

PhD THESIS

**ORGANIC-INORGANIC HYBRID
PEROVSKITE SOLAR CELL MATERIALS:
DFT STUDIES**



by

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**DEPARTMENT OF PHYSICS
UNIVERSITY OF MALAKAND
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ORGANIC-INORGANIC HYBRID PEROVSKITE SOLAR CELL MATERIALS: DFT STUDIES



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*Thesis submitted to the Department of Physics in partial fulfilment of the
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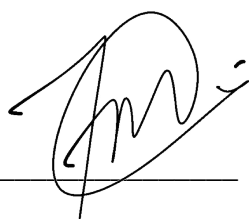
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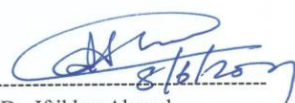
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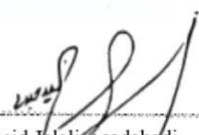
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Abstract

In this thesis, density functional theory studies are carried out for the structural, electronic and optical properties including the excitonic effects of $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ alloy and cubic, tetragonal and hexagonal systems of FAPbI_3 . The electronic structures are calculated using both Perdew-Burke-Emzerhof (PBE) and quasiparticle Green's function with the screened Coulombic interactions GW, methods while the excitonic optical properties are explored through Bethe-Salpeter Equation (BSE) method in the frame work of GW calculations. Our results show that for the mixed type $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ the bandgap value increases as a function of Br concentration showing stronger correlation with the structural behavior. The BSE based optical properties reveal that the overall excitonic spectra are blue-shifted with the Br fraction. Our results further reveal stronger anion concentration dependence of the variation in the exciton binding energies and the carrier effective masses as well as high frequency dielectric constants. These findings provide a way to improve short circuit currents and power conversion efficiencies in multijunction solar cell devices through doping in OIHPs (organic-inorganic hybrid perovskites). Similarly, the bandgap value increases across cubic-tetragonal-hexagonal phases due to temperature dependent structural transition. The excitonic spectral peaks are blue-shifted and exciton binding energies increases on transforming from room temperature cubic phase to low temperature hexagonal phase. Such findings could have important impacts on the practical uptake of HOIP based solar cells under different climatic conditions.

Dedicated to my parents.

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List of Publications

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2. Revealing the quasiparticle electronic and excitonic nature in cubic, tetragonal and hexagonal phases of FAPbI_3 , **Zeeshan Muhammad**, Peitao Liu, Rashid Ahmad, Saeid Jalali Asadabadi, Cesare Franchini and Iftikhar Ahmad (Under Review in *ACS Omega*).
3. Quasiparticle electronic and excited state excitonic properties of organic-inorganic hybrid perovskites, **Zeeshan Muhammad**, Cesare Franchini and Iftikhar Ahmad (In preparation).

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Chapter 1

Introduction

Electricity is obtained from petroleum products, such as coal, oil and flammable gas in various parts of the world beside hydro and nuclear power stations. These conventional energy sources are facing many hurdles including rising costs, security concerns due to reliance on few countries and environmental change. Therefore, governments, businesses, consumer and other organizations are continuously supporting the alternative options for energy sources. Sustainable power sources, for example, sun based, biomass, geothermal, hydroelectric and wind have attracted enormous attention in the recent years, as they address some of the present-day worries as mentioned earlier. Instead of non-renewable energy sources, that comes from limited assets which may eventually turn out to be extremely costly, making it inconceivable to recover, renewable energy sources are generally vast in accessibility. Generating solar power has come out to be as one of the fast-growing renewable sources of electrical energy.

Experimentally, the photovoltaic activity was first demonstrated in 1839 by French physicist E. Becquerel who observed that voltage develops between positive and negative electrodes dipped in an electrolytic solution, under the exposure of light [1]. The same effect was further studied by C. Fritts in selenium, when exposed to light [2]. Silicon based solar cells were reported initially by Pearson *et. al.* at Bell Telephonic Laboratories [3]. They found that silicon is more efficient than selenium thus enabling solar cells to power

electrical equipment. During mid-seventies, more research efforts were carried out to make efficient solar cells for terrestrial applications. In last few decades, newer device technologies and material study leads to deduction in cost and hence opening new perspectives for commercial applications of solar cells [4].

A solar cell is a photovoltaic device that transforms the energy of light (commonly sunlight) directly into electricity using the principle of photoelectric effect which is both physical and chemical processes. There are three basic attributes that requires for the operation of a solar cell:

- the generation of electron-hole (e-h) pairs or excitons by the absorption of light,
- the separation of the oppositely charged carries,
- the extraction of the carriers to the external circuit.

The performance of a photovoltaic device can be determined by the efficient separation of photo-generated charges due to the built-in potential at the terminals. The main issue which the researchers are facing in the solar cell technology is the search for efficient materials with high photon-to-electron-conversion-efficiency (PCE).

There are various distinctive semiconductor materials capable to transform the energy of photons into electrical energy. Photons having energy smaller than bandgap energy of the semiconducting material will not be absorbed while photons absorbed having much higher excess energy than the bandgap E_g of the material will lost rapidly due to thermalization. So, on the bases of these considerations and few other assumption, Shockley and Queisser [5] established the efficiency limit for solar cells with a single absorbing material and a single bandgap. On earth's surface (the AM1.5 spectrum), efficiency can reach up to 34%, when $E_g \approx 1.4$ eV. Presently, crystalline Silicon dominates the PV market. It has energy conversion efficiency more than 26% [6]. Since, Si is an indirect bandgap material, therefore poor absorber of light. To have well absorption of light, Si layer must be hundreds of micro-meters thickness, requiring extremely high-quality pure crystals. Thus, crystalline

Si based solar cells are expensive despite the abundance of Si. Gallium arsenide based (GaAs) solar cell has higher efficiency up to 29% than Si solar cells [7]. Similarly, Cadmium Telluride (CdTe) and thin film CIGS (copper indium gallium diselenide) and many other photons absorbing materials were used but they are prohibitively expensive for many PV applications [8].

Organic-inorganic hybrid perovskites (OIHPs) have demonstrated exceptional electronic and optical properties for potentially low-cost efficient photovoltaic technologies. Such materials do not require expensive elements and are easy to synthesize than traditional expensive solar cell materials (e.g. Si or GaAs). Since, advancements in theoretical methods and thin film processing, enable us in understanding the underlying structural, electronic and photophysical properties of solar cell materials and thus paves way to the fabrication of OIHPs based solar cells having power conversion efficiencies (PCEs) from 3.8% [9] to 27.0% [10] during the last decade. Now it only seems a matter of time to test the impact of such materials on real-world in commercialized energy sectors.

The development of the revolutionary mixed type hybrid organic-inorganic perovskites has sparked much interest in the field of photovoltaics [11–32] because of their low-cost compositional chemical management of constituents, allowing tailoring of electrical and optical parameters. Some of the key characteristics of these materials that make them exceptional are their tunable optimal bandgap for appropriate sunlight absorption [11, 13–18, 20–27, 29, 33], longer carrier lifetimes [11, 34, 35], higher charge carrier mobility [36–39], longer charge carrier diffusion length [35, 36, 40] and weak exciton binding energy [41–48]. Mixing of halides at X-site such as Br and Cl, provides wide range of fine-tuning property suitable for designing and boosting the performance of multijunction devices. In addition to $\text{MAPb}(\text{I}_{1-x}\text{Cl}_x)_3$ [12, 49] and $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3$ [21, 29, 30, 50], $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ [15, 22, 33] has also been successfully synthesized and demonstrated in solar cells.

Moreover, the power conversion efficiency of a solar cell material varies with its electrical and optical properties. These properties depend on various physical parameters such as lattice parameters, bandgaps, and absorption. Also, the structural transition upon change

in temperature strongly influences the performance of a solar cell. Such change in temperature affects the mechanism of electron-hole (e-h) pair interactions in the photo-excited states. Due to the higher contribution of e-h interactions in the optically excited systems, the interplay of excitonic effects cannot be ignored [41–48]. According to the published works in literature, the interaction of the e-h pair can be influenced by three basic factors. First, according to the ferroelectric domain theory [51–55], alignment of organic cations causes to generate nanoscale ferroelectric domains which make spatial separation of photoexcited electron and hole pairs and thereby degrading their process of recombination. Second, from the Rashba-Dresselhaus splitting effect [56–59], the orbital and spin motion of the inorganic atoms interact with the induced electric field due to the organic cations, thus resulting in the splitting of electronic band structure for different spins and results in enhanced carrier lifetime and indirect bandgap. Third, the formation of large polarons due to orientation of organic cations causes charge separation in response to optical excitation and thus reduces the quasiparticle energy of electron and hole [34, 42, 59, 60]. Experimentally, it has also been found that ionic screening is affected with a change in temperature [42–45, 48]. Previously, the photoluminescence (PL) studies of FAPbI₃ in the temperature range of 400 K to 100 K showed degradation in PL spectra going from cubic-to-hexagonal phase [61]. But in some reported articles, screening effects do not seem to be directly influenced by the change in temperature [46, 47]. In another study, kinetic trapping also influences the electronic and optical excitonic properties during the phase transition of FAPbI₃ [62].

Although the mixed FAPb(I_{1-x}Br_x)₃ alloy and transitional phase behavior of FAPbI₃ have been experimentally studied, a thorough in-depth theoretical description and understanding of the structural parameters, electronic density of states (DOS), bandgaps, carrier excitations and exciton binding energies has not been fully addressed. In the present work, we carried out the density functional theory (DFT) which proves to be a powerful tool for modeling and simulations of materials [63, 64]. The commonly used generalized gradient approximation (GGA) in Perdew-Burke-Ernzerhof (PBE) [65, 66] provides structural lattice parameters close to the experimental values, but it is well known that DFT fails

to describe the excited state properties such as quasiparticle (QP) bandgaps and excitonic properties [67, 68]. An additional complication in relativistic HOIPs is the need to include spin-orbit coupling (SOC) effects which causes further reduction of the bandgaps [42, 69–75]. Moreover, the use of hybrid functionals like HSE06 including SOC does not satisfactorily improve the issue of bandgap underestimation [74]. The state-of-the-art approach to improve the bandgap is the GW method [76, 77] which provides a good approximation in evaluating the self-energy operator as contraction of the one-body Green’s function (G) with the screened Coulomb interaction (W). The GW method has been widely used for many systems ranging from elemental semiconductors [67, 68, 78] to HOIPs [42, 69, 70, 72–75, 79], yielding bandgaps in better agreement with experiments. Since during the optical excitation the interactions of the electron-hole (e-h) pairs create excitons which strongly couple to the incoming photons, this leads to substantial modification of the optical spectrum both below and above the quasiparticle bandgaps. To explore the excitonic peaks in the optical spectra, it is important to account for e-h pair interaction which is normally done by solving the Bethe-Salpeter equation (BSE) on top of GW calculations [42, 80–83].

So, theoretically, it is necessary to explore the fundamental material properties of mixed $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ system and the temperature dependent structural transitions of FAPbI_3 from one phase to another. Such known information is exclusively requisite for the device architecture since a significant variation in the material’s electronic and optical characteristics typically is linked with doping level and structural phase transition. In addition, transitional behaviors are not easy to accommodate in a photovoltaic device whilst keeping efficient extraction of the carrier with proper metallization as they are required to be precisely compatible with the light-absorber under any climatic environment.

Chapter 2

Literature Review

2.1 Historical Overview

In 1839, a German mineralogist Gustave Rose, firstly discovered and reported the structure of calcium titanium oxide (CaTiO_3). The distinctive features of such material were later studied by Lev Alekseyevich von Perovski, a Russian mineralogist who was the first to describe its crystalline structure and thus named after him as *Perovskite*.

This crystallographic family follows the ABX_3 chemical formula, where A and B represents divalent cations of different nature and/or size, while X stands for monovalent anions. Among perovskites, since after their first appearance, metal-oxide (i.e. $\text{X} = \text{O}$) are broadly studied, mainly due to their captivating magnetic and ferroelectric properties, and possibly used as superconductive materials. In 1984, Tapøse *et. al.* was the first to report the crystal structure of hybrid halide perovskite with gold as metal and chlorine as halogen [84]. The interest in lead-based halide perovskite emerged in 1958, when Møllar *et. al.* demonstrated the photoconductive nature of CsPbX_3 material [85]. In 1978, Weber used methylammonium ($[\text{CH}_3\text{NH}_3]^+$ or MA) instead of Cs and was first to synthesize and described the structure of organic-inorganic hybrid perovskite [86].

Before the end of the twentieth century, perovskite were utilized as semiconducting materials in electronic gadgets. The pioneering works of Kagan and Chondroudis in 1999,

demonstrated the application of thin films of organic-inorganic halide perovskites as active semiconducting layer in low cost thin-filmed field-effect transistors (TFETs) and light emitting devices (LEDs) [87]. The novel major application of organic-inorganic hybrid perovskites for photovoltaics was emerged in 2006 when Miyasaka *et al.* employed methylammonium lead bromide (MAPbBr_3) as photo-active layer on nanoporous TiO_2 substrate within an electrolytic solution based dye-sensitized solar cell (DSSC) framework, generating a 2.2% of power conversion efficiency (PCE) [88]. After this development, the OIHP based solar cells achieved a rapid improvement in power conversion efficiencies. In 2009, Miyasaka *et al.* replacing the dye pigment and substituting I instead of Br, achieved 3.8% of PCE by using a thin layer of MAPbI_3 on mesoporous TiO_2 as electron-collector [9]. To improve the stability, Park *et al.* in 2011 employed perovskite nanoparticles on mesoporous TiO_2 to serve as sensitizer for high absorption of photon energy over conventional dyes, realizing an efficiency of 6.5% [89]. However, these devices based on liquid electrolyte, gained little attention due to lower efficiencies. In 2012, a breakthrough came, when Snaith *et al.* achieved relatively high efficiency of 9.7%, by replacing liquid electrolyte as electron-transporter spiro-OMeTAD as hole-transporter [90]. Later, Snaith and his co-workers demonstrated an efficiency of 10.9%, by replacing TiO_2 with inert Al_2O_3 substrate. These reports showed ambipolar nature of hybrid perovskites, leading the intensive employment of planar heterojunction design in these devices [91]. In March 2013, Snaith *et al.* used mixed hybrid perovskite, achieving power conversion efficiency up to 12.3% [92]. They demonstrated that the ambipolar nature of hybrid perovskites can transport both electrons and holes and transform the absorbed photons into collected carrier with approximately 100% efficiency. In July 2013, Burschka *et al.* used sequential deposition method by two step solution processing to overcome the precipitation of the perovskite which widely hampers the performance of the device and achieved 15% efficiency [93]. In December 2013, Liu *et al.* used a thin layer of ZnO nanoparticles as an electron-transporter replacing mesoporous TiO_2 in MAPbI_3 based solar cell, exceeding efficiency up to 15.7% [94]. In 2014, Yang *et al.* boost the photovoltaic efficiency up to 19.3% by lowering the de-

fects density of the perovskite film with controlled humidity [95]. In 2015, Seok *et al.* used FAPbI₃ (fomamidinium iodide or CH(NH₂)₂) layer for the first time and revealed broader absorption of solar spectrum [96]. Their best devices showed photovoltaic efficiencies up to 20.1% . In March 2016, Hagfeldt *et. al.* used mixed Cs/CH₃NH₃/CH(NH₂)₂ as triple cation, achieving highly efficient and stabilized solar cells, with maximum PCEs of 21.1% [97]. Seok and coworkers improved the conversion efficiency upto 22.1% by fixing the deep-level defects in perovskite-halides [98]. As a turning point the mixed system onwards takes on, not only modifies the stability but also paves way to tune the bandgap as well as carrier transport properties. In June 2018, Sahili *et. al.* reported two terminal perovskite/Si tandem solar cell and attained PCE upto 25.2% [31]. Later in 2020 Gharibzadeh *et. al* used mixed-cation lead mixed-halide perovskite/Si heterojunction tandem solar cell and efficiency jumped to 25.7% for perovskite based solar cells [32]. To date, the record certified efficiency of 27.0% has been obtained by Wang *et. al.* by using 4-terminal perovskite/Si based tandem architecture with multilayer of transparent MoO₃/Au/MoO₃ electrode [10].

OIHPs have attracted tremendous research efforts. These compounds require no rare elements for synthesis and are simpler to fabricate than many traditional technologies. Thus, the cost of perovskite solar cell could potentially be low. During a decade, there have seen an unprecedented rise in PCEs of OIHP based solar cells. The high efficiency and affordable cost are the motivation for studying such materials.

2.2 Structural Stoichiometry

In this section, we shortly review the structural framework of OIHP. The OIHP having wide range of applications in photovoltaics as well as in optoelectronics, generally follows the stoichiometric formula of ABX₃ just like CaTiO₃ as discussed in previous section. Traditionally, the unit cell of OIHP comprised of A, B and X sites referred to three distinct lattice locations. The A site mainly contains the larger organic cations (MA, FA or Cs), B site having smaller divalent inorganic/metal cations (Pb or Sn) and X site is composed

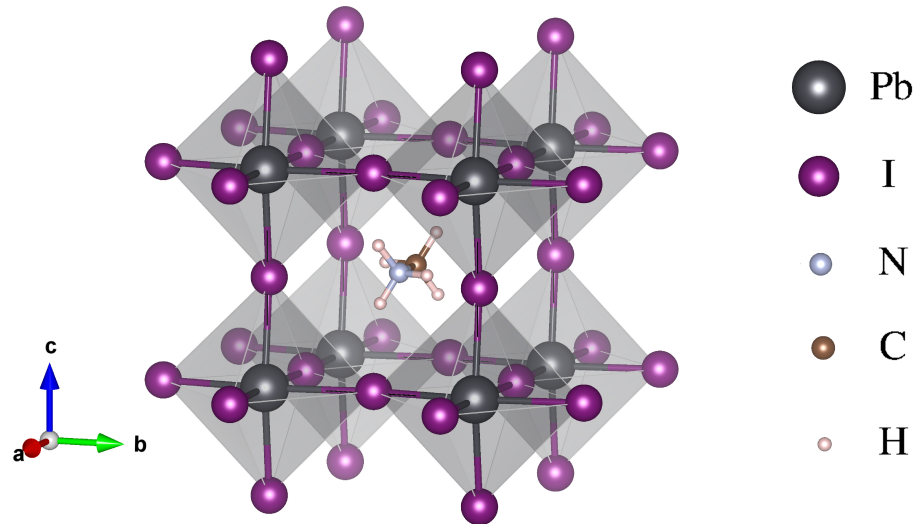


Figure 2.1 Unit cell of cubic MAPbI₃ belong to space group Pm-3m (221).

of monovalent anions or halogens (I, Br or Cl). Figure 2.1 shows the cubic (Pm3m-221) phase of the most studied MAPbI₃ unit cell with 12-fold coordination of the organic cation at A site, 6-fold coordination of inorganic atom at B site, and BX₆ octahedra residing at the eight corners of the cube. Moreover, the rotational dynamics of the organic molecule gives rise to steric effects which causes distortion in BX₆ octahedra and thus transforming from ideal cubic phase to pseudo-cubic phase. It is BX₃ octahedra distortion that is responsible for adverse effects in structural symmetry due to changes in Pb–I bond lengths which are directly linked with the electronic and optical behaviors of the material.

2.3 Tolerance and Octahedral Factors

Tolerance factor is the semi-empirical mathematical tool to predict the foamability of 3D perovskite structure. Having the ionic radii r_A , r_B and r_X of the constituents A, B and X respectively, the Goldsmith tolerance factor t can be found according to the following

expression [99]:

$$t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)} \quad (2.1)$$

In general, for halide based ABX_3 structures, the value t occurs in the range between 0.80 to 1.06 [100, 101]. Beyond this range, the density of lattice mismatch enhances due to the octahedral tilting and thus causes deviation from the ideal perovskite-like structure. For instance, when $t < 0.80$, the B–X bonds tends to compress and excess area inside the cage will be covered by A–X bonds strain. To adjust such stresses, BX_6 octahedra tilts and the degree of symmetry declines. Such effects will favor the formation of non-perovskite motif like NH_4CdCl_3 [102]. For the case when $t > 1.06$, the larger size of A or smaller size B and X species provides higher degree of symmetry, leading to form highly stable hexagonal structures. Based on the size of A site cation, various dimensionalities of perovskites can be obtained. For example, occupation of species like $[CH_3NH_3]^+$, $[HC(NH_2)_2]^+$ and $[Cs]^+$ at A site will form 3D motif. Whereas the extra-large A site cation like $[CH_3CH_2NH_3]^+$, $[C_3H_6N_2]^+$ or $[C_3H_5N_2]^+$ will disrupt the 3D motif and thus adopts 2D and 1D structures.

In conjunction to tolerance factor, Li *et. al.* introduced octahedral factor which directly provides information about the stability of the BX_6 octahedron to determine the formation of possible perovskite-like structure [101]. The octahedral factor λ is defined as ratio of ionic radii of B-site atom (r_B) to the X-site atom (r_X), given by: $\lambda = r_B/r_X$.

For a particular case to form halide perovskite, the B and X species are selected in such way that $0.442 < \lambda < 0.895$, otherwise outside such range, the stable BX_6 octahedron disrupts and results in non-perovskite formation [100, 101]. Though the above two factors in together provide a sufficient idea for predicting the formability of halide perovskite, but they fail entirely in predicting the formations all perovskite-like structure within the perovskite type family [101]. A comparative illustration for tolerance and octahedral factors of commonly used halide perovskites are shown in Figure 2.2.

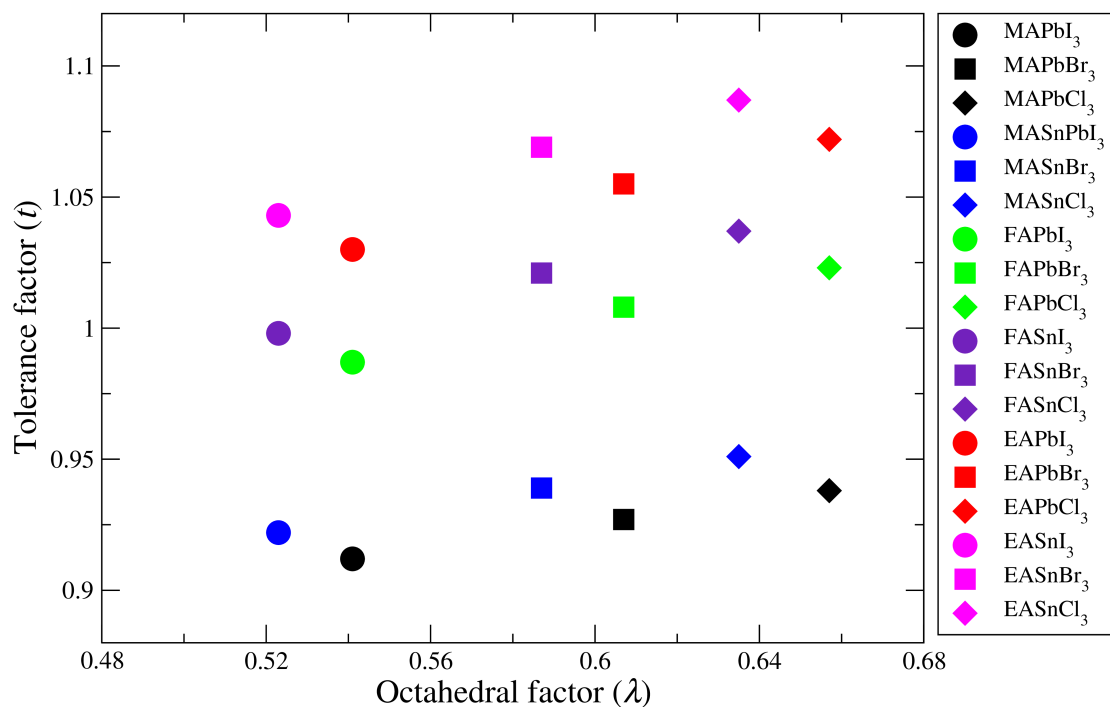


Figure 2.2 Calculated tolerance and octahedral factors for commonly studied OIHPs. Data collected from Ref. [101, 103].

2.4 Mixed Compositional OIHPs

According to the recent studies, the progress in the efficiency and chemical stability of the perovskite based solar cells can be accomplished by the compositional chemical management of A site having larger organic cation like Cesium $[\text{Cs}]^+$, Methylammonium MA $[\text{CH}_3\text{NH}_3]^+$ and Formamidinium FA $[\text{CH}(\text{NH}_2)_2]^+$ [18–20, 23, 104], of B site having smaller divalent inorganic cations e.g., Pb^{2+} and Sn^{2+} [25, 26, 28], and of X site containing monovalent metal halides including I^- , Br^- and Cl^- [12, 15, 21, 22, 29, 30, 33, 49]. For example, gradual substitution of the FA cation in MAPbI_3 will reduce the bandgap from 1.55 eV to 1.48 eV [16, 23], thus improving the carrier transport properties, long photoluminescence (PL) lifetimes [33], lower recombination and device hysteresis and high PCEs [33, 105]. Similarly, slowly replacing the Pb^{2+} cation with less toxic Sn^{2+} at B site will vary the bandgap from 1.51 eV to 1.28 eV [25, 28]. Due to the rapid oxidation of Sn^{2+} with the surrounding environment, it restricts its widespread use because of the stability and poor

PCEs issues [106]. In order to have a wide range of variations in electronic as well as in optical properties, the mixing of halogens at X site provides an effective way to meet such a fine-tuning property suitable for designing and meliorate performance of multijunction solar cell devices. In addition to MAPb(I_{1-x}Cl_x)₃ [12, 49] and MAPb(I_{1-x}Br_x)₃ [21, 29, 30], FAPb(I_{1-x}Br_x)₃ [15, 22, 33] has also been successfully synthesized and demonstrated in solar cells.

In present study, we carried out DFT-based theoretical investigation of FAPb(I_{1-x}Br_x)₃ system. The structural, electronic and excitonic photophysical properties of FAPb(I_{1-x}Br_x)₃ alloy are discussed in detail in Chapter 4.

2.5 Phase Transition

The structural symmetry of OIHPs also varies with temperature. As a function of temperature, OIHPs undergo change in lattice constants and octahedral distortions, thus resulting in different structural phases. According to the magnitude of distortion, OIHPs mainly adopts cubic (α), tetragonal (β), orthorhombic (γ) and hexagonal (δ) phases. For example, MAPbX₃ (where X = I, Br, Cl), exhibits in three different structural phases with change in temperature [107]. At higher temperature, MAPbX₃ exist in cubic form with fully disordered MA cations having higher degrees of rotational movement. As the temperature lowers, MAPbX₃ transforms to tetragonal phase with partially ordered MA cations and thus causing tilting of X–Pb–X bond angles. On further decrease in temperature, the tetragonal phase of MAPbX₃ become orthorhombic. During this phase, the rotational motion of MA cations ceases with strongly deformed PbX₆ octahedra. Temperature induced phase transitions of commonly studied OIHPs are listed in Table 2.1

The structural phase transitions of OIHPs directly linked to electronic and optical properties. The bandgap straightforwardly affected with the change in structural phase. Depending on the crystal system, the change in phase took place with tens of meV reduction in the bandgap energy [45, 108]. Moreover, dielectric screening also influenced by the

Table 2.1 Temperature dependent phase transitions for MAPbX₃ (X = I, Br, Cl). Data collected from Ref. [107].

Material	α	β	γ
MAPbI ₃	327 K	327 K $\sim$ 162 K	162 K
MAPbBr ₃	240 K	240 K $\sim$ 155 K	145 K
MAPbCl ₃	179 K	179 K $\sim$ 172 K	172 K

temperature dependent structural phase transition. At low temperatures, the organic cations barely to move, resulting in high exciton binding energies due to low dielectric screening. Whereas at higher temperature the movement of organic cations increases the screening effects there lowering the exciton binding energies [43].

2.6 Electronic Properties of OIHPs

For the manufacturing and designing of OIHP solar cells, it is requisite to have deep knowledge of the material electronic properties. Here, we briefly present the known electronic properties of OIHP material.

2.6.1 Band Structure

The Band structure or energy band structure refers to quantum mechanical relationship between the energy and momentum of the electrons and holes in a material. It gives description for the energy levels range in which electron may exist as well as energy range where it does not that belongs to forbidden bands (known as bandgap).

For 3D semiconductor case, the single electron can be treated as N interacting system within crystal lattice. In such model, it is assumed that each electron interacts with both nuclei as well as all other residing electrons. However, for the electron inside the lattice to behave independently, one may ignore the interacting electron-electron potential $V_{e-e}(\mathbf{r})$

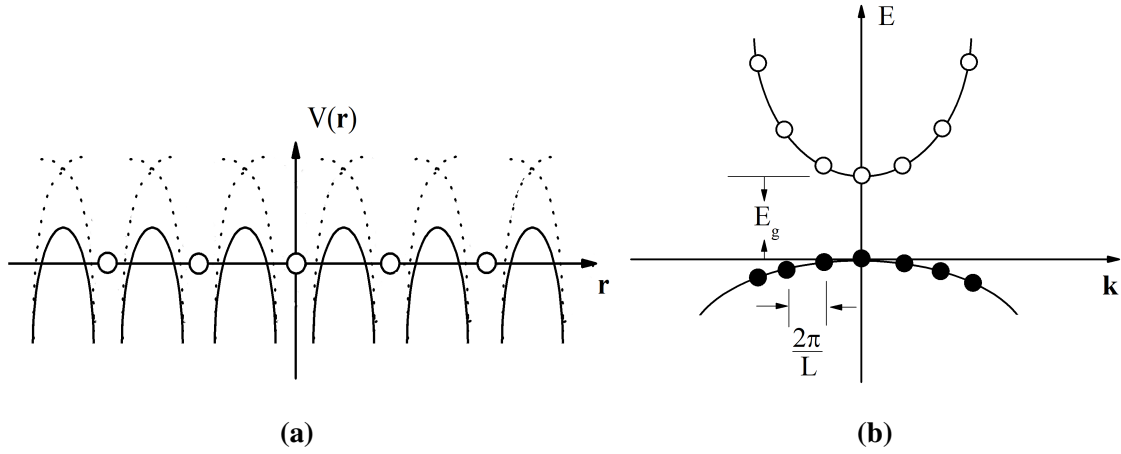


Figure 2.3 (a) Periodic potential for 1D lattice (solid lines) superimpose to the isolated atomic potentials (dotted lines). (b) Dispersion relation for a semiconductor.

and treat the lattice-electron interaction with one electron effective potential $V_{eff}(\mathbf{r})$ as accordingly to the underlying crystal periodicity. The $V_{eff}(\mathbf{r})$, however represents a qualitative term and attains the shape as displayed in Figure 2.3a, where the effective potential (solid lines) superimposes the individual ions potential (dotted lines) near to lattice sites and gets flatten at the center between them.

As according to the theory of single electron potential, the many electron problem can be treated as the solution of one electron Schrödinger equation:

$$H_0\psi(\mathbf{r}) = \left[-\frac{\hbar^2}{2m}\nabla^2 + V_{eff}(\mathbf{r}) \right] \psi(\mathbf{r}) = E\psi(\mathbf{r}) \quad (2.2)$$

where $\psi(r)$ belongs to Bloch states. From the statement of Bloch theorem [109], the periodicity of $V_{eff}(\mathbf{r})$ causes the Bloch states to act in the form of plane waves with respect to periodicity of the lattice:

$$\psi(\mathbf{r}) = u_k(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{r}}, \quad (2.3)$$

where u_k represents the lattice periodicity term. By solving Eq 2.2 to obtain a wavefunction of the form of Eq. 2.3, it can be found that the problem eigenvalues reside between

two allowed energy regions that are defined as conduction (E_c) and valence (E_v) band, respectively. The minimum point at conduction band mainly refers to the conduction band minimum (CBM) and maximum point at the top of valence band belongs to valence band maximum (VBM).

Moreover, the energy associated with each allowed state is related to its wave-vector $\mathbf{k}$ which usually refers to dispersion relation $E(\mathbf{k})$ as in Figure 2.3b. From the band structure, one can examine the nature of carrier transitions between the bands either direct or indirect and the bandgap as the shortest distance between CBM and VBM.

2.6.2 Density of States

The density of states (DOS) mainly provides the numerical data about the states or orbital character at each energy level. A steep value for the DOS represents a high contribution for the occupied energetic states.

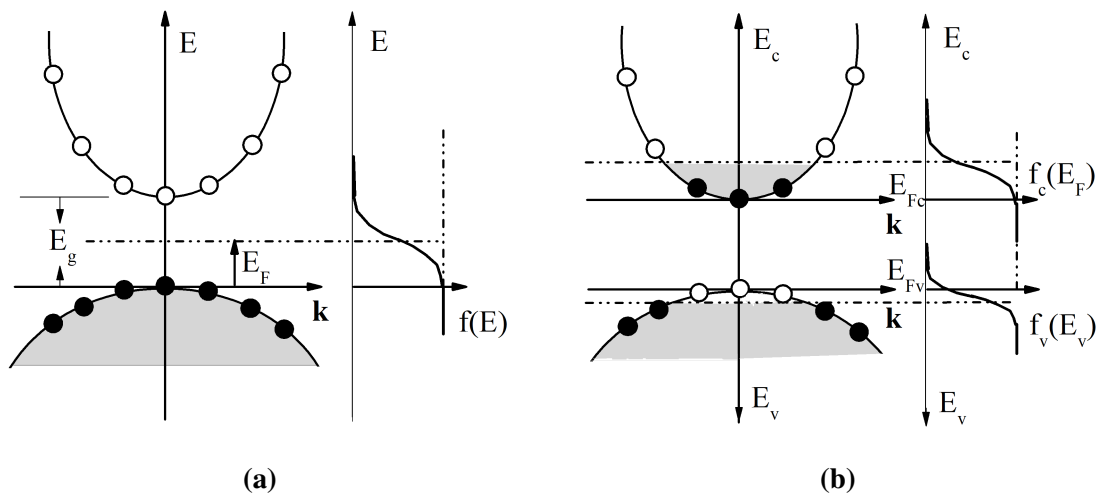


Figure 2.4 Dispersion relations and functions for occupation probability in (a) thermal and (b) quasi-thermal equilibrium states.

Here, we consider an intrinsic 3D semiconductor with a direct bandgap. For the k -space,

the number of allowed energetic states with wave vector $0 \rightarrow k$ can be evaluated as

$$N(k) = 2 \frac{(4/3) \pi k^3}{(2\pi)^3 / L_x L_y L_z} = \frac{V k^3}{3\pi^2}, \quad (2.4)$$

where V represents the spherical volume having radius k . The factor 2 accounts for the electron spin up and down motions. The DOS per unit volume or formula unit Δk is then calculated as

$$\rho_{c, v}(k) = \frac{dN}{V dk} = \frac{k^2}{\pi^2} \quad (2.5)$$

which can be extended to energy function as

$$\rho_{c, v}(E_{c, v}) = \frac{1}{2\pi^2} \left(\frac{2m_{c, v}}{\hbar^2} \right)^{\frac{3}{2}} \sqrt{E_{c, v}}, \quad (2.6)$$

Since electrons as fermion obeys Fermi-Dirac statistics, therefore, for a semiconducting material in thermal, the probability to occupy given energetic level E will be:

$$f(E) = \frac{1}{1 + e^{(E - E_F)/k_B T}}, \quad (2.7)$$

where for the above Eq. 2.7 k_B corresponds to the Boltzmann constant and E_F is the Fermi energy level. For a pure semiconductor, E_F lies in the middle of the bandgap which gives rise to a completely occupied VB and an unoccupied CB as illustrated in Figure 2.4b.

In the photo-excited state some electrons gain energy and will upraise from VB to CB leaving behind electron vacancies known as holes. As the intraband relaxation rate (≈ 1 ps [110, 111]) for the carries within both CB and VB is much higher than that of carrier recombination intraband relaxation (1 sin 100 ns [36, 112, 113]), we can readily assume that under the thermal equilibrium for each band allows the definition of occupation probability f_c and f_v for CB and VB respectively. Such theory normally refers to quasi-equilibrium approximation in which E_{Fc} and E_{Fv} corresponds to the quasi-Fermi level for each energy

band, which describe the states up to which each band is occupied entirely at $T = 0K$, as shown in Figure 2.4b where the shaded regions correspond to filled states.

We can evaluate, the number of electron density in CB and hole density in VB by using the following expressions:

$$N_e = \int_0^\infty \rho_c(E_c) f_c(E_c) dE_c \quad (2.8)$$

$$N_h = \int_0^\infty \rho_v(E_v) f_v(E_v) dE_v \quad (2.9)$$

where $\bar{f}_v$ belongs to hole occupation probability in VB defined as $\bar{f}_v = 1 - f_v$.

2.6.3 Spin-Orbit Interactions

Spin-orbit coupling (SOC), generally refers to the relationship between the spinning electron and its orbital (p, d and f) motion around the nucleus. The spin-orbit coupling in the Hamiltonian can be introduced using the term

$$H_{so} = \frac{1}{2rm^2c^2} \frac{\partial V(r)}{\partial r} \mathbf{L} \cdot \mathbf{S}, \quad (2.10)$$

where m , c and V are the electron mass, speed of light and electron spherical potential, respectively whereas L and S represents the electron angular and spin angular momentum operators, respectively. The Eq. 2.10 usually yields an excellent approximation as the spin-orbit coupling is entirely dominated by the spherically symmetric regions near to the nuclei.

In most 3D semiconductors, the bandgap is governed by a strong relativistic spin-orbit coupling (SOC) effects due to the presence of elements with higher atomic masses. Due to such effects, the conduction band edge splits (known as Rashba-Dresselhaus splitting) and significant reduction in bandgap occurs. For instance, the calculated bandgap for MAPbI₃ reduces significantly up to 53% sin 68% [42, 70, 72, 74] with SOC effects. Figure 2.5 shows the band structures for cubic MAPbI₃ both without and with inclusion of SOC effects.

Moreover, with decrease in temperature, the SOC show smaller effect due to the tilting

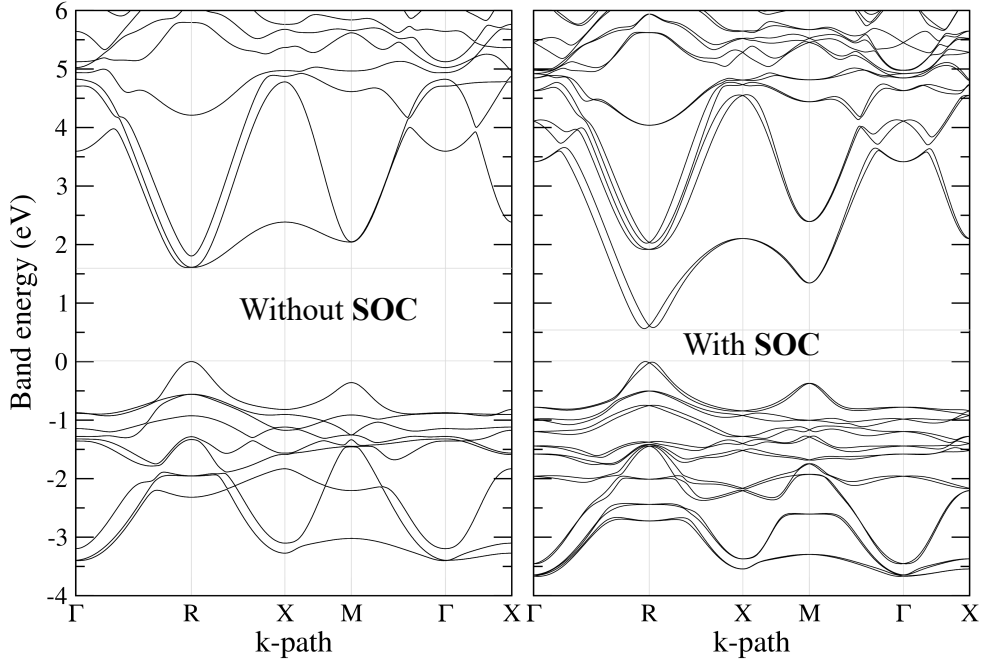


Figure 2.5 Band structure for MAPbI₃ without and with SOC effects.

of X–B–X bond angle which lowers the splitting effect and thus results in larger bandgap. For example, in orthorhombic phase of MAPbI₃, the tilting is much more pronounced than tetragonal phase which results in larger B–X bond length. This causes small splitting near conduction and valence band edges with reduced SOC effects [114]. The variations in strength of SOC effects are much smaller for changing halide components.

2.6.4 Carrier Effective Masses

In a lattice, the electron behaves differently as in the case of free space. For crystal, the electron moves through energy band packed with electrons and some with only a few. The internal and external forces together also alter the electron movement and for such system the $F_{net} = F_{int} + F_{ext} = ma$ is not valid. Therefore, we define effective mass that considers both carrier mass and the effects induced by internal forces.

The effective mass for electrons and holes in 3D semiconductor can be approximated by fitting a parabolic curve at the bottom of conduction band (CB) and at the top of valence band (VB) respectively. According to the relationship between energy in k-space (E_k) and

momentum (or wave vector) ($\mathbf{k}$) that can be expressed as

$$E = \frac{\hbar^2 k^2}{2m^*}, \quad (2.11)$$

where $\hbar$ represents the reduced Plank's constant and m^* corresponds to carrier effective mass. The single particle in a lattice can be regarded as wave-packet with the group velocity (v_g) is given by

$$v_g = \frac{d\omega}{dk} = \frac{1}{\hbar} \frac{dE}{dk}, \quad (2.12)$$

By using Newton's Law and Eq. 2.12 we get,

$$\frac{F}{m^*} = \frac{\partial v_g}{\partial t} = \frac{1}{\hbar} \frac{\partial^2 E_k}{\partial k \partial t}, \quad (2.13)$$

Since the external forces acting on the particle within the crystal is

$$F_{ext} = \hbar \frac{dk}{dt}, \quad (2.14)$$

Therefore, Eq. 2.13 takes form

$$m^* = \hbar^2 \left[\frac{\partial^2 E_k}{\partial k^2} \right]^{-1} \quad (2.15)$$

The above dispersion relation commonly refers to parabolic band approximation. Some of the material's calculated effective masses for both electrons (m_e^*) and holes (m_h^*) are summarized in Table 2.2.

Table 2.2 Calculated carrier effective masses for some well known materials.

Material	m_e^*/m_0	m_h^*/m_0	Reference
MAPbI ₃	0.381	0.351	[115]
	0.228	0.330	[69]
	0.13	0.17	[116]
	0.217	0.23	[117]
	0.18	0.22	[118]
	0.22	0.23	[119]
	0.19	0.25	[70]
	0.32	0.36	[120]
	0.247	0.276	[121]
	0.19	0.28	[42]
MAPbBr ₃	0.654	0.359	[115]
	0.271	0.306	[69]
	0.29	0.31	[121]
	0.26	0.35	[42]
MAPbCl ₃	1.135	0.400	[115]
	0.315	0.319	[69]
	0.39	0.38	[42]
MASnI ₃	2.65	1.03	[122]
	0.28	0.13	[70]
MASnBr ₃	3.15	1.11	[122]

Table 2.2 continued from previous page

MASnCl ₃	4.06	1.17	[122]
FAPbI ₃	0.403	0.302	[123]
	0.22	0.26	[121]
FAPbBr ₃	0.25	0.4	[123]

2.7 Optical Properties of OIHPs

The performance of a solar cell can be unveiled by analyzing its optical properties. In this thesis, we briefly summarized the main features of optical phenomena for 3D OIHP material.

2.7.1 Real and Imaginary Parts of Dielectrics

In semiconductors, real and imaginary parts of the dielectric are the primarily data for the description of optical terms such as absorption coefficient, complex refractive index, reflectivity, and extinction coefficient. The real part describes the ability of the material to permit electric field through it for storing electrical energy while the imaginary part explains the absorption ability and energy gain in the material.

Under photo-excitation, the total frequency dependent dielectric response function $[\varepsilon(\omega)]$ is given by

$$\varepsilon(\omega) = Re[\varepsilon(\omega)] + Im[\varepsilon(\omega)] , \quad (2.16)$$

where $Re[\varepsilon(\omega)]$ and $Im[\varepsilon(\omega)]$ represents the real and imaginary parts of dielectrics with

respect to photon frequency (ω), respectively. By solving the Kramer-Kronig relations [124], the mathematical expressions for real and imaginary part of the dielectric can be obtained as

$$Re[\epsilon(\omega)] = \frac{2}{\pi} \mathcal{P} \int_0^\infty \frac{\omega' Im[\epsilon(\omega')]}{\omega'^2 - \omega^2} d\omega', \quad (2.17)$$

$$Im[\epsilon(\omega)] = -\frac{2}{\pi} \mathcal{P} \int_0^\infty \frac{\omega' Re[\epsilon(\omega')]}{\omega'^2 - \omega^2} d\omega', \quad (2.18)$$

where $\mathcal{P}$ means that the Cauchy principal value of the integral is used. So $Re[\epsilon(\omega)]$ and $Im[\epsilon(\omega)]$ shows Hilbert transforms of one another and corresponds to the group of conjugate functions [125].

2.7.2 Excitonic Carriers

For a semiconductor, when a photo-excited electron raises towards conduction band it leaves behind a hole in the valence band. Due to their opposite charges, they attract each other via electrostatic coulombic force and form a bound state of e-h pair, known as exciton. The first prediction of excitons was made in 1931 by Frenkel [126] and discovered for the first time by Hayashi and Katsuki [127] in 1950 while analyzing the absorption spectra of CuO_2 .

Excitons in a semiconductor can exist in two types i.e. Frenkel and Wannier-Mott excitons [128]. Frenkel excitons are tightly bound e-h pairs which are mainly generated in organic semiconductors upon light exposure because of their high carrier effective masses and low dielectric constants. While the Wannier-Mott excitons are generally found in inorganic semiconductors (Si, Ge and GaAs) due to corresponding low effective masses and high dielectric constants [128]. Therefore, accounting for such excitonic nature in semiconducting materials is of crucial importance in manipulating their applications in optoelectronic as well in photovoltaics.

2.7.3 Exciton Binding Energy

In an optically excited system, it has been observed that the onset optical bandgap (E_{opt}) is fractionally less than that of fundamental electronic bandgap (E_g). The higher contribution of electron-hole pair during the excited state leads to the difference between E_g and E_{opt} values which refers to exciton binding energy (E_b).

From classical point of view, Wannier-Mott excitons can be treated in terms of Hydrogen atom-like model. In such approximation, (i) the electron and nucleus masses are replaced by effective masses and (ii) introducing dielectric constant (ϵ) of the material instead of Hydrogen. The exciton binding for a semiconductor with ion-clamped dielectric constant ϵ_∞ can be calculated as

$$E_b = \left(\frac{m_r^*}{\epsilon_\infty^2} \right) R_\infty, \quad (2.19)$$

with reduced mass $m_r^* = \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right)^{-1}$, where m_e^* and m_h^* represents the effective masses for electron and hole respectively. R_∞ is the Rydberg constant ≈ 13.56 . In hydrogenic model binding energy corresponds to the carrier transition energy of nth state. Exciton binding energies for selected 3D OIHPs along with their experimental and theoretical values are listed in Table 2.3.

Table 2.3 Exciton binding energies for some well-known 3D OIHPs with different temperatures/phases and methodologies.

Material	Exciton Binding energy, E_b (meV)	Temperature (K)/Phase	Methodology	Reference
MAPbI ₃	19	Cubic	Theory	[129]
	12.4	30 ~ 120	Temperature-dependent photocurrent	[130]
	9	300	Optical absorption	[131]
	34±3	less than 140	Optical absorption (f -sum rule)	[46]
	29	170 ~ 300		
	16	2	High-field magneto-absorption	[41]
	12	155 ~ 190		
	16±2	less than 150	High-field magneto-absorption	[43]
	30 ~ 6	13 ~ 300	Temperature-dependent PL	[45]
	13		Optical absorption	[132]
	32	80 ~ 300	Temperature-dependent PL	[133]
	48	Cubic	Theory	[72]
	5	215 ~ 300	Optical absorption	[134]
	15	50 ~ 160		

Table 2.3 continued from previous page

	19	10 ~ 300	Temperature dependent PL	[135]
	50	4.2	Magneto-absorption	[136]
MAPbBr ₃	25	2	High-field magneto-absorption	[41]
	71	Cubic	Theory	[42]
	60±3	80 ~ 300	Optical absorption (<i>f</i> -sum rule)	[46]
	84	240 ~ 350	Temperature dependent PL	[137]
	65	50 ~ 300	Temperature dependent PL	[138]
	76	4.2	Magneto-absorption	[136]
MAPbCl ₃	106	Cubic	Theory	[42]
MASnI ₃	8	Cubic	Theory	[129]
	29	Cubic	Theory	[42]
MASnBr ₃	65	Cubic	Theory	[42]
MASnCl ₃	257	Cubic	Theory	[42]
FAPbI ₃	17	Cubic	Theory	[129]
	8.1	150 ~ 295	Temperature -dependent PL	[139]
	35	Cubic	Theory	[42]
	14	2	High-field magneto-absorption	[41]

Table 2.3 continued from previous page

	10	140 ~ 160		
	18	5 ~ 110	Temperature-dependent PL	[139]
FAPbBr ₃	25	2	High-field magneto-absorption	[41]
	24	160 ~ 170		
	60	Cubic	Theory	[42]
FAPbCl ₃	110	Cubic	Theory	[42]
FASnI ₃	31	Cubic	Theory	[42]
FASnBr ₃	95	Cubic	Theory	[42]
FASnCl ₃	165	Cubic	Theory	[42]

Chapter 3

Methods

3.1 Density Functional Theory

All the electronic as well optical properties in this thesis are presented by using the theory as suggested by P. Hohenberg, W. Kohn and L. J. Sham [140, 141] known as density functional theory (DFT). Such approach is suitable to calculate materials properties by using first-principles. Its applications cover all types of electronic systems such as molecules, atoms, crystals, and interfaces. Within DFT the electronic density distribution $n(\mathbf{r})$ is the main object rather than the wave function Ψ for many-body problem. Hohenberg and Kohn showed that having the information of the ground state density, we can obtain all ground state properties of interest. Let us consider a system having N electrons and M ions, then from time-independent Schrödinger equation

$$\hat{H}\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N; \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_M) = E\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N; \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_M) , \quad (3.1)$$

where r_i and R_i represents the coordinates and spin motion of electrons and ions respectively, and $\hat{H}$ is the Hamiltonian operator acting on the N -electrons system with mass m

and charge $-e$ and M ions with mass M_j and charge $Z_j e$,

$$\hat{H} = -\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2 - \sum_{i,j} \frac{Z_j e^2}{|\mathbf{r}_i - \mathbf{R}_j|} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \frac{\hbar^2}{2} \sum_{j=1}^M \frac{\nabla_j^2}{M_j} + \frac{1}{2} \sum_{i \neq j} \frac{Z_i Z_j e^2}{|\mathbf{r}_i - \mathbf{R}_j|}, \quad (3.2)$$

As we our main interest is the electronic properties of the system, so the multi-body problem can be solved by making use of Born-Oppenheimer approximation [142]. The theory behind such approximation is that the ions being heavier move much slower than that of electrons. Therefore, it is possible factorize the wave function associated with many body as a product two wave functions that is electronic (Φ) and ionic (Θ). By keeping the ions fixed, we solve Schrödinger equation related to the electronic part as

$$\hat{H}\Phi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = E\Phi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N), \quad (3.3)$$

$$\hat{H}_e = -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 - \sum_{i,j} \frac{Z_j e^2}{|\mathbf{r}_i - \mathbf{R}_j|} + \frac{1}{2} \sum_{i,j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}, \quad (3.4)$$

where $\mathbf{R}_j$ now depends parametrically and acts only on the electronic wave functions. In Eq. 3.4, the first term on right side is the kinetic energy while the second and third terms belongs to electrostatic interactions of electron-ion and electron-electron, respectively. The electron density for the present system is defined as

$$n(\mathbf{r}) = \langle \Phi | \hat{n}(\mathbf{r}) | \Phi \rangle, \quad (3.5)$$

where $\hat{n}(\mathbf{r})$ represents electron density operator and is given by

$$\hat{n}(\mathbf{r}) = \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i). \quad (3.6)$$

P. Hohenberg and W. Kohn in 1964 presented their theory inspired by the method of Thomas and Fermi in which the electron density plays a vital role. This leads to the foundation of DFT which is based on the following two theorems [140];

1. For a ground state many-electron system, the nuclei potential and any external forces acting on it that feel their mutual Coulombic interactions is a unique functional for the electron density $n_0(\mathbf{r})$.
2. There exist a universal functional $E[n]$ which can be used for many-particle system and external potentials. In ground state, the minimum energy functional E_0 for the electron density $n_0(\mathbf{r})$ is given by

$$E_0 = E[n_0(\mathbf{r})] \langle \Phi_0(\mathbf{r}) | \hat{H}_e | \Phi_0(\mathbf{r}') \rangle , \quad (3.7)$$

which follows density variational principle.

The DFT method based on Hohenberg and Kohn models, although gives useful information about the ground state electronic properties of any system, but it fails to offer any means for practical calculations. In 1965, Kohn and Sham made some modification to it by using DFT variational properties to derive Schrödinger equation for one particle. They took a non-interacting system having identical ground state density as that of original interacting system and used this to derive the equations for the independent particle

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + V_{eff} \right) \phi_n^{KS}(\mathbf{r}) = \epsilon_n^{KS} \phi_n^{KS}(\mathbf{r}) , \quad (3.8)$$

where V_{eff} is the effective potential

$$V_{eff} = V_{ext} + e^2 \int \frac{n(r)}{|\mathbf{r} - \mathbf{r}'|} dr + \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} \quad (3.9)$$

Here the exchange-correlation functional E_{xc} associates two types of energies such as exchange E_x that belongs to the energy of electrons spinning oppositely and correlation E_c which is associated with the similar spin motion of electrons.

Summing over all the squares wave functions for single particle yields the electron density

$$n(\mathbf{r}) = \sum_n^N \left| \phi_n^{KS} \right|^2 \quad (3.10)$$

We can obtain results out of the above method by solving Eqs. 3.8, 3.9 and 3.10 self consistently. Thus, selecting some vectors $\{\phi_n^{KS}\}_n^N$ on trial basis, the calculation of $n(\mathbf{r})$ with $\hat{H}_e$ as operator will create a new set of vectors $\{\phi_n'^{KS}\}_n^N$ along with calculation of new $n(\mathbf{r})$. Such cycle is repeated until a well converged results has been achieved.

3.2 Plane Wave Pseudopotential Method

To solve the Kohn Sham equations for a single independent particle, it is requisite to define the basis set in which $\phi_n(\mathbf{r})$ can be expressed. Plane waves give rise to an orthonormal basis set that can be made more accurate by incorporating plane waves having shorter wave lengths. From the orthonormality of the plane wave basis, we have

$$\frac{1}{\Omega} \int_{\Omega} e^{-i\mathbf{q}\cdot\mathbf{r}} e^{-i\mathbf{q}'\cdot\mathbf{r}} d\mathbf{r} = \delta_{\mathbf{q}', \mathbf{q}} = \langle \mathbf{q}' | \mathbf{q} \rangle, \quad (3.11)$$

where Ω is the space volume with single period having the wave vector $\mathbf{q}$. According to Fourier theorem, any continuous periodic function can be presented in terms of Fourier series. We are mainly interested in periodic structures, either that of crystal structures or structures inside a supercell, which results in a periodic effective potential (V_{eff}). From Blöch theorem statement, the eigenstates can be chosen for a single electron Hamiltonian to have the form as given by;

$$\phi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}), \quad (3.12)$$

with $u_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) = u_{n\mathbf{k}}(\mathbf{r})$ for all $\mathbf{R}$ in the crystal. Therefore, straightforwardly plane waves are a basis for the wave function $u_{n\mathbf{k}}(\mathbf{r})$.

$$u_{n\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} \sum_m c_{\mathbf{G}_{n\mathbf{k}}} e^{i\mathbf{G}_m \cdot \mathbf{r}}, \quad (3.13)$$

where $\mathbf{G}_m$ denotes the reciprocal lattice vector and $c_{\mathbf{G}_{n\mathbf{k}}}$ stands for the Fourier coefficients. The single particle Schrödinger equation can then be expressed for any $\mathbf{k}$ vector as the following matrix equation

$$\sum_m H_{\mathbf{q}, \mathbf{q}'}(\mathbf{k}) c_{n, \mathbf{q}'} = \varepsilon_n(\mathbf{k}) c_{n, \mathbf{q}}, \quad (3.14)$$

where $\mathbf{q} = \mathbf{k} + \mathbf{G}_m$, $\mathbf{q}' = \mathbf{k} + \mathbf{G}_{m'}$ and

$$H_{\mathbf{q}, \mathbf{q}'}(\mathbf{k}) c_{n, \mathbf{q}'} = \langle \mathbf{k} + \mathbf{G}_m | \hat{H}_{\text{KS}} | \mathbf{k} + \mathbf{G}_{m'} \rangle = \frac{\hbar^2}{2m} |\mathbf{k} + \mathbf{G}_m|^2 \delta_{m, m'} + v_{eff}(\mathbf{G}_m - \mathbf{G}_{m'}) , \quad (3.15)$$

$\mathbf{G}_{m'}$ represents the set of reciprocal lattice vectors and differs from $\mathbf{G}_m$ through $\mathbf{G}_{m'} = \mathbf{G}_m - \mathbf{G}_m$ [143]. The Bloch state framework shows that all the possible eigenstates are presented in terms of the wave vectors $\mathbf{k}$ inside a primitive cell.

In general, a basis set with $3N_{pw}$ plane waves can be described having energies up to $\frac{\hbar^2}{2m} |\mathbf{k} + \mathbf{G}_m|^2 < E_{cut}$. As a result, the corresponding eigen values vary with respect to $\mathbf{k}$. Calculating the contributions of kinetic energy in the Hamiltonian Eq. 3.1 leads to complex N_{pw} operations, as $\langle \mathbf{k} + \mathbf{G} | \nabla^2 | \phi \rangle = \frac{\hbar^2(\mathbf{G} + \mathbf{k})^2}{2m} c_{n, \mathbf{q}}$ is diagonal in reciprocal space and is thus simple to operate. An issue arises when $\langle \mathbf{k} + \mathbf{G} | \nabla^2 | \phi \rangle$ calculations are performed in reciprocal space which requires evaluation of a double sum, consequently an expensive $\mathcal{O}(N_{pw}^2)$ calculation. The solution for such a problem can be understood by the fact that evaluation of $\langle \mathbf{k} + \mathbf{G} | \nabla^2 | \phi \rangle$ in real space acquires only the number of grid points N_R operations in real space. If we consider a method of switching from reciprocal to real space and return in less than N_{pw}^2 calculations, then it is possible to go to real space and calculate the contribution of the effective potential to the Hamiltonian there. Such a mechanism refers to Fast Fourier

Transform (FFT). A drawback for such approach is that NR must be an order of magnitude greater than N_{pw} to retain the same accuracy. Since charge density is squared of the wave function causing the periodicity to be doubled and thus double Fourier components are required in each direction. One can calculate $V_{eff}(\mathbf{r})\phi(\mathbf{r})$ concisely at every point in real space and then switch to reciprocal space by using FFT.

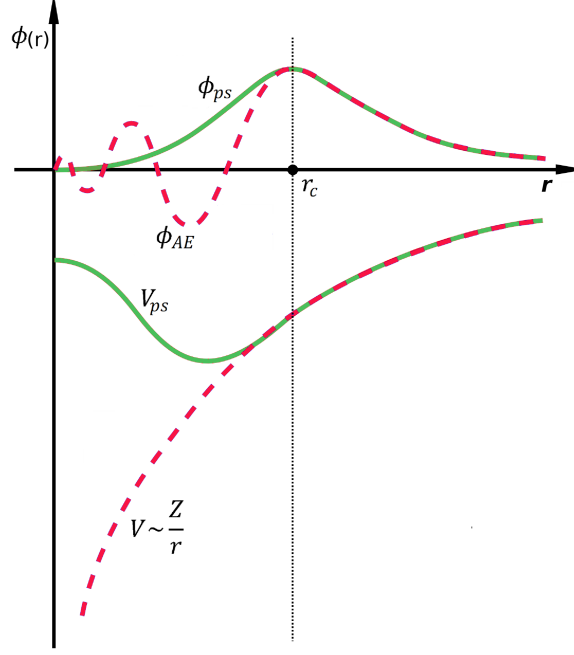


Figure 3.1 Schematic illustration for the all-electron potential (V) with corresponding wave function (ϕ_{AE}) and the pseudopotential (V_{ps}) with corresponding wave function (ϕ_{ps}). The all-electron/pseudo with their wave functions meet at $r = r_c$. Image redrawn from Ref. [144].

The plane wave basis is beneficial for the exact diagonalization of kinetic energy operator. The major issue arises for a plane wave basis when considering the abrupt changes in the shape of the wave function near the nucleus as depicted in Figure 3.1. The accurate description for such behavior would need a large quantity of plane waves. Also, the electrons in these states are highly localized and take no part in bonds formation or conduction process. To tackle such problem, one may use a uniform pseudopotential instead of real potential. The fundamental concept behind the pseudopotential is that the core electrons

are kept fixed and therefore do not change while evaluating a specific system. The pseudopotential approach constrains the lowest orbitals to be occupied. The core electrons cover the valence electrons against the Coulomb potential. Thus, pseudopotentials are smoothed potentials in which electrons likely to move.

The underlying basic concept for pseudopotential method can be understood by considering the norm-conserving pseudopotentials built for atoms. Hamann, Schluter and Chiang in 1979 introduced a method to create pseudopotentials obeying the following four conditions:

- Both real and pseudo with the corresponding atomic wave functions are equivalent beyond the core radius r_c , i.e.,

$$\psi_l^{AE}(\mathbf{r}) = \psi_l^{PS}(\mathbf{r}) \quad (3.16)$$

- Both the real and pseudo related valence eigenvalues are identical for a specified atomic reference configuration,

$$\epsilon_l^{AE} = \epsilon_l^{PS} \quad (3.17)$$

- The norms of the real and pseudo wave functions must be same for $r \leq r_c$ (refers to norm-conservation condition which states that the total charge is conserved throughout the core region).

$$\int_0^{r_c} |\phi(r)|^2 4\pi r^2 dr = \int_0^{r_c} |\phi^{ps}(r)|^2 4\pi r^2 dr \quad (3.18)$$

- Any change in the real and pseudo wave functions and in their first energy must be equal at r_c .

$$D_l^{AE}(\epsilon, r_c) = D_l^{PS}(\epsilon, r_c) \quad (3.19)$$

Constructing a norm-conserving pseudopotential for an atom involves three main steps:

- Integrate the radial Schrödinger equation to carry out all-electron calculation.
- Within a chosen reference energy ϵ_l^{AE} having corresponding ϕ_l^{AE} , calculate some ϕ_l^{ps} ensuring that it is nodeless and follows the norm-conservation condition.
- The pseudopotential V_{ps} can then be obtained by using the radial Schrödinger equation

$$-\frac{\phi_{ps}''}{2} + \left(\frac{l(l+1)}{2r^2} + V_{ps} - \epsilon_l^{AE} \right) \phi_{ps} = 0 \quad (3.20)$$

Such pseudopotential is not unique for an atom, one can make changes to the core radius to produce soft or hard pseudopotentials. Moreover, in projector augmented wave (PAW) potentials, the smaller radius of the core leads to higher cut-off energies which demands for heavier computational work due to the larger basis sets. However, they can be better understood for a system having smaller cut off radius such that they can recreate the nodes in core region. For calculations using the PAW method, it is necessary to have well defined plane wave basis set. Therefore, approximation to such approach are necessary. First the number of plane waves are reduced at the plane wave cut off, E_{cut} that can be described in terms of maximum of $G^2/2$. Second the projectors, real and pseudo partial waves are finite.

3.3 Projector Augmented Wave Method

P.E. Blöchl in 1994 introduced a method [145] that unifies an all-electron (AE) and a pseudopotential method. Such mechanism has been compiled in the electronic structure code VASP (Vienna ab-initio Simulation Package) [146] which is used in the present study. In this transformation theory, the space is divided into two parts as the region near the nucleus known as augmentation region and outside away from it as interstitial regions

as schematically presented in Figure 3.2. The all-electron (or real) wave function oscillates strongly inside the augmented region while they vary uniformly in interstitial regions. These two terms are then combined thereby subtracting the overlapping part to get a wave function similar in shape to the all-electron wave function.

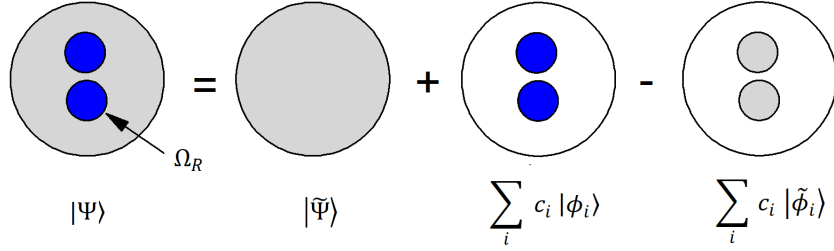


Figure 3.2 Schematic illustration for the projected augmented wave (PAW) method.

Consider the linear transformation $\mathcal{T}$ that operates on the PS wave function to give AE wave function that is $|\Psi\rangle = \mathcal{T} |\tilde{\Psi}\rangle$. $\mathcal{T}$ can be made as sum of local projectors with the assumption that $|\tilde{\Psi}\rangle = |\Psi\rangle$,

$$\mathcal{T} = 1 + \sum_R \mathcal{T}_R, \quad (3.21)$$

where R belongs to coordinates of the spheres. $\mathcal{T}_R$ operates inside the augmentation region Ω_R at every spherical site and must work for every atom type. It is useful to expand PS wave function into set of PS partial waves while inside Ω_R ,

$$|\tilde{\Psi}_n\rangle = \sum_i c_{i,n} |\tilde{\phi}_i\rangle, \quad (3.22)$$

where the subscript n denotes the band index. The operator $\mathcal{T}$ also works on $|\Psi_n\rangle$ thus leading to the expansion of $|\Psi_n\rangle$ set of partial waves,

$$|\Psi_n\rangle = \sum_i c_{i,n} |\phi_i\rangle = \mathcal{T} \sum_i c_{i,n} |\tilde{\phi}_i\rangle, \quad (3.23)$$

inside Ω_R . Since $\mathcal{T}$ operates linearly, the coefficients $c_{i,n}$ which are identical for both

partial waves, can be expressed as a scalar product of projectors projections (p_i) with the PS wave function,

$$c_{i, n} = \langle p_i | \tilde{\Psi}_n \rangle, \quad (3.24)$$

p_i are localized within Ω_R and obeys the condition $\langle p_i | \phi_j \rangle = \delta_{i, j}$.

In practice, the coefficients x can be evaluated on a radial support grid. The set of PS wave functions are plotted over this grid and $c_{i, n}$ coefficients are then obtained by a pointwise multiplication. The AE wave function can now be written as,

$$|\Psi_n\rangle = |\tilde{\Psi}_n\rangle + \sum_i c_{i, n} |\phi_i\rangle - \sum_i c_{i, n} |\tilde{\phi}_i\rangle. \quad (3.25)$$

The second term of Eq. 3.25 shows that PS wave function is summed over the entire grid and the third term yields the solution of PS inside Ω_R . According to Blöch linear transformation,

$$\mathcal{T} = 1 + \sum_R |\phi_i\rangle - |\tilde{\phi}_i\rangle \langle p_i| \quad (3.26)$$

Within the PAW formulism, the total kinetic energy E_{kin} can be written as combination of three terms

$$E_{kin} = \sum_n f_n \left\langle \tilde{\Psi}_n \left| \frac{\nabla^2}{2} \right| \tilde{\Psi}_n \right\rangle + \sum_R \sum_{i, j} \rho_{i, j} \left\langle \phi_i \left| \frac{\nabla^2}{2} \right| \phi_j \right\rangle - \sum_R \sum_{i, j} \rho_{i, j} \left\langle \tilde{\phi}_i \left| \frac{\nabla^2}{2} \right| \tilde{\phi}_j \right\rangle, \quad (3.27)$$

where $\rho_{i, j}$ is the density matrix given by

$$\rho_{i, j} = \sum_n f_n c_{i, n}^* c_{j, n}. \quad (3.28)$$

A similar approach can also be applied to the exchange energy.

3.4 Generalized Gradient Approximation

In a standard DFT calculation, the accuracy of the calculated self-consistent ground state density n_0 and associated energy E_0 is limited only by exchange-correlation functional E_{xc} . For a known exact functional, this approach would produce the exact ground state for the many body problem. For the case of unknown exact functional, the method of approximating functional have been introduced which are still under development. Although there are different types functionals like local density approximation (LDA), generalize gradient approximation (GGA), hybrid functional (HF) and so on, but here we limit our discussion only up to GGA.

Since LDA provides structural parameters up to 1% remarkable accuracy [147] but it underestimates the electronic bandgap [148]. The issues with LDA can be fixed by considering the spatially density gradient within the system that helps to provide better overview for inhomogeneities. The exchange-correlation functional for GGA E_{xc}^{GGA} can be expressed as

$$E_{xc}^{GGA} = \int f[\rho(\mathbf{r}) \nabla(r)] d\mathbf{r} . \quad (3.29)$$

GGA functionals are generated by incorporating a gradient correction to the LDA functionals and this can be parametrized by the experimental data. There are several different types of GGA functionals, which have a slightly different function f . Among them the functional of Perdew and Wang (PW91) [149] and Perdew, Burke and Enzerhof (PBE) [65] have been widely used in DFT calculations.

3.5 The G_0W_0 Approximation

The GW approximation [150] is an orbital based approach that provides a more accurate description of the excitation spectra. Since LDA and sometimes GGA yield the bandgaps of semiconductor and insulators less than that of experimental values. The GW method

corrects such underestimation and mostly provides better agreement with the experimental results. In the GW method, the self energy $\Sigma = iGW$, the contribution to energy of bare particle due to its interaction with the system, is approximated as

$$\Sigma(r, r', E) = \frac{i}{2} \int_{-\infty}^{\infty} e^{-i\omega\delta} G(r, r', E - \omega) W(r, r', \omega) d\omega \quad (3.30)$$

where G stands for Green functions and $W = \varepsilon^{-1}V_C$ for screened Coulombic interactions. The dielectric matrix (ε^{-1}) can be calculated by using random phase approximation (RPA) [77]. In Eq. 3.30, the term δ is a positive infinitesimal number which insures for closed contour integral just above the real axis and only encloses poles that correspond to occupied states. The quasi particle GW (QPGW) equations that have to be approximated look like

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + v_{ext} + e^2 \int \frac{n(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} \right) \psi_{n\mathbf{k}}(\mathbf{r}) + \int \Sigma(\mathbf{r}, \mathbf{r}', E_{n\mathbf{k}}) \psi_{n\mathbf{k}}(\mathbf{r}') d\mathbf{r}' = E_{n\mathbf{k}} \psi_{n\mathbf{k}}(\mathbf{r}) \quad (3.31)$$

where the first term on the left side belongs Kohn-Sham equations of DFT while in the second term the exchange potential (XC) is replaced by GW self energy. The quasi particle energies then obtained are given by [148]

$$E_{n\mathbf{k}} = \langle \psi_{n\mathbf{k}}(\mathbf{r}) | E_{kin} + v_{ext} + V_H + \Sigma(E_{n\mathbf{k}}) | \psi_{n\mathbf{k}}(\mathbf{r}) \rangle . \quad (3.32)$$

$E_{n\mathbf{k}}$ needs to solve iteratively to obtain the quasi particle eigenvalues. In the present work we use only one iteration step. Such a single iteration step usually refers to one-shot GW or G_0W_0 . This modifies the Kohn-Sham eigenvalues $\varepsilon_{n\mathbf{k}}$

$$E_{n\mathbf{k}} = \varepsilon_{n\mathbf{k}} + Z_{n\mathbf{k}} Re \left[\psi_{n\mathbf{k}} | E_{kin} + v_{ext} + V_H + \sum (\varepsilon_{n\mathbf{k}}) | \psi_{n\mathbf{k}} \rangle | - \varepsilon_{n\mathbf{k}} \right] , \quad (3.33)$$

where $\psi_{n\mathbf{k}}$ is the DFT based Kohn-Sham orbitals and $Z_{n\mathbf{k}}$ is renormalization factor given by

$$Z_{n\mathbf{k}} = \left(1 - \left\langle \psi_{n\mathbf{k}} \left| \frac{\partial \Sigma(\omega)}{\partial \omega} \right|_{\epsilon_{n\mathbf{k}}} \right| \psi_{n\mathbf{k}} \right)^{-1}, \quad (3.34)$$

Since, evaluating the elements of $\langle \psi_{n\mathbf{k}} | \Sigma(\epsilon_{n\mathbf{k}}) | \psi_{n\mathbf{k}} \rangle$ involves several factors such as the number of bands (N_b), frequencies (N_ω), k-points (N_k) and plane waves (N_{pw}), which makes the GW calculations more expensive as compare to DFT calculations.

3.6 Wannier Interpolation Method

For most semiconductors, obtaining the band structure is sometime tough where it has to deal not only with the ionic and excited states but also to the extended states. The energy of electron in a band structure is defined as $E_{n\mathbf{k}}$, where n represents the band index and $\mathbf{k}$ is the Blöch vector. $E_{n\mathbf{k}}$ continues for each n along the designated high symmetry points and known as energy band. To describe the extended states, we consider the spatially localized Wannier functions (WFs) centered at lattice site $\mathbf{R}$ which can be written using the Blöch states

$$w_{\mathbf{R}\mathbf{i}} = \frac{V}{(2\pi)^3} \int_{BZ} \left[\sum_{n=1}^{N_k} U_{ni}^k \psi_{n\mathbf{k}}(\mathbf{r}) \right] e^{-i\mathbf{k} \cdot \mathbf{R}} d^3\mathbf{k}, \quad (3.35)$$

where V is the volume of unit cell in real space and U_{ni}^k represents the unitary matrix $N_k \times N$. The Blöch functions $\psi_{n\mathbf{k}}$ are taken within the energy range including $N_k \geq N$ within the Brillion zone (BZ). While generating the WF, N is chosen for all $\mathbf{k}$ and U_{ni}^k must be unitary to get well localized WF. The localization can be checked by the spread which is valid for molecular orbital theory [151] and can be defined as Ω

$$\Omega = \sum_n \left[\left\langle w_{0i}(\mathbf{r}) \left| \mathbf{r}^2 \right| w_{0i}(\mathbf{r}) \right\rangle - \left| \langle w_{0i}(\mathbf{r}) | \mathbf{r} | w_{0i}(\mathbf{r}) \rangle \right|^2 \right], \quad (3.36)$$

which shows that localization to the origin of host unit cell is possible through the lattice vector translation, $w_{\mathbf{R}i} = w_{0i}(r)(\mathbf{r} - \mathbf{R})$. Applying Eq. 3.35 to Eq. 3.36, the spread Ω , then becomes function of U_{ni}^k and represented in terms of matrix elements of $\mathbf{r}$ and $\mathbf{r}^2$ between $\psi_{n\mathbf{k}}$. The total spread can be decomposed into two parts, that is, gauge invariant term Ω_I and gauge-dependent term $\tilde{\Omega}$ which can be further split up into diagonal Ω_D and off-diagonal Ω_{OD} WFs basis. Maximally localized Wannier functions (MLWF) are obtained by reducing the spread $\tilde{\Omega}$ with respect to the unitary matrix as accordingly to Marzari and Vanderbilt [152].

In DFT calculations, the ground state density is obtained self-consistently with a uniform mesh and then band structure is calculated using the converged density in a non-self-consistent loop. While the GW although gives good description about the excited state but obtaining band structure within GW is not an easy task as in the case of DFT. Because GW is non-density functional method and one must only calculate the QP energies with uniform grid where DFT calculations are performed initially. Since obtaining the QP energies at desired k-points is inconvenient. Therefore, Wannier functions (WF) are used to obtain the QP band structures, instead of periodically extended Bloch orbitals $\psi_{n\mathbf{k}}$. At every k values the Bloch functions have different values which allows to generate Wannier functions by the superposition of Bloch orbitals along different k through unitary transformations. Therefore, the corresponding functions would provide information about the Bloch functions. WFs often refer to the localized basis functions and its implementation to band structure calculations are known as Wannier interpolation method.

With Wannier interpolation method as proposed by Hammann and Vanderbilt [153], it is possible to obtain QP bands at arbitrary points since evaluating the QP corrections along such points is extremely computationally demanding. For the case of G_0W_0 approximation, as in the present thesis, the Wannier interpolation is performed at the PBE level and the transformation matrices applied to the corrected QP energies.

In the present thesis, WANNIER90 is used through VASPTOWANNIER90 interface. Initially WANNIER90 acquires inputs from electronic structure calculations, that is pro-

jections (guess orbitals) of the Blöch states $|\psi_{kn}\rangle$. Reader may refer to the WANNIER90 manual for detailed information about its usage.

3.7 Bethe-Salpeter Equations

In GW approximations, the electron and hole propagation can be presented by the single-particle Green's function. Propagation of two or more particles can be calculated by using higher order of Green's function. The consideration of the e-h interactions usually refer to excitons during excitation is helpful to deal with certain optical phenomena like absorption, electron energy loss and inelastic X-ray scattering (neutral excitations). Addressing the inclusion of such excitonic effects in the excitation spectra leads to the Bethe-Salpeter equation (BSE). Bethe and Salpeter in 1951, formulated the equation of motion related to the two-particle Green's function for bound state problems [154, 155] which later extended to excitons. Afterwards, it was used to analyze the optical spectra of silicon and diamond [156, 157]. Strinati [158] in 1961 proposed to calculate the BSE excitons via GW method by using the theory of Baym and Kadanoff [159]. Strinati's way of approach has been implemented in 1995 by Onida *et. al.* to study the excitons in sodium tetramer [160]. Presently with modern computational resources, the combined GW and BSE (GW+BSE) method is usually applied to study the excitonic optical spectra of semiconductors [161]. In most cases GW along with SOC effects improves the underestimation of alone SOC based electronic bandgap while GW+BSE provide a way to calculate the exciton binding energy from optical spectra (see Appendix).

The schematic illustration for DFT, GW and GW+BSE calculations are shown in the Figure 3.3. The GW method improves the estimation of DFT-bandgap while GW+BSE accounts for the excitonic effects in the optical spectra which paves way to obtain the optical bandgap and thereby exciton binding energy.

The screening and excitonic effects can be treated by solving BSE using the GW QP

energies,

$$\left(E_{c\mathbf{k}}^{QP} - E_{v\mathbf{k}}^{QP}\right) A_{c\mathbf{k}}^S + \sum_{c'\mathbf{k}'} \left\langle v\mathbf{k} \left| K^{eh} \right| c'\mathbf{k}' \right\rangle A_{c'\mathbf{k}'}^S = \Omega^S A_{c\mathbf{k}}^S, \quad (3.37)$$

where $A_{c\mathbf{k}}^S$ is the S^{th} order exciton wave function, K^{eh} is the kernel for e-h interactions and Ω^S corresponds to exciton excitation energies.

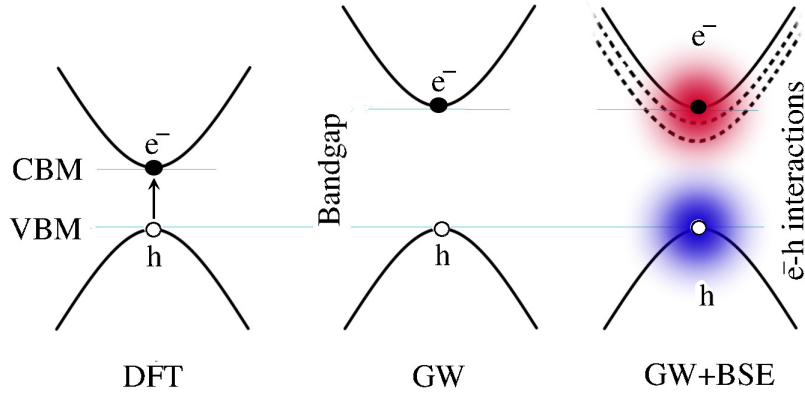


Figure 3.3 Schematic representation for DFT, GW and GW+BSE approaches.

In VASP, BSE calculations can be carried out in three basic steps. First, the PBE based ground state energies are calculated. Second, QP energies are updated within the GW approximations. Third, 4-point BSE Kernel is constructed along with the diagonalization of the BSE Hamiltonian.

It is known that to obtain converged optical spectra and excitation binding energies, many $\mathbf{k}$ points are normally needed [42, 80]. However, for the relatively large systems, this is prohibitive for the G_0W_0 calculations. To address this issue, we followed the strategy proposed in Ref. [42], where the optical spectra and exciton binding energies were calculated by a simplified approximation of BSE [termed as model BSE (mBSE)]. In mBSE calculations, the QP energies from G_0W_0 calculations are approximated by the PBE one-electron energies with a scissor operator on the unoccupied orbitals such that the PBE one-electron gap matches the G_0W_0 calculated bandgap. In addition, the expensive calculations of dielectric function matrix from G_0W_0 are approximated by a simple analytical model dielectric

function within the diagonal elements approximation [42, 80, 162, 163]:

$$\epsilon^{-1}(|\mathbf{G}|) = 1 - (1 - \epsilon_{\infty}^{-1})e^{-|\mathbf{G}|^2/4\mu^2}, \quad (3.38)$$

where ϵ_{∞} , μ , and $\mathbf{G}$ are ion-clamped (high-frequency) dielectric constant, range-separation parameter, and plane-wave vector, respectively. ϵ_{∞} is calculated from G_0W_0 calculations and is obtained by fitting Eq. 3.38 to the G_0W_0 calculated diagonal elements of dielectric function matrix. Such approach accurately describes the optical spectra as well as exciton binding energies for the systems considered in the present thesis.

Chapter 4

Results and Discussions

In this chapter, we present the detailed structural, electronic and excitonic optical properties of $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ alloy as well FAPbI_3 phase transformation along cubic, tetragonal and hexagonal phases. The related mBSE approach are discussed in Appendix A and B.

4.1 The Mixed $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ Alloy

The mixed type hybrid organic-inorganic perovskites has sparked much interest in the field of photovoltaics [11–32] because of their low-cost compositional chemical management of constituents, allowing tailoring of electrical and optical parameters. Some of the key characteristics of these materials that make them exceptional are their tunable optimal bandgap for appropriate sunlight absorption [11, 13–18, 20–27, 29, 33], longer carrier lifetimes [11, 34, 35], high charge carrier mobility [36–39], long charge carrier diffusion length [35, 36, 40] and weak exciton binding energy [41–48]. Mixing of halides at X-site such as Br and Cl, provides wide range of fine-tuning property suitable for designing and boosting the performance of multijunction devices. In addition to $\text{MAPb}(\text{I}_{1-x}\text{Cl}_x)_3$ [12, 49] and $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3$ [21, 29, 30, 50], $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ [15, 22, 33] has also been successfully synthesized and demonstrated in solar cells.

By means of density functional theory and many-body methods with the inclusion of the

spin-orbit coupling, we have performed systematic first-principles study of structural, electronic, and optical properties of the $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ alloy with $0 \leq x \leq 1$. Our results show that as the Br concentration increases, the volume of the $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ alloy decreases, the bandgaps increases from 1.47 eV for pure α - FAPbI_3 to 2.20 eV for Br-rich α - FAPbBr_3 , and the excitonic peaks are blue shifted. Our results further reveal strong Br concentration dependence of the exciton binding energy (varies from 74 to 112 meV) and the carrier effective masses as well as high frequency dielectric constants. Our findings open the way to fine-tune the carrier transport properties of the material by chemical substitution and provide important insights to improve short circuit currents and power conversion efficiencies in solar cell devices.

4.1.1 Computational Details for Mixed $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$

Starting from the experimental geometry of α - FAPbI_3 at 298 K [164] and α - FAPbBr_3 at 275 K [165]. The position of FA molecule for the present system is adopted accordingly to molecular dynamics simulations of Taylor et. al. [166]. The modeling of $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ alloy was carried out by compositional assembling of seven independent configurations i.e., for $x = 0, 0.17, 0.33, 0.50, 0.67, 0.83$ and 1. The unit cell of FAPbI_3 is expanded to $1 \times 1 \times 2$ tetragonal supercell, where an appropriately random substitution of I atom with Br atom is performed to obtain the corresponding compositions [51, 167, 168]. Our DFT calculations were performed using the computational code VASP [146, 169] with the projector augmented wave (PAW) pseudopotentials [145]. For the exchange correlation functional, PBE was used [65, 66]. The energy cutoff of 600 eV and Γ -centered $6 \times 6 \times 3$ k-point sampling of the Brillouin zone was adopted for all structures. The valence electron configurations that were included in the calculations are $5d^{10}6s^26p^2$ for Pb, $5s^25p^5$ for I, $4s^24p^5$ for Br, $2s^22p^2$ for C. All the structural parameters were relaxed with the convergence threshold of 10^{-6} eV in total energy and the stopping convergence criteria for the forces on each atom was set to be 0.01 eV/Å. To account for the van der Waals dispersion interactions, we used

the rev-vdW-DF2 functional of Hamada [170]. Due to the presence of heavy elements, the relativistic SOC effect was included in calculating the electronic and optical properties.

For the accurate electronic structure, in particular the bandgap, we carried out delicate one-shot G_0W_0 calculations using Γ -centered $4 \times 4 \times 2$ k-point sampling with 2200 empty bands, dielectric cutoff energy of 150 eV and 128 points on the frequency grid. The e-h interactions were accounted for by solving the BSE for the polarizability. 16 occupied and unoccupied QP energies were employed in constructing the BSE Hamiltonian and the screened interactions W were from the preceding G_0W_0 calculations. The broadening parameter used in evaluation of polarizability was chosen to be 0.1 eV. For detailed GW+BSE methodology that the VASP code follows, we refer the readers to Ref. [162]

For well converged optical spectra and exciton binding energy E_b , we carried out mBSE calculations. This turns out to be a good approximation for the systems studied here (See good agreement between G_0W_0 +SOC and PBE+SCISSOR+SOC band structures in Figure A1). The ion-clamped (high frequency) dielectric constant ϵ_∞ is calculated from G_0W_0 calculations and μ is obtained by fitting Eq. 3.38 to the G_0W_0 calculated diagonal elements of dielectric function matrix. The obtained ϵ_∞ , μ and scissor parameters used in mBSE calculations for all systems studied are compiled in Table A1. As shown in Fig. A1a, PBE+SCISSOR+mBSE reproduces very well the optical spectra obtained from G_0W_0 +BSE for FAPbI₃ on the same $4 \times 4 \times 2$ k-point mesh, though the spectra are not k-point converged, validating the good performance of the PBE+SCISSOR+mBSE approach in accurately describing the optical spectra as well as exciton binding energies for the systems considered in the present work.

By performing PBE+SCISSOR+mBSE calculations, we are able to check the k-point convergence by adopting dense k-point mesh up to $18 \times 18 \times 9$. Our test calculations indicate that the spectra and excitation binding energies are well converged on a $16 \times 16 \times 8$ k-point mesh with an accuracy of about 3 meV in excitation binding energies [see Figure A1]. Therefore, the $16 \times 16 \times 8$ k-point mesh was used for all mBSE calculations. The exciton binding energies were calculated by the energy difference between the G_0W_0 bandgap and

the first bright mBSE eigenvalue. Furthermore, for comparison purpose, the exciton binding energies were also estimated by using the Wannier Mott model [171]: $E_b \approx 13.6m_r^*/\epsilon_\infty^2$, where m_r^* is the reduced mass ($1/(m_r^*) = 1/m_e + 1/m_h$).

4.1.2 Structural Properties for Mixed FAPb(I_{1-x}Br_x)₃

The possibly synthesis of halide mixed perovskite is confirmed through the effective Goldsmith tolerance factor t_{eff} [100, 101, 103, 172]. The atomic-ratio weighted average of the two different anions is used to calculate effective anion size r_{eff} given by

$$r_{eff} = xr_{Br} + (1 - x)r_{I} \quad (4.1)$$

Using Eq. 2.1, t_{eff} for FAPb(I_{1-x}Br_x)₃ composition can be expressed as

$$t_{eff} = \frac{(r_{FA} + r_{eff})}{\sqrt{2}(r_{Pb} + r_{eff})} \quad (4.2)$$

where r_{FA} , r_{Pb} , r_I and r_{Br} are the Shanon ionic radii of FA (2.53 Å), Pb (1.19 Å), I (2.20 Å) and Br (1.96 Å), respectively [103, 172]. The stability of BX₆ octahedra can be predicted by octahedral factor λ , which (for present case) is the ratio of size B-cation r_{Pb} and the effective halide size r_{eff} :

$$\lambda = r_{Pb}/r_{eff}. \quad (4.3)$$

Table 4.1 Calculated Goldsmith tolerance factor and octahedral factor for different Br composition in FAPb(I_{1-x}Br_x)₃ alloy.

Br fraction x	0	0.17	0.33	0.50	0.67	0.83	1
Goldsmith tolerance factor t	0.987	0.990	0.993	0.997	1.000	1.004	1.008
Octahedral factor λ	0.540	0.550	0.561	0.572	0.583	0.594	0.607

Generally, as mentioned in Chapter 2 for ABX₃ perovskite-like structures, the tolerance

factor is in the range $0.80 \leq t \leq 1.06$ and octahedral factor lies between 0.442 and 0.895 [100, 101]. The calculated effective tolerance factors for the $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ system ranges from 0.987 to 1.008, thus confirming the perovskite structure as summarized in Table 4.1. The octahedral factor values also affirm the stable perovskite structure as it lies between 0.541 and 0.607 for $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ composition.

Table 4.2 Calculated lattice parameters for different $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ compositions using the PBE functional.

Composition x	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)
0	6.33	6.51	12.66	90.00	92.80	90.00
0.17	6.31	6.50	12.32	90.00	93.05	90.00
0.33	6.29	6.52	11.99	90.00	93.28	90.00
0.50	6.30	6.37	12.00	90.00	93.34	90.00
0.67	6.30	6.17	12.09	90.00	93.49	90.00
0.83	6.01	6.17	12.27	90.00	94.51	90.00
1	5.96	6.16	11.92	90.00	94.90	90.00

Table 4.2 summarizes the calculated lattice parameters of $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ system for $x = 0, 0.17, 0.33, 0.50, 0.67, 0.83$, and 1. The calculated averaged ground state lattice parameters for FAPbI_3 ($a = 6.38$ Å) and FAPbBr_3 ($a = 6.01$ Å) using the PBE functional showing good agreement to the experimental data, i.e., 6.36 Å and 5.99 Å for FAPbI_3 and FAPbBr_3 , respectively [22, 35, 173, 174] and relaxed structure of α - FAPbI_3 is shown in Figure 4.1. In the full relaxation of the structures, the deviation from the tetragonal symmetry is caused by the steric effect of $[\text{FA}]^+$ cation.

Figure 4.2 shows the overall decrease in volume of $1 \times 1 \times 2$ supercell from 520.9 Å³ to 454.2 Å³ as the Br content increases, which is consistent with decreasing experimental lattice constants [22, 33]. Also, Pb–X (where X = I and Br) bond lengths reduce from 3.26 Å to 2.96 Å which can be attributed to the smaller ionic radii of Br atom which influences the interplanar geometry. Moreover, the electronic charge distribution is much stronger around

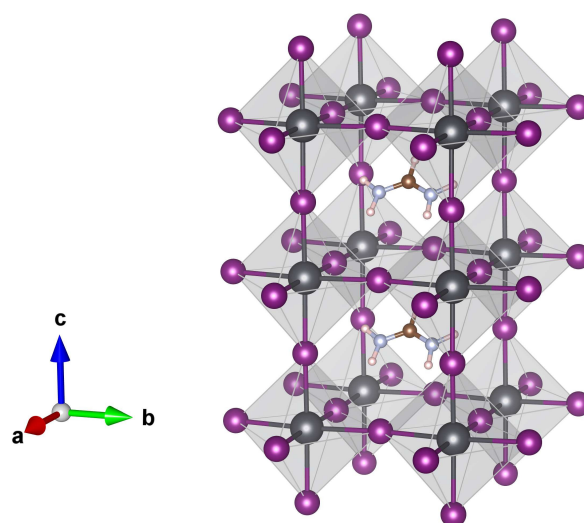


Figure 4.1 Crystal structure of $1 \times 1 \times 2$ supercell of FAPbI_3 . Pb (grey), I (purple), C (brown), N (light blue) and H (pink). $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ alloy is obtained by substituting I with Br.

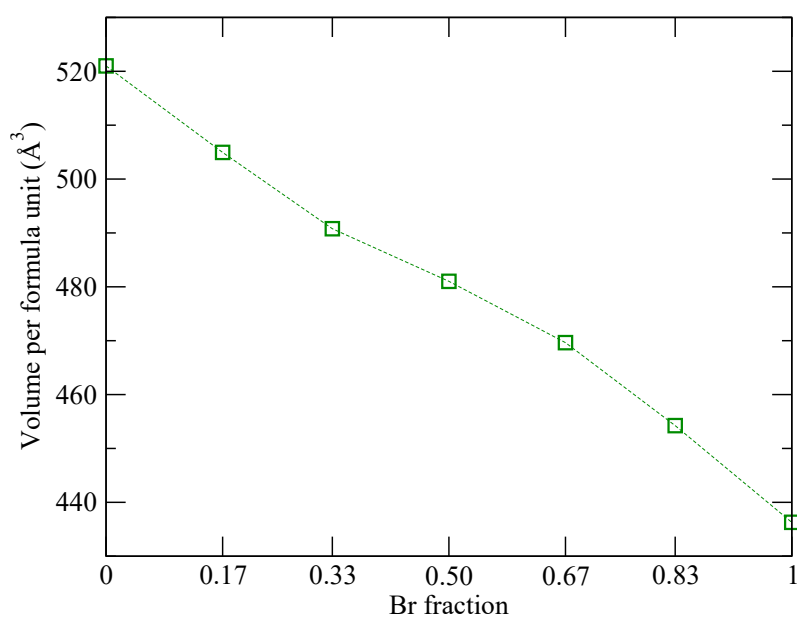


Figure 4.2 Optimized volume as a function of Br concentration.

Br atom due its higher electronegativity value (2.96) as compared to I (2.66). Thus, the heavy Pb atom will interact strongly with Br atom due to high electronegativity difference which leads to reduction in bond length [175].

4.1.3 Electronic Properties for Mixed $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$

In order to give an insight on the electronic structure, different approaches have been carried out. Table 4.3 summarizes the calculated bandgaps for the $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ system with increasing Br percentage obtained at various levels of theory. The comparison in the bandgaps clearly shows the underestimation in the calculated bandgaps of FAPbI_3 and FAPbBr_3 by PBE, as expected. Inclusion of the relativistic SOC effect reduces the bandgaps of FAPbI_3 and FAPbBr_3 to 0.41 eV and 0.87 eV respectively, underestimating the experimental bandgap further and consistent with previous SOC-DFT results for $\text{MA}(\text{Pb}, \text{Sn})\text{X}_3$ [42, 69–75, 79]. To improve the underestimation in the PBE derived gaps, we carried out the G_0W_0 calculations including the SOC effects. The $\text{G}_0\text{W}_0+\text{SOC}$ calculated bandgaps of 1.47 eV and 2.20 eV for FAPbI_3 and FAPbBr_3 respectively, are in excellent agreement with the experimental bandgaps [22, 33]. Similarly, we have calculated the electronic bandgaps using the $\text{G}_0\text{W}_0+\text{SOC}$ approach for all other configurations of $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ having different Br composition and the results are compiled in Table 4.3.

Table 4.3 Calculated bandgap values for different methods. The available experimental data are also shown for comparison.

Br fraction x		0	0.17	0.33	0.50	0.67	0.83	1
Bandgap (eV)	PBE	1.43	1.50	1.52	1.62	1.72	1.79	1.80
	PBE+SOC	0.41	0.52	0.57	0.61	0.71	0.82	0.87
	$\text{G}_0\text{W}_0+\text{SOC}$	1.47	1.63	1.72	1.79	1.94	2.11	2.20
	Expt.	1.47[22,	-	-	-	-	-	2.22[22], 2.23[33], 2.26[174] 33, 177]

The $\text{G}_0\text{W}_0+\text{SOC}$ calculated bandgaps for various Br fraction are plotted in Figure 4.3. Such linear trend in the bandgaps with the x composition in the mixed system can be rep-

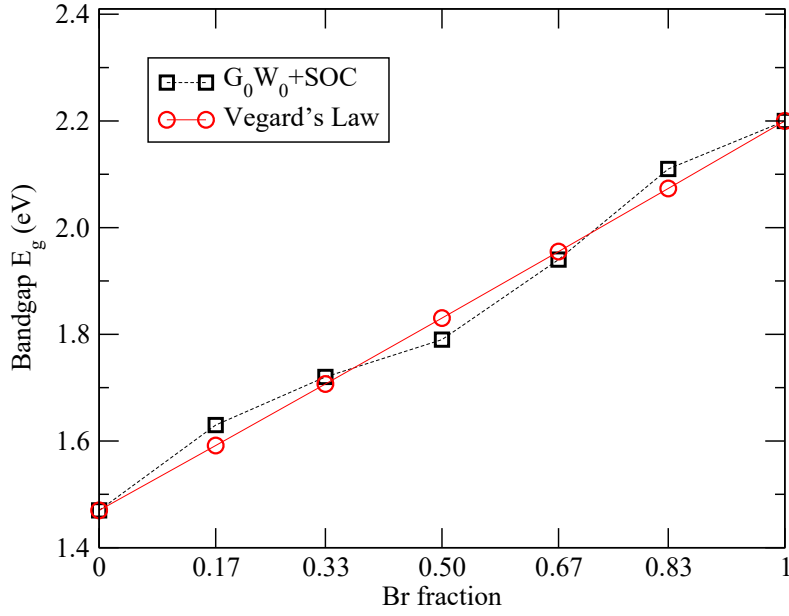


Figure 4.3 Linear variation in the G_0W_0 +SOC calculated bandgaps with respect to Br concentration.

resented by the quadratic equation known as Vegard 's law [178, 179]:

$$E_g[FAPb(I_{1-x}Br_x)_3] = E_g[FAPbI_3] + (E_g[FAPbI_3] - E_g[FAPbBr_3] - b)x + bx^2 \quad (4.4)$$

where b represents the bowing parameter and normally depends on the nature of the inter-substitutional atoms [178]. The bowing parameter shows the level of variations in the crystal field or the nonlinearity effect due to the anisotropic behavior of binding [179]. Eq. 4.4 yields the following expression:

$$E_{g(x)} = 1.47 + 0.71x + 0.02x^2, \quad (4.5)$$

which provides a good fitting to the G_0W_0 +SOC calculated bandgaps as shown in Figure 4.3, thus satisfying the Vegard 's law for mixed $FAPb(I_{1-x}Br_x)_3$ composition. The small bowing parameter $b = 0.02$ shows that $FAPbI_3$ and $FAPbBr_3$ have excellent miscibility yielding low compositional disorder for mixed $FAPb(I_{1-x}Br_x)_3$ system.

The G_0W_0 +SOC derived QP band structures along the high-symmetry points $\Gamma(0, 0,$

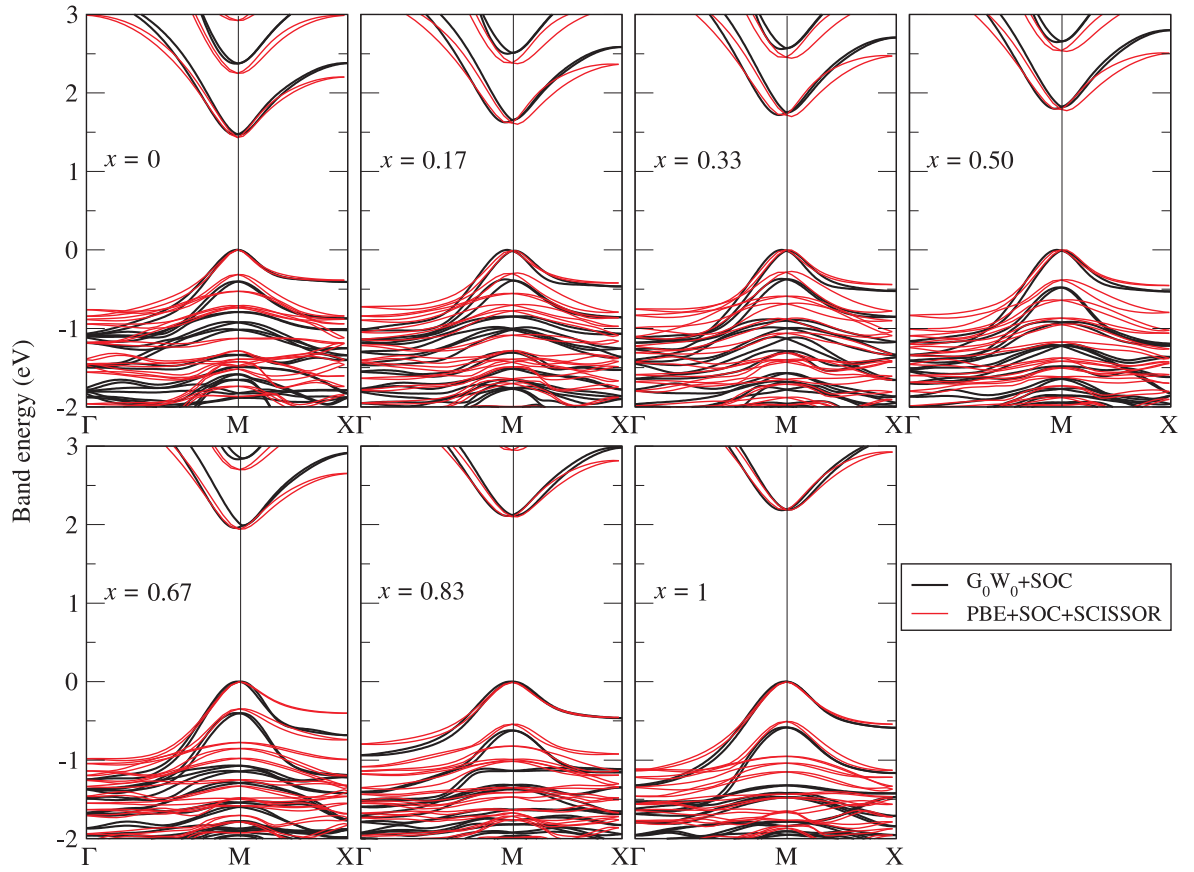


Figure 4.4 G_0W_0 +SOC calculated QP band structures obtained by the Wannier interpolation [180, 181] (black lines) superposed by the PBE+SOC band structures with a scissor operator to match the G_0W_0 bandgap (red lines). The Fermi level is set to zero.

0), M(0.5, 0.5, 0) and X(0.5, 0, 0) for each $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ configuration are shown in Figure 4.4. The band structures are plotted by using the Wannier interpolation scheme [180, 181], in which the Wannier orbitals are constructed at a Γ -centered $4 \times 4 \times 2$ k-point meshing and all the relevant orbitals are included for the initial representation of Kohn Sham states. With the $1 \times 1 \times 2$ supercell, both valence band maximum (VBM) and conduction band minimum (CBM) fold to the M-point and bandgaps are found to be direct in nature. Fractional deviations from M-point are observed for the VBM and CBM due to the presence of Rashba-Dresselhaus splitting [55–57]. The dispersion of both the conduction band as well as valence band slightly increases with the Br content leading to different effective masses for electron and hole near CBM and VBM. Such dispersions can be understood by

the enhanced orbital interaction with decreasing structural volume.

Table 4.4 Calculated effective masses for electron and hole from the G_0W_0 +SOC band structures.

Br fraction x	Effective mass		Effective mass		Average		Reduced effective mass m_r^*
	(M- Γ)		(M-X)				
	m_e^*/m_0	m_h^*/m_0	m_e^*/m_0	m_h^*/m_0	m_e^*/m_0	m_h^*/m_0	
0	0.212	0.267	0.225	0.279	0.218	0.273	0.121
0.17	0.227	0.288	0.234	0.298	0.231	0.293	0.129
0.33	0.232	0.279	0.228	0.287	0.230	0.283	0.127
0.50	0.253	0.296	0.255	0.304	0.254	0.300	0.138
0.67	0.275	0.336	0.277	0.372	0.276	0.354	0.155
0.83	0.369	0.467	0.364	0.431	0.367	0.449	0.202
1	0.351	0.412	0.353	0.404	0.352	0.408	0.189

To study the carrier transport properties for the $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ alloy, we calculated the effective masses m^* for electron and hole around CBM and VBM, respectively, by fitting the dispersion relation of Eq. 2.15 on the basis of parabolic approximation. Table 4.4 summarizes the effective masses of electrons (m_e^*) and holes (m_h^*) for the investigated $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ compositions along the directions M- Γ and M-X and their averaged values. Further, the corresponding reduced masses m_r^* are also evaluated using the averaged values for m_e^* and m_h^* . As can be seen in Figure 4.5, the overall effective masses for electrons and holes increase with Br fraction from $0.218m_0$ to $0.352m_0$ and $0.273m_0$ to $0.408m_0$, respectively. The slight deviation from linear behavior in m_e^* and m_h^* values for $x = 0.17$ and $x = 0.83$ can be attributed to the high internal structural strain as compared to the other configurations. Since the carrier effective masses and mobility are inversely related, Figure 4.5 clearly reveals that the mobility of the carriers varies with Br content. For all considered configurations, m_h^* is greater than m_e^* , so the mixed $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ system can be regarded as a good electron transporter.

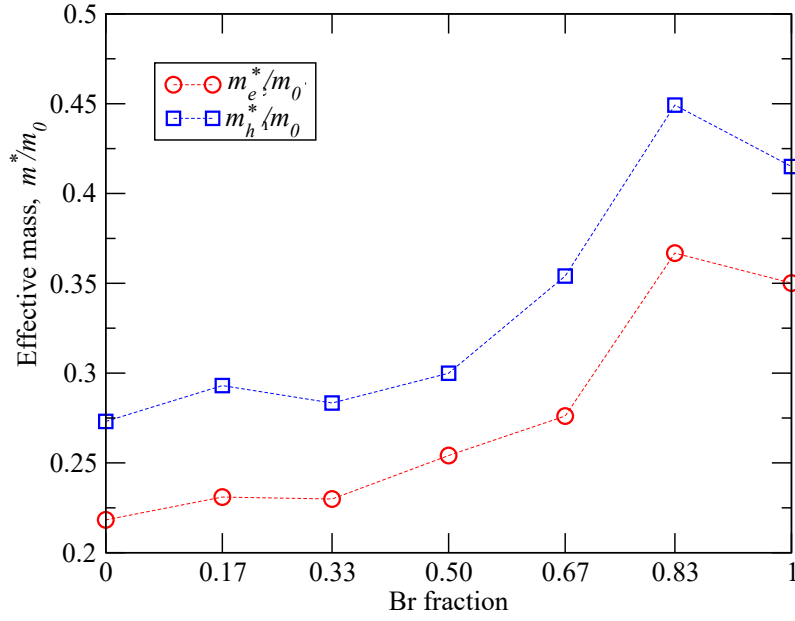


Figure 4.5 Calculated m_e^*/m_0 and m_h^*/m_0 ratios as a functions of Br contents, where m_e^* (m_h^*) is effective electron (hole) mass and m_0 is the mass of free electron.

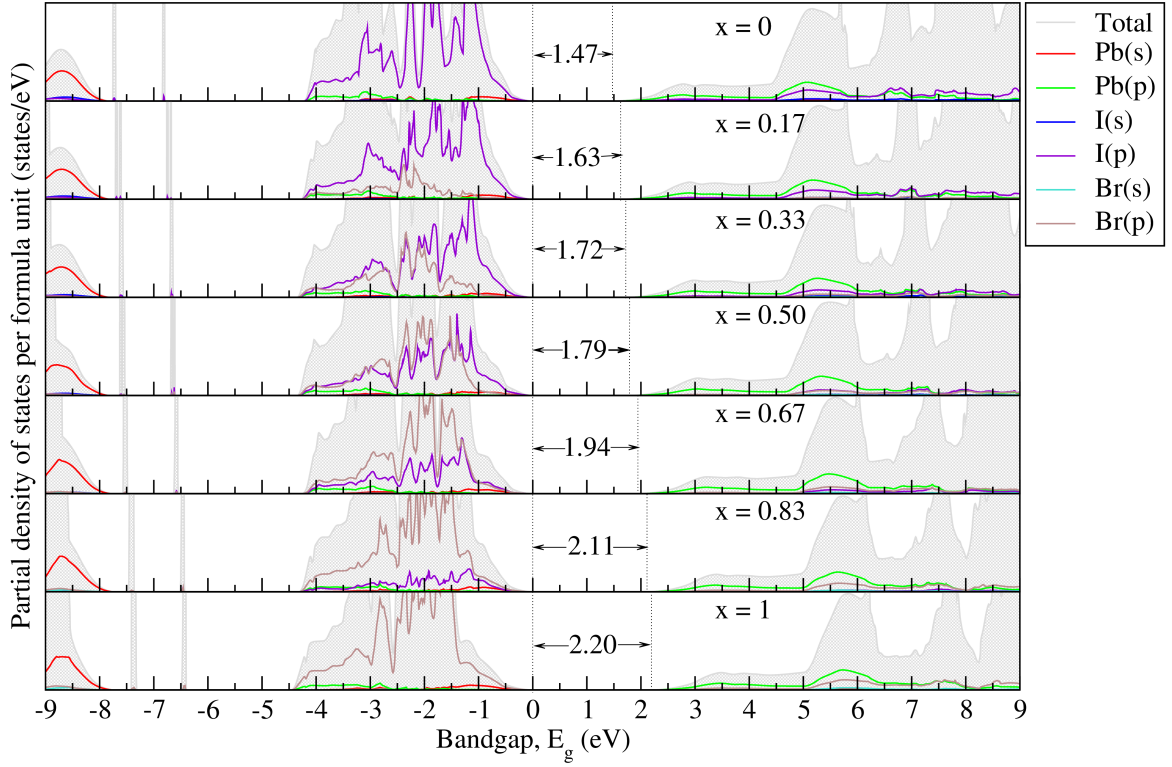


Figure 4.6 G_0W_0 +SOC calculated partial density of states for the $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ system.

The Fermi level is set to zero.

Figure 4.6 depicts the G_0W_0 +SOC calculated partial density of states (PDOS) to reveal the possible origin of responsible residual bandgap variations. One can see that the electronic states near the bandgap are mostly governed by the orbital overlap of the BX_6 octahedron. The organic part does not contribute to the fermi energy but acts as a charge compensating center, because of the weak interactions organic molecules with the inorganic part via hydrogen bonding through the organic cation groups. Thus, for the sake of clarity, around the bandgap only the contributions from the orbitals (s and p) of Pb, I and Br atoms are represented and analyzed. From the PDOS, the valence band is usually composed by X-p orbitals, mixed in minor fractions with B-s orbitals, whereas the conduction band is mostly contributed by B-p orbitals, partially hybridized with X-s states. The gradual replacement of I with Br causes the Br-4p orbital to dominate at the VBM, which tends to strongly hybridize with Pb-s states as compared to I-p states. This pushes the CBM towards high energy region and thus increases the bandgap. Such orbital behavior has also been observed in the DFT study of $MAPb(I_{1-x}Br_x)_3$ system [50].

4.1.4 Optical Properties for Mixed $FAPb(I_{1-x}Br_x)_3$

To explore the excitonic behavior for each $FAPb(I_{1-x}Br_x)_3$ configuration, we carried out PBE+SCISSOR+mBSE calculations including the SOC effect. Exciton is a neutral bound e-h pair which plays a crucial role in optical excitation process and is highly influential for both fundamental science and applications in solar cells [41–48]. Therefore, it is essential to consider the e-h Coulomb interactions for accurate excitonic description of the optical spectra.

Previously, it has been revealed that the polaronic effects in OIHPs contribute to excitonic features due to the interacting longitudinal optical phonons with electronic states of the carriers, thereby forming polarons which influences the dielectric behavior and exciton binding energies [34, 42, 44, 182]. However, the polaronic effects are not considered here since they are beyond the scope of this work. Figure 4.7 shows the imaginary parts of the

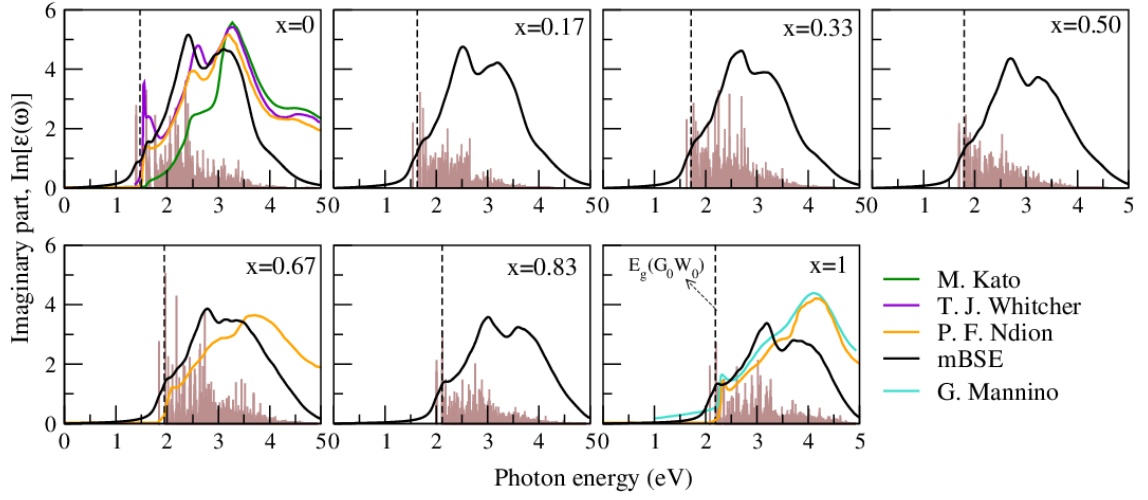


Figure 4.7 PBE+SCISSOR+mBSE calculated imaginary parts $\text{Im}[\epsilon(\omega)]$ of the dielectric function of the $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ alloy. The corresponding G_0W_0 derived fundamental gap $E_g(G_0W_0)$ and optical transition oscillator strengths are represented by dashed lines and brown histograms, respectively. The available experimental data on FAPbI_3 [183–185], FAPbIBr_2 [185] and FAPbBr_3 [186] are shown for comparison. Note that the $\text{Im}[\epsilon(\omega)]$ data shown here from Ref. [185] are indirectly calculated from the experimentally measured refractive index and extinction coefficient.

dielectric functions $\text{Im}[\epsilon(\omega)]$ with increasing Br compositions along with the corresponding optical transition oscillator strengths. One can see that $\text{Im}[\epsilon(\omega)]$ for all compositions show typical three peaks feature in considered energy range: two peaks are above the G_0W_0 bandgap and one peak is below the G_0W_0 bandgap, which is an exciton peak resulting from the e-h interactions upon photoexcitation. Our PBE+SCISSOR+mBSE calculated spectra for $x = 0$, $x = 0.67$, and $x = 1$ are in good agreement with available experimentally measured data [183–186], in particular the first two peaks. The spectrum of $x = 0$ from M. Kato *et. al.* [184] is largely blue-shifted for the first two peaks as compared to that of T. J. Whitcher *et. al.* [183] and P.F. Ndion *et. al.* [185] as well as our simulated one. As the Br fraction increases from $x = 0$ to $x = 1$, the optical spectra are systematically blue-shifted along with the gradual reduction in the overall amplitude of oscillator strengths. This trend is consistent with the increasing bandgaps and can be attributed to variation in electronic

charge distribution of X-p states with changing halide component as evident from PDOS of Figure 4.6.

Since changing in the halide components affects the bound state of electron-hole pair, we evaluated the exciton binding energies E_b within the Wannier-Mott theory by using the effective mass approximation as well as via mBSE. The resulting exciton binding energies are summarized in Table 4.5 and depicted in Figure 4.8. One can observe that the mBSE calculated exciton binding energies almost show linear behavior as the Br concentration increases and this trend is in general captured by the Wannier-Mott theory, though the values deviate. The mBSE calculated E_b for α -FAPbI₃ (74 meV) is significantly large as compared to the experimental value of 2.4 meV [187], whereas for the pure α -FAPbBr₃ the calculated E_b (112 meV) is in reasonable agreement with the experimental value of 170 meV [173]. For the latter, the Wannier-Mott theory yields a better value of E_b towards the experimental value. From the Wannier-Mott theory, we can infer that the overall increase in E_b with increasing Br concentration in FAPb(I_{1-x}Br_x)₃ is both affected by increasing m_r^* and decreasing ϵ_∞ . The smaller value of E_b in I-rich configuration requires smaller energy to dissociate the electron-hole pair, which in turn leads to high optical absorption and high PCE as compared to Br-rich material.

Table 4.5 Calculated high frequency dielectric constant ϵ_∞ and exciton binding energies E_b (meV) from both the Wannier Mott model and mBSE.

Br fraction x	0	0.17	0.33	0.50	0.67	0.83	1
ϵ_∞	5.320	4.929	4.746	4.613	4.447	4.266	4.173
E_b (Wannier Mott model)	58	72	77	88	107	151	149
E_b (mBSE)	74	85	90	95	99	108	112

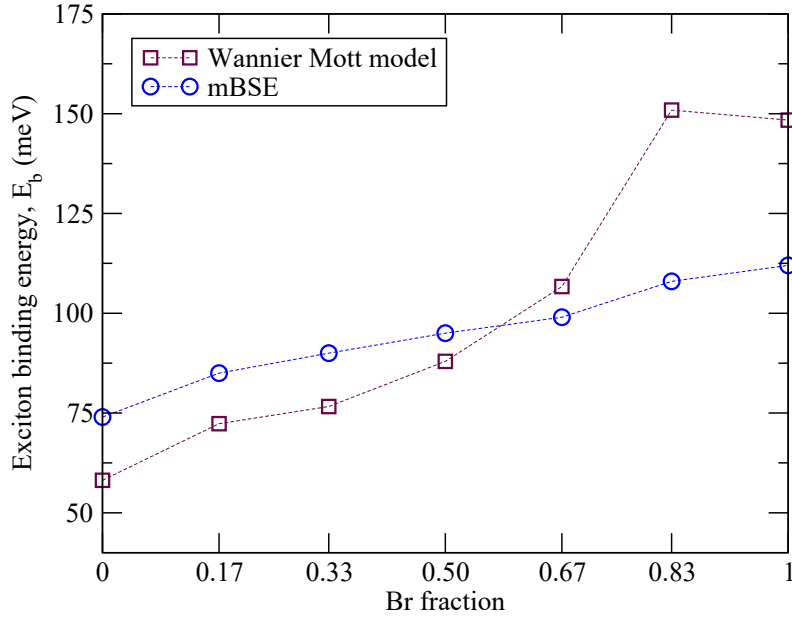


Figure 4.8 Calculated exciton binding energies as a function of the Br fraction.

4.2 Temperature-Dependent Phase Transformation Behavior for FAPbI₃

Here, we present the detail variations in quasi-particle electronic structures and optical excitonic behavior for FAPbI₃ system with respect to the structural transition from cubic to hexagonal phase. Along with the normal DFT calculations, the most reliable approach, many-body quasi-particle energies e.g. GW (QPGW) approximation is employed which is renowned for accurate prediction for the bandgap of the material. The GW bandgap increases from 1.47 eV to 3.52 eV while transforming from room temperature cubic phase to low temperature hexagonal phase. Both real and imaginary parts of the dielectric spectra shift towards the high energy region from room temperature α -phase to low temperature δ -phase. At the end, the evaluated exciton binding energies (E_b) scales with the calculated GW bandgaps and showed an increase from 74 meV for α -FAPbI₃ to 567 meV for δ -FAPbI₃. Such valuable information will play a requisite role in designing and manufacturing of an efficient solar cell.

4.2.1 Computational Details for Different Phases of FAPbI₃

Starting from the FAPbI₃ experimental geometry of cubic phase (α) at 298 K [164, 166], tetragonal phase (β) at 220 K [61] and hexagonal phase (δ) at 15 K [62], we performed DFT calculations using the computational code Vienna ab initio simulation package (VASP) [146, 169]. The pseudopotentials of projector augmented wave (PAW) [145] method were employed along with electron-ion exchange correlation functional known as the generalized gradient approximation (GGA) parametrized by Perdew-Burke-Ernzerhof (PBE) [64, 65]. The cutoff energy of 600 eV and $6 \times 6 \times 6$ Γ -centered k-points sampling of the Brillouin zone were used for all the three phases of FAPbI₃. The valence electronic states chosen for the calculations are $5d^{10}6s^26p^2$ for Pb, $5s^25p^5$ for I, $2s^22p^3$ for N, $2s^22p^2$ for C and $1s^1$ for H. The structural parameters for all the three phases were fully optimized with the minimum criterion of 0.05 eV/Å on the forces exerted on each atom applying energy convergence threshold of 10^{-4} eV. To take into consideration of the dispersion interactions of van der Waals, the rev-vdW-DF2 functional is used as proposed by Hamada [170]. Since the contribution of spin orbital motion in heavier elements is higher, therefore, the relativistic SOC (spin-orbit coupling) effect were included while exploring the electronic and optical behaviors of FAPbI₃ upon structural transformations.

For the accurate description of the electronic structure, we performed delicate one-shot G_0W_0 method using Γ -centered k-points sampling of $4 \times 4 \times 4$ for the α -phase and $3 \times 3 \times 4$ for the both β - and δ -phases with 2100 empty bands and 150 eV dielectric energy cutoff for each phase. The inclusion e-h interactions in the optical calculations are carried out by solving the BSE. For creating the BSE Hamiltonian 16 occupied and unoccupied QP energies were selected and the screened interactions W were chosen from the preceding G_0W_0 calculations. Evaluating the polarizability, a 0.1 eV was set as broadening parameter. The full description of GW+BSE approach that is compiled in VASP code is available in Ref. [162]

Since the GW+BSE calculations are prohibitive at denser k-points, so the exciton bind-

ing energies were calculated using an analytical model known as modeled BSE (mBSE) [42, 162] at the DFT level in which the GW screening part is replaced by a local model (See Eq. 3.38). The striking aspect of the mBSE approach is that the CPU time and memory used within mBSE calculations are much lower than those used within G_0W_0 +BSE calculations. The improvement in the exciton binding energy (E_b) increases as the sampling grid size increases. Since our main focus is to check the variation in E_b during the phase transition, so we restrict our k-points grid size for the α -phase to $18 \times 18 \times 18$, β -phase to $12 \times 12 \times 12$ and δ -phase to $12 \times 12 \times 12$ after careful convergence tests (see Appendix A for β -FAPbI₃).

4.2.2 Structural Properties for Different Phases of FAPbI₃

Using the PBE-GGA method we relaxed all the three structures, as shown in Figure 4.9. The calculated lattice parameters are summarized in Table 4.6.

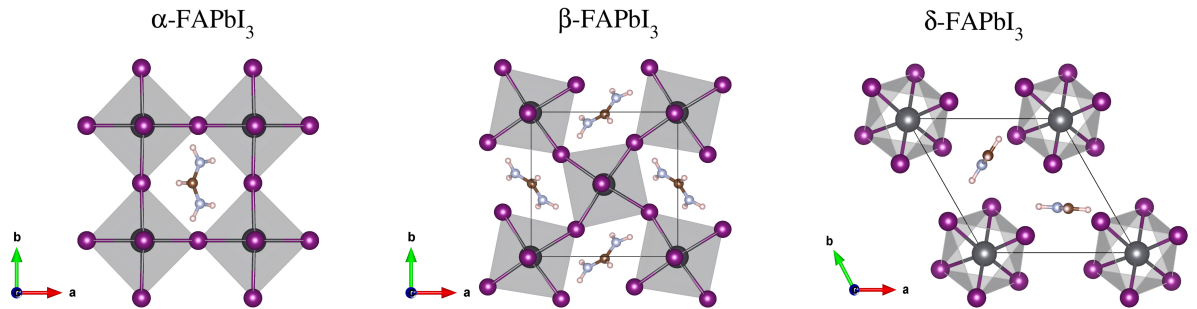


Figure 4.9 Relaxed structures of FAPbI₃ for different phases.

Using the PBE functional, the calculated ground state lattice parameters for three phases of FAPbI₃, that matches well with the experimental data. Slight variations in bond lengths of Pb–I (3.18 Å ~ 3.24 Å) occurs during the phase transformations and causing distortion of PbI₆ octahedra due to the irregular vibrational motion of the FA molecule and thus results in the tilting of bond angles of I–Pb–I. The fluctuations in the inorganic structure due to the motions of the organic cations are supported by the XRD analysis [61, 62, 188, 189]. Therefore, such a structural transition also leads to the change in electronic as well as optical

Table 4.6 Calculated lattice parameters for the three phases of FAPbI₃ using the PBE functional along with the published experimental data.

Phase	Calculated Lattice Constants			Experimental		
	a(Å)	b(Å)	c(Å)	a(Å)	b(Å)	c(Å)
α -FAPbI ₃	6.325	6.496	6.325	6.362	6.362	6.362 [164]
				6.352	6.352	6.352 [22]
				6.386	6.386	6.386 [62]
β -FAPbI ₃	8.900	8.925	6.344	8.926	8.926	6.326 [61]
				8.923	8.923	6.322 [188]
δ -FAPbI ₃	8.508	8.557	7.985	8.507	8.507	7.591 [62]

behavior of the material.

4.2.3 Electronic Structures and Bandgaps for Different Phases of FAPbI₃

Table 4.7 shows the calculated bandgaps at three different levels of theoretical methods. Comparing the bandgap of 1.43 eV for α -FAPbI₃ with the experiments, clearly indicates the underestimation in the calculated bandgap using the PBE method. With the inclusion of relativistic SOC effects in the calculations, the bandgaps for α -, β - and δ -FAPbI₃ reduce further up to 0.41 eV, 0.63 and 2.32 eV, respectively, thus making more underestimation of the experimental bandgaps. Such theoretical results agree well with the previous DFT+SOC calculations for MA(Pb, Sn)X₃ [42, 70, 74]. To overcome such underestimation in the bandgaps at PBE level, we performed the G₀W₀ calculations with the inclusion of SOC effects. Now the G₀W₀+SOC calculated bandgaps of 1.47 eV for α -FAPbI₃ shows an excellent agreement with the experimental bandgap.

Figure 4.10 represents the G₀W₀+SOC projected densities of states (PDOS) for the three phases of FAPbI₃, to unveil the possible responsible residual bandgap variations. The organic part interacts weakly with the inorganic content and does not contribute to the

Table 4.7 Calculated bandgaps parameters using different functionals.

	Method	α -FAPbI ₃	β -FAPbI ₃	δ -FAPbI ₃
Bandgap (eV)	GGA-PBE	1.43	1.63	2.70
	PBE+SOC	0.41	0.63	2.32
	G ₀ W ₀ +SOC	1.47	1.71	3.54
	Expt.	1.47[22], 1.48[23, 33, 177]	-	-

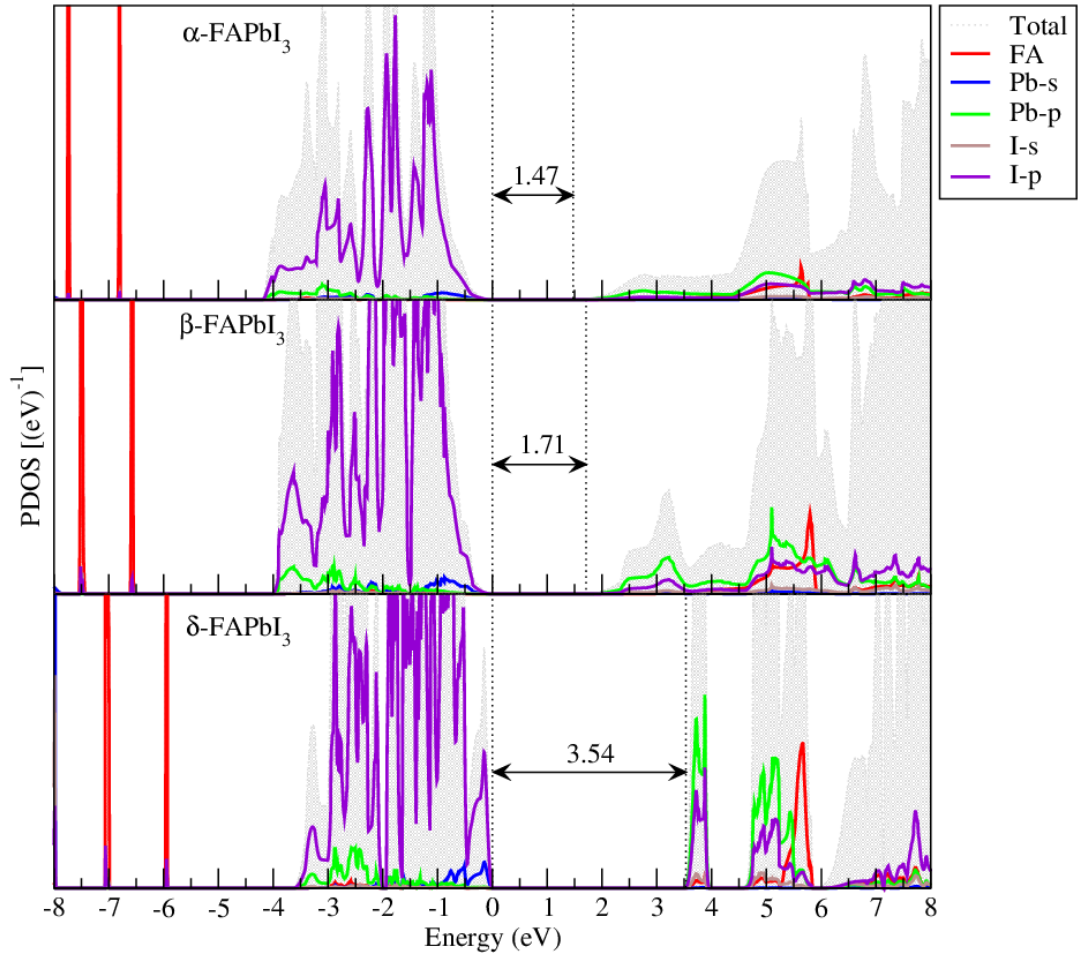


Figure 4.10 Calculated G₀W₀+SOC based projected densities of states (PDOS) for the three phases of FAPbI₃.

frontier electronic nature near the fermi level but behaves as a charge compensating center. Noticeably, the electronic states close to the bandgap region are mostly dominated by the orbital interactions of Pb and I. According to the PDOSs, the valence band maximum (VBM) is mostly contributed by p-orbitals of I, fractionally mixed with the s-orbitals of Pb, whereas the conduction band minimum (CBM) is mainly composed by the p-orbitals of Pb along with smaller portion of the p-orbitals of I. From the structural analysis, the rearrangement in the Pb–I–Pb angles increases the average Pb–I bond length along structural transition from α - to β - to δ -phases, thereby reducing the orbital interactions between Pb and I atoms. This results in an increase in the fundamental bandgap from 1.47 eV (α -FAPbI₃) to 3.54 eV (δ -FAPbI₃).

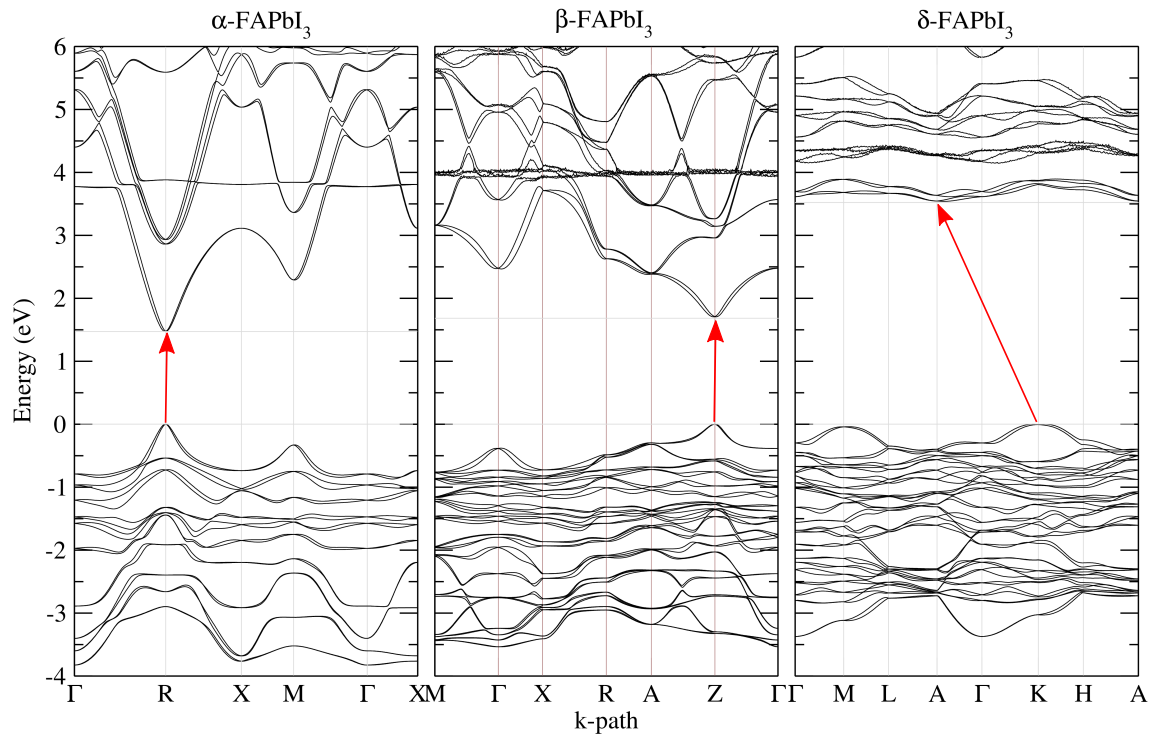


Figure 4.11 Calculated G_0W_0 +SOC band structures using DFT+scissor method for α -, β - and δ -FAPbI₃.

The G_0W_0 +SOC based band structures for the designated highly symmetric k-points for each phase are presented in Figure 4.11. These band structures are obtained by using DFT+scissor method. In this approach the CBM of the PBE+SOC band structure is shifted

in accordance with the GW based calculated bandgap. The validity of such results is consistent with the previously used Wannier interpolation method [42, 190]. For the cubic and tetragonal phase, both VBM and CBM fold to R- and Z-points respectively. Fractional deviations from highly symmetric point in α - and β -phases are observed for the CBM and VBM which is related to the splitting of Rashba-Dresselhaus [56–59], while such splitting is almost negligible for δ -phase. For both the α - and β -phases, the bandgaps are found to be direct in nature contrary to hexagonal phase which shows indirect bandgap. The dispersion both the valence band as well as conduction band slightly increases while going from α - to δ - phases, leading to increase in bandgap values. Such dispersions can be understood by the reduced orbitals coupling near both CBM and VBM. Also, the flattening of VBM and CBM in δ -phase reveals enhanced phonon-assisted electron scattering and thus has low carrier mobility in comparison to the α - and β -phases having sharper VBM and CBM. Such theoretical findings are consistent with previous experimental studies [189, 191].

4.2.4 Optical Properties for Different Phases of FAPbI₃

The excitonic effects during the photo-excited state plays a prominent role in understanding the relation between optical absorption and luminescence in hybrid organic-inorganic perovskites. Such optical behaviors of a material can be presented in terms of their complex real ($\text{Re} [\epsilon(\omega)]$) and imaginary ($\text{Im} [\epsilon(\omega)]$) dielectric functions. The ($\text{Re} [\epsilon(\omega)]$) indicates the ability of the material to permit electric field through it for storing electrical energy while ($\text{Im}[\epsilon(\omega)]$) describes absorption limits and the energy gain for the photovoltaic material.

Figure 4.12 shows the real ($\text{Re} [\epsilon(\omega)]$) and imaginary ($\text{Im} [\epsilon(\omega)]$) parts of the dielectric functions with the associated optical transition oscillator strengths, for all the three phases, as calculated by using mBSE approach. The whole optical spectrum shows a blue-shift with the decrease in overall amplitude of oscillator strengths which scales with the behavior of the optical spectra. The sharp dominant peaks in low energy region represent the presence

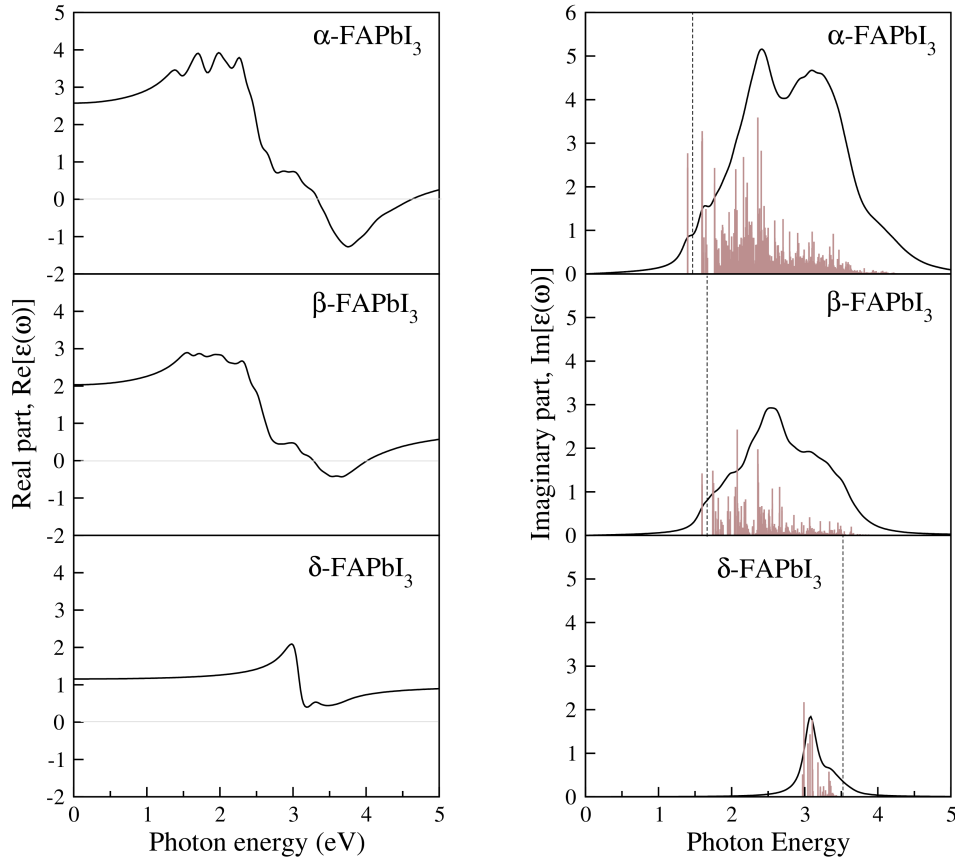


Figure 4.12 The mBSE based (a) real ($\text{Re} [\epsilon (\omega)]$) and (b) imaginary ($\text{Im} [\epsilon (\omega)]$) parts of dielectric functions with the optical transition oscillator strengths (brown histograms) and G_0W_0 derived electronic bandgap $E_{g(GW)}$ (dashed lines).

of strong electron-electron and e-h interactions for the α -FAPbI₃ and β -FAPbI₃. Such excitonic feature becomes weaker for δ -phase due to the reduced e-h recombination rate. Moreover, the calculated $\text{Im}[\epsilon (\omega)]$ values show a quite consistent behavior with reduced dielectric constants due to the structural transition of FAPbI₃ from α - to δ -phase. Such results can be attributed to the dominant intrinsic mechanism of Fröhlich interactions of optically excited charge carriers and longitudinal optical (LO) phonons, resulting in low momentum of charge-carrier with weak screening environment [34, 182]. Such optical characteristic is well documented in the experimental studies of phase-dependent emission-line broadening for MAPbI₃ and FAPbI₃ [192].

Since structural transition with temperature distorts PbI₆ framework which affects the

bound state of e-h pair and thus influences the excitonic binding energies. We can deduce the exciton binding energies for all the three phases of FAPbI₃ by making use of mBSE approach (See Appendix B).

Extracting the excitonic binding energies from the BSE based spectra are not relevant due to because of insufficient k-points sampling and interpreted only at qualitative level. The relevant static ion clamped dielectric functions ϵ_{∞} (high frequency dielectric constant) obtained from the G_0W_0 +SOC calculations along with the fitted screening parameter λ are used to obtain the optical bandgaps or first eigenvalue (Δ_{BSE}^1) at mBSE level at denser k-meshing. The calculated exciton binding energies as difference of G_0W_0 bandgap ($E_{g(GW)}$) and Δ_{BSE}^1 are summarized in Table 4.8. The increasing exciton binding energy with temperature-dependent structural transition is well consistent with decreasing dielectric constant and increasing bandgap. The first eigen value of 1.439 eV for α -FAPbI₃ which corresponds to the optical bandgap showing excellent agreement with the experimentally obtained results of 1.43 eV [193] and 1.45 eV [194]. The smaller values of E_b for α -FAPbI₃ and β -FAPbI₃ in comparison to that for δ -FAPbI₃, illustrates high quality ionic screening and prolonged carrier lifetime at excited level. Thus, the smaller value of E_b in α -FAPbI₃ and β -FAPbI₃ requires minimum energy for the dissociation of e-h pair, which results in high optical absorption and efficient solar cell performance. Such results also indicate that variations in exciton binding energies is directly related to the rotational entropy of FA molecule. Thus, lower rotational entropy results in localization of bound excitons and low carrier mobility thereby increasing E_b .

Table 4.8 The calculated high frequency dielectric constant ϵ_∞ and first mBSE eigen value Δ_{BSE}^1 . The exciton binding energies E_b (meV) are obtained as difference between $E_{g(GW)}$ and Δ_{BSE}^1 .

Phase	ϵ_∞	Δ_{BSE}^1 (eV)	$E_b = E_{g(GW)} - \Delta_{BSE}^1$ (meV)
α -FAPbI ₃	5.319	1.439	74
β -FAPbI ₃	4.608	1.595	93
δ -FAPbI ₃	3.968	2.977	567

Chapter 5

Conclusions and Future Projects

5.1 Main Conclusions

In the present thesis, we carried out first-principles study of structural, electronic, and optical properties of the $\text{FAPb}(\text{I}_{1-x}\text{Br}_x)_3$ alloy $0 \leq x \leq 1$ by means of density functional theory and many-body methods with the inclusion of the spin-orbit coupling. The calculated geometrical parameters show that the overall Pb–X bond length decreases with Br content and thus reduces the volume that is in agreement with the experiments. The G_0W_0 derived bandgap increases from 1.47 eV to 2.20 eV with increasing Br fraction which has been clearly demonstrated from the calculation of the electronic density of states. The G_0W_0 +BSE calculated optical spectra show that the overall excitonic peaks are blue shifted with increasing Br concentration, which shows strong correlation with the increase in the bandgap and is consistent with decreasing dielectric constants. The variation in the exciton binding energy from 74 meV to 112 meV reveals that excitons are more bound for Br rich compounds due to the reduced carrier mobility and thus require a higher energy for exciton dissociation. Our findings provide an efficient and controllable way to tune the electronic as well as optical properties for mixed HOIPs that will be beneficial for material design of high performance tandem solar cells.

Similarly we have investigated, the relativistic quasi-particle electronic and optical prop-

erties of FAPbI₃ in their cubic, tetragonal, and hexagonal phases. The computed G₀W₀ bandgap increases from 1.47 eV to 3.52 eV while transforming from cubic to hexagonal phase which can be related to the increase in Pb–I bond length in the inorganic framework. From the optical excitonic study, the overall spectrum is blue shifted going from cubic to hexagonal phase and the computed optical oscillator strength shows higher values for the cubic and tetragonal phases in comparison to hexagonal phase which indicates in localization of bound excitons and low carrier mobility. From the DFT based mBSE calculations, the exciton binding energies are higher as 567 meV for lower rotational entropy of hexagonal FAPbI₃ while it is lower for the cubic and tetragonal phases (74 meV and 93 meV respectively), thus indicating maximum light harvesting capabilities as compared to hexagonal phase. Such findings may provide conclusive information about the impact on efficiencies and designing of the solar cells during different thermal conditions.

5.2 Future Projects

Owing to the results obtained in present thesis, it paves way to further study the insight electronic and optical mechanism for OIHPs using more advance methods. The following new projects will be initiated in near future:

1. Quasiparticle electronic and optical properties for cation and metal mixed hybrid perovskite materials.
2. The role of Frölich interactions in the excited state of hybrid perovskite materials.
3. Electronic and photovoltaic study for molecular engineered hybrid perovskite materials.
4. Si/perovskite and perovskite/perovskite interface study for tandem type solar cells.
5. Low cost wide bandgap hybrid perovskite materials (alternative III-V compound semiconductors) for optoelectronic devices.

Appendix A

mBSE optical spectra and exciton binding energy convergence for $1 \times 1 \times 2$ FAPbI₃

In this appendix, we consider $1 \times 1 \times 2$ supercell of FAPbI₃ as an example to illustrate the performance of mBSE in comparison to the G_0W_0 +BSE and how the calculated optical spectra as well as exciton binding energies converge with respect to the number of k points. The required parameters used for PBE+SCISSOR+mBSE calculations are shown in Table B1.

Table A1 The parameters used for PBE+SCISSOR+mBSE calculations.

Br fraction x	0	0.17	0.33	0.50	0.67	0.83	1
ϵ_{∞}^{-1}	0.188	0.203	0.211	0.217	0.225	0.234	0.240
μ ($\text{\AA}^{-1}$)	1.055	1.060	1.070	1.073	1.081	1.095	1.109
SCISSOR (eV)	1.062	1.095	1.133	1.171	1.233	1.283	1.319

Figure A1(a) shows comparison of the imaginary part of the dielectric function calculated from G_0W_0 +BSE and PBE+SCISSOR+mBSE on a $4 \times 4 \times 2$ k-point mesh. One can see that PBE+SCISSOR+mBSE in general reproduces very well the spectra obtained from G_0W_0 +BSE, in particular the first bright peak, suggesting that PBE+SCISSOR+mBSE is a suitable method to describe the optical spectra with an accuracy that is comparable with more demanding G_0W_0 +BSE.

Figure A1(b) and A1(c) display the convergence of optical spectra and exciton binding energies calculated from PBE+SCISSOR+mBSE with respect to the number of k points. Clearly and expectedly, the convergence is very slow. Our calculations indicate that the spectra and exciton binding energies are converged with a $16 \times 16 \times 8$ k-point mesh, with an accuracy of about 3 meV in exciton binding energies.

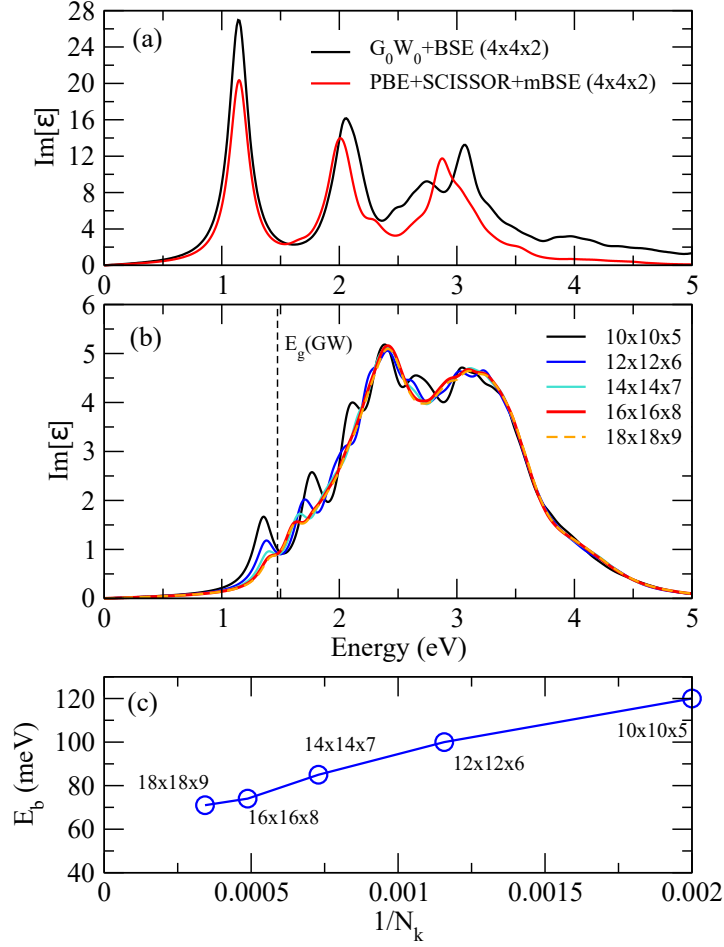


Figure A1 (a) comparison of the imaginary part of the dielectric function calculated from G_0W_0+BSE (black lines) and PBE+SCISSOR+mBSE (red lines) on a $4 \times 4 \times 2$ k-point mesh. Convergence of (b) spectra and (c) exciton binding energies calculated from PBE+SCISSOR+mBSE with respect to the number of k points. All calculations here are performed on $1 \times 1 \times 2$ FAPbI₃.

Appendix B

mBSE optical spectra and exciton binding energy convergence for β -FAPbI₃

Here, we consider β -FAPbI₃ as an example to illustrate the performance of mBSE in comparison to the G_0W_0 +BSE and to check the calculated optical spectra as well as exciton binding energies converge with respect to the number of k points. The required parameters used for PBE+SCISSOR+mBSE calculations are shown in Table B1.

Table B1 The parameters used for PBE+SCISSOR+mBSE calculations.

Parameter	α -FAPbI ₃	β -FAPbI ₃	δ -FAPbI ₃
ϵ_{∞}^{-1}	0.188	0.217	0.252
μ ($\text{\AA}^{-1}$)	1.055	1.081	1.112
SCISSOR (eV)	1.062	1.075	1.036

Figure B1(a) shows comparison of the imaginary part of the dielectric function calculated from G_0W_0 +BSE and PBE+SCISSOR+mBSE on a $3 \times 3 \times 4$ k-point mesh. One can see that PBE+SCISSOR+mBSE in general reproduces very well the spectra obtained from G_0W_0 +BSE, in particular the first bright peak, suggesting that PBE+SCISSOR+mBSE is a suitable method to describe the optical spectra with an accuracy that is comparable with more demanding G_0W_0 +BSE.

Figure B1(b) and B1(c) display the convergence of optical spectra and exciton binding

energies calculated from PBE+SCISSOR+mBSE with respect to the number of k points. As expected, the convergence is very slow. Our calculations indicate that the spectra and exciton binding energies are converged with a $12 \times 12 \times 12$ k-point mesh, with an accuracy of about few meV in exciton binding energies.

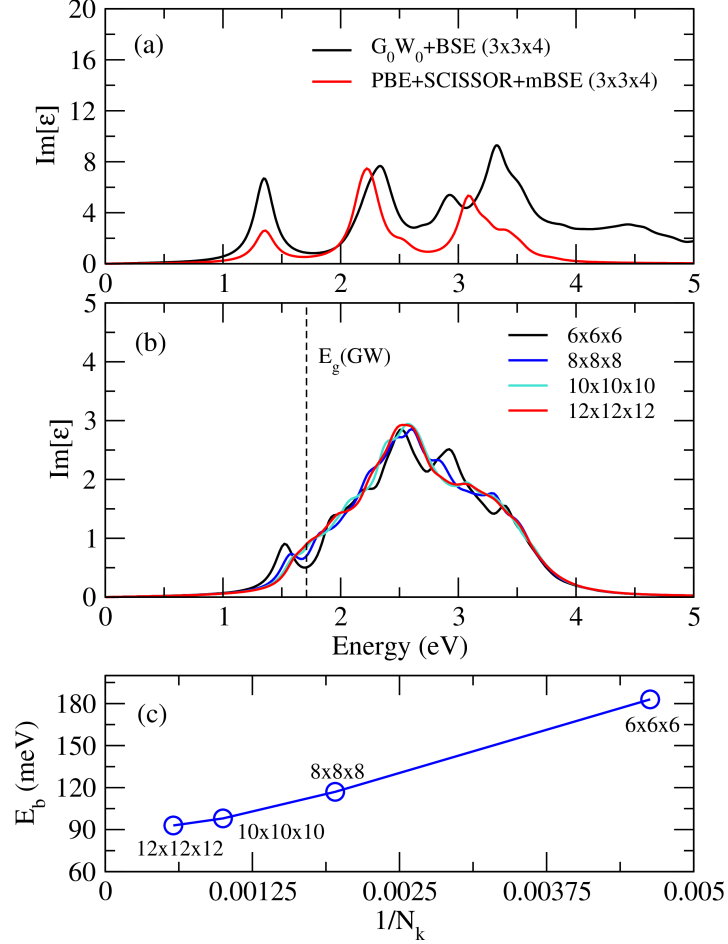


Figure B1 (a) comparison of the imaginary part of the dielectric function calculated from G_0W_0 +BSE (black lines) and PBE+SCISSOR+mBSE (red lines) on a $3 \times 3 \times 4$ k-point mesh. Convergence of (b) spectra and (c) exciton binding energies calculated from PBE+SCISSOR+mBSE with respect to the number of k points. All calculations here are performed on β -FAPbI₃.

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