A FIRST-PRINCIPLES STUDY OF HYBRID ORGANIC-INORGANIC PEROVSKITES FOR PHOTOVOLTAIC APPLICATIONS

by

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ABSTRACT

Hybrid organic/inorganic perovskites have attracted significant research interests due to the unprecedentedly rapid rise in energy conversion efficiency seen in photovoltaic devices based on PbI$_3$CH$_3$NH$_3$. Current research efforts in this field have focused on searching for similar perovskites with better properties, especially stability. However, properties relevant to photovoltaic performance, such as band gap size, remain unknown for some of these materials. Employing first-principles calculations based on density functional theory, we studied several hybrid perovskites: PbI$_3$CH$_3$NH$_3$ to check our methods, PbF$_3$CH$_3$NH$_3$ and SnF$_3$CH$_3$NH$_3$ as they had not been previously studied, and PbI$_3$CH(NH$_2$)$_2$ due to our colleagues at NREL believing it might have better properties. We find that the band gaps of FA (formamidnium, CH(NH$_2$)$_2$) based perovskites are smaller than those of corresponding MA (methylammonium, CH$_3$NH$_3$) based materials. PbI$_3$FA has black and yellow phases with close total energies, and the yellow phase has a much higher band gap than the black phase.
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CHAPTER 1
INTRODUCTION

This chapter discusses the motivation, background, and previous work for the topic of perovskite photovoltaics.

1.1 Motivation

Photovoltaic (PV) cells convert sunlight into electrical current. Among various renewable resources solar energy is very attractive because of its abundance; in addition, solar energy is clean and safe. However, current PV technology is not cost effective for bulk power generation under most circumstances.

As shown in Figure 1.1, many different types of solar cells have been investigated [1]. Among them crystalline silicon (Si) technologies are well established, with over 80% of the total PV market share as of 2011 [2] and a history of over 40 years [3]. Crystalline Si solar cells have relatively high energy conversion efficiency (\( \eta \)), up to 25%, because of a nearly optimum band gap (\( E_g \)) of 1.1 eV. Any photons with energy lower than the band gap of a semiconductor will not be absorbed, while any energy from an absorbed photon in excess of the band gap of the material is rapidly lost to thermalization. Based on these considerations and a few other assumptions, Shockley and Queisser [4] established the performance limit of solar cells with a single absorbing material and a single band gap. On earth’s surface (the AM1.5 spectrum), \( \eta \) can reach up to 34%, when \( E_g \approx 1.4 \) eV.

However, as an indirect gap material, Si is a poor absorber of light near its band gap compared to semiconductors with direct gaps [5]. In order to well absorb sunlight the Si layer in
Figure 1.1: Panel “a” is the NREL chart [1] of highest recorded efficiencies for various photovoltaic types. Panel “b” is a graph of the emerging PV using data from [1] and [3].

A solar cell must be hundreds of μm in thickness, requiring extremely high quality pure crystals to avoid the electron and hole recombining near a defect. Thus crystalline Si solar cells are...
a solar cell must be hundreds of μm in thickness, requiring extremely high quality pure crystals to avoid the electron and hole recombining near a defect. Thus crystalline Si solar cells are expensive despite the abundance of Si. Gallium arsenide (GaAs) solar cells have higher efficiency (up to 29% [2]) than Si solar cells because Eg of GaAs is 1.42 eV. But GaAs is prohibitively expensive for many PV applications.

Recent PV researches have focused on either using less (or cheaper) material to reduce cost or achieving higher efficiencies beyond the Shockley-Queisser limit. Cadmium telluride (CdTe) based solar cells are cheaper than Si solar cells [2], with a band gap of 1.45 eV and η as high as 21.5%. CdTe is one of the few types of PV cells commercially available for widespread use [2] with a market share of ~5%[6], and is the most successful of the “thin film” (absorber thickness ~10 μm or less [7]) technologies [3]. But Cd and Te are both toxic, and Te is as rare as platinum. Another promising bulk PV material is thin film CIGS (copper indium gallium diselenide) [3], which can reach high efficiencies in small scale but tends to have poor performance in large scale due to difficulty in manufacturing: simultaneous deposition of all four elements [7] is very challenging. It is nearly impossible to obtain the correct ratio of compounds over a large area [8]. CIGS systems have η up to 21.7%, while their band gaps vary in a range between 1.0 and 1.7 eV depending on the exact elements ratio present.

In addition to bulk semiconductors, nanostructured solar cells [9] including dye sensitized cells, organic photovoltaics, and quantum dot solar cells, are being developed. Dye sensitized solar cells separate the tasks of absorbing photons and transporting charge to different materials. Typically, a dye acts as an absorber for light. The electron and hole are separated on the interface between dye molecules and a scaffold of high band gap semiconductor such as titanium dioxide. This scaffold transports charge out of the cell to power the load. The dye is brought back to
ground state by an electron from a third material, either an electrolyte or another semiconductor, thus completing the cycle. Dye sensitized solar cells are typically made of inexpensive nontoxic materials and can be manufactured though simple techniques like screen printing [10]. However, the multitude of interfaces in such a system makes recombination losses high and reduces efficiency. The highest observed efficiency of a dye sensitized cell is only 11.9\% as of 2015, which is hardly above the 10.4\% record from 2001 [10]. Efficiencies around 4\% are typical of most dye sensitized cells architectures [2].

Organic solar cells are fabricated using organic molecules such as polymers or fullerenes [11]. These organic materials are abundant and the fabrication is simple solution processing or thermal evaporation [11], and organic PV cells can be very thin (~ 100 nm) because of strong optical absorption. While organic solar cells are inexpensive, their efficiencies are relatively low, with the maximum measured $\eta$ of 11.1 \% (efficiency is in the range of 1–3\% [2] is more typical). This is mainly due low carrier mobilities compared with those of bulk semiconductors. Also, $E_g$ of organic semiconductors are often larger than 2 eV [11]; above the optimal gap for solar cells. Furthermore, when exposed to oxygen or humidity while illuminated, these organic molecules will be degraded by photochemical reactions [12]. Due to the extremely thin nature of many organic solar cells, physical damage is also a concern [13].

Quantum dots are microscopic semiconductor crystals; due to their small sizes, the properties of the dots could be different from those of a bulk system of the same material. Quantum-dots have the potential to be made of inexpensive materials [2] and can be manufactured through spin coating [9], and their optical gaps are tunable by varying dot size, shape, and surface passivation [2]. In addition, excess energy from photons above the band gap could generate more electron-hole pairs through a process known as multiple exciton generation
(MEG) [9, 14]. MEG could lead to an optimal efficiency of 66% [2, 14], which is beyond the Shockely-Queisser limit. However, quantum dot technology is in its infancy and has yet to break 10% efficiency. As with the dye sensitized solar cells and the organic solar cells, quantum dot cells also suffer from high recombination losses on the multitude of interfaces [9].

Recently, hybrid organic/inorganic perovskite compounds have attracted tremendous research efforts. These compounds require no rare elements and are simpler to fabricate than many traditional technologies. Thus the cost of such a solar cell could potentially be low. The past few years have seen an unprecedented rise in efficiency of perovskite solar cells, which is especially evident in Panel b of Figure 1.1. The high efficiency and low cost are the motivation for studying perovskite compounds.

1.2 Perovskites and Photovoltaics

“Perovskite” refers to any compound that has a particular crystal structure, specifically the same crystal structure as CaTiO₃ [15, 3] and the ABX₃ formula. In Figure 1.2 a perovskite unit cell is shown. Two noteworthy properties are the cubic cage containing the A atom and the

*Figure 1.2: Perovskite Structure with the ABX₃ formula. It has a cubic unit cell, and the X atoms are purple, the B atoms are gray, and the A atoms are blue.*
octahedral arrangement of X atoms around each B atom which form when the structure is tiled.

There are a great many perovskite compounds with different properties, including piezoelectric materials, ferroelectric materials, and high-temperature superconductors [3]. The hybrid organic metal halide perovskites have been used to make efficient solar cells, which typically contain halogen (X) atoms, a lead or tin (B) atom, and a polyatomic organic ion (A). Although optoelectronic properties of these perovskite compounds were measured in the 1990s with the goal of adapting the material for light-emitting diodes (LEDs) [3], their usage in photovoltaics did not occur until 2006. Initially, PbI₃CH₃NH₃ and PbBr₂CH₃NH₃ were used as light absorbers in dye-sensitized solar cells with η of 2% or less. However, efficiency in perovskite solar cells was improved to about 10% [3] by 2012, when a breakthrough was made that allowed efficiencies to rise further: use the perovskite as both light absorber and charge transporter, eliminating possible recombination effects of electron–hole pairs on material interfaces. Solar cells made of PbI₃CH₃NH₃, whose band gap was reported to be 1.60 eV [16], 1.61 eV [17], and 1.52 eV [18], demonstrated η above 20% (see Figure 1.1) in 2014. It is expected that perovskite solar cells will perform at least as well as crystalline Si solar cells [3].

The high energy-conversion efficiency of perovskite solar cells is attributed to the facts that (1) these perovskite compounds are good light absorbers over a wide range of spectrum [5]; (2) they have low internal voltage loss. PbI₃CH₃NH₃ solar cells have the fourth lowest loss of open circuit voltage (0.45 V) among all known photovoltaic materials, after GaAs (~ 0.3 V), crystalline Si (~ 0.4 V), and CIGS (~ 0.4 V) [3].

Moreover, perovskites solar cells have the potential to be cheap, because they require no rare elements and the processing mechanism for producing these materials is simple aqueous chemistry [18], which is much easier than growing crystals by melting or vapor deposition.
Unfortunately the water solubility which makes these materials easy to fabricate also leads to their destruction; compound lifetimes in air range only up to a few weeks to months for lead based perovskite compounds, to mere hours for some of the tin based compounds [18]. Therefore, current researches in this field have been predominantly focused on how to increase the stability of these compounds, in addition to replacing lead (Pb) by other transition metals to avoid the environmental and health concerns. One approach is to change various components in these compounds to search for a combination that is more stable and maintains high efficiency for energy conversion, and first-principles calculations could help experimentalists to identify which systems are most promising.

1.3 Previous Theoretical Work

Because these hybrid perovskites are rather difficult to deal with from first principles, ab initio calculations were performed for these materials mainly in 2010s, although a paper published in 2008 modeled a few similar compounds based on tin (Sn) [19] using density functional theory (DFT). Most previous theoretical work investigated PbI3CH3NH3, the most successful perovskite PV material, either considering the cubic structure [2, 15, 20, 21] or the low-temperature tetragonal [16] or orthorhombic [22] structures. Equilibrium crystal structures, bulk moduli and electronic band structures were determined [15, 16, 20, 21, 23, 22]. In addition to PbI3CH3NH3, several similar compounds have been calculated using the DFT [16, 20, 23]. All possible cubic crystal combinations of Sn vs Pb for the B atom, Cl, Br, or I for the X atom, and Cs, CH3NH3 (methylammonium, MA), or NH2CHNH2 (formamidinium, FA) for the A ion, have been investigated [20]. Very recently, more complex crystal structures of FAPbI3 have been modeled, with interest shown in the effects slight structural changes have on electronic properties [24, 25].
DFT often severely underestimates band gaps of semiconductors. There are certain methods which attempt to correct this such as the hybrid functional. In the case of these perovskite systems, usage of spin orbit coupling with HSE06 hybrid functional have inconsistent results, in Kim et al [25] a band gap close to experiment is obtained for MAPbI$_3$, but Lang et al vastly underestimate the band gap of the same compound when they use the HSE functional. Many-body perturbation theory within the $GW$ approximation allows for quantitatively accurate determination of electronic band structures. $GW$ computations are much more demanding than DFT, and recent works [16, 23, 26, 24] investigated PbI$_3$CH$_3$NH$_3$ as well as CsSnI$_3$, CsPbI$_3$, SnI$_3$CH$_3$NH$_3$, NH$_4$PbI$_3$, and PbI$_3$HC(NH$_2$)$_2$ employing $GW$ calculations. Without considering spin-orbit coupling, the $GW$ method dramatically overestimates $E_g$ of PbI$_3$CH$_3$NH$_3$ to be 2.68 eV [16] or 2.73eV [23], as compared to the experimental value of around 1.6 eV. When spin-orbit corrections are taken into account, the GW band gap is 1.67 eV [16, 23], in good agreement with experimental data.

![Figure 1.3](image)

**Figure 1.3:** Important results from previous papers. “a” is a table from Lang et al. [20] which shows all of the different compounds they studied in an assumed cubic perovskite phase. “b” is a figure from Umari et al. [16] which shows the effects of spin orbit coupling and GW corrections on the calculated band gap of perovskites.
BSE calculations allow for theoretical determination of optical properties such as absorption. These computations seem to have only very recently been performed in detail for perovskites, in January 2015[27] and November 2014 (which included spin-orbit coupling)[26], although a BSE calculation was mentioned in an article from 2013[28].

1.4 Present Work

In this project we focus on hybrid perovskites containing different components. Of primary importance is treatment of FA (HC(NH$_2$)$_2$) instead of MA (CH$_3$NH$_3$), since FA-based compounds are expected to be more stable by our colleagues at NREL. Specifically, we study electronic structures of PbI$_3$HC(NH$_2$)$_2$ with two crystal structures: a black $\alpha$-phase and a yellow $\delta$-phase [8] employing density functional theory with spin-orbit interactions considered. Fluorine containing perovskites have also been largely ignored in previous work, so we modeled these in case they had desirable properties. In the next Chapter we will summarize computational methods used in this work, then our results and discussion will be presented in Chapter 3.
CHAPTER 2
METHODOLOGY AND THEORY

In this chapter the theory behind our work is summarized, topics include DFT, pseudopotentials/PAW, and spin-orbit coupling.

2.1 Density Functional Theory

All properties of a many-particle quantum system can be predicted by solving the many-particle Schrödinger equation; however, computationally this is prohibitive since the computational cost increases exponentially with the number of particles [29]. One approach for modern electronic-structure calculations is density functional theory, which in principle is an exact mapping of many-body quantum system to a single-particle system under an effective external potential [30].

DFT is based on the Hohenberg-Kohn theorem, which states that the ground-state electron density $\rho$ of a quantum system with $N$ electrons is uniquely determined by an external potential (up to a constant) [30, 31]. This has the important implication that all ground-state properties are uniquely determined by the electron density [29]. If functionals for: (1) kinetic energy $T[\rho]$, (2) external potential potential $V[\rho]$, (3) electron repulsion (Hartree) energy $W[\rho]$, and (4) exchange-correlation (XC) energy $XC[\rho]$ could be found such that they create identical energy contributions from the electron density as the operators would create from many-body wavefunction $\Psi$, then the ground state energy and electron density could be solved by creating an energy functional $E[\rho] = T[\rho] + V[\rho] + W[\rho] + XC[\rho]$ and solving for the density $\rho$ such that the total energy $E$ is minimized and $\int \rho(\mathbf{r}) * d\mathbf{r} = N$. 
In practice this method of direct minimization of the total-energy functional is not used [29] because the functionals T[ρ] and XC[ρ] remain unknown. Instead the Kohn-Sham equation [32] is solved. In this method, non-interacting single particle wave functions in an effective potential are treated [32]. The Kohn-Sham equations obtain the density from single particle wave functions using ρ(r) = ∑N i=1 |ψi(r)|2, and define a T operator in terms of these wave functions as T = ∑i h2 2m (∇ψi(r))2. Then one can formulate the Kohn Sham equation (2.1) with these ingredients by varying with respect to the wave functions [30].

\[-\frac{\hbar^2}{2m} \nabla^2 \psi_i(r) + \left( V(r) + \int \frac{\rho(r') e^2}{|r'-r|} dr' + \frac{\partial XC[\rho]}{\partial \rho} \right) \psi_i(r) = \varepsilon_i \psi_i(r). \tag{2.1}\]

Here \(\varepsilon_i\) and \(\psi_i\) are eigenenergy and eigenfunction for state \(i\). The exchange-correlation energy functional XC[ρ] must be approximated, and the simple local density approximation (LDA) and the generalized gradient approximation (GGA) are widely used in first-principles calculations.

### 2.2 Pseudopotentials and PAW

Other approximations are also used in practical DFT calculations. Very deep potentials near nuclei cause highly oscillatory behavior of the wave functions near the nucleus, which requires high spatial frequency expansion terms and thus increases computational cost dramatically when a plane-wave basis is used. We use pseudopotentials to overcome this problem. Pseudopotentials are approximations of the physical potential of an atom that reproduce the correct wave function and single particle eigenvalues outside a certain radius. Normally the nucleus and inner electrons are treated as a single entity and only the valence (and semi-core) electrons are modeled [29]. Norm-conserving pseudopotentials preserve normalization of the density, and are the most reliable pseudopotentials used in DFT calculations. More information about pseudopotentials can be found in Appendix B.
Another method that can be used to model the potential the electrons interact with is the projector-augmented wave (PAW) formalism proposed by Blochl in 1994 [33, 34]. One of the main ideas behind PAW is the use of a linear transform between “smooth” pseudo wave functions \( \psi_s \) and “full” wave functions \( \psi_f \),

\[
|\psi_f > = \hat{T} |\psi_s >
\]

Away from the atom centers, the real wave functions and the smooth wave function should be the same, but in the interior of the atoms they are different. We thus define \( \hat{T} = 1 + \sum_a \hat{T}_a \), where \( \hat{T}_a \) is a transformation defined in “augmentation spheres” around each atom. The wave function inside the augmentation spheres is expanded with partial waves

\[
|\psi_s > = \sum_i c_i |\phi_i >, \text{where } |\phi_i >\text{ is the } i\text{-th smooth partial wave}
\]

and \( \hat{T}_a |\phi_i > = |\phi_i > - |\phi_i >_s \). Instead of finding \( c_i \) directly from the inner product \( <\phi_i|\psi_s> \), another set of projector functions is chosen such that inside the augmentation sphere

\[
< p_i |\phi_j >_s = \delta_{i,j} \text{ and thus by completeness } \sum_i |\phi_i >_s < p_i | = I, \text{ the identity operator. This orthonormality allows } c_i \text{ to be written as } <p_i|\psi_s>. \]

The expression for \( \hat{T}_a \) is now obtainable by \( \hat{T}_a = \hat{T}_a \ast I = \sum_i \hat{T}_a |\phi_i >_s < p_i | = \sum_i (|\phi_i > - |\phi_i >_s ) < p_i | \), thus completing the full \( \hat{T} \) which is given by

\[
\hat{T} = 1 + \sum_a \sum_i (|\phi_i > - |\phi_i >_s ) < p_i |.
\]

PAW calculations allow for faster convergence with respect to plane wave energy than norm-conserving pseudopotentials and hence take less computational resources, because the real wave function is recovered by a transform of the smooth wave function; meanwhile, PAW calculations often provide results as accurate as those from norm-conserving pseudopotentials.

The PAW datasets for this project were obtained from http://www.physics.rutgers.edu/gbrv.

2.3 Difficulties

Although DFT is very successful and widely applied in materials simulations, this approach has three major challenges. First, the exact XC functional remains unknown, though simple LDA and GGA can provide accurate results for ground-state properties. A second flaw is
not in DFT per se, but rather in what DFT reduces. The Schrödinger equation is not the most accurate equation to model electrons as it ignores relativity. The third flaw is that DFT within LDA/GGA severely underestimate band gaps of insulators and semiconductors. We need to employ many-body perturbation theory to quantitatively predict band gap and band structures, a brief description of these methods can be found in Appendix D.

2.3.1 Relativity and Spin-Orbit Coupling

Relativistic effects are usually negligible for the valence orbitals [35], especially those of light atoms such as carbon; however, with heavier atoms such as Pb they can have significant impact [29]. There are two main relativistic effects which are typically accounted for when dealing with solid state systems: scalar-relativistic and spin-orbit. The Kohn Sham equation as we have defined it contains neither, but they can be added on. For scalar relativistic effects, the kinetic energy operator in the Hamiltonian is altered to include higher order elements of the relativistic energy expansion; but the wave function is still treated as a scalar wave function [29]. For perovskites, the dominant relativistic effect is the spin-orbit interaction due to magnetic coupling between the different angular momentum degrees of freedom. The spin orbit addition to the Hamiltonian is given by \( \Delta H = k \mathbf{S} \cdot \mathbf{L} \), where rigorously obtaining the correct form of parameter \( k \) involves treatment of the Dirac equation [36].

We used the ABINIT [37, 38, 39, 40] package to perform DFT calculations. ABINIT is an open source program for electronic structure simulations, using plane waves as basis to expand the wave functions. We used both norm-conserving pseudo-potentials and PAW to compute total energy and electronic structures of hybrid perovskites, and the spin-orbit coupling is evaluated using PAW. ABINIT uses a full two component spinor wave function to implement
spin-orbit interactions [41]. This is computationally more challenging; it requires more time and roughly 4 times as much memory due to the Hamiltonian matrix being quadrupled in size [42].

Much of the work done modeling MAPBI₃ with spin-orbit coupling was done using PAW, due in part to the fact that normal PAW datasets contain enough information to perform these spin orbit calculations. The Hamiltonian for standard PAW can be expressed

\[ H = T + V_{\text{eff}} + \sum D_{ij} \langle p_i \rangle \langle p_j \rangle, \]

where D is a density matrix. If the basis of projector functions is complete enough, and most of the electron density is in the augmentation spheres, then the spin orbit Hamiltonian for PAW becomes

\[ H \cong T + V_{\text{eff}} + \sum (D_{ij} + S_{Oij}) \langle p_i \rangle \langle p_j \rangle, \]

where \( S_{Oij} \) is the projection of \( \hat{L} \cdot \hat{S} \) onto the PAW spheres [42].

It is also possible to implement spin-orbit coupling with norm-conserving pseudopotentials in a plane wave basis, although this may not be well known [21]. ABINIT can implement spin-orbit interactions with the Hartwigsen-Goedecker-Hutter (HGH) pseudopotentials [42]. However, the available HGH pseudopotentials were inadequate. Not only did they require a high plane wave energy to converge, the results obtained when using them were not in good enough agreement with published results or our other results (more information in Chapter 3).
CHAPTER 3
RESULTS AND DISCUSSION

In this chapter we present our results for the properties of the various hybrid perovskite systems.

3.1 PbI₂CH₃NH₃

Since DFT calculations on these hybrid perovskites are non-trivial, we need to examine the methodologies by comparing results for PbI₂CH₃NH₃ against previously published data. Here we computed the electronic band structure using a number of methods, including norm-conserving pseudopotentials, PAW with and without spin-orbit interactions, and HGH type norm-conserving pseudopotentials.

We determined the crystal structure of PbI₂CH₃NH₃ first, which varies under different temperatures [18]. Stoumpos et al. [18] report the crystal is tetragonal $P4mm$ at 400K, tetragonal $I4cm$ at 293K, and a low-symmetry supercell at temperature below ~130K. Brivio et al. [23] claim that cubic $Pm\overline{3}m$, tetragonal $I4/mcm$, and orthorhombic $Pnam$ crystal structures were detected through X-ray diffraction in high quality PbI₂CH₃NH₃ crystals.

We are interested in the cubic phase, with initial coordinates obtained from Tingting Shi [43]. Our convergence tests were run for plane-wave energy cutoff (ECUT) and the k-point grid (for information about our criteria and convergence tests in general see Appendix C). For this particular material, a 6x6x6 k point grid and an ECUT of 50 Hartree were found to be sufficient for norm-conserving GGA-PBE pseudopotentials. For GGA-PBE PAW the k-point convergence behavior was much the same but the required ECUT was only 22 Hartree, and the additional PAW parameter of pawecutdg was set to 60 Hartree. HGH pseudopotentials, which used the
LDA exchange correlation functional, required a significantly higher ECUT of 100 Hartrees to have a converged result.

![Crystal structure of PbI$_3$CH$_3$NH$_3$](image)

**Figure 3.1**: Crystal structure of PbI$_3$CH$_3$NH$_3$ in cubic phase. Pb atoms are in dark gray, I purple, N blue, C light gray, and H white.

### 3.1.1 Ground State Properties of PbI$_3$CH$_3$NH$_3$

After the converged parameters were established, atomic positions at fixed lattice constants were relaxed until the maximum atomic force is less than $10^{-3}$ Hartree/bohr$^1$, using the GGA-PBE norm-conserving pseudopotentials. We varied volume and relaxed atomic coordinates at each volume, and the total energies of the system and the volumes of the unit cell were then fit to the Vinet equation of state [44] to obtain the equilibrium volume and bulk modulus, as illustrated in Figure 3.2.

The C-N bond length can be used to gauge the size of the interior MA ion. The C-N bond length is 2.346 bohr in the equilibrium structure with a lattice constant of 6.348Å, 2.307 bohr in

---

$^1$ The number of degrees of freedom made it such that using forces much smaller than this took prohibitively long
a compressed structure with a lattice constant of 5.82 Å, and 2.37 bohr in an expanded structure with a lattice constant of 6.77 Å. This variation in size is only 3% between the largest and smallest bond length, as opposed to 16% difference in linear dimension of lattice constant.

Table 3.1: Reduced coordinates\(^2\) of MAPBI\(_3\). The starting coordinates are reported as they were provided, equilibrium coordinates rounded to two decimal places.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Starting Coordinates [43]</th>
<th>Near equilibrium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>([0.5,0.5,0.5])</td>
<td>([0.50,0.50,0.50])</td>
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<tr>
<td>I</td>
<td>([0.0,0.5,0.5])</td>
<td>([0,0.49,0.49])</td>
</tr>
<tr>
<td>I</td>
<td>([0.5,0.0,0.5])</td>
<td>([0.49,0,0.50])</td>
</tr>
<tr>
<td>I</td>
<td>([0.5,0.5,0])</td>
<td>([0.50,0.49,0])</td>
</tr>
<tr>
<td>C</td>
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<td>([-0.05,-0.06,-0.05])</td>
</tr>
<tr>
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<td>([0.09,0.08,0.08])</td>
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<td>([-0.18,0.04,-0.11])</td>
</tr>
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<td>([0.04,-0.12,-0.18])</td>
</tr>
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<td>([-0.11,-0.18,0.04])</td>
</tr>
<tr>
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<td>([0.01,0.18,0.17])</td>
</tr>
<tr>
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<td>([0.20,0.16,-0.01])</td>
</tr>
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<td>([0.18,-0.01,0.18])</td>
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<tr>
<td>Lattice (bohr)</td>
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<td>12.04</td>
</tr>
<tr>
<td>Lattice (angst.)</td>
<td>6.00</td>
<td>6.39</td>
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</table>

\(^2\) These coordinates give atomic locations as fractions of lattice constant along the lattice transform vectors. In this case with the simple cubic lattice vectors, there is only 1 lattice constant and the directions are Cartesian.
Figure 3.2: Equation of state for cubic MAPbI3. Data points shown as blue circles, fitted equation shown as black line.

The ground-state properties of PbI$_3$CH$_3$NH$_3$ have not been as extensively published, except for the lattice constant. Numbers as high as 12.21 bohr [20] to as low as 11.89 bohr [15] are reported, with our present prediction being 12.04 bohr and a bulk modulus of 22.6 GPa, using GGA-PBE and norm-conserving pseudopotentials.

3.1.2 Electronic Band Structure of PbI$_3$CH$_3$NH$_3$

At the theoretical equilibrium lattice constant we computed electronic band structures of PbI$_3$CH$_3$NH$_3$ using three methods: (1) norm-conserving GGA pseudopotentials, (2) PAW, and (3) HGH pseudopotentials, without spin-orbit interactions. We want to compare the consistency of these three methods on electronic structures. Then the band structure was calculated with spin-orbit coupling employing PWA and the HGH pseudopotential.

The electronic band structure obtained using the norm-conserving pseudopotentials indicates that cubic PbI$_3$CH$_3$NH$_3$ has a direct gap at the R point, $\left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right)$ in the Brillion zone,
with a band gap of 1.46 eV, consistent with previous non-relativistic DFT band gaps of 1.46 eV [15] and 1.38 eV [23].

![Diagram](image)

**Figure 3.3:** Electronic band structures for PbI\textsubscript{3}CH\textsubscript{3}NH\textsubscript{3}. “a”: GGA-PBE PAW without spin-orbit coupling, “b”: GGA-PBE PAW with spin-orbit coupling, “c”: LDA HGH pseudopotential without spin-orbit coupling, “d”: LDA HGH pseudopotential with spin-orbit coupling. Note the GGA norm conserving pseudopotential band structure is almost identical to that from PAW without spin-orbit coupling so it is not shown.

The PAW band structure looks almost identical to that of norm-conserving pseudopotentials, with $E_g$ reduced slightly to 1.39 eV at the R point. The HGH band structure also looks similar to those of PAW and norm-conserving pseudopotentials, as shown in Figure 3.3, while the band gap is reduced noticeably to 1.2 eV. When spin-orbit interactions were considered, the calculated electronic band structure changes dramatically and $E_g$ vastly shrunk due to the splitting in the bottom conduction bands, as illustrated on the right panels in Figure
3.3. In the case of PAW, the band gap decreases to only 0.22 eV from 1.39 eV, in good agreement with previous calculations for this material [16, 20]. For HGH pseudopotentials, $E_g$ shrinks by a similar amount when spin orbit coupling was activated. However, since the band gap was smaller in the first place, it nearly closed, which would have made the material metallic. The band gap as calculated from the HGH pseudopotentials with spin-orbit coupling was only 0.07 eV.

3.1.3: A Brief Summary

Table 3.2: Properties of cubic PbI$_2$CH$_3$NH$_3$, in comparison with previous calculations and available experimental data. Areas marked with an X indicate that the information was not present in the work. Areas marked with n/a indicate that information is not applicable to the situation. Results in the same column separated “,” are from the same work and should be taken respectively to other such results.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
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<tr>
<td>XC</td>
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<td>GGA-PBE</td>
<td>GGA-PBE</td>
<td>PBEsol</td>
<td>LDA</td>
<td>GGA-PBE</td>
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<td>GGA-PBE</td>
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<tr>
<td>Spin-orbit</td>
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<td>no</td>
<td>no, yes</td>
<td>no, yes</td>
<td>no, yes</td>
<td>no, yes</td>
<td>no, yes</td>
</tr>
<tr>
<td>Bulk modulus</td>
<td>X</td>
<td>X</td>
<td>16.4</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>22.6,X,X</td>
</tr>
<tr>
<td>(GPa)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Band Gap (eV)</td>
<td>1.52</td>
<td>2.1, 0.95</td>
<td>1.38</td>
<td>1.46, 0.53</td>
<td>1.68,0.6</td>
<td>1.51,0.46</td>
<td>1.46, 1.39, 0.22</td>
<td></td>
</tr>
<tr>
<td>Lattice constant (bohr)</td>
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<td>12.21</td>
<td>11.92</td>
<td>11.89</td>
<td>11.89</td>
<td>n/a</td>
<td>11.83</td>
<td>12.04</td>
</tr>
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<td>Measured</td>
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<td>CASTEP</td>
<td>Vasp</td>
<td>Quantum Espresso</td>
<td>Vasp</td>
<td>ABINIT</td>
<td></td>
</tr>
<tr>
<td>Psp information</td>
<td>n/a</td>
<td>PAW</td>
<td>Norm conserving</td>
<td>X</td>
<td>X</td>
<td>Norm conserving, ultrasoft</td>
<td>ultrasoft</td>
<td>Norm conserving, PAW, PAW</td>
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<td>Notes</td>
<td>Experimental</td>
<td>Used HSE Functional</td>
<td></td>
<td></td>
<td></td>
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</table>
Table 2 lists our calculated ground-state properties and the band gap of MAPbI$_3$, compared with experimental data and previous theoretical works. GGA pseudopotentials and GGA PAW agree well with the previous work. Since the HGH pseudopotentials fail to provide consistent results with other methods, and have high computational cost (due to much larger ECUT), we will use the PAW method to compute electronic structures with spin-orbit corrections. Structural optimization will be performed with GGA pseudopotentials due to the difficulty using PAW for this purpose.

3.2 MAPbF$_3$ and MASnF$_3$

Replacement of halogens could offer greater stability and tunable band gaps, and a Sn-based perovskite compound with better stability and a favorable band gap would be desirable from an environmental/safety perspective. Most previous calculations on MA-halide perovskites have used one of three halides: I, Br, and Cl, while F was largely neglected. Here we consider MAPbF$_3$ and MASnF$_3$ using GGA-PBE exchange-correlation functional.

3.2.1 PbF$_3$CH$_3$NH$_3$

We found that a 6x6x6 k-grid was enough, while the required ECUT was 55 Hartree for norm-conserving pseudopotentials and 22 Hartree for PAW (see Appendix C for convergence criteria). Using a pattern from [20], the lattice constants of the different materials decreased by around 0.3 Å as the next smaller halogen was used; the initial guess for the lattice constant would be around 10 bohr. However, the equilibrium lattice constant of this compound was merely 9.29 bohr (4.91Å). Its bulk modulus is 63 GPa, about 3 times as high as the iodine variety.

The electronic band structure of this perovskite is similar in shape to the band structures for the I-based perovskite. It also has a direct gap at point R, which is standard for these hybrid perovskite systems in cubic phase. The most noticeable difference is the massive increase in
Figure 3.4: Band Structures of PbF3CH3NH3. The upper band structure “a” is without spin-orbit coupling (PAW and pseudopotential results again look the same so only one is shown). The lower band structure “b” is PAW with spin-orbit coupling activated.
band gap. The calculated $E_g$ are 3.56 eV using norm-conserving pseudopotentials and 3.43 eV using PAW, without considering the spin-orbit interactions. The spin-orbit coupling decreases the band gap by roughly 1 eV as before in I-based compound, reducing $E_g$ to 2.5 eV, which GW corrections would raise. In conclusion, this material has a band gap too high to be used for photovoltaic applications.

### 3.2.2 SnF$_3$CH$_3$NH$_3$

We also investigated a Sn-based perovskite, SnF$_3$CH$_3$NH$_3$. We tested the Sn pseudopotential and PAW dataset by computing the lattice constant and bulk modulus of gray tin, which has a diamond cubic structure. Our results are in good agreement with previous calculations. Our DFT calculations and Vinet equation fit predict that the cubic SnF$_3$CH$_3$NH$_3$ has an equilibrium lattice constant of 9.71 bohr, much larger than that of its Pb counterpart. Also, it has a bulk modulus of 14.8 GPa, which is much smaller than that of PbF$_3$CH$_3$NH$_3$ and more similar to the iodine containing perovskites.

The electronic band structure of this material is different from those for Pb-based perovskites, since it becomes an indirect-gap material, as plotted in Figure 3.6. Using norm-conserving pseudopotentials, we find that the direct gap at R is 3.48 eV, but at past R in the direction of X the conduction band moves slightly lower such that it is only 3.4 eV above the top of the valence band. PAW calculations without spin-orbit coupling also contain this feature of an extra trough between points R and X at the bottom conduction band. For PAW, the gap at R was 3.46 eV, and the indirect gap is 3.37 eV, slightly lower than those obtained using norm-conserving pseudopotentials.

Spin-orbit coupling did not have as large of an effect on the band gap for this Sn containing materials as it did for the for the Pb containing material, which is consistent with
Figure 3.5: Band Structures of SnF\textsubscript{3}CH\textsubscript{3}NH\textsubscript{3}. “A” does not include spin orbit coupling. “B” accounts for spin-orbit coupling; note that this restores the direct gap at R.

results found for other halides in other work [20, 16]. However, the spin orbit coupling was enough to restore the direct gap at R. With spin-orbit coupling activated, the band gap is
now 3.24 eV. GW corrections would raise this further, leaving this material as an unsuitable absorber for photovoltaics.

3.3 Formamidinium Perovskite

The systems studied previously in our investigation are all cubic, and Lang et al. [20] modeled cubic crystal phases of Pb and Sn based formamidinium\(^3\) perovskites with iodine, bromine, and chlorine. Experimentally however, PbI\(_3\)HC(NH\(_2\))\(_2\) was not found to be in a cubic phase at solar cell working temperatures; although Stoumpos et al. claim that a high-symmetry phase such as cubic may occur at higher temperatures than they tested [18]. As temperature decreases, the unit cell of the stable crystal structure of PbI\(_3\)HC(NH\(_2\))\(_2\) becomes larger and more complicated. At room and solar cell operating temperatures, two separate phases of PbI\(_3\)HC(NH\(_2\))\(_2\) are present\(^4\). The first one has a trigonal lattice with 36 atoms per unit cell, which has a band gap of 1.45 eV [18], and the other one has a hexagonal lattice with 24 atoms per unit cell, which has a much higher (but unspecified) band gap [18]. One of the main goals of this project is to accurately model these two crystal phases, in order to determine their relative energetics and electronic properties.

Due to the complexity of these structures, we used a few different models: (1) usage of space group defined coordinates and (1a) experimental unit cell or (1b) theoretical equilibrium unit cell volume; (2) Full relaxation of atomic positions and (2a) experimental unit cell or (2b) at theoretical equilibrium volume. Calculation of ground-state physical properties such as bulk moduli was performed with (1) and (2). Energy differences between the crystal phases were

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\(^3\) The chemical formula is written differently in [20] which caused early confusion

\(^4\) Specifically these phases can be found at temperatures above 200K to at least 400K [18]
computed assuming (1a), (1b), (2a), and (2b), respectively, while the electronic structure calculations employed model (1a).

For these calculations, a k-point grid of 6x6x6 was found to be sufficient, and the plane wave energy cutoff was set to 55 Hartree. For PAW results, the plane wave energy cutoff was 25 Hartree and the double-grid cutoff was set to 75 Hartree. The GGA-PBE exchange-correlation functional was used.

### 3.3.1 Yellow Phase Crystal Structure

Stoumpos et al. did extensive crystallographic tests on various phases of various perovskite materials [18]. The supplemental crystallography files associated with [18] gave coordinates of some of the atoms for the yellow phase, this initial configuration is shown in the top left panel of Figure 3.6.

Information about where the other atoms would be located can be found by using the given space group, P63mc. The space group gives lists of equivalent positions in the unit cell (equivalently could be defined by symmetry operations), which should be occupied by the same types of atoms. In the case of this material it seems that the FA ions are treated as a single entity centered on the carbon atom for purposes of defining the space group. Usage of the given space group provided the correct stoichiometric number of I, Pb, and C atoms, and provided information as to where the other N atoms should go. Once the space group is used, a plausible structure (minus the hydrogens) can be obtained, which is also shown in Figure 3.6, panels “B” and “C”.

The location of the H atoms was estimated from illustrations of the FA ion [18] and bond lengths in methane and ammonia. Then the coordinates of this material were relaxed using model 1 (see 3.3), the N atoms and H atoms were allowed to move, while the C atoms, I atoms, and Pn
atoms were kept fixed in coordinates determined by the space group. Our calculations predict that this system has an equilibrium unit cell size of 3877.5 bohr$^3$ and a bulk modulus of 16.8 GPa. This system has the extra space group constraint and is not fully relaxed.

**Figure 3.6:** Atomic positions of the yellow phase. “a” shows initial coordinates provided in the supplemental crystallography files of [18]. “b” and “c” are the unit cell atoms as could be determined from the information in these files given the space group. “c” shows a view from the top and lists the experimental geometry of the lattice and space group. “d” is an illustration from [18] provided for comparison. The color scheme for atoms is the same that was used before in Figure 3.1 except for in “d”, in which lead is green, iodine is purple, carbon is blue, and nitrogen is pink.

When this system is allowed to fully relax these properties constants change. The atoms do not move more than a few percent from their starting positions in most cases (with the
exception of the interior geometry of the FA atoms as the lattice constant is changed, see
discussion of MA bond length and Table 2) . The equilibrium primitive cell size is 4127.1 bohr$^3$,
which is roughly 6% greater than the other, but this translates to a difference in linear dimensions
of only 2%$^5$ . The large change was in the bulk modulus which massively decreased to 6.9 GPa.

Table 3.3: Reduced Coordinates for Yellow phase. Coordinates enforced by space group given to four
decimal places, those obtained through relaxation given to two decimal places.

<table>
<thead>
<tr>
<th></th>
<th>Full relax (2b)</th>
<th>Space Group+Exp Lattice (1a)</th>
<th>Space Group+Relaxed lattice (1b)</th>
<th>Exp Lattice (2a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>[0.00, 0.00, 0.00]</td>
<td>[0.0000, 0.0000, 0.0000]</td>
<td>[0.0000, 0.0000, 0.0000]</td>
<td>[0.00, 0.00, 0.00]</td>
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<tr>
<td>Pb</td>
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<td>[0.0000, 0.0000, 0.5000]</td>
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<td>[0.8312, 0.1688, 0.2510]</td>
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<tr>
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<tr>
<td>H</td>
<td>[0.63, 0.09, 0.64]</td>
<td>[0.63, 0.08, 0.64]</td>
<td>[0.63, 0.09, 0.64]</td>
<td>[0.63, 0.09, 0.64]</td>
</tr>
<tr>
<td>H</td>
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<td>[0.92, 0.38, 0.64]</td>
<td>[0.91, 0.38, 0.64]</td>
<td>[0.91, 0.37, 0.64]</td>
</tr>
<tr>
<td>H</td>
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<td>[0.90, 0.56, 0.66]</td>
<td>[0.89, 0.56, 0.66]</td>
<td>[0.90, 0.56, 0.67]</td>
</tr>
<tr>
<td>H</td>
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<td>[0.44, 0.1, 0.66]</td>
<td>[0.45, 0.10, 0.66]</td>
<td>[0.44, 0.10, 0.66]</td>
</tr>
</tbody>
</table>

Volume(bohr$^3$) 4127.1 3467.2 3877.5 3467.2

$^5$ Both of these are greater than the listed experimental volume of 513.27 Angstrom$^3$, (3467.2 bohr$^3$) but the error in linear dimension is 6% for the fully relaxed structure and 3.8% for the space group structure.
3.3.2 Black Phase Crystal Structure

The desirable black phase of this compound is simpler than the low-temperature phases but it is more complex than the unwanted yellow phase. This increased complexity leads to increased computational cost. Before any computations could be performed, the coordinates of the atoms had to be obtained. The supplemental crystallographic files [18] contained information about the positions of certain atoms as well as the space group, which allowed for possible positions of the other atoms to be calculated, following a similar process to that outlined in 3.3.1.

Positions of the other atoms show an interesting pattern. Cubic cages of the iodine and lead atoms would form, although some of the atoms would be in a different unit cell. This does not occur for the yellow phase where the lead atoms are arranged linearly. An octahedral substructure is also clearly visible in Figure 3.7, panel b. It is clear that they correspond, with the same restrictions that redundant atoms on edges (which would be counted by ABINIT as from different unit cells) are not shown, and the third “nitrogen” atoms are not present. This view from the top (panels C and D) has additional complication in that leads and carbons are superimposed.

This crystal was particularly challenging from a structural optimization standpoint due to the number of degrees of freedom present. Using model (1), the ground state volume was 5746.4 bohr$^3$ and the bulk modulus was 14.0 GPa. In this case the ground state volume is 8.4% above the listed experimental volume, which corresponds to an error in linear dimensions of 2.7%. Unlike with the previous yellow phase calculations when the atomic positions were allowed to fully relax (model 2) the material became stiffer and the equilibrium size agreed with the experimental data better. The bulk modulus increased to 17.8 GPA and the equilibrium volume was 5456.1 bohr$^3$. This corresponds to an error in volume from the experimental value of about 5%, so the error in lattice constant would be 1.7%.
Figure 3.7: Atomic positions of the Black phase. “a” shows initial coordinates provided in the supplemental crystallography files of [18]. “b” and “c” are the unit cell atoms as could be determined from the information in these files given the space group, note the formation of cage structures visible in “b”. “c” shows a view from the top. “d” is an illustration from [18] provided for comparison. The color scheme for atoms is the same that was used before in Figure 3.1 except for the “d”, in which lead is green, iodine is purple, carbon is blue, and nitrogen is pink.

Table 3.4: Summary of physical properties for both crystal phases. Model 1 overestimates the volume of the unit cell by a similar relative amount in both cases, Model 2 performs less consistently.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Parameter</th>
<th>Model 1</th>
<th>Model 2</th>
<th>Experimental data [18]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yellow</td>
<td>Unit Cell Volume (Bohr^3)</td>
<td>3877.5</td>
<td>4127.1</td>
<td>3467.2</td>
</tr>
<tr>
<td></td>
<td>Bulk Modulus (Gpa)</td>
<td>16.8</td>
<td>6.9</td>
<td></td>
</tr>
<tr>
<td>Black</td>
<td>Unit Cell Volume (Bohr^3)</td>
<td>5746.4</td>
<td>5456.1</td>
<td>5194.0</td>
</tr>
<tr>
<td></td>
<td>Bulk Modulus (Gpa)</td>
<td>14</td>
<td>17.8</td>
<td></td>
</tr>
</tbody>
</table>
Table 3.5: Black phase reduced atomic coordinates. Coordinates enforced by space group given to four decimal places, those obtained through relaxation given to two decimal places.

<table>
<thead>
<tr>
<th></th>
<th>Full relax (2b)</th>
<th>Space group+ Exp lattice (1a)</th>
<th>Space Group +Relaxed Lattice (1b)</th>
<th>Exp. Lattice (2a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>0.67, 0.34, 0.82</td>
<td>0.6667, 0.3333, 0.8300</td>
<td>0.6667, 0.3333, 0.8300</td>
<td>0.67, 0.34, 0.82</td>
</tr>
<tr>
<td>Pb</td>
<td>0.34, 0.66, 0.16</td>
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<td>0.3333, 0.6667, 0.1700</td>
<td>0.34, 0.66, 0.16</td>
</tr>
<tr>
<td>Pb</td>
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<td>0.0000, 0.0000, 0.5000</td>
<td>0.0000, 0.0000, 0.5000</td>
<td>0.02, 0.01, 0.50</td>
</tr>
<tr>
<td>I</td>
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<td>0.1662, 0.8338, 0.3376</td>
<td>0.1662, 0.8338, 0.3376</td>
<td>0.23, 0.89, 0.33</td>
</tr>
<tr>
<td>I</td>
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<td>0.1662, 0.3324, 0.3376</td>
<td>0.1662, 0.3324, 0.3376</td>
<td>0.10, 0.29, 0.29</td>
</tr>
<tr>
<td>I</td>
<td>0.67, 0.82, 0.34</td>
<td>0.6667, 0.8338, 0.3376</td>
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<td>0.67, 0.82, 0.34</td>
</tr>
<tr>
<td>I</td>
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<td>0.8338, 0.6667, 0.6624</td>
<td>0.8338, 0.6667, 0.6624</td>
<td>0.82, 0.68, 0.67</td>
</tr>
<tr>
<td>I</td>
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<td>0.8338, 0.1662, 0.6624</td>
<td>0.8338, 0.1662, 0.6624</td>
<td>0.89, 0.29, 0.67</td>
</tr>
<tr>
<td>I</td>
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<td>0.3324, 0.1662, 0.6624</td>
<td>0.29, 0.10, 0.71</td>
</tr>
<tr>
<td>I</td>
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<td>0.5000, 0.5000, 0.0000</td>
<td>0.5000, 0.5000, 0.0000</td>
<td>0.54, 0.46, 0.06</td>
</tr>
<tr>
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<td>0.5000, 0.0000, 0.0000</td>
<td>0.5000, 0.0000, 0.0000</td>
<td>0.48, 0.01, 0.01</td>
</tr>
<tr>
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<td>0.0000, 0.5000, 0.0000</td>
<td>0.00, 0.55, 0.01</td>
</tr>
<tr>
<td>C</td>
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<td>0.3333, 0.6667, 0.6200</td>
<td>0.3333, 0.6667, 0.6200</td>
<td>0.33, 0.67, 0.62</td>
</tr>
<tr>
<td>C</td>
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<td>0.6667, 0.3333, 0.3800</td>
<td>0.67, 0.33, 0.38</td>
</tr>
<tr>
<td>C</td>
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<td>0.0000, 0.0000, 0.0000</td>
<td>0.0000, 0.0000, 0.0000</td>
<td>0.00, 0.00, -0.01</td>
</tr>
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<td>0.35, 0.54, 0.61</td>
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<td>0.46, 0.83, 0.62</td>
</tr>
<tr>
<td>N</td>
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<td>0.54, 0.35, 0.39</td>
</tr>
<tr>
<td>N</td>
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<td>0.08, 0.16, -0.02</td>
<td>0.08, 0.16, -0.02</td>
<td>0.09, 0.17, -0.02</td>
</tr>
<tr>
<td>N</td>
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<td>0.83, 0.46, 0.38</td>
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<tr>
<td>N</td>
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<td>-0.16, -0.10, -0.02</td>
<td>-0.16, -0.10, -0.01</td>
<td>-0.17, -0.09, -0.01</td>
</tr>
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<td>0.21, 0.65, 0.63</td>
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</tr>
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<td>H</td>
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<td>0.65, 0.21, 0.37</td>
<td>0.64, 0.20, 0.37</td>
</tr>
<tr>
<td>H</td>
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<td>0.07, -0.06, 0.02</td>
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<td>0.07, -0.07, -0.01</td>
</tr>
<tr>
<td>H</td>
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<td>0.46, 0.54, 0.60</td>
<td>0.47, 0.55, 0.61</td>
</tr>
<tr>
<td>H</td>
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<td>0.58, 0.86, 0.62</td>
<td>0.58, 0.87, 0.62</td>
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</table>
Table 3.5, continued

<table>
<thead>
<tr>
<th></th>
<th>Full relax (2b)</th>
<th>Space group+ Exp lattice (1a)</th>
<th>Space Group +Relaxed Lattice (1b)</th>
<th>Exp. Lattice (2a)</th>
</tr>
</thead>
<tbody>
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<tr>
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<td>{0.55, 0.47, 0.39}</td>
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<td>{0.91, 0.43, 0.37}</td>
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<td>{0.03, 0.23, -0.04}</td>
<td>{0.04, 0.24, -0.02}</td>
</tr>
<tr>
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<td>{0.21, 0.23, -0.01}</td>
<td>{0.21, 0.23, -0.01}</td>
<td>{0.22, 0.23, -0.01}</td>
</tr>
<tr>
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<td>{-0.2217, -0.23, 0.00}</td>
<td>{-0.22, -0.22, 0.00}</td>
<td>{-0.22, -0.22, -0.00}</td>
</tr>
<tr>
<td>Volume (Bohr^3)</td>
<td>5456.1</td>
<td>5194</td>
<td>5763.3</td>
<td>5194</td>
</tr>
</tbody>
</table>

3.3.3 Energetics

As both the black and yellow structures contain integer amounts of the same chemical formula, their energies can be compared directly. Note that the total energy is dependent on the pseudopotentials used, for instance a core correction could change the result, but since the same pseudopotentials were used a direct comparison should be possible. The bottom two rows of Table 6 are PAW results, the final row accounting for spin orbit coupling. The “Unit” in Table 6 is a chemical unit of PbI$_3$HC(NH$_2$)$_2$, the black phase contains three of these per crystal unit cell and the yellow phase contains two of these per crystal unit cell.

Note that in all models the yellow system has a slightly lower energy (more binding energy) per unit of chemical formula. Stoumpos et al. indicate that conversion from the yellow to the black phase occurs when the yellow phase is heated. This is consistent from a
thermodynamic standpoint when treating an equilibrium mixture of both phases given the basic relation between the energies.

**Table 3.6:** Energy differences between two phases of PbI₂HC(NH₂)₂ in the various models

<table>
<thead>
<tr>
<th>Model Description</th>
<th>Energy Difference (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space Group, Relaxed lattice (1b)</td>
<td>-0.22</td>
</tr>
<tr>
<td>Full relaxation (2b)</td>
<td>-0.29</td>
</tr>
<tr>
<td>Relaxed atoms, Experimental lattice (2a)</td>
<td>-0.07</td>
</tr>
<tr>
<td>Space group, Experimental lattice (1a)</td>
<td>-0.16</td>
</tr>
<tr>
<td>Space group, Experimental lattice (1a)+PAW</td>
<td>-0.19</td>
</tr>
<tr>
<td>Space group, Experimental lattice(1a)+SO</td>
<td>-0.16</td>
</tr>
</tbody>
</table>

**3.3.4 Formamidinium Perovskite Electronic Structures**

To calculate the electronic band structures and densities of states for these materials the experimental lattice geometry and enforced space group configuration were used (model 1a). Due to the large number of electrons present in the systems and the fact that some electrons could be tightly bound to the formamidinium ions, certain bands are significantly below the Fermi energy and are not relevant to optical absorption or emission. For clarity, these low lying bands are excluded in Figure 3.8 and the density of states and band structures are only shown to within 5 eV of the Fermi level, but calculations included bands well outside that range in both directions. A dense 16x16x16 k-grid was used to compute electron density of states (DOS), and
the paths in the Brillion zone for a hexagonal unit cell\(^6\) were taken to plot electronic band structures.

We note that the band gap difference is evident even at a DFT level. Using the same norm-conserving pseudopotentials as were used for structural optimization, the band gap for the yellow and black phases were predicted to 2.81 and 1.48 eV, respectively. As the location of the band edge was unknown and may not be present on the band structures both of these gaps were obtained using the density of states. It turns out the direct gap at A \((0,0,\frac{1}{2})\) in the black phase is equal to the gap in the DOS plot. The yellow phase indirect gap between the K \((1/3,1/3,0)\) point (valence) and the \(\Gamma\) \((0,0,0)\) point (conduction) agrees with the DOS gap.

The significant effect of spin-orbit coupling in both the MAPbI\(_3\) test case and the new MAPbF\(_3\) indicate that changes to the band gap from this could be non-negligible. As before, the implementation of spin orbit coupling requires PAW. This also allows for a consistency check, if the results were significantly off than one might expect something was wrong. The band structure and DOS calculated this way are fairly consistent with the pseudopotential results. The band gap of the black phase using PAW, as determined by the DOS, is 1.39 eV. This agrees exactly with the band gap at the A point in the band structure. The band gap for the yellow phase is 2.64 eV, again determined by the DOS. Both of these are about 6% smaller than the corresponding band gaps computed using norm-conserving pseudopotentials.

---

\(^6\) [18] lists the crystal system of the yellow phase as hexagonal and lists the crystal system of the black phase as trigonal, which is ambiguous between hexagonal and rhombohedral. However, the lattice vector angles of the unit cell for the black crystal structure were consistent with hexagonal and inconsistent with a rhombohedral representation. Further, when a hexagonal path is used, a direct gap point which agrees with the DOS is captured, whereas when a rhombohedral path is used no such point is found.
Figure 3.8: Band structures and density of state graphs for PbI3HC(NH2)2. “a” and “b” graphs are the yellow phase and the “c” and “d” graphs are the black phase. Graphs “a” and “c” were obtained with norm conserving pseudopotentials and graphs “b” and “d” employed PAW.

There are a few noteworthy properties of the electronic structures. The DFT band gap for the black phase is in good agreement with experimental data; the band gap is listed as being 1.45 eV [18]. From this and the behavior of the other perovskites studied with GW and spin orbit coupling [16, 23], it seems likely that the spin-orbit and GW effects cancel similarly to the Pb-based MA perovskites. References to the exact measured band gap of the yellow phase were not found, but the fact that it is described as being yellow indicates that the band gap is probably between 2.5 eV and 3 eV. Although the band gap is too high for photovoltaics, the band structure and DOS indicate a splitting of the conduction band at the uncorrected DFT level (see panels “a” and “b” of Figure 3.8). This is an unusual property that could potentially have applications.
3.3.5 Spin-Orbit Coupling Effects

For the yellow phase, the valence bands are relatively unchanged, but there are notable changes to the conduction bands. The band gap decreases to 2.27 eV with some bands being heavily decreased forming a sort of island, which could lead to interesting optical behavior. Also of note is that the original location of the splitting in the conduction band has a different behavior. States in the upper band were decreased in energy to a point such that there is now an energetic continuum of states at those energies, but the bands do not contact anywhere on the band structure.

The black phase behaved much more similarly to the previous methylammonium based materials with regard to spin-orbit coupling than the yellow phase. There was a strong band gap reduction due to a high deformation of the bands near the direct gap point. In this case, the band gap reduces to 0.22 eV. While it looks like there is a mismatch between the band gap from density of states and band structure, they actually agree but the density of states gap looks larger due to the fact that the density near the band gap is lower than can be seen on this scale. This reduction is very similar to that found by Kim et al, but their initial band gap is higher [25].

---

7 This is similar to the behavior of metalloids, although within the conduction bands as opposed to at the band gap
Figure 3.9: Band structures and Density of states graphs for PbI3HC(NH2)2 with spin orbit coupling included. Graph “a” of the yellow phase band structure shows some unusual behavior in that several bands are lowered past the main body of the conduction band. Graph “b” of the black phase band structure shows the significant reduction in the conduction band minimum at the direct gap point, similar to the cubic systems we previously studied.
CHAPTER 4

CONCLUSIONS

We conclude with a brief summary of our work and thoughts about the future of this topic.

4.1 Fluorine Perovskites

These F-MA-based perovskites have interesting properties that break some of the patterns associated with the heavier halogens. For instance, the Pb-based perovskite has a smaller lattice constant than the corresponding Sn-based perovskite. In addition, the Pb-based perovskite is more incompressible than the other perovskite systems we studied. The Sn-perovskite was surprising in that the DFT band structure no longer had a direct gap at R, which is described as being a universal feature of these cubic perovskite systems [20]. However, the direct gap is restored when spin-orbit coupling is taken into account. Finally, band gaps of F-based perovskites are much too high for photovoltaic applications. It might be of some limited use in tandem with something else in a multi-junction cell, or more likely as a possible dopant in a lower band gap material to improve stability, as our colleagues at NREL claim chlorine can be used for this purpose.

4.2 Formamidinium perovskites

These particular crystals are more complex than the cubic perovskites, which have been previously studied theoretically. The black phase shares many properties with the well-studied MAPbI$_3$ cubic structure. They both have small bulk moduli on the order of 20 GPa, and their DFT band gaps are very similar, which is in good agreement with the experimental data. In the case of MAPbI$_3$, this is because the significant spin-orbit coupling effect on band gap almost
perfectly cancels the many-body correction to the band gap [16, 23]. PbI₃HC(NH₂)₂ has similar properties, including a spin-orbit coupling of similar magnitude, so presumably the many-body correction would also largely cancel the spin orbit correction for this crystal phase as it does for a similar crystal phase [24].

On the other hand, the yellow phase could have interesting properties due to the unusual structure of the conduction band. When spin-orbit coupling is activated, some bands are pulled down off of the main conduction band, and in all cases there is an area shortly above the band gap where the bands do not cross, although the exact behavior in the density of states changed whether pseudopotentials, PAW, or PAW with spin orbit coupling were introduced.

Ideally, the black phase would be highly favorable from an energetic standpoint or there would be some sort of property such as vastly different behavior under pressure that would allow for the black phase to be isolated easily for photovoltaics. This is unfortunately not the case. The yellow phase was slightly favorable energetically in all models.

4.3 Future of Perovskite Photovoltaics

There is a great deal more work that could be done in this field. From the experimental side, finding methods of increasing stability is of paramount concern. Conventional photovoltaics can last for decades, so the current short lifespan of perovskites when exposed to water or air is a major detriment. Additionally it would be desirable to improve efficiencies by refining manufacturing techniques. More fundamentally, similar compounds to those already in use should be investigated to determine if they would be suitable for photovoltaics.

It is in this last area that theory is best suited to help. However, there are many complications which have to be dealt with. A large factor in whether a material is a possible candidate for photovoltaics is its band gap. Theoretical determination of the band gap for these
materials in general requires treatment of spin orbit coupling in addition to many-body corrections. Several organic metal halide perovskites have not yet been studied to this degree. However, we observe that for PbI$_3$CH$_3$NH$_3$ [16, 24], SnI$_3$CH$_3$NH$_3$ [16], and PbI$_3$HC(NH$_2$)$_2$ [24] the combined calculation gives a similar band gap to taking adding the corrections to the DFT gap separately. This could be advantageous as many programs, such as ABINIT and BerkelyGW, do not yet implement GW calculations with spin orbit coupling. Also, many of these are direct gap materials, so a GW correction would only need to be computed at one point. Despite these advantageous properties, GW calculations of these materials are computationally very challenging should not be taken lightly.

Strong absorption of light is another attribute needed to perform well as a photovoltaic collector. Absorption properties can also be theoretically predicted with BSE calculations. For these calculations it is almost certain that spin orbit coupling would have to be taken into account directly in order to obtain a meaningful result. As with GW corrections, many software packages do not yet have the ability to perform BSE calculations with spin orbit coupling.

A final difficulty is illustrated by the yellow phase of PbI$_3$HC(NH$_2$)$_2$; there might be certain other compound which take this crystal structure, or even something completely different. If the crystal structure is not experimentally known, one might compare the energies of various crystal phases to determine if a crystal phase that has desirable band gap and absorption is stable. Luckily, comparatively simple DFT is sufficient for the ground state energy calculations needed to determine this.
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[16] P. Umari, E. Mosconi, F. De Angelis, “Relativistic GW calculations on CH$_3$NH$_3$PbI$_3$ and CH$_3$NH$_3$SnI$_3$ perovskites for solar cell applications”, Scientific Reports 4, Article 4467 (2014)


[43] Personal communication with Tingting Shi, 6-27-2014


APPENDIX A: VINET EQUATION

Equations of state are relationships between various thermodynamic properties in material systems, a simple and famous equation of state is the Ideal Gas Law $PV = nRT$.

Equations of state for solids tend to be more complicated than the ideal gas law, and have more parameters that are dependent on the particular system being modeled. An early equation of state for solids is known as the Murnhagan equation of state, now the similar and more accurate Vinet equation of state is used [44]. The Vinet equation of state was first described in 1987 in “Temperature effects on the universal equation of state of solids” [44], in which the authors state that if phase transitions are forbidden, the equation of state only requires the three parameters: equilibrium volume, isothermal bulk modulus, and bulk modulus pressure derivative; which will describe the solid at any given constant temperature. In practice, the Vinet equation is capable of describing ionic, metallic, and covalent solids.

$$P = 3B \frac{1-X}{X^2} e^{2(\frac{\partial B}{\partial P} - 1)(1-X)} \quad (A.1)$$

In (A.1) is the isothermal bulk modulus, $\frac{\partial B}{\partial P}$ is the bulk modulus pressure derivative, and

$$X = \frac{3}{\sqrt[3]{V_o}}$$

with $V_o$ being equilibrium volume.

Calculation of physical properties was done with a FORTRAN program. Initial data regarding total energy as calculated by ABINIT and primitive cell volume were fit to the Vinet equation of state. This program gave good results for simple systems like crystalline silicon and an analogous structure known as “gray” tin, as well as for the more advanced PbI$_3$CH$_3$NH$_3$ perovskite test case.

For instance, it is known that crystalline silicon has an equilibrium lattice constant of 5.43 Angstroms (10.26 bohr), a bulk modulus of 98.8GPa, a bulk modulus pressure derivative of 4.09
[35]. Crystalline silicon is a simple system (for modern computers) and theoretical DFT calculations reproduce these numbers well, with slight variation from usage of different exchange correlation functionals[35]. In the case of the following calculations, LDA exchange correlation and an LDA silicon pseudopotential from the ABINIT tutorials were used. The results from the VINET program were excellent. The equilibrium volume of the primitive cell was 265.338 bohr$^3$, which corresponds to a lattice constant of 10.2 bohr or 5.4 Angstrom. The calculated bulk modulus was 96.255 GPa, and the pressure derivative of the bulk modulus was 4.276. The graphs of the fitting are shown below; the graph of total system energy vs. primitive cell volume shows both the fit equation as output by the FORTRAN program in black as well as the initial data points from ABINIT calculations marked in blue.

![Graph of total system energy vs. primitive cell volume](image)

**Figure A.1:** Results of fitting to the Vinet equation for silicon, data from ABINIT is blue and the fitted energy vs primitive cell volume curve is shown in black.
Figure A.2: The program also outputs a graph of pressures versus primitive cell volume from the Vinet equation.
APPENDIX B: PSEUDOPOTENTIALS AND OPIUM

Pseudopotentials are potential functions which approximate the physical potential and true wave function beyond a certain radius, but have smoother behavior towards their cores for computational ease. This is partly done by treating certain electrons as “core” and combining them with the nucleus as a single entity [33], which is a suitable approximation in many systems where only the valence electrons contribute to interaction behavior.

There are several different types of pseudopotential. Two families are the ultrasoft pseudopotentials and the Norm-conserving pseudopotentials. In the case of pseudopotentials, “soft” refers to convergence with respect to energy and corresponds to lower energy plane waves required for modeling, and “hard” refers to higher energy plane waves required to model.

![Graph)](image)

**Figure B.1:** A singular $1/r$ potential in blue and an approximating smooth nonsingular pseudopotential in red ($V(r) = -\frac{2}{\pi} \text{ArcTan}[5r]/r$). The potential functions matching away from the origin is not sufficient, the wave functions they produce should also match.
Figure B.2: Hydrogen wave functions from OPIUM: the dotted pseudo wave function matches well with the solid physical wave function.

Figure B.3: Iodine shows more of a difference: inside the cutoff (shown by vertical lines) the real wave functions rapidly oscillate while the pseudo wave functions do not, but outside the cutoff they match perfectly.
Ultrasoft pseudopotentials have the advantage of being very easy to implement from a computational standpoint, however, they do not preserve normalization of the density outside the core region [45]. Norm-conserving pseudopotentials are explicitly designed to preserve normalization of density, but are often more computationally challenging than ultrasoft. Due to the computational ability available in modern computers, no ultrasoft pseudopotentials were used in this project, all pseudopotentials were norm conserving. Pseudopotentials are also classified by which exchange correlation functional they use. Finally, there are a variety of schemes for representing pseudopotentials. Trollier-Martins type pseudopotentials were used for most of the calculations, and should be assumed whenever pseudopotentials are mentioned unless stated otherwise.

Hartwigsen-Goedecker-Hutter pseudopotentials (referred to as HGH) were tested due to the ability to model the effects of spin-orbit coupling; any results from HGH pseudopotentials will be clearly labeled as such. HGH pseudopotentials have a relatively simple analytic form in both real and Fourier space [46], with adjustable parameters to model different types of atoms. These were created by generalizing the earlier Gaussian dual space pseudopotentials to a fully relativistic calculation based on the Dirac equation, which is why they are suitable for spin-orbit calculations.

Historically, pseudopotentials were originally created by manually creating functions that had the desired properties such as recreating atomic eigenvalues and wave function shapes. These were not norm-conserving in general and had no well-defined method of production [45]. Methods of rigorously creating pseudopotentials now exist with various properties via software such as OPIUM. OPIUM is capable of generating pseudopotentials with various schemes, such as Kerker, optimized/RRKJ, and Trollier-Martins[47], in multiple file formats supported by
different programs such as ABINIT. The cutoff radius can be changed when generating the pseudopotential, with the tradeoff of small cutoff radius leading to more “transferable” pseudopotentials, but these pseudopotentials require higher energy plane waves to accurately model. Small cutoff radius increases the energy of the plane waves due to a property of Fourier transforms: when something is confined in position space its size in frequency space increases\(^8\).

In terms of pseudopotentials, “Transferability” refers to how well the pseudopotential performs when it is put under conditions different from those in which it assumed during generation. It is possible to generate pseudopotentials which recreate wave functions for configurations other than neutral atoms. In a halogen for instance, it might be prudent to choose an ionized “reference” configuration, although if the transferability is good enough then the reference configuration should not matter.

Other available options for OPIUM include choice of exchange correlation functional, energy cutoff, treatment of core states, and number of Bessel functions used to create the pseudopotential [48]. The core states can often be ignored, which is called the frozen core approximation [33]. However, there are instances where electrons that are not considered valence normally have effects on the valence electrons beyond what could be safely treated this way. In instances where such effects occur, the pseudopotential can model these as “semicore” states, which are treated similarly to valence states [49]. Also, sometimes the density of core electrons significantly extends into the region of interest; in this case a partial core correction can be

\[^8\] This property can be used as an alternate derivation of the standard position-momentum Heisenberg Uncertainty principle, as well as the energy-time uncertainty principle, which is not as easily derived from the standard noncommutation procedure due to the lack of a time operator.
performed by which the actual core density inside the region of interest is replaced by a smooth function which matches in that region.
APPENDIX C: PROCEDURE FOR TESTING CONVERGENCE

There are several parameters in ABINIT which need to be adjusted to get accurate enough results in a reasonable time frame. The two that were applicable for every system tested are ECUT (the highest energy for the plane waves used to Fourier expand the wave function) and the k-point grid (which/how many points in reciprocal space are used- analogous to momenta in real space). The procedure used to evaluate convergence of ECUT was usually simple: choose a k-point grid for which you expect the results to be converged, then simulate the system in ABINIT using progressively higher ECUT values. These ECUT values and their corresponding output values for a parameter (total energy was used, although in principle something else could be) are then fit to an exponential decay curve using Mathematica. As a first illustrative example of this, the results from an early calculation of PbI$_3$CH$_3$NH$_3$ (prior to the adoption of the custom made iodine pseudopotential) are shown.

![Sample ECUT convergence](image)

**Figure C.1:** ECUT convergence data fitting. Data points from ABINIT are shown in red, and Mathematica’s fitted exponential decay is shown in blue.

Due to what is probably a bug in Mathematica’s fitting capabilities, the values of ECUT cannot be too high or a reliable fit will not be obtained. When this occurred (which was most
cases), the values of ECUT were divided by 10 then the equation fit. Note that the units along the x axis in Figure C.1 are in tens of Hartrees. Figure C.2 shows what occurs when these numbers are given their actual values: Mathematica fits to some strange curve that does not even have the correct asymptotic behavior.

![Sample ECUT convergence Problem](image)

**Figure C.2:** Mathematica Makes Mistake!

After an equation was obtained, an acceptable level of error was chosen (this project used 3meV/atom) and the equation was inverted to determine at what ECUT the total energy should be within tolerance from the asymptote. For the example above, the (properly done) fitting was calculated as \( F(\text{ECUT}) = 0.360274 \cdot e^{-3.27744 \cdot \text{ECUT}} - 1.28727 \), but due to the unit change care is required to invert \( F \) to obtain an estimate for the value of ECUT that results in a converged calculation. First, note that \( F = A + T \), where \( A \) is the asymptotic value and \( T \) is the tolerance. It is clear which part of \( F \) corresponds to \( A \), so that can be subtracted from both sides, leaving \( T = 0.360274 \cdot e^{-3.27744 \cdot \text{ECUT}} \). Further, \( T \) is determined from the error criterion and the number of atoms in the unit cell, leading to:

\[
T = \frac{3\text{meV}}{\text{atom}} \cdot 12(\text{atoms}) \cdot \frac{1\text{Ha}}{27211\text{meV}} \cdot \frac{\text{ETU}}{100\text{Ha}} = 1.323 \cdot 10^{-5} \text{ETU} \quad (C.1)
\]
where ETU is energy total units which for the fitted dataset is equivalent to 100 Hartrees. Next use algebra to get an expression for ECUT:

$$ECUT = \frac{l n\left(\frac{1.323 \times 10^{-5}}{0.360274}\right)}{-3.27744} \approx 3.12$$  \hspace{1cm} (C.2)

Note that this value is in ECUT fitting units, so the actual value in Hartrees used by ABINIT will be ten times as high. Another parameter for PAW that is similar is pawecutdg, for which the procedure for testing convergence is identical. In practice values of these parameters that were slightly higher than what was predicted to be converged were used in calculations to improve chances of convergence if the fit was off.

The k grid convergence can be similar (but is not always), although it takes a different turn due to the nature of the variable. While ECUT is relatively continuous, the k point number is necessarily discrete. Further, only certain types of k point grid would have important k points in them\(^9\). These particular k point grids are used with a high ECUT that is either expected to be converged or an ECUT that was indicated to be converged in a previous test. Using the total energy and the number used in ngkpt (such as using 8 for an 8x8x8 k point grid) from ABINIT an exponential decay curve could then be fitted, and whatever possible k point grid was closest but greater than the tolerance value from the asymptote was used. For instance, if the fit exponential decay passed through the tolerance value at 5.4, then a 6x6x6 grid should be used (assuming it contained the important K points). In general these perovskite systems converged quickly with respect to K points.

\(^9\) R \(_{\text{com}}, (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})\) is the direct gap point for cubic perovskites and was hence important to include, to ensure its presence even numbers are used when specifying the k point grid.
This approach worked in many instances. However, there were occasions where the data points were not following an exponential decay pattern, so such a fit could not give a reliable answer.

Figure C.3: k-point convergence data sometimes does not lend itself to an exponential fit.

If this was the case, relative change between consecutive values rather than distance from an asymptote was used. For instance, if the difference between consecutive points (say the points at 4 and 8) differ by a value smaller than this tolerance, then the 4x4x4 k point grid would be considered converged.
APPENDIX D: EXCITED STATES AND MANY BODY EFFECTS

As solar cells typically operate via absorption of a photon which excites an electron from a valence state into a conduction state, this could leave DFT unsuitable for these calculations. Anything above the band gap in an insulator is unoccupied the ground state. States above the Fermi level can be solved for using the Kohn Sham equations, but these could be fully meaningless. In practice, although DFT is not theoretically rigorous in these circumstances, it can often qualitatively describe some behavior of excited states. For instance, the shape of the Kohn-Sham bands above the Fermi level can be very similar to the shape of the bands obtained with more advanced calculations or experiment\(^\text{10}\). However, their energy relative to the states below the Fermi level is usually wrong. DFT often miscalculates the band gap, severely underestimating it [16]. The band gap is an important quantity for photovoltaic absorbers because it is a major determining factor of their efficiency. One method of correcting the underestimated band gap is known as the GW approximation. The GW approximation takes into account the screened coulomb interaction between an excited electron and its surroundings, treating an effective quasiparticle. Implementation of this screened interaction allows for calculation of accurate band gaps for many materials. The quasiparticle is taken to follow a Schrödinger type equation. In Equation D.1, \( T \) stands for kinetic energy, \( V \) for external potential, and \( C \) for coulombic interaction of the quasiparticle with the electrons. \( \Sigma \) is the quasiparticle self-energy operator.

\[
(T + V + C)\psi(r) + \int \Sigma (r, r', E)\psi(r')dr' = E\psi(r) \tag{D.1}
\]

\(^\text{10}\) Even below the Fermi level there is no known theoretical reason why the Kohn-Sham bands take such an accurate shape
Self-energy takes into account that the changes to the background caused by the presence of the particle. The self-energy operator $\Sigma$ is approximated by $G$ and $W$. The “$W$” in GW is related to the $W[p]$ functional above in the DFT derivation in that they are both coulombic in nature, but $W$ takes into account the polarizability of the material in question such that the interaction between the electrons is dielectrically screened. The “$G$” in GW stands for Green’s function. Although it is possible to create a higher order expansion to accurately determine $\Sigma$, in practice a low order expansion can be taken where $\Sigma = i * G * W$, [50] hence the naming of the GW approximation. While GW can give better accuracy than DFT for electronic band structure, it also requires orders of magnitude more computational resources to implement.

The Bethe-Salpeter equation\(^{11}\) (BSE) allows for calculation of optical properties such as absorption and emission of light. BSE calculations model the behavior of electron-hole pairs treating both particles simultaneously as an exciton. Like GW, BSE calculations are incredibly demanding in general because the electron and hole interact with the same screened coulomb interaction $W$ used in GW calculations[26].

\(^{11}\) Despite the what the name seems to suggest, this doesn’t always look the same. It would in some sense be better labeled as a Bethe-Salpeter framework.
APPENDIX E: BRILLOUIN ZONES

At the request of a committee member, the relevant Brillouin zones are shown in this appendix. Note that hexagonal lattices and simple cubic lattices are self-dual.

Figure E.1: Brillouin zones and high symmetry K points for hexagonal and simple cubic lattices.