

AB INITIO COMPUTATIONAL MODELING OF SURFACE SUPERCELLS OF
PSEUDO-CUBIC HALIDE PEROVSKITES

by

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A thesis submitted to the Graduate Council of
Texas State University in partial fulfillment
of the requirements for the degree of
Master of Science
with a Major in Physics
May 2023

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ACKNOWLEDGEMENTS

I would like to thank Dr. Alex Zakhidov for taking a chance on me. The support and guidance you provided shaped my academic life and will continue to do so. Your foresight in introducing the experimental and theoretical sides of research will benefit me greatly. I would like to thank Drs. Luisa Scolfaro, Mark Wistey, and Eric Welch. This work would not be complete without your willingness to step up during challenging times. To Samuel Cantrell, your training sessions laid the foundation for my understanding of VASP and DFT. Thank you for your time. I would also like to thank Drew Amyx. Whether we were creating devices in the cleanroom or running DFT calculations, being able to bounce ideas off one another was always enlightening. I would like to thank all the professors and support staff at Texas State University. Lastly, I would like to thank my family for their unwavering support and patience while I pursued this work.

This work was supported in part by the Office of Naval Research (N00014-19-1-2576) and by the NSF through an STTR Phase II grant (1927020) and an ECCS grant (1906492)

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LIST OF ABBREVIATIONS

Abbreviation	Description
HP	Halide Perovskite
MHP	Methylammonium lead halide perovskite
DFT	Density Functional Theory
VASP	Vienna Ab-initio Simulation Package
LED	Light Emitting Diode
MA	Methylammonium
HF	Hartree-Fock
KS	Kohn-Sham
XC	Exchange-Correlation
LDA	Local Density Approximation
GGA	Generalized Gradient Approximation
PBE	Perdew-Burke-Ernzerhof
PBEsol	PBE revised for solids
SOC	Spin-Orbit Coupling
PAW	Projector Augmented Wave
AE	All Electron
PBC	Periodic Boundary Condition
BZ	Brillouin Zone
RL	Reciprocal Lattice
SCF	Self-consistent Field
DOS	Density of States
HSE06	Heyd-Scuseria-Ernzerhof
eV	electron volts
DFT+U	Density Functional Theory plus Hubbard U
MAI	Methylammonium – Iodide
PbI	Lead – Iodide
IBZ	Irreducible Brillouin Zone
MP	Monkhorst-Pack
DOS	Density of States
PDOS	Projected DOS
STM	Scanning Tunneling Microscopy
XPS	Xray photoelectron spectroscopy
VESTA	Visualization for Electronic and Structural Analysis

ABSTRACT

Hybrid organic-inorganic perovskites (HP) such as methylammonium lead halide (MHP) are an exciting class of semiconductors with compelling advantages for solar cell applications, such as strong absorption and very low cost. HPs also exhibit balanced carrier mobilities, long carrier diffusion lengths, and shallow defect levels, making them even more attractive for photovoltaics and other optoelectronic devices. However, HPs face two significant challenges, which may be related: a lack of material stability as well as anomalous and unpredictable charge carrier transport. The performance of perovskite solar cells can vary wildly and unpredictably depending on their history of exposure to light, heat, mechanical stress, oxygen, or moisture, which raises serious questions about device reliability and the interpretation of experimental data. Furthermore, surfaces and grain boundaries likely play a fundamental role in charge transport, localization, and trapping in polycrystalline HP thin films. Previous work demonstrated polaron formation using hybrid functionals leveraging density functional theory (DFT) when modeling MHP surfaces which may contribute to lattice instability. Hybrid functionals are computationally expensive, creating a hurdle in studying polaronic effects in these materials. Through alternative computational methods known as the Hubbard U correction, polarons were modeled in the bulk, which significantly reduced the need for computational resources.

In this work, DFT implemented in the Vienna Ab-initio Simulation (VASP) was used to model several MHP bulk materials and surfaces, including surface termination by different halides (Cl, Br, I) and methylammonium (MA). These calculations used a semi-local exchange functional (PBEsol) and compared the results after implementing the Hubbard U correction

(PBEsol+U) to verify the feasibility of extending the DFT+U model for modeling halide perovskite surfaces.

A non-constant potential was eliminated in the vacuum by implementing dipole corrections. The minimum vacuum size for the MAPbCl, MAPbBr, and MAPbI terminated slabs (both MAX and PbX) was determined to be 28.4 Å, 29.6 Å, and 31.56 Å using 7 monolayers. MA ions reoriented so that the NH₃ group was pointing toward the vacuum within the Pb-X lattice using both PBEsol and PBEsol+U functionals in the bulk and all slab supercell models (with the latter functional reducing the amount of reorientation observed). The Pb-halide bond lengths shrank in the bulk as well as for both surface slab terminations after adding a U correction. The bulk band gaps for MAPbCl, MAPbBr, and MAPbI changed from 2.22 eV, 1.84 eV, and 1.52 eV to 2.44 eV, 1.79 eV, and 1.27 eV after including an 8 eV U correction. A smaller U value used for MAPbBr (4 eV) and MAPbI (1 eV) in the bulk resulted in band gaps much closer to experimental values, 1.83 eV and 1.5 eV. MAPbCl experienced octahedral tilting that resulted in a tiny band gap increase while the MAPbBr and MAPbI bandgap shrank due to lattice contractions. The 8 eV U correction changed the bandgap for the MAX terminated slabs from 1.68 eV, 1.39 eV, and 1.27 eV to 1.77 eV, 1.36 eV, and 1.07 eV for MAPbCl, MAPbBr, and MAPbI, respectively. The 8 eV U value also changed the PbX terminated slab bandgaps for MAPbCl, MAPbBr, and MAPbI from 1.31 eV, 1.03 eV, 0.88 eV to 1.35 eV, 0.90 eV, and 0.61 eV, respectively. The smaller bandgaps for the PbX slabs were determined to be due to surface reconstruction caused by dangling bonds on the PbX surfaces. The smaller bandgaps of the PbX slabs suggest the MAX surface would be less prone to radiative recombination occurring. Midgap states were not observed in the bulk nor in either the PbX or MAX surface slabs suggesting defect assisted recombination does not occur in the bulk nor the neutral surface slabs.

The DFT+U method was shown to significantly reduce computational resources for simulating surfaces, however, results show the U value needs to be individually reoptimized for each perovskite compound studied in this work as the U correction changes the physical bond lengths and electronic properties (band gap) of each compound differently in the bulk as well as both PbX and MAX slab supercells.

1. INTRODUCTION AND MOTIVATION

MHPs exhibit qualities that make them a good candidate for optoelectronic material in LEDs [1], lasers [2], photovoltaic devices and photodetectors [3]. These qualities allowed MHP solar cells to experience a significant rise in efficiency over the past 13 years from 3% in 2009 to 25% in 2022 [4]. MHP semiconducting material is created using Earth-abundant elements such as C, N, H, Pb, Br, and I. Creating MHP semiconducting precursor ink is inexpensive and can be done at room temperature allowing for easy and cost effective device fabrication [5].

One barrier preventing widespread MHP device adoption is device structure stability lifetime. Exposure to oxygen, moisture, heat, mechanical stress, reverse bias, and light illumination causes the MHP structure to degrade [6].

First principles Density Functional Theory (DFT) calculations have proven to be a reliable method for modeling the physical and electronic properties of various materials including perovskites. This work aims to use DFT to compare the structural and electronic properties using a semi-local functional with a Hubbard U correction on the surface of MHP slabs using the supercell method.

Perovskites are an abundant structural family of various compounds with an ABX_3 stoichiometry. The “B” ions are bonded by the “X” ion. For halide perovskites, the “A” cation is often smaller than the “B” cation and forms an organic framework while the former forms an inorganic framework with the “X” anion. In this study, $CH_3NH_3^+$ (methylammonium, MA) serves as the “A” site cation and Pb as the “B” cation. Three halides (Cl, Br, and I) are then substituted for the “X” anion. These elements are chosen based on criteria (such as the Goldschmidt tolerance factor in equation 1.1) that can predict which compounds would best form a perovskite structure.

$$t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)} \quad (1.1)$$

Here, r_A , r_B are the ionic radius for the “A” and “B” cations while r_X is the ionic radius of the anion. The tolerance factor is used to confirm if the “A” site cation fits within the cavities of the BX_3 framework. The tolerance factor is a measurement of the amount of distortion (from ideal) of the perovskite structure (from the ideal cubic structure), so as the tolerance factor goes to unity, a perovskite becomes more cubic. A tolerance factor of $1.00 < t < 1.13$ is hexagonal, $0.9 < t < 1.0$ is cubic, and $0.75 < t < 0.9$ is orthorhombic [7]. MAPbCl has a tolerance factor of 0.94, MAPbBr has a tolerance factor of 0.93, and MAPbI has a tolerance factor of 0.91 [8] so all are expected to be nearly cubic or pseudo-cubic. Figure 1.1 shows the MAPbI perovskite structure.

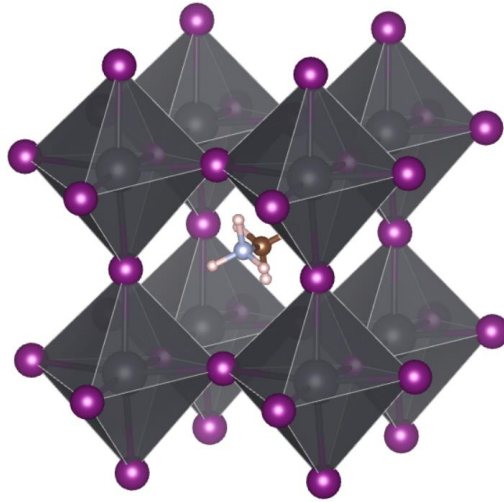


Figure 1.1: MAPbI Perovskite Structure

The electronic properties of semiconductors are dependent on the three-dimensional repetitive crystalline structure (lattice) of the material. Charge carriers can interact with this ionic lattice (the Pb-halide bond is ionic) which may alter its structure. This interaction is characterized by a quasiparticle called a polaron. Localized “small” polarons are thought to contribute detrimental effects resulting in: structural instability (and degradation) at ambient

temperature and humidity, hysteresis for current vs voltage measurements, and a reduced power conversion efficiency [6]. This reduction in power conversion efficiency is caused by recombination centers created when a small polaron is trapped at a lattice site. Delocalized “large” polarons are thought to contribute positively to the long charge carrier diffusion lengths, long charge carrier lifetimes, high defect tolerance, and enhanced charge carrier motion across grain boundaries for MAPbX devices [6]. To our knowledge, polaronic effects have only been modeled for slab surfaces of MAPbI using a semi-empirical hybrid functional [9]. Polaronic effects have been modeled using DFT+U in the bulk [10] for MAPbX (X = Cl, Br, I). This work looks to expand the DFT+U method for use in modeling polarons in slab surface structures. The DFT+U method was used to model different slab surface terminations and study the structural and electronic properties of MAPbCl, MAPbBr, and MAPbI.

In Chapter 1, we covered some of the barriers currently facing the improvements of HPs, a brief on what a perovskite structure is, and the motivation for studying HP systems. Chapter 2 of this study covers DFT foundational topics, spin-orbit coupling, dipole correction effects, Hubbard U corrections, and a background on polarons. Chapter 3 presents the methodology used to conduct the DFT calculations. Chapter 4 presents the results of the DFT modeling and analysis of the effects observed and conclusions are given in Chapter 5. Chapter 6 provides a summary of perspectives on any future studies that may be performed. Lastly, bulk structural optimization graphs and surface Pb-halide bond length tables are included in the Appendix Section.

2. TOWARDS DFT: THEORETICAL FUNDAMENTALS

2.1 Crystal Structures and the Unit Cell

In 1912 Max von Laue used XRD to show solids are composed of repetitive atomic structures [11]. These repetitive structures are called the crystalline structure. A crystal is grown using these repetitive structures. A unit cell is the smallest volume of these repetitive structures that constitute the crystalline structure. A set of mathematical points called a lattice plus a basis of atoms attached to each lattice point constitute the crystalline structure. A translation operator relates these points to one another

$$\mathbf{T} = u_1 \mathbf{a}_1 + u_2 \mathbf{a}_2 + u_3 \mathbf{a}_3 \quad (2.1.1)$$

where u_1, u_2, u_3 are integers and $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ are lattice vectors. Every lattice point with s atoms and positions is given by:

$$\mathbf{r}_j = x_j \mathbf{a}_1 + x_j \mathbf{a}_2 + z_j \mathbf{a}_3 \quad (2.1.2)$$

These lattice points form the crystal. This lattice is invariant such that:

$$\mathbf{r}' = \mathbf{r} + u_1 \mathbf{a}_1 + u_2 \mathbf{a}_2 + u_3 \mathbf{a}_3 \quad (2.1.3)$$

where u_1, u_2, u_3 are arbitrary integers and $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ are translation vectors (lattice vectors).

There are 14 different lattice types [12].

2.2 Quantum Mechanics

Computational modeling starts with solving the time-independent non-relativistic Schrödinger equation.

$$\hat{H}\psi(\mathbf{r}_i, \mathbf{r}_l) = E\psi(\mathbf{r}_i, \mathbf{r}_l) \quad (2.2.1)$$

$\hat{H}$, (the Hamiltonian), is an energy operator acting on a wavefunction ψ (called the eigenfunction). E is the eigenvalue of $\hat{H}$ associated with the wavefunction ψ . $\mathbf{r}_i$ and $\mathbf{r}_l$ represent vectors that define electron and nuclei positions. Solving the Schrödinger equation amounts to

finding the ground-state energy. Doing so returns a set of energy values (called eigenvalues) of the eigenfunction. For ψ to be an eigenfunction an operator must act on it and return a multiple of the original wavefunction. Wavefunctions that satisfy this criterion are called eigenvectors/eigenstates. ψ can represent everything about an electron (and by extension the system). Solving the wave equation for a system produces a set of wavefunctions as solutions where each solution applies to an electron. Relativity can often be ignored because the speed of an electron is smaller than the speed of light. Restricting our calculations to the ground-state energy of electrons causes the potential energy of the system to be constant, allowing time to be ignored. The Hamiltonian operator for this version of the Schrödinger equation is the sum of all energy terms for potential and kinetic energy.

$$\hat{H}=E_l^{\text{kin}}+E_i^{\text{kin}}+U_{li}+U_{ij}+U_{lj} \quad (2.2.2)$$

The first two terms are the kinetic energy of the nuclei and electrons. The final three terms are due to the attractive potential energies of electron-nuclei interactions, repulsive potential energies between electron-electron interactions, and the repulsive potential energies of nucleus-nucleus interactions.

The Born-Oppenheimer Approximation can be used to further simplify the Schrödinger equation [13]. This approximation allows for the decoupling of nuclear and electronic dynamics. The nuclei are considered “stationary” due to their much larger mass (compared to the electrons). The electrons will respond to nuclear motion instantaneously and occupy the ground-state of that nuclear configuration. A final simplification is made by ignoring atomic spin. With these simplifications, the wavefunction of the Schrödinger equation now only depends on the electron positions at r_i .

$$\hat{H}\psi(\mathbf{r}_i)=E\psi(\mathbf{r}_i) \quad (2.2.3)$$

Due to the Born-Oppenheimer approximation, the nuclei terms are dropped from the Hamiltonian.

$$\hat{H}=E_i^{\text{kin}}+U_{li}+U_{ij} \quad (2.2.4)$$

Substituting in the kinetic energy, electron-nuclei attractive potential interaction, and repulsive electron-electron interactions terms (using atomic units) and the resulting Hamiltonian is:

$$\hat{H}=-\frac{1}{2}\sum_i^n \nabla_i^2 - \sum_l^N \sum_i^n \frac{Z_l}{|\mathbf{r}_{li}|} + \frac{1}{2}\sum_{i \neq j}^n \frac{1}{|\mathbf{r}_{ij}|} \quad (2.2.5)$$

(A list of atomic units is given in the Appendix.) N and n are the number of nuclei and electrons in the system and Z_l are the nuclei charges. The double sum indicates the interactions occur from all electrons to all nuclei. The $\frac{1}{2}$ term is added as a correcting factor to account for double counting. Substituting this Hamiltonian into the Schrödinger wave equation gives the many-body electronic Schrödinger equation:

$$\left[-\frac{1}{2}\sum_i^n \nabla_i^2 - \sum_l^N \sum_i^n \frac{Z_l}{|\mathbf{r}_{li}|} + \frac{1}{2}\sum_{i \neq j}^n \frac{1}{|\mathbf{r}_{ij}|} \right] \psi(\mathbf{r}_i) = E\psi(\mathbf{r}_i) \quad (2.2.6)$$

This equation gives the electronic structure of a system. The dimensionality of this problem makes it extremely difficult to solve numerically.

2.3 Hartree Method – One-electron model

The electronic wavefunction for the many-body Schrödinger equation is a function of each of the spatial coordinates of each of the electrons. This is a $3N$ dimensionality, where N is the number of electrons in the system. Studying a single atom of Pb results in a wave function with 246 dimensions. The wave function for a nanocluster of 100 Pb atoms would require 23,600 dimensions, truly a difficult calculation. The problem can be simplified by assuming

each electron is independent and interacts with other electrons in an averaged way (also called a mean-field). This method is known as the Hartree method. The wave equation then looks like this:

$$\left(-\frac{1}{2}\nabla^2 + U_{\text{ext}}(\mathbf{r}) + U_H(\mathbf{r})\right)\psi(\mathbf{r}) = E\psi(\mathbf{r}) \quad (2.3.1)$$

where: $U_{\text{ext}}(\mathbf{r})$ is the attractive electron-nuclei interaction and $U_H(\mathbf{r})$ is the Hartree repulsive potential between each electron and the electron mean-field. Using this simplified method, Douglas Hartree introduced the self-consistent field method for solving the wave equation [14]. Using this simplistic approximation method, he was able to calculate the ground-state energy of hydrogen (-13.6 eV) but failed to do so for other atomic systems. These failures were a result of not incorporating Pauli's exclusion principle nor including the exchange and correlation energies of these alternate atomic systems. Exchange and correlation energies are discussed in section 3.5.3.

2.4 Hartree-Fock Equations

The Hartree Method was soon refined by Vladimir Fock into the Hartree-Fock Method. Fock was able to express a wavefunction that included the missing pieces from the Hartree method by approximating it as a linear combination of non-interacting one-electron wavefunctions as a Slater determinant [15]. The Slater determinant incorporated anti-symmetry and Pauli's exclusion principle. The generalized Slater determinant (not including spin) is:

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \psi_1(\mathbf{r}_1) & \dots & \psi_n(\mathbf{r}_1) \\ \vdots & \ddots & \vdots \\ \psi_1(\mathbf{r}_n) & \dots & \psi_n(\mathbf{r}_n) \end{vmatrix} \quad (2.4.1)$$

The wave equation including the Slater determinant becomes:

$$\left(-\frac{1}{2}\nabla^2 + U_{\text{ext}}(\mathbf{r}) + U_{ij}(\mathbf{r})\right)\psi(\mathbf{r}) = E\psi(\mathbf{r}) \quad (2.4.2)$$

where $U_{ij}(r)$ represents the “true” electron-electron interaction which contains both classical and quantum terms. Multiplying by the complex conjugate and integrating over all space gives the energy:

$$E = \sum \int \psi_i^*(\mathbf{r}) \left(-\frac{1}{2} \nabla_i^2 + U_{\text{ext}}(\mathbf{r}) + U_{ij}(\mathbf{r}) \right) \psi_i(\mathbf{r}) d\mathbf{r} \quad (2.4.3)$$

Solving this equation gives a sum for all the contributing energies.

$$E = E_{\text{kin}} + E_{\text{ext}} + E_H + E_x \quad (2.4.4)$$

where E_H is the Hartree energy (Coulomb energy due to electron-electron interactions) and E_x is the exchange energy. E_x is negative, lowers the total energy, and gives a better approximation of the ground-state energy. The exchange energy is a result of the Slater determinant and anti-symmetry. Additionally, Fock used the variational process to improve the wavefunction. This process is as follows. Assuming no degenerate states, there is only one ground-state energy for a given system. Continuously minimizing the system energy (with respect to the wavefunction) will eventually return the ground-state energy. Therefore, the initial approximated wavefunctions of the Slater determinant approach the wavefunctions that truly calculate the ground-state energy. The self-consistent method for the HF method is iterative (whereas the Hartree method is not). The HF method is another good step toward solving the many-body Schrödinger equation, however, it is limited in the size of the system that can be studied [16]. Additionally, the HF method does not account for electron correlation. Electron correlation occurs when electrons with the same spin tend to remain separated.

2.5 DFT Foundations: Electron Density

The key concept of DFT is electron density. This is the number of electrons per unit volume at a point. Electron densities are observable whereas wavefunctions are not. Therefore,

leveraging the electron density as the single variable for electronic system calculations presents a very real and viable method for material modeling compared to the previous wavefunction based methods. In DFT, electrons are assumed to be non-interacting in a decoupled coordinate system represented as a sum over a set of occupied noninteracting Kohn-Sham (KS) orbitals:

$$\rho(\mathbf{r}) = \sum_i |\phi_i(\mathbf{r})|^2 = 2 \sum_i^{\text{occ}} |\phi_i(\mathbf{r})|^2 \quad (2.5.1)$$

The amplitudes of each orbital are converted to a positive density of electrons. Integrating over all space gives the total number of electrons (n):

$$n = \int \rho(\mathbf{r}) d\mathbf{r} \quad (2.5.2)$$

Adding up the overlapping atomic electron densities resembles the electron densities of solids allowing for a solid to be modeled (only roughly at this stage). The electron density of a system can also be used to represent the wavefunction and orbital. It is also related to potentials, energies, and (by extension) all system properties.

2.5.1 Hohenberg-Kohn Theorems

Hohenberg and Kohn proposed two theorems that showed a link between electron density, external energy, the Hamiltonian, and the wavefunction [17]. The first theorem states the ground-state electron density solely determines a unique external potential. This means different external potentials always generate different electron densities. Deducing the total energy (or other properties) is possible by focusing on the ground-state properties of a system using the electron density at a given external potential.

The second Theorem provided an energy minimization method and used the variational principle to search for the ground-state of a system. Like the HF Method, minimizing the system

energy with varying electron density eventually leads to the lowest energy state.

2.5.2 One-electron systems

In 1965, using the Hohenberg and Kohn theorems, Kohn and Sham used a fictitious one-electron system to solve the many-body Schrödinger time-independent wave equation [18].

Starting with a full Hamiltonian (in atomic units):

$$\hat{H} = -\frac{1}{2} \sum_{i=1}^n \nabla_i^2 - \sum_{l=1}^N \sum_{i=1}^n \frac{Z_l}{|\mathbf{r}_i - \mathbf{r}_l|} + \frac{1}{2} \sum_{i \neq j}^n \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (2.5.2.1)$$

where $\mathbf{r}_i$ and $\mathbf{r}_j$ are electron coordinates and $\mathbf{r}_l$ are the nuclei coordinates. The Hartree potential is the last term and contains interactions that are difficult to calculate. Kohn and Sham assumed each electron was non-interacting and the system was in the ground-state. They then decomposed the energies of n electrons and regrouped them into a framework of independent electrons. The interacting n -electron system was mapped to a non-interacting one-electron system (for a given external energy). Thus equation 3.4.4 becomes:

$$E = (E_{\text{kin}}^{\text{non}} + E_{\text{kin}}^{\text{int}}) + E_{\text{ext}} + (E_{\text{H}} + E_{\text{x}} + E_{\text{c}}^{\text{int}}) \quad (2.5.2.2)$$

Here $E_{\text{kin}}^{\text{non}}$ and $E_{\text{kin}}^{\text{int}}$ replaced the E_{kin} term and represent noninteracting and interacting correlated kinetic energies. $E_{\text{c}}^{\text{int}}$ represents a new correlation energy which the HF method does not account for. Grouping the interacting terms where $E_{\text{c}} = E_{\text{c}}^{\text{int}} + E_{\text{kin}}^{\text{int}}$ and $E_{\text{xc}} = E_{\text{x}} + E_{\text{c}}$ shows the total energy to be:

$$E = E_{\text{kin}}^{\text{non}} + E_{\text{ext}} + E_{\text{H}} + E_{\text{xc}} \quad (2.5.2.3)$$

where E_{xc} is the exchange-correlation energy and E_{c} is the correlation energy. The non-interacting kinetic energy ($E_{\text{kin}}^{\text{non}}$) term can be calculated using equation 3.5.2.4. (Recall Kohn and Sham assumed the system was non-interacting). This energy accounts for the largest percentage of the total kinetic energy in the system.

$$E_{\text{kin}}^{\text{non}} = -\frac{1}{2} \sum_{i=1}^n \phi_i^*(\mathbf{r}) \nabla^2 \phi_i(\mathbf{r}) \quad (2.5.2.4)$$

The external energy (attractive electron-nuclei Coulomb interaction) and the Hartree energy (electron and electron density interactions) are both a functional of the electron density and are represented by the following equation(s):

$$E_{\text{ext}}[\rho(\mathbf{r})] = \int \phi^*(\mathbf{r}) U_{\text{ext}}(\mathbf{r}) \phi(\mathbf{r}) d\mathbf{r} = \int U_{\text{ext}}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} \quad (2.5.2.5)$$

$$E_{\text{H}}[\rho(\mathbf{r})] = \int U_{\text{H}}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} = \frac{1}{2} \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}' \quad (2.5.2.6)$$

Notice the Hartree energy has double integrals and represents the mean-field for all electrons on all other electrons. This leads to a double counting of the energy for an electron and is called self-interaction. This interaction is unphysical and is corrected in the exchange energy term.

2.5.3 Exchange-correlation energy

The exchange-correlation energy is also a functional of the electron density. Recall the exchange-correlation energy is a sum of two energies:

$$E_{\text{xc}} = E_{\text{x}} + E_{\text{c}} \quad (2.5.3.1)$$

where E_{x} is the exchange energy between electrons with the same spin and E_{c} is the correlation energy between electrons with a different spin. The exchange energy can be thought of as an interaction over the distance between an exchange hole and the electron density. Orbital antisymmetry for electrons with the same spin causes spatial separation between them resulting in a reduction of electron density. This electron density reduction is called an exchange hole (also referred to as a Fermi Hole) and results in a reduction in the repulsion between electrons thus lowering the energy of the system. This separation of electrons removes the self-interaction (double counting) in the Hartree energy. [19]

The correlation energy is a result of the correlation hole (also called a Coulomb Hole). Electrons with differing spins avoid each other when occupying the same orbital because of the same negative charge. This reduces the electron density around the electron(s) resulting in a small attractive energy. The exchange and correlation holes are known collectively as the exchange-correlation hole (XC). The exchange hole will alter the size of the XC hole while the correlation hole will alter the shape. The exchange hole is dominant when electron density is high while the correlation hole increases in importance when electron density is low.

The exchange energy is represented by:

$$E_x = -\frac{1}{2} \sum_{ij}^n \iint \frac{\phi_i(\mathbf{r})^* \phi_j^*(\mathbf{r}') \phi_i(\mathbf{r}) \phi_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \quad (2.5.3.2)$$

The exchange-correlation energy is the smallest contributor to the total energy but is important because it is involved in the atomic changes of solids such as bonding, spin-polarization, and band gap formation [16]. The exchange energy can be calculated using equation 2.5.3.2 but doing so requires using the HF method which scales badly for large systems and becomes computationally prohibitive. For this reason, the exchange-correlation is approximated and solved analytically. Although the exact exchange functional is not known, there must exist a functional which gives the exact ground-state energy and density.

2.6 Kohn-Sham Equations

The total energy of a system is now expressed as a functional of the electron density (except for the non-interacting term, E_{kin}^{non}):

$$E[\rho(\mathbf{r})] = E_{kin}^{non}[\phi(\mathbf{r})] + E_{ext}[\rho(\mathbf{r})] + E_H[\rho(\mathbf{r})] + E_{xc}[\rho(\mathbf{r})] \quad (2.6.1)$$

This equation can be minimized to find the ground state using the differentiation of functionals, the variational principle, and a Lagrange multiplier. Using the variational principle, the variation

of the energy functional(s) is zero when the energy is minimized.

$$0 = \frac{\delta E[\rho(\mathbf{r})]}{\delta \phi_i^*(\mathbf{r})} \quad (2.6.2)$$

$$0 = \frac{\delta}{\delta \phi_i^*(\mathbf{r})} \left(E[\rho(\mathbf{r})] - \sum_{ij} \lambda_{ij} \left[\int \phi_i^*(\mathbf{r}) \phi_j(\mathbf{r}) d\mathbf{r} \right] \right) \quad (2.6.3)$$

(λ ensures orthonormality for the orbitals.)

$$0 = \frac{\delta E_{\text{kin}}^{\text{non}}}{\delta \phi_i^*(\mathbf{r})} + \left[\frac{\delta E_{\text{ext}}}{\delta \rho(\mathbf{r})} + \frac{\delta E_{\text{H}}}{\delta \rho(\mathbf{r})} + \frac{\delta E_{\text{xc}}}{\delta \rho(\mathbf{r})} \right] \frac{\delta \rho(\mathbf{r})}{\delta \phi_i^*(\mathbf{r})} - \sum_j \lambda_{ij} \phi_j(\mathbf{r}) \quad (2.6.4)$$

Simplifying the equation results in the Kohn-Sham equations:

$$0 = \left(-\frac{1}{2} \nabla^2 + U_{\text{ext}} + U_{\text{H}} + U_{\text{xc}} - \lambda_i \right) \phi_i(\mathbf{r}) \quad (2.6.5)$$

$$0 = \left(-\frac{1}{2} \nabla^2 + U_{\text{eff}} - \epsilon_i \right) \phi_i(\mathbf{r}) \quad (2.6.6)$$

where U_{eff} is the effective potential that manipulates the noninteracting ground-state electron density so that it is identical to the interacting system. The associated Schrödinger wave equation now becomes:

$$\left[-\frac{1}{2} \nabla^2 + U_{\text{eff}}(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}) \quad (2.6.7)$$

where the KS Hamiltonian is:

$$\hat{H}_{\text{KS}} = -\frac{1}{2} \nabla^2 + U_{\text{eff}} \quad (2.6.8)$$

The KS eigenvalues, ϵ_i , represent the energies of each electron and describe various properties such as the band structure and density of states. After removing the double counting error, the sum of the KS eigenvalues is the actual total energy of the system.

$$E = \sum_i \epsilon_i - E_H[\rho(\mathbf{r})] + E_{xc}[\rho(\mathbf{r})] - \int \frac{\delta E_{xc}}{\delta \rho(\mathbf{r})} \rho(\mathbf{r}) d\mathbf{r} \quad (2.6.9)$$

2.7 Exchange-correlation functionals

Recall, the exact functional for E_{xc} is unknown, therefore approximations are used to make up for this shortcoming and are an active topic of research. For solids, the XC energy can be either local or semi-local functionals. The next few sections will cover a few of the commonly used XC functionals and provide benefits and drawbacks to each type. These functionals include the Local Density Approximation (LDA), Generalized Gradient Approximation (GGA), and hybrid functionals.

2.7.1 Local Density Approximation (LDA)

LDA is a local functional. This means the functional does not depend on the density gradient of the functional. LDA assumes the density in the local area containing the electron is homogenous throughout the system. The exchange energy is represented by the following analytical form (where C is constant):

$$E_x^{\text{hom}}(\rho) = -C\rho^{\frac{1}{3}}(\mathbf{r}) \quad (2.7.1.1)$$

The surveyed area is broken into uniform pieces of electron densities. The exact exchange and correlation energies can be calculated using the HF method, however, common practice dictates these energies are approximated using the simple analytical form. The final values are summed to calculate the total energy for the XC energy.

$$E_{xc}^{\text{LDA}}[\rho(\mathbf{r})] = E_x^{\text{LDA}}[\rho(\mathbf{r})] + E_c^{\text{LDA}}[\rho(\mathbf{r})] \quad (2.7.1.2)$$

LDA is exact for densities which vary slowly and work well for covalent and simple metallic systems. Known numerical values from quantum Monte Carlo calculations for a homogenous

gas are interpolated allowing $E_{xc}^{hom}[\rho(\mathbf{r})]$ to be parameterized. Multiplying $E_{xc}^{hom}[\rho(\mathbf{r})]$ by the local electron density and integrating over all space gives the XC energy.

$$E_{xc}^{LDA}[\rho(\mathbf{r})] = \int \rho(\mathbf{r}) E_{xc}^{hom}[\rho(\mathbf{r})] d\mathbf{r} \quad (2.7.1.3)$$

$$= \int \rho(\mathbf{r}) [E_x^{hom}[\rho(\mathbf{r})] + E_c^{hom}[\rho(\mathbf{r})]] d\mathbf{r} \quad (2.7.1.4)$$

Taking the derivative of the energy functional gives the XC potential:

$$U_{xc}^{LDA}[\rho(\mathbf{r})] = \frac{\delta E_{xc}^{LDA}}{\delta \rho(\mathbf{r})} \quad (2.7.1.5)$$

LDA is an older function and has fallen out of use with the advent of newer functionals.

Unfortunately, LDA is prone to many shortcomings including underestimating lattice constants (called overbinding) and band gap values. [20] Overbinding results in an overestimation of the cohesive energy and the bulk modulus of solids. Band gaps are underestimated due to only partial cancellation of self-interaction.

2.7.2 Generalized Gradient Approximation (GGA)

GGA is a semi-local functional, so it depends on the density gradient of the functional. This is needed because systems (generally) are not homogeneous. GGA accounts for both local and semi-local information. The GGA XC functional is expressed in a form that satisfies various physical constraints. GGA is based on LDA and incorporates an enhancement factor (corresponding to the gradient of the electron density) that directly modifies the LDA energy.

$$E_{xc}^{GGA}[\rho(\mathbf{r}), s] = \int \rho(\mathbf{r}) E_x^{GGA}[\rho(\mathbf{r})] \rho(\mathbf{r}) F(s) d\mathbf{r} \quad (2.7.2.1)$$

where:

$$s=C \frac{|\nabla\rho(\mathbf{r})|}{\rho^{4/3}(\mathbf{r})} \quad (2.7.2.2)$$

$F(s)$ typically varies from 1.0 to 1.6 for solids when s is in the range of 0-3 [21]. GGA provides better values for bond lengths by resolving the overbinding issues of LDA but can still underestimate the band gap.

2.7.3 Perdew-Burke-Ernzerhof revised for solids (PBEsol)

The GGA PBE (not the same as PBEsol) functional was introduced in 1996 and provided more accurate results compared to LDA and other early GGA functionals. PBE resolved the under binding of LDA but introduced an overbinding (meaning it overestimates lattice constants). Given this dilemma, the creators of PBE released the PBEsol functional in 2008 with the explicit intent of providing accurate equilibrium properties for solids and surfaces. PBE and PBEsol are extremely similar. The main difference between them are two terms used in the enhancement factor $F(s)$ and E_c .

The enhancement factor for GGA approximations has the form (as $s \rightarrow 0$):

$$F(s)=1+\mu s^2+\dots \quad (2.7.3.1)$$

As previously stated GGA was built on LDA so it must recover the uniform gas limit. Given this constraint, μ is limited to a value of ~ 0.2195 . Likewise, E_c is given by:

$$E_c[\rho(\mathbf{r})]=\int \rho(\mathbf{r}) E_c^{\text{GGA}}[\rho(\mathbf{r})]+\beta t^2(\mathbf{r})+\dots d\mathbf{r} \quad (2.7.3.2)$$

Most GGA approximations chose β so the uniform gas limit is recovered making $\beta = 0.0667$.

This value works well for the exchange energy of free atoms. PBEsol revised these values to $\mu = 10/18$ and $\beta = 0.046$, respectively [22]. These values provide a better estimation of surface energies. PBEsol becomes exact under intense compression where E_x is dominant (compared to

E_c) which minimizes error cancellation between E_x and E_c . This work used the GGA functional PBEsol (Perdew-Burke-Ernzerhof revised for solids) to perform DFT calculations.

2.7.4 Hybrid functionals

Hybrid functionals are exchange-correlation functionals that mix an amount of the accurate exchange energy from the HF method (by default in VASP) with a local or semi-local density functional. Hybrid functionals describe systems with rapid electron density variations or with long-range van der Waals interactions and are best suited for modeling bond energies, chemical transition-state barriers, and band gaps [16]. A transition-state is defined as a thermodynamic bottleneck experienced by a system in a chemical reaction going from the reactant state to the product state. [23] There are two types of hybrid functionals: unscreened and range-separated (screened). The unscreened hybrid functional, PBE0, is considered non-empirical. Range-separated functionals (such as HSE03, HSE06, and HSESol) are more commonly used in solid-state physics and are considered semi-empirical. Hybrid functionals incorporate corrections to the self-interaction error and have been used to model polarons. [9] Unfortunately, hybrid functionals incur a high computational cost, and identifying the correct exchange values can be time-consuming.

2.8 Projector Augmented Wave Pseudopotentials

Pseudopotentials mimic the characteristics of potentials for atoms. These approximated potentials combine and “freeze” the nucleus and core electrons resulting in simpler and quicker DFT calculations. The core electrons can be treated like this because they are bound tightly to the nuclei in a deep potential well. This configuration means the core electrons are unaltered (for the most part) when system conditions change. Valence electrons, however, are affected by changes in the system. A valence wavefunction oscillates rapidly near the nucleus due to the

deep well. A linear transformation can be used to create a well-behaved function without oscillations. Modeling the nodes of this rapidly oscillatory (RO) wavefunction is computationally expensive so a modulating function for the frozen nuclei and core electrons is used. This function reduces the computational cost and is called pseudization. The distance from the center of the nucleus to the outermost pseudized electrons is called the augmentation sphere. The basis set for this transformation operator has the following basis sets: RO partial wave, Pseudo partial wave, and a projector function. (Partial waves are plane waves decomposed into a series of spherical waves.) The RO partial wave will provide solutions to the Schrödinger equation. The Pseudo partial wave is identical to the RO partial wave outside the augmentation sphere but is also well-behaved inside of it. The projector function ensures the pseudo partial waves are solutions to the Schrödinger equation as well. The KS equation (using pseudopotentials) is now:

$$\left[-\frac{1}{2} \nabla^2 + U_{PP}[\rho(\mathbf{r})] \right] \psi_i^{PP}(\mathbf{r}) = \epsilon_i \psi_i^{PP}(\mathbf{r}) \quad (2.8.1)$$

where:

$$\rho(\mathbf{r}) = \sum_i |\psi_i^{PP}(\mathbf{r})|^2 \quad (2.8.2)$$

In 1994 F. Blochl proposed Projector-augmented wave (PAW) potentials which aimed to leverage frozen core potentials while maintaining the accuracy of RO potentials. [12] The charge density for PAW is no longer the actual charge density but is instead a pseudo-charge density. This is due to the approximation sum of the atomic contributions inside the augmentation sphere. Blochl's implementation of PAW potentials is:

$$E_{xc}^B = E_{xc}[\tilde{n}_v + \tilde{n}_{core}] + \sum_a (E_{xc}^a[n_v^a + n_{core}^a] - E_{xc}^a[n_v^a + \tilde{n}_{core}^a]) \quad (2.8.3)$$

where $\tilde{n}_v$ is the valence density and $\tilde{n}_{core}$ is the core density.

In 1998, Kresse and Joubert modified Blochl's PAW implementation by adding a valence compensation charge density [24].

$$E_{xc}^K = E_{xc}[\tilde{n}_v + \tilde{n}_{core} + n] + \sum_a (E_{xc}^a[\tilde{n}_v + n_{core}^a] - E_{xc}^a[\tilde{n}_v + \tilde{n}_{core}^a + n]) \quad (2.8.4)$$

This was done to make PAW's relationship explicit with DFT.

2.9 Periodic Boundary Conditions and the Slab Model

The structure of a solid is a periodic crystal. To reduce computational cost DFT relies heavily on this periodicity of solids by reducing the size of a solid to a supercell made up of several periodic unit cells. Periodic boundary conditions (PBCs) extend the supercell to infinity. The supercell extended by PBCs then can be used to simulate a bulk solid with a reduced computational cost. This method means the KS equations need only be solved in that single supercell. PBCs can be used for neutral slabs with no dipole moment.

2.9.1 Reciprocal Lattice and the First Brillouin Zone

Recall that pseudopotentials speed up DFT calculations by “eliminating” electrons from the calculation. Likewise, a Brillouin zone can be used to reduce the system further. The first BZ is a coordinate system used to characterize the behavior of electrons. Characterizing the system in the reciprocal lattice (RL) makes it easier than in real space. The grid of the RL is matched to the wave vectors. This means RL points define allowed wave vectors. (This is like identifying positional points in a real lattice.) Information transformed from real space to reciprocal space shrinks. This is done by expanding the KS wavefunctions and electron density using a Fourier series. The Fourier transform of the wavefunction is given by:

$$U_k(\mathbf{r}) = \sum_{\mathbf{G}} C_k(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}} \quad (2.9.1.1)$$

where $C_k(G)$ is the Fourier complex numbers of the replacement wavefunctions. Fast Fourier transformations discretize the charge distribution onto a finite grid in reciprocal space. e^{iGr} is the phase factor at each $\mathbf{G}$ (RL vector) representing a plane wave in space perpendicular to $\mathbf{G}$. Similarly, other quantities such as the electron density can be transformed. The first BZ can be thought of as an RL unit cell. K-points outside of the first BZ are folded back into the first BZ via the RL vector so DFT calculations can focus purely on the first BZ.

2.9.2 Irreducible Brillouin Zone and KPOINTS

Rotation and inversion symmetry also speed up DFT calculations by creating an irreducible Brillouin zone (IBZ). The IBZ can be represented by a minimum number of distinct k-points. Any point in the IBZ can represent a k-point so there are an infinite number of k-vectors. These k-vectors are well-behaved in the IBZ so a smaller sample can be used. For large systems, the IBZ volume is small and only a few k-points are needed to describe the sampled zone. Two types of commonly used k-point meshes are the Monkhorst-Pack (MP) [25] and a “Regular” mesh centered at the Gamma Point (GP). The MP method creates k-points evenly spaced in the IBZ. The Regular mesh is commonly used for large systems as it is computationally efficient. This is due to the gamma central point being located at $k = 0$ where the real and reciprocal coordinates coincide. Wavefunctions at this point are real and so complex number evaluation is not needed.

2.9.3 Bloch Theorem

The topic of free atoms was briefly mentioned in Section 2.7.3. A free atom is an atom that has minimal interaction with other electrons and nuclei inside a bulk structure and travels freely within the solid. The Bloch theorem allows the KS orbitals to be rewritten and solved for each k and band index in a matrix equation. Since the structure of a solid is periodic its

properties are also periodic. Therefore, the electron density is periodic (and invariant) since it depends on position

$$\rho(\mathbf{r}) = \rho(\mathbf{r} + \mathbf{R}) \quad (2.9.3.1)$$

where $\mathbf{R}$ is a lattice translational vector.

While the magnitude of the wavefunction will be periodic the wavefunction will not be due to associated complex numbers. Wavefunctions have a plane wave of the form (with C as a constant):

$$\psi(\mathbf{r}) = Ce^{i\mathbf{k}\cdot\mathbf{r}} \quad (2.9.3.2)$$

Bloch mapped these plane waves to the periodic structure of a solid [26]. This made the plane waves quasi-periodic. He also introduced a periodic function ($u_k(\mathbf{r})$) with the same periodicity as the potential.

$$\psi_k(\mathbf{r}) = u_k(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}} \quad (2.9.3.3)$$

This allowed a new phase factor to be included in the wavefunction.

$$\psi_k(\mathbf{r} + \mathbf{R}) = u_k(\mathbf{r} + \mathbf{R})e^{i\mathbf{k}\cdot(\mathbf{r} + \mathbf{R})} \quad (2.9.3.4)$$

$$\psi_k(\mathbf{r} + \mathbf{R}) = \psi_k(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{R}} \quad (2.9.3.5)$$

The new plane wave differs by a periodic modulation implying free electrons are simply perturbed free electrons allowing for all relevant properties to be expressed in periodic forms in real space. Substituting equation 3.9.1 into 3.9.3.3 and simplifying gives:

$$\psi_k(\mathbf{r}) = \sum_{\mathbf{G}} C_k(\mathbf{G})e^{i(\mathbf{k} + \mathbf{G})\cdot\mathbf{r}} \quad (2.9.3.6)$$

This form is a superposition of multiple plane waves differing by $\mathbf{G}$, where $\mathbf{G}$ is a reciprocal lattice vector. The Bloch theorem allows a small piece of a solid to be used for reliable DFT calculations.

KS orbitals come in many shapes, so approximating them as a linear combination of simple plane waves makes DFT calculations of large crystalline materials easier. Plane waves are a nonlocal basis set (meaning they span all space). The charge density is a quantity from the KS theorem and thus can be expanded using plane waves by squaring the expanded orbitals:

$$\rho(\mathbf{r}) = \sum_{\mathbf{G}} \rho(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}} \quad (2.9.3.7)$$

Summing over $\mathbf{G}$ in equation 2.9.3.7 will be infinite, however, introducing a cutoff energy (E_{cut}) truncates the plane wave basis set. The cutoff energy is defined as:

$$E_{\text{cut}} \geq \frac{1}{2} (\mathbf{k} + \mathbf{G})^2 \quad (2.9.3.8)$$

The E_{cut} will vary per system and must be optimized using convergence testing to ensure the specified energy is high enough for accurate results. G_{cut} is a spherical radius in reciprocal space which represents the plane wave. Charge density is quadratic in the wavefunction so charge density calculations in reciprocal space require the Fourier grid to contain all wave vectors up to $2G_{\text{cut}}$ otherwise wrap-around errors occur.

2.9.4 Band structure, Band gap, and Density of States

Plotting all KS orbitals and energies for a supplied set of $\mathbf{k}$ -points allows for the creation of band structure and density of states (DOS) plots. The band structure shows how electrons travel through the material and displays the electronic states along high symmetry lines in the IBZ. Valence electrons in solids form energy bands separated by energy ranges where no electron states exist called a band gap. Waves propagating in a crystal experience Bragg diffraction and form the band gap as there is no solution to the Schrödinger equation in this range. This creates two separated band regions above and below the highest occupied energy level called the Fermi level (energy). Bands above the Fermi energy are unoccupied and called

the conduction bands. Bands below the Fermi energy are occupied and called valence bands. Excited electrons transition from the valence band to the conduction band when external energy is supplied. The conduction and valence bands that are closest to the Fermi energy are called the conduction band minimum (CBM) and the valence band maximum (VBM). A DOS diagram provides the number of electronic states per unit energy range. The DOS is essential for determining carrier concentrations and energy distributions in a semiconductor. Figures 2.9.4a and 2.9.4b show a sample band structure and DOS plot.

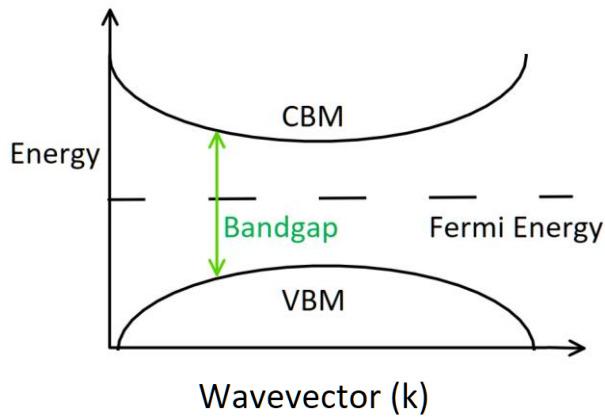


Figure 2.9.4a: Example Band structure including band gap

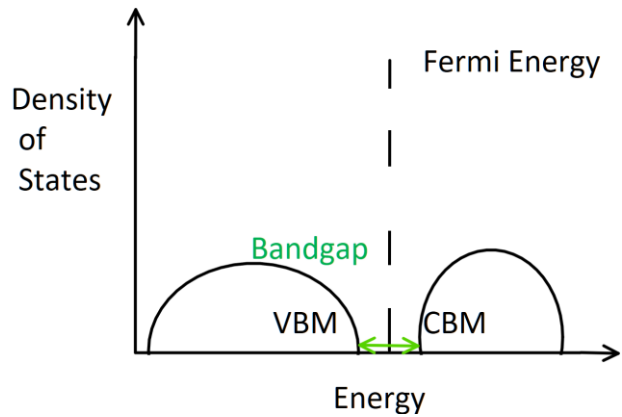


Figure 2.9.4b: Example DOS including band gap

2.9.5 Surfaces, Slabs, Supercells, and Dipole Corrections

A flat surface is created by cutting a bulk crystal material. This cutting will expose the atoms in the plane where the cutting occurred. In this work, the atoms at the surface will be in contact with a vacuum region. Surface simulations can be modeled using a supercell method. This method is comprised of a slab that is infinite and periodic in a parallel direction and finite in the perpendicular direction to the surface. Electronic properties are being investigated in this work so the slab supercell model was used as it allows for band formation with correct dispersions. Figure 2.9.5 depicts the supercell model with a slab in the center of the supercell and a vacuum region above and below the slab with a surface layer highlighted in yellow.

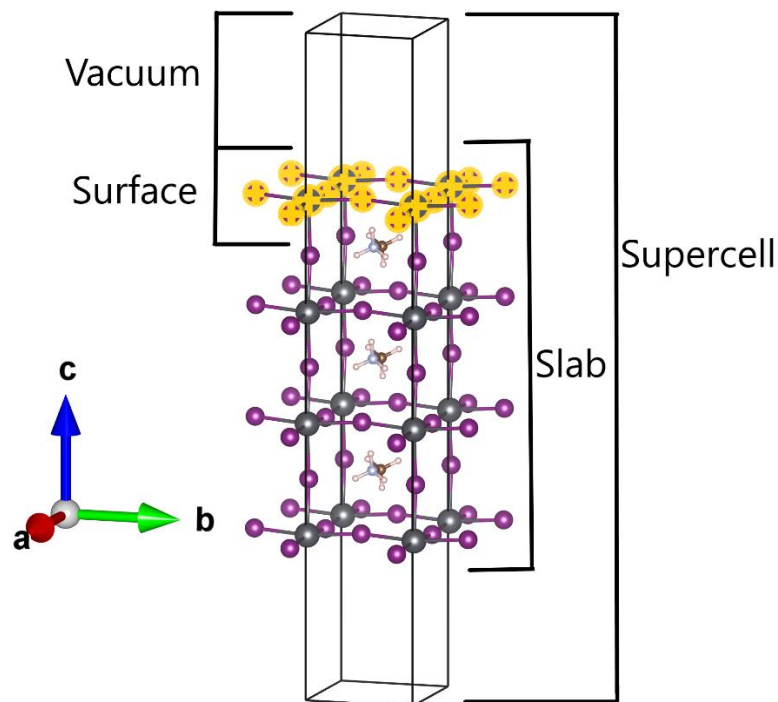


Figure 2.9.5: Supercell model containing a surface slab atomic structure

Many materials can have an asymmetric structure when creating surfaces using the slab model. The slab model includes a supercell representing a thin film oriented on a specific facet that is separated by a vacuum region. The asymmetrical structure of the surfaces is due to different arrangements of the atoms on the top and bottom surfaces resulting in differing electrostatic potentials for each surface. This potential difference induces an artificial electric field in the vacuum represented as a non-constant potential shown in Figure 2.9.6.

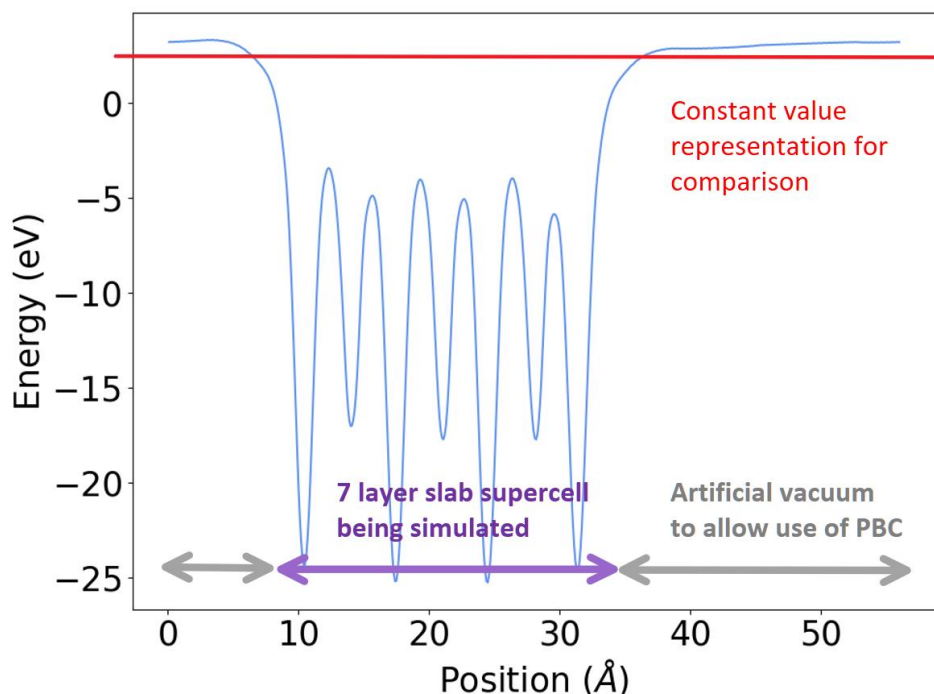


Figure 2.9.6: Non-constant potential in vacuum due to an artificial electric field

The artificial electric field is non-physical as the potential in a vacuum should be constant throughout since there is no electric field present. This effect can be compensated for by applying a planar dipole layer in the middle of the vacuum thereby negating the artificial electric field [27]. The size of the vacuum will need to be optimized until a constant potential is achieved. Additionally, the slab model presents two additional problems the dipole corrections resolve. Firstly, the supercell is being modeled using infinitely uniform plane waves whereas the surface creates a finite dimensionality. Secondly, certain slab terminations simulate a “cutting” of the material which results in broken “dangling” bonds violating the assumption of an infinite crystal that serves as a basis for the usage of periodic boundary conditions.

2.10 Energy Corrections in DFT

The first step in DFT calculations is optimizing the bulk unit cell of the system being studied. LDA and GGA have shortcomings that provide a close approximation for structural and

electronic properties. Hybrid functionals provide better approximations but can be computationally prohibitive. Additionally, there is the need to account for relativistic effects for heavy atoms such as Pb. The following section will discuss a method to improve the LDA and GGA approximations with a Hubbard U correction and will address how to incorporate relativistic effects such as spin-orbit coupling (SOC) to account for the heavy atoms.

2.10.1 Relativistic mass-velocity, Darwin, and SOC corrections

Equation 3.10.1.1 shows the fully relativistic Hamiltonian.

$$\hat{H} = \hat{H}_0 - \frac{1}{2mc^2} \frac{\mathbf{p}^4}{4m^2} + \frac{\hbar^2}{8m^2c^2} \nabla^2 v(\mathbf{r}) + \frac{\hbar}{4m^2c^2} \boldsymbol{\sigma}^* (\nabla v(\mathbf{r}) \times \mathbf{p}) \quad (2.10.1.1)$$

The terms (from left to right) are the non-relativistic Hamiltonian, the mass-velocity term, the Darwin term, and the spin-orbit interaction term. The mass-velocity term correction for the variation of mass with the velocity of the electron results in a small decrease in kinetic energy as evidenced by the negative sign. The Darwin term (proposed by C.G. Darwin, the grandson of Charles Darwin, in 1928 [28]) is a correction to the non-local interaction between the electron and the Coulomb field. This term smears the potential felt by the electron resulting in a change in the electron's potential energy. The last term is the spin-orbit coupling term. The mass-velocity and Darwin terms together are often called the scalar relativistic corrections and are included by default in the VASP PAW POTCARs. [29] [30] [31] Note that to perform full relativistic calculations the SOC correction must be included. Here, $\hat{H}_0$ is the default scalar relativistic Hamiltonian included in VASP which includes the mass-velocity and Darwin correction terms.

$$\hat{H} = \hat{H}_0 + \hat{H}_{\text{SOC}} \quad (2.10.1.2)$$

$$\hat{H}_{\text{SOC}} = \frac{e^2}{8\pi\epsilon_0} \frac{1}{m^2 c^2 r^3} \mathbf{L} \cdot \mathbf{S} \quad (2.10.1.3)$$

The SOC effect increases as atomic mass increases. [32] Previous work has shown that SOC effects should be incorporated when modeling Pb-based halide perovskites. [33]

2.10.2 Hubbard U Correction (DFT + U)

The Hubbard U correction is an empirical correction to the delocalized charge distributions in DFT. DFT includes self-interaction errors which result in delocalized charge distributions [34]. In 1963 John Hubbard proposed that systems with strongly localized orbitals have an extra-repulsive interaction [35]. This occurs in the d and f orbitals of strongly correlated metals. In this work, the U correction was considered to provide a better description of halide p-orbital interactions. This approach of adding a U correction to the halide p-orbitals was previously used in the bulk by Welch et al [10], and similarly, it was also used to study polarons in TiO₂. [36] The Hubbard U correction is a corrective term that can be employed with local or semi-local functionals. Leveraging HF-like methodology, the repulsive energy is added to the KS Hamiltonian to shift the localized orbitals. The DFT+U method ensures the cancellation of the self-interaction error in semi-local approximations. Adding the U correction provides improved results for electronic properties while only slightly increasing computational times compared to local and semi-local functional calculations. The U correction is significantly quicker than hybrid functionals but the results are not as precise. There are a couple of different versions of the Hubbard model implemented in VASP. The Dudarev model simplifies the Hubbard model while producing relevant results [37]. It is given by:

$$E_{\text{DFT+U}} = E_{\text{LSDA}} + \frac{(U-J)}{2} \sum_a \left[\left(\sum_{m1} n_{m1,m1}^a \right) - \left(\sum_{m1,m2} n_{m1,m2}^a n_{m2,m1}^a \right) \right] \quad (2.10.2.1)$$

The U term represents the strength of the effective on-site Coulomb interactions. J is the strength of effective on-site exchange interactions. The U and J terms replace the intra-atomic coulomb and exchange integrals in the local or semi-local functional. n is the occupation number(s) while $m1$ and $m2$ are electronic states with spin a . [38] In the Dudarev model, $J = 0$. The total energy will depend on U and J , so it is not meaningful to compare total energies with differing U and/or J values. The LDAUL tag specifies which atom and orbital to apply the U correction to. There are four options: -1 (no on-site interaction terms added), 1 (p orbital), 2 (d orbital), 3 (f orbital). Each atomic species will need to have a U value specified.

2.11 Polarons Basics

Phonons are the quanta of ion vibrations (lattice distortions) in a crystal. Electrons moving in the crystal interact with the phonons and this interaction is called electron-phonon coupling. In 1933 Lev Landau proposed an electron could be trapped by lattice distortions. [39] The term polaron was later coined by Solomon Pekar who further advanced Landau's polaron concept. Pekar proposed an electron "dressed" by lattice polarizations would move through the crystal with increased effective mass [40]. Today, polarons are thought of as the combination of a charge carrier (not just an electron) and the resulting induced polarization around the charge carrier. Polarons are fermionic quasiparticles.

Polarons which localize in a single unit cell are called small and move incoherently. The incoherent movement is due to the small polaron needing to overcome a potential barrier when moving from one lattice position to the next. Small polarons effectively hop from one location to the next. Polarons which delocalize across multiple cells are called large and move coherently. [41] Additionally, the charge carrier associated with the polaron will alter how the surrounding ions adjust their positions based on the charge of the surrounding ions. Positively

charged ions will attract towards a negative charge carrier but repel away from a positive charge carrier. This is demonstrated in Figure 2.11.

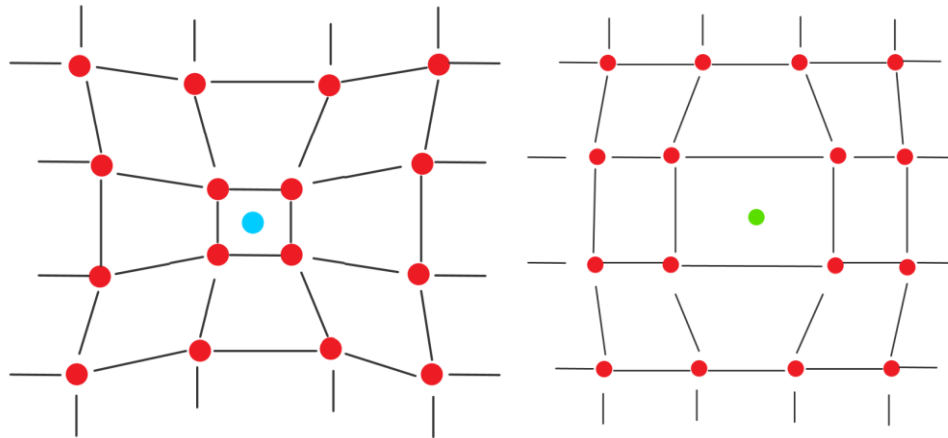


Figure 2.11: Lattice Distortion caused by an Electron Polaron (left) and Hole Polaron (right)

3. SIMULATION METHODS

3.1 Computational Details

This work used the Vienna Ab Initio Simulation Package (VASP) version 5.4.1 for both SOC and non-SOC calculations. PAW pseudopotentials with the PBEsol (semi-local) functional were used. Several files need to be created to run a VASP calculation including INCAR, POTCAR, POSCAR, and KPOINTS. The INCAR file provides input parameters that control how the calculation is performed. The KPOINTS file dictates how the 1st BZ is sampled. The POSCAR file contains the structural information for the compound/material being studied. The POTCAR contains pseudopotential information for each specific element to be used in the calculation. The order of the elements in the POSCAR and the POTCAR must match to run a successful calculation. VASP offers a couple of different pseudopotentials and PAWs to use. The PAWs are concatenated (appended) together to create the POTCAR. All pseudopotentials used were PAW_PBE. The Pb_d PAW was chosen over the standard Pb PAW. This treats the semi-core 5d states as valence states resulting in higher accuracy [42]. The bulk system is the starting point for all DFT calculations so it is imperative to ensure it is correctly modeled. Parameters such as the lattice constant, bulk modulus, and band gap can be used to check/verify if the structure is correctly modeled by matching against experimentally measured quantities.

3.2 Unit Cell Geometric Optimization

A pseudo-cubic unit cell POSCAR consisting of 12 atoms was taken from a GitHub repository from the Materials Design group at Imperial College London [43]. There are three commonly studied temperature-dependent polymorphs of MHPs: orthorhombic, tetragonal, and pseudo-cubic [6]. Specifically, MAPbI becomes pseudo-cubic at temperatures above 328 K [44]. Experiments show that the pseudo-cubic geometry has the benefit of maintaining a

uniform alignment of PbI_3 octahedra [45]. The rotation of MA cations causes MHPs to display a pseudo-cubic structure rather than a cubic structure [45].

Computational simulations perform numerical integrations over finite grids and infinite series. As the number of operations approaches infinity, so too does the time required to perform them. As such, the numerical calculations are truncated by selecting kinetic energy cut-off (E_{cut} or ENCUT) and the integration grid size for reciprocal space (k -point mesh). Firstly, convergence calculations to determine an appropriate KPOINT mesh size and kinetic energy cut-off (E_{cut}) were run. For KPOINT mesh size optimization, a minimum mesh size of $2 \times 2 \times 2$ and a maximum of $9 \times 9 \times 9$ were tested using an increasing $1 \times 1 \times 1$ mesh size increment. (All meshes were Γ -centered.) The largest energy value from the POTCAR was used as the ENCUT (cut-off energy) value in the INCAR file for KPOINT mesh optimization. To optimize the ENCUT value, a minimum energy of 250 eV and a maximum of 700 eV was used with increments of 50 eV. The cell shape and cell volume were held fixed by setting the ISIF tag to 2 in the INCAR. The ISIF tag specifies which degrees of freedom are allowed to change. These degrees of freedom include ionic positions, cell volume, and cell shape.

After optimizing the KPOINT mesh and ENCUT value, the lattice constant for each bulk material was determined. The lattice scaling factor in the POSCAR was varied from 95% to 105% (with increments of 1%) using the conjugate gradient algorithm for ionic relaxation. The conjugate gradient method moves ions in the negative direction of the gradient. After determining the initial result, subsequent minimization steps are used until the forces acting on the ions are orthogonal with the previous step. [46] Setting the IBRION tag to 2 directs VASP to use the conjugate gradient method. Setting the NSW tag to an integer value specifies the number of subsequent minimization steps to use for the minimization algorithm. Ionic minimization was

allowed to run until all forces were smaller than 0.01 eV by setting the EDIFFG tag in the INCAR. The equilibrium volume for each unit cell of all MHPs leveraged the Birch-Murnaghan equation of state fit to calculate the lattice constant as well as the bulk modulus. (Details follow in the next section.) The optimized KPOINT mesh, ENCUT energy, and lattice constant values were then used to create a fully optimized unit cell structure for use in a self-consistent calculation for the electronic structure of each system. To use the PBEsol functional, an additional tag (GGA = PS) needs to be added to the INCAR file. This overrides the default exchange functional supplied in the POTCAR. As of the writing of this document the exchange functional tag in the POTCAR (LEXCH) should not be changed. Note the CONTCAR file contains the final atomic positions after the job has finished running. Figure 3.1 shows the resulting optimized unit cell for MAPbI.

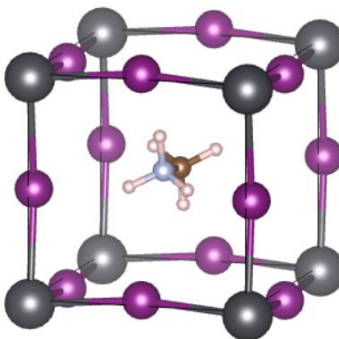


Figure 3.1: Optimized MAPbI Bulk structure

3.2.1 Birch-Murnaghan equation of state

Identifying the optimized k-point mesh and ENCUT is straightforward. Calculating the equilibrium volume, bulk modulus, and lattice constant is more involved. The bulk modulus is the amount of volume change based on the pressure applied. The equilibrium volume is determined by fitting the Birch-Murnaghan equation parameters to the data. The equilibrium volumes are then plotted as a volume-energy curve and the Birch-Murnaghan equation of state is

used to fit the data. The Birch-Murnaghan equation was proposed in 1947 and provides a relationship between the volume of a body and the pressure exerted on it [47].

$$E(V)=E_0+\frac{9}{16}V_0B_0\left\{\left[\left(\frac{V_0}{V}\right)^{\frac{2}{3}}-1\right]^3B_0'+\left[\left(\frac{V_0}{V}\right)^{\frac{2}{3}}-1\right]^2\left[6-4\left(\frac{V_0}{V}\right)^{\frac{2}{3}}\right]\right\} \quad (3.2.1.1)$$

Here, E_0 is the minimum energy of the curve, B_0 is the bulk modulus, V_0 is the ground state volume, and B_0' is the partial derivative of the bulk modulus with respect to pressure.

3.3 Bulk Electronic Properties

Generating electronic properties is a two-step process. First, the CONTCAR from the optimized unit cell was used as the POSCAR to create a charge density by running a self-consistent field (SCF) job with no ionic relaxation. The density of states (DOS) and band structure calculations were then performed using the charge density from the SCF job while keeping it constant throughout the run. The tetrahedron method was used for the DOS calculations while Gaussian smearing was used for the band structure. The Gaussian smearing width for band structure jobs was 0.001 eV. The k-points used for a band structure calculation are as follows: M1-R-X1-M2-R-X2-M3-R-X3- Γ -R-M1 (see figure 3.3.1).

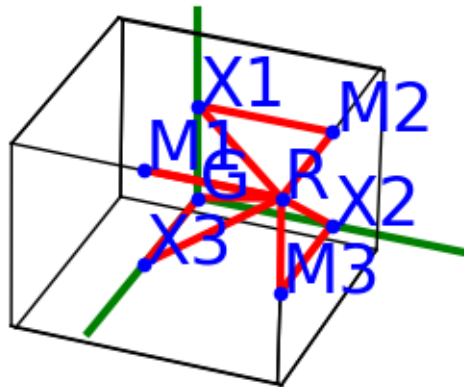


Figure 3.3.1: K-points used for band structure

After the initial DOS calculation, it was decided to run additional DOS calculations while increasing the NEDOS value. This value specifies the number of grid points used to evaluate the DOS. A larger value gives a better evaluation (at the expense of additional computation time). The default NEDOS value of 301 was unable to resolve all peaks sufficiently. A final NEDOS value of 10000 was chosen as an increase beyond that number did not result in a marked improvement.

Additional calculations leveraging the Hubbard U correction as well as the HSESol hybrid functional were performed for additional data comparison of band gap and band structure values in the bulk. For calculating band structures for the hybrid jobs, additional k-points with zero weight were used. This method is referred to as the 0-weight (Fake) SCF procedure. [48] This involves running a standard DFT band structure calculation at the PBE level to automatically generate a k-point mesh (IBZKPT), charge density file (CHGCAR), and wavefunction (WAVECAR) file. These additional files are used as inputs for the hybrid functional band structure calculations. HSESol calculations used an HF exact exchange value of 25%. The hybrid job used Gaussian smearing and removed symmetry. To save time while running hybrid calculations, the PRECFOCK tag was set to fast. The PRECFOCK tag is used to define which FFT grid is used to calculate the exact exchange contributions. This provides good accuracy for the energy while only introducing a small noise level in the forces (below 0.01 eV/Å). [49]

Previous work done to identify the correct U value in the bulk for MAPbX perovskites (using PBE) found that 8 eV provided the best results using band gap and hybrid ionic force matching. [10] This optimized U value was used to perform the PBEsol+U calculations in this work. The U values for C, H, and N were each set to -1 (meaning no correction was added) for

all calculations using the LDAUL tag in the INCAR. (Specifics on the LDAUL tag can be found in section 2.10.2) The U value was added to the p orbitals for the different halides. The simplified DFT+U method introduced by Dudarev was used. The bulk PBEsol+U calculations were then run again incorporating spin-orbit coupling by adding the LSORBIT tag. The python package pymatgen was then used to calculate the band gap [50]. Both HSEsol and PBEsol+U calculations included non-spherical contributions for gradient corrections inside the PAW spheres by setting the LASPH tag to true. Aspherical charge density contributions arise when using hybrid and Hubbard U calculations and must be included to calculate accurate total energies and band structures.

3.4 Surface Slab and Selective Dynamics

Two types of surfaces can be created depending on which plane of atoms the crystal is cut at. A 7-layer slab was created using VESTA [51] for two separate terminations, PbX and MAX (where X = Cl, Br, I), from the CONTCAR of a structurally optimized unit cell. A termination refers to where the slab ends and is determined by the atoms that construct the surface layer of the slab after it has been cut/sliced. Scanning tunneling microscopy (STM) measurements of an orthorhombic MAPbI thin film grown on Au surfaces showed the surface was terminated with an MAI layer. [52] X-ray photoelectron spectroscopy (XPS) measurements also showed that surface terminations will depend on the humidity present in the environment. The MAI termination was realized below 35% and the PbI was realized at higher humidity levels. [53] For these reasons, both surface terminations were modeled. The PbX slab termination (depicted in figure 3.4.2) was comprised of 39 atoms while the MAX slab termination (see figure 3.4.3) had 45. A vacuum was added “on top” of the slab so the supercell method can be used. The slab structure was shifted “to the middle” (roughly) so that vacuum

was on the top and the bottom of the slab inside of the supercell. The “top” and “bottom” of the slab contact the vacuum, so the slab has two surfaces. Multiple supercells with vacuums of varying sizes were created. The vacuum size variances were needed to decide the optimal vacuum size using selective (molecular) dynamics (plus dipole corrections) to ensure the top and bottom surfaces did not interact with each other. (That scenario would be an unphysical situation.) Selective dynamics specified (per atom) whether atomic coordinates were allowed to change during relaxation for structural simulations. The bottom 3 layers of the slab were held fixed to mimic a bulk structure while the top 4 surface layers were allowed to move. Structural relaxation was run until the structures were fully electronically relaxed with an energy minimization break condition of 1×10^{-6} eV using tetrahedron smearing. Supercell calculations used a $6 \times 6 \times 2$ k-point mesh. Figure 3.4.1 shows a layer-by-layer description of which layers were held fixed and which were allowed to move. Figures 3.4.2 and 3.4.3 show the supercells with differing PbX and MAX slab terminations.

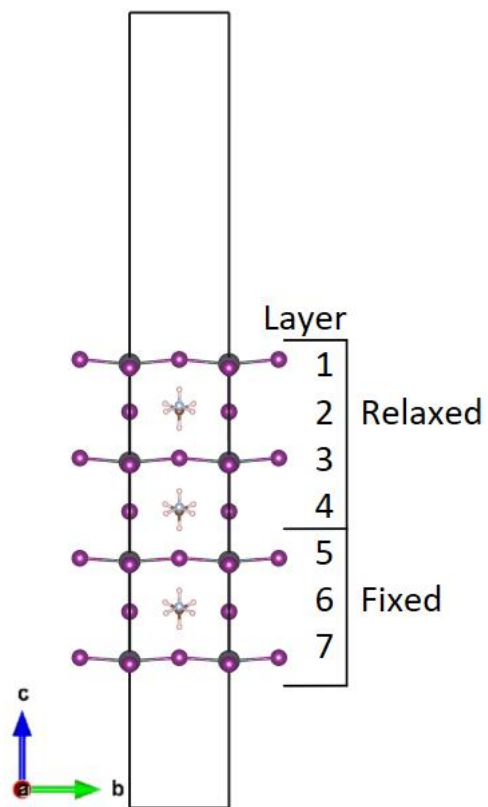


Figure 3.4.1: MAPbI Supercell showing relaxation strategy by layer

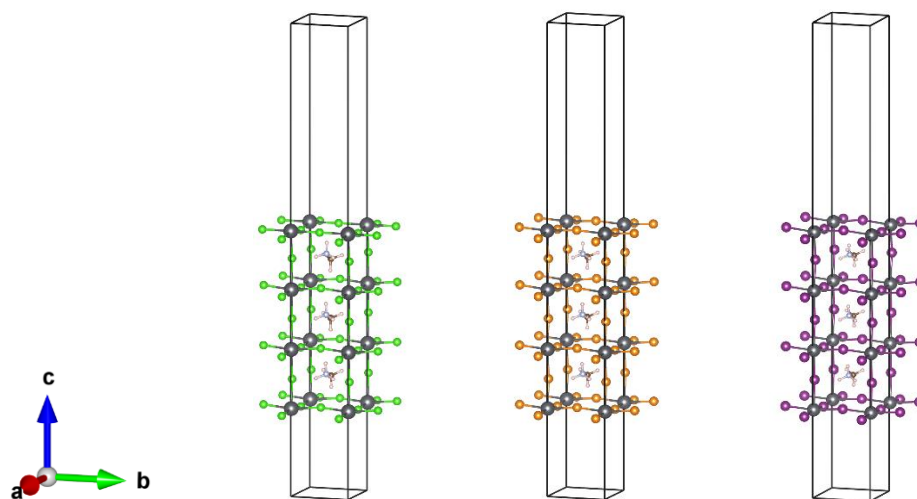


Figure 3.4.2: PbX Terminated Supercells with 5 units of vacuum:
MAPbCl (left,) MAPbBr (middle), MAPbI (right)

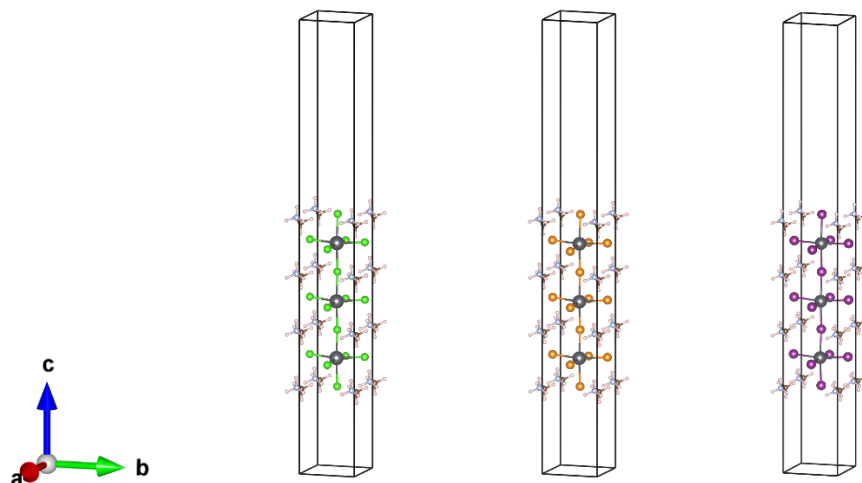


Figure 3.4.3: MAX Terminated Supercell with 5 units of vacuum:
MAPbCl (left,) MAPbBr (middle), MAPbI (right)

3.4.1 Surface Slab Local Potential and Vacuum optimization

After the slabs were relaxed using selective dynamics, dipole corrections were applied to the neutral supercells as recommended by VASP. [54] The CONTCAR from the relaxed (using selective dynamics) slabs was used as the POSCAR for the first dipole correction calculation. The dipole correction was calculated in the third lattice vector (z-axis) direction (since the vacuum added to the supercells was in this direction). The Potential-and-Forces correction (2nd dipole step) was then added. The python program MacroDensity (created by the Materials Design Group at Imperial College London) [55] was used to extract the planar average potential data and then plotted using python. The vacuum which exhibited the least deviation from a constant value was chosen. This process was performed for both PbX and MAX (where X = Cl, Br, I) slab terminations. (Note the potential-and-forces correction step cannot currently be applied to charged supercells.)

4. RESULTS AND DISCUSSION

4.1 PBEsol and PBEsol+SOC Bulk Results

Previous work to optimize the U value leveraged band gap matching as well as ionic force matching with a hybrid functional. [10] Insufficient time prevented a re-optimization of the Hubbard U value using ionic force comparisons with hybrid functionals; however, band structures were studied various U values in the bulk on all halide bulk materials with the aim of investigating changes in the band gaps due to different U values.

Unit cell geometric calculations determined the best gamma-centered k-point mesh size was 6x6x6 with a plane wave energy cut-off value (ENCUT) of 500 eV for use with all MHPs. Graphs of the convergence calculations are in the Appendix. The calculated lattice constants and bulk moduli values are given in Tables 4.1.1 and 4.1.2.

Table 4.1.1: Lattice Constants using PBEsol

Lattice Constant	This work (Å)	Other DFT Studies (Å)	Experimental Values (Å)
MAPbCl	5.68	5.68 [56]	5.68 [57], 5.68 [58]
MAPbBr	5.93	5.92 [56]	5.90 [57], 5.91 [59], 5.92 [58]
MAPbI	6.31	6.29 [60]	6.33 [57], 6.27 [61], 6.311 [58]
MAPbI	-	6.3*[46]	-

* PBE (cubic) with modified POTCARs

Table 4.1.2: Bulk Modulus using PBEsol

Bulk Modulus	This work (GPa)	Other DFT Studies (GPa)	Experimental Values (GPa)
MAPbCl	16.81	17.0 [56]	-
MAPbBr	15.96	15.9 [56]	16.8 [62]
MAPbI	13.29	15.6 [56]	13.1-13.3 [62], 13.9 [63]
MAPbI	-	16.6* [46]	-

* PBE (cubic) with modified POTCARs

The lattice constants for all the halides fell within <1% of other DFT studies and reported experimental values. MAPbCl, MAPbBr, and MAPbI had a calculated cell volume of 183.48 Å³, 208.90 Å³, and 251.31 Å³, respectively.

The calculated bulk modulus for MAPbCl and MAPbBr both fell within 1% of other DFT studies. The calculated bulk modulus for MAPbI improves on the value compared to other DFT studies and was within <1% for experimental values. The bulk modulus from the previous work in the bulk overestimated the bulk modulus by 25% for MAPbI. [46] Recall the bulk modulus is a measure of a materials resistance to uniform compression. Bulk modulus fitting graphs are in the Appendix Section.

Lattice constant optimization and bulk modulus calculations that included SOC and U corrections (U = 8 eV) were performed on a bulk MAPbI system. The calculated lattice constant for SOC was 6.30 Å with a bulk modulus of 39.34 GPa. The lattice constant for PBEsol+U (U = 8 eV) was 6.33 Å with a bulk modulus of 13.06 GPa. The lattice constant and bulk modulus calculated values for PBEsol+U (U = 8 eV) were close to the PBEsol values. Structural parameter optimization did not include the U correction, given how closely the resulting values were for PBEsol+U and PBEsol. Non-SOC calculations resulted in a closer match to experimental values for the bulk modulus, so the non-SOC optimized bulk structures were used.

The band gap is an essential property for photovoltaic applications. Therefore, achieving a good band gap and band structure for the bulk was imperative for comparison with experimentation. As previously stated, SOC affects the band gap of these perovskites as it breaks degenerate bands apart. All elements in these halide perovskites have a p orbital except for hydrogen. As such, the SOC effect will be present for C, N, Pb, Cl, Br, and I. C and N have small masses, so the SOC effect is negligible. In Figures 4.1.1 we show the band structures for

MAPbCl, MAPbBr, and MAPbI obtained using PBEsol and PBEsol+SOC functionals. Table 4.1.3 shows the atomic mass of each element. [64]

Table 4.1.3: Atomic Mass Values

Element	Atomic Mass (AMU)
C	12.022
N	14.0067
H	1.00797
Pb	207.2
Cl	35.453
Br	79.904
I	126.9045

The largest energy contribution occurs in Pb due to the large SOC effect on the p orbital splitting in the conduction band. As the halide size increased, so did the SOC energy contribution. The SOC splitting was smallest in chlorine and largest in iodine. Adding SOC to the PBEsol calculation for MAPbCl reduced the band gap by 40% from 2.2243 eV to 1.3504 eV. Likewise, MAPbBr and MAPbI experienced a 45% and 35% reduction, respectively. Unfortunately, adding the SOC correction at a GGA level (alone) did not reproduce the band gap for these halide perovskites. Studies showing the use of quasi-particle approximations (GW) and SOC can reproduce the experimental band gap value, but these calculations are computationally expensive and are not covered in this work. [65] [66] Fortunately, the scalar-relativistic POTCARs used by VASP cancel out errors between the relativistic SOC and the GGA functional resulting in a fairly good band gap and band structure description. [67] [68] Additionally, as determined by other studies, the inclusion of SOC does not significantly alter the structural properties (such as the lattice constant) in the bulk, confirmed by previous work. [67] [69] [70] Thus, SOC effects were neglected for the remainder of this work. SOC Band structures are shown in Figures 4.1.1a, 4.1.1b, and 4.1.1c.

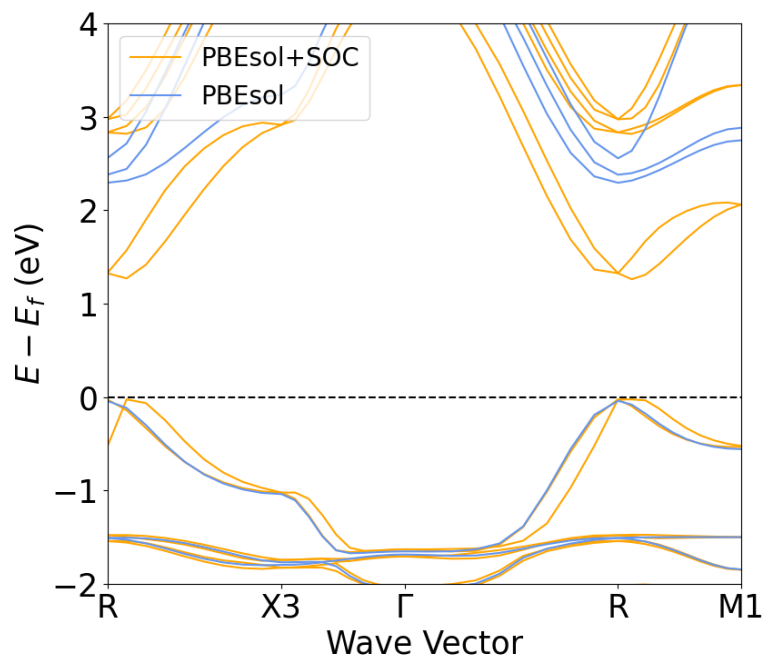


Figure 4.1.1a: MAPbCl band structure PBEsol vs PBEsol+SOC corrections

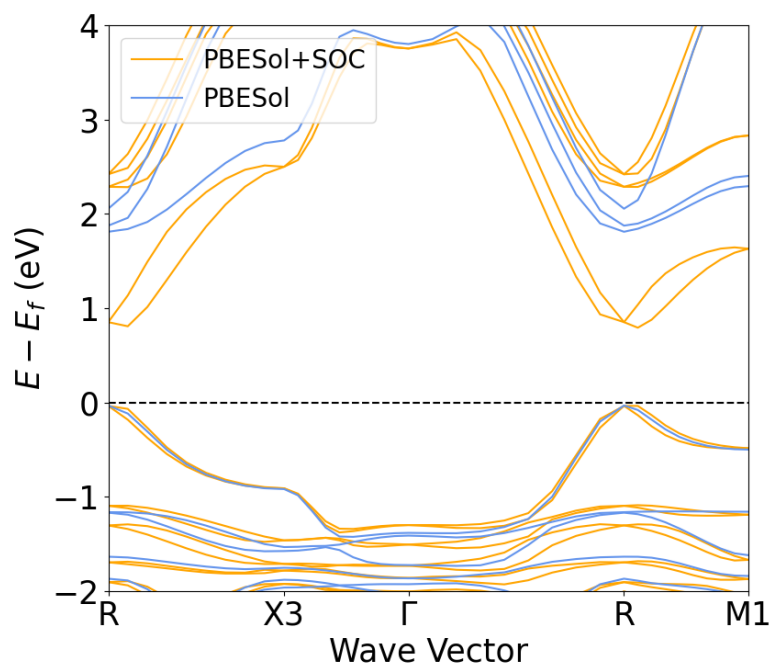


Figure 4.1.1b: MAPbBr band structure PBEsol vs PBEsol+SOC corrections

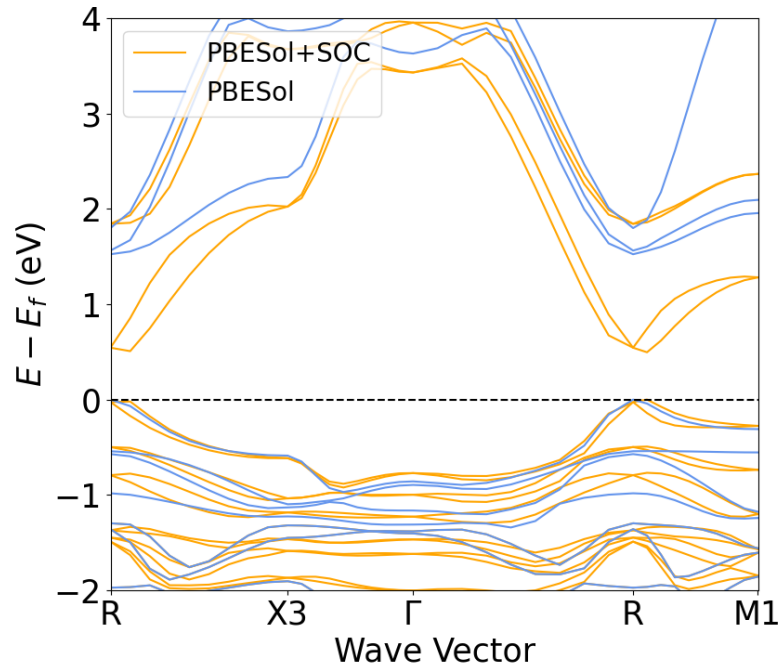
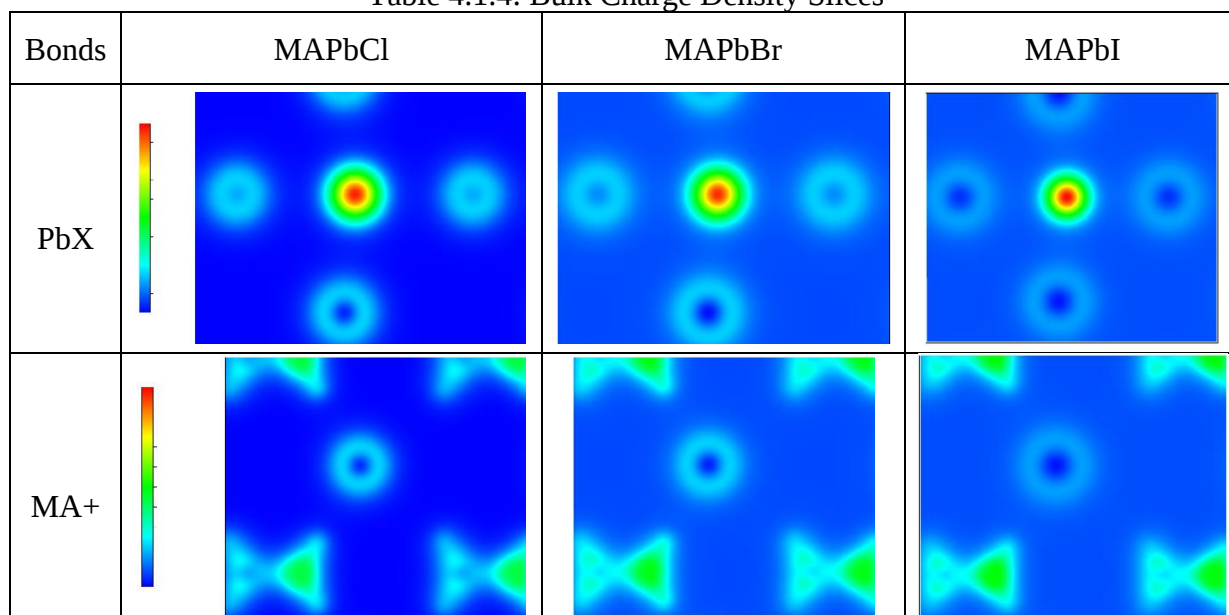


Figure 4.1.1c: MAPbI band structure PBESol vs PBESol+SOC corrections

Characterization of the bonding between the MA⁺ ion and the Pb-X inorganic lattice was performed using a slice of the charge density for each halide perovskite. The spherical electron distribution around the Pb and I atoms suggest an ionic bond characterization while the distortion and overlapping electron distributions in the MA⁺ ion suggest a covalent bond between C and N. This is confirmed by previous work for halide perovskites. [71] The atoms in the PbX row show a Pb atom in the center surrounded by the halide atoms. The atoms in the MAX row show the halide in the center surrounded by MA⁺ cations. Table 4.1.4 shows the charge density slice.

Table 4.1.4: Bulk Charge Density Slices



Electronic structure information about the material being studied can be analyzed using a density of states plot. Plotting the partial density of states (PDOS) using PBEsol demonstrates the halide (Cl, Br, and I) p and the Pb p orbitals are the primary contributors to the top of the valence band and the bottom of the conduction band, respectively. These orbitals are responsible for photoexcitation in a solar cell. Photons interact with electrons in the halide p orbitals exciting them to states in the Pb p orbital. The PDOS for the bulk of all three halides shows the MA ion does not contribute to the band edges directly. Figures 4.1.2a, 4.1.2b, and 4.1.2c show the density of states plots at the band edges.

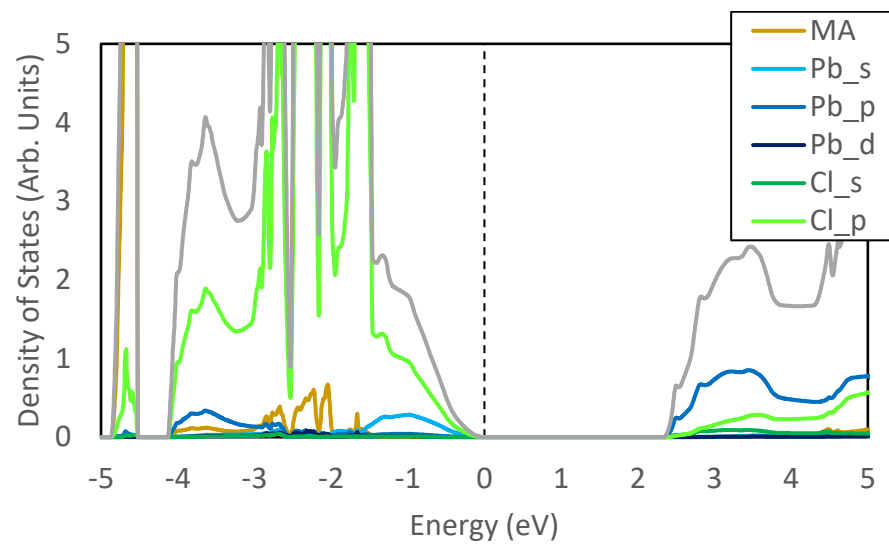


Figure 4.1.2a: MAPbCl Bulk PDOS using PBEsol

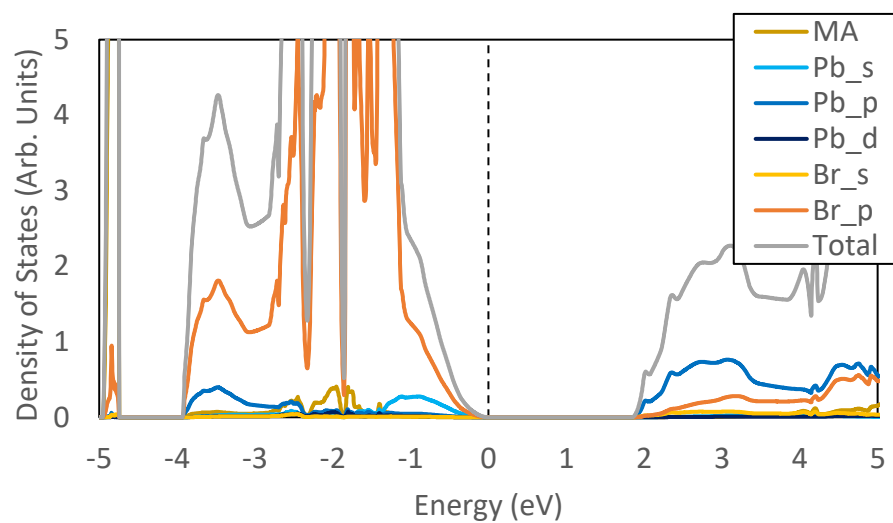


Figure 4.1.2b: MAPbBr Bulk PDOS using PBEsol

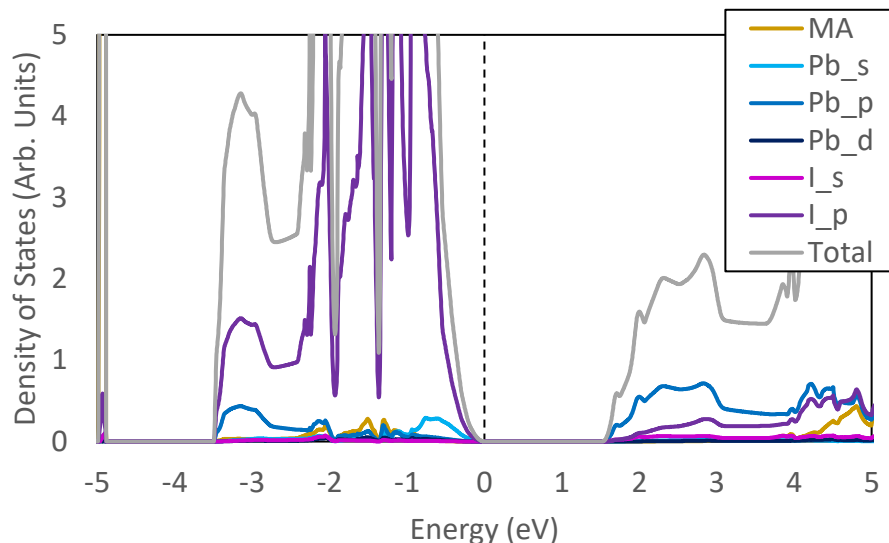


Figure 4.1.2c: MAPbI Bulk PDOS using PBEsol

Specifically, the valence band gap edges are composed of hybrid bonds for X-p (X = Cl, Br, and I), Pb-s, and Pb-p orbitals for all three compounds. The halide p orbitals for the hybrid bonds were Cl-p, Br-p, and I-p. The conduction bandgap edges were a hybrid bonding of Pb-p, X-p, and X-s orbitals. As the size of the halide increased a broadening of the DOS occurred coinciding with a reduction in the intensity beginning at the Fermi energy to -1.5 eV for MAPbCl. MAPbBr also displays a broadening from the Fermi energy to -1.2 eV. A broad band in the band structures results in a lower intensity caused by a larger variation in the energy. MAPbI shows the least broadening in the PDOS indicating less hybridization.

4.2 PBEsol+U Bulk Electronic Results

To investigate the effect of the U value on charge localization, an incrementally increasing U value (increments of 2) was added to the halide p orbitals in the bulk. This data was used to perform a comparison of the band gap with experimental values and compare them against other XC functionals. As the U value increased, the band gap for the MAPbBr bulk shrank up to 3% but increased for the MAPbCl bulk up to 10%. At 8 eV, the bandgap for the

MAPbCl bulk was within 1% of the band gap for the PBEsol functional with no U correction applied. For the MAPbI bulk, as U increased up to 8 eV, the band gap deviated significantly from experimental values resulting in a 19% decrease from the PBEsol value. Based on band gap data, the best U values were 8 eV, 4eV, and 1eV for MAPbCl, MAPbBr, and MAPbI, respectively. These values were chosen as they provided band gap values closest to experimental values. The U value used in this work (4 eV) for MAPbBr was close to the U value used by Kovalenko et al (5 eV) in their study of MAPbBr. [72] Recall U values were needed to remove the self-interaction error which results in delocalized charge distributions in local and semi-local functionals. These bandgap results are depicted in Figures 4.2.1a to 4.2.1c.

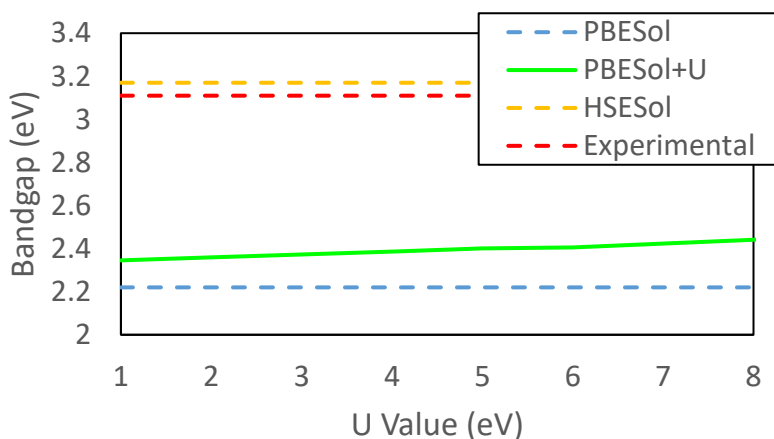


Figure 4.2.1a: MAPbCl band gap

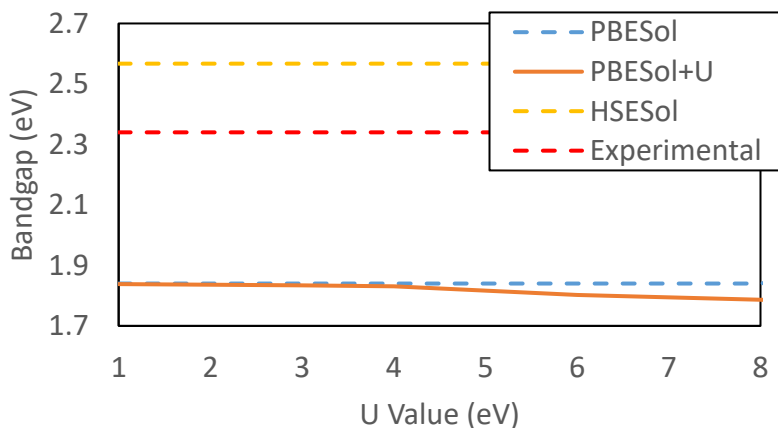


Figure 4.2.1b: MAPbBr band gap

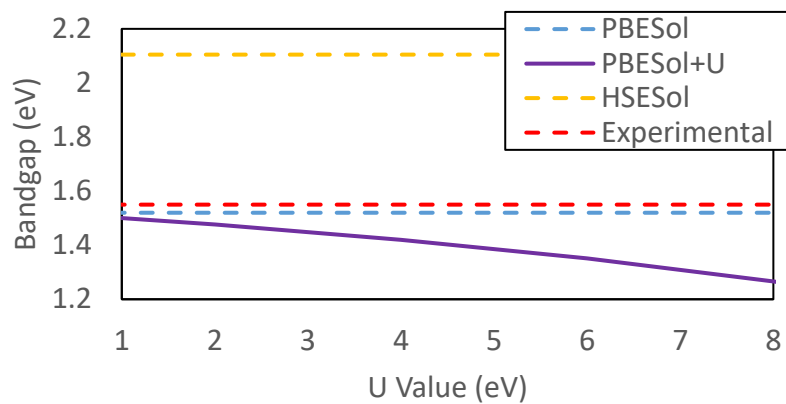


Figure 4.2.1c: MAPbI band gap

Next, a comparison of electronic changes in the total and partial density of states (TDOS and PDOS) as well as the band structure is presented. The TDOS and PDOS for the halide perovskite bulk structures are shown in Figures 4.2.2a to 4.2.4b.

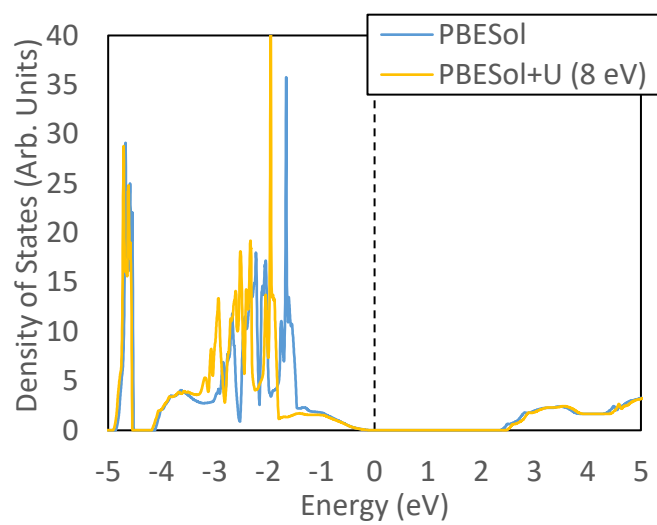


Figure 4.2.2a: MAPbCl Bulk TDOS

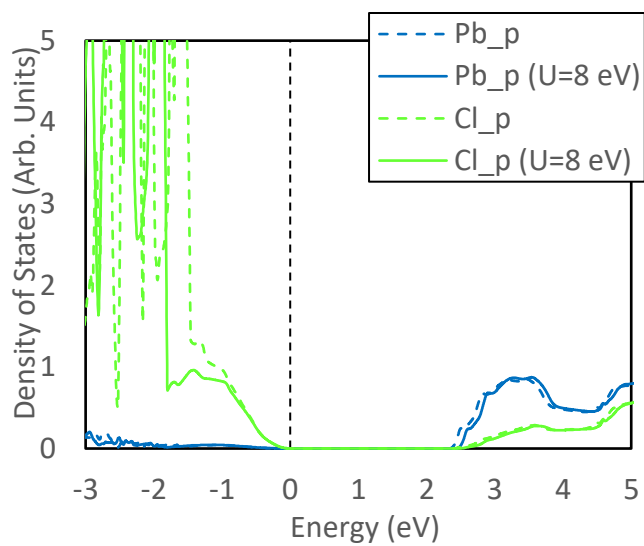


Figure 4.2.2b: MAPbCl Bulk PDOS

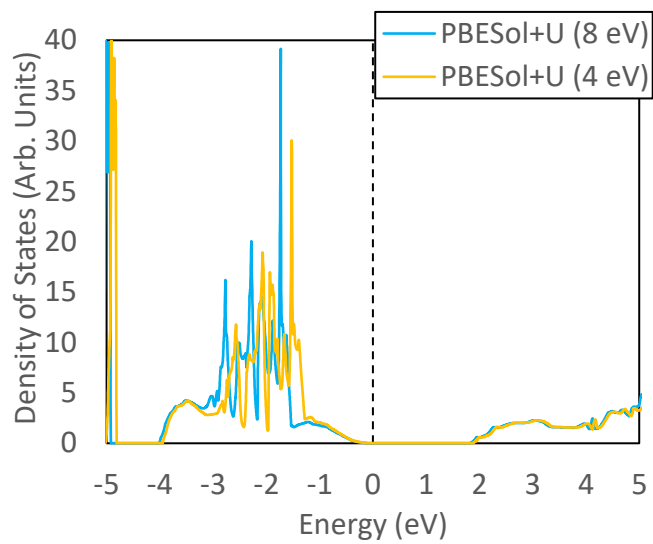


Figure 4.2.3a: MAPbBr Bulk TDOS

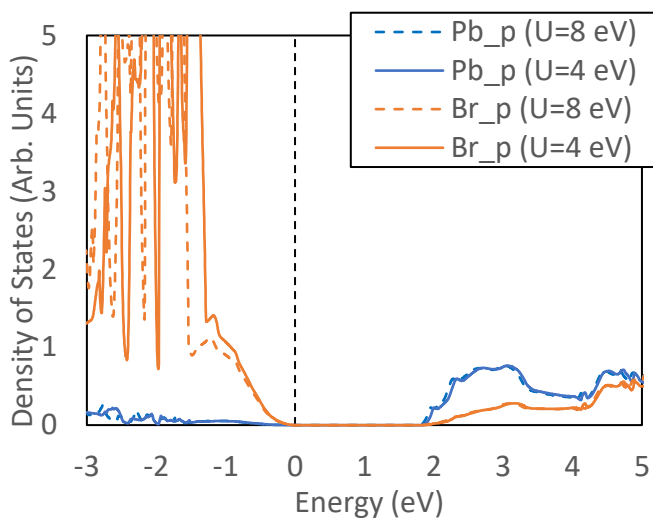


Figure 4.2.3b: MAPbBr Bulk PDOS

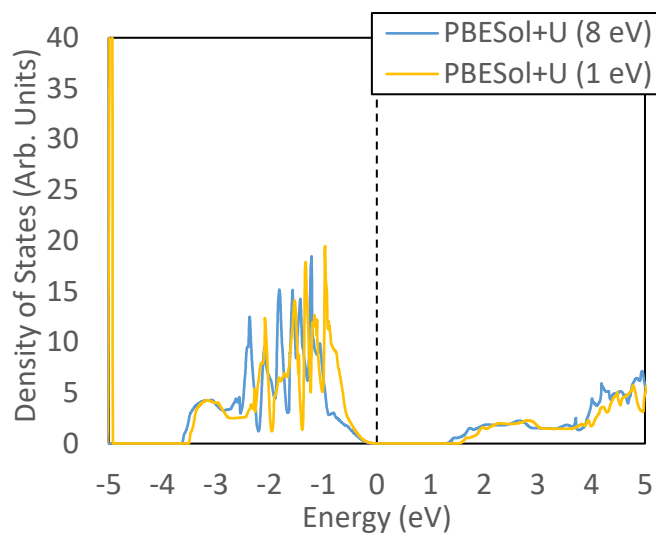


Figure 4.2.4a: MAPbI Bulk TDOS

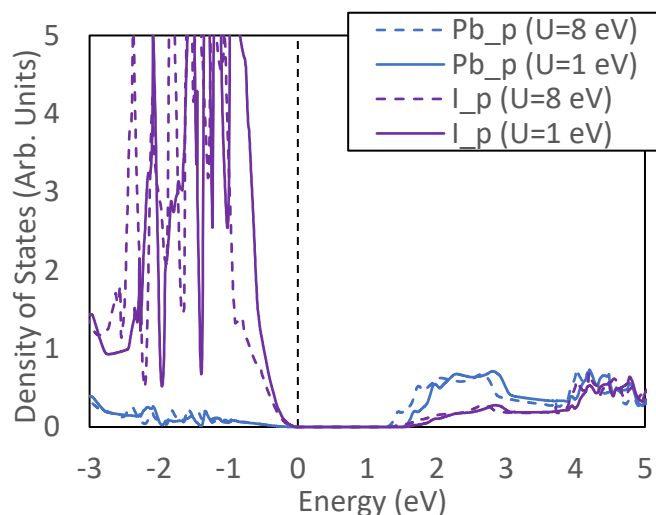


Figure 4.2.4b: MAPbI Bulk PDOS

Given that no alternative U value was determined for MAPbCl using band gap matching, a comparison between the PBEsol and PBEsol+ U ($U = 8$ eV) functionals was done using Figure 4.2.2a and 4.2.2b. Figures 4.2.3a to 4.2.4b give a comparison between U values of 4 eV and 8 eV for MAPbBr and 1 eV and 8 eV for MAPbI. As expected, the U correction that was added to the halide p-orbital caused a broadening of the valence band edges and an energy shift in the

conduction bands. Broadening of the halide p orbital resulted in a lowering of the DOS intensity at the band edges. This showed a reduction in the number of states that can be occupied in this region. The conduction band edge for MAPbCl was shifted to a higher energy level by 4.3%. The MAPbBr conduction band edge energy was reduced by 2.3% going from a U value of 4 eV to 8 eV. Additionally, the MAPbI conduction band edge saw a reduction of 15% going from a U value of 1 eV to 8 eV. This demonstrated that as the size of the halide increased, the effect of the U value on the system increased (as expected.) Adding the U correction does not alter the contribution by the MA ion at the band edges (contribution remained non-existent). Conduction band edge shifting was expected as the halide p-orbital was hybridized with the pb p-orbital and therefore is a contributor to the band edge.

A discussion concerning the band gap values calculated in the bulk using various functionals follows. The PBEsol functional provided a band gap in good agreement with other DFT studies as seen in Tables 4.2.1a to 4.2.1c.

Table 4.2.1a: Bandgaps for MAPbCl

Theory Level	This Work (eV)	DFT Studies (eV)	Experimental (eV)
PBEsol	2.22	2.34 [78], 2.46 [79]	3.11 [78]
PBEsol+SOC	1.35	-	
PBEsol+U (8 eV)	2.44	-	
HSEsol	3.17	3.08 [80]*	
-	-	-	

*HSE

Table 4.2.1b: Bandgaps for MAPbBr

Theory Level	This Work (eV)	DFT Studies (eV)	Experimental (eV)
PBEsol	1.84	1.8 [78], 1.95 [79]	2.33 [81], 2.35 [78]
PBEsol+SOC	0.89	0.8** [33]	
PBEsol+U (4 eV)	1.83	-	
PBEsol+U (8 eV)	1.79	-	
HSEsol	2.57	2.61* [80]	

**PBE

Table 4.2.1c: Bandgaps for MAPbI

Theory Level	This Work (eV)	DFT Studies (eV)	Experimental (eV)
PBEsol	1.52	1.6 [79], 1.57 [78]	1.55 [78]
PBEsol+SOC	0.57	0.56** [45], 0.5**[33]	
PBEsol+U (1 eV)	1.50	-	
PBEsol+U (8 eV)	1.27	-	
HSESol	2.10	2.10 [80] *	

However, the band gap was underestimated compared to experimental values due to overbinding common in semi-local functionals. [73] Comparing the PBEsol functional band gaps with experimental values, MAPbCl, MAPbBr, and MAPbI had a difference of 28%, 20%, and 1.6%, respectively. The MAPbCl band gap difference was reduced to 22% after adding the U value of 8 eV. U values of 4 eV and 8 eV for MAPbBr changed the band gap difference to 22% and 24%, respectively. The MAPbI band gap differences were also changed to 3.2% and 18% using U values of 1 eV and 8 eV. The band structures for the three MHPs in Figures 4.2.5a to 4.2.5c demonstrated how HSESol separated the top valence band from the second valence band. The amount of energy separation between bands decreased from MAPbCl to MAPbBr and finally to MAPbI. This separation was present but less pronounced in the PBEsol band structures but adding the U value increased this band separation energy at the expense of the band gap value. This energy separation corresponded to the low-intensity areas seen in the DOS at the band edges. This means the HSESol functional produced orbitals with a greater variation of energy compared to the semi-local functionals in the bulk. Additionally, the U values also increased this orbital energy variation but to a lesser extent. From the data, it was evident that as the halide size increased, the broadening of the bands near the band gap edge increased after adding the U correction. The band gap remained at the R k-point (and direct) for both the PBEsol and PBEsol+U functionals as shown in Figures 4.2.5a to 4.2.5c

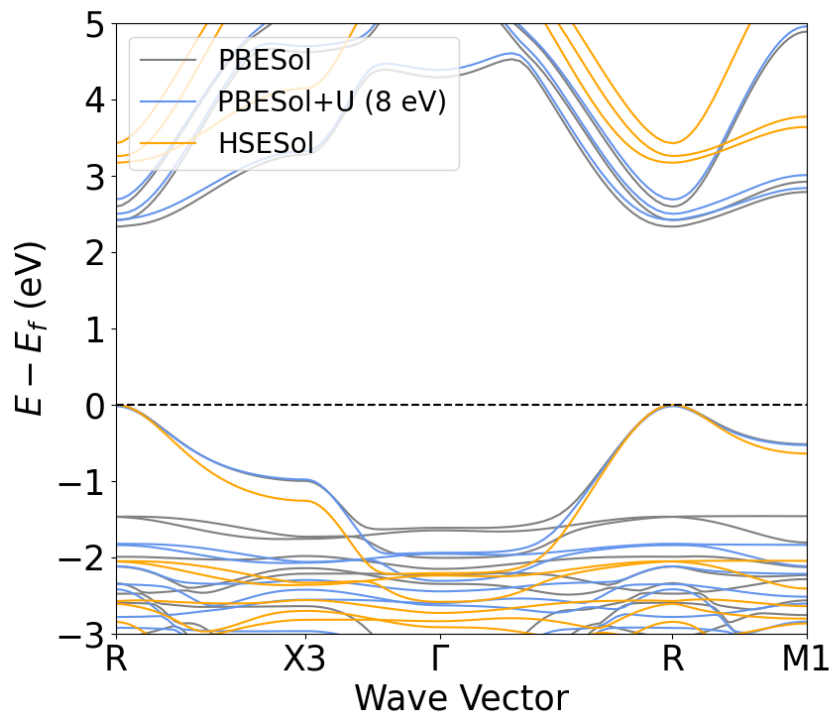


Figure 4.2.5a: MAPbCl Bulk Band structure

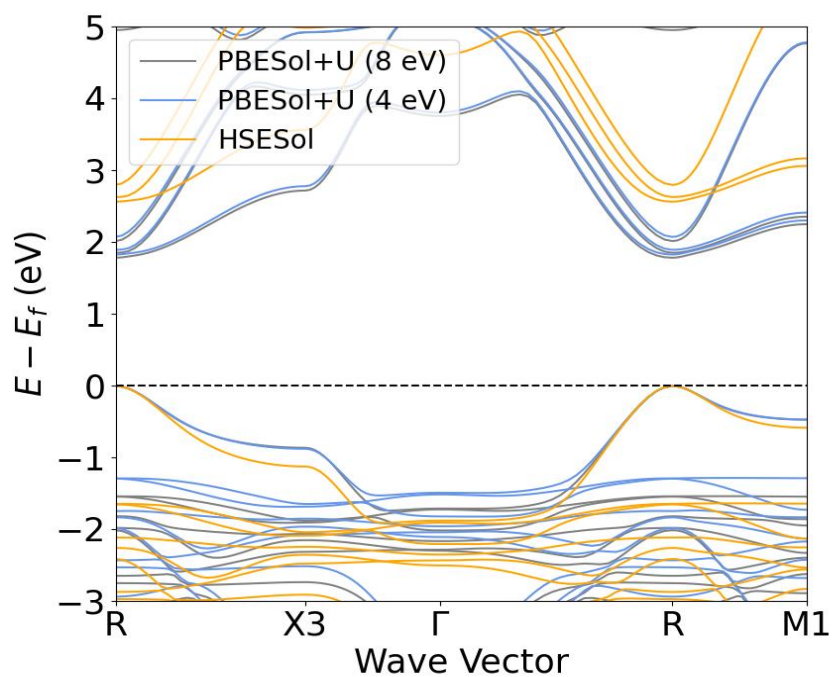


Figure 4.2.5b: MAPbBr Bulk Band structure

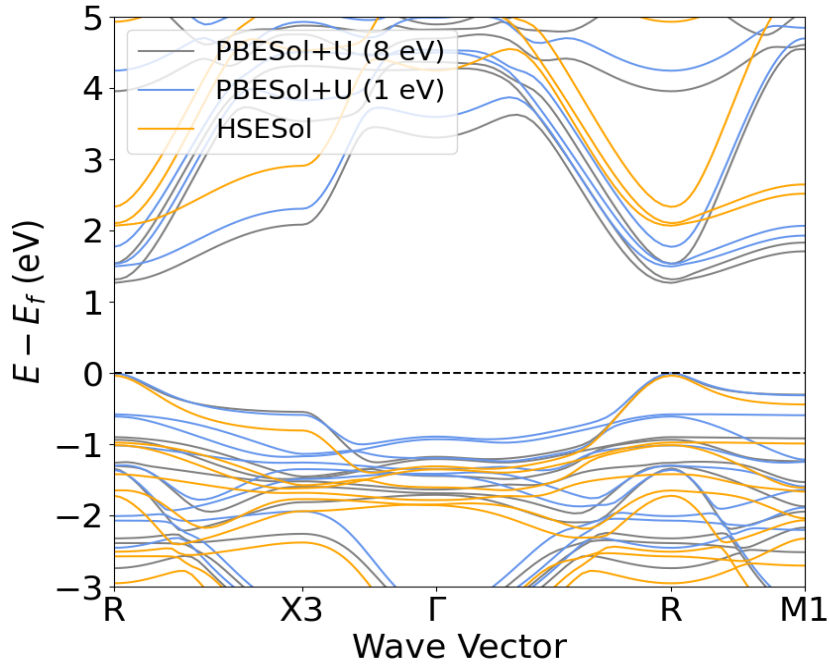


Figure 4.2.5c: MAPbI Bulk Band structure

Previous work attributed lattice contraction to an increased metal-halide orbital overlap that raised the bands to lower energy levels and decreased the band gap. [74] Band gap reduction and band energy shifting were experienced for MAPbI and MAPbBr for all U values used compared to the PBEsol band gap. This could be attributed to lattice contraction as previously reported. The band gap for MAPbCl increased. Previous work has demonstrated that octahedral tilting reduced metal-halide orbital overlap which increased the band gap and resulted in deeper energy states. [61] Octahedral tilting was experienced in the bulk lattice of MAPbCl. Octahedral tilting is present when a rotation of the inorganic PbX lattice occurs. [75] The band structure and band gap were altered differently for each HP.

HSEsol provided the closest bulk band gap value to experiment for MAPbCl compared to PBEsol and the PBEsol+U values. However, HSEsol overestimated the band gaps for MAPbBr and MAPbI compared to experimental values. This overestimation behavior was expected as the

exact exchange value (α) was shown to be material-dependent and therefore will need to be fine-tuned for each perovskite compound. [76] It could be argued that the overestimation of the band gap for MAPbI is preferable, as the addition of SOC to the system would reduce the band gap closer to experimental values. Meggiolaro and Angelis achieved a band gap of 1.58 eV for bulk MAPbI using HSE06 with SOC and an exact exchange value (α) of 0.43. [77]

As previously mentioned, hybrid functionals require more computational time than semi-local functionals to complete. Figure 4.2.6 displays the computational time required to complete a band structure job for each functional.

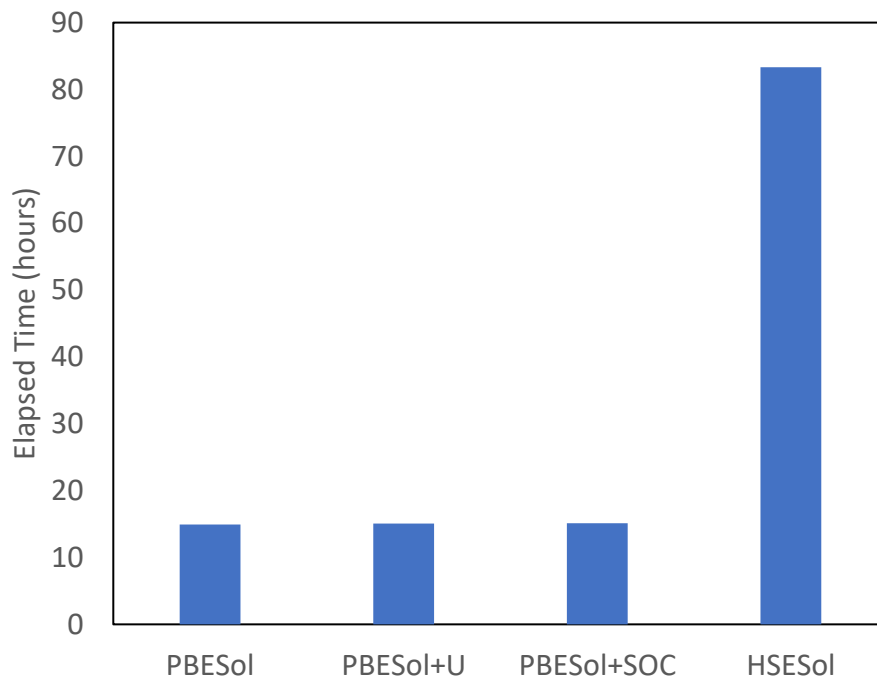


Figure 4.2.6: Bulk Bandstructure Jobs Comparisons

Adding a U value of 8 eV increased the total computation time by 8 minutes while the hybrid functionals saw a 5-fold increase in computational time for a 12-atom bulk system. Considering time constraints, the U value method was used instead of hybrid functionals for the remainder of this work.

4.2.1 Bulk Structural Results

Adding the 8 eV U correction to the PBEsol bulk shifted the Pb atom in the negative x (a-axis into the paper) direction and shifted the CH₃ molecule (of the MA ion) in the negative z (c-axis) direction, towards the halide atoms. The Pb atom shifting caused a change in the Pb-X (X = Cl, Br, and I) bond lengths and angles for all perovskites. For example, the shifting of the Pb atom in MAPbCl coincided with a bond elongation from 2.8464 Å to 2.8835 Å in the Pb-Cl bond on the positive side of the Pb atom as seen in Figure 4.2.1.1a. Additionally, a Pb-Cl bond length reduction occurred, from approximately 2.86 Å to 2.81 Å on the negative x-axis. These bond length changes for the Pb-Cl bond were the largest in bond lengths for all perovskites using any functional. This same scenario (of the Pb atom shifting that coincided with bond elongation and reduction) between the Pb-Br and Pb-I bonds also occurred (as well as MA ion reorientation). The amount of shifting for the Pb atoms and MA ions decreased as the halide size increased for both PBEsol and PBEsol+U functionals. These effects are shown in Figures 4.2.1.1a to 4.2.1.1c below where a reduction in the amount of shifting of the Pb atom occurred using the smaller U values (4 eV and 1 eV) for MAPbBr and MAPbI.

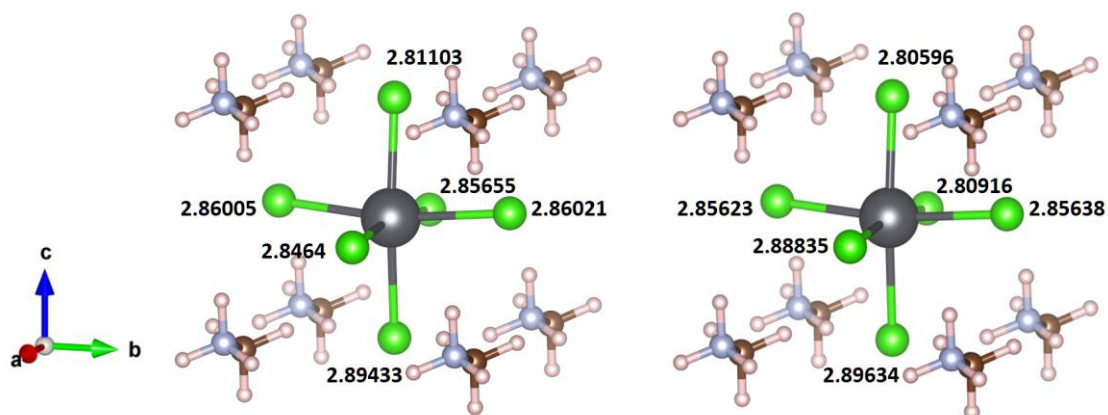


Figure 4.2.1.1a: MAPbCl PBEsol (left) vs PBEsol+U (8 eV) (right) Bond Length comparison (Å)

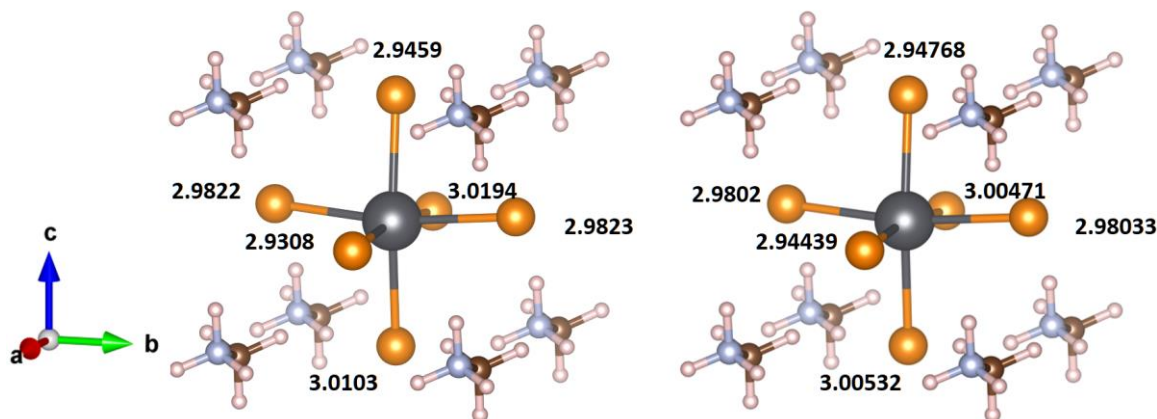


Figure 4.2.1.1b: MAPbBr PBEsol+U Bond Length comparison (Å) | Left U=4 eV, Right U=8 eV

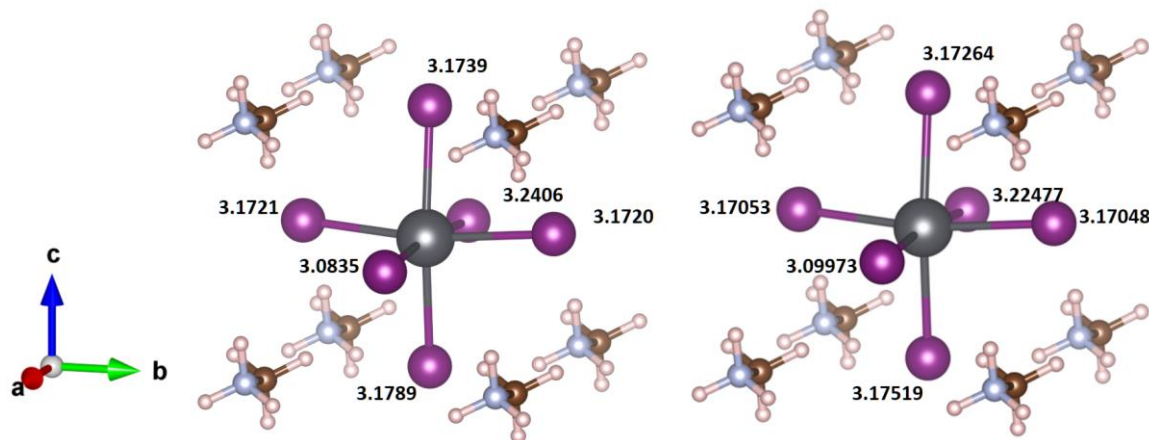


Figure 4.2.1.1c: MAPbI PBEsol+U Bond Length comparison (Å) | Left U =1 eV, Right U =8 eV

The largest bond length changes occurred for MAPbCl which resulted in a lattice contraction in the negative x direction for the bulk. As a result of this contraction, octahedral tilting also occurred in the inorganic lattice. The octahedral tilting increased the band gap for the bulk MAPbCl. Lattice contraction was also seen in MAPbBr and MAPbI although to a smaller extent. However, no lattice tilting was observed in MAPbBr and MAPbI, so the band gap was reduced. These results suggest octahedral tilting takes precedence over lattice contraction when calculating band gap values as previous studies have also shown. [74]

The average bond length for the 6 Pb-X bonds was calculated as it provided an easy way

to visualize lattice contraction holistically and is shown in Figures 4.2.1.2a to 4.2.1.2c.

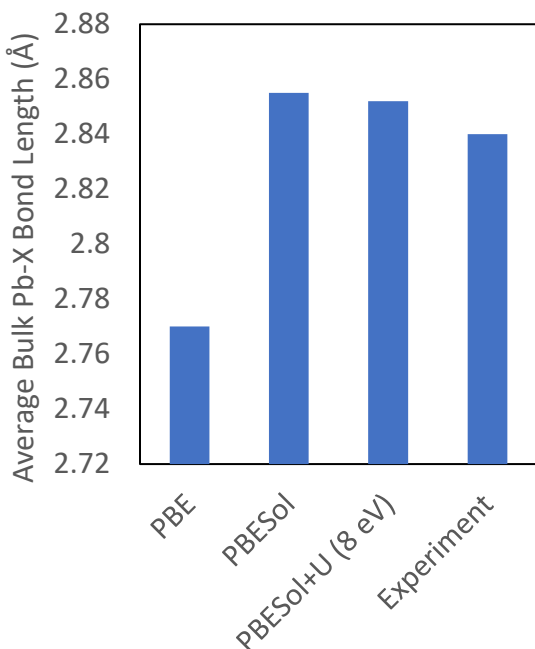


Figure 4.2.1.2a: MAPbCl Bulk Bond Length Comparisons

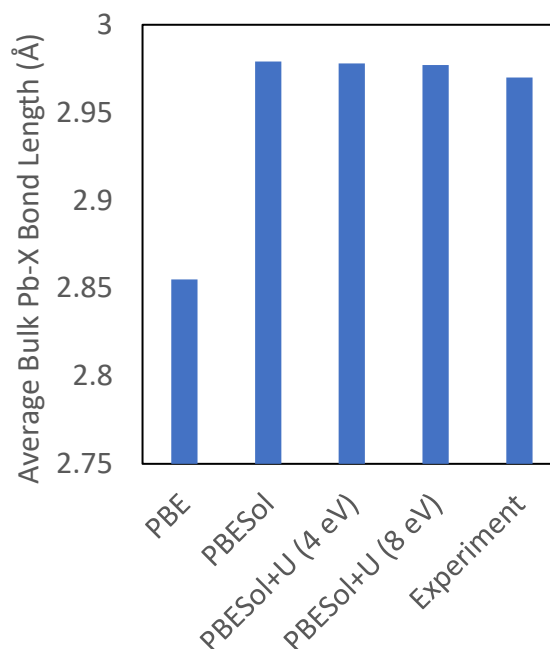


Figure 4.2.1.2b: MAPbBr Bulk Bond Length Comparisons

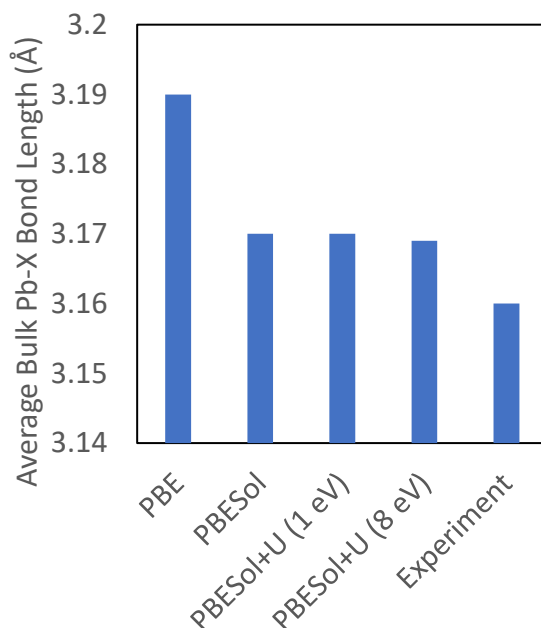


Figure 4.2.1.2c: MAPbI Bulk Bond Length Comparisons

The average bond length for Pb-Cl was calculated to be approximately 2.85 Å using the PBESol functional and suffered a reduction of 0.09% after adding the 8 eV U value. Both the PBESol

and PBEsol+U values matched well with the experimental value of 2.84 Å for the Pb-Cl bond length. [58] Similarly, the average bond lengths for Pb-Br and Pb-I were approximated to be 2.98 Å and 3.17 Å using PBEsol. These values were reduced by 0.05% and 0.04% after adding an 8 eV U correction. These Pb-Br and Pb-I bond lengths (using 8 eV) were close to the experimentally measured powder X-ray diffraction values of 2.97 Å and 3.16 Å, respectively. [58] The band gap matched U values for MAPbBr and MAPbI (4 eV and 1 eV) resulting in a slightly longer bond length for the Pb-Br and Pb-I bonds compared to the 8 eV U value as shown in Table 4.2.1.1.

Table 4.2.1.1: Average Bulk Pb-X Bond Length

Perovskite	PBE* (Å)	PBEsol* (Å)	PBEsol+U* (Å)			Experiment (Å)
			1 eV	4 eV	8 eV	
MAPbCl	2.77	2.855	-	-	2.852	2.84 [58]
MAPbBr	3.01	2.979	-	2.978	2.977	2.97 [58]
MAPbI	3.19	3.170	3.170	-	3.169	3.16 [58]

*Calculated values from this work

The longer bond length values calculated using 1 eV and 4 eV were expected as they do not “restrict” the charge density as much as the 8 eV U value. The bond length changes experienced in the bulk ranged from 0.001 for Pb-Br and Pb-I to 0.003 for Pb-Cl (considerably small), yet the electronic properties (such as band gap) were affected. Given this relationship, a correct U value optimized using the PBEsol functional needs to be calculated individually for each perovskite system.

4.3 Supercell Vacuum Optimization for Surface Slabs

After optimizing the bulk parameters using PBEsol, supercells were created from the fully optimized bulk unit cells which included varying sizes of vacuum. One unit of vacuum had

the same volume as 1 unit cell of each perovskite. In this figure, the purple potential line showed the non-corrected supercell matched exactly the potential of the supercell with Dipole corrections only (meaning no Potential-and-Forces Corrections applied). This suggested that MAPbX perovskites are not polar compounds. This agreed with other experiments. [82] Using Dipole corrections only did not result in a constant potential in the vacuum region of the supercell, so the Potential-and-Forces Corrections were applied. It was determined 3 units of vacuum were insufficient for any MAPbX system after applying dipole and potential-and-forces corrections to the neutral supercells. The potential in the vacuum was not constant indicating an interaction between the top and bottom of the slab. [83] Figure 4.3.1 shows the potential versus distance across the supercell in the z-direction.

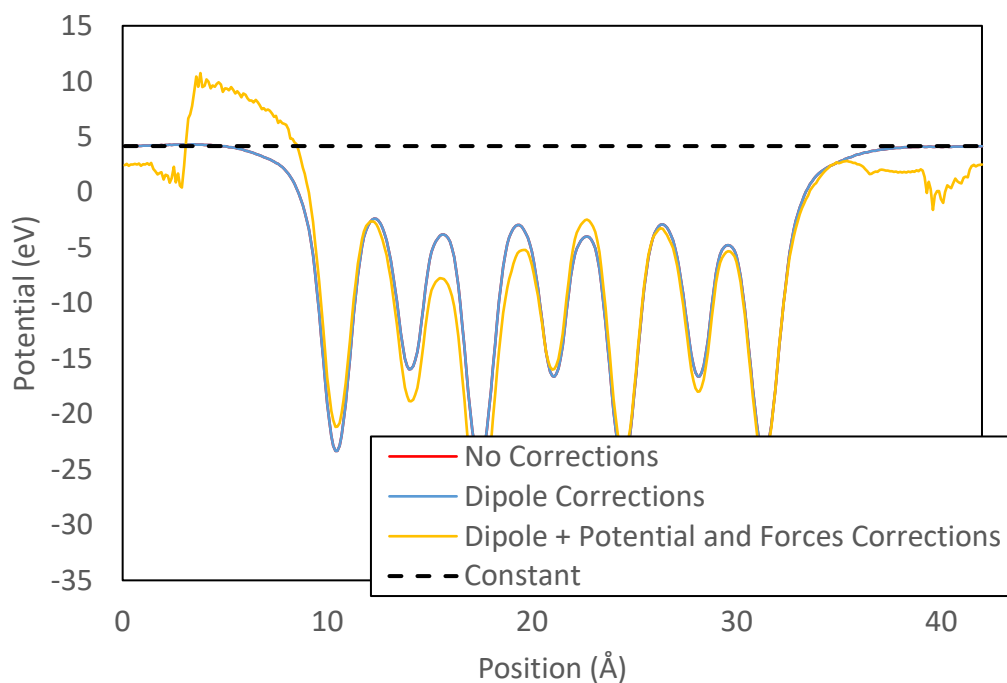


Figure 4.3.1: MAPbI PbI Termination with 3 units vacuum and Dipole Corrections

The vacuum size was increased until the dipole corrections applied to the neutral supercells showed a near-constant potential inside the vacuum. These results are shown in Figures 4.3.2a to

4.3.4b respectively for MAPbCl, MAPbBr, and MAPbI.

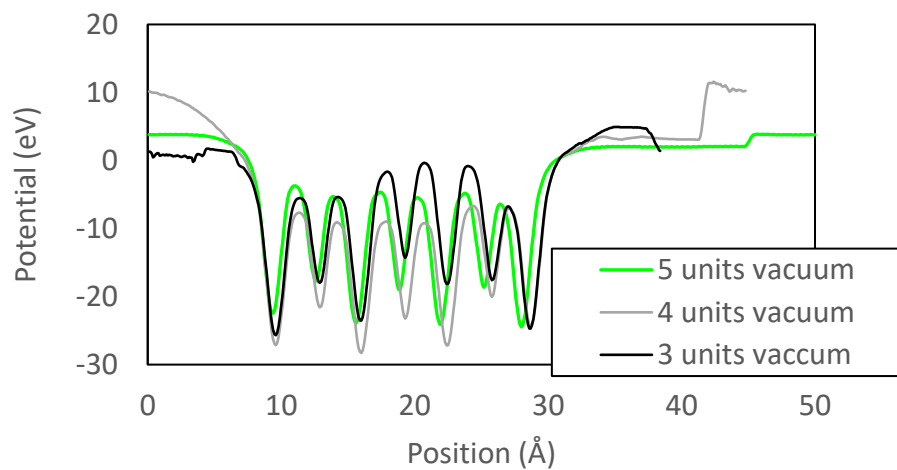


Figure 4.3.2a: MAPbCl Vacuum Optimization Potential: PbCl termination

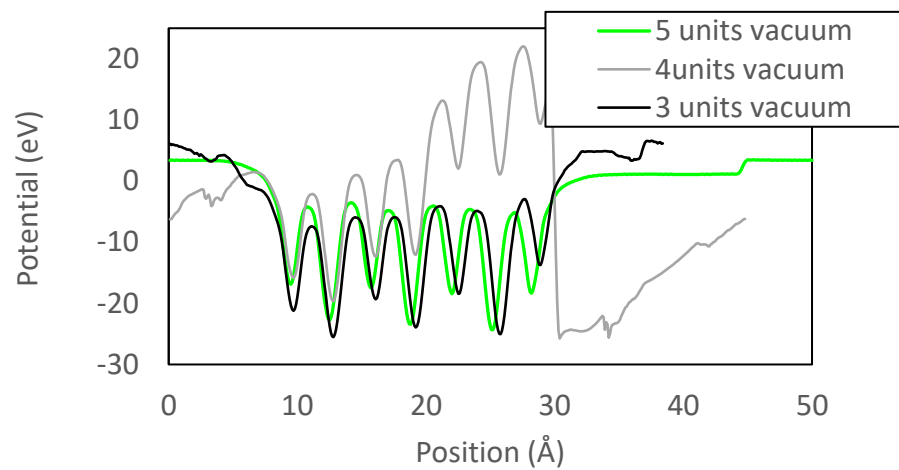


Figure 4.3.2b: MAPbCl Vacuum Optimization Potential: MACl termination

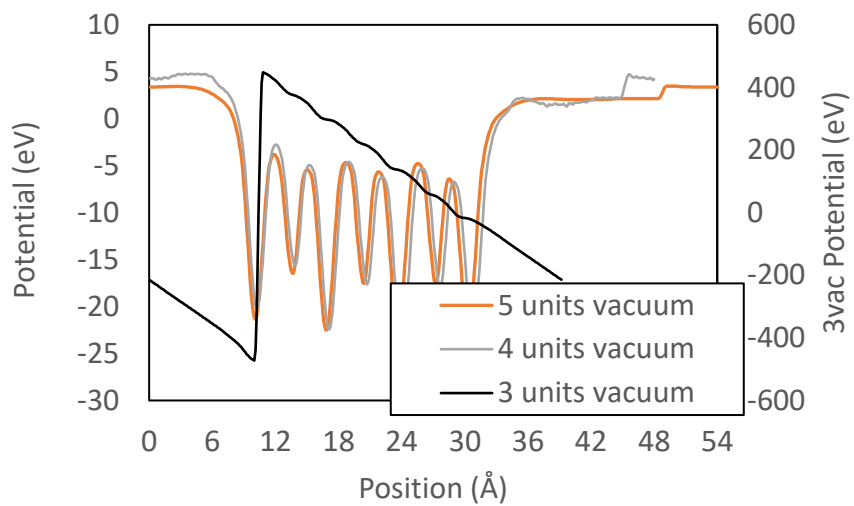


Figure 4.3.3a: MAPbBr Vacuum Optimization Potential: PbBr Termination

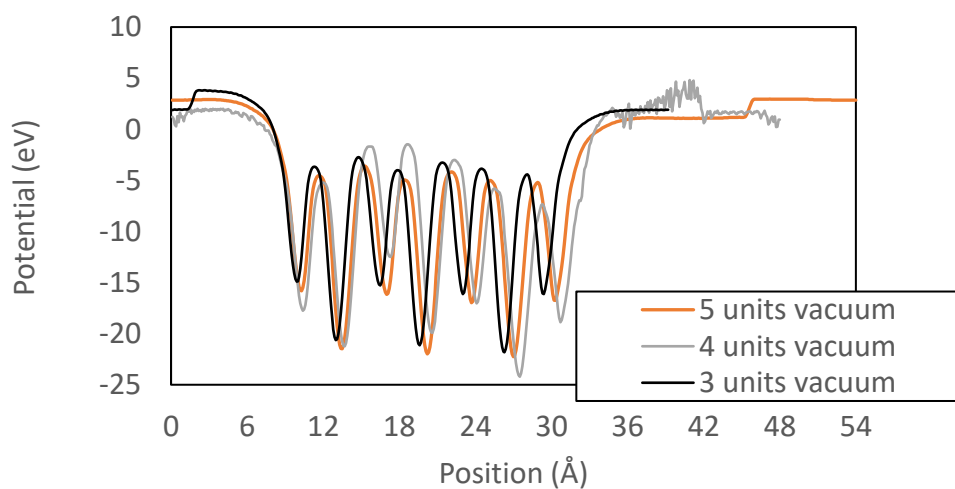


Figure 4.3.3b: MAPbBr Vacuum Optimization Potential: MABr Termination

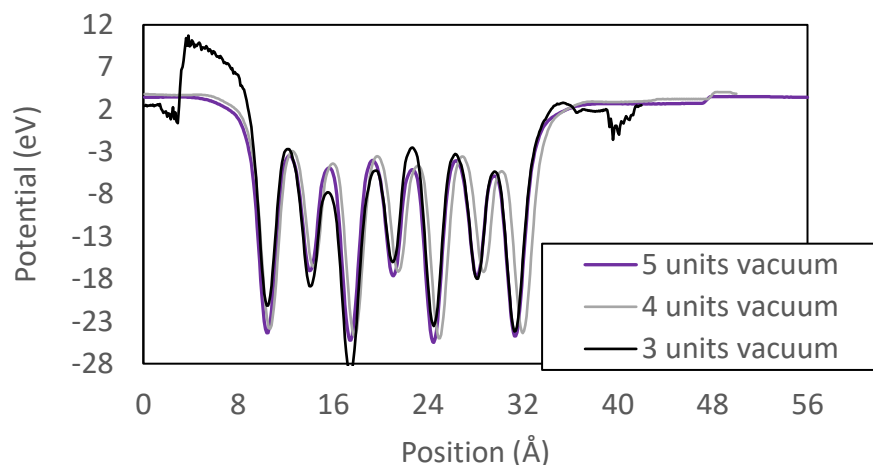


Figure 4.3.4a: MAPbI Vacuum Optimization Potential: PbI Termination

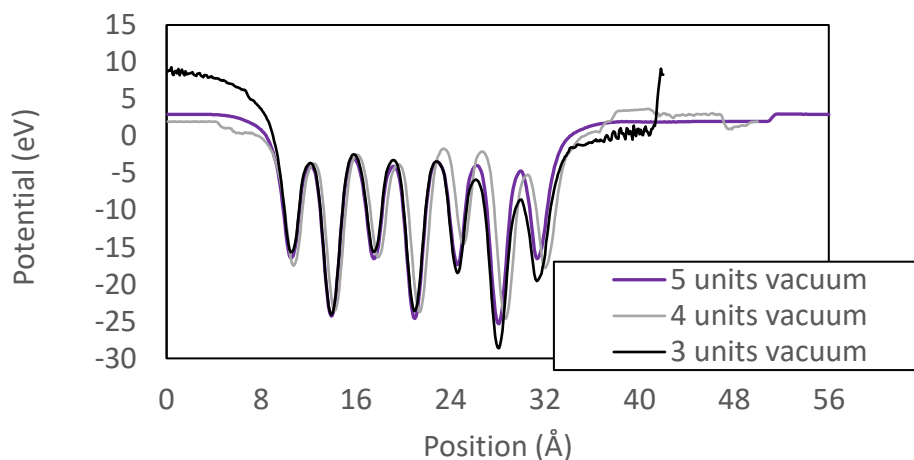


Figure 4.3.4b: MAPbI Vacuum Optimization Potential: MAI Termination

As the vacuum size increased the potential gradually trended towards a constant (ignoring the dipole step discontinuity). Increasing the size of the vacuum will increase computation time. Therefore, a fine balance between an acceptable value of the deviation of the potential in the vacuum and the time required to complete the calculation was needed. The change in the potential in the vacuum is merely a difference in the potential at the top and the bottom surfaces. After calculating this value, the step size (applied by the Potential-and-Forces corrections) was

subtracted resulting in the “corrected” potential difference. Figure 4.3.5 compares the vacuum potential difference for differing vacuum sizes after applying both Dipole and Potential-and-Forces corrections. Table 4.3.1 displays the values used in Figure 4.3.5.

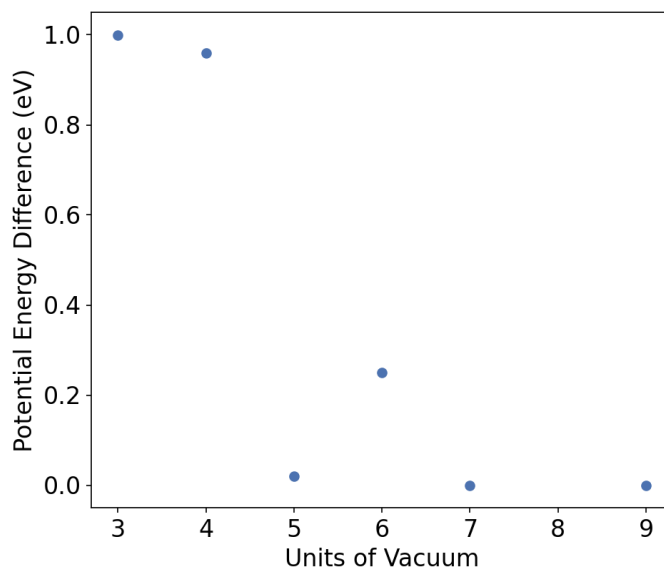


Figure 4.3.5: MAPbI Vacuum Corrected Potential Difference | PbI Termination

Table 4.3.1: MAPbI Vacuum Potential Difference | PbI Termination

Vacuum size	No Correction (eV)	Dipole Correction (eV)	Potential Forces Correction (eV)	Step Size (eV)	Corrected Potential Difference (eV)
3	0.21	0.21	14.2	-	14.2
4	0.33	0.33	1.75	0.79	0.96
5	0.45	0.45	0.82	0.8	0.02
7	0.53	0.53	0.79	0.79	0
9	0.57	0.57	0.79	0.79	0

A vacuum size of 5 was chosen as the potential difference was only marginally larger compared with 7 and 9 units of vacuum. Table 4.3.2 shows the size of the discontinuity step and the calculated “corrected” potential difference over the vacuum region for each slab. The MAX slabs had smaller “corrected” potential differences in the vacuum compared to the PbX slabs.

Table 4.3.2: Potential Difference for 5 units vacuum

Termination	Step Size (eV)	Corrected Potential Difference (eV)
PbCl	1.83	0.072
MACl	2.30	0.049
PbBr	1.33	0.034
MABr	1.79	0.001
PbI	0.8	0.020
MAI	0.81	0.004

4.4 Slab Surface Structural Results

As demonstrated by the PDOS for the bulk, the band edges arise from the bonding of Pb and halide p orbitals which means the inorganic lattice is responsible for electronic excitation. [66] Thus, an analysis of the Pb-X bond lengths was conducted. Specific bond length calculated values are in the Appendix for both PbX and MAX terminated slabs in Tables 7.5 to 7.9

Although the MA cation is not a contributor at the band edges of these halide perovskites, it does indirectly affect the structural features of the inorganic PbX cage. Three mechanisms influence the MA ion interaction with the inorganic PbX cage. These mechanics include an electrostatic potential between the positive (MA) cation and the negative PbX cage, an electrostatic contribution due to charge-dipole interaction, and an additional electrostatic contribution. The final electrostatic contribution source is currently disputed between an induced dipole interaction (called the Debye force) [71] or hydrogen bonding [84] [85]. The orientation of the MA⁺ ion for the PbX and MAX terminations was situated in the same direction as in the bulk. Namely, the dipole moment of the cation was pointing out away from the supercell towards the vacuum. This structural configuration was used because it produced band gap values in good agreement with experimental results in the bulk.

Following relaxation using the PBEsol functional, the MA⁺ cations in layers 2 and 4

reoriented so that the NH_3 group was pointing towards the vacuum. The MA^+ ion at layer 2 (just under the surface PbX layer) shifted more so than the MA^+ at layer 4 (located deeper in the supercell structure). The shifting of the cation was greatest in the PbCl terminated slab compared to the PbBr and PbI slabs. Adding the 8 eV U value to the PbCl slab calculations decreased the shifting of the cation in layer 4 but the MA^+ ion in layer 2 was unaltered. Both MA ions in layers 2 and 4 experienced a reduction in the shifting by the same amount for the PbBr and PbI slabs. The smaller U values (1 eV and 4 eV) allowed for a greater reorientation of the MA^+ compared to the 8 eV U value.

Results discussing how the U correction affected the MAPbX inorganic lattice structures are presented next. The distance from the first fixed layer (layer 5) and the top surface layer (layer 1) increased by .032 Å, 0.007 Å for the PbCl and PbBr slabs but shrank by 0.07 Å for the PbI slab. Adding a U value of 8 eV resulted in a reduction of 0.02 Å, 0.03 Å, and 0.06 Å for the PbCl , PbBr , and PbI slabs between these layers compared to PBEsol . All three PbX slabs experienced a bond elongation between the Pb and halide bond in the 4-5 and 2-3 bilayers and a contraction of the Pb -halide bond in the 1-2 and 3-4 bilayers. This change in bond lengths resulted in a shrinking of the lattice cavity above the MA^+ ion and an expansion below the MA^+ ion. This shrinking and expansion of the bonds also occurred after adding the 8 eV U value. Adding the U values of 1 eV and 4 eV also resulted in a shrinking above and an expansion below the MA^+ ion. However, the bond lengths using these smaller U values were larger than the 8 eV bond lengths. This allowed for a greater reorientation of the MA^+ ion within the lattice as was mentioned earlier.

The MA^+ ion is surrounded by the Pb-X lattice and the reorientation is dictated (partially) by the amount of volume in the Pb-X cavity. A decreasing halide size increased the

inorganic lattice cavity volume and also increased the reorientation of the MA⁺ ion. [86] Adding the U correction decreased the amount of charge density surrounding the halide atoms which resulted in a weaker attraction between the hydrogen atoms of the NH₃ group and the halide. This resulted in a reduction in the reorientation of the MA⁺ ion as the U value increased. Adding the U value seems to suggest that hydrogen bonding was the predominant interaction force dictating MA⁺ ion reorientation as opposed to the alternately suggested Debye force previously mentioned. Figures 4.4.1 to 4.4.3 show the resulting structures. Tables 4.4.1 to 4.4.3 show the comparison between the PBEsol values and the changes incurred after adding the 8 eV U correction.

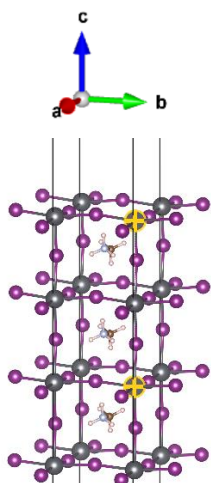


Figure 4.4.1:
MAPbI PbI slab
Pb layers 1 to 5
distance

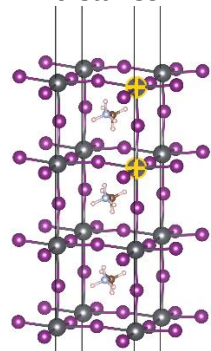


Figure 4.4.2:
MAPbI PbI slab
Pb layers 1 to 3
distance

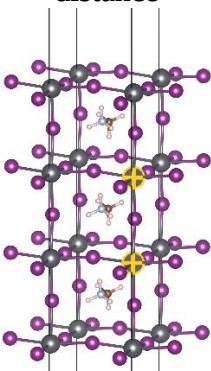


Figure 4.4.3:
MAPbI PbI slab
Pb layers 3 to 5
distance

Table 4.4.1: PbX Term. | Layers 1 to 5 Distance

System	PBEsol (Å)	PBEsol+U (Å)			Difference (Å)
		1 eV	4 eV	8 eV	
MAPbCl	11.39212	-	-	11.33502	-0.0571
MAPbBr	11.87877	-	-	11.84382	-0.03495
MAPbBr	11.87877	-	11.86805	-	-0.01072
MAPbI	12.54496	-	-	12.58282	0.03786
MAPbI	12.54496	12.53787	-	-	-0.00709

Table 4.4.2: PbX Term. | Layers 1 to 3 Distance

System	PBEsol (Å)	PBEsol+U (Å)			Difference (Å)
		1 eV	4 eV	8 eV	
MAPbCl	5.65539	-	-	5.6231	-0.03229
MAPbBr	5.91135	-	-	5.89501	-0.01634
MAPbBr	5.91135	-	5.90169	-	-0.00966
MAPbI	6.24593	-	-	6.2684	0.02247
MAPbI	6.24593	6.24191	-	-	-0.00402

Table 4.4.3: PbX Term. | Layers 3 to 5 Distance

System	PBEsol (Å)	PBEsol+U (Å)			Difference (Å)
		1 eV	4 eV	8 eV	
MAPbCl	5.73847	-	-	5.71446	-0.02401
MAPbBr	5.96779	-	-	5.94911	-0.01868
MAPbBr	5.96779	-	5.96682	-	-0.00097
MAPbI	6.29912	-	-	6.31481	0.01569
MAPbI	6.29912	6.29601	-	-	-0.00311

The MA⁺ ion shifted by the same amount for both PBEsol and PBEsol+U (8 eV) at layer 1 (which was in contact with the vacuum) for the MACl terminated slab. However, for the MABr and MAI slabs, the MA⁺ ion shifted more using PBEsol than it did for PBEsol+U. This was attributed to the U value altering the charge density in the same manner as in the PbX slabs. The NH₃ end of MA⁺ ion at layer 1 reoriented towards the vacuum. The MA⁺ ions in the layer 1 surface were not confined by the inorganic lattice and were in direct contact with the vacuum. Therefore, they had a greater volume for reorientation resulting in a larger reorientation of the MA⁺ ions in the MAX terminations as opposed to the PbX terminations. MA⁺ ion reorientation has been reported in recent studies. [86] [87] Torres and Rego reported the MAX surface termination configuration showed the greatest effects from relaxation in their study. [88] This result was confirmed in this work as the combination of the MA⁺ ion reorientation and the shifting of the Pb-X lattice was larger in the MAX slab than in the PbX slab. Again, smaller U values (1 eV and 4 eV) resulted in a larger MA⁺ ion reorientation due to the increased cavity volume created by slightly larger bond lengths in the Pb-X lattice. MA ion reorientation has been confirmed on MAI surfaces using STM. The reorientation of these surface MA ions are proposed to weaken surface polarity and should be considered a stabilizing force for surface structures. [52] Using STM, the underlying Pb-X layer was observed to move in plane or upwards. [89]

The MACl and MABr terminated slabs saw a reduction in the distance between layers 1 and 5 by 0.45%, and 0.25% after adding the 8eV U value. Like the PbX terminated slabs, there was a reduction in the bond lengths “above” the MA⁺ ion and an elongation “below” it for the MACl and MABr terminated slabs. The MAI terminated slab did not display this behavior. Instead, the distance between layer 1 and layer 5 increased by 0.3%. The 4-5 bilayer in the MAI

slab did show a reduction in bond length but the 2-3 bilayer experienced a bond length expansion. Using smaller U values again resulted in longer bond lengths for the MABr and MAI slabs compared to the 8 eV U value. Figures 4.4.4 to 4.4.7 show the resulting structures.. Tables 4.4.4 to 4.4.7 show a comparison between the values obtained using the PBEsol and PBEsol+U functionals.

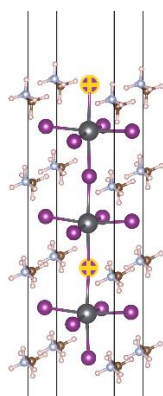


Figure 4.4.4:
MAPbI MAI
slab halide
layers 1 to 5
distance

Table 4.4.4: MAX Term. | Layers 1 to 5 Distance

System	PBEsol (Å)	PBEsol+U (Å)			Difference (Å)
		1 eV	4 eV	8 eV	
MAPbCl	11.5709	-	-	11.51901	-0.05189
MAPbBr	12.03059	-	-	12.00101	-0.02958
MAPbBr	12.03059	-	12.02226	-	-0.00833
MAPbI	12.81788	-	-	12.85681	0.03893
MAPbI	12.81788	12.83090	-	-	0.01302

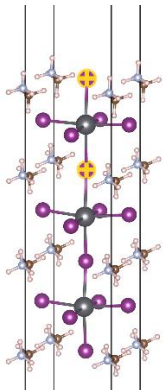


Figure 4.4.5:
MAPbI MAI
slab halide
layers 1 to 3
distance

Table 4.4.5: MAX Term. | Layers 1 to 3 Distance

System	PBEsol (Å)	PBEsol+U (Å)			Difference (Å)
		1 eV	4 eV	8 eV	
MAPbCl	5.79883	-	-	5.77473	-0.0241
MAPbBr	6.01284	-	-	5.99881	-0.01403
MAPbBr	6.01284	-	6.01535	-	0.00251
MAPbI	6.40469	-	-	6.42245	0.01776
MAPbI	6.40469	6.41817	-	-	0.01348

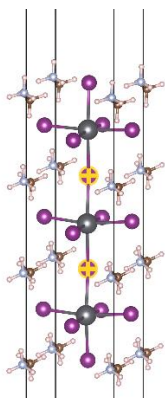


Figure 4.4.6:
MAPbI MAI
slab halide
layers 3 to 5
distance

Table 4.4.6: MAX Term. | Layers 3 to 5 Distance

System	PBEsol (Å)	PBEsol+U (Å)			Difference (Å)
		1 eV	4 eV	8 eV	
MAPbCl	5.77235	-	-	5.74468	-0.02767
MAPbBr	6.01939	-	-	6.00439	-0.015
MAPbBr	6.01939	-	6.00880	-	-0.01059
MAPbI	6.41321	-	-	6.4344	0.02119
MAPbI	6.41321	6.41276	-	-	-0.00045

The average surface bond length for both the PbX and MAX terminated slabs (using PBEsol and PBEsol+U) was compared with the bulk. These results are depicted in Tables 4.4.7 and 4.4.8.

Table 4.4.7: Bulk vs MAX Slab Average Bond Lengths

System	Bulk	MAX Slab Surface			
	PBEsol (Å)	PBEsol (Å)	PBEsol+U 1 eV (Å)	PBEsol+U 4 eV (Å)	PBEsol+U 8 eV (Å)
MAPbCl	2.854762	2.864803	-	-	2.859327
MAPbBr	2.978515	2.992847	-	2.991445	2.988773
MAPbI	3.170198	3.17731	3.17763	-	3.180835

Table 4.4.8: Bulk vs PbX Slab Average Bond Lengths

System	Bulk	PbX Slab Surface			
	PBEsol (Å)	PBEsol (Å)	PBEsol+U 1 eV (Å)	PBEsol+U 4 eV (Å)	PBEsol+U 8 eV (Å)
MAPbCl	2.854762	2.8257	-	-	2.822048
MAPbBr	2.978515	2.955314	-	2.953816	2.951688
MAPbI	3.170198	3.144586	3.145382	-	3.146202

The results suggest that the MAX slab was a more stable structure that produced band gaps closer to bulk values. For the MAX termination, PBEsol functional produced larger changes in the Pb-X average surface bond length for the MAcl and MABr slabs compared to the

8 eV PBEsol+U values. The MAI slab, on the other hand, increased the average surface bond length after the 8 eV U correction was added. The 8 eV U correction increased the average surface bond length of the MAI, MABr, and MACl slabs by 0.34%, 0.34%, and 0.16% compared to the bulk. The 8 eV U correction for the MAX slabs showed that as the halide size increased, the amount of change in the bond length increased.

For the PbX terminated surface slabs, the 8 eV U correction resulted in a larger change in average surface Pb-X bond length for the PbCl and PbBr slabs. The PbI slab average surface bond length decreased after adding the 8 eV U correction. The 8 eV U correction reduced the Pb-X surface bond lengths by -0.76%, -0.90%, and -1.15% for the PbI, PbBr, and PbCl slabs compared to the bulk. The larger deviation in surface bond length for the PbX terminations should result in larger deviations in the bandgap compared to the bulk. As the halide size increased (and electronegativity decreased), the amount of change in the bond length also increased after adding the 8 eV U correction for the PbX slabs. This was expected as the smaller atoms are lighter and therefore more susceptible to reorientation or distortion during relaxation.

Holistically speaking, surface bond lengths for the MAX and PbX terminated surface slabs experienced a maximum change in the Pb-X bond length of 1.15% (where U was 8 eV) from the PBEsol bulk. A recent paper showed the bond lengths deviated by <2.5% for MAX and PbX terminations. [86] The MAX terminated slabs all experienced an elongation in average surface bond lengths. The PbX terminated slabs all experienced a reduction in average surface bond lengths except for MAPbI which expanded by approximately 0.0016 Å (a negligible change). Both the changes in surface bond lengths and angles were attributed to surface reconstruction. Figures 4.4.7a to 4.4.7c show a comparison of the values for the average surface bond length for the MAX and PbX slab surfaces between the PBEsol and PBEsol+U functionals.

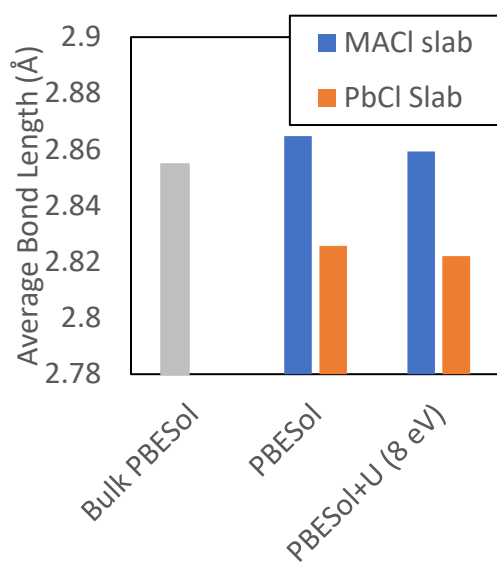


Figure 4.4.7a: Average MAPbCl bulk bond length and average slab surface bond lengths for MACl and PbCl slabs

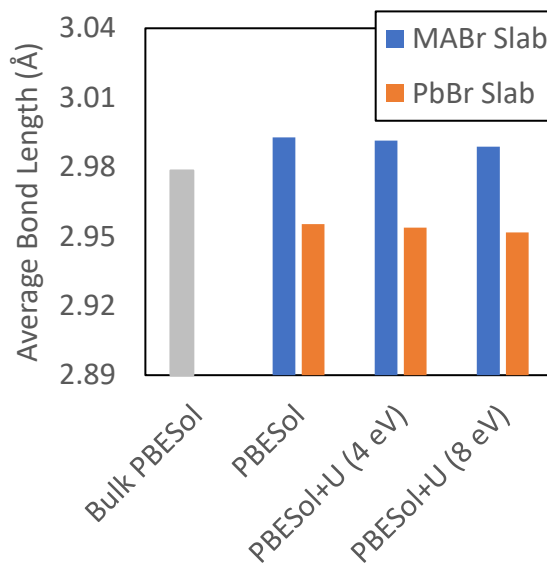


Figure 4.4.7b: Average MAPbBr bulk bond length and average surface bond lengths for MABr and PbBr slabs

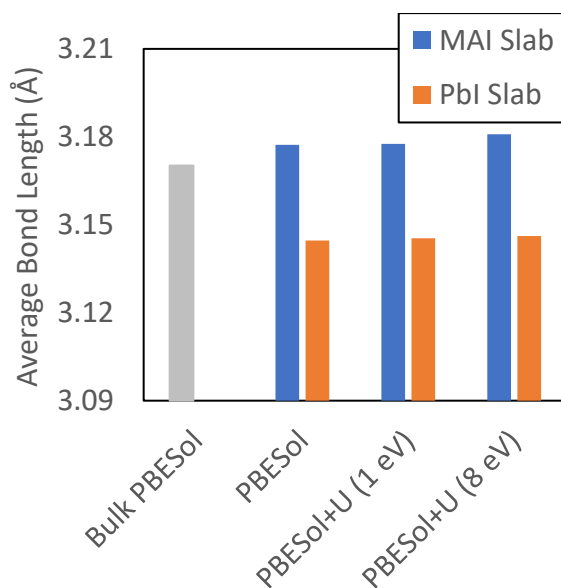


Figure 4.4.7c: Average MAPbI bulk bond length and average surface bond lengths for MAI and PbI slabs

Tables 4.4.7 and 4.4.8 shows a comparison of the values for the average surface bond length for the MAX and PbX slab surfaces between the PBESol and PBESol+U functionals. The MACl and MABr slab data in Table 4.4.7 showed that as the U value increased the average surface

bond length decreased. The MAI data showed that as the U value increased the bond length slightly increased. The PbCl and PbBr slab data in Table 4.4.8 showed that as the U value increased the bond length decreased. Additionally, the PbI slab data did show an increase in the average surface bond length as the U value increased.

4.5 Slab Surface Electronic Results

Plotting the PDOS for PbX slabs showed adding the 8 eV U correction had a marginal effect on the CBM edge energy for the PbCl slab but did move the PbBr and PbI slab CBM edges closer to the Fermi energy compared to the PBEsol functional. The shifting of the CBM increased as the halide size increased, with MAPbI showing the largest CBM movement. A similar scenario occurred in the bulk with MAPbI showing the largest CBM energy shift in the bulk as well. The CBM energy shifted because the CBM is composed of halide p orbitals as part of the hybrid bonds at the band edges. The PbCl slab shifted by 0.0298 eV away from the Fermi energy, while the PbBr and PbI slabs shifted toward the Fermi energy by 0.13 eV and 0.28 eV. This shift resulted in the valence band edge (and other valence bands) for all PbX terminated slabs shifting away from the Fermi energy and a reduction in DOS intensity as the valence band energy decreases. The PDOS for MAX surfaces showed adding the 8 eV U correction had a small effect on the CBM energy for the MAcl slab, moving it 0.8 eV away from the Fermi energy. The MABr slab experienced a 0.006 eV shift while the MAI slab shifted by 0.20 eV toward the Fermi energy. Unlike the PbX terminated slabs, the valence bands of the MAX terminated slabs did not shift away from the Fermi energy when adding the 8 eV U value. The smaller U value for MAPbBr (4 eV) reduced the amount of shifting by the CBM edge for the PbBr slab but hardly any shifting occurred in the MABr slab. The smaller U value for MAPbI (1 eV) reduced the CBM edge shifting towards the Fermi energy significantly for the PbI slab and

slightly for the MAI slab. As U increased, orbital overlap was reduced which caused a decrease in the band gaps of the PbX slabs compared to the MAX slabs. The MA cation remained far away from the band edges in both the MAX and PbX slabs. No midgap states were seen in the DOS plots of either the MAX nor the PbX slabs. The MAX slabs had no dangling bonds so surface reconstruction did not occur which resulted less of a change in the band gap value. DOS plots shown in Figures 4.5.1a to 4.5.6b have had the top valence band aligned to the Fermi energy that was taken as zero energy. The TDOS plots sample a large range of energy values. The PDOS energy range corresponds to the same energy range that was plotted for the band structures of the MAX and PbX slabs in this chapter.

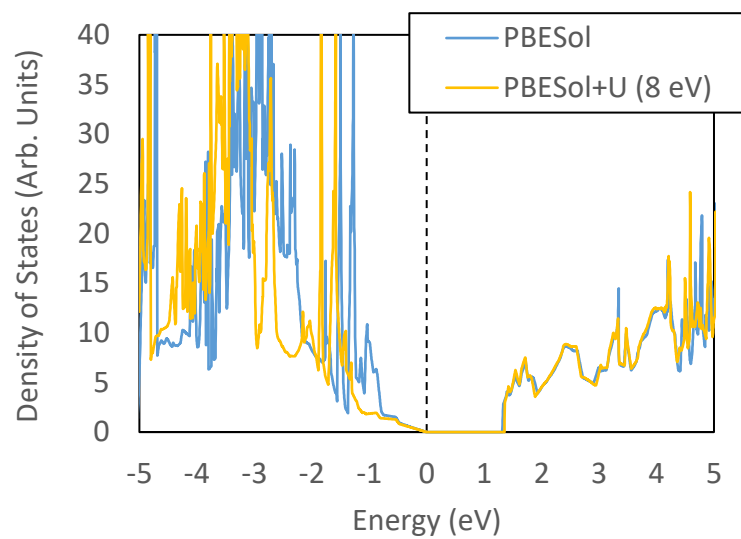


Figure 4.5.1a MAPbCl PbCl Slab Surface Supercell TDOS

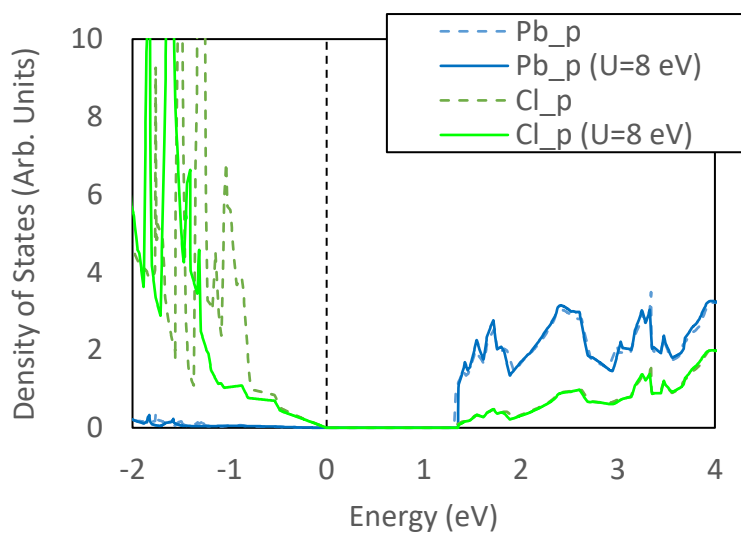


Figure 4.5.1b MAPbCl PbCl Slab Surface Supercell PDOS

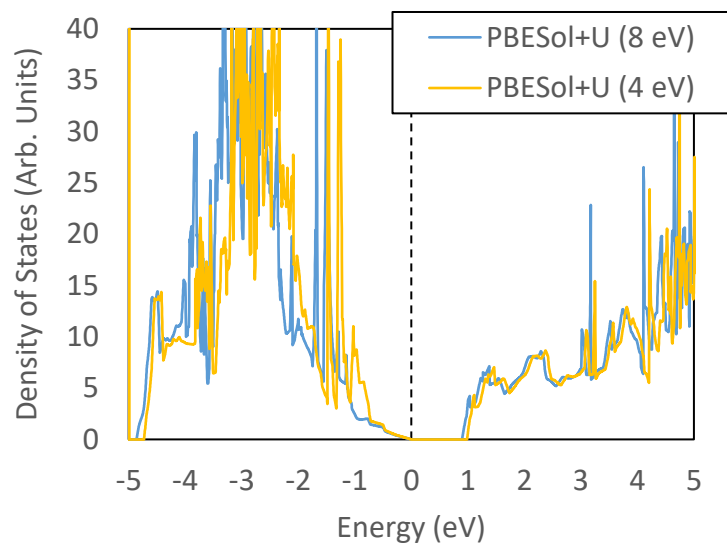


Figure 4.5.2a MAPbBr PbBr Slab Surface Supercell TDOS

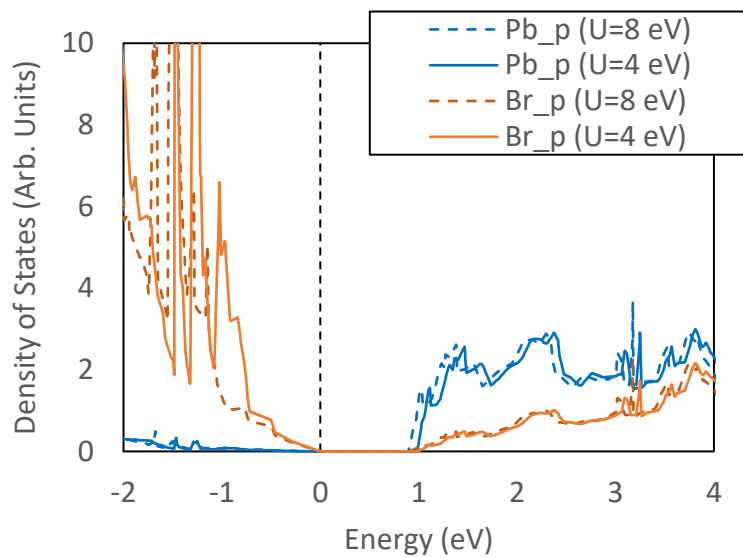


Figure 4.5.2b MAPbBr PbBr Slab Surface Supercell PDOS

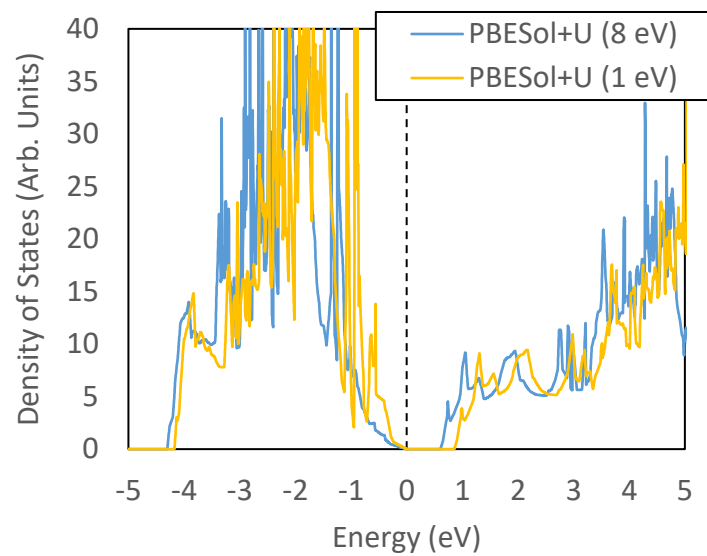


Figure 4.5.3a MAPbI₃ PbI Term. Surface Supercell TDOS

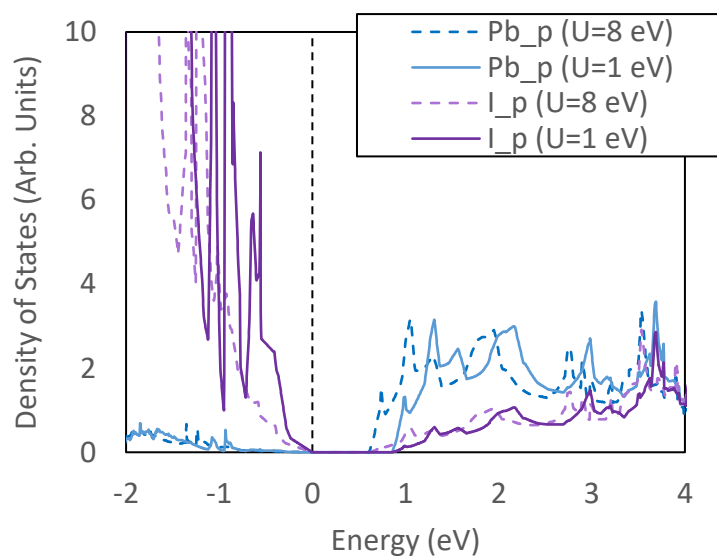


Figure 4.5.3b MAPbI₃ PbI Term. Surface Supercell PDOS

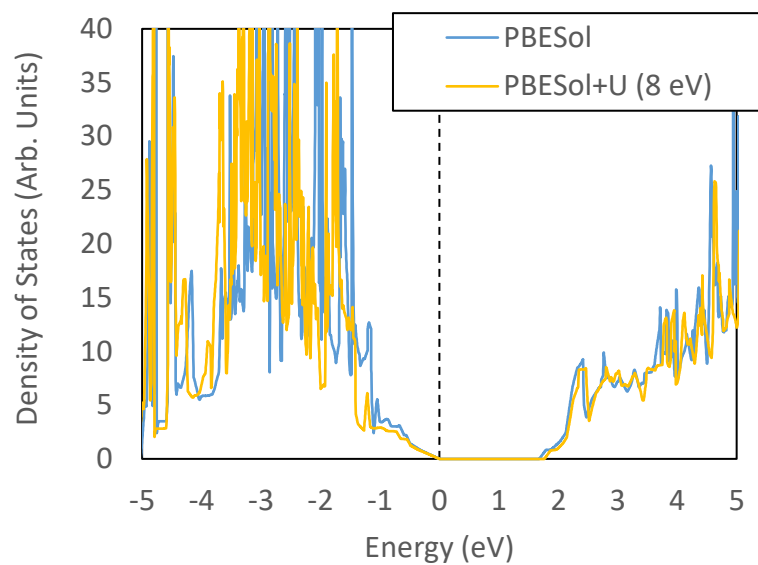


Figure 4.5.4a MAPbCl MACl Term. Surface Supercell TDOS

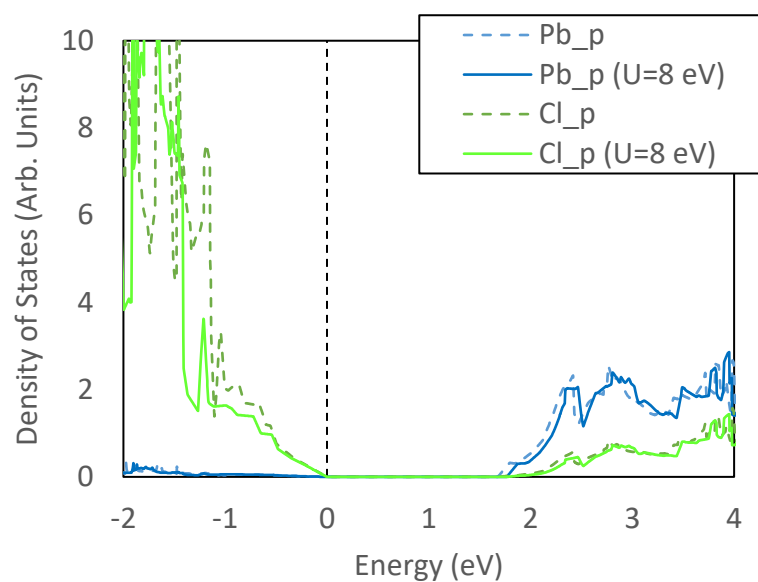


Figure 4.5.4b MAPbCl MACl Term. Surface Supercell PDOS

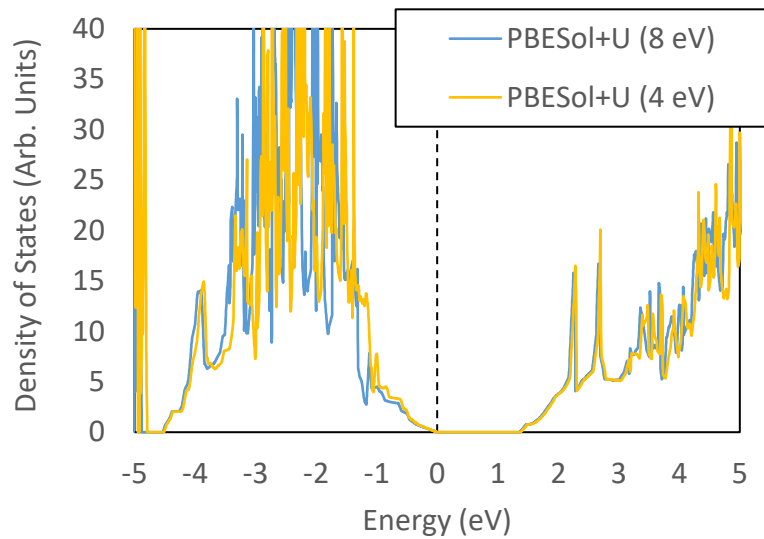


Figure 4.5.5a MAPbBr₃ MABr Term. Surface Supercell TDOS

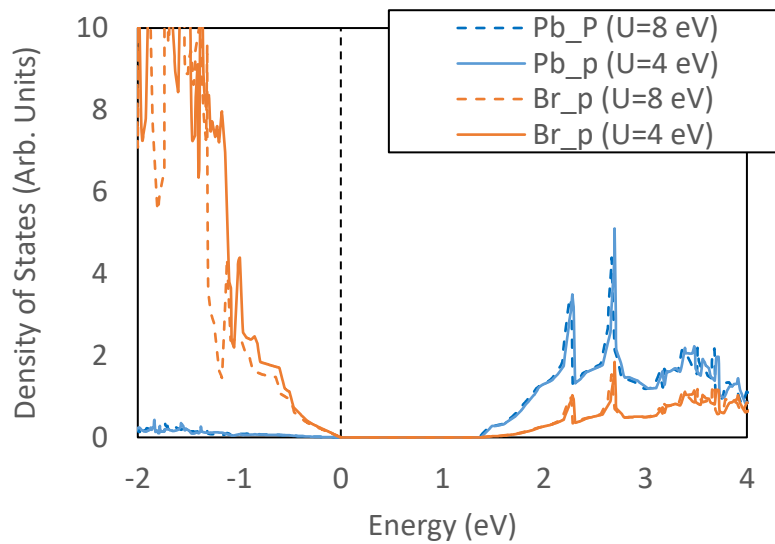


Figure 4.5.5b MAPbBr₃ MABr Term. Surface Supercell PDOS

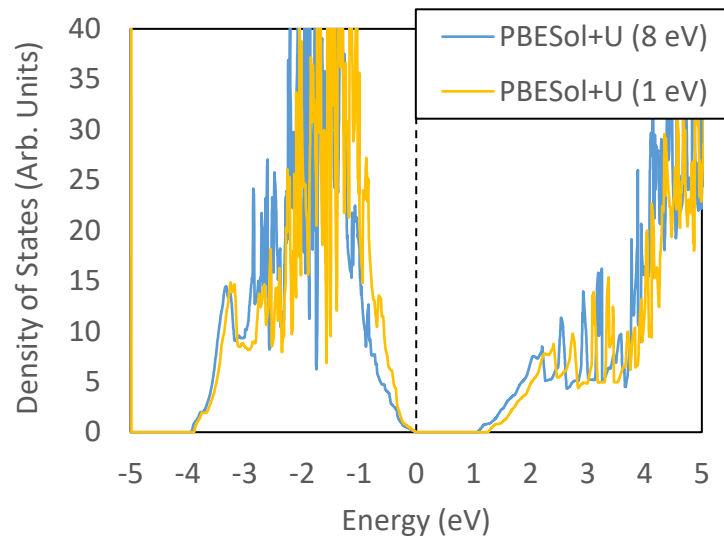


Figure 4.5.6a MAPbI MAI Term. Surface Supercell TDOS

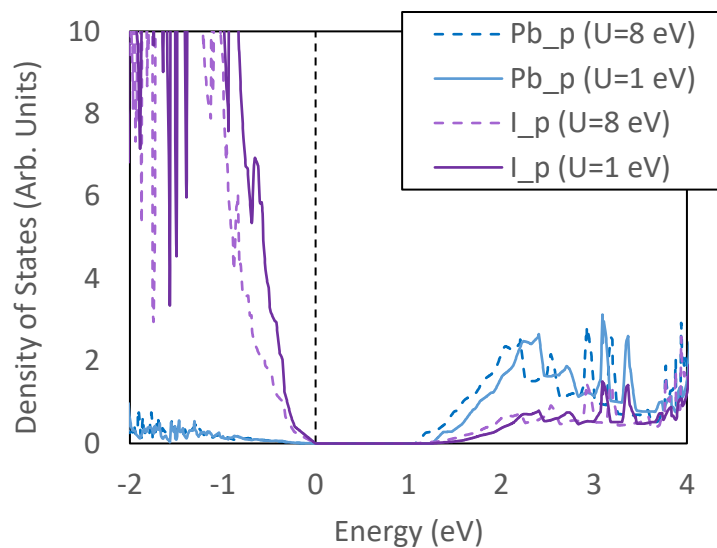


Figure 4.5.6b MAPbI MAI Term. Surface Supercell PDOS

Table 4.5.1 summarizes the results of the CBM shifts.

Table 4.5.1: PBESol+U CBM Energy Shift with respect to PBESol Energy

System	CBM Energy Shift (U = 1 eV)		CBM Energy Shift (U = 4 eV)		CBM Energy Shift (U = 8 eV)	
	PbX (eV)	MAX (eV)	PbX (eV)	MAX (eV)	PbX (eV)	MAX (eV)
MAPbCl	-	-	-	-	+0.0298	+0.8
MAPbBr	-	-	- 0.0405	+0.0234	-0.13	-0.006
MAPbI	-0.0274	-0.0187	-	-	-0.28	-0.20

The following paragraphs will discuss results from the PbX and MAX slabs in comparison with the bulk using the PBEsol functional only. The band structures in Figures 4.5.7 to 4.5.9, for the PbX and MAX terminated slabs, show the top valence band shifted towards the Fermi energy at the X3 and Γ k-points compared to the bulk. Given the different atomic configurations for the slabs (compared to the bulk), band rearrangement was expected for all slabs and both terminations. The band gap remains at the R k-point for both the PbX and MAX slabs. The conduction bands shifted toward the Fermi energy for both the PbX and MAX terminated slabs.

The shifting of the conduction bands was greatest for the PbX slabs. Broadening between the conduction bands decreased as the halide size increased for the PbX slabs. As shown earlier, there was a dangling bond on the PbX terminated slabs that resulted in surface reconstruction trying to compensate for this missing bond. The surface reconstruction resulted in a large change in the band structure for the PbX terminated slabs. The dangling bond was not present in the MAX terminated slabs, so the band structures were not altered as severely.

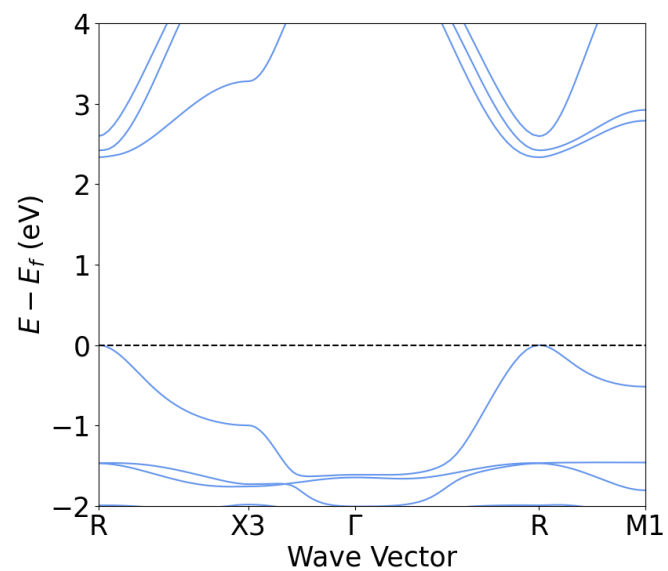


Figure 4.5.7a MAPbCl bulk band structure using PBEsol

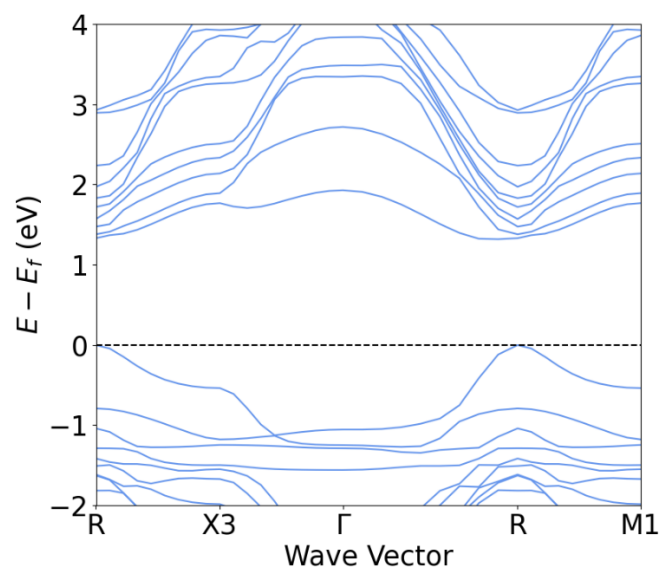


Figure 4.5.7b MAPbCl PbCl terminated slab band structure using PBEsol

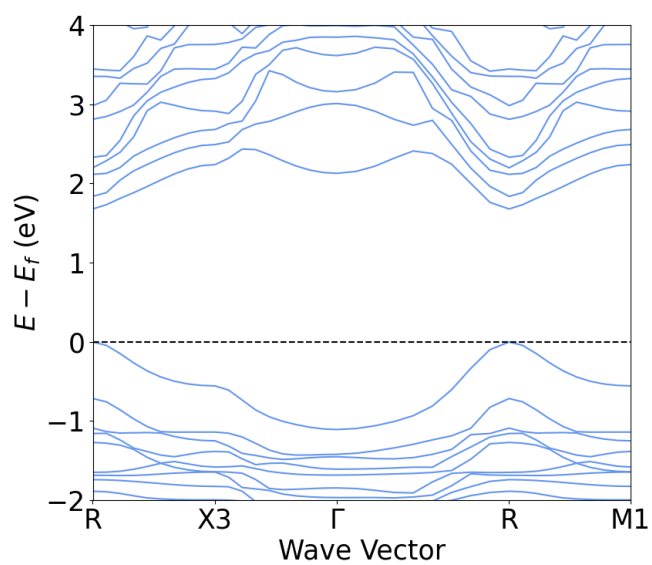


Figure 4.5.7c MAPbCl MACl terminated slab band structure using PBEsol

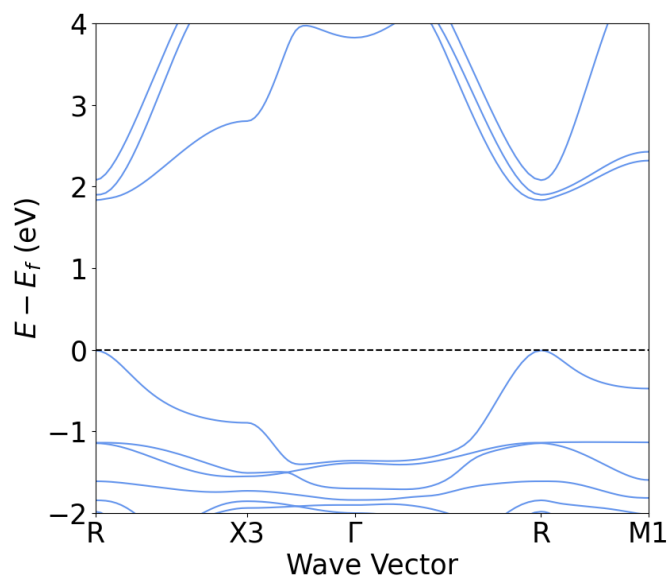


Figure 4.5.8a MAPbBr bulk band structure using PBEsol

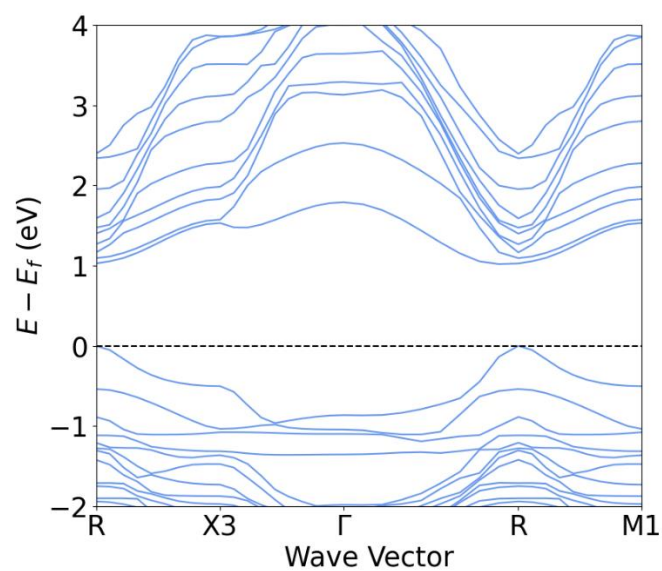


Figure 4.5.8b MAPbBr₃ PbBr terminated slab band structure using PBEsol

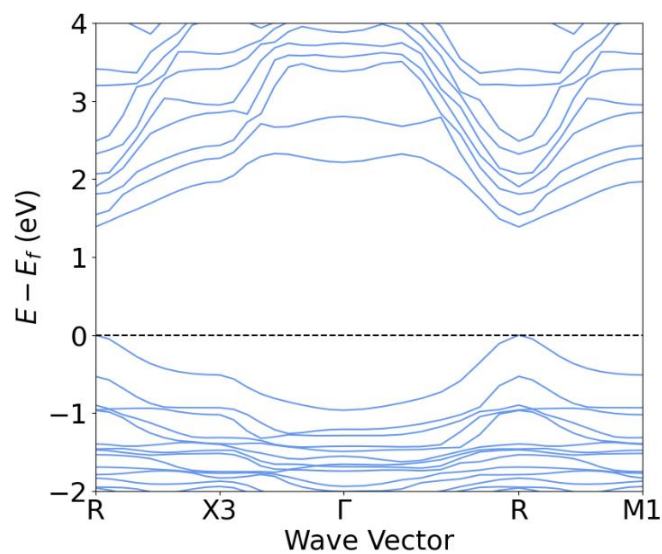


Figure 4.5.8c MAPbBr₃ MABr terminated slab band structure using PBEsol

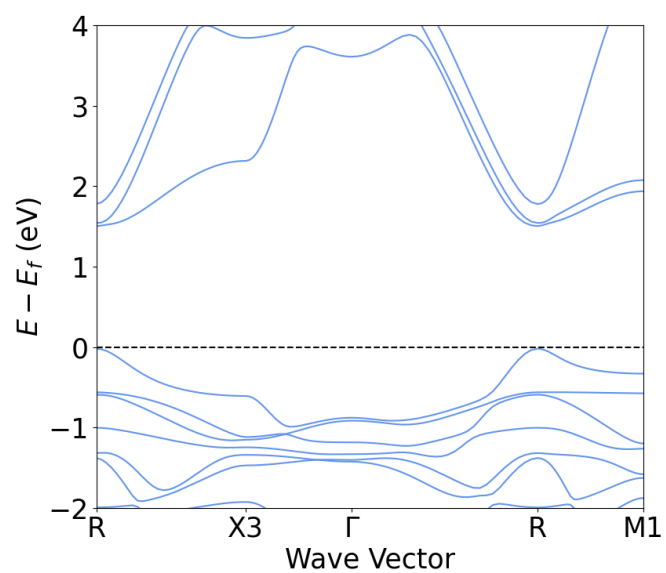


Figure 4.5.9a MAPbI bulk band structure using PBEsol

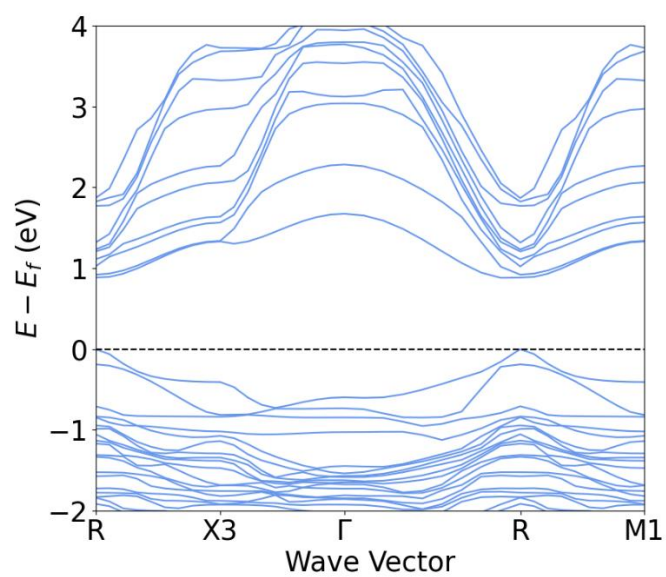


Figure 4.5.9b MAPbI PbI terminated slab band structure using PBEsol

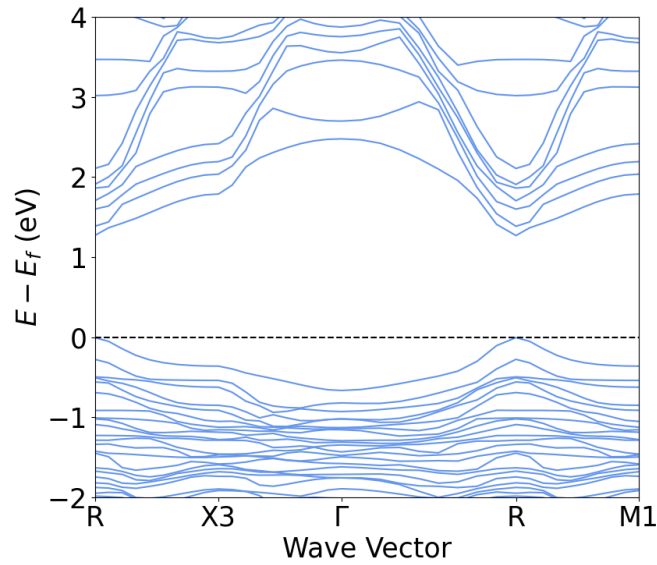


Figure 4.5.9c MAPbI MAI terminated slab band structure using PBEsol

Next, the data for the PBEsol+U (8 eV) functional are presented for the PbX and MAX slabs compared to the bulk. Adding the 8 eV U correction to PBEsol for the PbX and MAX slabs shifted the top valence band towards the Fermi energy around the X3 and Γ k-points compared to the bulk. No changes occurred at the band gap R k-point. Additionally, most of the valence bands shifted to a smaller negative energy towards the Fermi energy. Adding the 8 eV U correction decreased the energy at the Γ k-point in the top valence band and shifted most of the conduction bands towards the Fermi energy for both the PbX and MAX slabs. The shifting of the conduction bands decreased as the halide size increased. The 8 eV U correction showed a similar trend to the PBEsol functional regarding band rearrangement. Band rearrangement occurred most significantly in the PbX terminated slabs compared to the MAX terminated slabs. Again, this was attributed to surface reconstruction due to the dangling bonds in the PbX terminated slabs. [90] The band structures for the PbX and MAX slabs using PBEsol+U (8 eV) are shown in Figures 4.5.10a to 4.5.12c.

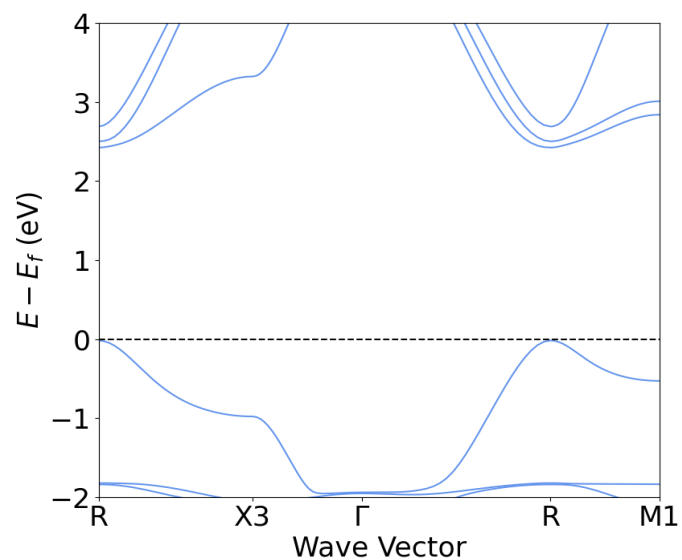


Figure 4.5.10a MAPbCl bulk band structure using PBEsol+U (8 eV)

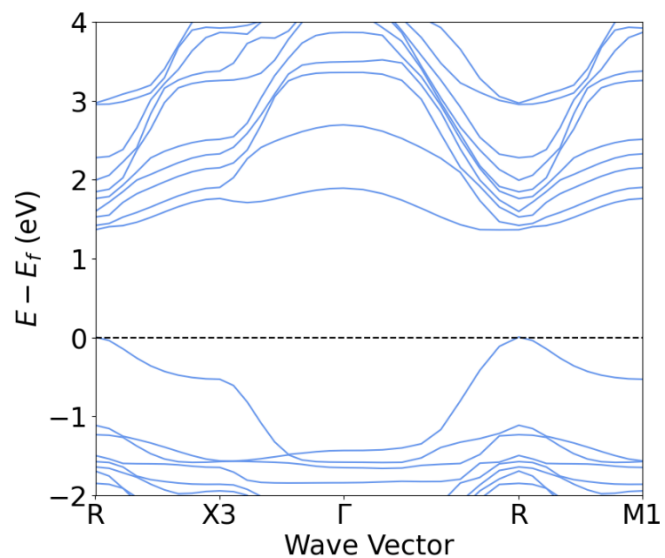


Figure 4.5.10b MAPbCl PbCl terminated slab band structure using PBEsol+U (8 eV)

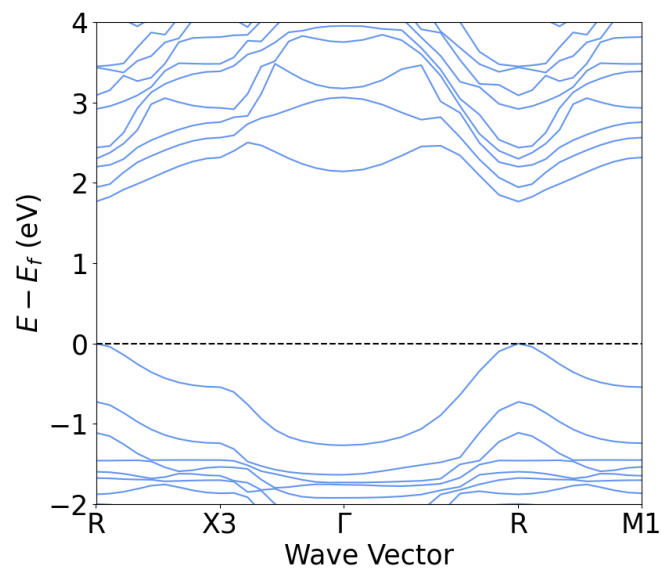


Figure 4.5.10c MAPbCl MACl terminated slab band structure using PBEsol+U (8 eV)

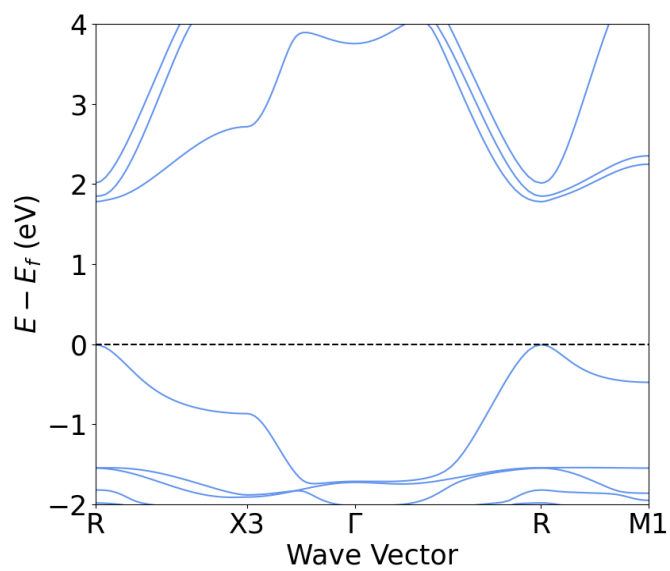


Figure 4.5.11a MAPbBr bulk band structure using PBEsol+U (8 eV)

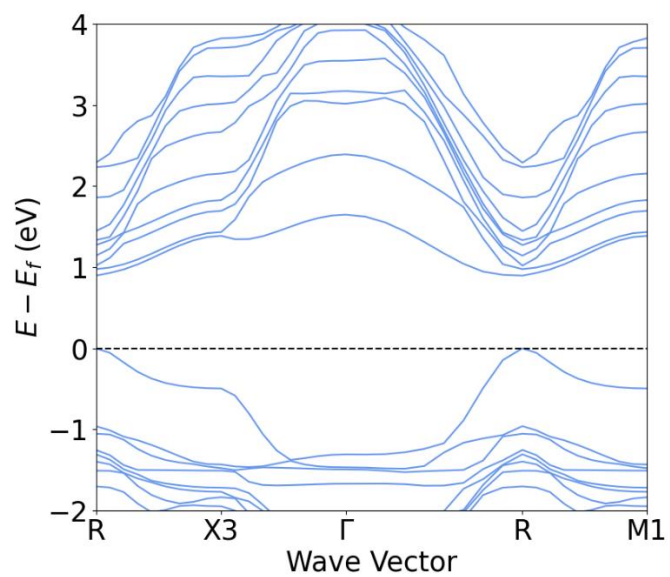


Figure 4.5.11b MAPbBr PbBr terminated slab band structure using PBEsol+U (8 eV)

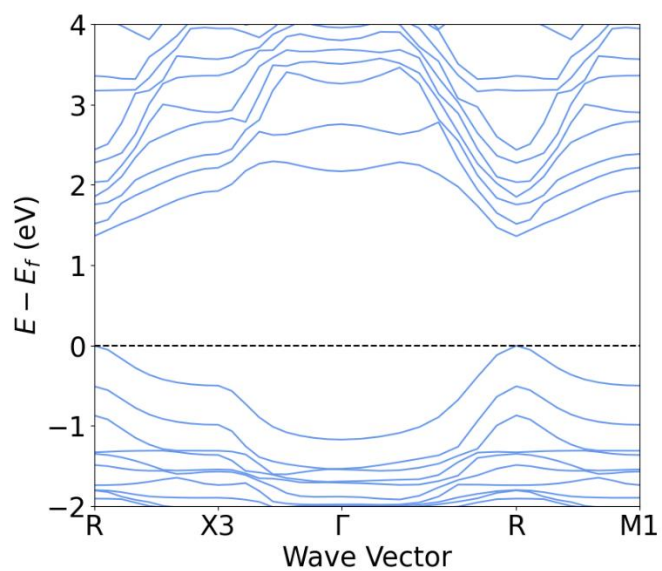


Figure 4.5.11c MAPbBr MABr terminated slab band structure using PBEsol+U (8 eV)

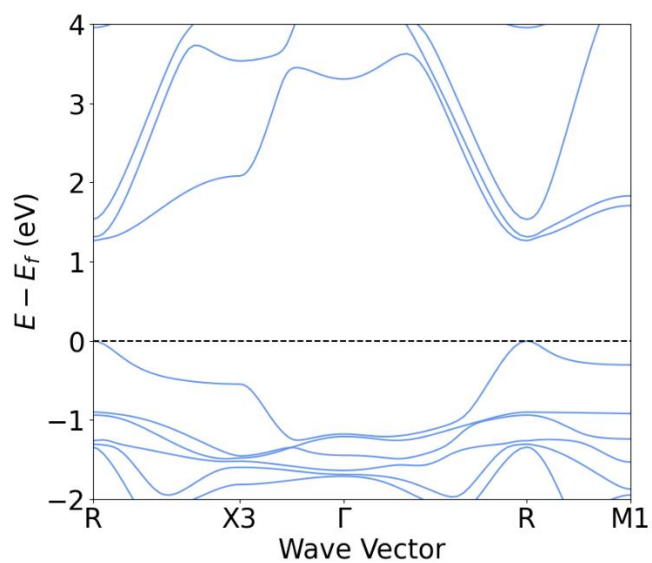


Figure 4.5.12a MAPbI bulk band structure using PBEsol+U (8 eV)

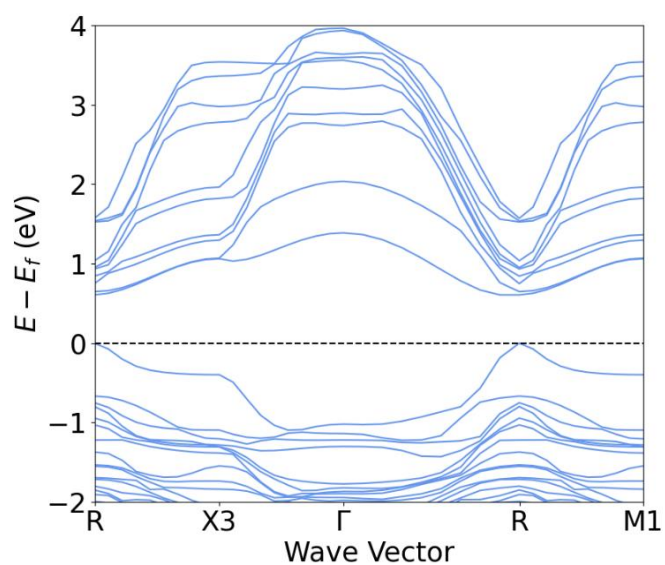


Figure 4.5.12b MAPbI PbI terminated slab band structure using PBEsol+U (8 eV)

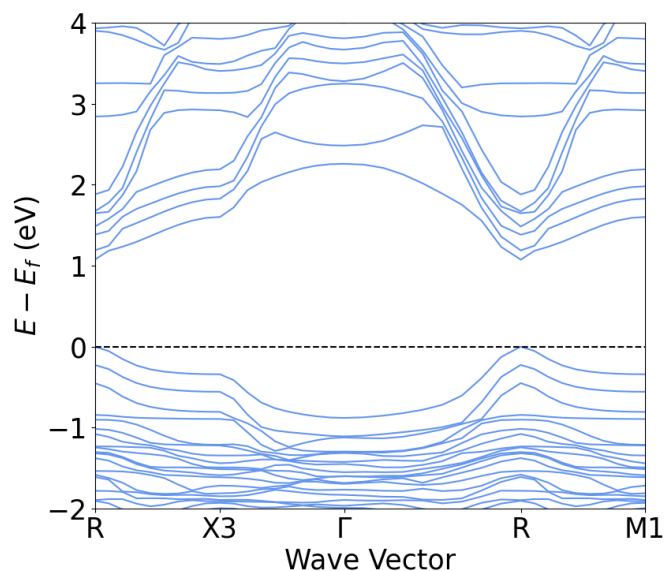


Figure 4.5.12c MAPbI MAI terminated slab band structure using PBEsol+U (8 eV)

Next, the PbX and MAX slab data for PBEsol and PBEsol+U (8 eV) will be compared. No mid-gap states were detected in any of the band structures for the PbX and MAX slabs using either functional. Band rearrangement was seen for all PbX and MAX slabs after adding the 8 eV U correction compared to the PBEsol functional.

Adding the 8 eV U correction to PBEsol for the PbCl and MAI slabs shifted the top valence band down around the Γ k-point only. The PbCl slab shifted more so than the MAI slab. Additionally, the valence bands for the PbCl slab were shifted to a larger negative energy compared to the MAI slab after adding the U correction.

The PbBr slab CBM was shifted slightly towards the Fermi energy, while the MABr slab CBM remained nearly unchanged. Again, adding the 8 eV U correction resulted in an energy decrease at the Γ k-point, while the MABr slab displayed a smaller shift in energy at this point.

For both the PbI and MAI slabs, the CBM moved towards the Fermi energy, although the PbI slab displayed a larger shift. Adding the 8 eV U correction resulted in a decrease in energy

as the Γ k-point for both the PbI and MAI slabs. Band structure comparisons are given in Figures 4.5.13a to 4.5.15c comparing the PBEsol+U (8 eV) and the PBEsol functionals.

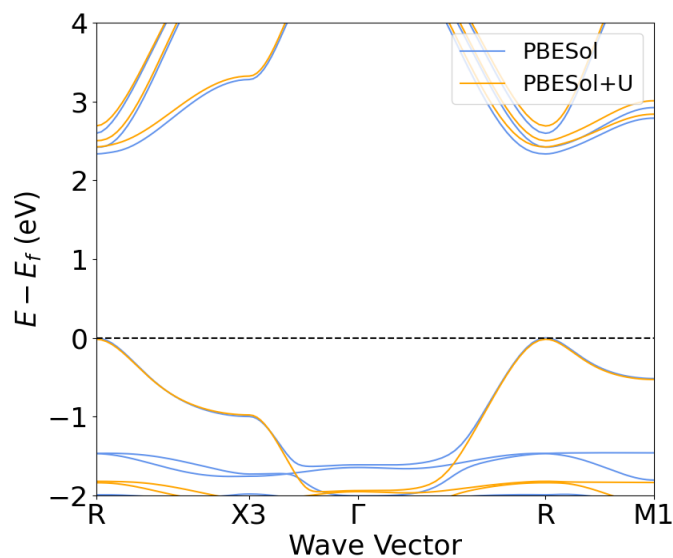


Figure 4.5.13a MAPbCl bulk band structure comparing PBEsol vs PBEsol+U (8 eV)

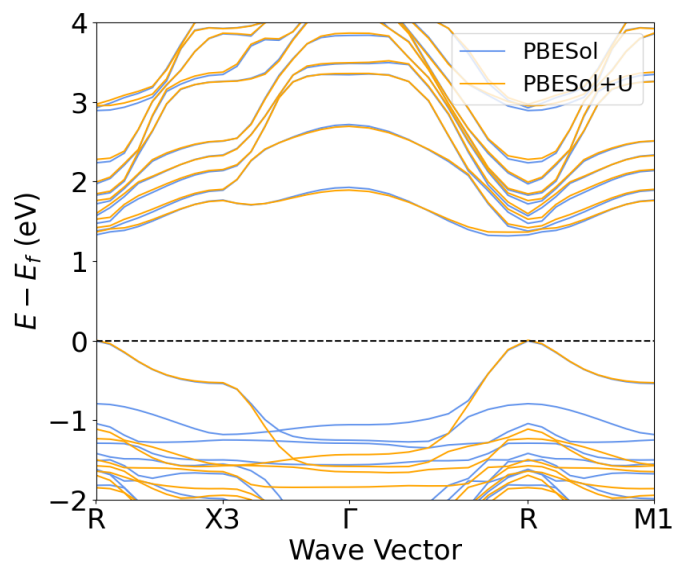


Figure 4.5.13b MAPbCl PbCl terminated slab band structure comparing PBEsol vs PBEsol+U (8 eV)

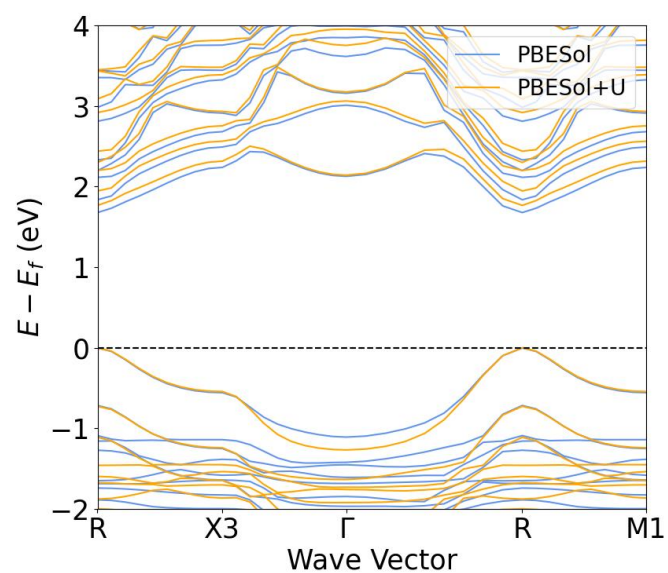


Figure 4.5.13c MAPbCl MACl terminated slab band structure comparing PBESol vs PBESol+U (8 eV)

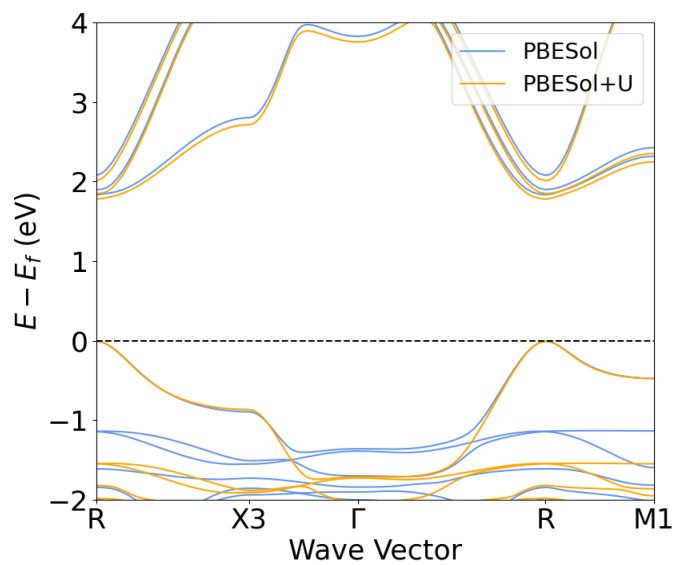


Figure 4.5.14a MAPbBr bulk band structure comparing PBESol vs PBESol+U (8 eV)

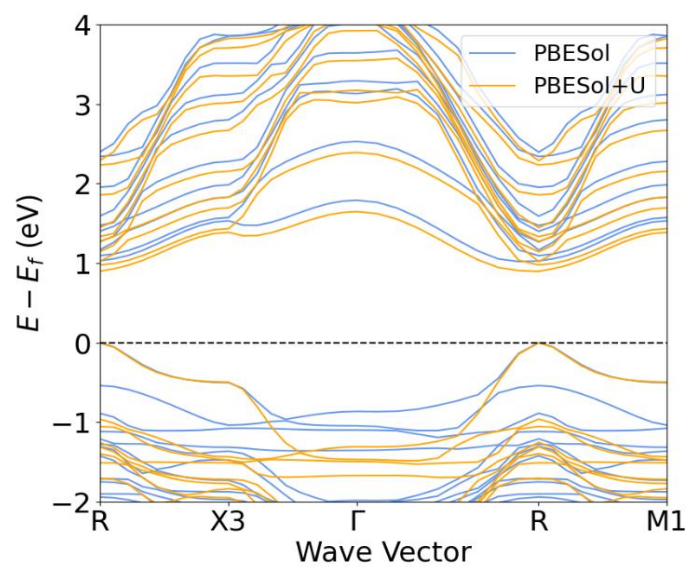


Figure 4.5.14b MAPbBr PbBr terminated slab band structure comparing PBESol vs PBESol+U (8 eV)

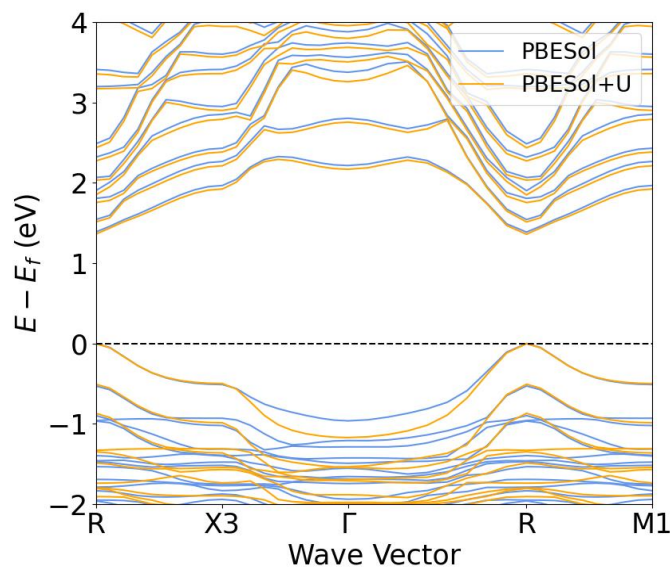


Figure 4.5.14c MAPbBr MABr terminated slab band structure comparing PBESol vs PBESol+U (8 eV)

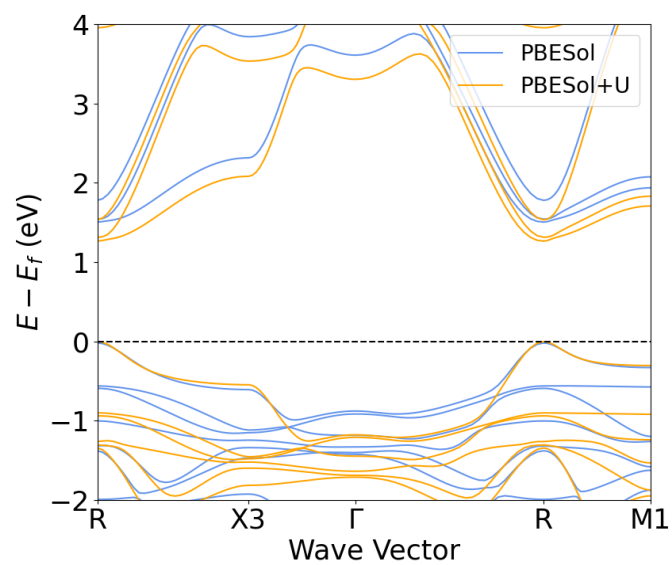


Figure 4.5.15a MAPbI bulk band structure comparing PBEsol vs PBEsol+U (8 eV)

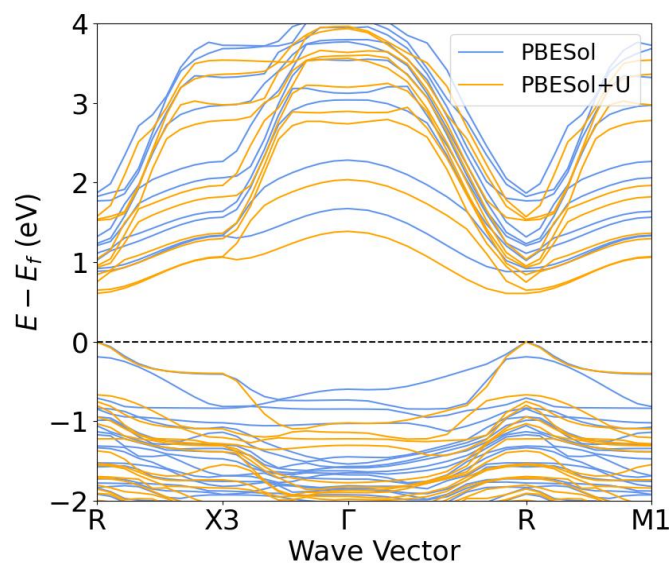


Figure 4.5.15b MAPbI PbI terminated slab band structure comparing PBEsol vs PBEsol+U (8 eV)

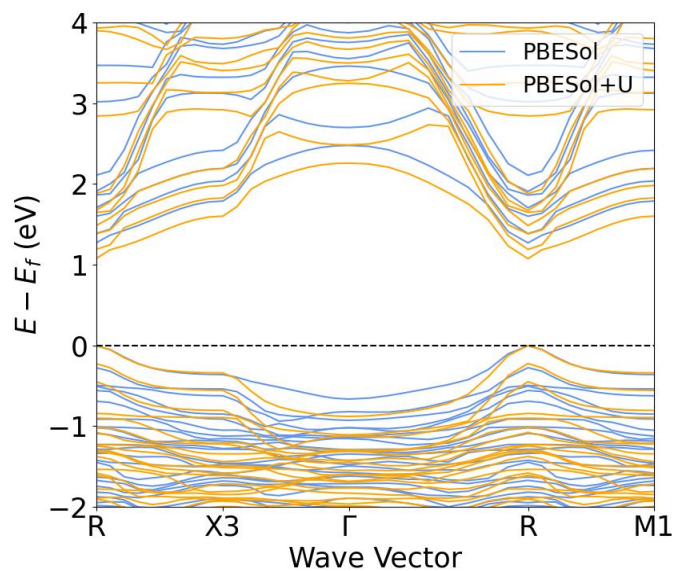


Figure 4.5.15c MAPbI MAI terminated slab band structure comparing PBEsol vs PBEsol+U (8 eV)

A comparison between the band structures for the different U values for MAPbBr and MAPbI will be presented. Recall the band gap matched U values for MAPbBr and MAPbI in the bulk were 4 eV and 1 eV, respectively. The band structures for these U values applied to MAX and PbX slab structures are depicted in Figures 4.5.16a to 4.5.17b.

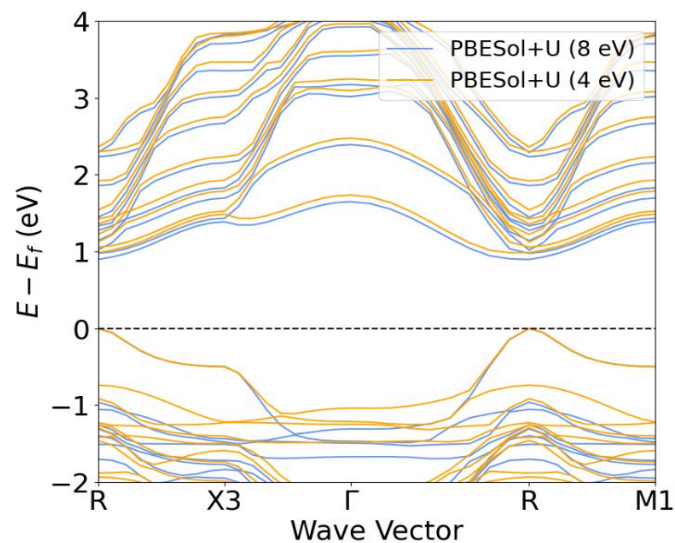


Figure 4.5.16a MAPbBr PbBr terminated slab band structure comparing U values

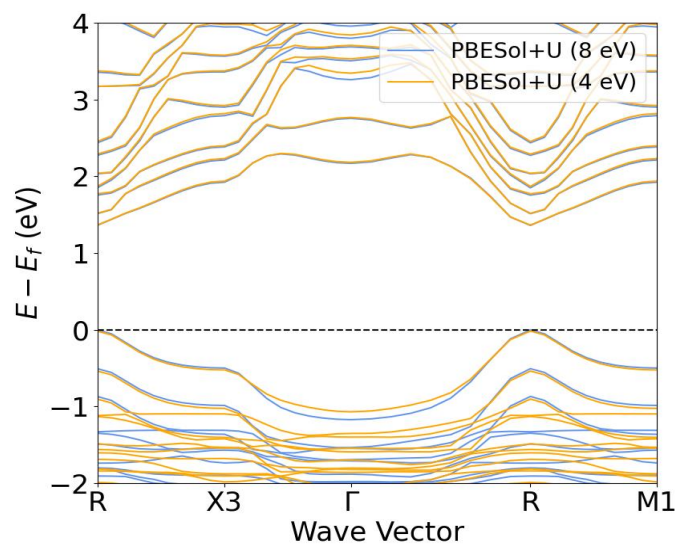


Figure 4.5.16b MAPbBr MABr terminated slab band structure comparing U values

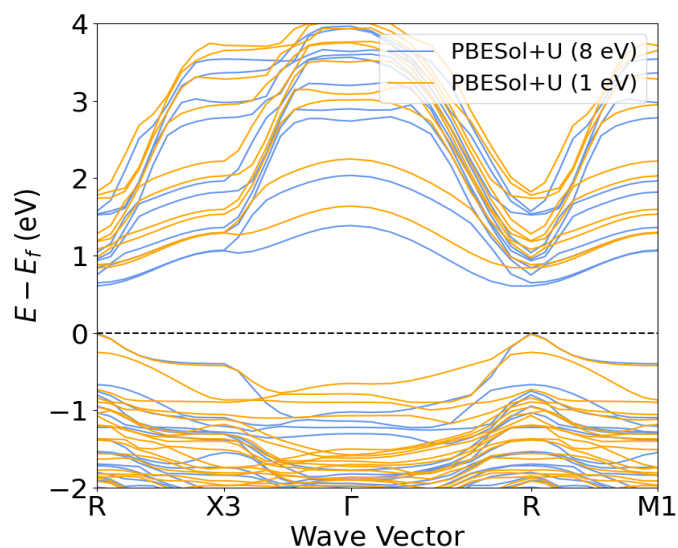


Figure 4.5.17a MAPbI PbI terminated slab band structure comparing U values

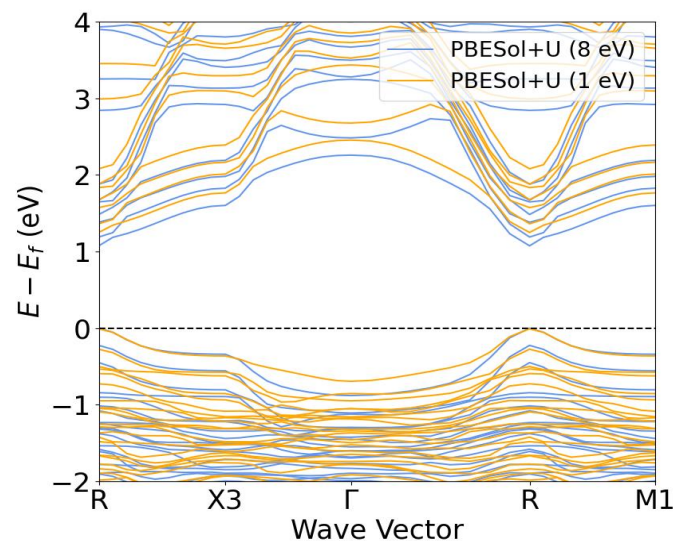


Figure 4.5.17b MAPbI MAI terminated slab band structure comparing U values

The band structure for the PbBr slab showed a slight decrease of the CBM band across all k-points after applying a U value of 4 eV. The top-most valence band shifted towards the Fermi energy at the Γ k-point. The conduction band closest to the Fermi energy was unchanged across all k-points for the MABr slab using either the 8 eV or 4 eV U values. The valence band closest

to the Fermi energy in the MABr slab experienced an energy reduction around the Γ k-point.

The band structures for the PbI slab in Figure 4.5.17a showed the top valence band shifted to a smaller energy resulting in the band moving towards the Fermi zero energy after adding the 1 eV U value. Additionally, the lowest conduction band shifted to higher energy resulting in a larger band gap for the 1 eV U value compared to the 8 eV U value. The MAI slab depicted in Figure 4.5.17b showed an energy shift at the Γ k-point (like the PbI slab), however, the energy shift was smaller in the MAI slab. The lowest conduction band in the MAI slab also shifted to higher energy after adding the 1 eV U value. The band gap values for the band gap matched U values are given in Table 4.5.2.

Table 4.5.2: Band gap values for PbX and MAX Slabs

Slab	System	PBEsol (eV)	PBEsol+U (eV)			DFT Literature
			U = 1	U = 4	U = 8	
MAX	MAPbCl	1.68	-	-	1.77	2.49 [86]*
	MAPbBr	1.39	-	1.38	1.36	1.6 [86]*
	MAPbI	1.27	1.26	-	1.07	1.15 [95]*, 1.265 [86]*
PbX	MAPbCl	1.31	-	-	1.35	2.49 [86]*
	MAPbBr	1.03	-	0.98	0.90	1.25 [86]*
	MAPbI	0.88	0.86	-	0.61	0.8 [96]**, 0.85 [86]*

* PBE Tetragonal ** PBE Cubic

The next paragraph will discuss band gap data for the PbX and MAX slabs using both the PBEsol and PBEsol+U (8 eV) functionals. The band gap values of the PbX and MAX slabs were smaller than the bulk values for both the PBEsol and 8 eV PBEsol+U functionals as shown in Figure 4.5.16. The PbX terminated surface slabs showed band gaps smaller than MAX slabs using both functionals. Similar results were found for the tetragonal structure. [86] The percent difference in the band gap increased for both PbX and MAX slabs as the halide size increased. A discussion of the band gap and band structure changes that occurred is given later when a

comparison is made between the PBEsol and 8 eV PBEsol+U results for both the PbX and MAX terminated slabs. For PbX terminated slabs, PbCl showed the least deviation of the band gap. This suggests the PbCl terminated slab displayed the least amount of orbital overlap. As a trend, the orbital overlap increased as the size of the halide increased.

The PbX terminated slabs experienced a reduction in the band gap of 3%, 12%, and 31% for PbCl, PbBr, and PbI after adding the 8 eV U correction. The MAX terminated slabs experienced a bandgap increase of 5% for MACl and a reduction of 2% and 16% for the MABr and MAI terminated slabs. The reorientation of the MA⁺ ion in the Pb-X lattice for both the PbX and MAX slabs changed after adding the 8 eV U value. The orientation of the MA⁺ ion has been shown to influence the band structure. [71] [86] It is postulated a buildup of charge is dependent on the MA⁺ ion orientation. [86] Adding the 8 eV U correction directly affected the amount of charge around the halide ions. This impacted the bond length and angles between the Pb and halide atoms that resulted in electronic property changes such as reduced band gap. The MAX-terminated slabs produced a larger band gap than the PbX slabs. This was confirmed in previous work. [91] [92] Figure 4.5.16 shows a comparison of the band gap values in the bulk and MAX and PbX surface slabs using both PBEsol and 8 eV PBEsol+U functionals. Table 4.5.2 shows the calculated band gap values for the MAX and PbX slabs for PBEsol and 8 eV PBEsol+U and a comparison with results found in the literature.

Band gap reduction could result in an increase in recombination events. Two types of recombination mechanisms are radiative (band-to-band) and defect assisted. Radiative recombination is the most dominant type in direct band gap semiconductors. Radiative recombination occurs when an electron in the conduction band stabilizes at a lower energy level in the valence band causing the removal of a hole and releasing a photon. The photon will have

an energy similar to the band gap and will only be weakly absorbed, allowing it to exit the semiconductor. [93] Defect assisted recombination occurs when there are midgap states within the band gap. These midgap states trap electrons (or holes) in the bandgap. A hole (or electron) can move up to the same trap state causing recombination to occur before the electron (or hole) can be re-emitted into the conduction band. [94]

5. CONCLUSIONS

This work studied the properties of MHP perovskites using VASP. An introduction to DFT, VASP, polarons, SOC, exchange functionals, and the Hubbard U correction and all associated physics with these topics has been presented. Bulk calculations were performed using PBEsol, PBEsol+SOC, PBEsol+U, and HSEsol. The optimal k-point mesh was determined to be 6x6x6 with an energy cutoff of 500 eV. PBEsol was shown to provide a good structural basis for the bulk parameters on its own as all lattice constants fell within 1% of experimental values. Additionally, all calculated bulk moduli values fell within 1% of other DFT simulations found in the literature.

Adding a U correction to the bulk structures altered the Pb-X bond lengths that caused lattice contraction in the inorganic lattice for all halide perovskites. Octahedral tilting also occurred in the MAPbCl bulk Pb-Cl lattice which marginally improved the bandgap towards experimental values and superseded the band gap reduction that accompanies lattice contractions. Octahedral tilting is an undesirable distortion in the inorganic lattice that would contribute to the instability of the lattice resulting in semiconductor device degradation or even failure. Meanwhile, the band gap for MAPbBr and MAPbI diverged from experimental values (significantly for MAPbI). The band gap values for MAPbBr and MAPbI diverged due to lattice contraction as there was no octahedral tilting observed in either of these compounds. Bulk band gap calculations identified alternate U values (MAPbCl was 8 eV, MAPbBr was 4 eV, and MAPbI was 1 eV) which provided values closer to experimental values. These differing U values altered the lengths of the bonds between the pb and halide ions in the bulk. Larger U values resulted in a larger reduction of the pb-halide bond. Average bond length values in the bulk were calculated and fell within 1% of experimentally verified values. The HSEsol hybrid

functional provided electronic properties closest to experimental values but at a significant cost increase in computational time. DOS plots showed band broadening increased at band gap edges as the halide size increased. For supercell simulations, all calculations were carried out using the PBEsol functional and with a U correction added to the halide p orbital.

To study surface properties, supercells were built with differing surface terminations using the optimized bulk values and structures. To our knowledge, no studies have been conducted using the Hubbard U correction for MHPs to study surface properties. A minimum of 5 volume units of vacuum was necessary to eliminate artificial potentials from the cyclic boundary conditions in VASP. Dipole corrections were applied to the neutral supercells negating the potential difference in the surrounding vacuum created by the pseudo-cubic nature of these halide perovskites. Dangling bonds on the PbX terminated slabs resulted in surface reconstruction for both PBEsol and PBEsol+U functionals. Adding the U correction resulted in a reorientation of the MA ion so that the NH_3 group was pointing toward the vacuum region. The MA ion indirectly influences the band gap through several interactions such as dipole-dipole interactions between MA ions or through hydrogen bonding between the positive MA ion and the negatively charged Pb-X lattice. Smaller U correction values resulted in slightly larger Pb-X bond lengths allowing for the MA ion to reorient to a larger extent. Adding a U correction also resulted in band broadening at the band gap edges in both the MAX and PbX slabs. The band gap was calculated for PbX and MAX slabs using PBEsol and PBEsol+U functionals. The PbX slabs consistently exhibited smaller band gap values compared to the MAX slab band gaps. A decrease in the band gap at the surface might lead to trapping of electrons and holes together there, which would likely result in unwanted radiative recombination rather than carrier separation. The smaller band gaps of the PbX surface suggest recombination events are more

likely to occur in the PbX surface compared to the MAX surface. It was observed that larger U values decreased the band gap for both the PbX and MAX slab structures. Band gap reduction was not accompanied by midgap states in the slab structures. The lack of midgap states being induced in the surface slabs is beneficial when using these perovskite materials in heterostructures and interfaces of devices as defect assisted recombination would not occur. Lastly, the impact of the U correction on the band gap and bond length changes varied for each halide in both the bulk and both the PbX and MAX slabs. These results lead us to conclude each perovskite will need to have a specific U value optimized for it. Further work optimizing the U value is needed relying on the hybrid ionic force matching as previously done for the bulk or model these slabs using hybrid functionals as the Texas State High Performance Computing Cluster can perform this work nowadays.

6. FUTURE WORK

Five topics were identified for follow-up studies. 1. As previously mentioned, insufficient time prevented a re-optimization of the Hubbard U value using ionic force comparisons with hybrid functionals. As such the U values used in this work need to be reoptimized. 2. The HSESol hybrid functional produced a band gap closest to the experimental value and would provide the best choice for simulating the surface of these materials. 3. The inclusion of SOC to the hybrid functional would also be possible without shrinking the bandgap to an unacceptable value which occurs when using a local or semi-local functional. 4. Larger supercells need to be considered to investigate how slab size affects surface properties. 5. The dipole and potential-and-forces corrections were applied after the supercells were allowed to relax. This means the atoms were relaxed with a non-constant potential in the vacuum, which may provide erroneous results. Applying the dipole and potential-and-forces corrections during relaxation calculations would eliminate the non-constant potential and provide better results.

APPENDIX SECTION

Table A.1: Atomic Units

Atomic Units	Value
electron charge	$1.60218 \times 10^{-19} \text{ C}$
electron mass	$9.11 \times 10^{-31} \text{ kg}$
Bohr (length)	$0.529 \text{ \AA}$
Hartree (energy)	27.21 eV
Reduced Planck's Constant	$1.05457 \times 10^{-34} \text{ J}\cdot\text{s}$
Coulomb	$8.98755 \times 10^9 \text{ kg}\cdot\text{m}^3\cdot\text{s}^{-2}\cdot\text{C}^{-2}$

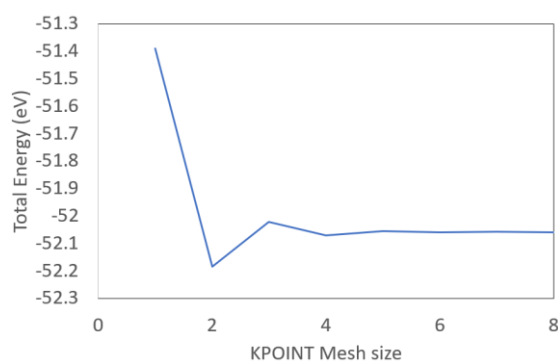


Figure A.1: MAPbCl Bulk kpoint Optimization

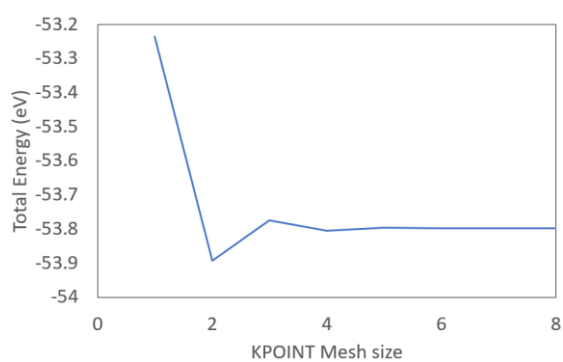


Figure A.2: MAPbBr Bulk kpoint Optimization

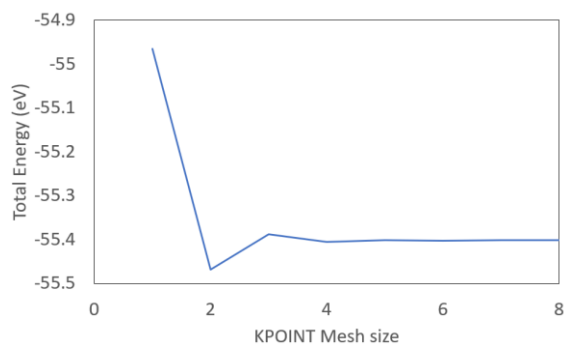


Figure A.3: MAPbI Bulk kpoint Optimization

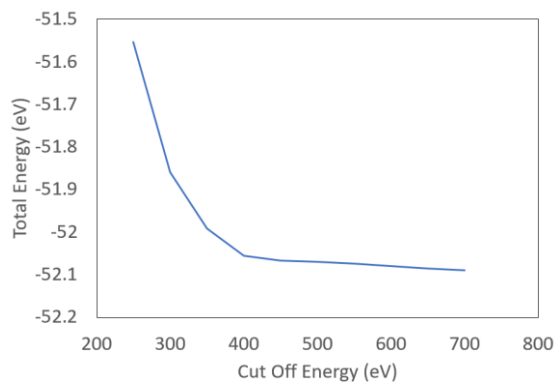


Figure A.4: MAPbCl Bulk ENCUT Optimization

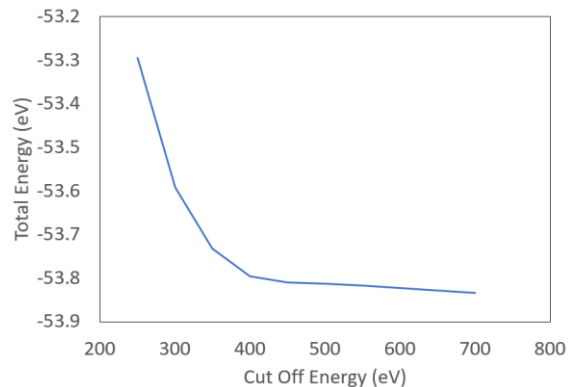


Figure A.5: MAPbBr Bulk ENCUT Optimization

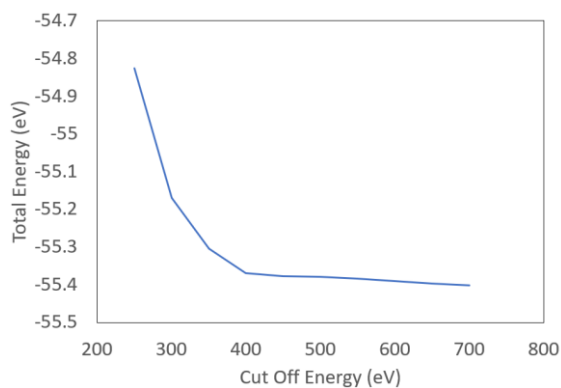


Figure A.6: MAPbI Bulk ENCUT Optimization

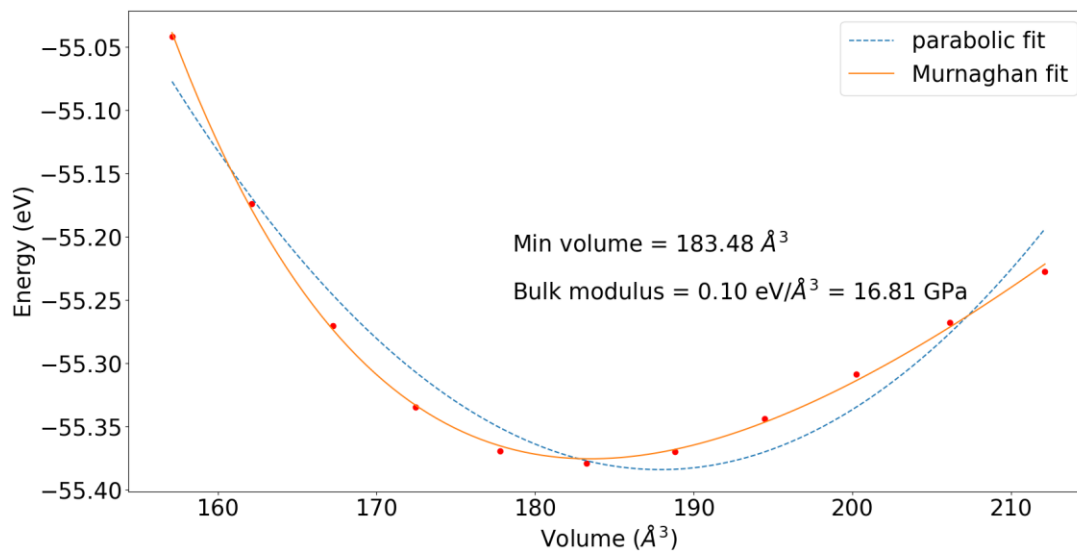


Figure A.7: MAPbCl Bulk Modulus

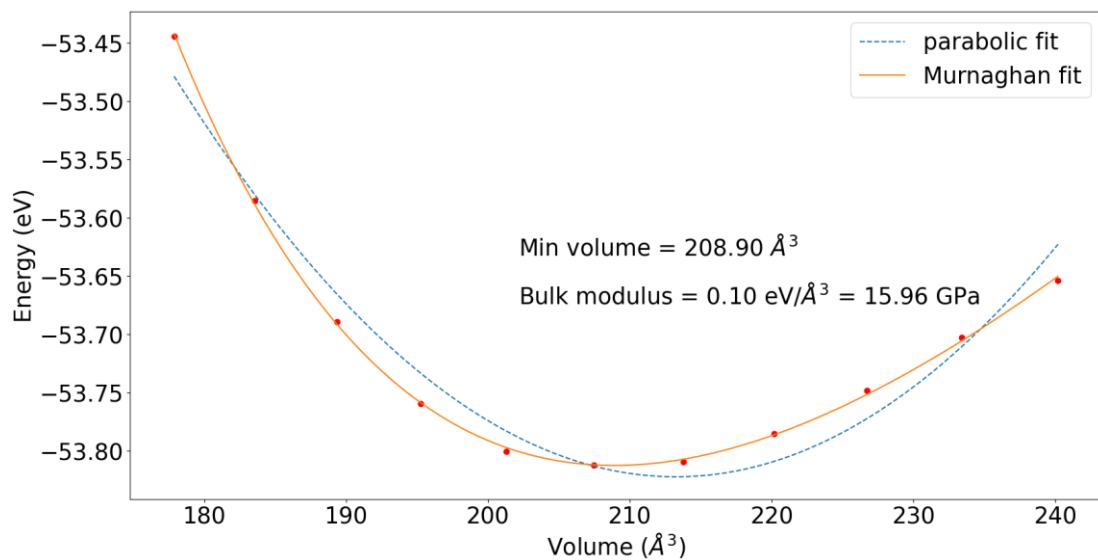


Figure A.8: MAPbBr Bulk Modulus

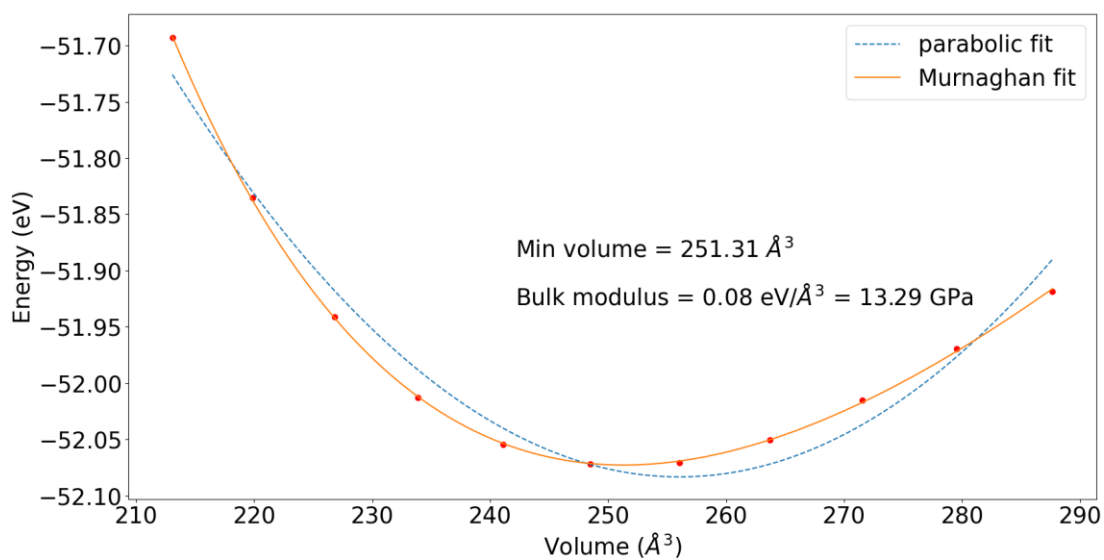


Figure A.9: MAPbI Bulk Modulus

Table A.2: Supercell with varying vacuum sizes for MAPbCl

Vacuum Units	Supercell Size (Å)	Vacuum Size (Å)	Total Size (Å)
0	17.04	0	17.040
3	17.04	17.040	34.08
4	17.04	22.72	39.76
5	17.04	28.4	45.44
6	17.04	34.08	51.12
7	17.04	39.76	56.8

Table A.3: Supercell with varying vacuum sizes for MAPbBr

Vacuum Units	Supercell Size (Å)	Vacuum Size (Å)	Total Size (Å)
0	17.79	0	17.79
3	17.79	17.76	35.579
4	17.79	23.68	41.509
5	17.79	29.6	47.439
6	17.79	35.52	53.369
7	17.79	41.44	59.299

Table A.4: Supercell with varying vacuum sizes for MAPbI

Vacuum Units	Supercell Size (Å)	Vacuum Size (Å)	Total Size (Å)
0	18.94038	0	18.94038
3	18.94	18.94	37.86
4	18.94	25.25	44.17
5	18.94	31.56	50.48
6	18.94	37.87	56.79
7	18.94	44.18	63.10

Table A.5: Pb-X Bond Lengths

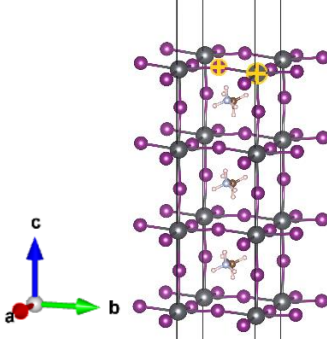
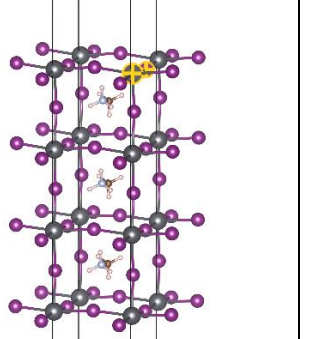
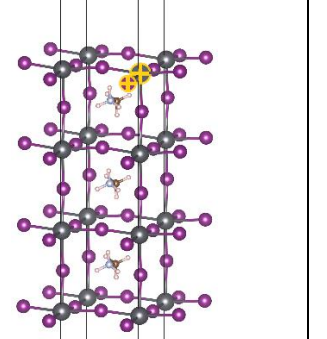
Pb-X Bond Length (Å)				Pb-X Bond Length (Å)				Pb-X Bond Length (Å)			
											
MAPbCl				MAPbCl				MAPbCl			
Layers	PBEsol	PBEsol+U	Delta	Layers	PBEsol	PBEsol+U	Delta	Layers	PBEsol	PBEsol+U	Delta
1	2.84064	2.84082	0.00018	1	3.02827	3.04864	0.02037	1	2.70256	2.68422	-0.01834
3	2.86513	2.86103	-0.0041	3	2.87921	2.82242	-0.05679	3	2.82344	2.87752	0.05408
5	2.86005	2.86005	0	5	2.85654	2.85654	0	5	2.84641	2.84641	0
MAPbBr				MAPbBr				MAPbBr			
Layers	PBEsol	PBEsol+U	Delta	Layers	PBEsol	PBEsol+U	Delta	Layers	PBEsol	PBEsol+U	Delta
1	2.97445	2.97130	-0.00315	1	3.11433	3.10041	-0.01392	1	2.85736	2.86927	0.01191
3	2.99176	2.98369	-0.00807	3	3.04111	3.02083	-0.02028	3	2.90898	2.92265	0.01367
5	2.98222	2.98222	0	5	3.01951	3.01951	0	5	2.93075	2.93075	0
MAPbI				MAPbI				MAPbI			
Layers	PBEsol	PBEsol+U	Delta	Layers	PBEsol	PBEsol+U	Delta	Layers	PBEsol	PBEsol+U	Delta
1	3.17606	3.17459	-0.00147	1	3.28848	3.26291	-0.02557	1	3.04196	3.07210	0.03014
3	3.18297	3.17826	-0.00471	3	3.26093	3.23554	-0.02539	3	3.05879	3.08458	0.02579
5	3.17210	3.17210	0	5	3.24066	3.24066	0	5	3.08351	3.08351	0

Table A.6: Pb-X-Pb Bond Angles

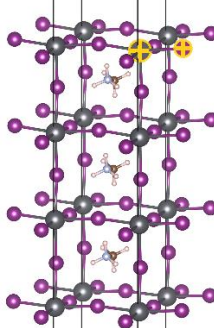
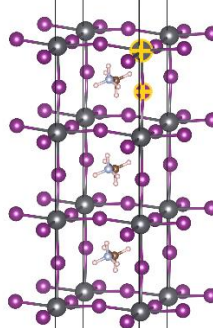
Pb-X Bond Length (Å)				Pb-X Bond Length (Å)			
							
MAPbCl				MAPbCl			
Layers	PBEsol	PBEsol+U	Delta	Layers	PBEsol	PBEsol+U	Delta
1	2.84078	2.84102	0.00024	1 – 2	2.71625	2.69554	-0.02071
3	2.86522	2.86113	-0.00409	3 – 4	2.82512	2.81301	-0.01211
5	2.86021	2.86021	0	5 – 6	2.89433	2.89433	0
MAPbBr				MAPbBr			
Layers	PBEsol	PBEsol+U	Delta	Layers	PBEsol	PBEsol+U	Delta
1	2.97454	2.97142	-0.00312	1 – 2	2.85589	2.84604	-0.00985
3	2.99189	2.98389	-0.008	3 – 4	2.94463	2.93618	-0.00845
5	2.98234	2.98234	0	5 – 6	3.01046	3.01046	0
MAPbI				MAPbI			
Layers	PBEsol	PBEsol+U	Delta	Layers	PBEsol	PBEsol+U	Delta
1	3.17596	3.17418	-0.00178	1 – 2	3.04047	3.04723	0.00676
3	3.18282	3.17815	-0.00467	3 – 4	3.12189	3.12687	0.00498
5	3.17207	3.17207	0	5 – 6	3.17899	3.17899	0

Table A.7: Pb-X-Pb Bond Angles

Table A.7: Pb-X-Pb Bond Angles

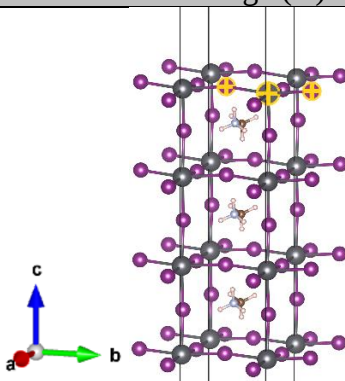
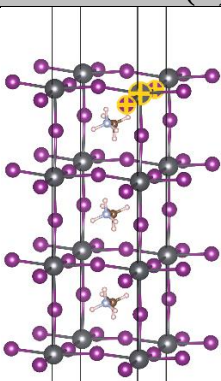
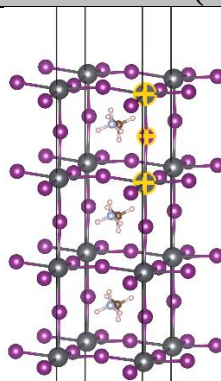
X-Pb-X Bond Angle(Å)	X-Pb-X Bond (Å)	Pb-X-Pb Bond (Å)																																																																				
																																																																						
<table><tr><th colspan="4">MAPbCl</th></tr><tr><th>Layer</th><th>PBEsol</th><th>PBEsol+U</th><th>Delta</th></tr><tr><td>1</td><td>177.4383</td><td>177.0813</td><td>-0.357</td></tr><tr><td>3</td><td>164.7986</td><td>166.0813</td><td>1.2827</td></tr><tr><td>5</td><td>166.3975</td><td>166.3975</td><td>0</td></tr><tr><td>7</td><td>166.3975</td><td>166.3975</td><td>0</td></tr></table>	MAPbCl				Layer	PBEsol	PBEsol+U	Delta	1	177.4383	177.0813	-0.357	3	164.7986	166.0813	1.2827	5	166.3975	166.3975	0	7	166.3975	166.3975	0	<table><tr><th colspan="4">MAPbCl</th></tr><tr><th>Layer</th><th>PBEsol</th><th>PBEsol+U</th><th>Delta</th></tr><tr><td>1</td><td>164.7013</td><td>164.3956</td><td>-0.3057</td></tr><tr><td>3</td><td>169.7836</td><td>170.4111</td><td>0.6275</td></tr><tr><td>5</td><td>169.7158</td><td>169.7158</td><td>0</td></tr><tr><td>7</td><td>169.7171</td><td>169.7171</td><td>0</td></tr></table>	MAPbCl				Layer	PBEsol	PBEsol+U	Delta	1	164.7013	164.3956	-0.3057	3	169.7836	170.4111	0.6275	5	169.7158	169.7158	0	7	169.7171	169.7171	0	<table><tr><th colspan="4">MAPbCl</th></tr><tr><th>Layers</th><th>PBEsol</th><th>PBEsol+U</th><th>Delta</th></tr><tr><td>1 - 3</td><td>168.4348</td><td>168.45</td><td>0.0152</td></tr><tr><td>3 - 5</td><td>171.4137</td><td>172.209</td><td>0.7953</td></tr><tr><td>5 - 7</td><td>169.1899</td><td>169.1899</td><td>0</td></tr></table>	MAPbCl				Layers	PBEsol	PBEsol+U	Delta	1 - 3	168.4348	168.45	0.0152	3 - 5	171.4137	172.209	0.7953	5 - 7	169.1899	169.1899	0
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7	170.5408	170.5408	0																																																																			
MAPbBr																																																																						
Layers	PBEsol	PBEsol+U	Delta																																																																			
1 - 3	169.8322	171.2767	1.4445																																																																			
3 - 5	171.3415	171.2745	-0.067																																																																			
5 - 7	169.2348	169.2348	0																																																																			
<table><tr><th colspan="4">MAPbI</th></tr><tr><th>Layer</th><th>PBEsol</th><th>PBEsol+U</th><th>Delta</th></tr><tr><td>1</td><td>166.8123</td><td>167.3297</td><td>0.5174</td></tr><tr><td>3</td><td>164.8181</td><td>166.1454</td><td>1.3273</td></tr><tr><td>5</td><td>168.1017</td><td>168.1017</td><td>0</td></tr><tr><td>7</td><td>170.9413</td><td>170.9413</td><td>0</td></tr></table>	MAPbI				Layer	PBEsol	PBEsol+U	Delta	1	166.8123	167.3297	0.5174	3	164.8181	166.1454	1.3273	5	168.1017	168.1017	0	7	170.9413	170.9413	0	<table><tr><th colspan="4">MAPbI</th></tr><tr><th>Layer</th><th>PBEsol</th><th>PBEsol+U</th><th>Delta</th></tr><tr><td>1</td><td>170.7828</td><td>169.8094</td><td>-0.9734</td></tr><tr><td>3</td><td>173.6397</td><td>173.5131</td><td>-0.1266</td></tr><tr><td>5</td><td>172.3266</td><td>172.3266</td><td>0</td></tr><tr><td>7</td><td>172.3281</td><td>172.3281</td><td>0</td></tr></table>	MAPbI				Layer	PBEsol	PBEsol+U	Delta	1	170.7828	169.8094	-0.9734	3	173.6397	173.5131	-0.1266	5	172.3266	172.3266	0	7	172.3281	172.3281	0	<table><tr><th colspan="4">MAPbI</th></tr><tr><th>Layers</th><th>PBEsol</th><th>PBEsol+U</th><th>Delta</th></tr><tr><td>1 - 3</td><td>166.0011</td><td>168.5031</td><td>2.502</td></tr><tr><td>3 - 5</td><td>168.0173</td><td>169.4214</td><td>1.4041</td></tr><tr><td>5 - 7</td><td>169.7254</td><td>169.7254</td><td>0</td></tr></table>	MAPbI				Layers	PBEsol	PBEsol+U	Delta	1 - 3	166.0011	168.5031	2.502	3 - 5	168.0173	169.4214	1.4041	5 - 7	169.7254	169.7254	0
MAPbI																																																																						
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3 - 5	168.0173	169.4214	1.4041																																																																			
5 - 7	169.7254	169.7254	0																																																																			

Table A.8: MAX Termination | Pb-X Bond Lengths

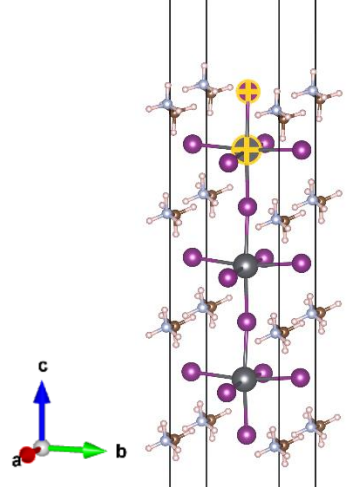
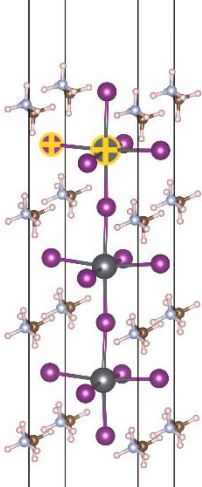
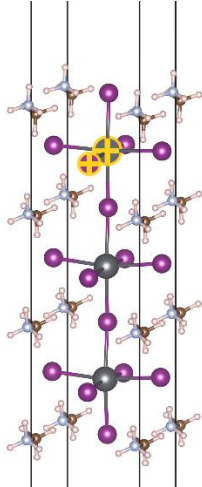
MA-X Bond Length (Å)				MA-X Bond Length (Å)				MA-X Bond Length (Å)			
											
MAPbCl				MAPbCl				MAPbCl			
Layers	PBEsol	PBEsol+U	Delta	Layers	PBEsol	PBEsol+U	Delta	Layers	PBEsol	PBEsol+U	Delta
1 – 2	2.89259	2.87521	-0.01738	1	2.85315	2.85196	-0.00119	1	2.87917	2.90834	0.02917
3 – 4	2.94448	2.93150	-0.01298	3	2.86338	2.86028	-0.0031	3	2.84931	2.89428	0.04497
5 – 6	2.81107	2.81107	0	5	2.86005	2.86005	0	5	2.84641	2.84641	0
MAPbBr				MAPbBr				MAPbBr			
Layers	PBEsol	PBEsol+U	Delta	Layers	PBEsol	PBEsol+U	Delta	Layers	PBEsol	PBEsol+U	Delta
1 – 2	3.04294	3.03602	-0.00692	1	2.97629	2.97403	-0.00226	1	2.99442	3.01115	0.01673
3 – 4	3.05438	3.04621	-0.00817	3	2.98750	2.98401	-0.00349	3	2.92489	2.94160	0.01671
5 – 6	2.94581	2.94581	0	5	2.98222	2.98222	0	5	2.93075	2.93075	0
MAPbI				MAPbI				MAPbI			
Layers	PBEsol	PBEsol+U	Delta	Layers	PBEsol	PBEsol+U	Delta	Layers	PBEsol	PBEsol+U	Delta
1 – 2	3.21468	3.22958	0.0149	1	3.15895	3.15782	-0.00113	1 - 3	3.14671	3.16322	0.01651
3 – 4	3.26246	3.26736	0.0049	3	3.17478	3.17215	-0.00263	3 - 5	3.09347	3.11351	0.02004
5 – 6	3.17384	3.17384	0	5	3.17209	3.17209	0	5 - 7	3.08351	3.08351	0

Table A.9: MAX termination | Pb-X Bond Lengths

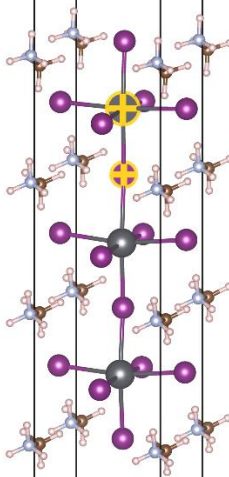
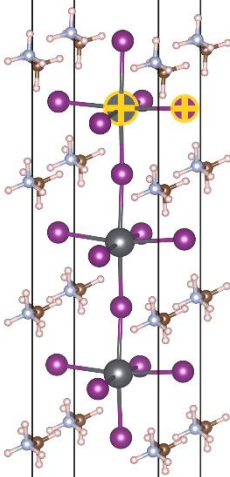
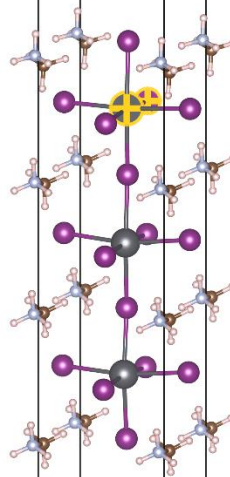
Pb-X Bond Length (Å)				Pb-X Bond Length (Å)							
											
MAPbCl				MAPbCl				MAPbCl			
Layers	PBEsol	PBEsol+U	Delta	Layers	PBEsol	PBEsol+U	Delta	Layers	PBEsol	PBEsol+U	Delta
2 – 3	2.89976	2.88860	-0.01116	2	2.85324	2.85205	-0.00119	2	2.81091	2.77980	-0.03111
4 – 5	2.87188	2.85875	-0.01313	4	2.86358	2.86051	-0.00307	4	2.84045	2.79381	-0.04664
6 – 7	2.89427	2.89427	0	6	2.86021	2.86021	0	6	2.85654	2.85654	0
MAPbBr				MAPbBr				MAPbBr			
Layers	PBEsol	PBEsol+U	Delta	Layers	PBEsol	PBEsol+U	Delta	Layers	PBEsol	PBEsol+U	Delta
2 – 3	2.99655	2.98806	-0.00849	2	2.97642	2.97415	-0.00227	2	2.97046	2.94923	-0.02123
4 – 5	2.97357	2.96497	-0.0086	4	2.98770	2.98419	-0.00351	4	3.01436	2.99664	-0.01772
6 – 7	3.01042	3.01042	0	6	2.98234	2.98234	0	6	3.01951	3.01951	0
MAPbI				MAPbI				MAPbI			
Layers	PBEsol	PBEsol+U	Delta	Layers	PBEsol	PBEsol+U	Delta	Layers	PBEsol	PBEsol+U	Delta
2 – 3	3.20982	3.21458	0.00476	2	3.15878	3.15756	-0.00122	2	3.17492	3.16225	-0.01267
4 – 5	3.16222	3.16947	0.00725	4	3.17495	3.17233	-0.00262	4	3.22182	3.20257	-0.01925
6 – 7	3.19013	3.19013	0	6	3.17207	3.17207	0	6	3.24066	3.24066	0

Table A.10: X-Pb-X Bond Angles (°)

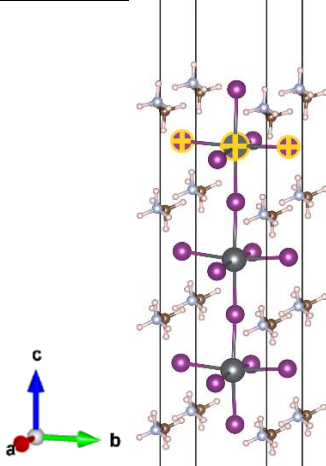
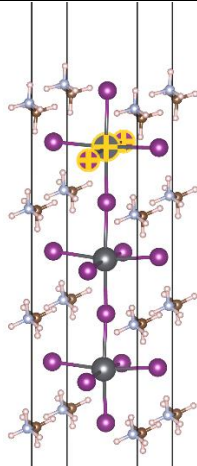
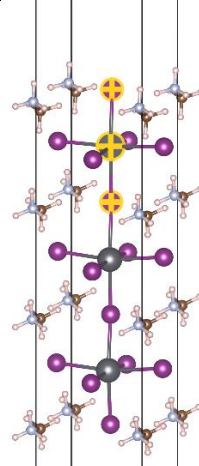
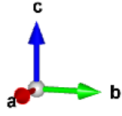
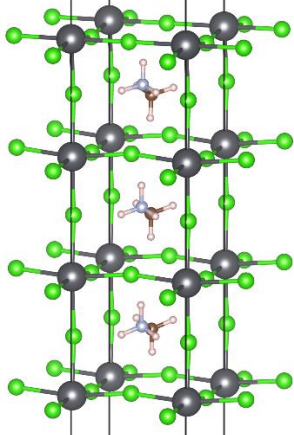
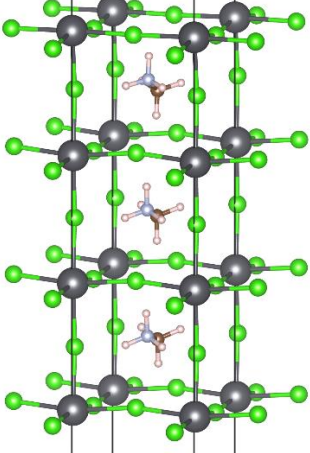
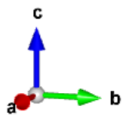
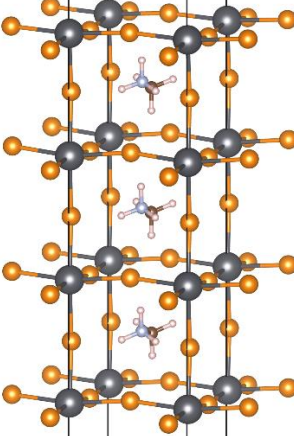
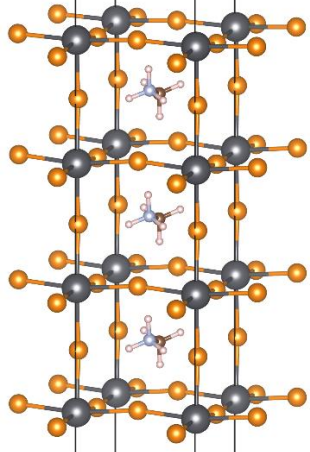
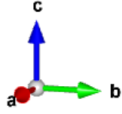
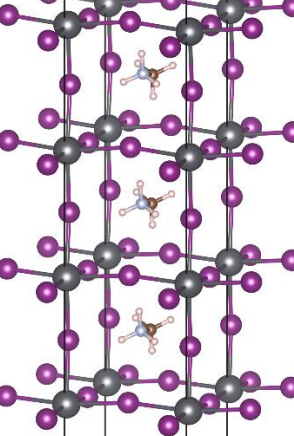
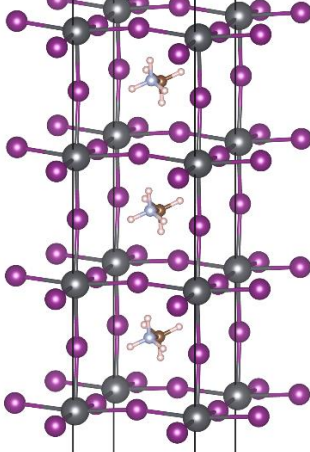
X-Pb-X Bond Angle(Å)	X-Pb-X Bond (Å)	X-Pb-X Bond (Å)																																																												
																																																														
<table><tr><th colspan="4">MAPbCl</th></tr><tr><th>Layer</th><th>PBEsol</th><th>PBEsol+U</th><th>Delta</th></tr><tr><td>2</td><td>168.976</td><td>169.4824</td><td>0.5066</td></tr><tr><td>4</td><td>165.315</td><td>166.3085</td><td>0.9935</td></tr><tr><td>6</td><td>166.397</td><td>166.397</td><td>0</td></tr></table>	MAPbCl				Layer	PBEsol	PBEsol+U	Delta	2	168.976	169.4824	0.5066	4	165.315	166.3085	0.9935	6	166.397	166.397	0	<table><tr><th colspan="4">MAPbCl</th></tr><tr><th>Layer</th><th>PBEsol</th><th>PBEsol+U</th><th>Delta</th></tr><tr><td>2</td><td>173.1767</td><td>173.8663</td><td>0.6896</td></tr><tr><td>4</td><td>173.2858</td><td>173.8899</td><td>0.6041</td></tr><tr><td>6</td><td>169.7158</td><td>169.7158</td><td>0</td></tr></table>	MAPbCl				Layer	PBEsol	PBEsol+U	Delta	2	173.1767	173.8663	0.6896	4	173.2858	173.8899	0.6041	6	169.7158	169.7158	0	<table><tr><th colspan="4">MAPbCl</th></tr><tr><th>Layers</th><th>PBEsol</th><th>PBEsol+U</th><th>Delta</th></tr><tr><td>1 - 3</td><td>170.474</td><td>170.661</td><td>0.187</td></tr><tr><td>3 - 5</td><td>171.101</td><td>171.606</td><td>0.5056</td></tr><tr><td>5 - 7</td><td>169.190</td><td>169.190</td><td>0</td></tr></table>	MAPbCl				Layers	PBEsol	PBEsol+U	Delta	1 - 3	170.474	170.661	0.187	3 - 5	171.101	171.606	0.5056	5 - 7	169.190	169.190	0
MAPbCl																																																														
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<table><tr><th colspan="4">MAPbBr</th></tr><tr><th>Layer</th><th>PBEsol</th><th>PBEsol+U</th><th>Delta</th></tr><tr><td>2</td><td>169.987</td><td>171.0387</td><td>1.0519</td></tr><tr><td>4</td><td>165.897</td><td>167.0285</td><td>1.1315</td></tr><tr><td>6</td><td>167.658</td><td>167.658</td><td>0</td></tr></table>	MAPbBr				Layer	PBEsol	PBEsol+U	Delta	2	169.987	171.0387	1.0519	4	165.897	167.0285	1.1315	6	167.658	167.658	0	<table><tr><th colspan="4">MAPbBr</th></tr><tr><th>Layer</th><th>PBEsol</th><th>PBEsol+U</th><th>Delta</th></tr><tr><td>2</td><td>167.6014</td><td>168.4239</td><td>0.8225</td></tr><tr><td>4</td><td>173.6036</td><td>173.9628</td><td>0.3592</td></tr><tr><td>6</td><td>170.5394</td><td>170.5394</td><td>0</td></tr></table>	MAPbBr				Layer	PBEsol	PBEsol+U	Delta	2	167.6014	168.4239	0.8225	4	173.6036	173.9628	0.3592	6	170.5394	170.5394	0	<table><tr><th colspan="4">MAPbBr</th></tr><tr><th>Layers</th><th>PBEsol</th><th>PBEsol+U</th><th>Delta</th></tr><tr><td>1 - 3</td><td>170.6474</td><td>170.7337</td><td>0.0863</td></tr><tr><td>3 - 5</td><td>171.8848</td><td>172.6451</td><td>0.7603</td></tr><tr><td>5 - 7</td><td>169.2347</td><td>169.2347</td><td>0</td></tr></table>	MAPbBr				Layers	PBEsol	PBEsol+U	Delta	1 - 3	170.6474	170.7337	0.0863	3 - 5	171.8848	172.6451	0.7603	5 - 7	169.2347	169.2347	0
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<table><tr><th colspan="4">MAPbI</th></tr><tr><th>Layer</th><th>PBEsol</th><th>PBEsol+U</th><th>Delta</th></tr><tr><td>2</td><td>174.332</td><td>175.2684</td><td>0.9369</td></tr><tr><td>4</td><td>167.174</td><td>168.0489</td><td>0.875</td></tr><tr><td>6</td><td>168.102</td><td>168.102</td><td>0</td></tr></table>	MAPbI				Layer	PBEsol	PBEsol+U	Delta	2	174.332	175.2684	0.9369	4	167.174	168.0489	0.875	6	168.102	168.102	0	<table><tr><th colspan="4">MAPbI</th></tr><tr><th>Layer</th><th>PBEsol</th><th>PBEsol+U</th><th>Delta</th></tr><tr><td>2</td><td>173.0486</td><td>171.9837</td><td>-1.0649</td></tr><tr><td>4</td><td>175.3081</td><td>174.9715</td><td>-0.3366</td></tr><tr><td>6</td><td>172.3253</td><td>172.3253</td><td>0</td></tr></table>	MAPbI				Layer	PBEsol	PBEsol+U	Delta	2	173.0486	171.9837	-1.0649	4	175.3081	174.9715	-0.3366	6	172.3253	172.3253	0	<table><tr><th colspan="4">MAPbI</th></tr><tr><th>Layers</th><th>PBEsol</th><th>PBEsol+U</th><th>Delta</th></tr><tr><td>1 - 3</td><td>173.2052</td><td>173.6922</td><td>0.487</td></tr><tr><td>3 - 5</td><td>170.9552</td><td>172.3372</td><td>1.382</td></tr><tr><td>5 - 7</td><td>165.2359</td><td>165.2359</td><td>0</td></tr></table>	MAPbI				Layers	PBEsol	PBEsol+U	Delta	1 - 3	173.2052	173.6922	0.487	3 - 5	170.9552	172.3372	1.382	5 - 7	165.2359	165.2359	0
MAPbI																																																														
Layer	PBEsol	PBEsol+U	Delta																																																											
2	174.332	175.2684	0.9369																																																											
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5 - 7	165.2359	165.2359	0																																																											

Table A.11: Perovskite Structural Comparison

Perovskite	PBEsol	PBEsol+U
MAPbCl 		
MAPbBr 		
MAPbI 		

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