AB INITIO STUDY OF THE EFFECTS OF HUMIDITY ON PEROVSKITE BASED HYBRID SOLAR CELL INTERFACES

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Renewable and Clean Energy Engineering

By

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B.E., University of Pune, 2014

2017
Wright State University
I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY
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ABSTRACT

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Despite the impressive success of perovskite-based hybrid solar cells, their widespread usage has been limited partially owing to stability issues under working environmental conditions. Among these, the effects of humidity are some of the most significant. Water intercalation generally degrades the material, shortens its useful life, and reduces the efficiency of photovoltaic energy conversion. Understanding the reasons for these effects can be achieved through detailed and accurate atomic-scale analysis.

Here, we study water intercalation at the interfaces of perovskite-based hybrid solar cell material and TiO$_2$ electrode. Accurate ab initio computer simulations are used to obtain structural and electronic properties. We systematically investigate interfacial geometry and determine the most stable configurations for different orientations of TiO$_2$ (001) surface and different layers of hybrid organic-inorganic tetragonal perovskite lead Iodide. We also determine water adsorption characteristic on reconstructed TiO$_2$ and hybrid perovskite surfaces. These are then used to obtain the most stable interfacial configurations upon water intercalation. Based on the obtained electronic properties we compare interface functionality with and without water and discuss consequent effects on solar cell performance.
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LIST OF ACRONYMS

VASP    Vienna ab initio Simulation Package
DFT     Density Functional Theory
LDA     Local Density Approximation
GGA     Generalized Gradient Approximation
TiO$_2$ Titanium Dioxide
PCE     Power Conversion Efficiency
MA      Methyl-Ammonium
PV      Photovoltaic
ETL     Electron Transport Layer
HTM     Hole Transport Material
FTO     Fluorine doped Tin Oxide
DOS     Density of states
DFT     Density Functional Theory
GGA     Generalized-Gradient Approximation
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CHAPTER 1 INTRODUCTION

Over the past few years, the world population has been going up on an average by 75 million per year now reaching to about 7 billion. The fact of increase in population is shown by US department of commerce. With this increase in population, there has been an increase in demand of all consumable resources. The industrial revolution began in the mid eighteenth century, changing human lives completely. This revolution boosted transportation and meanwhile the electrification of houses took place. In the 21st century we can now travel hundreds of miles in a few hours, connect with people thousands of miles away within seconds, change the temperature in a house according to comfort. To achieve this, the basic requirement is energy. We could successfully improve the technologies in this domain that consume fossil fuel. The fossil fuels currently being used are not just limited but cause climate change. After almost 150 years, scientists have realized the necessity of shifting the dependency from conventional to unconventional sources of energy. Unconventional sources can be solar energy, wind energy, geothermal energy etc. but solar and wind have grown because of their efficiency and feasibility over any other source of energy. As a clean source of energy, market of solar energy is wide. Since solar energy does not produce noise and utilizes less space as compared to any other renewable energy source, it is worth investing time in researching solar components to increase its efficiency.
The current photovoltaic solar cells are predominantly manufactured using crystalline silicon. In 2014, researchers at the University of New South Wales [1] [2], Australia claimed efficiency of greater than 25% for the crystalline silicon solar cells. This claim was supported by Panasonic (Japan) [3] and SunPower (USA) using silicon wafers [4]. The current problem with crystalline silicon solar cells is their expense and complication to fabricate. There are opportunities for other solar technologies if they can prove to give higher power conversion efficiencies or reduced manufacturing costs. Organic-inorganic perovskite solar cells seem to be promising in answering both challenges. In 2009, one showed efficiency of 3.8% [5] and it drastically increased to a confirmed efficiency of 22.1% [6]. The main reason behind researchers’ interest in perovskite solar cells are their rapid increase in power conversion efficiency within a brief period, simple assembly and low fabrication costs.

1.1 Thesis Aim

The main aim of this research is to understand the effect of moisture on hybrid perovskite, titanium dioxide (TiO$_2$), and in the interface of hybrid perovskite and (TiO$_2$). In this thesis, all results are produced using a computational approach. To obtain the initial structure, we will use reference literature for the basic coordinates. It will also help us understand the literature associated with perovskite humidity and Titanium oxide. Subsequently, we will optimize the structures using accurate ab initio approaches to ensure obtaining realistic interfaces.

In our research, we consider different settings for producing the results which will be elaborated upon explicitly. Here, minimum energy structures will be calculated for each
individual interface to find the stable structure. It is essential to identify a realistic interface to analyze the effect of humidity. To analyze this effect electrostatic potential and density of states are derived and utilized to assess the effects of humidity on photovoltaic performance of hybrid perovskite solar cells.

1.2 LITERATURE REVIEW

1.2.1 Overview

To work on a new idea, it is important to understand the relevant work performed by other researchers. This review will help us understand materials such as perovskite as well as the behavior of water with perovskite and Titanium oxide. Since the research mainly focuses on computer simulation, this survey will be discussing mainly the simulation aspect of the materials and interface.

1.2.2 PEROVSKITE

Perovskite as a solar cell material was first introduced by Kojima in 2009 [5]. The organic-inorganic hybrid perovskite compound is denoted with a chemical formula CH$_3$NH$_3$PbX$_3$ (X can be either Bromine, Chlorine or Iodine). In this thesis, discussion will be on the tetragonal structure of CH$_3$NH$_3$PbI$_3$ as it is preferred over others for this application, because of stability at room temperature and sensitivity to visible light frequencies. The properties that contribute in making a perovskite a favorable candidate for photovoltaics are its optical and excitonic properties and electrical conductivity [5]. The photoluminescence was checked before and after grinding organic-inorganic lead halide perovskite compound and it was found that photoluminescence of the material is strong.
after grinding [8]. This understanding led the thought of perovskite as a solar cell material. The perovskite material showed a strong band-gap adsorption despite being a semiconductor [9]. These properties provide staunch support for perovskite to be a potential material for solar cell applications [10] [11]. It is important to be able to visualize the perovskite structure to understand the material in detail. Schematics of a simple hybrid perovskite is depicted in Figure 1.1.

![Simple schematic diagram of CH₃NH₃PbI₃](image)

Figure 1.1 Simple schematic diagram of CH₃NH₃PbI₃ [12]

Chemical formula for representing hybrid perovskite is ABX₃. A is the positively charged organic cations (CH₃NH₃⁺) which is also denoted as Methyl-ammonium (MA), and B is lead (Pb) and X is the negatively charged halide anion which can be either chlorine, bromine or iodine (Cl⁻, Br⁻ or I⁻). The stability of perovskite depends on size of the lead (A) atom [13]. It can be clearly seen that the organic-inorganic molecules are not interconnected with chemical bonds. The forces that holds CH₃NH₃ together with the rest of perovskite structure are the van der Waals forces [14]. The shape of the perovskite
structure can change with respect to temperature between cubic, tetragonal and orthorhombic. The structure is cubic at elevated temperature and at around 327 K it tends to become tetragonal and when the temperature falls below 165 K it becomes orthorhombic [15] [16].

It is important to understand the formation of the tetragonal perovskite structure which can be used for solar cell applications. To understand this in detail, it is essential to be aware of its electronic properties of structure [17]. The model basically consists of 48 atoms as originally reported in the reference provided [16] [18] [19].

![Diagram of hybrid perovskite structures](image)

Figure 1.2 Hybrid perovskite structures from left to right: orthorhombic, tetragonal and cubic phases [17].

In Figure 1.2 the geometric parameters for tetragonal structure [18] are shown by dotted lines. In this structure “α” is the dihedral angle, “β” is the rotational angle, “γ” and “ω” are the apical and equatorial angle respectively.
In this thesis, to analyze the structure of the hybrid perovskite material, we first minimize the forces on the atoms to relax the structure. At minimum energy atoms tend to be stable giving the realistic structure. The settings that were implemented for relaxation of atoms are described in Chapter 2. To compute the forces and electronic structures, the Vienna Ab initio Simulation Package (VASP) [20] [21] software is used, which uses density functional theory (DFT) [22] [23] enhanced by inclusion of van der Waals forces for processing the results. For obtaining realistic results, the projector augmented wave approximation is also taken into consideration. Some of the basic settings that are used in VASP are (these terms are explained later in Chapter 2 of this report.): The energy convergence criterion is $10^{-7}$ eV per unit cell. The maximum allowed force on the atoms is $10^{-2}$ eV/Å. We use gamma-centered k-mesh of 3x3x2 for bulk calculations. The plane-wave energy cutoff is 400 eV. The structures are computed using both generalized gradient approximation (GGA) [24] PBE functional [25] as well as van der Waals’ correlation functional. Obtaining the correct structure is the first step in computational modeling of materials and this work focuses on this aspect at the beginning.

![Figure 1.3 Simple solar cell model](image)
Figure 1.3 gives a basic idea of the simple perovskite solar cell model. It constitutes of multiple layers and the perovskite layer is sandwiched between Hole Transporting Materials (HTM) and Electron Transporting Layer (ETL). It basically generates electron-hole pairs generated at interface due to sunlight. Gold layer is the metal contact, HTM is usually Spiro-OMeTAD [26]. In this research, ETL is TiO2 and is further discussed in detail.

**1.2.3 WATER ON PEROVSKITE**

The stability issue due to environmental condition is a significant aspect that is stopping the commercialization of perovskite solar cell. It is important to understand the effect of moisture on the perovskite surface to understand the penetration of water molecules in the surface at the interface. There are two surfaces to investigate the effect of moisture. One is the MAI (Methyl-ammonium(CH3NH3)-iodide) terminated surface and the other one is the PbI (lead-iodide) surface. Finding the minimum energy of water adsorption on these structures is essential to understand moisture effect.
Figure 1.4 water adsorption with lowest energy structure of water on the MAI and PbI terminated surface with different polarities [27].

In Figure 1.4, the researchers did not just consider different surfaces but also considered the effect of orientation of CH$_3$NH$_3$ molecules on the interface of water and perovskite. Dependence of adsorption energy on the polarities (which is either the CH$_3$ end or NH$_3^+$ end pointing towards the interface) plays a significant role.
Figure 1.5 MAI and PbI terminated surface with water adsorption sites [28]

Figure 1.5 shows a study performed with water on perovskite surface using computational approach. The perovskite slab consists of six layers, which is justified to be enough for performing this analysis. In this study, three different sites are considered on each (001) surface of perovskite. As shown in (a) and (b) in Figure 1.5 the bottom two layers are fixed, and top three layers are fully relaxed. The sites considered on the PbI terminated surface are: a) on top of Pb atom b) on top of I atom c) on top of hollow site. And similarly, sites considered for MAI surface are: a) on top of I atom b) on top of organic cation (MA) and on top of hollow cite. All these sites are shown by green dots in figure 1.5 (c) and (d).
After optimization, adsorption energies are found using the relation:

\[
\Delta E_{\text{ads}} = E_{(\text{total})} - E_{(\text{perovskite slab})} - E_{(\text{water molecule})}
\]

[28]

If the value of \( \Delta E_{\text{ads}} \) is negative it shows there is attraction and vice-a-versa.

According to the experimental results by Berhe et al. [45], moisture induces degradation which diminishes the power conversion efficiency of perovskite solar cell. Different hydrophobic monolayers, hole selecting materials, carbon electrodes [46] can prevent degradation of material. Experimentally it is proven that moisture has negative effect on the performance of perovskite solar cell [46]. The open circuit photovoltage and short circuit photocurrent decrease with the exposure time to moisture. As the moisture percentage increases, the efficiency decreases. With subsequent decrease of humidity percentage, the efficiency value remains at that lower value. This means that the deformation in the structure caused by water is permanent and even with reduction of moisture the efficiency does not improve [45].
1.2.4 TITANIUM DIOXIDE

The arrangement of atoms is simple. Lattice vectors are taken from the work of Baur [30] [31]. The values are \( a = 4.594\pm0.003 \) Å, \( c = 2.959\pm0.002 \) Å, \( c/a = 0.6441 \) and \( x = 0.306\pm0.001 \). This value of \( x \) is used while deciding the position of atoms. The initial position of two Titanium ions are \((0,0,0)\) and \((\frac{1}{2}, \frac{1}{2}, \frac{1}{2})\). Four oxygen atoms are at position \( \pm (x,x,0) \) and \( \pm (\frac{1}{2}+x, \frac{1}{2}-x, \frac{1}{2}) \).
There are two phases of titanium dioxide. One is anatase and the other phase is rutile. It is shown that the rutile surface has better lattice match with perovskite dimensions as compared to anatase, and larger charge transfer, making it a better choice [32]. TiO$_2$ is used as ETL which can also be referred as n-type semiconductor in the perovskite solar cell sandwich [5]. The structure design [29] for rutile TiO$_2$ is taken into consideration for initial input. This structure later is optimized within our ab initio framework.

Table 1: Interatomic distances and angles [29].

<table>
<thead>
<tr>
<th>Bond</th>
<th>Type</th>
<th>Number of bonds of its type per unit cell</th>
<th>(a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti−O</td>
<td>1</td>
<td>4</td>
<td>1.944±0.004 Å</td>
</tr>
<tr>
<td>Ti−O</td>
<td>2</td>
<td>2</td>
<td>1.988±0.006 Å</td>
</tr>
<tr>
<td>O−O</td>
<td>3</td>
<td>8</td>
<td>2.780±0.002 Å</td>
</tr>
<tr>
<td>O−O</td>
<td>4</td>
<td>2</td>
<td>2.520±0.012 Å</td>
</tr>
<tr>
<td>O−O</td>
<td>5</td>
<td>2</td>
<td>2.959±0.002 Å</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Angle</th>
<th>Bonds types</th>
<th>Number of angles of its type per unit cell</th>
<th>(b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O−Ti−O 1, 1 (smaller angle)</td>
<td>2</td>
<td>80.8°</td>
<td></td>
</tr>
<tr>
<td>O−Ti−O 1, 1 (greater angle)</td>
<td>2</td>
<td>99.2°</td>
<td></td>
</tr>
<tr>
<td>O−Ti−O 1, 2</td>
<td>8</td>
<td>90.0° (by symmetry)</td>
<td></td>
</tr>
</tbody>
</table>
1.2.5 WATER ON TiO$_2$

![Ab initio molecular dynamics simulation cell of the water/TiO$_2$ interface](image)

Figure 1.7 Ab initio molecular dynamics simulation cell of the water/TiO$_2$ interface [45].

A wide range of studies has been performed on the TiO$_2$ surface due to its application in the field of photovoltaics [33] [34] [35] [36]. To understand the effect of water on TiO$_2$ there are multiple approaches. The method explained by Predota et al. [36] is based on the force field approach [37]. The main purpose of this analysis is to understand the behavior and penetration of water on TiO$_2$ surface. In the study performed by Liu et al. on $<110>$ surface of rutile TiO$_2$ [45], they reported results by using density functional simulations of the interface between TiO$_2$ and water. The results show that with the amount of water they used on TiO$_2$ there is no water dissociation on the surface. These results provide good insight into the dynamics of solid liquid interface. In Liu et al.’s work [45], higher coverage of water is considered and the effect of multiple layers of water on solid titanium dioxide is studied. The results show that the interfacial water has inhomogeneous
dynamics. The study also reveals that the second layer of water also tends to reorient the first layer. In this interface the adsorption energies are calculated for individual atom and for interface and is subtracted to find the flow of energy. This helped in understanding the effect of water coverage and provided the data of initial bond lengths for this research. The reference data for the input structure are taken from the paper published by Predota [36].

1.2.6 PEROVSKITE AND TITANIUM DIOXIDE INTERFACE

The reason behind the interest in perovskite and titanium dioxide interface is the rapid increase in its efficiency of corresponding solar cell system. In 2009 Kojima used the similar interface and came up with 3.8% efficiency. According to the first principle study performed by Geng et al. the rutile (001) surface has been considered as the best choice because of its minimum lattice mismatch with CH$_3$NH$_3$PbI$_3$ [32] (Figure 1.8).

![Figure 1.8 Optimized interfaces between methyl-ammonium hybrid perovskite layers (MAI and PbI) and anatase (A) as well as rutile (R) phases of TiO$_2$: MAI/A (a), PbI/A (b), MAI/R (c), and PbI/R (d). [32]](image)
In Figure 1.8 “A” stands for anatase surface of TiO$_2$ and “R” stands for rutile surface of TiO$_2$. In Ref. [32] both terminations are considered for both phases of TiO$_2$. It can be observed from the perovskite structure that not all atoms are interconnected, which gives it the ability to deform to some extent without generating higher forces on specific atoms. For this reason, the cell parameters for the interface are considered are those of TiO$_2$. After calculating results such as electron localization function and charge density difference, and after comparing all the results the better interface for solar cell application can be identified. In the results mentioned above, the electron localization function (ELF) offers visualization of charge interaction between individual atoms in the valence shell [7].

In Figure 1.9, ELF the color scheme has a significance: The red color shows that the electrons are highly localized, green means electron-gas like feature, whereas the blue means no localization. The value of ELF lies between 0 to 1. The most desired region is
the one with electron-gas like region which technically means the surface has better charge transfer. According to Figure 1.9, from ELF it can be observed that PbI terminated surface has better charge transfer [32].

Figure 1.10 charge density and electrostatic potential for MAI/A (a), PbI/A (b), MAI/R (c), and PbI/R (d) interfaces [32].

In Figure 1.11, for all listed structures charge density and electrostatic potential are plotted. The charge density plot is the difference of charge density of interface and
individual materials. In the right there is electrostatic potential which is used to find electronic level positions. Due to the presence of chemical-potential difference, there is charge transfer from perovskite to TiO₂ generating electric field. To analyze the difference quantitatively the Bader charge is calculated which helps to distinguish between different interfaces. It is observed in the Geng’s results [32] that the direction of charge transfer remains same whereas the charge transfer in the rutile interface is more.

Since the potential difference is larger in rutile interface as compared to anatase the charge transfer in rutile is higher. In rutile structure after comparison between MAI and PbI terminated surfaces, it is observed that the potential drop is higher at PbI terminated surface than at MAI, in which case electrons are accumulated at TiO₂. This causes better electron-hole separation in the solar cells. All these results eventually helped us to consider rutile structure for our research.
CHAPTER 2 METHODOLOGY

2.1 BACKGROUND THEORY

2.1.1 COMPUTATIONAL MATERIAL SCIENCE [38]

Over the past few years, computers have become powerful enough to complete resource intensive calculations relatively efficient. Computational Material Science (CMS) allows us to understand the characteristics and properties of a material with the help of modelling and simulation. This approach gives the engineer an opportunity to analyze the properties and nature of material with different levels of accuracy. In CMS, it is possible to put constraints on the model to study a specific behavior of a material.

In this thesis, the computer program that is used is for producing all results is Vienna Ab Initio Simulation Package (VASP) [20] [21]. Using the first principles plane wave basis, where first principle modelling refers to solving of Schrödinger equation in the form of matrix. The basis function that is used is plane wave basis which is a method for periodic structure [39]. This program performs modeling at the atomic level to compute electronic structure and quantum mechanical molecular dynamics. This software solves the Schrödinger equation either using Density Functional Theory in which Kohn-Sham (KS) equation must be solved or using Hartree-Fock method which involves solving of Roothaan equations, or by the combination of DFT/Hartree-Fock method. All the necessary terms associated with VASP are explained below.
To perform quantum simulations, the most important equation in quantum mechanics is Schrödinger equation. This is used to understand the properties of sub-atomic and atomic particles, in particular electrons, which also act as a wave. The simplest form of Schrödinger equation is the time-independent form:

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

In this $\hat{H}$ is the Hamiltonian operator which shows the total energy of the system, $\psi$ is the wave function which is in stationary state and $E$ is the energy of the wave function. Understanding properties in quantum studies can be achieved by solving Schrödinger equation. Directly solving this equation is not an efficient task for large systems of practical interest, so multiple iterative approaches have been proposed and are currently being used.

To briefly explain the history of different iterative approaches, the method that was initially introduced was Thomas-Fermi Dirac theory (TFD) which is used to approximate the electronic structure using electronic density [40]. This approach gives an approximate error of about 10% after finding TFD energies, thus this approach is used for approximate estimates of atomic properties [40].

The successor of TFD is Hartree-Fock (HF) theory. Although this theory is more precise and useful than TFD, it has drawbacks. This theory underestimates the bond energies. To overcome this problem post HF approaches [40] were developed which produced results with high accuracy but were computationally expensive.

In 1964 and 1965 three researchers named Hohenberg, Kohn and Sham published two papers successively discussing Density Functional Theory (DFT), [22] [41] which is one of the iterative approaches to find the properties of electronic structure. According to the paper published in 1964 [22] the total density of electrons is used to calculate the energy
as well as determine the ground state properties of the system. This is achieved by solving Kohn-Sham (KS) equation.

One of the terms entering the KS equation is exchange-correlation ter that specifies the quantum interactions between electrons. To define the exchange correlation term depending on the electron density there are two widely used approximations, Local Density Approximation (LDA) [42] and Generalized Gradient Approximation (GGA) [25]. This term helps in finding the complete correlation and exchange of a system’s energy [20]. The LDA approach is straightforward. It assumes that the density of electron gas is the same everywhere, while in the case of GGA it considers the inhomogeneities of electron density.

Interactions between electrons and atomic ions are usually included using pseudopotentials. The reason behind approximating pseudopotential is essential to understand. The core electron wave function remains the same in any chemical environment. These core electrons can be replaced by “ultrasoft” pseudopotentials. The reason for an ultrasoft potentials is to make the wave function form smooth, which influences all electrons behavior even outside the core region. Pseudopotential can produce the effect of core electrons in any environment. Introducing this is computationally efficient [43].

To understand the concept of projector augmented wave functions (PAW), it is important to know the behavior of wave functions. The wave function is fairly smooth at the bonding region while near the nucleus it oscillates rapidly. This is a difficulty of electronic structure method that is resolved using the PAW method. In this method the wave functions are divided into parts, which are now considered as partial wave expansions around the sphere of the atom center and envelope function around the sphere. The PAW
method has accuracy comparable to the electronic structure method which is LDA based, and by using this approach an excellent quality molecular dynamics simulation can be obtained [44].

2.2 PROCEDURE

2.2.1 Summary

To obtain the stable interface of perovskite and TiO$_2$ in the presence of moisture we use a systematic approach. Here we explain the design of individual structures, their optimization, surface reconstruction, water Intercalation and the settings required to achieve all these in VASP. Previously in background theory section we briefly mentioned the approaches that are applied in the VASP software to conduct the optimization. To begin, the primary requirement is to have the coordinates for the input structure. The two main structures are perovskite [17] and TiO$_2$ [29] whose coordinates are procured from the supplementary information of the former reference and the information included in the latter, respectively. The data for designing unit cell structures is used in addition to other data necessary for VASP simulations.

There are basically four main input files and one additional file to trigger the VASP program. The four main input files include information about atomic positions, reciprocal lattice (k-space), pseudopotentials, and detailed settings. The additional input file includes information about van der Waals interactions.
Figure 2.1 Bulk structures of hybrid perovskite \((\text{CH}_3\text{NH}_3\text{PbI}_3)\) and titanium dioxide \((\text{TiO}_2)\) optimized in our research.

At the beginning, the perovskite and TiO\(_2\) structures are individually optimized. Figure 2.1 shows the optimized structures after procuring the initial data from the Refs. [17] [29]. The optimized structures have minimum energy. They can be used further by making it a bulk structures and reconstructing its surfaces. These structures give the platform to explore in detail the effect of water inside the interface of perovskite and TiO\(_2\) using simulation techniques.

The next step is to obtain the realistic surface that is used for studying the interface. Using the structure viewing software GaussView, the bulk structure of TiO\(_2\) and \(\text{CH}_3\text{NH}_3\text{PbI}_3\) are prepared. On each structure \((001)\) surface is reconstructed by choosing 2 unit cells for perovskite and 3 unit cells for TiO\(_2\) facing a vacuum layer within a supercell, and putting constraints on half of the atoms so that they don’t move during optimization. In 2x2x3 TiO\(_2\) slab, 1.5 unit-cell is fixed by using selective dynamics. In case of
A $\text{CH}_3\text{NH}_3\text{PbI}_3$ 1x1x2 slab is prepared where two surfaces are obtained. One surface is MAI terminated and the other one is PbI terminated. For both of these surfaces, individually selective dynamics is applied on four layers which is one unit-cell. These are then optimized to obtain reconstructed surfaces.

Before understanding the behavior of water molecule inside the interface of $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{TiO}_2$, it is essential to understand the effect of moisture on each of these optimized bulk surfaces such as MAI, PbI and $\text{TiO}_2$ obtained after applying selective dynamics. The water molecule is first arranged on $\text{TiO}_2$ surface. Bond lengths of water on $\text{TiO}_2$ surface are referred from the research work by Predota et al. [37]. One water molecule is arranged on a bulk surface in two separate ways [45]. This gives a platform to compare two arrangements of water on $\text{TiO}_2$ on the criterion of minimum energy. Likewise, water is arranged on MAI and PbI terminated surfaces in two separate ways respectively [27]. According to the research performed on perovskite with water [27] the polarity of $\text{CH}_3\text{NH}_3$ is also taken into consideration which is complex in its own way. This leaves us with two structures of MAI with water, two structures of PbI with water and two structures of $\text{TiO}_2$ with water.

The structures with minimum energy after the completion of optimization process are the more stable structures. These structures are later required in the stage where the water intercalation is performed.

The step after this is developing interface structures using optimized $\text{CH}_3\text{NH}_3\text{PbI}_3$ slab of 1x1x2 and $\text{TiO}_2$ slab of 2x2x3. The structures that are used for constructing interface are not initially surface reconstructed. It is important to make sure that there is 20 Å vacuum in $c$-direction to avoid the unphysical interactions. With this setting twelve interface
structures are prepared. These structures are individually distinct because of multiple criterions. Basically there are two sets of six structures one set of MAI interface and one set of PbI interface. These two sets are further divided in the sets of three, here in three structures TiO$_2$ slab is rotated by $90^\circ$ as compared to other three. Now each structure in a set of three is different because of the initial distance between perovskite and TiO$_2$ at the interface. This difference is 0.5 Å. After preparing all these interfaces, single point energy calculations (without optimization) are performed to obtain the energy of each structure. All these values of energies are put together in an Excel file against the change of distance in each set of three. So basically, in each set of three there is one reference interface and two other interfaces with $\pm$ 0.5 Å distance. Next, the difference of energies from reference structure with respect to change in distance is plotted. To find the difference in energies the relations used are:

1. $E_0 \Rightarrow \Delta E = 0$
2. $E_\varsigma \Rightarrow \Delta E = E_\varsigma - E_0$
3. $E_\varpi \Rightarrow \Delta E = E_\varpi - E_0$

Here $E_0$ is the energy value of reference interface. $E_\varsigma$ is the value of energy of interface with 0.5 Å distance smaller than the reference interface. $E_\varpi$ is the value of energy of interface with 0.5 Å distance larger than the reference interface. The energy values are fitted with a parabolic curve. The equation for the parabolic curve generated is quadratic: $F(x) = ax^2 + bx + c$ by differentiating this equation with respect to $x$ the minimum value for $x$ can be calculated which can be referred to $x_0$:

$$x_0 = -\frac{b}{2a}$$

Using this equation and with each set of three among 12 structures four new structures are developed with $x_0$ as their initial interface distance. These are: MAI and TiO$_2$. 

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90° rotated TiO$_2$ with MAI, PbI and TiO$_2$, 90° rotated TiO$_2$ with PbI. Further these four structures with new interface distances are optimized using selective dynamics. There are now two sets of structures with two interfaces (MAI and PbI) in each set. For MAI, the structure with minimum energy is chosen, and similarly for PbI. This leaves us with two optimized minimum energy structures one of each kind. These two structures can now be used as most stable interfaces for intercalation of water.

2.2.2 Insertion of water molecule into the optimized interfaces of perovskite and TiO$_2$

Step 1: Measure the difference between the Z co-ordinates of waters oxygen atom and the average Z co-ordinates of carbon, nitrogen and Iodine (for MAI surface or Pb and I atoms for PbI surface) in the lowest energy optimized water on perovskite.

Step 2: Repeat step 1 for optimized water on TiO$_2$ (Between Z co-ordinate of water oxygen and average Z co-ordinate of oxygen on TiO$_2$ surface).

Step 3: Add the results of step 1 and 2. This will be the approximate distance between perovskite and TiO$_2$ after water intercalation.

Step 4: Take the corresponding (MAI or PbI) minimum energy structure. Determine the difference between average Z co-ordinates of C, N and I for MAI and subtract from it the average of Z co-ordinates from oxygens on TiO$_2$ surface. This will be the approximate distance between TiO$_2$ and perovskite without water intercalation.

Step 5: Subtract the results of step 4 from step 3.

Step 6: Add the result of step 5 to increase the distance between optimized minimum energy corresponding interface of TiO$_2$ and perovskite such that there will be room for water intercalation. (There is no water yet).
Step 7: Insert one oxygen atom such that it will be closest to the orientation of oxygen from water on the corresponding perovskite surface. Add two hydrogen atoms to oxygen to make a water molecule and adjust the orientation of hydrogens such that they closely resembles water on corresponding perovskite. Considering that we have two minimum energy perovskite interfaces the aforementioned procedure in step 7 will give us two interface structures with intercalated water.

Step 8: Repeat step 7 but use the orientation of water from optimized orientation of water on TiO$_2$. Considering that we have two interfaces between TiO$_2$ and perovskite (MAI and PbI) the aforementioned in step 8 will give us two interface structures with intercalated water.

Step 9: Use the four interfaces structure with intercalated water for constrained optimization.

2.2.3 WATER INTERCALATION GEOMETRY

We want to have four interface structures with water intercalation two coming from MAI and two from PbI. For each interface there are two water geometries, one according to water optimization corresponding to perovskite surface and one corresponding to TiO$_2$ surface. The idea is that we increase the average interface distance such that a water molecule can be accommodated in accordance with surface reconstruction upon water adsorption. Then arrange water molecule at the interface such that it closely resembles the adsorbed geometries on individual surfaces.

There are three problems that arise during initial structure setting for water intercalation:

1. The unit cell of interface is in accordance to TiO$_2$ surface and not that perovskite.
2. Rotation of MA molecules upon different optimizations.

3. Surface reconstructions are different from individual surface to interface surface reconstruction.

Despite these problems we arranged water molecules at different interfaces as close as possible to the geometries individually optimized for different surfaces.

For PbI terminated interface, for example, we choose the result whose water molecule was initially set according to the water optimization on perovskite surface. This structure is energetically favored by 84 meV over the same interface whose water was initially set according to water optimization on TiO$_2$. We will continue the rest of the calculation with this minimum energy structure. The structure characteristic are as follows:

- Optimized interface distance before water intercalation = 2.59 Å
- Increase in distance with water intercalation = 1.51 Å

The next step is to decrease this distance and optimize the structure with water and compare energies at different interlayer distances. We decrease the distance in steps of 0.5 Å. To do that we moved the whole structure of perovskite and TiO$_2$ by 0.25 Å each while water is kept at the same position. And, by applying the selective dynamics two ends are fixed and the structure is optimized. After optimizing the structures three times, they are brought close to the original distance which was obtained without water intercalation. In these three steps, a plot is obtained with difference in minimum energies against distance from the reference structure. This plot is fitted with a parabolic curve that is described by a polynomial equation, which, when differentiated and equated to zero, gives a minimum energy value for distance with respect to the reference curve. This distance calculated is
set between slabs and is allowed to relax. In this way, from the scratch the structures are prepared and finally the effect of moisture is added in the interface.
CHAPTER 3 RESULTS AND DISCUSSION

3.1 Structure Optimization and Surface Reconstruction

The first and foremost step is to optimize the bulk structures using the structures given in references [32] [29] utilizing the settings explained in the previous chapter. The perovskite-structure unit cell has 48 atoms. The initial coordinates are those at 293K for tetragonal structure including van der Waals interactions [32]. Similarly, TiO$_2$ unit cell structure is prepared based on the coordinates included in reference [29] and is optimized using our settings. These optimized structures are used for subsequent modelling and simulations.

The purpose of surface reconstruction is to obtain the realistic surface that accounts for the boundary interface without crystal continuation. Surface reconstruction is achieved by using a supercell that contains two-unit cells of perovskite and a vacuum layer, and fixing one-unit cell while allowing the other unit cell of perovskite to optimize. The fixed unit cell represents the bulk part of the material whereas the optimizing unit cell represents boundary interface. Similarly, for TiO$_2$ we use a super cell containing three unit cells of TiO$_2$ plus a vacuum layer with 1.5 TiO$_2$ unit cells fixed and 1.5 TiO$_2$ unit cells optimizing. The surface reconstruction structures are presented in Figs 3.1, 3.2 and 3.3.
3.1.1 MAI surface of Perovskite as Interface

Figure 3.4 Two views, with second one rotated 90° with respect to the first, of bulk MAI layer (a,b), and of the reconstructed MAI interface at vacuum (c,d)

In Figure 3.1 one can observe that there are two-unit cells extended in c-direction. These two-unit cells include a total of eight layers of perovskite. Eight layers are considered thick enough to represent the surface as explained by Mosconi [12]. Figure 3.1 (a) and (b) are the two views of the same structure to clearly visualize the geometry of bulk structure without surface reconstruction. The (a) and (b) structure is fully relaxed bulk and the structure represented in (c) and (d) includes surface reconstruction. The PbI side is on the top and MAI side is in the bottom for all the structures in this figure. In Figure 3.1 (c) and (d) the unit cell size is larger because of the vacuum layer included. The vacuum is included
in c-direction to avoid the interaction between atoms in c-direction (it can happen if vacuum is not included since the structures are periodic). In Figure 3.1 one can compare (a,c) and (c,d) to observe the difference between bulk and surface reconstructed structures. In (c,d) structure the top four layers from PbI to MAI are fixed and the bottom four layers are allowed to relax. It can be clearly observed that the MA molecules reoriented, and both of the iodine atoms moved a little from their regular location, whereas the Pb atoms are less dislocated. If (b,d) views are compared one can tell that the bottom four layers tend to move towards negative b-axis after surface reconstruction. These structures show the significant effect of surface reconstruction clearly.

As explained by Hao et al. [28] in their research of perovskite with water on (001) surface, they just included six layers of perovskite which was considered sufficient to represent the properties of surface. They used three fixed layers out of their total six layers in case of MAI interface, which is less than our four fixed layers. Similarly, in this thesis half of the layers (one unit cell) away from the interface are fixed with selective dynamics. The super cell dimension used in this thesis for perovskite includes 20 Å of vacuum as compared to 15 Å mentioned for six layered structure by Hao et al.
3.1.2 PbI surface of Perovskite as Interface

Figure 3.5 Two views, with second one rotated 90° with respect to the first, of bulk PbI layer (a,b), and of the reconstructed PbI interface at vacuum (c,d)

Similar to what we explained for Figure 3.1, in Figure 3.2, PbI terminated surface is reconstructed since it can also form the interface. Figure 3.2 (c,d) represents surface optimized with selective dynamics that has a vacuum of 20 Å. Similar vacuum layer is used for all the structures which are surface reconstructed. In Figure 3.2 (c,d), the bottom four layers of structure are allowed to optimize while the top four layers are kept fixed. The surface reconstruction in Figure 3.2 is not as significant as in Figure 3.1. At MAI interface the dipole moments of MA cations cause a relatively significant movement compared to the initial orientation, as MA molecules are not connected with chemical bonds to the PbI
structure. These are minimum energy surfaces and at minimum energy the van der Waals forces play a significant role in holding the MA molecule in place.

3.1.3 Surface reconstruction of TiO$_2$ surface

![Diagram of TiO$_2$ surface reconstruction]

Figure 3.6 Two views, with second one rotated 90° with respect to the first, of bulk TiO$_2$ layer (a,b), and of the reconstructed TiO$_2$ (001) interface at vacuum (c,d)

For TiO$_2$, three layers facing the vacuum are reconstructed. These are 1.5 unit cells as shown in Figure 3.3 (c,d). However, in perovskite just one-unit cell is fixed. The TiO$_2$ structure is shown at the bottom of the vacuum and perovskite is shown at the top of the vacuum (Figures 3.1 and 3.2), as these depict the conventional view of the interface with light absorbing perovskite on top and electron collecting TiO$_2$ electrode at the bottom.
The TiO$_2$ 2x2x3 slab size is considered to match the surface area of perovskite structure in a-b plane. In Figure 3.3 (c,d), the structure is reconstructed. It is observed that the oxygen atoms are slightly shifted towards the vacuum which is not the case in bulk shown in Figure 3.3 (a,b). This slight shift of atoms is specified in the work published by Geng et al. [32]. Although this change is not very large, it is noticeable.

3.1.4 Surface Reconstruction of Perovskite with water

Before observing effect of water molecule within the interface, it is essential to determine its effect on the surface of the individual materials. It allows us to analyze the lattice elongation in the perpendicular direction in the presence of water, dissociation on the surface, and the degradation of material similar to previous studies [27] [28]. In Figure 3.4, the results of structure optimization of water adsorption on reconstructed MAI and PbI terminated surfaces are shown. These are the minimum-energy structures.
Figure 3.7 Two views if the most stable hybrid perovskite surfaces after water adsorption, with second one rotated 90° with respect to the first, of reconstructed MAI interface at vacuum (a,b), and of the reconstructed PbI interface at vacuum (c,d)

Two initial positions of water molecule on the MAI perovskite layer are chosen in accordance with Koocher et al. [27]. For the MAI terminated surface in Figure 3.4 (a,b), in one case water molecule is placed on the hollow site which is also considered by Hao et al. [28] and in the other case water molecule is placed on one iodine atom. After optimization of both structures the molecule on top of the hollow site showed the minimum energy for the structure. For performing this optimization, the MAI surface reconstructed structure from Figure 3.1 is used.
Similarly on PbI terminated surface, two initial structures are used for the optimizations depicted in Figure 3.4 (c,d): in one case water molecule is placed on the hollow site and in other case water molecule is placed on a Pb atom. After optimization of both the structures the water molecule on top of the Pb atom showed the minimum energy for the structure which is Figure 3.4 (c,d). The work performed by Koocher et al. [27] includes extensive study of water on perovskite surfaces with the effect of orientation of MA molecules.

The structures with minimum energy value after optimization of water on MAI and PbI layers are shown in Table 2 and in Figure 3.4.

<table>
<thead>
<tr>
<th>Structure Layer</th>
<th>Initial Position</th>
<th>Energy Values</th>
<th>Selection</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAI layer</td>
<td>hollow site</td>
<td>0.000 eV</td>
<td>Most stable</td>
</tr>
<tr>
<td>MAI layer</td>
<td>on I</td>
<td>0.023 eV</td>
<td></td>
</tr>
<tr>
<td>PbI layer</td>
<td>on Pb</td>
<td>0.000 eV</td>
<td>Most stable</td>
</tr>
<tr>
<td>PbI layer</td>
<td>hollow</td>
<td>0.365 eV</td>
<td></td>
</tr>
</tbody>
</table>

Table 2 Energy values of MAI and PbI layer with water
3.1.5 Surface Reconstruction of TiO$_2$ surface with water

![Diagram](image)

Figure 3.8 Two views, with second one rotated 90° with respect to the first, of TiO$_2$ slab reconstructed at vacuum with water adsorbed.

On TiO$_2$ surface water molecule is placed on two distinct positions. The initial bond length details are taken from the work by Predota et al. [37]. The structure with minimum energy value is used for understanding the effect of water adsorption on TiO$_2$ surface. In Figure 3.5 we present the minimum-energy optimized geometry of water molecule on TiO$_2$ surface reconstructed slab.
<table>
<thead>
<tr>
<th>Structure</th>
<th>Initial Position</th>
<th>Energy Values</th>
<th>Selection</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$ layer</td>
<td>position 1</td>
<td>0.000 eV</td>
<td>Most stable</td>
</tr>
<tr>
<td>TiO$_2$ layer</td>
<td>position 2</td>
<td>1.098 eV</td>
<td></td>
</tr>
</tbody>
</table>

Table 3 Energy values of TiO$_2$ structure with water

The effect of water adsorption on TiO$_2$ is as important as the effect of water adsorption on perovskite. For our simulations, one water molecule is placed on 2x2x3 slab of TiO$_2$. As TiO$_2$ is the electron transport electrode in the perovskite solar cell system, inclusion of water can cause the change in performance of the system in terms of efficiency or light absorbing capacity of solar cell. In this thesis, TiO$_2$ is considered as electron transport electrode therefore it is essential to understand the effect of water on it. We observe that water adsorption on TiO$_2$ cases less surface deformation as compared to water adsorption on hybrid perovskite. The reason is that TiO$_2$ is a much denser crystal compared to hybrid perovskite, and internal bonding in the former are stronger than those in the latter.
3.2 Interface Structures

3.2.1 Perovskite-TiO$_2$ interface without water

In Figure 3.6 the minimum energy structures for MAI and PbI interfaces with TiO$_2$ are shown. These structures are obtained from a parabolic fit of total energies at three different distances between the two surfaces. The interface is set 0.5 Å closer and 0.5 Å far from the initial position set for the interface based on typical interfacial atomic bond lengths. The difference of energy with respect to initial position energy is placed in a
tabular format against the value of displacement. From the parabolic fit curve a polynomial is obtained which is differentiated to find the equation for minimum energy distance. In this way, from twelve energy calculations at different interfacial distances, four minimum energy structures are obtained. Two for MAI and two for PbI, corresponding to two structures with 90º relative rotation of the perovskite structure parallel to the a-b plane. Table 4 includes the energy values of these four interfaces upon optimization. The minimum energy value for two MAI structures has a difference in of 3.264 eV which is significant. In case of the two PbI structures the difference of energies is 0.815eV. As the energy of the most stable PbI structure is less than that of most stable MAI structure by 2.004 eV, the PbI structure is chosen for understanding the effect of water intercalation inside interface since it has least energy which makes it the most stable interfacial structure overall.

<table>
<thead>
<tr>
<th>Rotation angle</th>
<th>Structure</th>
<th>Energy Values</th>
<th>Selection</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>MAI interface</td>
<td>2.004 eV</td>
<td>Most Stable MAI</td>
</tr>
<tr>
<td>90º</td>
<td>MAI interface</td>
<td>5.268 eV</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>PbI interface</td>
<td>0.815 eV</td>
<td></td>
</tr>
<tr>
<td>90º</td>
<td>PbI interface</td>
<td>0.000 eV</td>
<td>Most Stable PbI and</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>overall</td>
</tr>
</tbody>
</table>

Table 4 Energy values of hybrid perovskite-TiO₂ interfaces without water

The two final structures with minimum energy for each of MAI and PbI interfaces are shown in Figure 3.6. These structures can be compared with the work published by
Geng et al. [32]. These are basically the optimized stable structures with rutile TiO$_2$ and two surfaces (MAI and PbI) of perovskite. In this thesis, the optimized cell parameters of TiO$_2$ in a-b (horizontal) plane are used to build the supercell of the interface. The structures deform and there is a lattice mismatch. To understand the behavior of moment of electrons, electrostatic potential plot is useful and to understand the energy required to transfer the electron at the interface the density of plot is useful. These plots are derived in subsequent chapters for the interfacial structures depicted in Figure 3.6, as well as for the PbI interface including water intercalation.
3.2.2 Final minimum energy PbI interface structure with water intercalation.

Figure 3.10 Two views, with second one rotated 90° with respect to the first, of reconstructed PbI-TiO$_2$ interface with intercalated water (a,b)

In a previous study by Geng et al. [32], the interfaces with rutile TiO$_2$ and perovskite without water are studied, but in this thesis the focus is to understand the effect of moisture inside the interface. The procedure for obtaining this structure is mentioned in the computational procedure section explained above, and includes a parabolic fit to the energy versus distance curve to obtain the interfacial distance with minimum energy. Initial structures are prepared with water situated in accordance with optimized geometries on perovskite and TiO$_2$ (depicted in Figures 3.4 and 3.5). The result of water intercalation within the PbI interface is shown in Figure 3.7. In Figure 3.7 (a,b), it can be observed that
the PbI layer is severely deformed with the intercalation of water. This damage contributes to reducing the performance of the system when used as a solar cell. With introduction of one water molecule over one-unit cell there is degradation of the perovskite surface. The damage to the performance of the interface is studied in the next sections when the electrostatic potential plots are compared against the interface without water shown in Figure 3.6 (c,d).

This study of interface with moisture gives an in-depth knowledge of structures with respect to the change in properties of materials at the interface. In figure 3.7 (a,b), the introduction of water did not cause much deformation on TiO₂ whereas perovskite molded to adapt the foreign material which is water molecule. This change is shown to modify some of the internal characteristics of the interface structure and degrades the photovoltaic application, as explained in the next sections.
3.3 Electronic Properties of Interface and Effects of Water Intercalation

3.3.1 Electrostatic Potential for the MAI interface structure

Figure 3.11 Minimum (blue), maximum (black) and average (red) electrostatic potential of MAI-TiO$_2$ interface (a) and magnified average electrostatic potential for MAI-TiO$_2$ (b). Vacuum is at the left, TiO$_2$ is in the middle and perovskite is at the right of each graph.

Figure 3.8 is the plot for electrostatic potential of MAI-TiO$_2$ interface without water. On x-axis, the length of supercell including interface is shown (vacuum at the left) and on the y-axis the values of electrostatic potential are shown in electron-volts. Figure 3.8 (b) shows the magnified average of electrostatic potential for MAI-TiO$_2$ interface. In
this curve, average electrostatic potential of perovskite material is higher than TiO$_2$ which shows the flow of electron is from perovskite to TiO$_2$.

This result can be compared with the results produced by Geng et al. [32]. The variations are almost same and so are the curves. In case of MAI the potential drop between perovskite and TiO$_2$ is not significant (as compared to the PbI case explained in the next section). The potential values of perovskite are not too high but are higher than TiO$_2$. This causes potential difference and electrons flow from perovskite to TiO$_2$. If this potential drop is higher then there is more electron saturation on TiO$_2$ side with better electron-hole separation.
3.3.2 Electrostatic Potential for PbI interface structure without and with water

![Electrostatic Potential Graphs](image)

Figure 3.12 Minimum (blue), maximum (black) and average (red) electrostatic potential of PbI-TiO$_2$ interface without water (a) and with water (b). Vacuum is at the left, TiO$_2$ is in the middle and perovskite is at the right of each graph.

Figure 3.9 gives the overview of perovskite PbI-TiO$_2$ interface with and without water. The deflection in curve is significant and can be clearly observed from the graph in Figure 3.9 (a,b). The region of interface where water is located can be easily located by just looking at the plot.

Due to the introduction of water there is noticeable drop of potential values of perovskite layers at the interface. This drop caused by water reduces the flow of charge transfer. The drop in potential means drop in transfer of electrons. Thus humidity effect
reduces the amount of charge transfer. This can also be clearly observed in the average plots in Figure 3.10 (a,b).

### 3.3.3 Average electrostatic potential for PbI interface structure without and with water

![Graphs](image)

Figure 3.13 Magnified average electrostatic potential of PbI-TiO₂ interface without water (a) and PbI-TiO₂ interface with water (b). Vacuum is at the left, TiO₂ is in the middle and perovskite is at the right of each graph.

Figure 3.10 is the magnified version of the average electrostatic potential curves from Figure 3.9. In this plot only the averages of maximum and minimum curves are plotted. It can be observed from Figure 3.10 (a,b) that the overall electrostatic potential
value of the perovskite structure is lower in perovskite with water compared to perovskite without water. However, the electrostatic potential of TiO₂ is almost constant. Thus, the difference in electrostatic potential of perovskite and TiO₂ with water is lower and, therefore, there is reduction in the flow of charge compared to the case of interface without water. Thus, moisture adversely affects the photovoltaic performance of solar cell, and humidity effect should be eliminated for obtaining better performance of perovskite in solar cell application.

To describe the efficiency for a solar cell, the following relation can be used.

$$\eta = \frac{I_{sc}V_{oc}(FF)}{P_{input}} \times 100\% \ [47].$$

Here, $I_{sc}$ is the short circuit current, $V_{oc}$ is the open circuit voltage, $FF$ is the fill factor, and $P_{input}$ is the input light power. The input power for the structure with water and without water remains the same. There are several contributions to $V_{oc}$ corresponding to potential drop at all interfaces in the solar cell. What we studied here is just one of those interfaces. The average voltage difference between perovskite and TiO₂ without water is 1.749 eV whereas with water it is 1.555 eV. This suggests lowering of $V_{oc}$ by 0.194 eV. The total open circuit voltage cannot be determined within the scope of the current work, but the inclusion of the change in electrostatic potential drop at perovskite-TiO₂ interface after water adsorption reduces efficiency. The reduction in short circuit current because of the interfacial disorder caused by water intercalation further reduces efficiency.
3.3.4 Density of States

Figure 3.14 Density of states (DOS) of PbI-TiO₂ interface without water (a) and with water (b). Top of the valence band is at zero.

Density of states (DOS) provides another measure for assessing water intercalation effects on perovskite solar cell performance. Figure 3.11 shows that upon water intercalation, the band gap of interface increases. This means that the radiation frequency needed to excite charge carriers in the case with water is larger than that in the case without water. Water intercalation therefore can reduce the efficiency of carrier excitation by visible light, thereby reducing efficiency of photovoltaic performance.
CHAPTER 4 CONCLUSIONS

Hybrid organic-inorganic perovskite materials are excellent candidates for photovoltaic solar energy harvesting, owing to their high efficiency and relatively low cost. Their widespread usage, however, is diminished because of important limitations including stability under working conditions. Humidity is known to degrade these materials and reduce the efficiency of solar energy conversion. In order to understand details of water inclusion effects on solar cell performance, here we perform ab initio simulations on interfaces of hybrid perovskite lead-iodide material and TiO$_2$ electrode. Surface reconstructions and interface geometries are obtained in absence and presence of water, along with electronic structures (electrostatic potential and density of states).

Our results show that water intercalation at interface results in significant rearrangement of interface geometry. The corresponding electronic structure shows degradation of photovoltaic performance upon water intercalation. Specifically, the electrostatic potential difference between perovskite and electrode diminishes in presence of water, indicating less charge transfer between hybrid perovskite and electrode. Density of states shows increased gap in presence of water indicating less efficient carrier excitation in optical range of radiation. These results provide detailed insight into solar cell performance degradation in presence of water, and can be used for addressing this stability issue of hybrid perovskite solar cells.
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