ELECTRONIC, OPTICAL PROPERTIES AND RASHBA DRESSELHAUS EFFECT IN INORGANIC HALIDE PEROVSKITE

M.Sc. Thesis

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ELECTRONIC, OPTICAL PROPERTIES AND RASHBA DRESSELHAUS EFFECT IN INORGANIC HALIDE PEROVSKITE

A THESIS

Submitted in partial fulfillment of the requirements for the award of the degree of Master of Science

> by PRIYANKA YADAV



DEPARTMENT OF PHYSICS INDIAN INSTITUTE OF TECHNOLOGY INDORE JUNE 2021



INDIAN INSTITUTE OF TECHNOLOGY INDORE

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **ELECTRONIC**, **OPTICAL AND RASBHA DRESSELHAUS EFFECT IN INORGANIC HALIDE PEROVSKITE** in the partial fulfilment of the requirements for the award of the degree of **MASTER OF SCIENCE** and submitted in the **DEPARTMENT OF PHYSICS**, **Indian Institute of Technology Indore**, is an authentic record of my work carried out during the time period from July 2020 to June 2021 under the supervision of Sudip Chakraborty.

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



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This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

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ABSTRACT

In this thesis, the electronic and optical properties of Lead-free perovskites, CsPbI₃ and Cs₂AgBiBr₆ were investigated. The stability of these modified crystals was verified through structural factors and formation energy. We studied the projected density of states, band structure plot, absorption coefficient and refractive index graphs, hence verifying its credibility for photovoltaic application.

Lead is renowned for its toxic nature and instability towards moisture, stress etc, thus dampening the commercialization of Lead halide perovskite. To subdue this limitation, lead-free materials are being promoted, two of the suggested alternatives have been discussed in this thesis. Some of the lead atoms in Caesium lead iodide were substituted by similar cations like Barium, Calcium, Magnesium and Strontium and their respective projected DOS were plotted. The second material inspected was halide double perovskite, to ascertain its stability the formation energy and structural factors were calculated. As we know the halide double perovskites do not exhibit Rashba Effect in the 3D system, we reduced the dimensionality by introducing vacuum along a particular direction, as for 2D we increased the lattice parameter along (001) direction. On increasing separation between lattices, a reduction in van Der Wall interaction between the two layers is observed, hence transforming the 3D structure to 2D. The projected DOS, bandstructure plot, absorption coefficient and refractive index plots were observed with and without the spin-orbit coupling in materials. There is a substantial decrease in bandgap observed as 2D structure shows metallic bandstructure while the 3D material corresponds to IR bandgap with SOC and Visible region without SOC.

Therefore we infer that on reducing dimensionality we observe narrowing of the bandgap of the crystal but the reduction can be done only to a limit as it fragments the crystal structure, 1D and 0D materials were found unstable.

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Chapter 1

Introduction

Energy has always been the driving force for the continuous and rapid development of science and technology. For several centuries we had been majorly dependent on energy resources from fossil fuels because of high energy efficiency and abundance in nature. However, the overexploitation of these resources has led to depleting reservoirs, drastic emission of CO₂ hence Global warming. After nearly destroying nature, we turned towards alternative energy sources along with a sustainable development perspective. Numerous attempts have been made to explore and develop technologies for harvesting renewable energy from natural sources such as solar, wind, and geothermal. In 1954 Daryl Chapin, Calvin Fuller, and Gerald Pearson developed the silicon photovoltaic (PV) cell at Bell Labs. It was the first solar cell capable of converting solar energy into an adequate amount of power to run standard electronic equipment. With global growing energy demands, the search for a material that exhibits high power conversion efficiency, ease in fabrication and better stability became prevalent. We have witnessed the evolution of solar cells from Si to Hybrid Perovskite, and the search has yet not come to an end.

1.1 Perovskites and Evolution

In the history of minerals, perovskite was discovered by the Prussian mineralogist Gustav Rose in 1839 and

was named after the renowned Russian mineralogist Count Lev A. Perovskiy. The mineral had the composition of CaTiO₃, and perovskites represent a class of crystal structure with the chemical formula ABX₃, where A and B are cations while X is an anion. In an ideal cubic structure, the B cation has 6-fold coordination at the body-centre position, surrounded by an octahedron of anions at face-centred sites, and the A cation has 12-fold coordination at corner positions.



The first class of perovskite considered for study was oxide; they are used for various ferroelectric, piezoelectric, dielectric, and pyroelectric applications. Most of the metal oxide perovskites do not exhibit good semiconducting properties hence, are not suitable for PV applications.

The next class we considered was halide perovskites (ABX_3 ; A = cation, B = divalent metal cation, X = halogen anion). They exhibit semiconducting properties that are desirable for PV applications.

The crucial factors that support superior performance and high efficiency of halide perovskite solar cells are high optical absorption coefficient, long carrier diffusion length, suppressed recombination (defect tolerance), and well-balanced charge transfer. The defect-tolerant nature of halide perovskites leads to the generation of high voltage, which is most important in PV applications.

1.2 Stability

Both the structural/intrinsic stability and the long-term environmental stability of perovskites have become the most critical issues in present times. Several key developments have been implemented in the engineering of perovskites

One significant development has been incorporating different cations in the A-site and halides in the B-site. The cations in the A-site are considered not to contribute directly toward the band structure. However, they provide structural stability by charge compensation within the PbI_6 octahedra, primarily based on their electrostatic (van der Waals) interactions with the inorganic cage. Changing the size of cations in the A-site leads to a contraction or expansion of the crystal lattice, thereby altering the optical properties of the perovskite. Smaller cations like Cs and Rb contract the lattice hence increase the bandgap. In contrast, larger cations expand the lattice resulting in decreased Pb–I bond distance, therefore lowering the bandgap. The inclusion of cations like Cs also improves the moisture stability in the perovskite.

Goldschmidt tolerance factor (t) is used for verifying structural stability of perovskite compounds, it predicts the formation of different crystal structures of perovskites. The value of τ varies with the size of the ions in ABX₃ formulated as

$$t = \frac{R_A + R_X}{\sqrt{2} \left(R_B + R_X\right)}$$

 R_A corresponds to the ionic radius of A cation, R_B to B cation, while R_X to the ionic radius of X anion. Specifically, 0.9 < t < 1 favors a cubic perovskite structure while for 0.8 < t < 0.9, a distorted perovskite structure is formed. Values of t < 0.8 and t > 1 diminish the possibility for the formation of perovskite structures. τ lying in the middle of range 0.8 to 1, is away from both the non-perovskite zones, hence forming a stable perovskite. Other structural stability indicators are octahedral factors (μ) and tolerance factor (τ) given by the following formulae, where R_B is the average of B' and B"

$$\mu = \frac{R_B}{R_X} \qquad \tau = \frac{R_X}{R_B} - n_A (n_A - \frac{R_A/R_B}{\ln(R_A/R_B)})$$

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The acceptable range of octahedral and tolerance factor is $0.44 < \mu < 0.90$ and $\tau < 4.18$, respectively, indicating a perovskite structure.

The long-term stability and toxicity of Pb are two formidable obstacles to the commercialisation of PSCs (Perovskite solar cells). For outdoor installation like Si PV panels, PSCs must guarantee stable power production at operating conditions of natural sun radiation, raised temperature due to heating, under atmospheric moisture and oxygen for a longer duration, thus are of the inevitable characteristics.

CHAPTER 2

THEORETICAL AND COMPUTATIONAL METHODOLOGY

Density Functional Theory

DFT is a computational quantum mechanical modelling method used to investigate the various properties of atoms, molecules, and condensed phases using spatially dependent electron density functionals. This segment gives an overview of fundamental principles and methods applied to conduct all of the studies in this thesis. We start the calculation by considering a many-body problem, using approximations and theorems to simplify our problem.

2.1 The Many-Body Problem

The nature of matter is defined by its fundamental particles, i.e., electrons and nuclei. One can find a vast range of material properties if we describe the complexity of interactions between a large number of these particles in matter, also known as the many-body problem. A crystal has several lattices; each lattice plane consists of atoms arranged periodically; they contain nuclei and electrons. Based on quantum mechanics, it is theoretically possible to tackle such complexity in the form of the wave function for the coupled motion of these particles. The ground state energy of the crystal can be calculated by solving the Schrodinger Equation of the coupled motion of electron and nuclei. The Hamiltonian of this system can be represented as, where $\mathbf{R}_{\mathbf{I}}$ is the position vector for the nucleus and $\mathbf{r}_{\mathbf{i}}$ is the position vector for the electron. The total number of electrons is represented by N_e and nuclei by N.

$$\hat{\mathbf{H}} = \frac{-\hbar^2}{2m_e} \sum_{i}^{Ne} \nabla_i^2 - \frac{\hbar^2}{2M} \sum_{I}^{N} \nabla_I^2 + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J e^2}{R_I - R_J \vee} - \sum_{i,I} \frac{Z_I e^2}{r_i - R_I \vee} + \frac{1}{2} \sum_{i \neq J} \frac{e^2}{r_i - r_j \vee}$$

The Hamiltonian is t sum of the following terms, kinetic energy operators of electrons and nucleus, Coulombic interaction between nuclei-nuclei, electron-nuclei and electron-electron, respectively.

$$\hat{H}\Psi = E\Psi$$

2.1.1 Born Oppenheimer Approximation

This approximation is based on the fact that the nucleus has a much larger mass than an electron. The distance travelled by a nucleus during the time taken by an electron to reach its ground state is negligible; hence, nuclei appear to be relatively stationary. We, therefore, consider a system where the nuclei are fixed, hence neglecting

the corresponding Kinetic energy of nuclei; also, the electrons experience an external potential due to these static nuclei particles. This consideration thus decouples the motion of these particles. We can now represent the total wave function as the product of two individual wavefunctions.

$$\Psi(ri, Ri) = \Psi_e(r_i)\Psi_N(R_i)$$

We are solving the Schrodinger equation for the motion of electrons only.

$$\hat{\mathbf{H}} = \frac{-\hbar^2}{2m_e} \sum_{i}^{N_{el}} \nabla_i^2 + \sum_{i}^{N_{el}} V_{ext}\left(r_i\right) + \sum_{i=1}^{N_e} \sum_{i \neq j} U(r_i, r_j) \qquad \qquad \hat{\mathbf{H}} \Psi = (\mathbf{T} + \mathbf{U} + Vext) \Psi$$

In this purely electronic Hamiltonian \hat{H} , Coulombic interaction U and Kinetic energy T are the universal operators. At the same time, V_{ext} is the static external potential observed by electrons, which is system dependent.

2.1.2 Hartree Approximation

The above approximation still couldn't wholly simplify the problem to solve the many-body wavefunction due to the correlation of electrons. The Hartree approximation is based on the assumption that the electrons are uncorrelated; the motion of the ith electron and its interactions with the fixed nuclei are no longer influenced by the Coulomb repulsion from the other N_e -1 electrons in the N_e -electron system. This approximation, therefore, converts the many-body problem with **U** to a singular body problem without **U**. This method takes into account an average of the electron-electron interaction.

The total electronic wavefunction can now be represented as the product of individual electron wavefunctions known as the **Hartree product**, while the single electron wavefunction is called **Molecular orbital**.

$$\Psi(r_1, r_2, r_3 \dots r_N) = \Psi(r_1)\Psi(r_2)\Psi(r_3)\dots\Psi(r_N)$$

The limitation here is that it doesn't hold for the spin of the electrons; hence, the **Hartree-Fock Approximation** was introduced where the Slater determinant gives the antisymmetric wavefunction. Therefore, the wavefunction of the electrons should consist of 4 coordinates rather than just three spatial coordinates, where the fourth is the spin of the electron, hence obeying Pauli's Exclusion Principle.

The Hartree-Fock (HF) method defines the wavefunction in a Slater determinant (Ψ_{HF}) of single-electron wavefunctions $\Psi_j(x_j)$ as given below,

$$\Psi_{HF} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\mathbf{x}_1) & \psi_2(\mathbf{x}_1) & \cdots & \psi_N(\mathbf{x}_1) \\ \psi_1(\mathbf{x}_2) & \psi_2(\mathbf{x}_2) & \cdots & \psi_N(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(\mathbf{x}_N) & \psi_2(\mathbf{x}_N) & \cdots & \psi_N(\mathbf{x}_N) \end{vmatrix}$$

In the determinant, $\psi_j(x_j)$ is a product of a function of the position $\psi(r_j)$ and the spin variable $\phi_i(\sigma_j)$. Based on this approximation, one can obtain the Hartree-Fock equation by using the variation principle to minimise the expectation value of the Hamiltonian.

2.2 DFT

The approximate solution of the Hartree-Fock approximation is not exact, the true wavefunction is not a product of two orbitals but is a complicated function of both variables simultaneously. The true wavefunction satisfies the exact Schrodinger equation and minimises the ground state energy functional for external potential.

To overcome the shortcomings of this approach, that is, to replace 4 N_e variable wavefunction (three spatial and one spin variables for each of N_e electrons) with a simpler 3-variable function of the electron density was proposed in the remarkable theorems, known as the density functional theory. However, it is challenging to solve the Schrodinger equation because of the complicated electron-electron interactions. Density functional theory (DFT) can simplify this complex problem. Therefore, in this thesis, DFT has been performed through the Vienna Ab-initio simulation package (VASP) code.

2.2.1 Thomas Fermi Model

In 1927, Thomas and Fermi proposed the approximate functional for electronic energy.

$$E_{TF}[n] = C_1 \int n(r)^{5/3} dr + \frac{1}{2} \iint \frac{n(r)n(r')drdr'}{|r-r'|} + \int V ext(r)n(r)dr$$

This model replaces the atom's nuclei with a uniform background of positive charge. At the same time, the electrons are still treated as quantum particles, moving in this medium, thus forming Uniform Electron Gas (UEG). The Kinetic Energy functional was approximated using the UEG model, as the kinetic energy of electrons in the system is proportional to $n(\mathbf{r})^{5/3}$. In the Local density approximation, we assume that in an actual molecule, the contribution to the electronic kinetic energy from an infinitesimal volume element is proportional to $n(\mathbf{r})^{5/3} d\mathbf{r}$. Dirac corrected this in 1930, adding the exchange energy proportional to $n(\mathbf{r})^{4/3} d\mathbf{r}$ to the energy functional.

$$E_{TFD}[n] = C_1 \int n(r)^{5/3} dr + \frac{1}{2} \iint \frac{n(r)n(r')drdr'}{|r-r'|} + C_2 \int n(r)^{4/3} dr + \int V ext(r)n(r)dr$$

2.2.2 Hohenberg-Kohn Theorem

Density functional theory was proposed to simplify a many-body problem into a practical single-particle problem that also includes correlations among particles. Instead of dealing with the $4N_e$ - variable wavefunction, the ground state is uniquely described based on a simpler 3-variable electron density function (n[r]). This formulation of DFT was first proved to be valid in any interacting particle system under the effect of $V_{ext}(r)$ by Hohenberg and Kohn (HK). They proposed the core foundation for DFT, stating the two most important theorems.

Theorem I states that for a system of interacting particles in an external potential $V_{ext}(\mathbf{r})$, the potential is a unique functional of the electron density $n(\mathbf{r})$. The ground state energy E can be written as a functional of ground-state electron density. Considering $n_g(\mathbf{r})$ is the ground-state electron density, we can determine the electron number, external potential, Hamiltonian.

$$E[arPsi_{n_0}]] = ig\langle arPsi_{n_0}]|\hat{T} + \hat{V} + \hat{U}|arPsi_{n_0}]ig
angle$$

Theorem II states that a universal functional for the energy E[n(r)] in terms of the density n(r) can be defined, for any external potential $V_{ext}(r)$. The electron density minimizing the overall energy functional is the true electron density. The exact ground state is the global minimum value of this functional. This universal functional consists of the Kinetic Energy of N_e electrons and the inter electronic interaction and not the external potential.

$$\mathbf{E}_{\mathbf{V}}[\mathbf{n}(\mathbf{r})] = \mathbf{F}[\mathbf{n}] + \int d^3 \mathbf{r} \, \mathbf{n}_g(\mathbf{r}) \mathbf{V}(\mathbf{r}) \ge \mathbf{E}_g$$

The Electronic energy and Hohenberg and Kohn functional are written as:

$$E_{el} = F_{HK}[n] + E_{ext}[n] \qquad \qquad F_{HK}[n] = E_{kin}[n] + E_{coul}[n] + E_{X}[n] + E_{C}[n] + E_{ext}[n]$$

 E_{Kin} : Kinetic energy; E_{Coul} : Coulomb energy E_x : Exchange energy E_C : Correlation energy **Eext**: External energy

The limitation here is the attempt of computing energy of interacting particles as a functional of density also the inaccuracy in the approximations of Kinetic energy functional.

2.2.3 Kohn-Sham Equations

HK theorems hence proved that the electron density could be a fundamental variable to determine the ground state wavefunction of many-particle systems, allowing the formulation of energy functional with the help of variational principle. Kohn-Sham proposed a simple approach to deal with the complex interacting system by replacing it with an auxiliary system of non-interacting electrons having the same electron density. The wavefunction of the non-interacting particles is different from that of the interacting particles; similarly, the density would also vary for the two systems. This approach removes the limitation of HK theorems as the expression for Kinetic energy of non-interacting electrons is known; hence no approximation is required.

The KS Hamiltonian is as follows.

$$\left[\frac{-\hbar^2}{2m_e}\nabla^2 + V_{ext}(r) + V_H(r) + V_{XC}\right]\Psi_j = \epsilon_j\Psi_j \qquad V_H: \text{Hartree potential, } V_{XC}: \text{Exchange correlation}$$

In the Kohn Sham approach, the exact electron density is obtained from the molecular orbitals of the noninteracting electrons.

$$n(r) = 2\sum_{j} \Psi_{j}^{*}(r)\Psi_{j}(r)$$

The energy functional of the Kohn Sham Molecular orbitals is given as

$$E_{KS}[n] = 2\sum_{i=1}^{N_e/2} \int \Psi_i^*(\mathbf{r}) \left(-\frac{1}{2}\nabla^2\right) \Psi_j(\mathbf{r}) d\mathbf{r} + E_{coul}[n] + E_{ext}[n] + E_{XC}[n]$$

If the exact $V_{XC}(r)$ is known, then the ground state wavefunction and energy can easily be determined by solving the KS equation using the SCF procedure.

Self-Consistent (SCF) procedure

- An iterative approach is followed to obtain the true charge density. A trial charge density is selected initially.
- Then KS Hamiltonian and the effective potential are



constructed and operated on the trial density, giving new KS wavefunctions.

- A new charge density is determined from these obtained wavefunctions and is refined by mixing the previous density.
- If the energy difference between this mixed density and the previous analogue satisfies the expected tolerance (energy convergence criteria), we obtain the true ground state wavefunction; otherwise, the process mentioned earlier will be iteratively repeated based on the mixed density.

2.3 Exchange-correlation Functionals

In KS method, the exchange-correlation functional $E_{XC}(\mathbf{r})$ is introduced by integrating the unknown terms accounting for the difference between the interacting and non-interacting systems. This term cannot be expressed in an exact form due to the complexity of the electron correlation of the many-body system. However, we can represent it with the help of several approximations.

2.3.1 Local Density Approximation

LDA assumed that the electrons in a solid could be represented as uniform electron gas (UEG), such that the electron density at any point in space is constantly expressed as $n(\mathbf{r}) = n_0$. The exchange-correlation functional under LDA is dependent on electronic density only.

$$E_{XC}^{LDA}[n(r)] = \int n(r) \, \varepsilon_{xc}^{UEG}[n(r)] dr$$

The LDA has been a very successful method to simulate various material properties in several systems, especially the ones resembling UEG model like valence electrons in metals. However, it is problematic while dealing with highly inhomogeneous systems, such as atoms and molecules.

2.3.2 Generalised Gradient Approximations

In GGA, an approximation of exchange-correlation energy for inhomogeneous systems was made in the form of a generalised gradient approximation GGA. It proposed to add the gradient of electron density $\nabla n(\mathbf{r})$ to incorporate the effect of inhomogeneities.

$$E_{XC}^{GGA}[n(\boldsymbol{r})] = \int n(\boldsymbol{r}) \, \varepsilon_{XC}[n, \nabla n] d\boldsymbol{r}$$

As a result of the inclusion of the density gradient, the GGA functionals can give us better information regarding the electron exchange and correlation hence correcting the LDA functional, especially for systems with fluctuating electron density. We can't clearly state that results provided by GGA are always accurate as

there can be a situation where due to self-interaction error or absence of van der Waals interaction, both LDA and GGA might not provide accurate results. The self-interaction errors refer to the unphysical interaction of electrons with themselves in Hartree term, resulting in the delocalisation of electrons in both solids and molecules. This error leads to the wrong prediction of the material's nature as the underestimated bandgap in LDA and GGA functionals because of weak localisation of electrons. The energy level corresponding to the valence band maximum becomes excessively high. This situation can be even worse for systems with strongly correlated and highly localised electrons.

2.3.3 DFT+U Approach

In this approach, we apply the Hubbard Hamiltonian to selectively correct the strongly correlated electronic states (like d and f orbitals), while other states are treated with LDA and GGA functionals.

$$E^{DFT+U}[n] = E^{DFT}[n] + E_{Hub}[l^{\sigma}_{mm'}] - E_{dc}[l^{\sigma}_{mm'}]$$

 E^{DFT} [n] is the KS energy functional, $E_{Hub}[I^{\sigma}_{mm'}]$ is the Hubbard Energy correction for the localised state, $E_{dc}[I^{\sigma}_{mm'}]$ is the correction to remove the double-counting of the strongly localised states in $E^{DFT}[n]$. E_{dc} and E_{Hub} are functions of occupation numbers $[I^{\sigma}_{mm'}]$ defined by the projections of occupied KS orbitals on localised states. Different formulations have treated this functional like rotationally-invariant formulation proposed by Lichtenstein et al. and another simplified formulation proposed by Dudarev et al. where a spherical average replaces the orbital-dependent interactions. Therefore enabling us to use an effective potential $U_{eff} = U - J$, where U is the Hubbard Coulomb repulsion and J is the Hund exchange interaction. The energy functional is modified as

 $E^{DFT+U}[n] = E^{DFT}[n] + U_{eff}/2 \sum Tr[n^{\sigma}(1-n^{\sigma})]$

The correction for this functional is controlled by U_{eff} parameter but, determining an appropriate value for this parameter is difficult.

2.3.4 Hybrid Functional

Integrating the exchange-correlation energy based on two different methods is the central ideology behind Hybrid functionals. As we know, GGA functional provides us good prediction at affordable computational resources but suffers inaccuracy due to self-interaction error. But if we consider the HF approach, this error is completely eradicated in the exact exchange energy formalism as the electron correlation is excluded, but it requires high computational resources. Some of the proposed formulations for this functional are PBE0, B3LYP and Heyd-Scuseria-Ernzerhof (HSE) functionals. The HSE functional is represented as a linear combination of energies. LR and SR refer to long-range and short-range respectively, α is a mixing parameter, and ω is the screening parameter controlling the short ranges of exchange interaction.

$$E_{xc}^{HSE} = \alpha E_x^{HF,SR} (\omega) + (1-\alpha)E_x^{PBE,SR}(\omega) + E_x^{PBE,LR} (\omega) + E^{PBE}$$

2.4 Plane-wave basis sets and Bloch's Theorem

DFT methods provide us with a solution to our many-interacting electron system problem. However, it is still too difficult to handle an infinite number of electrons moving under the influence of a static potential due to an infinite number of ions. This leads to an infinite expansion of wavefunctions over an entire space in the crystalline solid system, requiring many basis sets. The periodicity of the crystal makes it possible for the wavefunctions to be represented on a plane-wave basis set with a periodic function by Bloch's theorem. By this theorem, the electronic wavefunction at the ith band index is defined as product of a periodic cell term and wavelike function.

$$\Psi_{i,k}(\mathbf{r}) = u_{i,k}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}$$

k represents the reciprocal lattice vector of a Bravais lattice in the first Brillouin zone (in k-space) and $u_{i,k}(\mathbf{r})$ is the periodic function of the crystal lattice such that $u_{i,k}(\mathbf{r}) = u_{i,k}(\mathbf{r}+\mathbf{T})$ for all lattice vectors **T**. The $u_k(\mathbf{r})$ can be written in Fourier series as,

$$u_{i,k}(\boldsymbol{r}) = \sum_{\boldsymbol{G}} \boldsymbol{C}_{i,\boldsymbol{G}} e^{(i\boldsymbol{G}.\boldsymbol{r})}$$

Where $C_{i,G}$ are plane wave expansion coefficients and **G** represent reciprocal lattice vectors satisfying the condition **G.T**= $2m\pi$ (m is an integer).

2.5 Projector-augmented wave method

The unique characteristics of wavefunctions show that electrons near the nuclei experience strong Coulombic interactions, resulting in highly rapid oscillations of the wavefunction in the nuclear region, requiring a vast number of plane waves for accurate representation. Due to the Screening effect, the wavefunctions vary slowly outside this region. Therefore, we can categorise these regions as **core** and **valence** that are separated at a certain cutoff radius (r_c). The core electrons are tightly bound in the vicinity of the nucleus, while valence electrons are outside and are responsible for the physical properties, thereby introducing the concept of *pseudopotential* approximation where the electrons in different regions are treated separately, hence reducing the number of required plane waves.

We used the Vienna Ab initio Simulation Package (VASP), implementing the plane-wave basis within Projector-augmented wave (PAW), one of the most efficient methods for DFT calculations. An all-electron single-particle wavefunction is mapped into a smooth auxiliary wavefunction in the PAW method, which is more computationally convenient, known as a pseudo wavefunction.

2.6 Force Theorem

The equilibrium of crystal structure can be justified by force acting on each atom in the system. The groundstate structure is achieved when during the process of geometry optimisation, we achieve zero total interatomic force. We can evaluate the force acting on the i^{th} atom at position R_i with total energy E of the system as,

$$F_i = - \nabla_{Ri} E$$

2.7 Computational Details

Geometrical optimization and total energy computations of CsPbI₃ were done using the VASP package by solving Kohn-Sham equations within the DFT framework. To define the electronic exchange-correlation effects, the projector augmented wave (PAW) method was used in conjunction with the PBE parameterization and Hybrid functional. The PAW pseudopotentials of Cs, Pb, I, Ba, Ca, Mg and Sr were analysed for 6s¹, 6s²4f¹⁴5d¹⁰6p², 4d¹⁰5s²5p⁵, 6s², 4s², 3s² and 5s² respectively. For all the substituted system studied kinetic energy cut off of 500 eV was defined.

The unit cell of four compounds was constructed with 90 atoms (18 Cs, 17 Pb, 54 I, 1[Ba, Ca, Mg, Sr]). The mesh was sampled using Monkhorst-pack mesh (5 x 5 x 5). The self-consistent electronic steps have an energy convergence criterion of 10⁻⁴ eV.

Geometrical optimization and total energy computations of Cs₂AgBiBr₆ were done using the VASP package by solving Kohn-Sham equations within the DFT framework. To define the electronic exchange-correlation effects, the projector augmented wave (PAW) method was used in conjunction with the PBE parameterization and Generalised Gradient Approximation (GGA). The PAW pseudopotentials of Cs, Bi, Br and Ag were analysed for 6s¹, 4f¹⁴5d¹⁰6s²6p³, 4s²3d¹⁰4p⁵ and 4d¹⁰5s¹ respectively. For all the substituted system studied kinetic energy cut off of 100 eV was defined.

The unit cell of four compounds was constructed with 40 atoms (8 Cs, 4 Bi, 4 Ag, 24 Br). The mesh was sampled using a Monkhorst-pack mesh (5 x 5 x 5) for Bulk and (5 x 5 x 1) for 2D. The self-consistent electronic steps have an energy convergence criterion of 10 $^{-5}$ eV.

• ALGO

The ALGO tag is used to specify the electronic minimisation algorithm and to select the type of GW calculations. We have used ALGO = Normal, which selects IALGO = 38.

• EDIFFG

By default, the tag is defined as $EDIFFG = EDIFF \times 10$. EDIFFG tag defines the break condition for the ionic relaxation loop. When EDIFFG is positive, the relaxation stops when the change of the system's total energy is smaller than EDIFFG between successive ionic steps. In contrast, for negative value, the relaxation is contained when norms of all forces are smaller than |EDIFFG|.

• ENCUT

ENCUT specifies the cutoff energy for the plane-wave basis set in eV. The plane waves with kinetic energy smaller than E_{cut} are included in the basis set and components greater are removed.

• IBRION

IBRION tag determines how ions are updated and moved. For complex relaxation problems, it is better to use the conjugate gradient algorithm (IBRION=2). We have used IBRION = -1 which refers to no ions' movement, but NSW outer loops are performed. In each outer loop, the electronic degrees of freedom are re-optimised; if no ionic update is required, NSW=0 is used instead.

• ISIF

ISIF tag determines whether the stress tensor is calculated and which principal degrees of freedom

(ionic positions, cell volume, and cell shape) are allowed to change in relaxation and molecular dynamics runs.

• ISPIN

ISPIN specifies spin polarisation. On selecting ISPIN=1 non spin-polarised calculations are performed while for SPIN=2 spin-polarized calculations (collinear) are performed. Collinear magnetism can be studied if we combine ISPIN with MAGMOM.

• IVDW

This tag controls whether van der Wal corrections are calculated or not and how they are to be calculated.

Popular local and semilocal density functionals are unable to describe correctly the van der Waal interactions due to dynamical correlations between fluctuating charge distributions. A pragmatic method used to work around this problem is by adding a correction to the conventional Kohn-Sham DFT energy E_{KS-DFT} :

The correction term E_{disp} is computed using some of the available approximate methods. We have used IVDW = 11 for zero dampings.

• LOPTICS

LOPTICS tag calculates the frequency-dependent dielectric matrix after the electronic ground state has been determined. If we select LOPTICS= TRUE, it requires a significant number of empty conduction band states. Usually, the parameter NBANDS is roughly doubled or tripled in the <u>INCAR</u> file with respect to the VASP default.

• LSORBIT

LSORBIT tag specifies if the spin-orbit coupling is taken into account. This option only works for PAW potentials and is not supported by ultrasoft pseudopotentials. If the spin-orbit coupling is not included, the energy becomes independent of the direction of the magnetic moment, i.e. rotating all magnetic moments by the same angle results in the same energy; therefore, no need to define the spin quantisation axis. Spin-orbit coupling, however, couples the spin to the crystal structure.

VASP reads in the WAVECAR and CHGCAR files, aligns the spin quantisation axis parallel to SAXIS, implying that the magnetic field is parallel to SAXIS, and performs a non-self-consistent calculation. On comparing the energies for different orientations, magnetic anisotropy can be determined.

Switching on spin-orbit coupling (SOC) in a conventional DFT calculation adds term $H_{soc}^{\alpha\beta} \propto \vec{\sigma} \cdot \vec{L}$ to the Hamiltonian that couples the Pauli-spin operator with the angular momentum operator $\mathbf{L} = \mathbf{r} \times \mathbf{p}$.^[1] As a relativistic correction, SOC acts predominantly in the immediate vicinity of the nuclei, such that it is assumed that contributions of H_{SOC} outside the PAW spheres are negligible. VASP, therefore, calculates the matrix elements of H_{SOC} only for the all-electron one-centre contributions

$$E_{soc}^{ij} = \delta_{\mathbf{R}_i \mathbf{R}_j} \delta_{l_i l_j} \sum_{n \mathbf{k}} w_{\mathbf{k}} f_{n \mathbf{k}} \sum_{lpha eta} \langle ilde{\psi}_{n \mathbf{k}}^{lpha} | ilde{p}_i
angle \langle \phi_i | H_{soc}^{lpha eta} | \phi_j
angle \langle ilde{p}_j | ilde{\psi}_{n \mathbf{k}}^{eta}
angle$$

• **PREC** tag specifies how precise the real space projectors should be.

CHAPTER 3

CASE STUDY I: CsPbI3

As we already know, hybrid perovskites exhibit desirable properties for solar cell applications like broad absorption spectrum, fast charge separation, long carrier separation lifetime, exceptionally higher power conversion efficiency and easy fabrication. Even with such high qualities, the degradation of hybrid perovskites as the hydrogen bonding between monovalent organic cation and octahedral PbI₂ is very weak hence degrades quickly to PbI₂ under external stresses like the electric field, moisture, photo-oxidation, hinders commercialisation of the perovskite solar cells. Substituting the organic cation with inorganic Caesium improves the stability of the crystal, as an all-inorganic perovskite is effective under such conditions. The unique photovoltaic properties of the Pb halide perovskites, like suitable direct bandgaps, high optical absorption coefficients, balanced electron and hole effective masses, defect tolerance, super-long carrier diffusion lengths and lifetimes, and small exciton binding energies, all have contributed to record high PCEs.

The development of Caesium lead halide perovskites also led to problems like the toxic nature of Pb and longterm instability against moisture, heat and light; hence finding new, stable and Pb-free perovskites has been the recent research interest. Among the few suggested strategies, substituting lead atom with another similar in size and properties element was studied by us.

We had substituted 5% of the Lead ions in the Caesium lead iodide crystal with Barium, Calcium, Magnesium and Strontium ions. We verified the structural and thermodynamical stability of the corresponding crystals structures.

Element	Coordination	Ionic Radius		Crystal	Tolerance	Octahedral
	number	(Angstrom)			Factor (t)	Factor (µ)
Caesium	12	1.88		CsPb _{0.95} Ba _{0.05} I ₃	0.832	0.578
Lead	6	1.19				
Iodine	6	2.2		CsPb _{0.95} Ca _{0.05} I ₃	0.876	0.498
Barium	6	1.35	-	CsPb _{0.95} Mg _{0.05} I ₃	0.915	0.434
Calcium	6	1				
Magnesium	6	0.72		$CsPb_{0.95}Sr_{0.05}I_3$	0.852	0.539
Strontium	6	1.18	L			

The octahedral and tolerance factors for the systems have been tabulated below:

Table 1(a) Coordination Numbers and ionic Radii, 1(b) Stability factors

It is observed that the Tolerance factor t for all the crystals was between the permissible range of 0.8 < t < 1and octahedral factor $0.44 < \mu < 0.90$ for stable perovskite structure.

The formation energy verified the thermodynamic stability of the crystals. The formula used for calculating the formation energy is $E_{C_sPbI3_x} = -(18E_{C_s} + 17E_{Pb} + 54E_{I+}E_x)/18$ where (X= Ba, Ca, Mg, Sr)

The following tables, Tables 2(a), represent the energies of isolate atoms, and Table 2(b) denotes the formation energy and formation energy per unit cell, respectively, for corresponding crystals.

Element	Energy (eV)	Material	Energy (eV)	Formation
Caesium	-0.864			Energy / unit
Lead	-3.88			cell (eV)
Iodine	-1.49	CsPb _{0.95} Ba _{0.05} I ₃	-314.77191	-8.372
Barium	-2.11	CaDh Ca I	214 (1100	0 272
Calcium	-1.93	CSP00.95Ca0.0513	-314.01109	-8.373
Magnesium	-1.53	CsPb _{0.95} Mg _{0.05} I ₃	-312.34554	-8.269
Strontium	-1.64	CsPb _{0.95} Sr _{0.05} I ₃	-314.61237	-8.389

Table 2(a) Elements Energy, 2(b) Energy of the crystal and corresponding formation energy

Projected DOS

1. CsPb0.95Ca0.05I3



Figure 3(a), 3(b) Dos and electronic structure of Calcium substituted CsPbI₃

The DOS plot shows that 5p orbitals of Iodine contribute majorly in the Valence band while 6p orbitals of Lead and 4s orbitals of Calcium contribute in the conduction band. It is observed that there is a hybridisation between 6p orbital of Lead and 5p orbital of Iodine. Similarly, the 4s orbital of Calcium and 6s of Caesium hybridise, forming the octahedral configuration in the crystal. In the crystal structure, Cyan: Cs, Black: Pb, Purple: Iodine and Blue: Ca atoms.



2. CsPb0.95Ba0.05I3

Figure 4(a), 4(b) Dos and electronic structure of Calcium substituted CsPbI₃

The DOS plot shows that 5p orbitals of Iodine contribute majorly in the Valence band while 6p orbitals of Lead and 4s orbitals of Barium contribute in the conduction band. It is observed that there is a hybridisation between 6p orbital of Lead and 5p orbital of Iodine. Similarly, the 4s orbital of Barium and 6s of Caesium hybridise, forming the octahedral configuration in the crystal. In the crystal structure, Cyan: Cs, Black: Pb, Purple: Iodine and Green: Ba atoms.

200 CsPb_{0.95}Mg_{0.05}I₃ 100 15 Cs 10 Pb Mg 0 -4 -2 0 100 I 50 $\mathbf{E}_{\mathbf{f}}$ -2 2 Energy(eV)

3. CsPb0.95Mg0.05I3

Figure 5(a) Dos, 5(b) Dos and electronic structure of Calcium substituted CsPbI₃

The DOS plot shows that 5p orbitals of Iodine contribute majorly in the Valence band while 6p orbitals of Lead and 3s orbitals of Magnesium contribute in the conduction band. It is observed that there is a hybridisation between 6p orbital of Lead and 5p orbital of Iodine. Similarly, the 3s orbital of Magnesium and 6s of Caesium hybridise, forming the octahedral configuration in the crystal. In the crystal structure, Cyan: Cs, Black: Pb, Purple: Iodine and Orange: Mg atoms.

4. CsPb0.95Sr0.05I3



Figure 6(a), 6(b) Dos and electronic structure of Calcium substituted CsPbI₃

The DOS plot shows that 5p orbitals of Iodine contribute majorly in the Valence band while 6p orbitals of Lead and 5s orbitals of Strontium contribute in the conduction band. It is observed that there is a hybridisation between 6p orbital of Lead and 5p orbital of Iodine. Similarly, the 5s orbital of Strontium and 6s of Caesium hybridise, forming the octahedral configuration in the crystal. In the crystal structure, Cyan: Cs, Black: Pb, Purple: Iodine and Green: Sr atoms.

CHAPTER 4

CASE STUDY II: Cs₂AgBiBr₆

We already know why there is a need to switch from lead halides; another proposed method was by replacing Lead cations with two different cations resulting in the formation of Halide double perovskites.

Initially, it was proposed to substitute Pb(II) with similar divalent lone-pair cations Sn(II) and Ge(II) cations. However, this led to more severe instability issues as these two cations were oxidated to Sn(IV) and Ge(IV) states, thus losing optoelectronic properties. Then trivalent lone-pair cations Bi(III) and Sb(III) were employed for substitution, but obtained compound with formula $A_3B_2X_9$ adopted a low-dimensional structure to maintain the charge neutrality, resulting in large bandgaps, high anisotropic carrier effective masses, defect intolerance which was all undesired characteristics for photovoltaic application. All these failed attempts led us to an essential inference that the material should exhibit high electronic dimensionality; therefore, high structure dimensionality became a necessary condition. It was now suggested that we substitute Pb with a combination of one monovalent and another divalent cation, resulting in a 3D double perovskite, $A_2B(I)B'(III)X_6$ composition. The B(I) and B(III) cations usually adopt the rock-salt-ordered configuration due to the charge difference.

Theoretical studies have shown that the $6s^2$ lone-pair states of Pb^{2+} , that is, the B cation and X anion play a critical role in determining the optoelectronic properties of perovskites. In contrast, the A cation does not contribute to the band edges.

Based on the presence or absence of lone pairs states in B(I) and B(III), they have been classified into three categories.

<u>Type I</u> $(s^2 + s^2)$: both the cations have lone pair electrons, exhibit 3D electronic dimensionality, high optical absorption, small effective masses as well as small exciton binding energies.

Suitable for: Solar cell applications

<u>Type II</u> ($s^0 + s^2$): only one of the cations have lone pair electrons, BX6 octahedra determine the band edges, Bi 6p states determine CBMs while VBMs comprise of antibonding of Bi 6s and X p orbitals and no contribution from B(I) cation. The highly ionic B(I) cation's octahedra [B(I)X₆] results in passivation of the BiX₆ octahedra hence disturbing the band edge-determining octahedra to connect 3 dimensionally, resulting in 0D electronic dimensionality. They exhibit characteristics like large bandgaps and carrier effective masses.

Suitable for: Light emission device (natural electronic confinement), solar cells

<u>Type III</u> ($s^0 + s^0$): none of them has lone pair electrons, generally comprise of elements B(I) with occupied d¹⁰ states and B(III) with dispersive unoccupied s⁰ states. They show low bandgaps as the occupied d¹⁰ states raise the VBM energy levels and s⁰ states lower the CBM. The p orbitals of X anions and d orbitals of B(I) cations cannot connect 3D dimensionally in the valence band corresponding to 0D electronic dimensionality. At the same time, in CBM, there is a 3D connection between the antibonding s states of B(I) and p orbitals of X, signifying the mobility of electrons in 3D.

Suitable for: Photodetector laser and light emission device

The halide double perovskites of type II do not possess suitable optoelectronic properties; their carrier transport property has been drastically affected by low electronic dimensionality, resulting in large bandgaps. Therefore, the substitution of monovalent cations like Ag(I), In(I), Cu(I) help in narrowing the bandgap as their filled s² or d¹⁰ orbitals can elevate the VBM energy level.

The material studied by us was $Cs_2AgBiBr_6$. The structure is formed by alternating Ag^+ - and Bi^{3+} - centred octahedra of $(AgBr_6)^{5-}$ and $(BiBr_6)^{5-}$ in three crystallographic axes. Similar to single perovskites, $Cs_2AgBiBr_6$ single crystals also possess a cubic structure with a space group of *Fm3m*.

The structural stability factors were obtained as Tolerance factor: 0.89, Octahedral factor: 0.56, and τ as 3.96 thus, indicating reasonable structural stability.

OBSERVATIONS

CRYSTAL STRUCTURES



3D structure

2D structure

Figure 7(a) 3D structure, 7(b) 2D structure

1. Bulk Cs₂AgBiBr₆ with SOC



1.1 Projected Density of States

1.2 Optical Properties and Band structure

The projected Density of States denotes that 6s orbital of Caesium, 6p orbital of Bismuth together contribute to the conduction band while 4p orbital of Bromine has a major contribution in the valence band. We observe hybridisation between 6s orbital of Caesium and 4p orbital of Bromine overlapping states and undergoing hybridisation. Similarly, the 5s orbital of Silver and 6p of Bismuth hybridise in the crystal.



Figure 8(a) Dos, 8(b) Refractive Index, 8(c) Reflectivity 8(d) Absorption Cross-section 8(e) Band structure of 3D SOC

Materials	${m_h}^*$	me*			Cs ₂ AgBiBr ₆	eV
	$\Gamma \rightarrow I \qquad \Gamma \rightarrow X$		$I \rightarrow \Gamma$ $I \rightarrow W$		Indirect Band Gap	0.297
		1 1			Direct Band Gap	1.136
Cs ₂ AgBiBr ₆	52AgBiBr ₆ -0.455 -1.476 0.260 0.184	Conduction band minima	1.034			
(50)					Valence band maxima	0.737

Table 2(a) Elements Energy, 2(b) Energy of the crystal and corresponding formation energy

10 Cs, AgBiBr, No Soc Bulk 5 0-6 -4 -2 2 4 ¹⁰ Cs 5 Density of States (states/eV) 0 L -6 2 4 10 Ag 5 0^L -6 10 Bi 5 0└ -6 2 -4 -2 4 10 Br 5 0-6 .2 E, Energy (eV)

2.2 Projected Density of States

2. Bulk Cs₂AgBiBr₆ without SOC

The projected Density of States denotes that 6s orbital of Caesium, 6p orbital of Bismuth together contribute to the conduction band while 4p orbital of Bromine has a significant contribution in the valence band. We observe hybridisation between 6s orbital of Caesium and 4p orbital of Bromine overlapping states and undergoing hybridisation. Similarly, the 5s orbital of Silver and 6p of Bismuth hybridise in the crystal.



2.3 Optical Properties and Band Structure



Fig 9(a) Dos, 9(b) Refractive Index, 9(c) Reflectivity 9(d) Absorption Cross-section 9(e) Band structure of 3D No SOC

Materials	${m_h}^*$		me*		Cs ₂ AgBiBr ₆	eV
					Indirect Band Gap	1.297
	Γ→L	$\Gamma \rightarrow X$	$L \rightarrow \Gamma$	$L \rightarrow W$	Direct Band Can	2 200
					Direct Danu Gap	2.200
Cs ₂ AgBiBr ₆	-0 445	-0 768	0 406	0.322	Conduction band	1.998
(3D)	01110	0.,00	0.100	0.322	minima	
(02)					Valence band maxima	0.701

Table 3(a) Elements Energy, 3(b) Energy of the crystal and corresponding formation energy

3. 2D Cs₂AgBiBr₆ with SOC

We synthesised the 2D structure from bulk by increasing the separation by 50 Å along the miller indices (001). The Vander wall force effect reduces due to this increase in separation hence lowering the interaction between the layers, converting the 3D bulk to 2D.

3.2 Projected Density of States

The projected Density of States denotes that 6s orbital of Caesium, 6p orbital of Bismuth together



contribute to the conduction band while 4p orbital of Bromine has a significant contribution in the valence band. We observe hybridisation between 6s orbital of Caesium and 4p orbital of Bromine have overlapping states and undergo hybridisation. Similarly, the 5s orbital of Silver and 6p of Bismuth hybridise in the crystal.

3.2 Optical Properties and Band Structure







Fig 10(a) Dos, 10(b) Refractive Index, 10(c) Reflectivity 10(d) Absorption Cross-section 10(e) Band structure of 2D SOC

4. 2D Cs₂AgBiBr₆ without SOC



4.1 Projected Density of States

The projected Density of States denotes that 6s orbital of Caesium, 6p orbital of Bismuth together contribute to the conduction band while 4p orbital of Bromine has a significant contribution in the valence band. We observe hybridisation between 6s orbital of Caesium and 4p orbital of Bromine overlapping states and undergoing hybridisation. Similarly, the 5s orbital of Silver and 6p of Bismuth hybridise in the crystal.



4.2 Optical Properties and Band Structure



11(a) Dos, 11(b) Refractive Index, 11(c) Reflectivity 11(d) Absorption Cross-section 11(e) Band structure of 2D No SOC

CHAPTER 5

CONCLUSIONS

5.1 SUMMARY

Hybrid perovskites exhibit intrinsic properties like broad absorption spectrum, fast charge separation, long carrier separation lifetime, exceptional power conversion efficiencies, enhanced stability and relative ease of fabrication.

The first approach for reducing the lead content in halide perovskite that has been discussed in this thesis is lead substituted by Calcium, Barium, Magnesium and Strontium in CsPbI₃. Based on structural and thermodynamic stability it was observed that Strontium doped CsPbI₃ was most stable.

The second material studied was halide double perovskite $Cs_2AgBiBr_6$ at different dimensionalities. It was observed that 1D and 0D material are not stable hence, their electronic and optical properties have not been studied. There is a reduction in bandgap observed on incorporating the spin-orbit coupling. The 3D material without SOC exhibits a direct bandgap of 2.2 eV corresponding to the visible region (Green). The 3D material with SOC corresponds to a direct bandgap of 1.136 eV, near the IR region.

On reducing the dimension of the sample, we observe a decrease in band gap as there is a transition from a 3D semiconductor to a 2D metallic system.

5.2 FUTURE OUTLOOK

We plan to study the effect of the Rashba and Dresselhaus phenomenon on halide double perovskite's electronic and optical properties.

RASHBA AND DRESSELHAUS EFFECT

Spin-Orbit Coupling

An electron with momentum p moving across a magnetic field B experiences a Lorentz force in the direction perpendicular to its motion $F = -e(p \times B)/m$. It also possesses Zeeman energy $\mu B \sigma \cdot B$, where σ is the vector of Pauli spin matrices, m and e are mass and charge of the electron, and $\mu B = 9.27 \times 10-24$ J/T is the Bohr magnetron. Similarly, when traversing in the presence of an electric field E, it experiences an effective magnetic field Beff ~ E × p / mc2 in its rest-frame, a field inducing a momentum-dependent Zeeman energy Hso ~ $\mu B (E \times p) \cdot \sigma /mc2$, known as SO coupling. In crystals, the electric field is defined by the gradient of the

crystal potential, $E = -\nabla V$. The breaking of inversion symmetry also results in the splitting of energy bands. This band splitting was explained by Bychkov and Rashba, where they considered an electric field E = Ez z resulting in an effective SO coupling of the form

$H_{R} = \alpha_{R} \ /\hbar \ (\boldsymbol{z} \times \boldsymbol{p}) \boldsymbol{\cdot} \boldsymbol{\sigma}$

where αR is called the Rashba parameter. This form is derived for 2D plane waves, does not apply to realistic systems. Theoretical investigations show that the lack of inversion symmetry creates an additional electric field, Ez and distorts the electron wave function close to the nuclei where the plane wave approximation is not valid. In other words, in the solid-state, the Dirac gap mc2 ≈ 0.5 MeV is replaced by the energy gap ≈ 1 eV between electrons and holes and $\alpha R /\hbar \gg \mu B \text{ Ez/mc}^2$. The inversion symmetry breaking implies that the SO coupling is odd in electron momentum p, i.e., HSO = w (p) $\cdot\sigma$, where w(-p) = -w(p).

The inherent spin-orbit coupling effect in the non-centrosymmetric crystal structure is responsible for discovering the Rashba splitting phenomenon. The presence of heavy atoms in the crystal results in the spin-orbit coupling, which, when combined with a break in inversion or crystal symmetry, leads to Rashba-type effects. The symmetry in three-dimensional centrosymmetric perovskite crystal structures can be broken by several means like an octahedral tilting of the inorganic lead-halide cage or by dynamic rotation of organic cation on the timescale of few picoseconds. The Rashba splitting governs the charge carrier recombination, eventually monitoring the carrier lifetime and diffusion length hence the solar cell efficiency of the perovskite materials.

In hybrid perovskites, the thermodynamically stable inorganic substructure exhibiting excellent charge carrier mobility when combined with the organic part with fine-tuning of optoelectronic properties makes these materials ideal for solar cells, light-emitting diodes and spintronics. However, the presence of a hydrogen bond in the material gives rise to octahedral tilting, resulting in structural distortion and broken inversion symmetry, transforming the crystal structure of hybrid perovskites into non-centrosymmetric. Furthermore, these structural re-arrangements cause the transformation of electronic band structures (conduction and valence band maxima).

Rashba-type effects lead to the possibility that the fundamental bandgap in hybrid perovskite systems may be indirect. The indirect band is shifted in k-space and has slightly lower energy than the direct band. Due to the SOC effect, we observe splitting in the extrema edges of conduction and valence band along the reciprocal lattice k. This change of energy eigenvalue in the k direction with respect to band edge shift is quantified as Rashba splitting parameter, which drastically affects the dynamics of charge carriers as, under the visible light illumination, the electrons get excited and jump to the conduction band but create a hole in the valence band

region. This pair of excited electron and hole are called charge carriers or excitons. The recombination of these excitons governs the power conversion efficiency. The possibility of recombination is determined by the carrier lifetime and diffusion length, but these two depend on three factors. The rate of recombination can be altered by charge carrier trapping, that is, the nonradiative recombination by the conversion of electronic energy into heat energy. Other factors controlling this rate are the polaronic screening effect and one of the consequences of the Rashba effect. Even though light absorption occurs through direct transition, but the recombination of the cooled charge carriers gets delayed due to the shift of band extremes. The electron now is unable to follow the direct path. Instead, it gets captured in the secondary conduction minima before reaching the valence band, following an indirect transition.



Figure 12 Rashba Effect

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