First Principle Study of Nitrogen Fixation on Molybdenum Containing Semiconductor Surface with a Developed Machine Learning Approach

Alhassan S Yasin

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First Principle Study of Nitrogen Fixation on Molybdenum Containing Semiconductor Surface with a Developed Machine Learning Approach

Alhassan S. Yasin

Dissertation submitted to the Benjamin M. Statler College of Engineering and Mineral Resources at West Virginia University in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Mechanical Engineering

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Keywords: Density Functional Theory, First Principle Calculations, Nitrogen Fixation, Machine Learning, Neural Network, DFT, ML, NN, High-Throughput

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ABSTRACT

First Principle Study of Nitrogen Fixation on Molybdenum Containing Semiconductor Surface with a Developed Machine Learning Approach

Alhassan S. Yasin

The Haber-Bosch (HB) process is the main industrial method for converting atmospheric nitrogen (N\textsubscript{2}) to ammonia (NH\textsubscript{3}). In the HB process, hydrogen is typically derived from steam reforming natural gas, which results in a large quantity of greenhouse emissions and considerable environmental concern. In providing a sustainable solution, the following research investigates a semiconductor-based photocatalytic approach that emulates the biological nitrogen fixation (BNF) pathway. By emulating the biological process, the overall reaction energy, pressure, and temperature are significantly reduced. Moreover, this allows ammonia to be produced from atmospheric nitrogen at atmospheric pressures. To aid in material selection and to provide fundamental insight into the process, the following research leverages first principle calculations to predict both the light absorption properties and the thermodynamic reaction barriers of the associative (BNF) and dissociative (HB) reaction pathways.

A major limitation in the throughput of alloy-based Density Functional Theory (DFT) studies for large design spaces is the wall time required to find the optimal position of the minority ions. A novel method was developed that involves a machine learning approach to predict the minority ion positions prior to simulation. This lead to a significant decrease in computational wall time required to identify and solve the most stable minority configuration. By training the positions based on a select number of DFT cases, it was found that positions of other species could be predicted with mean square error (MSE) less than 1.6x10\textsuperscript{-2}. Moreover, it was found that the total energy for these configurations could also be predicted with MSE less than 2.3x10\textsuperscript{-7} relative to the subsequent DFT calculations.

In applying the developed techniques, two design spaces were investigated, (M\textsubscript{x}Bi\textsubscript{y})\textsubscript{2}MoO\textsubscript{6} (M = Fe, La, and Yb) and sulfur desorbed M\textsubscript{x}Mo\textsubscript{y}S\textsubscript{2} (M = Co and Fe). In the case of M\textsubscript{x}Mo\textsubscript{y}S\textsubscript{2}, phases with a higher concentration of Co and Fe elements resulted in a lower reaction barrier. More specifically, by incorporating Co and Fe into the structure, the affinity toward hydrogen species was exchanged with increased nitrogen affinity. In turn, the Fe containing 1T phase of Fe\textsubscript{0.25}Mo\textsubscript{0.75}S\textsubscript{2} for the dissociative pathway was predicted to have the lowest overall reaction barrier within the M\textsubscript{x}Mo\textsubscript{y}S\textsubscript{2} design space. In the case of (M\textsubscript{x}Bi\textsubscript{y})\textsubscript{2}MoO\textsubscript{6}, higher concentration of Fe and Yb resulted in an increase of the Mo-O bond length and improved nitrogen affinity. The best composition for this design space was predicted to be the orthorhombic phase of (Fe\textsubscript{0.25}Bi\textsubscript{0.75})\textsubscript{2}MoO\textsubscript{6} for the associative pathway with a reaction barrier of 1.4 eV.
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CHAPTER 1

INTRODUCTION

The flowing study looks at two distinct problems that may seem trivial at first, but ultimately define a large area of computational science. The first distinct problem that this study aims to understand and explore is nitrogen fixing materials. Nitrogen fixation is an essential process of converting nitrogen into ammonia. This study explores two distinct design spaces for nitrogen fixation, that is the bismuth containing \((M_xBi_y)_{2}MoO_6\) \((M = Fe, La, \text{and } Yb)\) and sulfur desorbed \(M_xMo_yS_2\) \((M = Co \text{ and } Fe)\), which shares many attributes with biological processes. However, the problem of exploring capable material systems for nitrogen fixation and or tailorability in large design based studies encompasses immense design analysis. Thus gives rise to the second distinct problem that this study aims to address, which is the cost for computational complexity required for these large design based studies. The proposed method for reducing the computational cost is to use a machine learning approach which provides a promising starting point for high-throughput structure predictions. With the developed machine learning approach further predictions are done that assisted this study to reduce computational expense in three ways, first by reducing the wall time required for DFT calculations, second by predicting the total energy for each unit cell, and third by predicting candidate ions for future nitrogen fixation studies. Thus the two distinct problems are expressed and looked at by the preceding chapters and sections.

1.1 Nitrogen Fixation

Biological development and adaptation on this planet is possible due to an essential processes of converting nitrogen into ammonia, referred to as nitrogen fixation. [2–5] This essential process allows the production of reduced forms of nitrogen that living organisms
require for sustainability. These organisms utilize the reduced forms of nitrogen to activate an enzyme-catalyzed process where substances are converted into more complex products for basic building blocks [2], referred to as biogenesis [4]. Nitrogen is one of the most abundant elements on Earth, dominantly as nitrogen gas (N\textsubscript{2}) in the atmosphere [6, 7]. However, this form of nitrogen needs to be reduced in order for meaningful utilization by living organisms, thus taking forms through: (i) ammonia (NH\textsubscript{3}) and/or nitrate (NO\textsubscript{3}\textsuperscript{-}) fertilizer [5, 8, 9], (ii) utilization of released compounds during organic matter decomposition [2, 4], (iii) the conversion of atmospheric nitrogen by natural processes, such as lightening [10], and (iv) biological nitrogen fixation (BNF) [2].

Semiconductor photocatalysts have had much increase in attention due to the growing concerns with the environmental pollution and energy shortage. These photocatalysts prove to have applications in solar energy conversion and photo-oxidation of organic pollutants [11], key features of promising semiconductors are high reactivity, low cost, electrochemical stability, and environmental friendly applications. This is why much effort is put into exploring active oxide photocatalysts for visible sunlight harvesting like many binary, metal oxide, and ternary photocatalysts that show intense visible light absorption and high activity such as the reported materials of SrTiO\textsubscript{3}, ZrO\textsubscript{2}, BaTi\textsubscript{4}O\textsubscript{9}, bismuth oxides, etc. [11]. The aim of this study is to demonstrate key properties that characterize BNF processes for molybdenum containing photocatalysts. The following study combines the contribution of the latter process with recent advances in the inorganic synthesis of photocatalytic surfaces. More specifically, this study will focus the exploration of a computational design space of two material systems the bismuth containing (MBi)\textsubscript{2}MoO\textsubscript{6} (M = Yb, Fe, La) and sulfur desorbed MMoS\textsubscript{2} (M = Mo, Fe, Co), which shares many attributes with the BNF process.

First structure system, the MoS\textsubscript{2} based sulfur desorbed system tends to decrease the coordination of the Mo sites, which in contrast to the desorption of sulfur atoms the surface would lack affinity for nitrogen species. Experimentally, the desorption of sulfur has been achieved during ultra-high vacuum (UHV) annealing [12] of this transition metal
dichalcogenides (TMD). TMD or TMDC share similar properties to graphene, which makes it an advantageous photocatalyst [13]. From a morphology perspective TMDs form two-dimensional structures, similar to graphene [13, 14]. However, differences are realized when expressing TMDs and graphene’s electronic properties. A commonly studied TMD and the focus of this study is a Molybdenite TMD, which is commonly referred to as MoS$_2$ monolayers. The optical band gap properties for MoS$_2$ range from 1.2 eV to 1.8 eV depending on the monolayer environment [15–17]. There are several experimental approaches to achieving the monolayer phase that include both mechanical and chemical exfoliation. It was found that during chemical exfoliation and a post anneal phase at UHV [12] that sulfur desorption is realized and sulfur vacancies are formed. With this experimental method being known, the approach taken is to study the photocatalytic properties of a desorbed MoS$_2$ monolayer.

Second structure system, the Bi$_2$MoO$_6$ based system, which have attained much attention due to the up-shifted valence band and a narrow band gap of 2.63 eV [18] that has the ability to utilize more sunlight. This small band gap is a result of hybridization between Bi 6s and O 2p states [11], and this hybridization makes the valence band more disperse which allows more easily transited photogenerated holes in the valence band. The system of interest for this study is based on Bi$_2$MoO$_6$ of an orthorhombic crystal structure and its counterpart Bi$_3$FeMo$_2$O$_{12}$ of a monoclinic crystal structure with substitution of Bi and Fe sites with combinations of Fe, La, and Yb.

1.1.1 Outline for Nitrogen Fixation

This study aims to calculate and present the reaction steps of nitrogen reduction for systems of (M$_x$Bi$_y$)$_2$MoO$_6$ (M = Fe, La, and Yb) and sulfur desorbed M$_x$Mo$_y$S$_2$ (M = Co and Fe), and to understand the workings of these structures for a viable source of self sustainable nitrogen reduction reactions. This will be done by identifying and exploring compositional design space of MoS$_2$ and Bi$_2$MoO$_6$ based structures by leveraging first principle density functional theory (DFT) calculations. This tool (DFT) does prove most beneficial from a
theoretical standpoint, because complex structures can be configured and analyzed within a fraction of the time and cost compared to experimental viewpoint. DFT calculations are no means of recording exact results, they are primarily used to see the trend and or pattern in the data.

This is why our group aims to explore design space for the expressed structures (MoS$_2$ and Bi$_2$MoO$_6$ based structures) for nitrogen fixation. This will allow us to record relevant information for molybdenum based structures regarding nitrogen fixation, by investigating the thermodynamics reaction barriers on inorganic photocatalytic surfaces. This investigation will primarily focus on Heyrovsky type reactions along both the associative and dissociative pathways, reference associative and dissociative pathways in Section 3.1.4. Most of the information regarding these pathways for MoS$_2$ based structures is demonstrated in results sections of Chapter 5 and Bi$_2$MoO$_6$ in Chapter 6, where key insight on roles taken by the substitution of Mo, Fe, Co in MoS$_2$ and Fe, La, Yb in Bi$_2$MoO$_6$ structures and the precise balance between nitrogen and hydrogen affinity on the respected surfaces. This provides evidence for minimizing the required over-potential needed to carry the nitrogen fixation reaction steps. This work focuses on nitrogen fixation of MMoS$_2$ (M = Mo, Fe, Co) and (MBi)$_2$MoO$_6$ (M = Yb, Fe, La) structures, information included in the background and theory sections are used to further gain insight.

1.2 Machine Learning Approach

Advancements have been made for first-principle material modeling and simulation techniques in response to modern day environmental prediction and protection, new chemical production, new applications, faster information processing, and a demand for sustainable and effective use of resources. Modern materials look to exhibit very non-novel properties such as rapid phase response to external stimuli like pressure, light, magnetic field, so that meaningful uses are possible in modern day or can be expected in the near future. These modern materials (magnetic, ferroelectric, superconducting) are often multicomponent systems.
such as but not limited to high temperature superconductors, magnetic tunnel-junctions, and perovskite materials with complex magnetic structures [19]. The underlying principle cohered with for these first-principle methods is that the parameters of the formulated theory are fixed by the basic assumptions and equations of quantum mechanics.

During the past two decades first-principle calculations based on density-functional theory (DFT) [20] in the generalized gradient approximation (GGA) [21–23] or the local density approximation (LDA) unfolded as a successful approach to solve the electronic structure of matter [19]. DFT is a widely used electronic structure method implement to assist in understanding a wide range of material properties. The theory is able to reduce the many body Schrödinger equation to an effective single electron problem by relying on Hohenberg-Kohn theorem [24] and Kohn-Sham method [20], thus making material property predictions computationally feasible [25]. The profound success of DFT for describing ground-state properties for vast classes of materials such as semiconductors, insulators, half metals, semimetals, transition metals, etc., at the nanostructure scale makes it one of the most used method for modern electronic structure analyses [19]. It’s noted that the goal of these calculations is to gain insight on a well defined model so that studies can find and predict trends that can better assist in developing different levels of understanding for any system in question [19].

Due to the extreme computational costs of most theoretical studies, limitations can and do arise when using approximation methods because accuracy is compromised in exchange for speed up time [26]. One of the most challenging aspects in modern theoretical calculations is to develop and apply an approximation method that expedite first-principle calculations speed up time without the loss of accuracy. Methods such as fragmenting the system [27], construction of empirical potentials, corrections through statistical methods [28], linear scaling [29], or semi-emperical methods have been applied to attain accurate first-principle calculations that are still computationally effective [26, 28]. In the case of semi-emperical tight binding approximations to DFT, the time expense is reduced by treating the Hamiltonian elements as parameters adjusted for the desired properties of the system.
such as band gap, effective mass, etc, also semi-emperical tight binding to DFT simplifies
the Hamiltonian to nearest neighbor interactions among atoms [30]. Introduction of the ex-
change and correlation functionals allowed DFT to improve cost even further when compared
to high level first principle methods like MP2 and CI, with very similar level of accuracy [28].
However, even the fastest DFT techniques, such as O(N) approach that is based on Local
Orbitals, use up most of the computational time to iteratively formulate the Hamiltonian
and solve self consistently for the ground state electron eigenstates [30]. Thus relies heavily
on the initial state of the system, the closer the final state of the system is to the initial state
specified as the input, the less iterations spent formulating the Hamiltonian and solving self
consistently the ground state.

1.2.1 Outline for Machine Learning Approach

The reader should note that each molecule is unique and thus to explore different
configurations, tailor or substitute various atoms into a structure, will only increase the
computational cost. This is not to say one can avoid computational cost but in practical-
ity greatly reduce it if the initial state of the system being explored is not just referenced
based on some configuration but slightly refined based on the referenced configurations and
based on what is being tailored or substituted. Thus exploring new configurations can be
more computationally feasible, especially in a time sensitive world where industry applica-
tions relies heavily on a number of material systems such as geometries, boundary conditions
need, and so on to be evaluated quickly and effectively to meet with the growing demand
for production and application. Machine learning approaches have demonstrated viable so-
lutions in attaining various forms of interacting and non-interacting atomistic potential by
utilizing regression algorithms in resent years [26]. Variety of applications such as chemistry
and physics have successfully applied machine learning methods to predict reaction path-
ways [31], formation energies [32], excited energy states [33], atomic forces and resonance
chemical shifts, etc., to assist in searching and classifying material systems [26]. Also, com-
putational material science has had several advancements made in applying various machine learning techniques such as predictions of DFT functionals [34], mapping of spacial atomic data for predicting total energies [35], and computation of electronic properties [36] in recent years. Thus machine learning express potential to predict molecular interactions with accuracy and reduction of computational cost.

To address the issue of computational expense, this study proposes a machine learning based method to predict positions of atoms (vectors that represent each atom) and the total ground state energy for each structure (unit cell). The predicted atomic positions that make up the unit cell and energy is then compared to that of the predicted DFT calculations. Note that this is predicting the fractional coordinates for each atom that makes up one primitive unit cell and the respected lattice constants. The machine learning model uses training sets based on DFT simulations done for various structures. This study focuses on bismuth-based photocatalysts (Bi$_2$MoO$_6$) in the orthorhombic configuration (Figure 4.1) and predictions made are validated with DFT calculations for configurations of (Bi$_x$M$_y$)$_2$MoO$_6$ where (M = La, Yb). However, this method is independent of material system and depends only on referenced DFT simulations for a specific structure. The aim of this study is to predict fractional coordinates and the total ground state energy for a bismuth-based photocatalysts (Bi$_2$MoO$_6$) by taking already attained DFT calculations for (Bi$_x$La$_y$)$_2$MoO$_6$ configurations as the training set to a neural network and then predict the ground state energy and the fractional coordinate vectors with respect to the DFT calculations for (Bi$_x$Yb$_y$)$_2$MoO$_6$ in the orthorhombic configuration. By using the training set, a much better approximation of the initial state of the system can be attained which reduces the effective iterative steps taken in the DFT calculations to solve self consistently the ground state.

1.3 Semiconductor Physics

This section is an overview of semiconductor physics that will better assist further discussions in this study and is introduced in this section. Typically semiconductors have
Figure 1.1 Bands and gaps in semiconductors. Evolution from looking at single atom with a potential to utilizing blocks theory for many electron in crystal. Then expressing the band gap energy form conduction band to valence band.

arranged atoms in a crystal lattice that contain tetrahedral bonded atoms (one atom located at center of four substituents that are located at corners of tetrahedron), allowing only certain bands of allowed energies that is separated by forbidden gaps [37]. The band gap is
just the difference between highest filled band, valence band, to the lowest unoccupied band, conduction band.

Dopants typically are atoms that have energy levels close to the conduction band (donors) or the valence band (acceptors) edge. Dopants contribute donors (electrons) and acceptors (holes, which are the absence of an electron in a particular place in an atom) bounded by parent atoms at low temperatures [38] However, at room and or higher temperatures, holes and electrons may have sufficient energy to escape the bound state of the parent dopant, thus allowing them to move freely through the crystal. Also, if a potential difference is applied across the semiconductor, exited electrons and holes will move in opposite direction with respect to each other [39], thus also becoming freely moving. Information regarding the movement of these freely mobile charges is what transport theory aims to understand.

These freely moving particles experience variations of Coulombic potential due to the present atoms in the crystal as shown in Figure 1.1. However, this is somewhat complex problem to solve, because semiconductors are not perfect crystals that have periodic in nature potential variations. Thus bringing about Blocks theorem which provides a simple solution, it turns out that in a perfect crystal, one can remove the periodic potential and express it as electrons effective mass.[37] This allows the fluctuating Coulombic potential to be reduced to electron in free space with a different mass [39]. By doing this one can solve the problem for the electron, taking into account the periodicity of a crystal structure, thus yielding the band structure of the semiconductor that allows information such as location of Brillouin Zone, the overall band structure, the simplified band structure around conduction band minimum and valence band maximum, etc., this band structure contains all the quantum mechanical states an electron can have in a semiconductor.[37]
CHAPTER 2

BACKGROUND & LITERATURE REVIEW

2.1 Biological Nitrogen Fixation (BNF)

Biological nitrogen fixation (BNF) process occurs naturally due to nitrogen-fixing bacteria in the soil, these bacteria are affiliated with specific groups of plants that utilize living organisms called prokaryotes. These organisms are very reliant on the enzyme nitrogenases [40, 2], which are enzymes that can be produced by certain bacteria, and are responsible for the reduction of nitrogen to ammonia. The nitrogen molecule, more specifically the dominant form of nitrogen on this planet is N\textsubscript{2} gas, which is comprised of two nitrogen atoms joined by a triple covalent bond, making the molecule highly inert [6, 7] and nonreactive. Microorganisms that fix nitrogen (nitrogenases) require 16 moles of adenosine triphosphate (ATP) to reduce each mole of nitrogen (approximately 5 eV) [41]. Typically the reduction of atmospheric nitrogen by nitrogenases occurs by initially weakening the N-N bond by successive protonation until the dissociation barrier is low enough that the N-N bond breaks (later in the reaction sequence) [1]. This barrier to overcome is referred to as the positive determinant step which requires the most energy to precede the reaction. This particular reaction sequence is referred to as the associative mechanism, and the energy required by the microorganisms to reduce nitrogen is obtained by oxidizing surrounding organic molecules. In other words, microorganisms that are non-photosynthetic must obtain this energy from other organisms, while photosynthetic capable microorganisms use sugars produced by photosynthesis to obtain the essential energy to oxidize other organic molecules [41, 42].

The active site in the nitrogenase enzyme is a cluster of FeMo\textsubscript{7}S\textsubscript{9}N, the FeMo-cofactor,
with an electrochemical reaction,

$$N_2 + 8(H^+ + e^-) \rightarrow 2NH_3 + H_2.$$  \hspace{1cm} (2.1)

These clusters have shown great stability in various configurations and sustainability in natural environments. Thus, most synthetically researched nitrogen fixation processes of transition metal configurations are based in some variation to molybdenum (Mo) structures.

A key insight into the nitrogen fixation process has been realized through several studies over the years on the biological nitrogen fixation processes. First, it was determined that nitrogenase of the BNF process is a two component system \([43–45]\) comprised of MoFe protein and the electron transfer Fe protein \([46–48]\). Second, a reducing source and MgATP are needed for catalysis \([49–52]\) and that the Fe protein and MoFe protein associate and dissociate in a catalytic cycle involving single electron transfer and MgATP hydrolysis \([47, 2]\). Third, the MoFe protein contains two metal clusters, the iron-molybdenum cofactor (FeMo-co) \([53, 54]\), which provides an active site for substrate binding and reduction, and P-cluster (which involves the electron transfer from the Fe protein to FeMo-co) \([55–58]\). Simply, the Fe protein is comprised of sub-units that contains one Fe\(_4\)S\(_4\) cluster that functions to transfer electrons from a reducing agent to the MoFe protein, which then transfers the electrons to the FeMo cofactors. Then, each FeMo cofactor acts as a site for nitrogen fixation that allows N-N to bind in the central cavity of the cofactor. Fourth, crystallographic structure are important for both Fe and MoFe proteins, this allows more localized minimum energy stability sites. \([59, 56, 60–62]\) These catalytic advancements have greatly assisted in the reduction of reaction pressure and temperature of the Haber-Bosch Process. However, no significant energy consumption reduction has been shown, thus yielding the catalytic mechanism to remain elusive and incomplete.
2.2 Haber-Bosch Process

The most known method of synthetically producing ammonia in large quantities for the modern world is through the utilization and production of the Haber-Bosch process [10, 2]. Fundamentally this process reduces nitrogen the same way as natural biological systems [63], but with a required energy substantially greater than that of biological processes. The way this process converts atmospheric nitrogen (N$_2$) to ammonia (NH$_3$) is by successive reactions of nitrogen gas with hydrogen gas (H$_2$), coupled with metal catalysts (usually an iron based catalyst). However, this synthetic process requires large amounts of energy and utilization of hydrogen, which is typically obtained by processing natural gas in large quantities that cause carbon dioxide emission (CO$_2$) [63, 2].

This reaction of nitrogen and hydrogen gas takes place under high temperature and pressure [64, 65], where some excess energy can be recovered and used to continue the manufacturing process, this is referred to as recuperation. During the process N and H gas molecules are heated to approximately 400 to 450 °C, while continuously being kept at a pressure of 150 to 200 atm [64]. At this point of the manufacturing process it is necessary to remove as much of the surrounding oxygen as possible prior to the exposure of gases to the catalyst to avoid catalytic oxidation. After the oxygen removing step is done, the dissociated nitrogen and hydrogen mixture is passed over a Fe-based catalyst to form ammonia as shown in Figure 2.1.

\[
N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \tag{2.2}
\]

Contrary to biological nitrogen fixation where the N$_2$ bond is broken late in the reaction sequence after initially weakening the bond by successive protonation, the Haber-Bosch process initially dissociates the N$_2$ bond on the first step and then protonates each nitrogen atom, referred to as the dissociative mechanism [1]. Nitrogen and hydrogen atoms do not react until the strong N$_2$ triple bond and H$_2$ bond have been broken [66] for the dissociative mechanism. Even though this reaction is reversible and an exothermic process, relatively high
temperature and pressure is needed still to allow the reaction evolve quickly [67]. However, this high temperature shifts the equilibrium point towards the reactants side thus resulting in lower conversion of ammonia [66, 1]. To correct for reactants equilibrium shift, external energy is thus needed to shift the equilibrium in favor of the reactions products [66].

Present day agricultural currently depends upon the Haber-Bosch to produce commercial fertilizer needed to grow most of the world crops. However, this synthetic process requires hydrogen utilization which is typically obtained by processing natural gas, which is energy intensive and causes carbon dioxide emission (CO₂) [63, 2]. Moreover, due to excess,
these chemical fertilizers have led to an upset in the nitrogen cycle and therefore pollution to surface water and groundwater as well. Excess load of nitrogen fertilizer to freshwater, as well as various ecosystem, has led to eutrophication (the process where excessive fertilizers run into lakes and rivers).[68]

2.2.1 History of Haber-Bosch Process

For the past couple of centuries, the staple of most human diet’s are that of cereal crops (corn, grain, rice, ect.), thus provoking farmers to develop and adapt more successful ways to grow and farm these crops to support the growing population. With time, farmers eventually realized that fields needed periods of rest between planting and harvesting to recover all the nutrients and minerals lost in the process of farming. Farmers eventually found that planting other crops, such as legumes, after harvesting will result in better cereal crops. Later it was found that the crops that proved to better restore the fields added nitrogen to the soil. By the industrial period, human population had grown exponentially, as a result grain production needed to increase, thus resulting in farmers exploration for ways to add nitrogen to their soil to make more productive crops [69], by utilized manure, guano, and nitrate from fossil bones.

Chemists in early 1900’s, began to explore and develop fertilizers by artificially inducing nitrogen fixation the same way as the roots do in legumes. By 1909, German chemist Fritz Haber was able to successfully fix atmospheric nitrogen by producing a continuous flow of liquid ammonia by mixing hydrogen and nitrogen gases that flowed into a hot, pressurized iron based tube over osmium metal catalyst [70]. This accomplishment presented military, industrial, agricultural benefits, and within five years a research team led by Carl Bosch from BASF, German chemical company, developed and worked to industrialize ammonia synthesis for world-wide scale utilization, thus referring to this process as the Haber-Bosch process. With the success of this process in 1910, Haber and Bosch were respectfully awarded Nobel prizes in 1918 and 1931 for the work done in surpassing the chemical and engineering issues
faced for large scale utilization of nitrogen fixation.

The prolonging of WWI was due to this process, which provided the necessary gun-
powder and explosives for war efforts. During this time, ammonia extraction cost was at an
all-time low because of the inexhaustible source of atmospheric nitrogen, which allowed the
contribution of developmental agriculture with high levels of input and output per unit of
agricultural land area. Thus allowed the continuous support for the worldwide population
influx at the time. During WWII, industrialization of Haber-Bosch process greatly benefited
from the Bergius process (method to produce liquid hydrocarbons for synthetic fuels), which
allowed areas to access synthesized fuels thus decreasing imported oil.

2.3 Material for Nitrogen Fixation

Even with the well-established Haber-Bosch process which has been the major artifi-
cial way to fertilize the earth, the intensive energy consumption of this process has motivated
many researchers to learn from nitrogenase, what can fix atmospheric nitrogen to ammonia
under mild conditions with precisely arranged proteins. Some studies indicate that efficient
fixation of nitrogen can be proceeded; for example, at room temperature and atmospheric
pressure, BiOBr nanosheets can reduce nitrogen by utilizing water using visible light illumi-
native BiOBr nanosheets of oxygen vacancies in the absence of organic scavengers with fine
metal cocatalysts.[71–73] The designed catalytic oxygen vacancies of BiOBr nanosheets have
the ability to activate the adsorbed nitrogen by interfacial electron transfer from excited
BiOBr nanosheets which can thus efficiently reduce to ammonia.[71, 73] These nanosheets
allow tunable exposing proportion of (0 1 0) facets, due to different n-alcohols in use by the
synthesis process, this also allows the modulation of size and thickness of BiOBr nanosheets
in a wide range.[71, 72] Also, these nanosheets demonstrated efficient photodegradation
activity on salicylic acid (SA) and rhodamine B(RhB).[72, 73] This great photocatalytic ac-
tivity was due to thin lamellar thickness and the exposure of (0 1 0) facets, this allows the
facilitation of photo-induced holes and electrons separation.[72, 73]
Another group reports a carbon-tungstic-acid (\(\text{WO}_3\text{H}_2\text{O}\)) hybrid for co-optimization of nitrogen activation as well as subsequent photo-induced protonation.\[74, 75\] In this study effective ammonia evolution reached 205 mol/gh under simulated sunlight, which demonstrates efficient solar driven nitrogen fixation over \(\text{WO}_3\text{H}_2\text{O}\) hybrid.\[74, 75\] The photo-activated material allowed the supply of protons and electrons for continuous protonation to the system \(\ni \text{(WO}_3\text{H}_2\text{O})\).\[74\] Photo-reduction of nitrogen proves to be a most interesting and challenging method for nitrogen fixation. Allot of these studies try to free nitrogen fixation processes from interference by outside gases to element any external source to the system. One such study determined that nitrogen vacancies (NVs) could endow a graphitic carbon nitride (g-C\(_3\)N\(_3\)), thus allowing the photocatalytic nitrogen fixation induced by NVs to not be subjected to these interfering gases.\[76\] The idea is that NVs have the same shape and size as nitrogen atom and thus can selectively adsorb an active nitrogen.\[76\]

It is noted that the proteins in the BNF contain two distinct sub-units with different active sites with the primary nitrogen site being FeMoS core cluster that is reduced by neighboring iron-sulfur clusters.\[77\] Based on nitrogen site being FeMoS cluster, studies have demonstrated chalcogels containing this inorganic cluster (FeMoS) to be capable of photochemical reduction of nitrogen. Reported for chalcogels containing FeMoS cluster, under white light irradiation, in aqueous media, under ambient pressure and room temperature are photochemical reduction of nitrogen.\[77\] The chalcogels are composed of \((\text{Mo}_2\text{Fe}_6\text{S}_8\text{(SPh)}_3)^{3+}\) and \((\text{Sn}_2\text{S}_6)^{4-}\) clusters in solution and demonstrate good aqueous stability, high surface area, and strong optical absorption that results in a light-driven nitrogen conversion by MoFe sulfides that has implications in solar energy utilization.\[77\] Evidently, chalcogels of \((\text{Mo}_2\text{Fe}_6\text{S}_8\text{(SPh)}_3)^{3+}\) don’t require Mo itself to carry nitrogen conversion process and this was observed experimentally\[78\] under illumination of the structure with in situ diffuse-reflectance Fourier transform infrared spectroscopy (DRIFTS). Also, demonstrated by this group was a Mo-free chalcogels containing Fe\(_4\)S\(_4\) clusters accomplish nitrogen fixation with even higher efficiency then \((\text{Mo}_2\text{Fe}_6\text{S}_8\text{(SPh)}_3)^{3+}\)[78] and also that DFT electronic
structure calculations suggest that nitrogen binding is thermodynamically more favorable with the reduced active cluster (Fe4S4).[78]

### 2.3.1 Candidate Materials for Nitrogen Fixation

Bi$_2$MoO$_6$ structure is feasible compound for nitrogen fixation [11, 79, 80, 18], with a shifted valence band and smaller band gap resulted from hybridization between Bi 6s and O 2p states make bismuth-based material attract attention. This is because hybridization makes the valence band more disperse, which can benefit the transportation of photogenerated holes in the valence band. Bi$_2$MoO$_6$ has been identified as a promising photocatalytic material due to Aurivillius layered structure comprised of the MoO$_6$ octahedron and Bi-O-Bi layers as shown in Figure 2.3A.[11, 18] Experimental observations have approximated the band gap of Bi$_2$MoO$_6$ to 2.56-2.63 eV, [11, 79, 80, 18] with unique physical and chemical properties, such as environmentally friendly, chemical inertness and photo-stability features, making them ideal photocatalytic materials.

![Figure 2.2](image)

**Figure 2.2** Powder X-ray diffraction (XRD) pattern and SEM image for the conventional Bi$_2$MoO$_6$ catalyst.[80]
Figure 2.3 Illustration of the Bi$_2$MoO$_6$ (A) and La$_2$MoO$_6$ (B) unit-cell structure. Reference Figure 3.4 for unit-cell in orthorhombic and monoclinic configurations.

It was reported that Bi$_2$MoO$_6$ structure possesses intrinsic activation ability for nitrogen-splitting.[80] The edge exposed coordinatively unsaturated Mo atoms can effectively achieve activation, chemisorption, and photo-reduction of dinitrogen, because Mo atoms act as a nitrogen activation center in the Mo-O coordination polyhedron.[80] On the same basis, Bi$_2$MoO$_6$ based artificial photosynthesis system was successfully constructed by controllable crystal structure and defect engineering.[80] The result was effective energy coupling with photons, excitons, and dinitrogen in this system enables impeccable sunlight-driven nitrogen fixation performance (Figure 2.2).

It was also reported that a class of inorganic compounds, MBiMoO$_6$ (M = Pr, Nd,
Table 2.1 Color co-ordinates and band gap of Bi$_2$MoO$_6$ and MBiMoO$_6$ (M = Pr, Nd, Sm, Tb and Yb). Noted band gap decreases with implementation of M$^{3+}$ into Bi$_2$MoO$_6$.\cite{18}

<table>
<thead>
<tr>
<th>Sample</th>
<th>Color co-ordinates</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$L^*$</td>
<td>$a^*$</td>
</tr>
<tr>
<td>Bi$_2$MoO$_6$</td>
<td>93.4</td>
<td>-4.3</td>
</tr>
<tr>
<td>BiPrMoO$_6$</td>
<td>84.3</td>
<td>-12.6</td>
</tr>
<tr>
<td>BiNdMoO$_6$</td>
<td>74.2</td>
<td>4.7</td>
</tr>
<tr>
<td>BiSmMoO$_6$</td>
<td>91.2</td>
<td>-7.4</td>
</tr>
<tr>
<td>BiTbMoO$_6$</td>
<td>79.1</td>
<td>16.0</td>
</tr>
<tr>
<td>BiYbMoO$_6$</td>
<td>78.3</td>
<td>17.7</td>
</tr>
</tbody>
</table>

Sm, Tb and Yb) was synthesized by solid state route. These substitutions of different rare earth metals for Bi$^{3+}$ in Bi$_2$MoO$_6$ structure yields visible light activated compounds that gently red shifting the absorption edge to low energy side.\cite{18} This visible light absorption was based on transitions of charge transfer from O$_2$p valence band to conduction band that was primarily made of secondary Bi$_6$p and Mo$_4$d.

The rare earth metals that can be seen in Figure 2.4, partially occupied 4f electronic levels in between the band gap (impurity states: states in band gap), and the position of these levels depend on the number of f electrons, which indirectly allows tuning of the band gap.\cite{18} That means the rare earth metals provides opportunities to tailor the band gap from 2.99 eV to 2.19 eV for Bi$_2$MoO$_6$ structure.\cite{18} The group that demonstrated this \cite{18} showed that these compounds exhibit different shades of yellow hue and good coloration to plastics. What is interesting about this study is the recorded band gap for these rare earth metal Bi$_2$MoO$_6$ structures, as shown in Table 2.1. These recorded band baps would dramatically increase charge transfer between the valence band and conduction band, thus allowing for reaction steps of nitrogen fixation to yield very promising results.
2.4 Nanomaterial Synthesis

Success of industrial methods for nanomaterial synthesis are attributed to how well the nanomaterial manufacturing techniques can be scaled up and scaled out for large-scale production. Large-scale nanotechnologies have to deal with production of smaller than 100 nm in at least one-dimension nanoparticles contained in these materials. Due to the size of these nanomaterials, distinct attributes are expressed for mechanical, catalytic, and optical properties. Properties like large amount of grain boundaries for bulk materials that allow extended grain boundary sliding that leads to high plasticity, interesting catalytic properties for transition element oxides due to large surfaces, and tuning of index refraction due to distributions of non-collected nanoparticles in a polymer that may also demonstrate non-linear optical properties. This section will express some different methods that nanomaterials ex-
pressed in this study can be synthesized for large-scale production. Nanotechnologies can be divided into two groups: (i) dry manufacturing methods like mechanical attrition (milling), combustion synthesis, flame pyrolysis, and plasma synthesis, etc. (ii) wet manufacturing methods such as sol-gel, hydrothermal synthesis, etc.

Two different techniques have been developed for mechanical attrition (MA), first being to mill a single phase powder by controlling the balance point between cold welding and fracturing [81, 82]. This allows particles larger than 100 nm to not excessively be cold welded, resulting in the reduction of average grain size from 50-100 nm up to 2-20 nm [81–83]. This reduction of one magnitude for the average grain size occurs due to the creation and self organization of large-angle grain boundaries between powdered particles. The second technique is mechanochemical processing, which utilizes ball mill as a low temperature chemical reactor [82, 83]. The ball mill allows reaction kinetics to increase for the reaction powder mixture, due to intermediate mixing and refinement at the nanometer scale of the corresponding grain structure. MA methods have demonstrated to overcome quantity limitations for nanocrystalline preparation, thus resulting in large scale nanocrystalline powder production [81]. Moreover, this method can be implemented in different number of structures in preparing structures within nanostructured powders like crystalline to crystalline, crystalline to amorphous, and atomic bonding of metal to metal, metal to semiconductor, and metal to ceramic, etc.

The MA is a ‘top down’ method but one of many dry manufacturing method, and currently the most commercially use dry based techniques are of ‘bottom up’ approaches for manufacturing nanomaterials from molecular to nano-assembly. Often processes produce low specification dry powders that show attributes of wide particle size distribution or high collection of basic material particles, these powders tend to be reprocessed before use. This is where combustion synthesis and or flame pyrolysis methods are implemented. These two methods are dry based techniques that utilize high temperature zone to convert nanoparticles from dissolved metal species [81, 83]. Similarly, plasma synthesis methods relies on
metal precursors that travel in a spray through the plasma under vacuum to form nanoparticles [81]. The expressed dry techniques are relatively simple from a lab prospective and can be easily salable, thus appealing to commercial and industrial manufacturing that requires large quantities of nanomaterials.

Figure 2.5 Illustration of the stages for Sol-Gel method from mixing the solution, formation of gel, drying, and finally heating to high temperatures (calcination) to form nanoparticles.

Wet based techniques give an alternative method that also demonstrates great opportunities for synthetically producing high quality nanoparticles. For example sol-gel method, which is a long established industrial process for generation of colloidal nanoparticles from liquid phase [81, 83] for production of coating and advanced nanomaterials. This process is based on condensation reactions or hydrolysis as shown in Figure 2.5. With implementation of appropriate amount of reactants, nanosized particles will undergo precipitation. Low temperature during processing, versatility, easy shaping and embedding are some of the key advantages that sol-gel methods demonstrate.

The other expressed wet method is hydrothermal synthesis. The reactor technology is based on continuous hydrothermal synthesis to produce inorganic nanoparticles for both crystalline oxide and or non-oxide materials suspended in water as an aqueous dispersion [81, 83]. To allow the synthesis of nanoparticles, supercritical/superheated water or high pressured water is used. In these synthesis the high pressured water is mixed with metal salt
based solution, like iron nitrate, thus allowing reaction to occur and nanoparticles to form in the solution.

2.5 Hydrogen Evolution Reaction (HER)

Critical challenges occur when trying to contribute to the world’s growing population for clean, affordable, and sustainable energy sources. Fossil fuels dominate the global energy landscape, thus yielding an increasing concern over the effect of carbon dioxide emissions which makes sustainable energy technologies such an attractive option. Electrochemical hydrogen evolution reaction (HER) materials offer promising ways to form hydrogen, which has a high energy density and potentially without carbon emissions, and most effectively catalyzed by Pt and its alloys. However, the high cost and limited supply of Pt group metals prevent wider adoption for HER.[84] Critical requirement for HER is the feasibility of highly active developmental, stable, and sustainable material to allow widespread implementation of HER economically viable. On the note of nitrogen fixation, which requires hydrogen in conjunction with nitrogen to form ammonia as a byproduct, the MMOs$_2$ (M = Co Fe) electro-catalyst systems as a source of possible hydrogen evolution reaction (HER) and in recent work MMOs$_2$ has demonstrated promise as HER catalyst, [84–86] due to their high activity and excellent structure stability.

Hydrogen evolution reaction is thought to involve three reaction steps (asterisk ’*’, denotes a site on the surface),

\[ * + (H^+ + e^-) \rightleftharpoons H^* \quad Volmer - Step, \]  
\[ H^* + (H^+ + e^-) \rightleftharpoons H_2^g + * \quad Heyrovsky - Step, \]  
\[ 2H^* \rightleftharpoons H_2^g + 2 * \quad Tafel - Step. \]  

HER may occur via Volmer-Heyrowsky mechanism or Volmer-Tafel mechanism. However,
Figure 2.6 Current density as a function of $\Delta G_{H^*}$ for HER catalyst materials. (a) Experimental volcano plot for HER which shows Pt having the least negative hydrogen absorption energy and has the highest HER activity. (b) Theoretical HER volcano plot, which predicts catalysts with hydrogen binding energy equal to zero will have highest HER activity.[85]

hydrogen atoms adsorbed at the electrode surface ($H^*$) in both cases, and thus the overall reaction rate is influenced by Gibbs energy of hydrogen adsorption ($\Delta G_H$). Also, the adsorption step will limit overall reaction rate if the hydrogen to surface bond is to weak,
and respectful if the hydrogen to surface bond is to strong the reaction desorption step will limit the overall reaction rate as well. Usually, catalysts for HER have hydrogen adsorption energies close to $\Delta G_H = 0$, with hydrogen bonded neither too strongly nor too weakly. This idea gives rise to the volcano relationship as expressed by Figure 2.6, which illustrates HER measure of catalytic activity as a function of $\Delta G_H$. Also, Figure 2.6 shows the several classes of materials that have currently been investigated as active HER catalysts, such as platinum, nickel alloys, metal oxides, metal phosphides, and metal sulfides.

### 2.5.1 Insight for MoS$_2$ Structure

Hydrodesulfurization (HDS) is a widely used catalytic chemical process to remove sulfur from refined petroleum products and natural gas. The main reason for removal of sulfur from products is to greatly reduce the sulfur dioxide emissions, which is attributed with fuel combustion equipment and even at low concentrations sulfur can prove dangerous. Thus materials that prove to be candidates for active HDS catalyst must bond well with hydrogen when removing sulfur as H$_2$S. Work directed toward MoS$_2$ research involves the increase in overall edge site turnover frequency, inspired by success of molybdenum sulfide catalysts reported for HDS. The approach taken in improving the activity of MoS$_2$ by this study is to sub Fe and Co into MoS$_2$ to better activate S-edge; however, this is also looked at quite extensively in literature reference [85, 86] from a theoretical and experimental point of view. The reference literature [85, 86] expresses doping and approaches such as modifying the H-binding energy through substrate interaction, tuning electronic properties through Li ion interaction, and utilizing the conductive 1T polymorph of MoS$_2$ for improving the intrinsic activity of molybdenum sulfide. Thus this will primarily be a review of some highlighted points for doping of transition metals into MoS$_2$.

More than one order of magnitude is increased for catalytic activity for HDS when incorporating small amounts of transition metal dopants into molybdenum sulfide. Researchers
have demonstrated that location of dopants tend to be at the S-edge sites of doped MoS$_2$ clusters, and the doped transition metal (Co, Ni, Fe) modification of hydrogen bonding energy at S-edge is attributed to the activity enhancement of MoS$_2$ cluster [85]. Binding energy at the S-edge is decreased from 0.18 eV to 0.10 eV when Co dopants are incorporated into MoS$_2$ [85]. The role of transition metals is thus associated with the increase of the activated site number in MoSS$_2$ catalysts by indirect activation of S-edges.

Binding energies of pure MoS$_2$ for Mo 3d and S 2p orbitals are shifted negatively with different degrees as transition metals are incorporated [86]. This shift of binding energies is due to diverse electronic densities of MoS$_2$ as more transition metals are doped. Thus modulation of electronic densities will yield changes to catalytic activity for MoS$_2$ and for Fe/Co doped MoS$_2$, electrocatalytic activities are greatly reduced toward HER [86].
3.1 Nitrogen Fixation Methodology

There is a growing concern and need for synthetically producing ammonia that will need to be addressed with the growing population. What this study aims to understand is the potential utilizing concepts of electrochemistry that can aide to further investigate synthetically production ammonia. This is enhanced by the demand for ammonia to sustain the very apparent population influx. Great strides have been made to address the obstacles faced while developing catalytic materials for nitrogen reduction in the past several years from a theoretical [1, 40, 2] and experimental [1, 87, 88] perspective, which gives a starting point for further investigation on these catalytic materials. In fact, some of these studies showed that ammonia synthesis to be very structure sensitive on metal surfaces that can occur on surface steps of Fe and Ru [1], and potently could expect the associative mechanism to be even more so. Thus, bringing about this study to investigate the highly under coordinated MoS$_2$ and bismuth containing Bi$_2$MoO$_6$ structures, which provides a means to investigate this structure sensitive mechanism.

First principle density functional theory (DFT) calculations allow reliable modeling of chemical reactions for the expressed MoS$_2$ and Bi$_2$MoO$_6$ structures to investigate the electrocatalytic production of ammonia. This study focuses on the highly under coordinated structures, which has shown oxidation reactions performed on transition metal nanoparticles consisting of metals at lower temperatures [89, 1, 11, 79, 80], and has shown to dramatically change the reactivity of inert metals. [1, 11] Also, due to the fact that various experimental work has demonstrated this structure to have good: light absorption, band gap variability, charge mobility, thermal stability, and structure mobility. [41, 42, 6, 7, 53, 54, 18] The
edge exposed coordinatively unsaturated Mo atoms in Bi$_2$MoO$_6$ structure can effectively achieve activation, chemisorptions, and photo-reduction of dinitrogen, because Mo atoms act as a nitrogen activation center in the Mo-O coordination polyhedron [80, 11]. On the same basis, Bi$_2$MoO$_6$ based artificial photosynthesis system was successfully constructed by controllable crystal structure and defect engineering [80, 18]. The result was effective energy coupling with photons, excitons, and di-nitrogen in this system which demonstrates impeccable sunlight-driven nitrogen fixation performance [80]. While previous studies primarily looked at step metal surfaces of these structures, this study performed calculations on a consistent basis for configurations of MoS$_2$ and Bi$_2$MoO$_6$ and their respected sub configurations. This allows the investigation of the reaction intermediates for the dissociative and associative mechanisms on MoS$_2$ structure for Mo, Co, Fe (M$_x$Mo$_y$S$_2$ (M = Fe, Co)) and Yb, Fe, La ((M$_x$Bi$_y$)$_2$MoO$_6$(M=Yb, Fe, La)) transition metals, and develop stepped and closed packed metal surface relations. These calculations construct Gibbs energy diagrams for both reaction pathways based on entropy and zero-point energy corrections. These diagrams are then used to determine the lowest potential across the investigated metal configurations.

3.1.1 Nitrogen Reduction

The loss and gain of electrons in a chemical reaction is referred to as oxidation and reduction reactions. Biochemical reactions of C, H, and O are the foundations in which oxidation and reduction chemical reactions take place [90] in elements for which nitrogen reduction is most importantly associated with. This is because, nitrogen valence range can undergo a biochemical cycling [90, 3] from which nitrogen can lose all five of its outer shell electrons to surrounding elements or gain three electrons from other elements to complete all orbitals of its outer-most electron shells.

Nitrogen can take two cycling forms in this reduction; first nitrogen atom can lose outer shell electrons if the surrounding element has a higher electron affinity (to be more electronegative). For example, if the surrounding element was oxygen, which is more elec-
tronegative then nitrogen (affinity for electrons is greater than nitrogen), the nitrogen will eventually lose all five outer shell electrons, thus nitrogen can eventually become fully oxidized as nitrate (NO$_3^-$). In contrast to losing electrons, nitrogen can eventually fill all outer shell electron orbitals (gain three electrons) from elements such as H and C, which are less electronegative than nitrogen. With this gain of electrons, nitrogen can be fully reduced to ammonia (NH$_3$), and thus potentially allowing nitrogen to be fully to partially reduced in various organic compounds. Similar to C, H, and O, nitrogen cycling involves a zero valence form (N$_2$ gas), for which the charge of the seven protons in nitrogens nucleus are balanced by seven electrons orbiting the nucleus by the two electrons of the inner electron shell and the five of the outer shell. The depicted nitrogen reduction is greatly idealized and can therefore contain many intermediate oxidation and reduction forms that nitrogen can assume; however, not all are expressed in this work, but are discussed in great detail in references [90, 3, 91].

Furthermore, these oxidation and reduction reactions of nitrogen is regulated by biological, chemical, and physical factors [90] that play key roles in reducing nitrogen. These factors do not only influence the form that nitrogen takes, but also the flux, accumulation of nitrogen, and the nature/extent of the reactions in which nitrogen contributes. From thermodynamic examination of nitrogen reduction, one can express the importance of these mediating factors for which nitrogen exists in forms other than its most thermodynamically stable form (NO$_3^-$) [3, 91]. This suggests that any applied external source of energy that are directed by mediating chemical, physical and biological factors truly contribute to the possibility of driving nitrogen reduction.

3.1.2 Photocatalysis

The main concern of successfully reducing nitrogen by synthetic means is the energy required to implement these processes. Usually the main source of energy utilized by these synthetic processes are attained by burning fossil fuels that yield environmental pollution
as discussed in Section 2.2. This prompted studies to investigate and advance better reaction pathways for ammonia production through the mimicry of biological organisms, thus allowing various researchers to develop catalysts for this process. Thus allowing many researchers to investigate the mechanism of nitrogen fixation and produce photocatalytic and photoelectrochemical processes to utilize solar energy conversion.

The presence of a catalyst allows photo-reaction to be accelerated, this is because the photocatalytic activity is dependent on the catalyst to create hole pairs (electron charge carriers), which generate free unpaired valence electrons that can contribute to secondary reactions. Typically, these photocatalysts are comprised of transition metal oxides and or semiconductors that have void energy region (band gap) where no energy levels are present to undergo an electron and hole recombination produced by photoactivation (light/photon absorption). When the energy of an absorbed photon is equal to or greater than that of the materials band gap, an electron becomes excited from the valence band (HOMO) to the conduction band (LUMO), thus producing a positive hole in the valence band. This excited electron and hole can then become recombined, and release heat from the energy gained by the photon exciting the surface of the material. The idea is to have a reaction that produces an oxidized product by reaction of generated holes with a reducing agent, and to have a reduced product by the interaction of the excited electron and an oxidant. Simply-put, photoelectrochemical and photocatalytic processes rely on semiconductor materials to absorb sunlight and generate excited charge carriers that allow for reactions to take effect without any external input.

Thus the presented work aims to yield a photocatalytic and electrochemical investigation for sunlight-driven nitrogen fixation to reduce energy consumption, which will also provide flexibility in designing materials for nitrogen conversion. This work prompts to gain a crucial understanding of nitrogen to ammonia reaction process on the photocatalytic and electrochemical level and to develop means of approaching a sustainable solar driven conversion process of nitrogen to ammonia.
3.1.3 Electrochemical Reaction

DFT calculations approximations of the Gibbs energy for the adsorbed species relative to the gas phase molecules of nitrogen and hydrogen, which can be obtained from the expression,

\[
\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S, \quad (3.1)
\]

where \(\Delta E\) is the DFT calculated enthalpy, \(\Delta E_{ZPE}\) is the reaction zero point energy, and \(\Delta S\) is the reaction entropy. In this study, only the ZPE is considered for the gas phases.

The driving electrochemical reaction is set to that of the standard hydrogen electrode (SHE) for the applied reference potential, which this study also takes into account in addition to zero point energy. This study is able to include the effect of the potential on the expressed reactions for surface sites by using the computational standard hydrogen electrode.

Thus the reference potential used by this study is that of the standard hydrogen electrode, which expresses the Gibbs energy per hydrogen (chemical potential of \((H^+ + e^-)\) as related to that of \(\frac{1}{2}H_2(g)\), which is Equation 3.2 in the state of equilibrium. This implies that the \(\text{pH} = 0\), the potential is that of \(U = 0 \text{ V}\) relative to the SHE, and a pressure of 1 bar of \(H_2\) in gas phase at 298 K, thus reaction (2.2) Gibbs energy is equal to that of net reactions of (3.4)-(3.12) and or (3.13)-(3.22) at an electrode.

3.1.4 Associative and Dissociative Reaction Pathways

In the electrochemical process of forming ammonia, it is ideal to reference the source of protons and electrons to model the anode reaction,

\[
H_2 \rightleftharpoons 2(H^+ + e^-). \quad (3.2)
\]

Initially, protons are exposed into the proton conducting electrolyte to maintain the equilibrium and diffuse into the cathode while an external circuit is used to transport electrons
to the cathode side through substrate. At this instant, a nitrogen molecule will react with surrounding protons and electrons at the cathode as described by the following reaction,

$$N_2 + 6(H^+ + e^-) \rightarrow 2NH_3,$$

(3.3)
to form ammonia at the catalytically active site. This is known as the overall electrochemical reaction.

In theory, the reaction can take two different possible pathway forms in which there are two different possible types of mechanism for each pathway in order to synthesize ammonia electrochemically. Pathways correspond to either the Tafel-type mechanism or the Heyrovsky-type mechanism. [87] In the Tafel-type mechanism, solvated protons from the solution are first adsorb [88] on the surface and combine with electrons, then the hydrogen adatoms react with the adsorbed species($N_2H_x$ or $NH_x$). Indirect effect through interchangeable concentrations of the reactants can only be done by this type of mechanism. [87] It is noted that this study focuses on room temperature processes, and that activation barriers for Tafel-type reactions are about 1 eV or higher for most transition metal surfaces [89, 92], thus most likely yielding very slow reactions for this type of mechanism. Also, it is further noted that this type of mechanism is known to require hydrogenation steps [92] of the reaction barriers to be overcome, and thus will also require higher temperature as well to drive the process forward. This is because, initially there is a requirement of the reaction to merge protons and electrons to form hydrogen adatom on the surface. [88] Thus the process will therefore either go through an associative and or dissociative Heyrovsky-type reaction.

In Heyrovsky-type reactions [87], the adsorbed species are known to be directly protonated in order to form a coordinate bond to the proton and the species. These protons directly attach to molecules from the electrolyte and then electrons merge from the surface with the protons to form hydrogen bonded to the molecule. By applying a bias in later steps of the mechanism, a thermochemical barrier can be directly affected efficiently. Ideally,
this study considers the possibility of reactions to take an associative Heyrovsky mechanism which proves to be more efficient from a biological standpoint then that of the dissociated mechanism. The associative Heyrovsky mechanism is similar to that of the mechanism for BNF, where the N-N bond is initially weakened by successive protonations until the dissociation barrier is low enough so that the N-N bond can be broken later in the reaction steps. For this Heyrovsky mechanism, nitrogen molecule is first attached to the surface and is then protonated before N-N bond dissociates. The below equations express reaction steps of BNF, which is the associative Heyrovsky mechanism (asterisk ‘*’, denotes attachment to the surface),

\[ N_2(g) + 6(H^+ + e^-) + \ast \leftrightarrow N_2\ast + 6(H^+ + e^-), \tag{3.4} \]

\[ N_2\ast + 6(H^+ + e^-) \rightarrow N_2H\ast + 5(H^+ + e^-), \tag{3.5} \]

\[ N_2H\ast + 5(H^+ + e^-) \rightleftharpoons N_2H_2\ast + 4(H^+ + e^-), \tag{3.6} \]

\[ N_2H_2\ast + 4(H^+ + e^-) \rightleftharpoons N_2H_3\ast + 3(H^+ + e^-), \tag{3.7} \]

\[ N_2H_3\ast + 3(H^+ + e^-) + \ast \rightarrow 2NH_2\ast + 2(H^+ + e^-), \tag{3.8} \]

\[ 2NH_2\ast + 2(H^+ + e^-) \rightleftharpoons NH_3\ast + NH_2\ast + (H^+ + e^-), \tag{3.9} \]

\[ NH_3\ast + NH_2\ast + (H^+ + e^-) \rightarrow 2NH_3\ast, \tag{3.10} \]

\[ 2NH_3\ast \rightarrow NH_3\ast + NH_3(g) + \ast, \tag{3.11} \]

\[ NH_3\ast + NH_3(g) \rightleftharpoons 2NH_3(g) + \ast. \tag{3.12} \]

Addition of the fourth H to the N_2H_3\ast molecule allows weakening of the N-N bond to readily dissociate molecules into the NH_x species on the surface. In addition, there is a possibility of reaction (3.7) to split into NH and NH_2 on the surface and has been observed on some metals.[1]

The second mechanism, dissociated Heyrovsky mechanism, is also considered and
compared to that of the associative mechanism. Where in this type of mechanism the nitrogen molecule is initially dissociated on the surface and then followed by subsequent protonation by direct attachment of protons. Below equations express reaction steps of Haber-Bosch process, this is the dissociated Heyrovsky mechanism,

\[ N_2(g) + 6(H^+ + e^-) + \ast \rightleftharpoons N_2 + 6(H^+ + e^-), \quad (3.13) \]

\[ N_2 + 6(H^+ + e^-) + \ast \rightleftharpoons 2N + 6(H^+ + e^-), \quad (3.14) \]

\[ 2N + 6(H^+ + e^-) \rightleftharpoons NH + N + 5(H^+ + e^-), \quad (3.15) \]

\[ NH + N + 5(H^+ + e^-) \rightleftharpoons NH_2 + N + 4(H^+ + e^-), \quad (3.16) \]

\[ NH_2 + N + 4(H^+ + e^-) \rightleftharpoons NH_3 + N + 3(H^+ + e^-), \quad (3.17) \]

\[ NH_3 + N + 3(H^+ + e^-) \rightleftharpoons NH_3 + NH_2 + (H^+ + e^-), \quad (3.18) \]

\[ NH_3 + NH_2 + (H^+ + e^-) \rightleftharpoons 2NH_3, \quad (3.19) \]

\[ 2NH_3 \rightleftharpoons NH_3 + NH_3(g) + \ast, \quad (3.20) \]

\[ NH_3(g) + NH_3 \rightleftharpoons 2NH_3(g) + \ast. \quad (3.21) \]

### 3.1.5 Kinetic Considerations

Reduction potential is the measurement of the tendency of chemical groups to attain electrons and thereby reduce (gain of electrons).\[93, 94\] The use of reduction potentials to predict the course of reactions is limited to thermodynamic considerations, and if the overall reduction potential for the reaction is positive, which is the difference of the reduction potentials of the individual couples, then there is a negative Gibbs reaction energy and the
reaction is thermodynamically spontaneous. With that in mind, even if a thermodynamic potential for a reaction is favorable, the reaction at times can proceed slowly or not at all, and whether the reaction occurs or the rate at which it does occur, depend on the kinetic factors which influence the process. This is due to an additional impedance that is related to the kinetics of the reaction and system electrical losses, this additional voltage that’s required to proceed the reaction is called the over-potential.[93] 

**Figure 3.1** Electrochemical cell consists of two half-cells. One half-cell consists of metal electrode of a certain metal submerged in aqueous solution. The electrode is connected to the other half-cell, which contains an electrode of different metal submerged in aqueous solution. Over-potential is the potential (voltage) difference between half-cell potential with
current flow and the equilibrium zero-current half-cell potential.\cite{95} In one half-cell the oxidation of metal electrode (loss of electrons) occurs, and reduction of metal ions (gain of electrons) in solution occurs in the other half-cell (Figure 3.1).\cite{96, 97, 95} Half-cell potential is altered when there is current flowing in the electrode due to electrode over-potential, reference Figure 3.1. In the first half-cell (marked as anode in Figure 3.1), metal atoms in electrode become oxidized and join metal ions in the aqueous solution.\cite{95} The electrons lost from anode will then transfer to the second half cell (marked by cathode in Figure 3.1). As electrons pass metal electrode in the cathode, the ions of the solution will become reduced and become a metal atom on the electrode.\cite{95} In order to balance the charge on both sides of the cell, half-cells are connected by a salt bridge. As anode half-cell becomes overwhelmed with metal ions, the negative anion of salt will enter the solution and stabilize the charge and similarly for the cathode, as solution become negatively charged, cations from salt bridge will stabilize the charge.\cite{96, 95}

The over-potential takes the following form,

$$\Delta V = \Delta V_A + \Delta V_R + \Delta V_C$$  \hspace{1cm} (3.23)

Over-potential losses originate primarily from activation over-potential ($\Delta V_A$), ohmic over-potential ($\Delta V_R$), and gas concentration over-potential ($\Delta V_C$).\cite{96, 97} The first of these losses, activation over-potential, is very noticeable in the low current region and electronic barriers must be overcome before the advent of current and ionic flow in this region. This activation loss is directly proportional to increase in flow current and is represented as

$$\Delta V_A = \frac{RT}{\alpha \eta F} \ln\left(\frac{i}{i_0}\right)$$  \hspace{1cm} (3.24)

Where R is universal gas constant, T the temperature, $\alpha$ the charge transfer coefficient, $\eta$ the number of electrons involved, F the Faraday constant, $i$ the current density, and $i_0$ is the exchange current density.\cite{96} Activation over-potential becomes present due to slow
electrochemical reactions at electrode surface, where species are reduced or oxidized in the cell reaction. This makes activation over-potential directly related to the rate at which the oxidant is reduced or oxidized. Since activation energy barriers for reduction and oxidation are different, the net activation energy depends on the direction of current and appears as a voltage.

The second, ohmic over-potential, varies proportionally to the increase in current and the increase over the entire range of currents, this is due to constant nature of the cell resistance, and is represented by

$$\Delta V_R = iR_c$$ (3.25)

Where $R_c$ is the cell resistance and $i$ is the current density. The origin of ohmic over-potential is derived from resistance to the flow of ions in the electrolyte and flow of electrons with respect to the electrodes and external electrical circuit. Ohmic over-potential’s voltage drops along the path of the current and the current changes resistance of electrolyte.

Lastly, the concentration over-potential, which happens over the entire range of the current density; however, at high limiting current, it becomes much more difficult for gas reactant flow to reach the cell reaction sites, and these loses become much more prominent. This concentration over-potential is represented as

$$\Delta V_C = \frac{RT}{\eta F} \ln(1 - \frac{i}{i_\Delta})$$ (3.26)

Where $R$ is universal gas constant, $T$ the temperature, $\eta$ the number of electrons involved, $F$ the Faraday constant, $i$ the current density, and $i_\Delta$ is the limiting current density. As reactant gas is consumed at electrode by means of electrochemical reaction, a drop of potential will occur due to the drop in the initial concentration of bulk fluid in surroundings (aqueous solution), thus this leads to concentration gradient formation in the system. In other words, current alters the distribution of ions at the interface of the electrode-electrolyte.

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3.2 Density Functional Theory

This study leverages the predictions of ground state electronic structures by using quantum mechanical modeling tool based on first principle density functional theory (DFT) [98]. This theory uses functionals (functions of another function), to determine properties of the many electron system, which in this study is the spatially dependent electron density. Solving the Non-relativistic Kohn-Sham equations, which are used to calculate fundamental properties that implement proven methods like DFT. Where DFT is based on Hohenberg-Kohn theorem which suggests that:

1. All ground state properties of a system, including total energy, are some functional of the ground state charge density.

2. The correct ground state charge density minimizes the functional.

The total energy of the system is given by,

\[
E(n) = T_s(n) + E_H(n) + E_{xc}(n) + \int V_{ext}(r)n(r)dr,
\]

(3.27)

where \(T_s(n)\) is the kinetic energy of the non-interacting system, \(n\) is the charge density, \(E_H(n)\) is the Hartree energy, \(E_{xc}(n)\) is the exchange-correlation energy functional that contains information regarding the exchange interactions between electrons and all other correlational effects in a many-electron system, and \(V_{ext}(r)\) is the exchange-correlation potential.

The ground state of the system is achieved by varying the charge density until the global minimum in the energy functional is reached. Local Density Approximation (LDA) method is used in order to solve equation (3.27) which requires approximating the exchange-correlation functional. LDA is a way to approximate exchange-correlation energy, which only depends on the density where the functional being evaluated an expressed as fallows:

\[
E_{xc}^{LDA}(n) = \int n(r)\epsilon(n(r))dr
\]

(3.28)
where $\epsilon(n(r))$ is the exchange-correlation energy per particle with electron density $n$. To better improve LDA, a generalized gradient approximation (GGA) is used, which assumes a gradient of the electron density at any specified point in space. It is noted that this study used an improved approximation method similar to GGA to approximate the functional and is also implemented for electronic structure calculations.

For ground state calculations, several parameters are required such as effective mass ($m^*$), fermi energy, band gap energy, and lattice parameters. The parameters specified can be attained from band structure and the material force constants which depend on the composition and configuration of the substituents parts that make up intermediate compositions. DFT method implemented in this work utilizes Perdew-Burke-Enzerhof (GGA-PBE) [99] exchange-correlation function, as well as the projected augmented wave (PAW) pseudo-potentials implemented in ABINIT package [100, 101]. In strongly correlated condensed matter, the GGA-PBE is selected based on its potential for correcting the over-binding. Through minimization of the total lattice energy and the inter-atomic forces, the energy of each configuration, band structure, and lattice constants can be obtained.

Pseudo-potential is an approximation method used to generated an effective potential that describes an atom from the surrounding core region of the valance electrons. The valance electrons surrounding the core region effectively are the ones contributing to the binding properties, assuming core elections to be at steady state. The present core electrons of an atom are assumed at steady state (frozen), because core electrons are highly localized and tightly bound to the nucleus of an atom, moreover the energy of these core electrons falls way below the conduction band. Thus fewer nodes are need to describe the valance electrons by the pseudo-wavefunctions and hence making the plane-wave basis practical, hence using effective potential will reduce the computational time.
3.3 MoS$_2$ Design Space

Typically a good strategy to design new catalyst for nitrogen reduction is by combining components that lie from both the dissociative and associative side. Initial DFT calculations show that MoS$_2$ to favor the dissociative side and with the addition of Fe and or Co, which typically favor the associative mechanism, the material of interest takes the form of M$_x$Mo$_y$S$_2$ ($M = Mo, Fe, Co$). The main structural modification that was done is the substitution of the non-organic ion with various combinations in all possible positions in the unit cell (MMoS$_2$, $M = Mo, Co, Fe$). The 8 (1T) and 7 (2H) atomic positions that were modified are clearly shown in Figure 3.2 of the unit cell for the 1T and 2H structures. Every configuration combination of the three elements (Mo, Co, Fe) is implemented and tested in the metal positions expressed in Figure 3.2 of the unit cell. These configurations are classified under one element case (pure Mo, Co, Fe structure), two element cases (combination of Co and Fe, Co and Mo, Fe and Mo), and three element cases (combination of Co and Fe and Mo).

![1T and 2H unit cell structures](image)

**Figure 3.2** Illustration of the sulfur desorbed MMoS$_2$ 1T and 2H supercell structure. A 1T unit cell made up of 16 atoms 8 transition metal atoms and 8 S atoms, whereas the 2H unit cell is comprised of 18 total atoms 7 transition metal atoms and 11 S atoms. The transition metal atoms in the structures are alloyed with all combinations of Mo, Fe, Co atoms.
It is noted that while the MoS$_2$ material is coupled with Fe and Co, all combination of the three elements are and will be evaluated in this study to better vary the mechanism of interest for each distinct adsorption species ($\text{N}_2\text{H}_x$, $\text{NH}_x$). For cases of elemental combination (two element and three element cases), there are different configurations possible for same elemental ratios. This makes a total of 6561 (3 elements for 8 positions $3^8$) unique configurations for 1T and 2187 (3 elements for 7 positions $3^7$) unique configurations for 2H structures. Only the best configurations (lowest energy of the relaxed structure) for each distinct structure will be evaluated for the electrochemical reactions. For example, configuration of 1T structure of 1 atom Co and 7 atom Mo (Co1Mo7) can have 8 distinct configurations of Co being in any of the 8 metal positions, so only the lowest energy structure after the relaxation will be implemented in the electrochemical reactions, and this is the same for every other configuration for 1T and 2H (Co2Mo6, Co3Mo5, ...).

Also, it is noted that for each configuration there are various operations that had to be done in sequence to obtain proper data, this resulted in a total of 45 configurations for 1T and 36 configurations for 2H that had the lowest energy structure for a specific configuration. The reader should note that this is a tremendous amount of computational and analytically challenging process. This is an area that needs to be investigated from a statistical point of view. Then only the 45 (1T) and 36 (2H) unique structures went on to be implemented in the electrochemical reactions. This will significantly allow every configuration of 1T and 2H structure to be explored and give the best configuration of MMoS$_2$, $M = \text{Mo, Co, Fe}$ structure as a means of nitrogen reduction catalyst.

Figure 3.3 illustrates the pure S-Mo-S layers for the MoS$_2$ without any sulfur desorption. In contrast to the MoS$_2$ based sulfur desorbed system (Figure 3.2), the sulfur layer illustrated by the top row of Figure 3.3 would lack affinity for nitrogen species because there is a much higher affinity for HER. Thus this study looks at the sulfur desorbed system (Figure 3.2), which is just the removal of the exposed sulfur layer at the surface of the MoS$_2$ system (Figure 3.3). Sulfur desorption has been experimentally achieved during ultra-high
Figure 3.3 Illustration of the pure S-Mo-S layers for MoS$_2$ 1T and 2H phase without any sulfur desorption. This structure is used to demonstrate the removal of the sulfur layer on the surface of the MoS$_2$ structure as shown in Figure 3.2.

vacuum (UHV) annealing [12]. These experimental approaches known to achieve desorption of the sulfur layer including both mechanical and chemical exfoliation. Thus sulfur desorption was realized, which demonstrated formation of sulfur vacancies during chemical exfoliation and a post anneal phase at UHV [12]. With the experimentally known method, this study focuses on photocatalytic properties of the sulfur desorbed MoS$_2$ based structure system (Figure 3.2) and not the MoS$_2$ contrast structure (Figure 3.3).

3.3.1 MoS$_2$ Phase

The material of interest is a MMoS$_2$ (Figure 3.2) that has received tremendous attention due to the earth-abundant composition and attractive optical, catalytic, electronic properties, and high chemical stability. However, the focus of MoS$_2$ has mainly been on the hydrogen evolution reaction (HER) [102, 85, 86]. The bulk crystal is indirect gap semiconductor that has an energy gap of approximately 1.29 eV and is built up of van der Walls bonding of the S-Mo-S units. Due to their large surface areas and highly dense active sites along edges, MoS$_2$ are potentially promising material for electrochemical reaction studies. However, MoS$_2$ have proven to have poor conductivity, which has limited their electrochem-
ical response. The fact that MoS$_2$ monolayers is known to have two phases, the trigonal prismatic (2H) and octahedral (1T), makes it a unique structure to investigate[103, 74]. The 2H phase has proven to be very stable, but with poor conductivity. However, the 1T phase is particularly favoring a stable structure at room temperature, but is metallic and better conductivity in nature.[103] This is why the combination of Fe and Co into the MoS$_2$ is being looked at in this study, to allow ideal properties to be demonstrated for distinct structures. If the properties of the two phases are combined in a monolayer structure, such as higher stability of the 2H phase and the high conductivity of the 1T phase [103, 104, 74], this will result in the very favorable structure for N reduction. The resulting structure would have both large specific surface area and high charge transfer abilities that can be achieved simultaneously.

The structural transformation between semiconducting (2H) and metallic (1T) phases of MoS$_2$ has been a topic of interest in the past. These phase transitions (1T/2H) is made up of Mo and or S atomic glide planes that require a precursor intermediate phase (α-phase) [104]. Also, the phase transition is found to be associated with movement between B and y-boundaries [104]. In a thermodynamic system, the phase transition is fundamental phenomena and of great technological importance in the material science research, due to the fact that properties of a material are able to be altered without the need on additional atoms into the system.

The MoS$_2$ crystal (Figure 3.2) structure is made of atomic layers stacked by van der Walls forces, each layer is comprised of strong in-plane binding of S-Mo-S triple atomic planes.[104, 74] Depending on the arrangements of the S atom, the crystal structure can appear in two distinct symmetry(2H and 1T) as expressed by Figure 3.2, the phases can be easily converted to each other through an inner layer atomic plane glide, which involves a transverse displacement of one of the S-planes. The 2H phase demonstrates hexagonal lattice with a threefold symmetry with an atomic stacking sequence of ABA (S-M-S), whereas the 1T phase similarly shows atomic stacking sequence of ABA (S-M-S) however, the S-
plane occupies the hollow center of the 2H hexagonal lattice.[104, 74, 103] This S plane glide occupies the hollow center site of the 2H hexagon, thus resulting in a 2H→1T phase transition (Figure 3.2). Due to weak interactions between these monolayers coupled with much stronger interlayer interactions, the formation of ultrathin crystals of MoS$_2$ by micromechanical cleavage technique has been demonstrated. Systematic studies of the evolution of the optical properties and electronic structure of ultrathin MoS$_2$ crystals have been demonstrated and shown to be as a function of layer numbers. To further modify the activity of the structure towards nitrogen, sulfur atoms have been desorbed from the top surface. This has been achieved experimentally using a UHV anneal process [12].

3.4 Bi$_2$MoO$_6$ Structure

Researchers have previously studied step metal surfaces of the Bi$_2$MoO$_6$ orthorhombic structure, and very little research has been done on Bi$_3$FeMo$_2$O$_{12}$ monoclinic structure. The following study has performed calculations on a basis for configuration of (Bi$_x$M$_y$)$_2$MoO$_6$ where (M = Fe, La, Yb) sub-configurations of both the orthorhombic and monoclinic structures. It is noted that ratios of the expressed systems are the same; however, the Bi$_2$MoO$_6$ based structures are of orthorhombic crystal structure and Bi$_3$FeMo$_2$O$_{12}$ based structures are of monoclinic crystal structure. This permits investigations of reaction intermediates for both the dissociative and associative mechanisms on Bismuth containing structures for Fe, La, and Yb transition metals, and also allows the study of stepped and closed packed metal surface relations. The expressed analyses of this study utilize fundamental calculations to construct Gibbs energy diagrams for both the dissociative and associative reaction pathways. These diagrams will be used to determine the lowest potential barrier across the investigated metal configurations, this will be the barrier required to overcome in each configuration to evolve the reaction.

The material of interest is Bi$_2$MoO$_6$ shown in Figure 3.4 for the orthorhombic and monoclinic configuration, has received tremendous attention due to the attractive opti-
Figure 3.4 Illustration of the Bi$_2$MoO$_6$ in orthorhombic and monoclinic configurations. Sub-figure A is orthorhombic unit cell made up of 24 O atoms, 8 transition metal atoms (Bi) and 4 Mo atoms, sub-figure B is monoclinic unit cell of the same ratio number of atoms making a total of 36 atoms in each configuration. Fe, La, and Yb are subbed into the 8 metal atom positions (Bi) for both structures. The 10 Å vacuum in A is placed along the [010] plane and in B is placed along the [100] plane. Indicated distances for sub-figure A shows the internal bond length between M-O-Bi.

Bi$_2$MoO$_6$ has been identified as a promising photocatalytic material due to Aurivillius layered structure comprised of MoO$_6$ octahedron and Bi-O-Bi layers as shown in Figure 3.4A and B.[11, 18, 105] Aurivillius is a form of perovskite structure that is built by alternating layers of (Bi$_2$O$_2$)$_{2+}$ and pseudo perovskite blocks and these perovskite layers are ’n’ octahedral layers in thickness, thus making (Bi$_2$O$_2$)$_{2+}$ layers in-between MoO$_6$ octahedral layers that are connected to each other corner-sharingly. Electron-hole pairs will migrate easily and transfer effectively to the surface of a corner-sharing structure, due to the contribution of photocatalytic performance under visible light.[80, 105] Experimental observations have approximated the band gap of Bi$_2$MoO$_6$ to 2.56-2.63 eV, [11, 79, 80, 18, 105] with unique physical and chemical properties, such as environmental friendly, chemical inertness and...
photo stability features, making them ideal photocatalytic materials.

Bi$_2$MoO$_6$ structure is unique in it forms a layered structure where individual layers are primarily held together with electrostatic forces. The main structural modification that was done is the substitution of the non-organic ion Bi with various combinations in all possible positions in the unit cell of (BiM)$_2$MoO$_6$ (M = Yb, Fe, La). It is noted that calculations are done for Bi$_2$MoO$_6$ based structures in both the orthorhombic Figure 3.4A and monoclinic Figure 3.4B configuration. It is further noted that for BNF Mo-O plays an important role in attracting nitrogen to the surface which proves to be ideal for nitrogen fixation (Mo acts as a N activation center in the Mo-O coordination [80, 11]), thus even though the monoclinic configurations of Bi$_2$MoO$_6$ (Figure 3.4B) demonstrate similar properties as the orthorhombic configuration (Figure 3.4A), its still theorized that monoclinic structure will not yield dramatically better results [105]. This is because the Mo-containing complexes are located in the center of the monoclinic structure Figure 3.4B, thus making the recombination between the holes and electrons to be weak [105], and ideally for nitrogen fixation the interaction of Mo and N species are of most importance. Looking at orthorhombic configuration, Figure 3.4A, the first layer N species will see in this configuration is the aliened Mo atoms, reference Figure 6.1, that prove to better stabilize N species then that of monoclinic configuration. Never the less the monoclinic configuration is still looked at for comparability and data collection.

To further validate calculations on the two phase of the orthorhombic structure (that is based on Bi$_2$MoO$_6$) and the monoclinic structure (that is based on Bi$_3$FeMo$_2$O$_{12}$), calculations of the powder diffraction patterns are analyzed to ascertain the calculations done for the reaction pathways for the correct configurations. Figure 3.5 demonstrates the XRD pattern of the two configurations calculated for the theoretical and experimental results. The theoretical calculations are for unit-cells of relaxed structure where as the experimental is for polycrystalline unit-cells that may contain impurity states. This means that one would expect the experimental to produce broader peaks that may result from the resolution and combination of various peaks detected by the equipment and that the theoretical calculations
Figure 3.5 Illustration of the diffraction patterns for Bi$_2$MoO$_6$ in orthorhombic and Bi$_3$FeMo$_2$O$_{12}$ in monoclinic configurations of the experimental and theoretical calculations. The theoretical calculations are of T = 0 K for ideal crystalline unit cells, whereas experimental is done at room temperature for polycrystalline unit cells which tend to have some impurities, thus resulting in some variations in diffraction pattern.

will result in sharper peaks, which is true of Figure 3.5. It is noted that peak positions are aliened in Figure 3.5, which suggests that calculations done on the expressed configurations in Figure 3.4 are consistent with the experimental configurations analyzed.

3.4.1 Bi$_2$MoO$_6$ Design Space

Utilizing components that lie from both the dissociative and associative side is also expressed for this structure. This will allow structures to be designed for more effective breaking of the N-N bond by allowing good ratios of N and H species affinity, where associative protonation requires better H affinity where as the initial braking of N-N for the dissociative will require more N affinity. Initial DFT calculations express Bi$_2$MoO$_6$ orthorhombic and Bi$_3$FeMo$_2$O$_{12}$ monoclinic structures to favor the dissociative side and with the addition of
Fe, La, and Yb, which can favor the associative mechanism, the material of interest takes the form of $(\text{Bi}_x\text{M}_y)_2\text{MoO}_6$ ($\text{M} = \text{Yb, Fe, La}$) for orthorhombic and monoclinic configurations. Main structural modification that was conducted is the substitution of the Bi atoms with various combinations of the 8 possible positions in the unit cell Figure 3.4A and B. The 8 atomic positions of both orthorhombic and monoclinic structures that were modified are clearly shown in Figure 3.4 of the unit cell. All element configuration combination of the three elements (Yb, Fe, La) is implemented and tested in the metal positions expressed in Figure 3.4 of the unit cell. These configurations are classified under one element case (pure Bi, Yb, Fe, La structure) and two element cases (combination of Bi and Yb, Bi and Fe, Bi and La).

It is noted that while the $\text{Bi}_2\text{MoO}_6$ material is subbed with Fe, La, and Yb, combination of the two elements are evaluated in this study to better vary the mechanism of interest for each distinct adsorption species of $\text{N}_2\text{H}_x$ and $\text{NH}_x$ respectively. Of the two element case combinations, there are different configurations possible for same elemental ratios. Meaning the minority ion can be placed in several substitutional locations. This makes a total of 768 (2 elements for 8 positions for 3 structures $2^8 \times 3$ of Bi and La, Bi and Yb, Bi and Fe) unique configurations for orthorhombic and 768 configurations for monoclinic structures. Only the configurations that yielded the lowest energy of the relaxed case for each distinct structure will be evaluated for the electrochemical reactions. For example, configuration of 1 atom Bi and 7 atom Fe ($\text{Bi1Fe7}$) can have 8 distinct configurations of Bi being in any of the 8 metal positions, so only the lowest energy structure after the relaxation will be implemented in the electrochemical reactions, and this is the same for every other configuration for $\text{Bi}_2\text{MoO}_6$ based orthorhombic and monoclinic structures ($\text{Bi2Fe6}$, $\text{Bi3Yb5}$, $\text{Bi4La4}$, ...). Each configuration also had various operations that must be done in sequence to obtain proper data, like initial relaxation, screening of best configurations, then vacuum implementation and relaxation.

This resulted in a total of 27 configurations for orthorhombic and 27 configurations
for monoclinic structures that had the lowest energy structure for a specific configuration. The reader should note that this is a tremendous amount of computational and analytically challenging process. The brute force approach allows every configuration of the orthorhombic and monoclinic structures to be explored and give the best configuration of (Bi$_x$M$_y$)$_2$MoO$_6$ (M = Fe, La, Yb) structure as a means of nitrogen reduction catalyst.

### 3.5 Experimental Synthesis for Bi$_2$MoO$_6$ Structures

Materials synthesis based on hydrothermal method, and are used to express the calculated results for (Bi$_x$M$_y$)$_2$MoO$_6$ in Figure 3.5 and Figure 3.6, and follows the listed procedures. Firstly for orthorhombic Bi$_2$MoO$_6$ structure: Na$_2$MoO$_4$·2H$_2$O was dissolved in 60 mL DI-water. Then Bi(NO$_3$)$_3$·5H$_2$O was slowly added to the above solution under vigorous stirring will pH was adjusted to 4-6. After stirring about 15 min, the suspension was transferred into 80 mL autoclaves and keep at 180°C for 20 h. Then when cooling down to room temperature, the product was centrifuged and washed three times with DI-water and ethanol. Finally, the powder was obtained by drying the solution at 60°C for 12 hours. For the 10% Lanthanum doped Bi$_2$MoO$_6$ and the 5% Iron doped Bi$_2$MoO$_6$ orthorhombic structure, an additional step was taken to add 10% La or 5% Fe respectfully into the precursor with same procedures taken as expressed above. Exactly the same steps are taken for Bi$_3$FeMo$_2$O$_{12}$ monoclinic structure synthesis with the addition of 25% Fe into the precursor solution.

Shimadzu 2550 UVVisible spectrometer equipped with an integrating sphere (UV 2401/2, Shimadzu) was used to obtain the absorption spectra under the diffuse reflection mode as shown for select compositions in Figure 3.6. XRD patterns are shown in Figure 3.5 were recorded by X-ray diffraction (XRD, X Pert Pro PW3040-Pro, Panalytical Inc.) with Cu K radiation.

The photocatalysis experiment is as follows, 50 mg catalysts disperse in 100 mL DI-water. Using high pressure Hg lamp as light source. N$_2$ was bobbled 30 min before illu-
minimized with light. During the photocatalytic reaction, $N_2$ was bubbling with 50 mL/min flow rate. 3 mL solution was taken out every 15 min. The concentration of ammonia was quantified by Indophenol blue method. The calibration curve is as follows, standard ammonium solution, phenol ethanol solution, sodium nitroprusside solution, sodium hypochlorite, mixture of sodium hydroxide and sodium citrate solution were pre-prepared. Oxidation solution was made by mix sodium hypochlorite and sodium citrate, sodium hydroxide solution before use. Standard ammonium solution was diluted to 0.5 $\mu$M, 1 $\mu$M, 5 $\mu$M, 10 $\mu$M, 25 $\mu$M, 50 $\mu$M, 75 $\mu$M and 100 $\mu$M respectively. 3 mL standard solution mixed with phenol, sodium nitroprusside and oxidation solution. Then maintained in the dark at room temperature for at least 1 hour to generate color. Then used DI-water as the reference and attained absorption intensity from spectrometer.

Figure 3.6 Plot of the experimental UV-Vis spectrum for orthorhombic structure of: $\text{Bi}_2\text{MoO}_6$, $\text{Bi}_2\text{MoO}_6$ doped with 10% La, $\text{Bi}_2\text{MoO}_6$ doped with 5% Fe, and monoclinic structure of: $\text{Bi}_3\text{FeMo}_2\text{O}_{12}$. The fraction of $(\text{Bi}_x\text{M}_y)_2\text{MoO}_6$ ($\text{M} = \text{Fe}, \text{La}, \text{Yb}$) correspond to the percentage of Fe, La, Yb implemented in structure synthesis for the eight positions available for substitution. The corresponding experimental band gap values can be found in Table 6.1.
Based on linear relationship between absorption intensity and standard ammonium concentration, a calibration curve is developed for quantification of ammonia in the reaction, shown in Figure 3.7. From Figure 3.8, for bare Bi$_2$MoO$_6$, ammonia product rate is $4.7 \mu$Mh$^{-1}$ (0.5 g/L catalysts). Compared with bare sample, 5% Fe doped Bi$_2$MoO$_6$ has ammonia product rate, which is $6.9 \mu$Mh$^{-1}$ (0.5 g/L catalysts) higher than that of undoped one. This experimental results illustrates that the dopant Fe could enhance N$_2$ activation and
Figure 3.8 Plot of ammonia concentration (production rate) vs. time maintained at room temperature to generate color for ammonia quantification of Bi$_2$MoO$_6$ and 5% Fe doped Bi$_2$MoO$_6$. Catalysts concentration 0.5 g/L, ammonia rate is 4.7 $\mu$Mh$^{-1}$ for Bi$_2$MoO$_6$ and 6.9 $\mu$Mh$^{-1}$ for 5% Fe doped Bi$_2$MoO$_6$.

reduction, which is consistent with our computational results as discussed in Chapter 6.

3.6 Implemented DFT Computational Parameters for Nitrogen Fixation

Thermodynamic ground state properties were approximated for thermodynamic steps that assisted this study to analyze various configuration reaction steps by means of density functional theory (DFT) approach. [98] DFT calculations relied on functional form of the pseudo-wave function that is based on Perdew-Burke-Ernzerhof [99] (PBE) exchange-
correlation function at potentials with a cut-off wave function energy of 1.5 keV (110 Ry) and a density cut-off radius of 1.8 keV (1320 Ry), which proved to be very accurate and stable for the studied unit cells. In addition, a ultra-soft pseudo-potential and pseudized wave function was implemented to allow the reduction of computational expense for which this study greatly benefited due to the various configurational combinations these structures had that this study aimed to explore. Also, to further reduce the computational expense, only a single primitive cell was simulated for each configuration. Monkhorst-Pack with a k-point mesh sampling 2x2x2 grid with an offset of 1/2,1/2,1/2. For relaxation a 10 Å vacuum was placed on top of the slab. The k-point grid for super-cells with vacuum was a gamma point grid. Van der Waals correction term [106, 107] was incorporated to account for the Van der Waals interaction, which allowed some empiricism into the calculation. Scaling parameters were specified to be 0.7.

By solving the electronic densities self-consistently, adsorbates (N, H, NH, etc.) sitting on the structure and unit cell, geometries were relaxed to a relative total energy less than $1 \times 10^{-10}$ and overall cell pressure of less than 0.5 kBar. It is noted that the unit cell was relaxed with the vacuum before any absorbates were implemented in the structure. Then once relaxation of the structure in the vacuum was done, the substrate atoms were kept fixed and the adsorbates were allowed to relax on the surface of the structure in the 10 Å vacuum. The reader should note that DFT predictions of energies and band gap are often under predicted due to the over-analyticity of the functionals and exchange-correlation terms that need to be calculated. Thus the reported energies in this study should not be used as absolute, but used to study the trends for various structure configurations.

3.7 Employed Computational Methods for High-Throughput Data Structuring & Analyzing

This section pertains to discussions regarding computational steps taken on large data analyses such as generating files, organizing and manipulating structure design space,
and screening of best possible configurations. From Section 3.3 and Section 3.4, one gets a brief overview on the large scale structure uniqueness needed to be analyzed for compositional design space. It should be noted that if a configuration demonstrates the capacity for substitutionalization of various elements in various potions, the task to find each configuration grows exponentially as the number of available substitution position grows. The total number of possible configurations for a system is given by,

\[ C(N, P) = N^P, \]  

(3.29)

where \( C \) is the number of possible unique configurations, \( N \) is the number of elements wanting to substitutionalize, and \( P \) is the number of available positions that the substitutionalized elements can be in. For example, the 1T MMOs\(_2\) system that has 3 elements (Mo, Fe, Co) to sub in 8 positions in any order, that is 6561 (3 elements for 8 positions \( 3^8 \)) unique configurations. That is why steps attained from various trial and error proceedings to automate these self generating and self analyzing tasks that implement Matlab for: large file generation, file editing, structural configuration management and large data analyses, bash scripting for: large file submission and management, quantum espresso tool for DFT calculations, and basic but extremely powerful scripting commands for quick data editing and simple manipulation of files. Also, demonstrate steps dealing on how to use most of these tools effectively and together with minimal effort.

### 3.7.1 Finding & Screening all Unique Configurations

The initial step in finding all possible configurations is to start with a structure that works, for example in the case of 1T MMOs\(_2\) (M= Mo, Fe, Co) system, the structure was based on pure MoS\(_2\) 1T phase. This structure will serve as a base for all other 1T MMOs\(_2\) (M= Mo, Fe, Co) structures. The initial step is to find the pure case atomic positions (related structure) and all parameters that work for this base structure, reference Appendix
A for reference input (’mos2.pw.in’) file that was implemented into quantum espresso plane wave solver for the 1T MoS\textsubscript{2}, this file should only be used as reference. Also, the run file used to submit the job for that input file is expressed in Appendix A (’run\_pw\_pbe.pbs’). After relaxation is done the output file should contain the atomic positions and cell parameter for the relaxed structure. Its noted that this initial step is the most important step because all other files of the 1T M\textsubscript{M}oS\textsubscript{2} (M= Mo, Fe, Co) system is based on this file, so cation is advised to correctly find the parameters that will work for this configuration. The rezone for this step is to reduce computational expense because the atomic positions and cell size for the pure 1T MoS\textsubscript{2} gives good initial atomic location for all configurations of 1T to start being relaxed from. Then once the parameters are found all configurations can thus be made according to those parameters, note this is repeated for 2H and bismuth containing structures of orthorhombic and monoclinic configurations. Making a total of 4 reference structures for this study (1T, 2H, orthorhombic, monoclinic), once these structures are found the process of finding all configurations can start.

Figure 3.9 shows the structure format of all files pertaining to the studied configurations. The next step is to generate the input and run files for all expressed configurations so that steps to find the relaxed atomic positions and unit cell can be calculated for the corresponding configurations. Examples of matlab source code used to do this is expressed in Appendix B 'configurations.m', where the corresponding configurations are of permutation of all possible positions Appendix B 'permn.m'. This is a way to generate the file structures expressed by Figure 3.9. The idea is to use the reference file from step one and only manipulate the positions for the subbed elements in the input file as expressed in Appendix A for input file (P1, P2, ...). Once these files are generated the relaxation of the unit cell and the atoms can thus be done. Its noted that the relaxation processes for all the configurations is the most computationally and time intensive step. Its also noted that on average trials for each case that proved to have the minimum energy and best relaxed configuration allays turns out to converge with less time due to the structure demonstrating better stability thus
Figure 3.9 Illustration of how the structures are organized. 2H has 2187 unique trials, 1T 6561 trials and both the orthorhombic and monoclinic has 768 trials making a total of 10284 unique configurations for this study. The last row represents trials 1 through 7 for Co1Mo6 case and 1 through 8 for Bi1La7 case.

The last row represents trials 1 through 7 for Co1Mo6 case and 1 through 8 for Bi1La7 case.

faster convergence/computational time. For example looking at Co0Mo7 in Figure 3.9, Trial 1 through 8 are relaxed and only the best case/lowest energy relaxed structure from the trials are used for more analyses, all other trials in that family are deemed not ideal.

Thus the screening process can further reduce the computational expense by running relaxation step for each structure with a low number of optimization steps and or electron maximum step. These parameters can be tuned in the input file for the respected configuration, and these parameters correspond to the number of structural optimization steps performed in run (optimization step) and number of iterations for molecular dynamics or ionic relaxation taken for each configuration (electron step). The rezone is that configurations that can converge with less iterations proved in this study to be the best cases, and anything that exceeds the number of iterations is deemed not converging because they would require allot more iteration steps. This is a perimeter that must be fine tuned in the initial step, but its noted that for this study the electron max step, the number of ionic relaxations...
done is 100 for each iteration of the optimization step for 200 maximum iterations. This allowed more than 50% of the trials to be screened out within the first four hours of each run. It’s noted that each case has to be run first to allow this screening process to work (all 10284 unique configurations), but after the first couple of hours only cases that prove to be more stable will continue running. Also, the cases that do continue to run will still take a long time before convergence, this step is to just utilize computational time for the best cases, by eliminating non ideal cases within the first couple of steps. On average each relaxation would be run for four hours on and off, this depended on which nodes the run was being submitted to, and for this study the standby q-system was the fastest to submit in the cluster, but had a limit of 4 hours. Thus the output file, which contained the relaxed atomic positions, energy, and unit cell parameter would need to be checked to see for convergence, none convergence, or need more iterations after the run was done each time and then resubmitted if need be.

3.7.2 Automating the Process of Checking & Submitting Files

Checking all the output files for relaxation steps proved to be quite a daunting task, thus source code generated to automate this process needed and is expressed in Appendix’s. Where matlab code was used to check the output file for ’JOB DONE.’, ’convergence NOT achieved after’, ’Begin final coordinates’, etc. reference Appendix B ’restart_trials.m’. These phrases are expressed for the generated output file for each run from the quantum espresso solver and may differ for other solvers. The only thing that this file needed is to be run inside the directory that houses the different configurations, like orthorhombic directory which houses all the configurations of BiXLaX, BiXYbX, BiXFeX (X= 0, 1,...,8) as seen in Figure 3.9. Note that the ’restart_trials.m’ file in Appendix B is just comprised of logic statements and can be manipulated very easily according to the needs of the user; this code generates output files that express the crashed cases and or the converged cases. Its noted that the restart file shown in Appendix B also changes the name of the run files from
'_runpw_pbe.pbs' to '_runpw0_pbe.pbs' for converged cases. This leads on to the next step, which is to submit the files that still need to continue running, the best method was found to submit all files at once like expressed in Appendix C for script '_submit_all_pw'. This file is run inside the directory and will go inside sub-directories and submit files that have the run file name '_runpw_pbe.pbs' thus allowing only the pw and not the pw0 files to be run. Another method was to take the files generated by the matlab 'restart' file, which are just the generated directory names of files, and to submit those without going inside all directories, this is expressed in Appendix C for '_submit_from_input_pw'. This file will only look at the text file named 'restart.out' that has the directory name for files needed to be submitted. Other useful scripts to quickly edit and modify large quantity of files are expressed in Appendix C; however, this is just examples and can be easily modified based on needs.

The example script called 'run' in Appendix C shows how these files can work in unison. To run this file one needs to execute the command .\run in the terminal. However, this file can be run in the background while the user is logged out by executing the command nohup .\run &. The nohup command is used to run script while the user is logged out the & is used to run in the background so that the user can still operate the terminal. Now upon executing the run file expressed in Appendix C 'run', the script will initially lode the matlab module. Then wait for 2 hours and run matlab code called 'restart_trials' (Appendix B) which generates a file called 'restart.out' that contains the directory name of all files that need to be submitted. After the matlab file 'restart_trials' is done the script will execute the '_submit_from_input_pw' (Appendix C) which will only read the generated file 'restart.out' and submit (qsub) the job '_runpw_pbe.pbs' into the cluster. After submitting is done the script will wait another 2 hours and repeat for 6 iterations till completion, the iteration count can be increased or decreased respectfully. It is noted that this is a very simple way to continuously check and submit jobs into the cluster with minimal user interference due to the nohup command, which allows continuous running of script when user is logged out.
This is effective for the 4 hour standby q-system that these files are submitted to; this was the quickest way found to submit large number of jobs. It is more effective to submit to q-system that is not limited to 4 hours if the number of jobs is low; however, there is a large wait time if user has to submit a large quantity of jobs as this study needed to complete calculations. Thus the 4 hour standby q-system is used, which had less wait time for job submission.
CHAPTER 4

THEORY & METHODOLOGY: PROPOSED MACHINE LEARNING APPROACH

Implementing a neural network to any problem requires input features (specified by user) to be mapped to some target output in some non-trivial way. In this study, a supervised neural network (NN) is applied to a data set consisting of inputs (features that describe atomic classification in a unit cell) to be mapped on desired output (expressing atomic positions in a unit cell and total ground state energy).

4.1 Model Design Space Implemented for the Machine Learning Approach

This study focused on the substitution of La and Yb into the bismuth-based structure \((\text{Bi}_2\text{MoO}_6)\) as shown in Figure 4.1. The main structure modification that was looked at is the substitution of La and Yb atoms for the Bi atoms in various combinations of the 8 possible positions occupied in the unit cell expressed in Figure 4.1 for atom position numbers 3, 16, 17, 18, 19, 20, 21, 22. Thus all combination of Bi and Yb, Bi and La are explored in an attempt to express a method for machine learning that can reduce the computational cost of exploring the substitution for a structure system. A usual method implemented for substitution is to calculate all possible combinations that the substitution can occur in the structure, which is a very computationally heave method. To put this in perspective, for the structure system explored in this study, more then 300 unique configurations are evaluated, this is a classical permutation problem. For example, if to say we are looking at 1 Yb atom and all 7 Bi atoms implemented into the structure, Yb could potentially occupy any of the 8 positions in the unit cell, thus 8 unique combinations can be expressed for the Yb 1/7 Bi ratio. Thus this study aims to express a viable solution to the permutation problem so that not all structures
Figure 4.1 Illustration of the Bi$_2$MoO$_6$ in orthorhombic configuration that is used as the example structure system to test the machine learning approach for this study. The orthorhombic unit cell is made up of 24 O atoms 8 transition metal atoms (Bi) and 4 Mo atoms making a total of 36 atoms in a unit cell. La, and Yb are subbed into the 8 metal atom positions (Bi) (atom position numbers 3, 16, 17, 18, 19, 20, 21, 22). These is the initial state of all DFT calculated structures and thus the numbers that correspond to each atom are the same for any configuration. All calculated DFT data is referencing the same atom position number to keep consistency, thus all attained calculations of position are for the same atom position number.

are needed to be explored in a system, and if structures are explored, to express a better production of the initial state (initial configuration of the unit cell) of the system to reduce computational cost. The way proposed in this study is to use machine learning technique to predict the fractional coordinates for all atoms that make up a unit cell (Figure 4.1), and predict the total ground state energy for structure system which expresses a more viable solution to screen large design spaces. The model for the machine learning approach is DFT simulations of atomic structures, and also the validated results are compared to the DFT simulations.
Figure 4.2 Illustration A is the vector representation of input (charge number $Z$) and output (positions along the lattice vectors ($a$, $b$, $c$) in each unit cell). Illustration B is the artificial neural network architecture implemented for this study. It’s noted that the numbers indicated in this figure (such as $a_1$ or $Z_{36}$) are referencing the same numbers initially started for each unit cell in Figure 4.1 to keep referencing atomic number positions in the NN consistent.
4.2 Input & Output Data Sets for the NN Model

The data set consists of inputs in a set of atomic charges (atomic numbers) that make up a structure while the output of the network consists of fractional coordinates along lattice vectors \((a, b, c)\) of each atom position that make up one unit cell and the corresponding total energy. The reference/training \([(\text{Bi}_x\text{La}_y)_2\text{MoO}_6]\) and validation \([(\text{Bi}_x\text{Yb}_y)_2\text{MoO}_6]\) data is attained by consistent DFT calculations. It is noted that all calculated DFT structures initially start in the same configuration, Figure 4.1, which allows referencing input and output features consistent with the number that correspond to each atom position for all unit cells as expressed by numbers in Figure 4.1. The way the input and output features are expressed for the data set is by decomposing the input features (charges of atoms in the unit cell) and output features (atomic positions in the unit cell) as the vector representation expressed in Figure 4.2A. It is noted, that operations such as rotation, translation, and permutation to atoms in the data set (input and output) would ultimately change the ordering and positions of referenced atoms that make up the unit cell. Thus it is very important that the input and output features formed for the neural network reflect the same corresponding number in the sequence of vector input and output given to the neural network for each unit cell. This is why the order in which the numbers expressed in Figure 4.1 is maintained when classifying input and output vectors for each unit cell represented as the vectors in Figure 4.2A. Thus allowing the network to progressively see how individual output feature changes as a consequence of input vectors.

To reduce the complexity of solving the atomic positions and gain insight into fundamental and meaningful solutions to the problem given. This study imposes dimensionless quantities given to the neural network for data set interpretation, thus fractional coordinates are used for atomic positions. Understanding the energy as substitution occurs in the structure plays a central role in studies of chemical and biological systems. Thus the ground state energy of the relaxed structure became another very important feature the neural network was trained to calculate. Keeping the same idea of dimensionless quantity in mind, this study
proposes to express the energy as a ratio of the calculated sum of the individual energy that make up the structure constituent parts divided by the total ground state energy, which is referred to as the energy ratio in this study.

\[
\text{Energy Ratio} = \frac{\sum \text{Individual Energy of Constituent Parts}}{\text{Total Energy of Structure}}.
\] (4.1)

Thus the ground state energy is the DFT calculated energy and the individual energy of atoms that make up the system is just solving the self-consistent calculation for each individual atom. From this point forward energy is expressed as energy ratio. Unlike the output vector corresponding to each input vector for the fractional coordinates, the energy ratio is just a scalar representation of energy for each input vector. Thus the total ground state energy for each unit cell can be calculated simply by using the sum of energies that make up the individual part of the unit cell divided by the energy ratio.

4.3 Artificial Neural Network (ANN) Model

This study trains a neural network with all configurations of \((\text{Bi}_x \text{La}_y)_2\text{MoO}_6\), inputs being the atomic number (charge) of atoms that make up the unit cell structure and outputs being the fractional coordinates for each atom in the unit cell, then to validate this with configurations of \((\text{Bi}_x \text{Yb}_y)_2\text{MoO}_6\). General ANN model is a simple information processing unit with multiple inputs and output. A simple neuron within the architecture of the network is attaining inputs from other neurons or from the exterior through path modeling. The artificial neuron output is computed as the weighted sum of all inputs modified by an activation function. These weights are adjusted through the learning process of the ANN. The idea is to train the network with a given set of non linear input to output data set, in order to express patterns in the data set. The method implemented in this study is that of Radial Basis Function (RBF) ANN, where the network is comprised of three layers (Figure 4.2B), the input layer (IL), the hidden layer (HL) and the output layer (OL) [108].
Each layer in the RBF-NN has a different task [109, 110], the general architecture of
the RBF is expressed in Figure 4.2B. From the IL to the HL of RBF network the distance
between the network input and hidden layer centers is calculated. From the HL to OL the
weighted sum is computed for each neuron. Each neuron of the HL has a vector parameter
called center, and the general expression of the network is given as [109, 110],

\[ \bar{y}_j = \sum_{i=1}^{N} w_{ij} \phi_i, \]  

(4.2)

where, \( N \) is the number of neurons in the HL (\( i \in \{1, 2, ..., N\} \)), \( w_{ij} \) are the weight of
the \( i^{th} \) neuron and \( j^{th} \) output, \( \bar{y}_j \) is the neural network’s response to the \( j^{th} \) output, and \( \phi_i \) is
the radial basis function for the \( i^{th} \) neuron. The radical basis function is refereed to as the
activation function which is taken as the Gaussian function defined as,

\[ \phi_i = \exp[-\sigma_i \|x - c_i\|^2], \]  

(4.3)

where, \( \sigma_i \) is the spread parameter of the \( i^{th} \) neuron, \( x \) is the input data vector, \( c_i \) is
the center vector of the \( i^{th} \) neuron, and \( \|x - c_i\|^2 \) is the Euclidean distance. Figure 4.2B
expresses the architecture of the used RBF network. Note that for the structure system this
study is exploring the input vector (\( x \)) is a 1x36 vector (\( Z_1, ..., Z_{36} \)), the vector is passed to
the HL comprised of N neurons. At the HL each neuron calculates the Euclidean distance
between its center vector and the input vector, then calculates the Gaussian function (activa-
tion function) with the spread parameter specified (Equation 4.3). Then the output layer
calculates the weighted sum for each input multiplied by the neurons activation response
(Equation 4.2) to that input vector to get the output of the RBF network (\( \bar{y}_1, ..., \bar{y}_j \), where
\( M \) denotes the number of outputs (\( j \in \{1, 2, ..., M\} \)), being in this study the fractional
coordinates.

The training part of the NN involves determining the number of neurons in the HL,
and to attain the desired output for the network, the \( w, \sigma, \) and \( c \) parameters can be adjusted
and attained. The most common error reference response of the NN typically used is mean square error and sum square error to train the NN. Thus for this study the error-based expression used (supervised learning) is that defined as,

\[
\text{error}(w, \sigma, c) = \sum_{j=1}^{M} (y_j - \bar{y}_j)^2, \quad (4.4)
\]

where, \(y_j\) indicates the desired output, and \(\bar{y}_j\) is the network output. Thus ultimately the training steps for the network entails the minimization of the error function. The training algorithm for the NN utilizes three approaches. The first, is to use k-means clustering [111] for initially attaining the centers (c) for each neuron based on the input vectors. The second, is to have the weights (w) updated based on the activation function for the training set by using pseudo-inverse [112] of the activation function matrix used for all training sets. Lastly, using a gradient decent algorithm (GD) [113] to progressively update the spread for each neuron (\(\sigma\)), thus ultimately minimizing the error function.

### 4.4 Training Algorithm used for the RBF Network

To attain the desired result for the neural network output to the training parameters, the training algorithm follows three steps. The reader should note that this section is only referencing the training set in order to teach the NN model, and not for validation set. The first step used in the training algorithm is a k-means clustering [111] for input vectors of all training set to find the centers. The point of k-means clustering is to partition all the input vectors of training set into N clusters, N being the number of neurons specified, in which each input vector belongs to the nearest mean cluster, cluster is the center specified for the \(i^{th}\) neuron. However if the user wants to increases or decreases the number of neurons for the model a new k-means clustering has to be done to attain the new center for each neuron.

Before the second step the spread (\(\sigma\)) is initialized. Since the output of the HL multiplied by the weights is supposed to approximate the output training data as given in
Equation 4.2 or represented as follows,

\[
\begin{bmatrix}
\bar{y}_1^{(j)} \\
\vdots \\
\bar{y}_O^{(j)}
\end{bmatrix} =
\begin{bmatrix}
\phi_1(x_1, \sigma_1^{(j)}, c_1) & \ldots & \phi_1(x_O, \sigma_1^{(j)}, c_1) \\
\vdots & \ddots & \vdots \\
\phi_N(x_1, \sigma_N^{(j)}, c_N) & \ldots & \phi_N(x_O, \sigma_N^{(j)}, c_N)
\end{bmatrix}
T
\begin{bmatrix}
w_1^{(j)} \\
\vdots \\
w_N^{(j)}
\end{bmatrix}.
\tag{4.5}
\]

Here, \( O \) is the number of training data set’s, \( N \) being the number of neurons, \( c \) being the center that corresponds to each neuron, \( j \) represents the output feature approximating for (such as \( a_1 \) in Figure 4.2B). For example \( \bar{y}_O^{(1)} \) is the \( a_1 \) value for the \( O \) vector input \((x_O)\) whereas \( \bar{y}_O^{(2)} \) is the \( b_1 \) for the \( O \) vector input, reference Figure 4.2B. A much simpler way to write Equation 4.5 is as follows,

\[
\bar{Y}^{(j)} = \Phi^{(j)T} \cdot W^{(j)}.
\tag{4.6}
\]

For the second step the weights are computed by using the inverse of \( \Phi^{(j)} \) if it is a square matrix, being the number of neurons is the same as the number of the tanning set \((N=O)\), note that in this case the centers will just be the input vectors and the ANN will provide exact estimations for the training data, this is not recommended because the estimation will tend to over fit all desired inputs to the training data. However, if less neurons are used then will need to compute the pseudo-inverse \([112]\) of \( \Phi^{(j)} \), which is done for most cases, thus the weights are,

\[
W^{(j)} = [\Phi^{(j)}]^{-1} \cdot \bar{Y}^{(j)}.
\tag{4.7}
\]

It’s noted that \( Y^{(j)} \) is the desired output for the training data and thus the weights are updated this way for each updated spread of the Gaussian function \((\sigma)\). The final step in the training algorithm is updating the spread for each neuron \((\sigma)\) for the next iteration of the training algorithm to further minimize the error in the NN output to the desired output.
of the training set. The method used is gradient descent algorithm (GD) [113] which is a first order derivative based optimization algorithm used for finding local minimums for a function. The method takes small steps proportional to the negative of the gradient for the error function at current iteration to update the spread to the next iteration. The error function is defined as follows,

\[ Error^{(j)} = \sum [Y^{(j)} - \bar{Y}^{(j)}]^2, \] (4.8)

where, \( Y \) is the desired output of the training set, \( \bar{Y} \) is the NN output, and \( j \) is the output feature of the tanning set, same \( j \) represented in Equation 4.5-4.9. Thus the GD [113] algorithm is used to minimize the error and optimize the adjusting spread for each neuron by iteratively computing the partial derivative and updating spreads (\( \sigma \)) in parallel and follows this update,

\[ \sigma^{(j)}_{i+1} = \sigma^{(j)}_i - \eta \frac{\partial Error^{(j)}}{\partial \sigma^{(j)}_i}, \] (4.9)

where \( j \) is the output feature of the tanning set, \( i \) is the current iteration step, \( \eta \) is a small step size (referred to as the learning rate). Thus a simple summery of training is as follows:

1) Select the number of neurons and initialize the spread parameter for each neuron.

2) For the training set do k-means [111] algorithm to attain the center for each neuron.

3) Compute the activation for each neuron and get the weights for each neuron by pseudo-inverse approach [112].

4) Check to see convergence, if not converged do a GD [113] algorithm to update the spread for next iteration and repeat step 3.

The convergence criteria specified for this study is that the training epoch are iterated until the NN training output data set stops improving in accuracy for 100 epochs. The
optimization process implemented, is to carry out the training method 5 times using an order of magnitude smaller learning rate each time. It’s noted that \( w, \sigma, \) and \( c \) parameters very much relies on the number of neurons used for the network. Ultimately having more neurons than the needed amount causes the model to over fit the output to the training data set and increases the complexity of the network. Therefore the number of neurons used directly affects the performance of the network and has to be investigated based on desired result.

Once training is done approximating any set becomes relatively simple. First, the input for the desired approximation wanting to be evaluated is taken through each neuron by computing the Euclidean distance to each center of each neuron specified in the training set. Second the neuron computes the activation function (Equation 4.3) which describes the relationship of input to the center of that neuron. Then lastly the approximated output for the desired input is computed as the sum of all neurons activation function multiplied by the corresponding weights attained in the training set, thus solving Equation 4.6 for desired input and follows Figure 4.2B.

4.5 Implemented DFT Computational Parameters for Attaining Input & Output Features

Ground state properties and total ground state energies are approximated for relaxed configurations of a bismuth oxide structure system (see Figure 4.1), which assisted this study to implement a neural network that can analyze the relevant trends in data set by means of density functional theory (DFT) approach [98]. The DFT calculations used in this study implemented pseudo-wave function functional representation based on Perdew-Burke-Ernzerhof (PBE) exchange-correlation function. The PBE exchange-correlation function implemented at potentials with a cut-off energy wave function of 1496 eV (110 Ry) that demonstrated quite accurate and stable results for the studied unit cells of this study. The various configurational combinations that the bismuth structure had and this study explored,
benefited greatly in the reduction of computational expense due to the implementation of pseudized wave function. It is noted that all the DFT simulations for all configurations had the initial system to be that of bismuth based structure expressed in Figure 4.1. For all expressed DFT simulations, a Monkhorst-Pack with a k-point mesh sampled at 2x2x2 grid with 1/2,1/2,1/2 offset was implemented. To account for Van der Waals interaction, a Van der Waals correction term [106, 107] is implemented in DFT simulations, however this correction did introduce some empiricism into the calculations.

For the dispersion interaction, a cut-off radius of 12 times that of cut-off wave function is implemented, 1320 Å, with the scaling parameter specified as 0.7 for DFT simulations. The unit cell for each configuration geometry were relaxed to a relative total energy less than 1x10^-10 with an overall unit cell pressure less than 0.5 kBar by computationally solving the electronic density self-consistently. It is noted that DFT predictions of energies, band bap, etc. are known to under predict results because of the exchange-correlation terms that are needed to calculate and due to the over-analyticity of the used functionals. Thus the calculated configurations and energies are used not as absolute but to express a relationship between input and output features that the network model will be trained on to predict the trends for various configurations.
CHAPTER 5

RESULTS & DISCUSSIONS: NITROGEN FIXATION FOR THE MoS$_2$ BASED STRUCTURE

Reaction states of the adsorption energies in (Equation 3.4)-(Equation 3.22) are calculated for the various combinations of M$_x$Mo$_y$S$_2$ (M=Fe, Co) in a 1T and 2H structure. These results are used to estimate Gibbs energy change in elementary reactions (Equation 3.4)-(Equation 3.12) for the associative mechanism and (Equation 3.13)-(Equation 3.22) for the dissociative mechanism. Gibbs energy differences of elementary steps assisted in approximating the theoretical over-potential needed to overcome for the reaction to evolve. It is noted that the calculated theoretical over-potential for all structures are approximated with the absence of any kinetic considerations (Section 3.1.5) that may increase the required over-potential.

5.1 Adsorption Sites

Adsorption sites illustrated in Figure 5.1 of MoS$_2$ are used to demonstrate characteristics of adsorption states for all metals studied in this report because these sites have very similar trends; however, this is not to say that the binding energy is the same for different structures. It’s sufficient to say that combinations of M$_x$Mo$_y$S$_2$ (M=Fe, Co) 1T and 2H structures produce very small variations in adsorption sites. These sites are usually classified as adsorption sites of hollow, bridge, and on top, and typically each classification will be slightly geometrically different. Thus each structure (M$_x$Mo$_y$S$_2$ (M=Fe, Co)) will yield unique electronic properties that can be analyzed and structures that prove more stable can be found and investigated.

Figure 5.1 demonstrates these adsorption sites on MoS$_2$ monolayer, first hydrogen
Figure 5.1 Adsorption sites of the MoS$_2$ 1T structure. The adsorption sites presented for the MoS$_2$ 1T structure is only used for the adsorption types and not for actual bonding for all other metals in this study. This means that the species of NH$_x$ could bind more strongly to Mo, Fe, Co structure configurations studied.

molecule proved to be quite unstable on the surface and tended to lie on the crystal surface. Thus hydrogen proved to have a bonding site of bridge classification; however, a very small difference of energies was found between adsorption sites. Whereas nitrogen adsorbed to the surface on a hollow site and preferred to bind in a sigma (strong covalent bond, formed by overlapping between atomic orbitals) bond on the surface with two metal atoms, thus proving edge sites to be the most stable. Similar in the adsorption of N$_2$, however it is noted that N$_2$ molecule proved to have few stable adsorption configurations, due to the strong N-N bond.
The NH molecule binds to hollow sites, NH$_2$ to bridge sites, and NH$_3$ on-top sites and all proved to be stable structures (Figure 5.1 bottom row). However, in the case of N$_2$H, N$_2$H$_2$, and N$_2$H$_3$ species (Figure 5.1 middle row), they typically preferred to bond in a bridge site, and each nitrogen atom bonded to a metal atom similarly to the sigma bonding expressed for N and N$_2$ species (Figure 5.1 top row). Based on the adsorption sites, species’ configuration orientation changed slightly as more hydrogen atoms are implemented in the surface species. Weakening of the N-N bond is demonstrated when looking carefully at Figure 5.1, as a visual representation of the internal bonding length dramatically increases as more hydrogen atoms are implemented in the species. It is very apparent when looking at NH$_3$ adsorbed on the structure, were the internal bonding length is much greater to that of other species. Also, it is very apparent that nitrogen atom becomes further away from the metal atom as more hydrogen atoms become bonded to the respected nitrogen atom, this is demonstrated for BNF for the associative mechanism and shows the weakening of bonds between nitrogen and metal atoms.

5.2 Ammonia Formation on Surface of MoS$_2$ based Structures

For each surface composition, two morphologies (1T,2H) with several adsorbate species that conform to the two reaction pathways were investigated to predict the electrochemical reaction of each step for different mechanism configurations. Figure 5.2 and Figure 5.3 illustrate the electrochemical reaction which refers to the Gibbs energy of reaction steps (Equation 3.4)-(Equation 3.12) ($\Delta G$4-$\Delta G$12) for the associative mechanism and (Equation 3.13)-(Equation 3.22) ($\Delta G$13-$\Delta G$22) for the dissociative mechanism of 1T and 2H structures.

DFT calculations show that a N$_2$ molecule binds to all surfaces of 1T and 2H structures with an adsorption energy that is always slightly more negative when compared to all other reaction steps, (Figure 5.2 and Figure 5.3 A,C dissociative $\Delta G$14 and B,D associative $\Delta G$5). The large loss in enthalpy in going from gas phase N$_2$ to a surface bonded molecule, this corresponds to a slightly negative Gibbs energy under ambient conditions for the 1T and
Figure 5.2 Cumulative Gibbs energy for the dissociative (A) and associative (B) mechanism for 2H morphology. Energies are attained from DFT calculations for an electrolyte with pH=0 at T = 0. The energies correspond to reaction steps (Equation 3.4)-(Equation 3.12) for the associative mechanism and (Equation 3.13)-(Equation 3.22) for the dissociative mechanism relative. Each grouping can be associated with the potential-energy curve for successive reactions.
Figure 5.3 Cumulative Gibbs energy for the dissociative (C) and associative (D) mechanism for 1T morphology. Energies are attained from DFT calculations for an electrolyte with pH=0 at T = 0. The energies correspond to reaction steps (Equation 3.4)-(Equation 3.12) for the associative mechanism and (Equation 3.13)-(Equation 3.22) for the dissociative mechanism relative. Each grouping can be associated with the potential-energy curve for successive reactions. The best performing structure and morphology is (Mo$_6$Fe$_2$)$_2$S$_2$ 1T phase (C).
2H structures. For the most part, the associative mechanism for both structures (1T and 2H) tend to have the potential determining steps (largest positive step to overcome) in the reduction to form ammonia, this is the addition of one hydrogen atom to transition from \( \text{N}_2 \) to \( \text{N}_2\text{H} \) (Figure 5.2 and Figure 5.3 from \( \Delta G_5 \) to \( \Delta G_6 \)), and addition of one hydrogen atom to go from \( \text{NH}_2 \text{NH}_3 \) (Figure 5.2 and Figure 5.3 from \( \Delta G_9 \) to \( \Delta G_{10} \)). This hydrogenation step corresponds to a positive step that is needed to overcome from Gibbs energy formation of \( \text{N}_2 \) and \( \text{NH}_2 \) on the surface, which is also deemed as a large energy barrier that is associated with the binding of hydrogen from the gas phase.

Typically the addition of hydrogen atoms promotes a positive step in Gibbs energy for most surfaces investigated and the first hydrogen step (from \( \Delta G_5 \) to \( \Delta G_6 \)) appears to be the most uphill in Gibbs energy for all hydrogen steps. However, the over-potential in the dissociative mechanism for both morphologies (1T and 2H) is most significant when initially trying to break the N-N bonding going from \( \text{N}_2 \) to N (Figure 5.2 and Figure 5.3 from \( \Delta G_{14} \) to \( \Delta G_{15} \)), this is very likely to occur due to N-N bond which binds in a di-sigma bond that is a very strong valent bond formed by overlapping between atomic orbitals that are very hard to overcome. Even thou \( \text{N}_2 \) binds to the surface with a negative adsorption energy from the significant loss in entropy from the gas phase, this is not enough to overcome this initial potential to brake N-N bonding without applying an external potential. It is also noted that for both the associative and dissociative mechanism of 1T and 2H structures (Figure 5.2 and Figure 5.3) the last three steps (associative B,D: \( \Delta G_{10} \) to \( \Delta G_{11} \) to \( \Delta G_{12} \) and dissociative A,C: \( \Delta G_{20} \) to \( \Delta G_{21} \) to \( \Delta G_{22} \)) are typically positive steps in Gibbs energy associated with the reduction of \( \text{NH}_3 \) on the surface to \( \text{NH}_3(g) \) this is due to a large gain of entropy going from surface bounded molecule to a gas phase.

5.3 Adsorption of \( \text{N}_2\text{H}_x \) and \( \text{NH}_x \) Species on Fe and Co Configurations

The associative mechanism initially relies on adsorbed configuration steps of \( \text{N}_2\text{H}_x \) molecules whereas the dissociative mechanism initially relies on adsorbed configuration steps
of NH$_2$ molecules. The associated Gibbs energies of these reactions depend on both the morphology and composition of the surface. In this study stable configurations of the surface, which is determined based on the formation energy predictions, are presented. The solid solution stability is important in the MoS$_2$ structure because both CoS$_2$ and FeS$_2$ forms pyrite structures. This means that only concentrations below fifty percent are stable in the MMoS$_2$ structure before pyrite is formed. Therefore, as shown in Figure 5.4 the results are depicted for only the stable compositions of MMoS$_2$ and not the pyrite phase.

First, it is known that the catalytic activity of the plane parallel to the lateral or horizontal axis (basal plane) of a pure 1T and 2H MoS$_2$ configurations mainly becomes apparent from the structure’s affinity for binding hydrogen at surface S sites. Meaning that one would expect configurations comprised of more Mo atoms to have hydrogenation steps (associative: $\Delta G_5$ to $\Delta G_6$, $\Delta G_9$ to $\Delta G_{10}$, and dissociative: $\Delta G_{15}$ to $\Delta G_{16}$) which corresponds to the largest positive step that needs to be overcome from Gibbs energy formations of N$_2$ to N$_2$H ($\Delta G_5$ to $\Delta G_6$), NH$_2$ to NH$_3$ ($\Delta G_9$ to $\Delta G_{10}$), and N to NH ($\Delta G_{15}$ to $\Delta G_{16}$). This can be seen in Figure 5.2 and Figure 5.3, where more concentrations of Mo in the structure yields positive steps at the depicted formation energy regions (associative: $\Delta G_5$ to $\Delta G_6$, $\Delta G_9$ to $\Delta G_{10}$, and dissociative: $\Delta G_{15}$ to $\Delta G_{16}$). Also, one would expect structures to have hydrogen as a large positive step, due to internal bonding length of N-N dramatically increases as more hydrogen atoms are implemented in the species (Figure 5.1).

Second, nitrogen binds in a sigma bond (that is formed by overlapping between atomic orbitals) on the surface with metal atoms, and that Co and Fe atoms have a higher affinity to nitrogen than Mo atoms. Thus causing structures having more concentration of Fe and Co to have the positive determining step associated with braking N-N bonding (dissociative: $\Delta G_{14}$ to $\Delta G_{15}$ going from N$_2$ to N) because nitrogen binds very strongly to Fe and Co atoms compared to Mo. This can be seen when looking at lower concentrations of Mo atom in conjunction with a higher concentration of Fe and Co atoms in Figure 5.2 and Figure 5.3 of the dissociative mechanism going from N$_2$ to N ($\Delta G_{14}$ to $\Delta G_{15}$).
Figure 5.4 Ternary plots of the maximum reaction barrier for all successive reactions for the three inorganic components and the 2H (top) and 1T (bottom) morphologies. The contour colors corresponds to the energy of the most difficult step to overcome for reaction steps (Equation 3.4)-(Equation 3.12) for the associative mechanism and (Equation 3.13)-(Equation 3.22) for the dissociative mechanism. The white region of ternary plots corresponds to pyrite structure formation, which was not considered. The star in the figures represents the best possible configuration for the given pathway and morphology. The best points are tabulated in Table 5.1.
Based on the two aforementioned ideas, one would expect a region where there is a
shift between which positive step to be more dominant, either hydrogenation step or N-N
bonding breaking step. In fact based on the dissociative mechanism illustrated by Figure 5.2
and Figure 5.3 (A,C), one can see the largest step going from $\Delta G_{14}$ to $\Delta G_{15}$ ($N_2$ to $N$) to
dramatically increase when more of Fe and or Co is implemented in the structure, because the
strong sigma bonding with N-N and metal atoms. However, when the ratio of Mo to Fe/Co
shifts from a structure containing more Mo atoms, the largest positive steps are affiliated with
the hydrogenation as expressed by the associative mechanism of Figure 5.2 and Figure 5.3
(B,D) going from $\Delta G_{5}$ to $\Delta G_{6}$ ($N_2$ to $N_2H$), $\Delta G_{7}$ to $\Delta G_{8}$ ($N_2H_2$ to $N_2H_3$), and $\Delta G_{9}$ to
$\Delta G_{10}$ ($NH_2$ to $NH_3$) due to the first expressed idea of this section. To better illustrate this
concept of shifting of positive steps and also to help determine the best structures for this
mechanism, ternary plots of the maximum positive (Gibbs energy) step to overcome for a
give reaction pathway is illustrated in Figure 5.4.

5.4 Onset Maximum Positive Determining Step for MoS$_2$ Based Structure

Figure 5.4A and Figure 5.4B illustrate the largest energy barrier that every composi-
tion for both morphologies must overcome. If this energy can be overcome by either an
applied electric field in the case of electrocatalyst or a photogenerate potential in the case of
photocatalyst, the reaction is free to evolve to completion. These values are in the absence
of any kinetic considerations that may increase the required over-potential. The white area
of the ternary plots corresponds to the formation of a pyrite structure. This is associated
with a high concentration of Fe/Co to Mo atoms are incorporated in the structure. The
points are associated with each DFT predictions. The contours are interpolation between
the DFT predictions. It is reasoned that the colored region is a continuous design space and
all compositions should be obtainable. The method of interpreting these plots is to recognize
that Mo, Fe, and Co bound the space at the corners of the triangle. Along the edges of the
triangle there is a binary composition of transition metals and within the triangle is a ternary
<table>
<thead>
<tr>
<th>Pathway</th>
<th>1T ($\eta$[eV])</th>
<th>2H ($\eta$[eV])</th>
</tr>
</thead>
<tbody>
<tr>
<td>Associative</td>
<td>Mo$<em>{0.75}$Co$</em>{0.25}$S$_2$ (1.23)</td>
<td>Mo$<em>{0.43}$Fe$</em>{0.57}$S$_2$ (1.14)</td>
</tr>
<tr>
<td>Dissociative</td>
<td>Mo$<em>{0.75}$Fe$</em>{0.25}$S$_2$ (0.10)</td>
<td>Mo$<em>{0.43}$Fe$</em>{0.57}$S$_2$ (0.35)</td>
</tr>
</tbody>
</table>

**Table 5.1** List of the best possible compositional points for each reaction pathway (associative and dissociative) and surface morphology (1T and 2H). These points correspond to the starred points in Figure 5.4. The associated over-potential determined is based on thermodynamic barrier energy and does not consider any kinetics. The best point overall is a Mo$_{0.75}$Fe$_{0.25}$S$_2$ 1T surface along the dissociative reaction pathway.

composition. Also, it is important to note that these plots are only representing the largest positive step attained from Figure 5.2 and Figure 5.3 by taking the difference between each step and only recording maximum positive step. This step is noted as the largest energy barrier to overcome, therefore, the lowest value in Figure 5.4 will be the best to implement because these structures will require the least amount of implemented potential.

Based on findings mentioned in Section 5.3, one can visually confirm in Figure 5.4 the shift in energy from a composition that has an affinity for hydrogenation to a composition with an affinity for N-N splitting. Where this shift is very clear for the dissociative mechanism of 1T and 2H structures, going from a pure Mo structure (bottom left corner) along the Fe/Co line. This region is saturated by higher energies toward the middle of the lower triangle for both the dissociative and associative mechanisms, but definitely more apparent in the dissociative mechanism. It is also noted that the highest energy for the associative 2H (Figure 5.4A) mechanism is attained for a pure Mo structure because the 2H structure has more Mo atoms and in turn, has higher affinity to H. The largest positive potential is associated with the hydrogenation, first point discussed in Section 5.3. This can be further convinced by the accept performance of 2H MoS$_2$ for HER.

Focusing on the minimum positive potential for the 1T and 2H associative (Figure 5.4(B,D)), where the associative mechanism tends to have more hydrogenation step to gradually weaken the N-N bonding till the very last steps. One would expect a structure
having more Mo atoms and few Co/Fe atoms to be more dominant. This is seen for the 1T and 2H associative mechanisms, where the mechanism preferred Co atom due to the fact that Co is more electronegative than Fe. That is way higher concentration of Fe that is needed to satisfy the same energy levels as fewer Co implemented in the structure. Of course, this is not a unary or binary transition metal composition because the mechanisms still need to have hydrogenation and N-N bond breaking steps to fully form NH\(_2\) from N\(_2\). Therefore, structures have to have a balance of atomic components that both have an affinity for hydrogenation and N-N bond breaking. The structure that proves to have the best performance for the associative mechanism is a combination of 2Co and 6Mo atoms (Mo\(_{0.75}\)Co\(_{0.25}\)S\(_2\)) in the 8 metal positions for 1T structure and 3Mo and 4Fe atoms (Mo\(_{0.43}\)Fe\(_{0.57}\)S\(_2\)) in the 7 metal positions for the 2H structure that resulted in approximately 1.23 eV for the positive limiting step (over-potential ignoring kinetic considerations). The 1.23 eV over-potential is within the band gap energy of MoS\(_2\). Further investigation is required to determine the change in and gap energy for the compositional space.

Contrary to the associative mechanism, for the 1T and 2H dissociative (Figure 5.4) mechanisms, the N-N bonding is broken on the second reaction and the latter steps in the reaction are responsible for hydrogenations. Based on the claims for the associative mechanism, a structure with lower affinity to nitrogen will be associated with Fe-containing composition and reactions associated with a hydrogen containing species tend towards Mo incorporated compositions. This requires a balance structure also needs to effectively associate the hydrogenation that happens late in the reaction. The 1T dissociative mechanism preferred to have 6Mo and 2Fe atoms (Mo\(_{0.75}\)Fe\(_{0.25}\)S\(_2\)) in the 8 metal positions and the 2H preferred to have 4Fe and 3Mo atoms (Mo\(_{0.43}\)Fe\(_{0.57}\)S\(_2\)) in the 7 metal positions that resulted in approximately 1 eV for the positive determining step. A summary of the best structure configurations for this study is shown in Table 5.1 with the respected theoretical over-potential calculated for both the associated and dissociated reaction mechanism for MoS\(_2\) base structures. It is also noted that these results should only be used as trends and not exact results because of
approximation in the DFT method. The surface can be expected to be covered with hydro-
gen atom that forms a natural environment that can’t be accounted for using the current approach. Also, the typical formation of hydrogen gas can end up being very fast unless the surface is covered with N adatoms rather than H adatoms, which contributes to possible discrepancies.
CHAPTER 6

RESULTS & DISCUSSIONS: NITROGEN FIXATION FOR THE Bi$_2$MoO$_6$ BASED STRUCTURE

All reaction states of the adsorption energies in (Equation 3.4)-(Equation 3.22) are calculated for the various combinations of (Bi$_x$M$_y$)$_2$MoO$_6$ (M = Fe, La, Yb) in the orthorhombic structure and the monoclinic structure. These results are used to estimate Gibbs free energy change in elementary reactions (Equation 3.4)-(Equation 3.12) for the associative mechanism and (Equation 3.13)-(Equation 3.22) for the dissociative mechanism. Gibbs free energy differences of elementary steps assisted in approximating the theoretical over-potential needed to overcome for the reaction to evolve. Note that the calculated theoretical over-potential for all structures are approximated with the absence of any kinetic considerations (Section 3.1.5) that may increase the required over-potential.

6.1 Adsorption Sites

Figure 6.1 illustrates the adsorption sites for the orthorhombic structure of Bi$_2$MoO$_6$, this is used to demonstrate characteristics of adsorption states for all configurations in the orthorhombic and monoclinic structures studied in this report. The orthorhombic and monoclinic structures demonstrate similar adsorption site trends, this is not to say that the binding energy is the same for different configurations of the orthorhombic and monoclinic structures. It is sufficient to say that combinations of (Bi$_x$M$_y$)$_2$MoO$_6$ (M = Fe, La, Yb) in the orthorhombic and monoclinic structures produce similar variations in adsorption sites. The expressed sites in Figure 6.1 are usually classified as adsorption sites of either bridge, hollow, and on top. It is also noted that typically each classification will yield slightly different geometries. Thus each structure of (Bi$_x$M$_y$)$_2$MoO$_6$ (M = Fe, La, Yb) in the orthorhombic
and monoclinic configurations will yield unique electronic properties that can be analyzed and studied, which allows structures that prove more stable to be found and investigated.

**Figure 6.1** Adsorption sites of the orthorhombic Bi$_2$MoO$_6$ structure configuration in the [010]. The expressed adsorption sites for the Bi$_2$MoO$_6$ orthorhombic structure is only used to demonstrate the adsorption types and not for actual bonding for all other metals in this study. This means that the species of N$_x$H$_y$ could bind more strongly to Fe, La, Yb orthorhombic and monoclinic structure configurations. The corresponding color for atoms are red = O, white = H, dark blue = Mo, light blue = N, and gray = Bi.
Figure 6.1 illustrates the adsorption sites on Bi$_2$MoO$_6$ orthorhombic structure surface. The hydrogen molecule proved to be stable on the exposed surface layer of metal sites and tended to lie on the crystal surface directly attaching to one metal atom. Thus allowing hydrogen to have a bonding site of bridge classification, in fact a very small difference of energies was found between adsorption sites that responded to hydrogen bonding. Nitrogen adsorbed to the surface on a hollow site and preferred to bind in a sigma (strong covalent bond, formed by overlapping between atomic orbitals) bond on the surface with two metal atoms, thus proving edge sites to be the most stable with respect to all other sites. However, this was not true for adsorption of N$_2$, this is because N$_2$ molecule prove to have limited stable adsorption configurations, due to the strong N-N bond and proved to have a bonding site of top classification.

The NH molecule was found adsorbed on the surface in hollow sites similar to N, NH$_2$ to bridge sites, and NH$_3$ on-top sites and all proved to be stable structures (Figure 6.1 bottom row). However, in the case of N$_2$H, N$_2$H$_2$, and N$_2$H$_3$ species (Figure 6.1 middle row), they typically preferred to bond in a bridge site, and only tend to favor the surface as more hydrogen was introduced in the species, one of the nitrogen atoms bonded to a metal atom similarly to the sigma bonding expressed for N and NH$_x$ species (Figure 6.1 top and bottom row). With respect to all the adsorption sites, species’ configuration orientation changed slightly as more hydrogen atoms are implemented in the surface species. When looking carefully at Figure 6.1, weakening of the N-N bond is demonstrated as a visual representation of the internal bonding length dramatically increases as more hydrogen atoms are implemented in the species. This can be seen when looking at NH$_3$ adsorbed on the structure, where the internal bonding length is much greater to that of other species as a result of the higher ratio of hydrogen to nitrogen. Also, it is very apparent that nitrogen atom becomes closer to the metal atom as more hydrogen atoms become bonded to the respected nitrogen atom as seen in Figure 6.1 middle row, this is demonstrated for BNF pathway and shows the weakening of N-N bond.
6.2 Ammonia Formation on Surface of Bi$_2$MoO$_6$ based Structures

Each surface composition of the orthorhombic and monoclinic configurations with the 9 adsorbate species of nitrogen and hydrogen that conformed to the two reaction pathways were investigated, which allowed this study to predict the electrochemical reaction of each step for the two mechanism pathways. Figure 6.2 and Figure 6.3 expresses the Gibbs energy of the electrochemical reactions of steps (Equation 3.4)-(Equation 3.12) ($\Delta G4-\Delta G12$) for both the associative and (Equation 3.13)-(Equation 3.22) ($\Delta G13-\Delta G22$) the dissociative mechanism of orthorhombic and monoclinic structures in configurations of (Bi$_x$M$_y$)$_2$MoO$_6$ ($M = Fe, La, Yb$). It is noted that some combinations of the (Bi$_x$M$_y$)$_2$MoO$_6$ in Figure 6.2 and Figure 6.3 proved to be unstable and propagated too much into the exposed vacuum after relaxation steps. Thus for the orthorhombic configurations, high Fe and Yb input into the structure is not present and for the monoclinic configurations high Fe input into the structure is not present. This was also recorded in the experimental results for high Fe, Yb, and La input into both configurations, which could not be stabilized and lost the orthorhombic and monoclinic phase. Also, it should be noted that theoretical calculations are expressed for ideal conditions, were as experimental calculations are of practical conditions. Thus some of the theoretically stabilized configurations may prove to be less than ideal for synthesis, never the less this study aims to express and compare calculations that better assist the explored structures.

Theoretical calculations express $N_2$ binding to almost all the surfaces of orthorhombic and some of the surfaces of monoclinic configurations of (Bi$_x$M$_y$)$_2$MoO$_6$ ($M = Fe, La, Yb$) structures, this resulted in adsorption energy that always expressed slightly negative reaction steps when compared to all other reaction steps as shown in Figure 6.2 and Figure 6.3 A,C dissociative $\Delta G14$ and B,D associative $\Delta G5$ and $\Delta G8$. The larges loss in entropy is associated from steps leading to gas phase $N_2$ to surface bonded molecules, this large loss of energy corresponds to slightly negative Gibbs energy steps expressed for the orthorhombic and monoclinic structures, Figure 6.2 and Figure 6.3. Most of the potential determining steps
Figure 6.2 Cumulative Gibbs energy for the dissociative (A) and associative (B) mechanism for orthorhombic structure configurations. The respected energies are attained from DFT calculations for an electrolyte with pH=0 at T=0 K. The expressed energies correspond to relative reaction steps of (Equation 3.4)-(Equation 3.12) for the associative mechanism and (Equation 3.13)-(Equation 3.22) for the dissociative mechanism. Each configuration can be associated with the potential-energy curve for successive reaction steps. The best performing structure for the associative mechanism is the orthorhombic configuration of \((\text{Bi}_{6/8}\text{Fe}_{2/8})_2\text{MoO}_6\) B and for the dissociative mechanism is the orthorhombic configuration of \((\text{Bi}_{6/8}\text{Fe}_{2/8})_2\text{MoO}_6\) A.
Figure 6.3 Cumulative Gibbs energy for the dissociative (C) and associative (D) mechanism for monoclinic structure configurations. The respected energies are attained from DFT calculations for an electrolyte with pH=0 at T=0 K. The expressed energies correspond to relative reaction steps of (Equation 3.4)-(Equation 3.12) for the associative mechanism and (Equation 3.13)-(Equation 3.22) for the dissociative mechanism. Each configuration can be associated with the potential-energy curve for successive reaction steps.

(largest positive step to overcome) in reducing N to form ammonia for both the associative and dissociative pathways in the structures, tended to be the braking of the N-N bond as
expressed in dissociative step $\Delta G_{14}$ of Figure 6.2 and Figure 6.3 A,C for both structures and for the monoclinic associative step $\Delta G_8$ of Figure 6.3D but not for the associative orthorhombic Figure 6.2B. This is because most of the monoclinic structures did not favor a direct attachment of $N_2$ on the surface, thus resulted in both the associative and dissociative pathways of the monoclinic structure to have the largest step requiring an external source to break the N-N bond. This is true for the dissociative mechanism where the N-N bond is broken early for the reaction thus the largest step is that of N-N bond braking as shown in Figure 6.2 and Figure 6.3 A,C $\Delta G_{14}$. However, this is not true for associative step of the orthorhombic configuration Figure 6.2B. Where the determining step is that of the addition of one hydrogen atom to transition from $N_2$ to $N_2H$, Figure 6.2B from $\Delta G_5$ to $\Delta G_6$, because for the most part the $N_2$ tended to better attach on the surface in the orthorhombic configuration. The expressed hydrogenation step in the orthorhombic configuration is also expressed as a large energy step to overcome from the binding of H from its gas phase, which corresponds to the step taken to overcome Gibbs energy formation of $N_2$ and NH$_2$ on the surface.

Looking at just the hydrogen steps, the first addition of hydrogen atom, from $\Delta G_5$ to $\Delta G_6$, typically is the most positive step in energy for most surfaces explored for all hydrogen steps. However, with respect to all steps taken for the dissociative mechanism of both configurations and associative mechanism of monoclinic configuration, the most significant over-potential is when initially breaking N-N bonding from $N_2$ to N, Figure 6.2 and Figure 6.3 A,C from $\Delta G_{14}$ to $\Delta G_{15}$ and Figure 6.3D from $\Delta G_7$ to $\Delta G_8$. This is expected due to the strong sigma bond expressed by overlapping atomic orbitals of N-N. For both configurations of both pathways the last three steps, Figure 6.2 and Figure 6.3 A,C going from $\Delta G_{20}$ to $\Delta G_{21}$ to $\Delta G_{22}$ and B,D going from $\Delta G_{10}$ to $\Delta G_{11}$ to $\Delta G_{12}$ are all negative steps expressed by the reduction of NH$_3$ on the surface to NH$_3(g)$ from large gains in entropy associated with transitions of surface bounded molecule to gas phase.
6.3 Adsorption of N$_2$H$_x$ and NH$_x$ Species on Fe, La, Yb Configurations

Initially, the two reaction pathways rely on configurations that have adsorption steps of N$_2$H$_x$ molecules for the associative and NH$_x$ molecules for the dissociative mechanisms. Morphology and composition of the monoclinic and orthorhombic surface structures greatly contribute to the Gibbs energies for reactions steps taken of associative and dissociative mechanisms. Presented in this study are stable configurations of the monoclinic and orthorhombic bismuth containing surfaces as shown in Figure 6.2 and Figure 6.3 and Figure 6.4, which are noted to be stable theoretically by calculations of the formation energy and by direct experimental synthesis for some configurations of (Bi$_x$M$_y$)$_2$MoO$_6$ (M = Fe, La, Yb). Calculations predict that high concentrations of Fe, La, and Yb to prove unstable. The configurations that DFT calculation are performed on are for structures that have energies within the scale factor attained from experimental results. The scale factor is a product of Boltzmann constant and temperature for the experimental sample (kT). Thus thermal energy greater than that of the formation energy for synthesized samples prove unstable. Also, experimental syntheses prove unstable for 40% or more implementation of La, Yb, and Fe into the orthorhombic and monoclinic structures, and forms secondary phases.

For any La, Yb, and Fe implemented in both structures, that the determinant step (Figure 6.4) is associated with the breaking of the N-N bond as seen in Figure 6.2 and Figure 6.3 A,C of $\Delta G_{14}$ for dissociative and D of $\Delta G$ for associative mechanisms, expect for the associative mechanism of orthorhombic structure in Figure 6.2B. This is because the orthorhombic structure has better affinity toward nitrogen attachment to the surface, due to exposed surface of Mo sites tending to have much higher affinity for N species. For the orthorhombic structure of the associative mechanism, Figure 6.2B, the determinant step is associated with hydrogenation steps $\Delta G_4$ to $\Delta G_5$ which is the addition of the first H step to form N$_2$H on surface or $\Delta G_5$ to $\Delta G_6$ which is the addition of second H step to form N$_2$H$_2$. This occurs because all configurations of the orthorhombic structure contain the same number of Mo atoms on the surface that directly interact with N species, Mo has
Figure 6.4 Plots of the maximum reaction barrier for all successive reactions for Fe, La, Yb implemented for the orthorhombic A,B and monoclinic C,D Bismuth based structures. The bars corresponds to the energies of the most difficult step to overcome for reaction steps (Equation 3.4)-(Equation 3.12) for the associative mechanism (B,D) and (Equation 3.13)-(Equation 3.22) for the dissociative mechanism (A,C). The best composition for orthorhombic and monoclinic structures are tabulated in Table 6.2.

6.4 Onset Maximum Determining Step for Bi₂MoO₆ Based Structure

Looking at the minimum positive potential for the orthorhombic and monoclinic structures one can directly observe that the most determinant step is associated within the breaking of N-N as expressed in Figure 6.2 and Figure 6.3 A,C,D. Which is expected for higher affinity to N atom species and acts as a precursor to directly attach N species as seen in Figure 6.1 reference biological nitrogen fixation Section 2.1 for Mo affinity for N atom species.
<table>
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<th>Design</th>
<th>DFT (eV)</th>
<th>Experimental UV-Vis (eV)</th>
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</thead>
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<tr>
<td>Bi₂MoO₆</td>
<td>2.40</td>
<td>2.61</td>
</tr>
<tr>
<td>(Bi₉₅Fe₀₅)₂MoO₆</td>
<td>2.11</td>
<td>2.30</td>
</tr>
<tr>
<td>(Bi₉₀La₀₁₀)₂MoO₆</td>
<td>2.30</td>
<td>2.51</td>
</tr>
<tr>
<td>Bi₃FeMo₂O₁₂</td>
<td>1.80</td>
<td>2.17</td>
</tr>
</tbody>
</table>

Table 6.1 Calculated and experimentally determined band gap energies for Bismuth based configurations of orthorhombic and monoclinic structure. The DFT calculations attained from DOS Figure 6.5, and the experimental data was determined using UV-Vis spectrometer, see Figure 3.6. As expected of the DFT calculations, the overall band gap is under approximated but dose demonstrate the correct trend as experimental results.

the dissociative mechanism as seen in Figure 6.2 and Figure 6.3 A,C where the N-N bond is broken initially. It is reasoned that the orthorhombic configurations behaves relatively as expected for both mechanisms. However, when it comes to the monoclinic configurations of the associated mechanism, Figure 6.3D, the structure is still having trouble stabilizing N-N near the surface as indicated by the determining step associated with breaking of the N-N as seen for ΔG₈s of Figure 6.3D that correspond to all determinant step for that configuration.

For the orthorhombic structure, there become two scenarios that determine the best structure for nitrogen fixation, scenario (i) which configuration better stabilizes N atom on the surface and scenario (ii) how well can the structure attract H atom. Scenario (i) is needed for the initial breaking of N-N bond for the dissociative mechanism Figure 6.2A and scenario (ii) is needed for the successive initial protonation as seen in the associative mechanism Figure 6.2B. In both scenarios the answer lies with the Mo-O atoms in the orthorhombic structure and how well can the structure influence the Mo-O atoms to better assist the attraction of N and H species on the surface (Mo-O layer). The Mo-O layer is what the N and H species interact with the most as seen in Figure 6.1 because the location of the vacuum which was found to only stabilize in the [010] plane for orthorhombic structures (from exploring all possible orientations) as seen in Figure 3.4A and thus forces that interaction of N species and H species with Mo-O layer.
Figure 6.5 Illustration of the density of states (DOS) calculated for the orthorhombic configurations of (Bi$_x$M$_y$)$_2$MoO$_6$ (M = Fe, La, Yb). DOS of monoclinic configurations proved to demonstrate similar trends when implementing Fe, La, and Yb, thus only orthorhombic configurations are shown. Note that all Fermi levels (red line) are aligned at 0 eV for direct comparison. Select band gap calculated values are expressed in Table 6.1. The trend suggests that more Fe, and Yb implemented into the structure further reduces the band gap by introducing impurity states in the band gap.

Figure 6.5 better illustrates what happens to the orthorhombic configuration as more Yb, La, and Fe are added in the structure. It is quite apparent that more states are able to be introduced in the band gap as more Yb and Fe are implemented thus resulting in impurity states in the band gap. This impurity states are associated with strong orbital interactions due to strong hybridization between the Bi 6p and Fe 3d orbitals and also the O 2p and Fe 3d orbitals. This is due to the energetic overlap in the Fe 3d bands with the Bi 6p bands and the O 2p and Fe 3d bands, this result is also expressed in literature [114]. Adding Fe will induce localized distortions of the Mo atoms and this modulates the affinity of N and H species toward the Mo atoms. This can be seen in Figure 6.6 for a Fe containing orthorhombic structure where enhancement of the bands due to hybridization causes strong interaction between Fe-O. The strong interaction can be visually represented with the de-
creased internal bonding length when comparing the same location of Fe-O of Figure 6.6 with Bi-O in Figure 3.4A which alters the bond length of Mo-O. This opens bonds to N and H species as shown in Figure 3.4A and Figure 6.6, where Mo-O distance increases from 0.186 nm to 0.190 nm as Fe is implemented in the structure thus resulting in Mo interacting better with N and H species on the surface. This can also be said for the Yb 4f orbitals which demonstrate strong interaction with O and Bi thus also causing this shift in states. Meaning that all surrounding atoms like Bi, O, and Mo will be affected due to the substitution of Fe and Yb atoms. Thus resulting in a shifting of stats that eventually will cause the strong interaction of Mo-O layer to N and H species.

**Figure 6.6** Illustration of the \((\text{Bi}_{6/8}\text{Fe}_{2/8})_2\text{MoO}_6\) in orthorhombic configuration. Fe atoms induce localized distortions of Bi, Mo, O as shown, and this modulates the affinity of N and H species toward Mo atoms.

Fe and Yb in the lattice cause a shifting of states due to changes in inter-atomic bond
lengths, which indirectly affect the interaction of N species to the surface of orthorhombic configurations that better assist the dissociative mechanism of Figure 6.2A. This indirect interaction expresses the best determinant step as \((\text{Bi}_{6/8}\text{Fe}_{2/8})_2\text{MoO}_6\) for all studied structures in this study for the dissociative mechanism of approximately 3.2 eV as seen in Figure 6.4A, which is associated with N-N breaking \(\Delta G_{14}\). Any Fe implemented in the orthorhombic structure resulted in greatly reducing the band gap as seen in Table 6.1 of the recorded experimental and DFT calculated band gap. The small band gap results in larger population of excited carriers as a result of increased utilization of the electromagnetic spectrum. The addition of Fe and Yb into the structure also results in changing the majority carrier concentration. This can be seen in Figure 6.5 as a shift in the Fermi level towards the valence band (HOMO) and conduction band (LUMO). The same idea of the Mo layer strong effect can also be made for the orthorhombic configuration of the associative mechanism for H species, Figure 6.2B. The better structure for the orthorhombic associative pathway proved to be Bi4Fe2 of Figure 6.5 \(((\text{Bi}_{6/8}\text{Fe}_{2/8})_2\text{MoO}_6)\), which tended to stabilize N species on the surface and still maintain good affinity with the H species. Thus resulting in better protonation steps taken for all studied structures in the associative mechanism. The \((\text{Bi}_{6/8}\text{Fe}_{2/8})_2\text{MoO}_6\) of orthorhombic configuration in Figure 6.2B had approximately 1.4 eV for the determinant step, which is the lowest for all studied structures in this study that are associated with \(\Delta G_6\) of H atom attachment to \(\text{N}_2\).

### 6.5 Partial Density of States

Figure 6.7 expresses the partial density of states (PDOS) for orthorhombic configuration of (A) \(\text{Bi}_2\text{MoO}_6\) and (B) \((\text{Bi}_{6/8}\text{Fe}_{2/8})_2\text{MoO}_6\) for all N and H cases implemented into the configuration. The PDOS plot provides information of how the states associated with each atom are interacting with each other. In Figure 6.7 the Fermi levels have been aligned (set to zero eV) across the plot. All states below the Fermi level are assumed bound. Because the density is determined from the expectation value of the wave function, it is reasonable...
Figure 6.7 Plot of the partial density of states (PDOS) for the orthorhombic configuration of (A) Bi$_2$MoO$_6$ and (B) (Bi$_{6/8}$Fe$_{2/8}$)$_2$MoO$_6$. The Fermi level has been aligned to 0 eV. Comparison between A and B illustrated the influence that the Fe ion has on the Mo-O bond state, which results in a modulation of the HOMO states. Moreover, the circles in both A and B illustrate the limiting step ($\Delta G_{8}$), where the incorporation of Fe eliminates the covalent bond of NH$_2$ with Mo, reducing the associated reaction barrier.
to assume that atoms with density peaks at similar energy levels have complimentary wave functions. These complimentary wave functions are associated with strong covalent bonds. While the directionality of the covalent bond is desirable, the strength of bond often leads to a thermodynamic limiting step in the case of surface bound states. In addition to surface bound states, the PDOS also provide information about the binding within the bulk material. As seen in Figure 6.7, there is a modulation of the Mo-O with and without Fe that induces strain. This in turn shifts the energy level and modulates the band gap energy as support by the band gap as a function of composition shown in Figure 6.5. Furthermore, in Figure 6.7, there is a noticeable modification of the Mo and O states as Fe is introduced into the orthorhombic configuration (Figure 6.7B) when compared to a pure Bi case (Figure 6.7A). This behavior of modifying the Mo-O bond is confirmed for Fe implemented in the structure, as Fe-O will more strongly bond (orbital hybridization) as seen in the PDOS for Fe-O compared to Bi-O. This is seen as the alignment of the Fe states with the O states (strong orbital interaction), note that Fe in Figure 6.7B shifts all states up toward the Fermi, thus modifying the composition of the structure with Fe will modify and cause strong covalent bonding. Note that Fe ion causes a considerable modulation of the HOMO Mo and O states, this is apparent in all cases in Figure 6.7B. Also, this stronger bond length between Fe-O compared to Yb-O and Bi-O is to be expected as a result of a lower atomic number of Fe. Note that this increased bonding is the cause for the change in the states nearest the HOMO level as seen in Figure 6.7B. Also, the contribution of Mo is further validated as being the absorption site for all N and H species, this is seen as alignment of the individual states to Mo states as seen in Figure 6.7A,B.

More interesting, Figure 6.7 provides information about how the surface species bind with the bulk surface. The circles in Figure 6.7 highlight the transition of the most difficult step, which is associated with ΔG8. Comparing between subfigure A and B where Fe is incorporated there is a clear difference. In the absence of Fe the N-Mo bond shift up as a result of the change in orientation relative to the surface (see Figure 6.1), which is desirable
from an energetic point of view but the associated number of bonds (number of states/energy level) at that energy level increases. Meaning that NH₂ has increased binding resulting in a larger thermodynamic barrier. However, the most intriguing finding comparing between subfigure A and B is that when Fe is incorporated the N-Mo covalent state is not present. And a lower N-Mo state is shifted up in energy. Because the product of the reaction (NH₂) is slightly less stable the Gibbs energy ends up being positive, as shown previously. Moreover, as reasoned earlier by measuring the bond lengths, by introducing Fe into the structure we can confirm that from Figure 6.7B that there is increased Mo-Fe binding, which modulates the covalent bonds of N-Mo.

The monoclinic configuration was the least desirable of the two configuration due to the limited affinity for nitrogen. This is attributed partially because the Mo-O atoms were not located at the free surface of the slab. It was determined that there were no high index planes which have the Mo on the surface as was the case in the orthorhombic configuration. In turn this did not permit the Mo-O atoms to interact very well with N species. Thus for the monoclinic configurations, all determinant steps of Figure 6.4C,D for the associative and dissociative mechanisms have the breaking of N-N as the highest to overcome as seen in Figure 6.3C,D ΔG8 and ΔG14. For the monoclinic configurations, the two scenarios that assist in explaining what is the better structure for each mechanism are, scenario (i) that for the dissociated mechanism the structure that proves more ideal is the one that has a good balance of N and H species affinity. This is because more energy will be required to break the N-N bond if the structure has a higher affinity for N species than H species. Thus the high combination of Fe, La, Bi, Yb, will tend to have a higher affinity for N species than H species in the monoclinic configuration, and will not prove suitable as seen in Figure 6.4C. (Bi⁷⁄₈Yb¹⁄₈)₂MoO₆ of the monoclinic dissociated mechanism had the right balance of N and H affinity that results in approximately 7.8 eV as seen for determinant step in Figure 6.4C for ΔG14 associated with N-N bond breaking. Scenario (ii), for the associative mechanism of monoclinic structure, the configurations that produce better affinity
of N species on the surface result in lower determining steps as seen in Figure 6.3D. This is reasoned because continuous protonation steps are required for the associative mechanism before any breaking of the N-N bond. Thus structures in the monoclinic configuration of the associative mechanism that demonstrate better stabilize of N species on the surface to be more effective. This better stability of N species on the surface allows each protonation step to more strongly affect the N-N bond breaking. \((\text{Bi}_{6/8}\text{Fe}_{2/8})_2\text{MoO}_6\) for the monoclinic configurations as seen in Figure 6.3D to result in a determinant step of approximately 1.7 eV as shown Figure 6.4D for N-N bond breaking associated with \(\Delta G_8\).

### 6.6 Volcano Plot

Figure 6.8 illustrates a volcano plot for the associative mechanism. The volcano plot allows for a visual representation of the onset potential required to evolve nitrogen fixation, this method is shown in reference [1]. In this method the reaction free energy, described by reaction steps corresponding to Equations 3.4-3.22, are used as a simple measure of the electrocatalytic activity. The reaction free energy for each step is expressed as a function of an applied bias. The idea is to find the required bias needed such that each forward reaction has a negative free energy that will make the limiting step zero, which ensures a spontaneous reaction [1].

Figure 6.8 describes the required bias needed to make each reaction step exothermic. The two solid lines in Figure 6.8 shows the limiting steps for the associative electrochemical ammonia synthesis. The red point express material systems experimentally tested in reference [1] for the two limiting steps and the blue points are the structure configurations theoretically calculated for the orthorhombic bismuth structure system. Where the two solid lines meet is the optimal point where the lowest onset potential for driving associative ammonia synthesis. Note that none of the investigated materials are at the lowest onset potential for driving associative ammonia synthesis electrochemically. However, higher concentration of Fe, La, and Yb seem to perform better at reaching the optimum point. Note that higher
Figure 6.8 Volcano plot which compares the associative limiting steps for different experimental [1] (red points) and investigated materials (blue points). Illustrates the volcano plot for the associative mechanism with free energy of $\Delta G_N^*$ as the descriptor. The two solid lines indicated in the plot are the limiting step for the associative mechanism, reference [1] for experimental results depicted by the red points in this figure.

concentration will yield stability issues as discussed in earlier section of this chapter, and thus the optimal point may not be achieved with the bismuth based material. Thus finding the optimum material system for the associative mechanism will lie between the Mo and Fe points illustrated in Figure 6.8, which is known to fit quite well with the active site in the nitrogenase enzyme of FeMo cofactor that drives BNF.

A summary of the best structure configurations for this study is shown in Table 6.2 with the respected theoretical over-potential calculated for both the associated and dissociated reaction mechanism. It is noted that all expressed over-potential energies are within the band gap energy for the material as expressed in Table 6.1 except $(\text{Bi}_{7/8}\text{Yb}_{1/8})_2\text{MoO}_6$ of the
Table 6.2 The best possible compositions for each reaction pathway of associative and dissociative mechanism of Bismuth bases structures of Orthorhombic and Monoclinic configurations. These correspond to determinant steps attained from Figure 6.4. The best structure is that of the orthorhombic Fe containing associative pathway for $(\text{Bi}_{6/8}\text{Fe}_{2/8})_2\text{MoO}_6$ structure.

<table>
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<th>Monoclinic ($\eta$[eV])</th>
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<td>Associative</td>
<td>$(\text{Bi}<em>{6/8}\text{Fe}</em>{2/8})_2\text{MoO}_6$ (1.4)</td>
<td>$(\text{Bi}<em>{6/8}\text{Fe}</em>{2/8})_2\text{MoO}_6$ (1.7)</td>
</tr>
<tr>
<td>Dissociative</td>
<td>$(\text{Bi}<em>{6/8}\text{Fe}</em>{2/8})_2\text{MoO}_6$ (3.2)</td>
<td>$(\text{Bi}<em>{7/8}\text{Yb}</em>{1/8})_2\text{MoO}_6$ (7.8)</td>
</tr>
</tbody>
</table>

monoclinic configuration for the dissociative mechanism, which resulted in an over-potential of approximately 7.8 eV. It should be noted that the closer the over-potential is to the band gap the better the prominence of the overall structure will be, due to more utilization of the electromagnetic spectrum for photocatalysis. Also, the reader should note that the approximated results throughout this study by means of DFT should not be used as exact results, because of the approximations of the DFT method and the expressed approximations should only be used to demonstrate the relevant trends in this study.

### 6.7 Comprehensive Efficiency Analysis of the Bismuth Based Structure for Nitrogen Fixation

This section addresses the efficiency and provides a perspective on how well the bismuth based structure material system studied in this work compares to the biological (BNF) and current commercial (Haber-Bosch) ammonia syntheses processes. Ammonia synthesis is known to exhibit fascinating engineering and scientific challenges such as the high temperature and pressure as described in Section 2.1 for BNF and Section 2.2 for Haber-Bosch process. Nitrogenase microorganisms requires 16 moles of ATP to reduce each mole of nitrogen ($\text{N}_2$), that is roughly 5 eV per molecule of nitrogen ($\sim$500 kJ/mole) [41, 115]. Therefore challenges presented in chemistry is to find new ways to allow the N-N bond to activate, thus bringing about the Haber-Bosch process which is a viable solution for nitrogen fixation being employed today. An overview and in-depth discussion pertaining to the methods
described for nitrogen fixation is depicted in Section 2.1 for BNF and Section 2.2 for Haber-Bosch process. Although the iron based ammonia synthesis catalyst has not differed over the past several decades, the energy consumption required for the Haber-Bosch process has been improved.

<table>
<thead>
<tr>
<th>Energy Cost</th>
<th>Associative</th>
<th>Dissociative</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Bi$<em>{6/8}$Fe$</em>{2/8}$)$_2$MoO$_6$</td>
<td>$\sim$135 kJ/mole</td>
<td>$\sim$308 kJ/mole</td>
</tr>
<tr>
<td>Process</td>
<td>$\sim$500 kJ/mole (BNF)</td>
<td>$\sim$525 kJ/mole (Haber-Bosch)</td>
</tr>
<tr>
<td>Improvement</td>
<td>73%</td>
<td>41.3%</td>
</tr>
</tbody>
</table>

Table 6.3 The table illustrates the required energy cost to reduce each mole of nitrogen (N$_2$). The best studied structure is that of the orthorhombic Fe containing associative pathway for (Bi$_{6/8}$Fe$_{2/8}$)$_2$MoO$_6$ structure. This table is used to compare the associative mechanism (BNF) and dissociative mechanism (Haber-Bosch process) of the studied structure system to the known and commercially implemented nitrogen fixation processes.

State of the art plants typically produce 2500 tons of ammonia a day. The total annual production amount is roughly 146 million tons at energy cost of 28 GJ/ton ($\sim$525 kJ/mole) [115], which is becoming much more comparable to the biological processes. Thus when comparing the biological and industrial processes for nitrogen fixation, this study ultimately proposes the bismuth based photocatalytic material as also a viable candidate for nitrogen fixation. Effectively for the studied structures, the orthorhombic (Bi$_{6/8}$Fe$_{2/8}$)$_2$MoO$_6$ resulted in the best overall effectiveness for nitrogen fixation as expressed in Table 6.2, which resulted in an over-potential of 1.4 eV ($\sim$135 kJ/mole) for the associative and 3.2 eV ($\sim$308 kJ/mole) for the dissociative mechanism. This over-potential accounts for adequate improvement when comparing the associative mechanism to the BNF and the dissociative mechanism to the Haber-Bosch process. For the associative mechanism this is an improvement of 73% and for the dissociative mechanism this is an improvement of 41.3%. A summary of the overall improvement demonstrated by the bismuth structure system is illustrated in Table 6.3.
RESULTS & DISCUSSIONS: MACHINE LEARNING APPROACH FOR PREDICTING ATOMIC POSITIONS & TOTAL ENERGIES

Understanding the characteristics that describe chemical and biological system behavior and attributes plays quite a role in guiding and predicting new material systems. The modeling tools used to simulate these quantum systems relies on first-principle calculations of electronic structures to predict interactions and attributes. This study proposes to use a NN to predict and refine the initial state of structure configurations and ground state energy to reduce the computational expense needed for first-principle calculations based on DFT simulations. As mentioned in Chapter 4, we express a NN to a training set consisting of all configurations of \((\text{Bi}_x\text{La}_y)_2\text{MoO}_6\), and test (validate) results with configurations of \((\text{Bi}_x\text{Yb}_y)_2\text{MoO}_6\). The input to the NN is the vector input that describe the charges that make up a structure and output being the desired feature. The first feature the NN is trained to approximate are the fractional coordinates (atomic positions) that make up a unit cell based on the bismuth structure (Figure 4.1). The second feature the NN predicts is the energy ratio that describes the total ground state energy of a unit cell.

7.1 Approximating Atomic Positions for the Tested Set

Predicting atomic positions that make up a unit cell in a sense determines the computational time required to achieve convergence for that structure. In DFT, the total energy of any given system of interacting atoms and electrons is a function of the atomic positions that make up the structure and the electron density [19]. The external potential used in DFT explicitly depends on the atomic position, which is changed by a small step to find optimized atomic structure. Thus the Hamiltonian and the wavefunctions used in DFT are also
Figure 7.1 Plot A is the maximum vector mean squared error (MSE), Equation 4.8, for the structures with Yb substitution in the 8 atomic positions specified in Figure 4.1, this is the error difference between NN and DFT. Plot B is showing the structure with the maximum error (worse case) difference between NN and DFT calculations for the 36 vectors and representing the ‘*’ in plot A, the 36 vectors represent the 36 atomic positions in the unit cell expressed in Figure 4.1. The vector errors shown in plot B correspond to 3 Yb atoms and 5 Bi atoms in the 8 positions as specified in Figure 4.1, that is (Bi_{5/8}Yb_{3/8})_2MoO_6.
dependent on the atomic positions. The initial routine of DFT code is to solve the charge
density self-consistently, which is solved iteratively by computing the potential terms in the
Hamiltonian by initial guess of the input density and comparing that to the output density
attained by using Kohn-Sham approach. This iterative step is considered converged when
the self-consistent energy is within a specified accuracy. After this self-consistent calculation
is done the atomic positions are moved by a small step, then re-evaluation of the density and
solving the self-consistent calculation is done till the problem is solved within some accuracy
specified. Thus its noted that the iterations requires to solve this problem relies heavily
on the atomic positions that make up the structure. It is quite simple to deduce that if
a structure system has atomic positions initially close to that of the final atomic positions
then the iterations requires to solve DFT calculations would be reduced. In practice the
initial atomic positions are specified by the structure system wanting to be tailored and or
substituted, as in this study all DFT structure systems had initial atomic positions specified
by Figure 4.1 which is the bismuth based structure.

Figure 7.1 illustrates the response of the neural network error for vector positions as
Yb is substituted in the 8 atomic positions specified in Figure 4.1. Its noted that for each
unit cell there is a total of 36 vectors that correspond to the 36 atomic positions specified
in Figure 4.1. Thus the maximum vector error is plotted for all cases as Yb is substituted,
Figure 7.1A, and the configuration that yielded the maximum overall error, Figure 7.1B.
Initial inspection of Figure 7.1A shows a random error of the NN response. However, that
is not the case when looking carefully, there seems to be a trend, as more Yb substitution
occurs the error progressively builds up. Which is to be expected, as lower concentration of
Yb tends to be dominated by Bi, thus the training set which has seen high concentration of Bi
will yield good results for higher Bi combination with Yb. Where as higher concentration of
Yb will result in error build up due to the training set not consisting of any Yb substitution.
Thus vectors of low concentration Yb will be evaluated more accurately, and based on
the results the concentration of 1 Yb 7 Bi resulted in the lowest maximum overall vector

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MSE as $1.0 \times 10^{-3}$ Figure 7.1A. However, for the maximum error response overall of the NN as expressed by '*' in Figure 7.1A and Figure 7.1B, the highest maximum vector MSE is $1.6 \times 10^{-2}$ of 3 Yb 5 Bi. Its noted for both the maximum and minimum MSE for all Yb substitution, the vectors are compared to that of DFT, thus the error is reasonable compared to the computational expense DFT takes to attain the final structure. The only downfall is that the NN needs a good interpretation for training set in order to accurately expresses input and output features.

Looking at the worst case, the overall error in the NN response, as in Figure 7.1B, atomic vector 35 is contributing to the maximum overall error for the $(\text{Bi}_{5/8}\text{Yb}_{3/8})_2\text{MoO}_6$ structure. Further inspection of the atomic position that corresponds to vector 35 in Figure 4.1 reveals the location in the unit cell it occupies. This position is located at the boundary of the unit cell, at the boundary the unit cell tends to be periodic in nature. Thus from a NN perspective the training set had periodicity in the unit cell structures but was never told how this periodicity existed for these structure. The NN only saw how the atomic position would change from one input vector to the next and so it was difficult for the NN to approximate the behavior of this structure at the boundary condition, a solution to this can be incorporating periodicity in the NN algorithm. However, for the intent of this study, it was more interesting to see if the NN could potentially predict the behavior at the boundary, and not by explicitly telling the network that behavior from user input. After further inspection of the tested set, most of the error was expressed at the boundary conditions, but was reasonably low. A visual interpretation of the error expressed for the vectors in Figure 7.1B of $(\text{Bi}_{5/8}\text{Yb}_{3/8})_2\text{MoO}_6$ structure is expressed in Figure 7.2.

It is very interesting to see how the NN predicts the structure configurations of the Yb substitution. Comparing the optimized DFT structure, Figure 7.2A, and the NN predicted structure, Figure 7.2B, we see that the NN tends to distribute the atoms more evenly in the unit cell. This goes back to the training set, where configurations containing La expressed very similar interactions as configurations containing Bi, were structures expressed more
Figure 7.2 Considering the worst case, structure A represents the DFT attained optimized structure and B is the NN approximated structure for \((\text{Bi}_{5/8}\text{Yb}_{3/8})_2\text{MoO}_6\). This configuration had the overall maximum error based on the NN approximations. Note that the individual vector MSE expressed in Figure 7.1B is comparing structure A (DFT) and B (NN).

Even distribution of atoms in the unit cell. It is noted that all configurations of La, including pure La in the 8 positions proved stable from a DFT convergence perspective. However, not all Yb configurations were stable, and from DFT simulations anything more the 50% would prove to not converge at all. Thus, this study tested (validate) Yb configurations to 50% substitution in the 8 possible positions in the unit cell from DFT simulations. We also see when comparing A and B of Figure 7.2 that the NN had progressively done a better job at predicting the atomic positions that are within the unit cell. Its noted that atoms closer to the boundary tended to be more evenly unformed for the NN, such as the 4 oxygen sites located at the top of the unit cell in Figure 7.2 A and B, this feature was expressed in configurations of the training set (La substitution) thus the network though it to be true for most cases. However, with this error in mind, this study found it to be quite difficult for the
NN to attaining exactly the atomic positions, this is quite an arduous task that requires very precise calculations of interactions in a structure system. Thus the NN predicted structure is used as a refinement of the initial atomic positions in the aim of reducing computational time spent for DFT calculations which has proven from time to time to have very accurate results.

\[
\text{(Bi}^{5/8}\text{Yb}^{3/8}\text{)}_2\text{MoO}_6
\]

<table>
<thead>
<tr>
<th>Initial Positions Specified</th>
<th>Computational Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 4.1</td>
<td>~30 hr</td>
</tr>
<tr>
<td>Figure 7.2B</td>
<td>~26 hr</td>
</tr>
</tbody>
</table>

Table 7.1 The table expresses the computational time required for DFT simulation to find optimized structure, for the worst case with maximum error, for \((\text{Bi}^{5/8}\text{Yb}^{3/8})_2\text{MoO}_6\) configuration starting from initial atomic positions specified by Figure 4.1 and NN positions specified by Figure 7.2B. All parameters for DFT calculations are described by the DFT computational details Section 4.5, the only thing that is changed are the initial atomic positions.

The structure with the maximum overall error (worst case), \((\text{Bi}^{5/8}\text{Yb}^{3/8})_2\text{MoO}_6\), was re-evaluated using DFT simulation with the initial positions specified by the NN, Figure 7.2B, and evaluation of the computational time spent reveals an overall improvement of 4 hours in wall time compared to the initial positions specified by Figure 4.1 for DFT simulation (Table 7.1). This improvement may seem trivial for a single structure, however when looking at the whole design space, this is quite an improvement. Overall the tested set consisted of 100 configurations and each of the configurations had required an average of 30 hours of continuous running time for each simulation. Thus the 4 hours would account for over 400 hour in reduction time in the overall study, if to say each structure would be improved on average of 4 hours. However, this reduction is based on the time spend for the worst case with maximum error, and in practicality most structures had much lower error, thus
the improvement would be more than 400 hours overall. For instance, when testing the NN
specified initial positions for the best case with the minimum error, being \((\text{Bi}_{7/8}\text{Yb}_{1/8})_2\text{MoO}_6\),
the overall reduction in computational time is more than 9 hours, thus overall this study
would account for way over 400 hours in computational wall time reduced. It is noted
that most design studies of structure systems account for hundreds and even thousands of
configurations, thus every possible method of improvement is explored, such as the expressed
refinement of the initial system positions. Ultimately tailoring a structure system is a means
to find a beater structure that expresses very specific behaviors. In structure simulations, first
principle calculations can be used to predict reaction steps that proceed chemical reactions
such as the hydrogen evolution reaction (HER) or oxygen evolution reaction (OER). These
reactions steps relies on the computation of the total energy for the structure system, thus
effectively simulating energy becomes a priority in this study.

7.2 Approximating Energy Ratio for the Tested Set

Total energy of the unit cell is ultimately effected by the atomic positions that make
up the unit cell. Thus it is possible to calculate the energy based on the predicted structure
attained from the NN. However, this study intended for the NN to find relevant trends
between input (charge) and the output features. With the error found based on the atomic
vectors, it was reasoned that ultimately back calculating the energy would ultimately result
in a similar magnitude for the error. So ultimately energy became a feature for the NN
to calculate and not attained by back calculating it relative to the NN predicted positions.
It is noted that energy is given as a energy ratio to the NN, thus dimensionless and more
manageable for this study (reference input and output data sets Section 4.2). Having the NN
to predict the energy and not back calculating it proved quite ideal as expressed by the error
for Yb substitution in Figure 7.3. Being able to predict the energy without the computational
expense really solves the permutation problem mentioned in the model design space for the
NN, Section 4.1. This is because not all configurations will require DFT simulation to
Figure 7.3 Plot A represents the energy ratio MSE for the structures contain Yb substituted in the 8 atomic positions. This error is comparing the NN predicted energy ratio to the DFT predicted energy ratio. Plot B expresses the predicted (\(E_{NN}\)) versus reference (\(E_{DFT}\)) energy ratio. The ideal line (\(x=y\)) is included to indict the quality of fit, when the predictions match the reference data perfectly, they will lie on the ideal line.
evaluate the energy. In some cases it's more ideal to take the structure system with the lowest total energy, such as the example stated in the model design space Section 4.1. For instance, finding the best ratio (configuration with lowest energy) of Yb 1/7 Bi ratio requires DFT simulations of 8 unique configurations. Thus by using the NN to evaluate the energy one can get a sense of the relevant trend as Yb is configured in different positions in a unit cell.

Figure 7.3A expresses the overall energy ratio MSE comparing the NN and DFT calculated energy for Yb substitution in the 8 positions. It's very interesting to see that the error expressed in Figure 7.3A behaves like a step increase from low to high concentration of Yb. This is due to the evaluation of energy by the NN for similar configuration ratios like the 1/7 Yb to Bi. Thus the energy for 1/7 Yb to Bi in one configuration is quite similar to a different configuration with the same ratio of 1/7 Yb to Bi. However, the error expressed for energy is of great accuracy, minimum error being $1.1 \times 10^{-8}$ MSE for low concentration of Yb (12.5%) and maximum error of $2.3 \times 10^{-7}$ MSE for high concentration of Yb in the 8 positions (50%). Figure 7.3B expresses the quality of fit for the evaluated energy ratio expressed by the error in Figure 7.3A, where comparison of the reference (DFT) versus predictions (NN) of energy for the training and tested set. The ideal line ($x = y$, along $45^\circ$) in Figure 7.3B indicates the quality for expressed predictions, thus predictions matching reference data (training set) would lie on the ideal line. It is quite reasonable to see that the energy attained from the NN is way within the energy computed by DFT simulations (ideal line in Figure 7.3B), without the computational expense required to evaluate each structure configuration. In Figure 7.3B, the red points indicate how well the NN responded to the training set, and expresses a visual interpretation of the NN performance for the training algorithm steps taken. The points indicated in blue represent the tested set, being all the configurations of Yb up to 50% substitution in the 8 positions. Ideally the network should be within the line indicated as Ideal in Figure 7.3B, this means that the energy calculated from DFT is exactly the same as the predicted NN energy ($E_{DFT} = E_{NN}$). Thus having the
network express energy based on training set proved quite ideal, and more so having the
energy expressed as a ratio between the sum of the individual energy that makes up the
structure constituent parts divided by the total ground state energy even more ideal. Thus
attain energy is feasible as long as the individual energy of the constituent parts is evaluated.

7.3 Computational Efficiency of the Proposed NN Approach

The reader should note that most structure based studies encompass huge design
spaces, on the order of hundreds and even thousands of unique configurations. Thus to
relatively evaluate the effective efficiency of the proposed NN approach, a control model
must be compared and evaluated for the overall wall time required. The control model for
this study is all the configurations that make up the training and tested set. The training
set is comprised of 230 unique configurations of \((\text{Bi}_x\text{La}_y)_2\text{MoO}_6\) and the tested set are 100
configurations of \((\text{Bi}_x\text{Yb}_y)_2\text{MoO}_6\). Note that on average the wall time required for relaxation
of each configuration took 30 hours of consistent DFT calculations. That is roughly 6900
hours of continuous calculations for DFT simulation for the tested set and 3000 hours for
the training set. The total wall time required for the control model is mostly used to find
the stable energy ratio configurations as expressed by Equation 4.1, and in practicality there
are vast amounts of structure analyses needed to be done for most structure based studies.
However, to demonstrate the potential of the NN approach proposed by this study, the overall
wall time is reduced by refining the initial atomic positions and predicting the energies prior
to DFT simulation for structure system.

For the first method of reducing the overall wall time by refining the initial atomic
positions as expressed on this chapter in Section 7.1. The overall wall time was shown to
reduce by 4 hours for the structure with the maximum error (worst case) and 9 hours for
the structure with the minimum error (best case). Thus since most structures expressed
error way lower then the worst case as shown in Figure 7.1A for the tested set. The overall
improvement in the wall time is way over 400 hours for the tested set, because this is taking
the worst case improvement. The overall wall time reduction for the tested set was calculated to averaged around 7 hours for each trail. That is calculating the average wall time for all the trails of the tested set, which ranged from 4 hours (worst case) to 9 hours (best case) in wall time reduction. Based on the calculated average wall time reduced, an overall 700 hours improvement for the tested set is shown. Thus reducing the 3000 hours of overall wall time to 2300 hours, which is a 1.3x speed up in computation for the tested set.

<table>
<thead>
<tr>
<th>Method</th>
<th>Control</th>
<th>Refining Atomic Positions</th>
<th>Energy Ratio Prediction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unique Configurations</td>
<td>100</td>
<td>100</td>
<td>4</td>
</tr>
<tr>
<td>Overall Wall Time</td>
<td>3000 hr</td>
<td>2300 hr</td>
<td>120 hr</td>
</tr>
<tr>
<td>Overall Speed Up</td>
<td>–</td>
<td>1.3x</td>
<td>25x</td>
</tr>
</tbody>
</table>

Table 7.2 The table expresses the computational wall time required for DFT simulation to find optimized structure for the overall configurations of the tested set by implementing the NN proposed approach. The first method is to refine the atomic positions prior to DFT simulation. The second method is to predict the energy ratio for all configurations of the tested set thus eliminating majority of the required trials for the tested set. Note that there are 100 unique configurations (trials) for the tested set and on average each trial required continuous wall time of 30 hours for DFT simulation.

For the second method, the overall wall time is reduced by predicting the energies for all the energy ratio trials for the tested set as expressed by Section 7.2. This way only the potential trial that represent a specific ratio can be evaluated as expressed in Section 4.1. Note that there is 100 trials for the tested set and the combination of Bi and Yb goes up to 50% substitution. That is to say only rations of Yb occupying 1/8, 2/8, 3/8, 4/8 for the 8 possible positions in the structure system as expressed in Figure 4.1. Thus by being able to predict the energies for the 100 trials prior to DFT simulation, vast amounts of trials can be eliminated and only trials that represent the specific trial ratio will need to be evaluated. That is only 4 trials of the 100 for the tested set because there is only 4 ratios being evaluated for in the Yb case (1/8, 2/8, 3/8, 4/8). Eliminating most of these trials greatly reduces the
overall wall time of 3000 hours to 120 hours, which is a 25x speed up in computation for the tested set. Reference Table 7.2 for a summery of the overall wall time reduced by the NN approach.

7.4 Overall Feasibility of the NN Approach

Results in the previous sections of this chapter demonstrate not only the NN feasibility in learning the expressed system, but can provide accurate and meaningful features that greatly reduced DFT simulations overall and DFT computational expense. It would be ideal to demonstrate the proposed method to other DFT simulations of structure systems, for understanding the limitations and feasibility of the proposed method. The two features that the network was able to predict is the atomic positions and the total energy of the unit cell. The first feature was that of fractional coordinates for atomic positions. Where the network saw various input vectors and the corresponding fractional coordinates as the output feature as described by the training algorithm. Outside of these features no additional assumptions are given to the network. The computed output features relied on the DFT optimized structure, where all assumptions such as boundary conditions are taken care of, thus the network saw pure input and output characteristics. Further investigations regarding the best set of input features that could express the uniqueness of the structure may need to be looked at in future studies. However the method expressed for this study, which are the inputs to the NN as charges that make up individual atoms in the unit cell, proves to express reasonable results, especially for the second feature the network was trained to predict (total energy). The second feature the NN was able to predict is the total energy, no modification to the NN architecture is done, except that the energy was the only output to each input vector.

Advantages of the expressed method versus alternate NN methods is the simplicity and ease of the algorithm used. When it comes down to the algorithm, the most arduous part was attaining the data input and output feature. Thus the referenced and training
sets were obtained by time consuming self-consistent calculations using DFT. The method expressed in this study links charge classification directly to structural information and total energy. While this approach is quite powerful and efficient for specific case studies, it does require having access to accurate DFT simulations to explore design space. Thus limitations are based on the data set used and having to train the NN on multiple configurations in order for a relevant trend to be presented for the network, and thus ideal for large design studies. For instance the training algorithm consisted of 230 training configurations of the \((\text{Bi}_x\text{La}_y)_2\text{MoO}_6\) and evaluated 100 configurations of \((\text{Bi}_x\text{Yb}_y)_2\text{MoO}_6\) for the tested set. It is also noted that introducing any Yb configuration in the training part would prove to reduce the overall error because the network would see configurations similar to the tested set. However, this study focused on the feasibility of predicting and refining initial positions on configurations that are not introduced to the NN. Thus this method is independent of material system and only depends on referencing DFT simulations for specific class of structure system like the bismuth bases structure \((\text{Bi}_2\text{MoO}_6)\) explored in this study. The expressed method is thus ideal for large design space based studies where structure systems could potently take multiple substantiational attributes, thus making such studies reliant on computationally effective methods.
A key goal of this work is to express a viable solution for exploring large design spaces, as expressed by the design space in chapters pertaining to nitrogen fixation for the two molybdenum containing semiconductor systems. The solution presented in Chapter 7, as expressed by the NN model, demonstrates a method that significantly reduce the computational expense required for large design based studies without sacrificing accuracy. The aim of this chapter is to predict candidate materials for nitrogen fixation by implementing the developed machine learning approach. Its noted that the machine learning approach relies on training data before any predictions can be made. Thus this section utilizes attained reaction energies for structure configurations of the Bi$_2$MoO$_6$ system from Chapter 6 for nitrogen fixation as the training data to the developed machine learning approach. The goal, is to use the reaction pathways for the associative and dissociative mechanisms described by Equations 3.4-3.22 and corresponding energies expressed in Figures 6.2 and 6.3 for the orthorhombic Bi$_2$MoO$_6$ system from Chapter 6 to predict reaction steps for candidate ions. The only modification to the NN model, described in Chapter 4, is the output feature, which is the reaction steps corresponding to each input vector. Note that everything else is maintained including the training method, input vector, architecture of the NN model, and all other characteristics. Reference Chapter 4 for description of the machine learning model used, and Chapter 7 for the results and predictions made by the developed machine learning model.
8.1 Candidate Ions

Predictions made in Chapter 6 for the orthorhombic Bi$_2$MoO$_6$ system express the attained reaction energies from consistent DFT calculations for Fe, La, Yb, and Bi configurations and are the bases for the NN model illustrated in this chapter. The reaction energy steps are used as the output feature for the NN model. Then predictions of each reaction step is calculated for other possible candidate ions that can be subbed in the orthorhombic Bi$_2$MoO$_6$ system expressed in Figure 3.4A and Figure 4.1. Candidate ions chosen for predictions express similar attributes to the studied ions of Fe, La, Yb, and Bi in the orthorhombic Bi$_2$MoO$_6$ system, and also have been known in sum way to express potential substitute for the studied ion in resent works. A good method for choosing potential substitutional ions adopted by this study are solid solution rules by Hume-Rothery. The Hume-Rothery rules [116] for substitutional solid solutions are as fallows:

1) Atomic radius of the solute and solvent atoms must differ by no more than 15%.

2) Crystal structures of the solute and the solvent must be similar.

3) Complete solubility occurs when the solvent and the solute have the same valency. Dissolution more likely occurs from metal of higher valency to a metal with lower valency.

4) The electronegativity of the solute and solvent should be similar. Metals tend to form intermetallic compounds if solute and solvent electronegativity differ greatly.

Using Hume-Rothery rules and resent works for potential ion substitution of Fe, La, Yb, and Bi the explored ions depicted in this chapter are listed as fallowed (ordered by atomic charge number): Ti, Cr, Ga, As, Zr, Mo, Ru, In, Sb, and Hf. The proceeding results will look at the NN model predicted reaction steps for associative and dissociative mechanisms for the candidate ions.
Figure 8.1 Plot A is the calculated associative and B is the calculated dissociative reaction steps corresponding to Equations 3.4-3.22 for pure orthorhombic Sb$_2$MoO$_6$ configuration. The Sb is substituted in all 8 atomic positions expressed in Figure 3.4A and Figure 4.1. This plot expresses the difference between NN and DFT calculated reaction steps, the resulting error is shown in Figure 8.2.

8.2 Validating Reaction Steps with DFT Calculations

Reaction steps attained from the machine learning approach expressed in this chapter are used as an evaluation of the trend and not absolute reaction energy steps for the candidate
ions. Configurations of \((\text{Bi}_x\text{M}_y)_2\text{MoO}_6\) \((\text{M} = \text{Fe}, \text{La}, \text{Yb})\) are used as the training data for the NN model input being the charge (same as Chapter 4) and output being the reaction energy steps. A detailed discussion of the NN model response to the training data is expressed in Chapter 7, which shows predictions of the total energy with great accuracy. However, this chapter deals with reaction energy steps of the associative and dissociative mechanism and not the total energy of the unit cell. Figure 8.1 illustrates the reaction steps attained from the NN and DFT calculations for pure orthorhombic \(\text{Sb}_2\text{MoO}_6\) configuration, that is \(\text{Sb}\) implemented in all 8 atomic positions shown in Figure 3.4A and Figure 4.1 that substituted ions can occupy. This figure is used to validate the NN predicted reaction energy steps with DFT calculations for the orthorhombic \(\text{Sb}_2\text{MoO}_6\) configuration.

As seen in Figure 8.1, the NN over approximates the reaction energy steps for both the associative (Figure 8.1A) and dissociative (Figure 8.1B) reactions compared to the DFT calculated reaction steps for pure \(\text{Sb}_2\text{MoO}_6\) configuration. The most distinct error overall is seen in both Figure 8.1A and B, the NN evaluates the first step \((\Delta G_4 \text{ and } \Delta G_{13})\) as a slightly positive step where DFT calculations express a slightly negative step. This error is more distinct than any other error in the reaction steps, because negative energy suggests spontaneous reaction where as positive energy suggests a reaction that requires an external bias to evolve the reaction step. Because the evaluated energy in this reaction step is so minuscule compared to all other reactions, it can be accounted for in the calculations. With that error in mind, the NN was able to correctly predict all other reaction steps, even though slightly over prediction, with relative accuracy compared to DFT calculations. All other reaction steps \((\Delta G_4-\Delta G_{22})\), comparing the NN to the DFT calculated reactions is shown in Figure 8.1A and B. Figure 8.2 illustrates the error response of the NN model for the \(\text{Sb}_2\text{MoO}_6\) configuration, the MSE comparing the difference between the NN and DFT calculated reaction steps as shown in Figure 8.1A and B.

Figure 8.2 provides a comprehensive depiction of the MSE for each reaction step, comparing the NN with DFT calculations. Its noted that the NN model performed much
Figure 8.2 Plot A is the MSE calculated for the associative and B is the MSE calculated for the dissociative reaction steps corresponding to Equations 3.4-3.22 for pure orthorhombic Sb$_2$MoO$_6$ configuration. This plot expresses the error difference between NN and DFT calculated reaction steps, comparing the NN and DFT calculations expressed in Figure 8.1. Better overall when predicting the associative mechanism for the Sb$_2$MoO$_6$ case compared to the dissociative mechanism, comparing the maximum MSE of Figure 8.2A with Figure 8.2B.
The NN model expressed a maximum MSE of $3.6 \times 10^{-1}$ ($\Delta G_{12}$) and minimum MSE of $1.0 \times 10^{-3}$ ($\Delta G_{5}$) for the associative pathway (Figure 8.2A) and maximum MSE of $9.5 \times 10^{-1}$ ($\Delta G_{13}$ and $\Delta G_{15}$) and minimum MSE of $1.0 \times 10^{-3}$ ($\Delta G_{16}$) for the dissociative pathway (Figure 8.2B) for the Sb$_2$MoO$_6$ case. It was found that even if the NN model was trained with lower learning rate and more neurons implemented in the NN model the overall error expressed for Sb$_2$MoO$_6$ case is maintained relatively the same. The reader should note that the training data makes up low concentration of (Bi$_x$M$_y$)$_2$MoO$_6$ ($M = Fe, La, Yb$) as described in Chapter 6, this is due to stability issues for high concentration of Fe, La, and Yb in the Bi$_2$MoO$_6$ structure. A solution to give better predictions is to introduce some Sb configurations into the training set, this way the network would have an idea how Sb would behave in the Bi$_2$MoO$_6$ structure and could better predict the reaction steps. However, the goal is to find and compare the limiting step (maximum positive reaction step) between different ion configurations, thus a trend can be demonstrated for different ions implemented and comparisons of the limiting step will narrow down the search for the orthorhombic Bi$_2$MoO$_6$ structure system. As seen in Figure 8.1A and B, the general trend, comparing the NN and DFT calculations, is quite similar and expresses the correct positive and negative steps, with a small over approximation, thus demonstrates great potential in predicting the relevant trend for different ions implemented for Bi$_2$MoO$_6$ structure system.

8.3 Predicting Reaction Steps with NN Model

As described in this chapter, predictions of the reaction steps for the chosen ions are made based on already attained reaction steps for configurations of orthorhombic (Bi$_x$M$_y$)$_2$MoO$_6$ ($M = Fe, La, Yb$). The orthorhombic (Bi$_x$M$_y$)$_2$MoO$_6$ ($M = Fe, La, Yb$) configurations act as the training data for the NN model, inputs being the charge number for each atom that make up a unit cell, as described in Chapter 4, and output being the reaction energy steps for the associative and dissociative mechanism. Note that the NN model is only trained on one mechanism at a time, thus the model first is trained on the associative mechanism and
Figure 8.3 Cumulative Gibbs energy for the associative (A) and dissociative (B) mechanism for candidate ions implemented in the orthorhombic Bi$_2$MoO$_6$ structure configuration. The respected energies are attained from NN model, which are based on training data of orthorhombic (Bi$_x$M$_y$)$_2$MoO$_6$ (M = Fe, La, Yb) configurations attained by consecutive DFT calculations. The expressed energies correspond to relative reaction steps of (Equation 3.4)-(Equation 3.12) for the associative mechanism and (Equation 3.13)-(Equation 3.22) for the dissociative mechanism. Each configuration can be associated with the potential-energy curve for successive reaction steps.
generates results for the validated and prediction data (candidate ions) then the same thing is done for the dissociative mechanism. This allows each individual mechanism to be evaluated separately without any chance of the NN model to see the results for both mechanism at the same time. Also, the predictions made for candidate ions are only expressed for low concentrations, because it was found that high concentration of Fe, La , and Yb implemented into the Bi$_2$MoO$_6$ structure would cause stability issues as described in Chapter 6. Thus this chapter predicts reaction steps for low concentrations of candidate ions (Ti, Cr, Ga, As, Zr, Mo, Ru, In, and Hf) implemented in the Bi$_2$MoO$_6$ structure, specifically 2 of the 8 positions allowed to occupy (Figure 3.4A and Figure 4.1). The 2 allowed positions for candidate ions to occupy make up more then 25% of the 8 possible positions, in practice stability issues can occurs at much lower concentration then 25% depending on lots of factors such as ion used, temperature, pressure, etc.

Before the NN model could predict the reaction steps, it had to find the best possible 2 of the 8 positions that the specific ion could occupy. Note that 2 of the 8 positions make up lots of different configurations with the same 2/8 ratio that the ion could occupy, basically solving the permutation problem described in Chapter 4. Thus the 2/8 ratio positions of a specific candidate ion is found by using the NN model developed for approximating the total energy, reference section Approximating Energy Ratio in Chapter 7, for the different permuted 2/8 ratio configurations and taking the most stable (lowest total energy) permutation case for each specific candidate ion. Then the NN model is given the input data (atomic number for each atom that make up a unit cell) to predict the reaction steps for each candidate ion. Figure 8.3 illustrates the reaction steps for the associative (A) and the dissoiative (B) mechanism predicted by the NN model for candidate ions implemented in the orthorhombic Bi$_2$MoO$_6$ structure.

It's noted that the expressed reaction steps in Figure 8.1 are slightly over predicted by the NN model as discussed in last section, that is validating the NN model with DFT calculations for the Sb$_2$MoO$_6$ structure. Thus it should be noted that the reaction steps attained by
Figure 8.4 Plots of the maximum reaction barrier for all successive reactions of candidate ions implemented for the orthorhombic Bismuth based structure. The bars corresponds to the energies of the most difficult step to overcome for reaction steps (Equation 3.4)-(Equation 3.12) for the associative mechanism (A) and (Equation 3.13)-(Equation 3.22) for the dissociative mechanism (B) as seen in Figure 8.3. The best composition predicted by the NN model for the orthorhombic structure are tabulated in Table 8.1.
the NN model for candidate ions are also over predicted. Reference Chapter 6 for in-depth discussions on the scenarios that determines the best material system for the associative and dissociative mechanism expressed by the orthorhombic bismuth based structure. Also discussed in Chapter 6, the implemented ions that best modulates the atomic bond length between M-O sites proves most promising for nitrogen fixation for the orthorhombic bismuth based structure by allowing a balance between nitrogen and hydrogen affinities. Most of the reaction steps for the candidate ions expressed in Figure 8.3 show similar attributes to reaction steps for Fe, La, and Yb ions, reference Chapter 6.

For the most part, the associative mechanism for candidate ion reaction steps (Figure 8.3A) did not dramatically fluctuate except for Hf ion implemented into the structure. In the case of the Hf ion implemented into the structure the limiting step for the associative mechanism is described by the first protonation step (Figure 8.3A $\Delta G_5$). Where as for all other candidate ions the limiting step is associated with the second protonation step (Figure 8.3A $\Delta G_6$) for the associative mechanism. The minimum limiting step is 1.51 eV expressed by (Bi$_{6/8}$Ti$_{2/8}$)$_2$MoO$_6$ for the associative mechanism. For the dissociative mechanism reaction steps did not fluctuate at all except by uniformly increasing as the candidate ion charge number is increased (Figure 8.3B going from left to right) and for all candidate ions the limiting step is that of the N-N bond breaking (Figure 8.3B $\Delta G_{14}$). The minimum limiting step is 3.9 eV expressed by (Bi$_{6/8}$Ti$_{2/8}$)$_2$MoO$_6$ for the dissociative mechanism.

Figure 8.4 gives a comprehensive illustration of the maximum limiting step for the associative (A) and the dissociative (B) mechanism for the candidate ions, that is taking the maximum step for each ions in Figure 8.3. The limiting step gives the overall maximum step required to evolve each reaction for the different candidate ions implemented into the bismuth based structure system. As illustrated in Figure 8.4A for the associative mechanism, the limiting step does not fluctuate to much and for the most part stays just under 2 eV for all candidate ions. For the dissociative mechanism illustrated in Figure 8.4B, candidate ions have a more gradual increase in the limiting step as the charge number increases for most
Pathway | Orthorhombic ($\eta$[eV])
--- | ---
Associative | (Bi$_6$/8Ti$_2$/8)$_2$MoO$_6$ (1.51)
Dissociative | (Bi$_6$/8Ti$_2$/8)$_2$MoO$_6$ (3.9)

Table 8.1 The best possible compositions for each reaction pathway of associative and dissociative mechanism of Bismuth bases structures of orthorhombic configuration predicted by the NN model. These correspond to determinant steps attained from Figure 8.3. The best structure is that of the orthorhombic Ti containing associative pathway for (Bi$_6$/8Ti$_2$/8)$_2$MoO$_6$ structure.

ions except for the Hf ion where the limiting step is around 9.7 eV. However, the overall goal is not to give absolute energies for reaction steps but to show a trend as illustrated by Figure 8.3 and Figure 8.4, which helps to show the relevant trend for the orthorhombic bismuth based structure system for the different candidate ions expressed in this chapter. This trend gives a good idea of what candidate ion will preform better for nitrogen fixation for the bismuth based structure by comparing the limiting step for the different configurations as illustrated in Figure 8.4. Table 8.1 gives a summary of the best structure configuration attained by the NN model with the respected theoretical over-potential (limiting step) calculated for the associative and dissociative reaction mechanism. The reader should note that predictions throughout this study by both DFT and NN model should not be referenced as exact calculation, and should only be used to demonstrate the relevant trend overall in this study.
CHAPTER 9

CONCLUSION

9.1 Nitrogen Fixation

This study implemented DFT and experimental methods to explore design space of \((M_x\text{Bi}_y)_2\text{MoO}_6\) where \((M = \text{Fe, La, and Yb})\) in both the orthorhombic and monoclinic configurations as well as DFT approach to explore \(M_x\text{Mo}_y\text{S}_2\) \((M = \text{Co and Fe})\) in 1T and 2H phases. The first principle approach allowed the understanding of additional physics that would be difficult to determine and express experimentally for this large design space. Investigations are done to predict the thermodynamic reaction barriers during nitrogen fixation for two reaction pathways, the associative and dissociative reaction pathways of the Heyrovsky-type mechanism with the absence of kinetic considerations.

First, for \((M_x\text{Bi}_y)_2\text{MoO}_6\) configurations, which had the same concentration of Mo sites, thus the affinity of N and H species are explored for the orthorhombic and monoclinic substitution of Fe, La, and Yb. Thus this study expresses the balance between affinity of N and H species for configuration compositions of La, Yb, and Fe that resulted in orthorhombic structure that followed the reaction pathway of the associated mechanism to yield the lowest energy barrier. The higher the concentration of Fe and Yb resulted in significantly modulation of the Mo-O bond length, resulting in increased nitrogen affinity. Whereas, when La concentration increased, there was a greater reaction barrier for the hydrogen containing species. Thus the resulting structure was found to be a combination of Bi and Fe in the orthorhombic configuration that tended to have both affinity properties of N and H species in the associative mechanism that is \((\text{Bi}_{0.75}\text{Fe}_{0.25})_2\text{MoO}_6\) optimal structure. The approximate over-potential was 1.4 eV that is well within the band gap for orthorhombic configuration.

Second, for \(M_xM_y\text{S}_2\) configurations, which this study found that strong affinity of
hydrogen species towards Mo and a similarly strong affinity of nitrogen towards Fe. The phases with higher concentration of alloying elements resulted in a lower reaction barrier. More specifically, by incorporating Fe and Co into the structure, the affinity toward hydrogen species was exchanged with increased relative nitrogen affinity. The resulting structure was determined to be an alloy that combined both Mo and Fe. While both reactions paths could be optimized to obtain over-potentials below 2eV the most desired and the lowest of the pathways was the dissociative pathway. The optimal structure allowed the dissociative pathway and is Mo$_{0.75}$Fe$_{0.25}$S$_2$ 1T phase with a over-potential of less than 1 eV in the absence of kinetic consideration. An additional benefit of the 1T phase, which is associated with higher electronic mobility. Overall for both structures, it was found that a balanced affinity towards hydrogen and nitrogen species is required to lower the overall reaction requirement.

9.2 Machine Learning Approach

This study proposed a neural network technique based on machine learning for evaluating large design spaces to reduce computational cost for DFT simulations. Predicting the optimized atomic structure and the total energy is ultimately the bases for most first principle calculations. Thus this study looks at bismuth bases system (Bi$_2$MoO$_6$) as the example structure system and the design space consists of configurations in (M$_x$Bi$_y$)$_2$MoO$_6$ where (M = La and Yb). We have demonstrated that this method can provide accurate predictions that will ultimately reduce the computational cost required to explore the structure unique configurations by applying one of the two methods. The first method to reduce the computational cost is by having the neural network better predict and refine the initial structure system based on a given set of training data. This way the DFT simulations will have a more refined method to initialize the unit cell being evaluated, which will allow less iterative steps to be taken in evaluating the optimized configuration for that specific structure. The second method proposed, exposes the network to a training data set for a given structure system, in order for the total energy of the optimized configuration to be predicted. This
way the total energy of any configuration that makes up a given structure system can be predicted accurately based on already attained training data set for that structure system.

The training set used for this study are configurations of \((\text{Bi}_x\text{La}_y)_2\text{MoO}_6\), and the tested set used are of \((\text{Bi}_x\text{Yb}_y)_2\text{MoO}_6\) configurations. Both the training and the tested set are evaluated with DFT simulations in order to see the error response from the DFT simulations to the neural network. Ultimately for the bismuth based system explored for this study, an overall maximum vector mean squared error of \(1.6 \times 10^{-2}\) was expressed by the neural network for structure configuration of \((\text{Bi}_{5/8}\text{Yb}_{3/8})_2\text{MoO}_6\) being the worst case. Then the predicted structure for this configuration was used as the refined structure for initializing the unit cell for DFT simulation, and allowed an overall 4 hour reduction in computational time. For the tested set, this overall reduction would account for 400 hours in reduction if all structures had on average 4 hour improvement, however most structures demonstrated over 4 hours reduction when implementing the refined positions from the NN. Thus over 400 hours in reduction is expressed for the design study of the tested set. Also, the network was trained to predict the total energy for the same tested configurations, and yielded a maximum mean squared error of \(2.3 \times 10^{-7}\). The described method is independent of material system and depends only on referenced DFT simulations for a specific structure system. Thus ultimately the machine learning technique expressed for this study provides a promising starting point for high-throughput electronic structure predictions for DFT simulations in large design space based studies.

### 9.2.1 Implementing Machine Learning Approach

This study relied on the developed machine learning approach to make future predictions for candidate ions that allows a more feasible way of exploring large design spaces. Huge part of this work is to predict reaction steps of associative and dissociative mechanisms expressed for nitrogen fixation on a bismuth based structure system. The implemented approach used nitrogen fixation reaction steps for the \((\text{Bi}_x\text{M}_y)_2\text{MoO}_6\) where \(M = \ldots\)
Fe, La, Yb) orthorhombic configurations attained by DFT calculations as the training data and predictions are then made for candidate ions implemented for M in the orthorhombic (Bi$_x$M$_y$)$_2$MoO$_6$ structure. Candidate ions are chosen to have similar attributes for the studied ions of Fe, La, Yb, and Bi as in the training data, also have been known in sum way to express potential substitute for the studied ion in resent works, and also chosen based on Hume-Rothery solid solution rules. The candidate ions chosen are as follows: Ti, Cr, Ga, As, Zr, Mo, Ru, In, Sb, and Hf. Using the developed approximation approach for the total energy, specific candidate ion most stable configuration is found (finding the lowest total energy for similar ion configuration ratio). Then for the candidate ion most stable configuration, the NN model predicts the reaction steps for nitrogen fixation of the associative and dissociative mechanism. Results reveal that structure configurations of the orthorhombic (Bi$_{6/8}$Ti$_{2/8}$)$_2$MoO$_6$ for both the associative and dissociative mechanism yielding the lowest determining step (over-potential), 1.51 eV and 3.9 eV respectively. The predictions throughout this study by both DFT and NN model should not be referenced as exact calculation, and should only be used to demonstrate the relevant trend in this study that helps to reduce the overall computational expense and predict candidate ions for different structure systems.

9.3 Contribution and Publication

The author’s contribution to the research community is developing fundamental understanding of nitrogen reduction on inorganic surfaces and the determination of a balanced affinity between H and N species. Also, analysis of desorbed MoS$_2$ structure, which has not previously been investigated from a computational perspective. In addition, identified physical material parameter responsible for modulating the hydrogen and nitrogen affinity in a Bi$_x$MoO$_6$ based structures. From the computational side, developed methods that can be used to evaluate and explore large design spaces for nitrogen reduction. Additionally, developed a machine learning approach that allowed significant reduction in computational time required to analyze large design spaces. The developed machine learning approach used
a neural network which allowed predictions to be made of the fractional coordinates and the total energies for a given structure system. Lastly, implemented the developed machine learning approach to make future predictions for other candidate ions that have potential in reducing nitrogen. The publications submitted for this work are,

1) Ab initio Screening of a Sulfur Desorbed MoS$_2$ Photocatalyst for Nitrogen Fixation

2) Density Functional Theory Evaluation of Cation-doped Bismuth Molybdenum Oxide Photocatalysts for Nitrogen Fixation


9.4 Future Work

With the work presented in this study for large scale nitrogen fixation analysis and the promising starting point for the developed machine learning approach, future work aims to be more promising. The aim is to find a way to implement the machine learning approach to any structure system without the need for large scale training data sets. Possible solution to reduce the number of training data is to use other characteristic input features that describes a structure system to the machine learning algorithm. It may be feasible to use atomic radii, ionic radii, electronegativity, etc. to better characterize the input data for the neural network model. Also, future work for the machined learning approach is to investigate other activation functions and architecture implemented by the neural network model that may prove more ideal then the one used in this study. Additionally, the nitrogen fixation study gave insightful characteristic information that describes the attributes needed to be present for structure systems that allows conversion of nitrogen to ammonia. For instance, the bismuth structure system relied on the interaction of the implemented ion and an oxygen sit on the surface to modulate the Mo-O sites which allowed the modulation of nitrogen affinity. Thus future
work will explore attributes, like the modulation of the Mo-O sites, which can better assist endeavors to define a more feasible method for ammonia conversion.


[72] Xuyang Xiong, Liyong Ding, Qingqian Wang, Yongxiu Li, Qingqing Jiang, and Juncheng Hu. Synthesis and photocatalytic activity of BiOBr nanosheets with tunable exposed {010} facets. *Applied Catalysis B: Environmental*, 188:283–291, 2016.


APPENDIX A

Quantum Espresso Files

**PW Input File 'mos2.pw.in'**

```
&control
  calculation = 'vc-relax'
title = 'XXXXXXXXXX'
  restart_mode = 'from_scratch',
  pseudo_dir = '/group/XX/pps/',
  outdir = '/scratch/XX/qe_out',
  tstress = .true.,
  tprnfor = .true.,
  wf_collect = .TRUE.,
  prefix = 'XXXXXXXXXX'
  verbosity = 'high'
  etot_conv_thr = 1.0E-8
  forc_conv_thr = 1.0E-5
  nstep = 200
  max_seconds = 14200
/
&system
  ibrav = 0,
  A = 1.00
  nat = 12,
  ntyp = 6,
  ecutwfc = 90,
  ecutrho = 900,
  nspin = 1,
  starting_magnetization(1) = 2.0
  starting_magnetization(2) = 0.0
  occupations = 'smearing'
  degauss = 0.025
  smearing = 'gaussian'
/
&electrons
  electron_maxstep = 100,
  mixing_mode = 'plain'
  mixing_beta = 0.7,
  diagonalization = 'david'
  conv_thr = 1.0d-10
/
&ions
  ion_dynamics = 'bfgs'
  bfgs_ndim = 1
/
&cell
  cell_dynamics = 'bfgs'
  cell_factor = 2.0
```
press=0.0
press_conv_thr=0.01
/

CELL_PARAMETERS (alat)
6.384657367 -0.000024292 0.000005421
-3.192349721 5.529263285 -0.000005421
0.000010555 -0.000006094 20.467711121

ATOMIC_SPECIES
Mo  95.95 Mo.pbe-spn-rrkjus.UPF
Co  65.95 Co.pbe-nd-rrkjus.UPF
Fe  95.95 Fe.pbe-nd-rrkjus.UPF
S   32.06 S.pbe-n-rrkjus.UPF
N   47.01 N.pbe-rrkjus.UPF
H   1.00 H.pbe-rrkjus.UPF

ATOMIC_POSITIONS (angstrom)
P1  -0.000977855 1.843834225 1.566672406
S   1.596668889 0.921353178 -0.000003280
S   1.596667300 0.921355109 3.133930717
P2  -1.597259139 4.608417055 1.566670358
S   0.000454763 3.686041241 -0.000591528
S   0.000453373 3.686041816 3.133914649
P3  3.191311820 1.843751452 1.566674606
S   4.789062627 0.921417075 -0.000595441
S   4.789060437 0.921418565 3.133927303
P4  1.595096284 4.608462484 1.566672588
S   3.192731747 3.685953804 -0.000571941
S   3.192729555 3.685953997 3.133899563

K_POINTS (automatic)
2 2 2 1 1 1

PW Run File _runpw_pbe.pbs'

#!/bin/csh

#PBS -M XXX.wvu.edu
#PBS -m bae
#PBS -l nodes=1:ppn=16
#PBS -l walltime=4:00:00
#PBS -l pvmem=3000mb
#PBS -o qe.pw.$PBS_JOBID
#PBS -j oe
#PBS -q standby

module load compilers/intel/14.0
module load libraries/mkl/4.1.1.036
module load mpi/intel/4.1.1.036

# *** Working Directory ***
set WORKDIR = ${PBS_O_WORKDIR}
set SCRATCH = /scratch/X/${PBS_JOBID}

echo Working dir: $WORKDIR

echo Scratch dir: $SCRATCH

#cd $PBS_O_WORKDIR
#cp /users/X/src/abinit/abinit-7.4.3_intel/src/98_main/abinit .

# *** Print Node Info ***
echo ”Node file: ${PBS_NODEFILE} :”
cat ${PBS_NODEFILE}
echo ” ”
set NUM_PROCS='/bin/awk 'END {print NR}' $PBS_NODEFILE'
echo ”Running on ${NUM_PROCS} processors.”
echo

#goto scratch directory
cd ${WORKDIR}

echo Starting...
echo Run started at: ‘date’
echo

echo mpirun -np $NUM_PROCS /shared/software/MAE/X/espresso/espresso-5.0.1/bin/pw.x < mos2.pw.in > mos2.pw.out
mpirun -np $NUM_PROCS /shared/software/MAE/X/espresso/espresso-5.0.1/bin/pw.x < mos2.pw.in > mos2.pw.out

echo Done...
echo Run finished at: ‘date’

```
APPENDIX B

Matlab Code

Permutation Function 'permn.m'

function [y] = permn(N,P)
%Gives matrix of all permutations for
%N is number of elements
%P is positions
y=zeros(NˆP,P);
for i=1:P
    s=1;
    while(s<=NˆP)
        for j=1:N
            y(s:s+Nˆ(1,P)-1,i)=j;
            s=s+Nˆ(1,P);
        end
    end
end
end

Make all Configurations 'configurations.m'

clc
clear all
ne={'Bi','Fe','La','Yb'};
cd('C:XX')
A=6; %number of positions
L=2; %number of elements
C=unique(permn(L,A),'rows'); %all possible combinations
c1=1; %element1
c2=2; %element2
c3=3;
ELM='Bi'; %element that will be replaced in the input file

final1=C(sum(C==3,2)==0,:); % matrix of 2 element combination
final2=C(sum(C==3,2)==0,:); % matrix of 3 element combination
final2=final2(sum(final2==2,2)==0,:);
final2=final2(sum(final2==1,2)==0,:);
strc='BiO12_2';
cd(strc);
In=fileread('mos2.pw.in'); % input file to reference
RUN=sprintf('%s_run_pw_pbe.pbs',pwd); % run file to reference

%% BiXFeX
e1=ne{1};
e2=ne{2};
directory=sprintf('%sX%sX',e1,e2);
try
    rmdir(directory,'s');
catchend
mkdir(diractory);
cd(diractory);
for i=0:A
    final=final1(sum(final1==1,2)==i,:);
    name=sprintf('%s%i%s%i',e1,i,e2,(A-i));
    mkdir(name);
    cd(name);
    for j=1:size(final,1)
        trial=sprintf('Trial%i',j);
        mkdir(trial);
        cd(trial)
        T=sprintf('%s%n%s%n%s',strc,name,trial);
        in=strrep(In,'XXXXXXXXXX',T);
        a=strfind(in,ELM);
        a(1:length(a)-A)=[];
        for jj=1:A
            if (final(j,jj)==1)
                in(a(jj):a(jj)+1)=e1;
            else
                in(a(jj):a(jj)+1)=e2;
            end
        end
        out=fopen('mos2.pw.in','wb');
        fwrite(out,in,'*char');
        fclose(out);
        copyfile(RUN,pwd)
    cd..
end
end
cd..
%% BiXLaX
%same as BiXFeX exept e2=ne{3};
.
.
Check output file status ‘restart_trials.m’

clear all
addpath(genpath(pwd));

F=sprintf('/users/X/BiO/BiO6/BiO_min/'); % directory name
r1=fopen(tf1,'w');
r2=fopen(tf2,'w');
r3=fopen(tf3,'a');
r4=fopen(tf4,'a');
r5=fopen(tf5,'w');
cd(F);
d=dir(F); % list of sub-directory
isub=[d(:).isdir];
nameFolds=d(isub).name’;
nameFolds(ismember(nameFolds,’.’,’..’))=[];
for i=1:length(nameFolds)
    cd(nameFolds{i})
    d=dir(); % list of sub-sub-directory
    isub=[d(:).isdir];
    name={d(isub).name’};
    name(ismember(name,’.’,’..’))=[];
    for j=1:length(name)
        cd(name{j})
        d=dir();
        isub=[d(:).isdir];
        namesub={d(isub).name’};
        namesub(ismember(namesub,’.’,’..’))=[];
        for jj=1:length(namesub)
            cd(namesub{jj})
            if (exist(’run_pv0_pbe.pbs’,’file’)>0)||(isempty(dir(’qe*’)))
                cd ..
                continue
            end
            try
                a=fileread(’mos2.pw.out’);
                catch
                    fprintf(r5,’%s
’,pwd);
                    try
                        AP_restart;
                    catch
                    end
                cd ..
                continue
            end
            if strfind(a,’Begin final coordinates’)
                try
                    movefile(’run_pv0_pbe.pbs’,’run_pv0_pbe.pbs’);
                    catch
                        warning(’File already in %s,%s’,namej,namesubjj);
                    end
                delete(’qe*’);delete(’CRAS*’);
                if strfind(a,’The maximum number of steps has been reached’)
                    fprintf(r2,’%s
’,pwd);
                else
                    fprintf(r3,’%s
’,pwd);
                end
                cd ..
                continue
            elseif strfind(a,’convergence NOT achieved after’)
                try
                    movefile(’run_pv0_pbe.pbs’,’run_pv0_pbe.pbs’);
                catch
                    warning(’File already in %s,%s’,namej,namesubjj);
                end
            else
                fprintf(r5,’%s
’,pwd);
            end
        cd ..
        continue
    end
else
    fprintf(r5,’%s
’,pwd);
end
catch
end
delete(('qe*'));
fprintf(r4,'%s
',pwd);

cd ..
continue
end
if(exist('CRASH','file')>0)||(isempty(strfind(a,'JOB DONE.')))
    fprintf(r5,'%s
',pwd);
delete(('CRAS*'));delete(('qe*'));
    try
        AP_restart;
catch
        end
    fprintf(r1,'%s
',pwd);
    cd ..
continue
end
fprintf(r1,'%s
',pwd);
try
    RESTART;
catch
    end
    delete(('qe*'));
    cd ..
end
    cd ..
end
fclose all;
quit

Read atomic positions and restart 'RESTART.m'

function RESTART
out=fopen('mos2.pw.out'); % open output file
in=fopen('mos2.pw.in'); % open input file
readfile=textscan(out,'%s','delimiter',\n');
readfile1=textscan(in,'%s','delimiter',\n');
fclose(out);
fclose(in);
readfile1=readfile1{:};
readfile=Read atomic positions and restart 'RESTART.m' readfile{:};

try
    a=find(strcmp(readfile,'ATOMIC
positions (angstrom)')); % read atomic positions
    a=max(a);
    n=find(strcmp(readfile,'number of atoms/cell')); % number of atoms
    n=Read atomic positions and restart 'RESTART.m'
    n=length(n)-2:length(n));
    n=str2num(n);

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ap=readfile(a+1:a+n); % atomic position
uc=readfile(a-4:a-2); % unit cell

b=find(strcmp(readfile1,'ATOMIC_POSITIONS {angstrom}')); % write atomic position
readfile1(b+1:b+n)=ap(1:n);

b=find(strcmp(readfile1,'CELL_PARAMETERS {alat}')); % write unit cell
readfile1(b+1:b+3)=uc(1:3);
catch
derend

b=find(strncmp(readfile1,'restart mode',11)); % restart from last known position
readfile1(b)=cellstr('restart mode="restart",');
fid=fopen('mos2.pw.in','wt');
for s=1:length(readfile1)
    fprintf(fid,'%s
',readfile1{1:s});
end
fclose(fid);
derend

**Read atomic positions and restart from scratch ’AP_restart.m’**

function RESTART
out=fopen('mos2.pw.out'); % open output file
in=fopen('mos2.pw.in'); % open input file
readfile=textscan(out,'%s','delimiter',\n');
readfile1=textscan(in,'%s','delimiter',\n');
fclose(out);
fclose(in);
readfile=readfile{1};
readfile1=readfile1{1};

try
    a=find(strcmp(readfile,'ATOMIC_POSITIONS (angstrom)')); % read atomic positions
    a=max(a);
    n=find(strncmp(readfile,'number of atoms/cell',16)); % number of atoms
    n=readfile{n};
    n=n(length(n)-2:length(n));
    n=str2num(n);
    ap=readfile(a+1:a+n); % atomic position
    uc=readfile(a-4:a-2); % unit cell
    b=find(strcmp(readfile1,'ATOMIC_POSITIONS {angstrom}')); % write atomic position
    readfile1(b+1:b+n)=ap(1:n);
    b=find(strcmp(readfile1,'CELL_PARAMETERS {alat}')); % write unit cell
    readfile1(b+1:b+3)=uc(1:3);
catch
b=find(strncmp(readfile1,'restart mode',11)); % restart from scratch
readfile1(b)=cellstr('restart mode="from scratch",');
fid=fopen('mos2.pw.in','wt');
for s=1:length(readfile1)
    fprintf(fid,'%s
',readfile1{s});
end
fclose(fid);
end

---

**Charge transport figures**

% Si constants
k=1.3806e-23;% Boltzmann constant
q=1.6e-19;%C
mob_n=[1400 1400]; %cm^-2/Vs for 100
mob_p=[1400/2.5 1400/2.5];
E=1:10:10^5; %Field v/cm
v_st=[2.4e7/(1+0.8*exp(100/600)) 2.4e7/(1+0.8*exp(100/600))];

for i=1:1
    for j=1:length(E)
        drift_n(i,j)=mob_n(i)*E(j)/(1+((mob_n(i)*E(j))/v_st(i)));
        drift_p(i,j)=mob_p(i)*E(j)/(1+((mob_p(i)*E(j))/v_st(i)));
    end
end
figure(1)
hold on
r1=loglog(E,drift_n,'r','linewidth',2);
hold on
r2=loglog(E,drift_p,'b','linewidth',2);
hold off
xlabel('Field (V/cm)','fontsize',20)
ylabel('Drift Velocity (cm/s)','fontsize',20)
set(r,'fontsize',20);
ylim([10^5.5 1e8])
xlim([10^1.5 1e5])

%%% mobilaty vs doping density
rat=1e20/1e14;
N(1)=1e14;
n=100;
for i=2:n
    N(i)=N(i-1)*rat^(1/n);
end
m_min=[44.9 68.5];
m_max=[470.5 1414];
Nr=[2.23e17 9.2e16];
a=[0.719 0.711];
for j=1:2
    for i=1:length(N)
        \(\text{mob}(i,j) = m_{\text{min}}(j) + ((m_{\text{max}}(j) - m_{\text{min}}(j))/(1+(N(i)/Nr(j))^a(j))));\)
        \(\text{ro}(i,j) = 1/(q*(\text{mob}(i,j)*N(i)))\);
    end
end
figure(3)
semilogx(N,mob(:,1),'b','linewidth',2);
hold on
semilogx(N,mob(:,2),'r','linewidth',2);
hold off
xlabel('Doping density (1/cm^3)','fontsize',20)
ylabel('Mobility (cm^2/V-s)','fontsize',20)
r=legend('Holes','Electrons');
set(r,'fontsize',20);
grid on

%% Resistivity vs doping
figure(4)
loglog(N,ro(:,1),'b','linewidth',2);
hold on
loglog(N,ro(:,2),'r','linewidth',2);
hold off
r=legend('p-type','n-type');
set(r,'fontsize',20);
xlabel('Doping density (1/cm^3)','fontsize',20)
ylabel('Resistivity (\Omega-cm)','fontsize',20)
grid on
APPENDIX C

Bash Code

Submit all run files (_run_pw_pbe.pbs) inside directory ’_submit_all_pw’

#!/bin/sh

echo "Submitting to qsub"
for a in */; do
   cd $a
   for b in */; do
      cd $b
      for d in */; do
         cd $d
         qsub run pw pbe.pbs
         cd..
      done
      cd..
   done
   cd..
done
echo "Done..."

Submit run files from input (restart.out) file ’_submit_from_input_pw’

#!/bin/bash

for i in $(<restart.out); do
   cd $i
   qsub _run_pw_pbe.pbs
done

Replace all files in directory text from ’text old’ to ’text new’

find ./ -type f -exec sed -i -e ’s/text old/text new/g’ {} \;

Replace files ’mos2.pw.in’ text from ’text old’ to text new’

find ./ -name ’mos2.pw.in’ -exec sed -i -e ’s/text old/text new/g’ {} \;

Rename files that are ’mos2.pw.in’ to ’mos2.org.in’

find ./ -type f -exec rename mos2.pw.in mos2.org.in {} \;

Find files ’mos2.pw.out’ that have ’convergence NOT achieved’ and log them

find ./ -name ’mos2.pw.out’ -exec grep -l ”convergence NOT achieved” {} \; > log.txt
Example of unison code called 'run'

#!/bin/sh

module load statistics/matlab/2014a
for a in 1..6; do
    sleep 2h;
    echo "$a"
    matlab -r restart_trials
    ./_submit_from_input_pw;
done
exit;