 1. Structure relaxation
- 2. Self-consistent calculation
- 3. Band structure

3.1 Structure Relaxation

For relax structure we have different parameters to be set in the INCAR file as follows:

ISTART = 0	#new calculation
ISMEAR = 0	#Gaussian smearing
#For Ionic relaxation	
ICIE 2	#Delevation stome call shape and call

ISIF = 3	#Relaxation atoms,	cell shape and co	ell volume

IBRION = 2#Conjugate algorithm method

For ISIF, it calculates the force and stress tensor. Also tells which

degree of freedom is allowed in the calculation for the relaxation of the

structure. IBRION determine how ion are updated and moved.

3.2 Self-Consistent calculation

For SCF (self-consistent field) calculation, we need the updated file the POSCAR that is CONTCAR. Use CONTCAR as POSCAR for the SCF calculation to get the electron density of the system. Also, we need denser k-points for the self-consistent calculation, so we increase the grid by 3 times as that for the pervious calculation.

For this step, we need to change little bit in INCAR file only.

IBRION = -1	#No update in the ion movement

NSW = 0 #no ionic calculation

As for next step, we need CHGCAR which contained the charge density of relaxed crystal.

3.3 Band structure calculation

For band structure calculation, we need the updated POSCAR that contain the relaxed structure and self-consistent charge density. CONTCAR act as updated POSCAR from first step of calculations and CHGCAR from second step calculation for input of final step.

Change in INCAR file as follows:

ISTART = 1 #Charge density read from CHGCAR

ICHARG = 11

ISMEAR = 0 #Gaussian Smearing

LORBIT = 11 #For total and partial Density of states

NEDOS = 100 #Maximum number of bands

High symmetry k-point can be obtained on the following

website for any material : (https://www.materialscloud.org/work/tools/seekpath)

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