A THEORETICAL STUDY OF STRUCTURAL AND ELECTRONIC PROPERTIES OF THE LaMnO₃ PEROVSKITE WITH THE APPLICATION

M.Sc. Thesis

By

NAVEEN SHARMA



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Submitted in partial fulfillment of the requirements for the award of the degree

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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled A Theoretical Study of Structural and Electronic Properties of the LaMnO₃ Perovskite with the application in the partial fulfillment of the requirements for the award of the degree of MASTER OF SCIENCE and submitted in the DISCIPLINE OF PHYSICS, Indian Institute of Technology Indore, is an authentic record of my own work carried out during the time period from July 2023 to May 2024 under the supervision of Dr. Srimanta Pakhira, Associate Professor, IIT Indore.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

Naveen shouma 17/05/2024

Signature of the student with date (Naveen Sharma)

This is to certify that the above statement made by the candidate is correct to

the best of my/our knowledge.

20th May 2024

Signature of the Supervisor of

M.Sc. thesis

(Dr. Srimanta Pakhira)

Dr. Srimanta Pakhira, Ph. D. Assistant Professor and Ramanujam Faculty Fellow Department of Physics, Centre for Advanced Electronics and Department of Metallurgy Engineering and Materials Sciences (MEMS) Indian Institute of Technology Indore Khandwa Road, Simrol, Indvre-453552, MP, India

NAVEEN SHARMA has successfully given his M.Sc. Oral Examination

held on 14/05/2024.

lin 20th May 2024

Signature of Supervisor of MSc thesis Date: May 14, 2024

Convener, DPGC Date:

Dr. Srimanta Pakhira, Ph. D. Assistant Professor and Ramanujam Faculty Fellow Department of Physics, Centre for Advanced Electronics and Department of Metallurgy Engineering and Materials Sciences (MEMS) Indian Institute of Technology Indore Khandwa Road, Simrol, Indore-453552, MP, India

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ABSTRACT

The oxygen reduction reaction (ORR) is crucial in electrochemical energy conversion systems like fuel cells. Typically, the kinetics of ORR are slow, necessitating practical electro-catalysts to enhance reaction rates. While Pt-based catalysts are thermodynamically suitable, their scarcity and high cost hinder commercial-scale industrial applications. In the pursuit of finding non-noble metal catalysts, this thesis presents a theoretical investigation of the LaMnO₃ perovskite material as a potential candidate for ORR.

The 3D bulk crystal structure of the LaMnO₃ perovskite exhibits a significant overlap of bands at the Fermi level, however with almost negligible electronic occupancy, rendering it inefficient as an electro-catalyst for ORR. To address this limitation, a basal plan of miller indices (001) is cleaved from the 3D LaMnO₃ perovskite and computationally designed a 2D monolayer slab structure of the LaMnO₃ material. This study unveiled that the 2D monolayer structure of LaMnO₃ shows overlap of bands and an increased density of states at the Fermi level, indicating its potential utility as a cathode material for fuel cell applications.

Emphasizing the 2D layered perovskite structure, first-principles-based density functional theory (DFT) calculations are employed to study its ORR kinetics. This investigation revealed that the basal plane of the 3D LaMnO₃ perovskite demonstrates remarkable electro-catalytic activity towards ORR, exhibiting a selectivity for the four-electron reduction pathway. Both dissociative and associative reaction mechanisms of ORR on the surfaces of the 2D monolayer LaMnO₃ perovskite are explored, by computing the change in Gibbs's free energy (Δ G) and calculating overpotential. Importantly, all the reaction intermediates investigated in this study were found to be thermodynamically favorable.

The findings of this study suggest that ORR proceeds via a $4e^{-}$ transfer mechanism on the surface of 2D LaMnO₃, with the associative mechanism favored over the dissociative pathway. This theoretical groundwork lays the foundation for future applications of 2D LaMnO₃ perovskite-based electrocatalysts, indicating their promise as Pt-free alternatives for fuel cell components.

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Chapter 1 Introduction

1.1 Fuel Cells and ORR

After the dawn of the industrial revolution, the burning of fossil fuels rapidly increased, directly resulting in the degradation of global environmental conditions, leading to global warming, depletion of the ozone layer, atmospheric pollution, and harsh climatic conditions. The interactive Figure 1.1 shows global fossil fuel consumption in terms of coal, oil, and gas. Due to the hazardous impacts of fossil fuel consumption, researchers all around the globe have shifted their attention to cleaner energy sources. These include solar, wind, hydrothermal, fuel cells, etc.



Figure 1.1. Global fossil fuel consumption.

Fuel cells have garnered significant attention as promising clean energy sources due to their high efficiency and minimal environmental impact.¹ They offer the potential to transform the energy landscape by providing a sustainable alternative to conventional fossil power generation methods. A fuel cell is an electrochemical device that uses the chemical energy of hydrogen or other fuels to cleanly and efficiently produce electricity.² If hydrogen is the fuel, the only products are electricity, water, and heat. Fuel cells offer numerous advantages compared to traditional combustion-based technologies in power plants and vehicles. They boast higher operational efficiencies than combustion engines, efficiently converting chemical energy from the fuel into electrical energy at rates surpassing 70%. In contrast to combustion engines, fuel cells exhibit lower or zero emissions. Hydrogen fuel cells, for instance, release only water, presenting a crucial solution to climate challenges by eliminating carbon dioxide emissions. Moreover, fuel cells contribute to improved air quality, as they produce no air pollutants responsible for smog and associated health issues at the operational level.



Figure 1.2. Conceptual representation of working of a fuel cell.

Fuel cells function similarly to batteries but distinguish themselves by not depleting or requiring recharging. They generate electricity and heat continuously as long as the fuel supply is maintained. A typical proton exchange membrane fuel cell contains two electrodes—an anode and a cathode encasing an electrolyte in a proton exchange membrane (PEM), as shown in Figure 1.3. For an H₂-O₂ fuel cell, at the anode area, hydrogen fuel supply is provided,² while air is directed at the cathode. A catalyst initiates the separation of hydrogen molecules into protons and electrons at the anode as the supplied hydrogen reaches and reacts at the surface of the electrode. These protons and electrons then follow distinct paths to the cathode. Electrons traverse an external circuit to reach the cathode, establishing an electric current. Simultaneously, protons migrate through the electrolyte to the cathode, where they combine with oxygen and electrons to produce water and heat. When a fuel cell operates, it creates

an electrochemical gradient (difference in chemical potential) across the PEM. This gradient is due to the difference in concentration of protons on each side of the membrane, as well as the electrical potential (voltage) difference that the cell operation establishes. Therefore, protons naturally move from areas of high potential to low, following this gradient. This continuous process ensures sustained electricity and heat generation if the fuel supply is maintained.



Figure 1.3. Simplified planar anode-electrolyte-cathode structure of a fuel cell.

A pivotal aspect within fuel cell technology revolves around the imperative advancement of efficient and economically viable catalysts designed for facilitating the oxygen reduction reaction (ORR) and hydrogen oxidation reaction (HOR), both of which constitute fundamental processes crucial to the core functionality of fuel cells.

A basic schematic of fuel cells is shown in Figure 1.3. Inside the fuel cells, the ORR occurs at the cathode.³ However, the rate of ORR at the cathode is comparatively slower than the HOR at the anode. Due to this difference, we need cost-effective and sustainable catalysts that can facilitate the rate of ORR at the fuel cell's cathode. The ORR can take place with either a 4e⁻ pathway in one step or a 2e⁻ sluggish pathway, and both pathways in acidic and alkaline electrolytes with their standard electrode potential values have been shown in Table 1.1.



Figure 1.4. The basic model of a fuel cell.

Conventionally, Pt-based catalysts have dominated the field due to their exceptional catalytic activity and stability. However, the exorbitant expenses associated with it and the restricted accessibility of platinum have spurred intensive research into finding alternative catalysts that can match or surpass its performance. Recent advances in the study of perovskite-based halide and oxide structures have shown that perovskite oxides offer an excellent alternative solution for catalyzing the ORR and HOR.^{4–7}

	In acidic electrol	In alkaline electro	lytes	
4e-	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ H	E° = 1.23V	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	$E^{\circ} = 0.40V$
transfer				
2e ⁻	$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$ I	$E^\circ = 0.68V$	$O_2 + H_2O + 2e^- \rightarrow HO^2 + OH^-$	$E^{\circ} = 0.08V$
transfer	$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	$E^{\circ} = 1.77V$	$\mathrm{HO}^{-}_{2} + \mathrm{H}_{2}\mathrm{O} + 2\mathrm{e}^{-} \rightarrow \mathrm{3OH}^{-}$	$E^{\circ} = 0.88V$

Table 1.1. Reaction pathways of ORR in fuel cells in acidic and alkaline medium.

<u>1.2 Perovskite Materials</u>

Perovskite materials belong to a distinct family and exhibit a crystalline structure with characteristics reminiscent of a cuboid or a diamond. A Russian mineralogist, L. A. Perovski, first discovered perovskites in 1839, when a mineral named calcium titanium oxide CaTiO₃ was found. Perovskites have the structural formula ABX₃, where A and B are two cations of different sizes, as shown in Figure 1.4. Perovskite materials have been used in various fields, including solar cells, nanotechnology, fuel cells, sensors, catalysts, lasers, memory devices, spintronic, LED, and photodetectors.^{8–12}



Figure 1.5. The crystal structure of a perovskite material.

In the context of fuel cells, perovskite catalysts have emerged as promising candidates due to their tunable structural and electronic properties and the ability to tailor their composition for specific reaction mechanisms.^{10,11} Perovskite oxides with the general formula ABX₃, where A and B are two cations of different sizes and X is an anion, exhibit diverse structural and electronic characteristics that can be engineered to enhance their catalytic activity. In particular, the investigation of double perovskites, where two different cations occupy the A and B sites, presents an intriguing avenue for catalytic exploration.

Lanthanum-based perovskite materials exhibit apparent optical, magnetic, and catalytic characteristics. They have found extensive use in various domains, including catalysts, chemical sensors, solid oxide fuel cell electrodes, hydrogen storage, optoelectronic devices, solar cells, and magnetic materials.^{13–16} These materials provide inherent stability, exhibit a wide range of oxidation states, offer

adaptable oxygen stoichiometry, enable efficient power conversion processes, and possess the capability to replace metals within their molecular structures.

This investigation delves into the catalytic potential of the LaMnO₃ perovskite for the Oxygen Reduction Reaction (ORR). Initially, a comprehensive analysis of the material's electronic properties, including the electronic band structure and density of states, is conducted within the bulk LaMnO₃ perovskite structure. A 2D 2 x 2 supercell monolayer of the LaMnO₃ was carefully modeled computationally. Subsequently, distinct pathways for ORR are explored in the 2D LaMnO₃ material. This specific 2D configuration is achieved by strategically cleaving a (001) basal plane from the 3D LaMnO₃ perovskite structure, allowing for a targeted and insightful examination of the catalytic behavior in a reduced dimensionality and a high number of active metal (Mn) sites. LaMnO₃ perovskite with a simple cubic crystal structure has been chosen, and it is one of the most studied perovskites in terms of its applications in spintronic, solid oxide fuel cells (SOFC), and nanomaterials. In the LaMnO₃ perovskite, lanthanum ions occupy the A-site within the perovskite crystal structure. Lanthanum typically has a 3⁺ oxidation state in this compound, and the manganese ions occupy the B-site within the perovskite structure. In the LaMnO₃, manganese ions are often in a mixed-valence state, with both Mn⁺³ and Mn⁺⁴ ions present. The combination of different valence states shapes the electronic and magnetic characteristics of the perovskite LaMnO₃.

The electronic characteristics of LaMnO₃ have been meticulously computed employing the Vienna Ab-Initio Simulation Package (VASP).¹⁷ This computational framework operates on the density functional theory (DFT) principles, a powerful method for investigating the electronic structure of materials. DFT is founded on quantum mechanics and enables the description of the electronic properties of a system by determining the electron density distribution. In the context of VASP, the electronic wave functions are expanded using a plane wave basis set, providing a versatile and accurate approach for representing the electronic states within the material.

Choosing a plane wave basis set is particularly advantageous when studying periodic systems such as crystals. By employing periodic boundary conditions inherent to crystal structures, the plane wave basis set can effectively capture the repetitive nature of the crystal lattice. This enables a comprehensive exploration of the electronic properties of LaMnO₃, considering the intricate interactions and behaviors of electrons within the crystal lattice. Overall, the integration of VASP and the plane wave basis set facilitates a detailed and reliable analysis of the electronic structure of LaMnO₃ within the framework of DFT.

<u>1.3</u> Outline of Thesis

Chapter 1: This chapter deals with an introduction to fuel cells, their urgent requirements, working principles, and the need for electro-catalysts.

Chapter 2: Density Functional Theory (DFT) calculations have been performed throughout this study; therefore, it becomes necessary to discuss DFT in this thesis's early chapters. Chapter 2 deals with the fundamentals of the DFT.

Chapter 3: As all the calculations have been performed in the Vienna Ab-Initio Simulation Package (VASP) software, Chapter 3 deals with VASP, the input and output files used in the VASP, and how these files are used for analysis of the results of the calculations performed.

Chapter 4: All the computational details of the calculations are included in Chapter 4.

Chapter 5: The results of the calculations performed on the LaMnO₃ perovskite material are discussed in this chapter.

Chapter 6: This chapter deals with conclusions and the future scope of this work.

Chapter 2 Density Functional Theory

Density Functional Theory (DFT) methods have emerged as a powerful and versatile computational tool in various fields such as condensed matter physics, material science, quantum chemistry, nanoscience, and biological sciences. It is an invaluable method for understanding the electronic structure, energetics, and properties of diverse materials, ranging from simple atoms to complex solids. In this chapter, we delve into the fundamentals of DFT methods.

The electronic structure of materials plays a crucial role in determining their properties and behaviors. Traditional quantum mechanical methods, such as Hartree-Fock (HF) theory, face significant challenges when applied to systems with many electrons. The computational cost and complexity escalate exponentially, making accurate simulations almost unachievable for many real-world materials. The need for a more efficient and computationally scalable approach was realized, leading to the development of the DFT. DFT method was formerly developed in 1964-1965 by Walter Kohn and Pierre Hohenberg.¹⁸

At its core, the DFT is a quantum mechanical method used to describe the electronic structure of a system by determining the electron density distribution. Unlike wave function-based methods, the DFT focuses on the electron density rather than individual electron wave functions. Hohenberg-Kohn theorems form the central basis of the DFT, which asserts that the ground-state electron density uniquely determines the system's external potential and, in effect, all the ground-state properties.

In the DFT method, the total energy of a system is expressed as a functional of the electron density. The Kohn-Sham Equations, derived from the Hohenberg-Kohn theorems, are solved self-consistently to obtain the electronic structure. The exchange-correlation energy, accounting for the non-classical correlation effects between electrons, is approximated using various functional forms. The success of DFT relies on the accuracy of these approximations.

2.1 Many-Body Schrodinger Equation

Building upon introductory of the quantum mechanical principles, a foundational understanding of the behavior of quantum particles necessitates the determination of their respective wave functions, denoted as $\psi(\mathbf{r})$. These wave functions must be computed for each spatial point $\mathbf{r} = x\mathbf{u}_x + y\mathbf{u}_y + z\mathbf{u}_z$ within the specified region of interest necessitating the solution of the Schrödinger Equation.

Focusing on stationary electronic states, the time-independent manifestation of the Schrödinger Equation is articulated as:

$$(\widehat{T} + \widehat{V})\psi = E\psi \tag{2-1}$$

In this context, \hat{T} represents the kinetic energy operator, \hat{V} symbolizes the operator for potential energy. The function ψ is the wave function. The Cartesian unit vectors \mathbf{u}_x , \mathbf{u}_y , and \mathbf{u}_z describe the spatial coordinates along the x, y, and z axes, respectively. Here, E is the energy eigenvalue for the stationary state $\psi(\mathbf{r})$. $|\psi(\mathbf{r})|^2$ represents the probability density of finding the particle at the point **r**.

In a material, we have three kinds of Coulombic interactions to be considered, which are (i) the repulsive term due to Coulomb interaction between electrons (r_{ee}), (ii) the repulsion between nuclei (r_{nn}), and (iii) the Coulombic attraction between the nucleus and the electrons (r_{ne}). Mathematically, these can be expressed as:

$$E_{ee} = \frac{e^2}{4\pi\epsilon_0 r_{ee}}$$
(2-2)
$$E_{nn} = \frac{Z^2 e^2}{4\pi\epsilon_0 r_{nn}}$$
(2-3)

$$E_{ne} = -\frac{Ze^2}{4\pi\epsilon_0 r_{ne}} \tag{2-4}$$

As the materials are not limited to one electron description and contain many electrons and nuclei, to study these systems, we need to define a many-body wave function, ψ , which depends on the positions of each electron and each nucleus in the system.

$$\psi = \psi(r_1, r_2, r_3, \dots, r_N; R_1, R_2, R_3, \dots, R_M)$$
(2-5)

Where, $r_1, r_2, r_3, ..., r_N$ are electron coordinates of an N electron system and, $R_1, R_2, R_3, ..., R_M$ are the coordinates of the M number of nuclei in the same system.



Figure 2.1. Interaction of electrons and ions in many-body systems.

Therefore, for a system of electrons and nuclei, the kinetic energy and potential energy terms inside the Schrodinger Equation can be written as:

Kinetic energy =
$$-\sum_{i=1}^{N} \frac{\hbar}{2m_e} \nabla_i^2 - \sum_{I=1}^{M} \frac{\hbar}{2M_I} \nabla_I^2$$
 (2-6)

(Potential energy)_{ee} =
$$\frac{1}{2}\sum_{i\neq j} \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$
 (2-7)

$$(Potential energy)_{nn} = \frac{1}{2} \sum_{I \neq J} \frac{e^2}{4\pi\epsilon_0} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}$$
(2-8)

(Potential energy)_{en} =
$$-\sum_{i,I} \frac{e^2}{4\pi\epsilon_0} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_J|}$$
 (2-9)

Putting these terms in Equation (2-1), the many-body Schrodinger Equation becomes:

$$\begin{bmatrix} -\sum_{i=1}^{N} \frac{\hbar}{2m_{e}} \nabla_{i}^{2} - \sum_{I=1}^{M} \frac{\hbar}{2M_{I}} \nabla_{I}^{2} + \frac{1}{2} \sum_{i \neq j} \frac{e^{2}}{4\pi\epsilon_{0}} \frac{1}{|\mathbf{r}_{i} - \mathbf{r}_{j}|} + \frac{1}{2} \sum_{I \neq J} \frac{e^{2}}{4\pi\epsilon_{0}} \frac{Z_{I}Z_{J}}{|\mathbf{R}_{I} - \mathbf{R}_{J}|} - \sum_{I,I} \frac{e^{2}}{4\pi\epsilon_{0}} \frac{Z_{I}}{|\mathbf{r}_{i} - \mathbf{R}_{J}|}] \psi = E_{tot} \psi$$
(2-10)

The Born-Oppenheimer (BO) approximation implies that as the nuclei are far heavier than the electrons present in the system, thus the contribution from the kinetic energy term of nuclei can be neglected, and the potential energy contribution can be treated as a constant, in Equation (2-10). After employing the Born-Oppenheimer (Clampednuclei) approximation, Equation (2-10) becomes:

$$\left[-\sum_{i=1}^{N} \frac{\nabla_{i}^{2}}{2} + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_{i} - \mathbf{r}_{j}|} - \sum_{I,I} \frac{Z_{I}}{|\mathbf{r}_{i} - \mathbf{R}_{I}|}\right] \Psi = E \Psi$$
(2-11)

$$\mathbf{E} = \mathbf{E}_{\text{tot}} - \frac{1}{2} \sum_{\mathbf{I} \neq \mathbf{J}} \frac{\mathbf{Z}_{\mathbf{I}} \mathbf{Z}_{\mathbf{J}}}{|\mathbf{R}_{\mathbf{I}} - \mathbf{R}_{\mathbf{J}}|}$$
(2-12)

The dummy index "I" was used atomic units to write the Equations (2-11, 2-12).

The nuclear coordinates, \mathbf{R}_{I} , can now be regarded as external parameters and ψ could be considered as a function of electron coordinates only: $\psi = \psi(r_1, r_2, \dots, r_N)$. The term representing the coulomb potential of nuclei experienced by electrons present in Equation (2-11) can be defined as:

$$V_{n}(\mathbf{r}) = -\sum_{I} \frac{Z_{I}}{|\mathbf{r} - \mathbf{R}_{I}|}$$
(2-13)

Therefore, the nuclear coordinates have now completely disappeared from Equation (2-11):

$$[-\sum_{i=1}^{N} \frac{\nabla_{i}^{2}}{2} + \sum_{i} V_{n}(\mathbf{r}_{i}) + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_{i} - \mathbf{r}_{j}|}] \Psi = E \Psi$$
(2-14)

Equation (2-14) is the fundamental Equation of electronic structure theory. The many-electron Hamiltonian is given by:

$$\widehat{H}(\mathbf{r}_{1}, \dots, \mathbf{r}_{n}) = -\sum_{i=1}^{N} \frac{\nabla_{i}^{2}}{2} + \sum_{i} V_{n}(\mathbf{r}_{i}) + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_{i} - \mathbf{r}_{j}|}$$
(2-15)

This many-electron Hamiltonian contains a single electron Hamiltonian (the first two terms) and an extra term due to Coulombic electron-electron interactions.

Solving Equation (2-14) itself is a complex process. Further approximations result in simplifying this process. One such approximation involves assuming that electrons do not see each other (independent electrons approximation) or do not interact with each other. Using the independent electron approximation, the last Columbic repulsion term from Equation (2-11) could be easily dropped, and Equation (2-14) becomes:

$$\sum_{i} \widehat{H}_{0}(\mathbf{r}_{i}) \psi = E \psi \qquad (2-16)$$

$$\widehat{H}_0(\mathbf{r}) = -\frac{1}{2}\nabla^2 + V_n(\mathbf{r})$$
(2-17)

This allows us to write the many-body wave function ψ as a slater determinant and obtain the single-particle wave functions as the solution of Equation (2-16). Also, the wave function can now be written in terms of the product of single electron wave functions:

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \phi_1(\mathbf{r}_1) \dots \dots \phi_N(\mathbf{r}_N)$$
 (2-18)

Supposing that the wavefunctions ϕ_i , are obtained by solving the single electron wavefunctions:

$$\widehat{H}_{0}(\mathbf{r})\phi_{i}(\mathbf{r}) = \epsilon_{i}\phi_{i}(\mathbf{r})$$
(2-19)

2.2 Hartree-Fock Equations

The Hartree-Fock Equations are derived from the variational method.¹⁹ To derive these Equations, the ground state energy of the system is minimized with respect to the single electron wave functions ϕ_i . The central idea of Hartree-Fock theory is to express the total energy of the system as some functional of the wave function, and then find the wave function (essentially these are ground state wave functions) that minimizes this energy.

In the Hartree-Fock theory, the many-body wave functions are expanded using the Slater determinant of one-electron wave functions (orbitals). Equation (2-18) does

not obey the Pauli exclusion principle, thus, expressing many-electron wave function in the form of a Slater determinant of single electrons is a preferred choice. These orbitals are constructed from a basis set of atomic orbitals. The total energy of the system can be formulated as a functional of the wave function ($E = \mathcal{F}[\Psi]$). According to the variational principle, the energy derived from any trial wave function will invariably surpass or match the true ground-state energy. The goal is to find the wave function that minimizes this energy.

$$\mathbf{E} = \int d\mathbf{r}_1 \dots \dots d\mathbf{r}_N \boldsymbol{\psi}^* \widehat{\mathbf{H}} \boldsymbol{\psi}$$
(2-20)

On minimizing the energy E with respect to the functions $\phi_i(\mathbf{r})$ in the Slater determinant, and requiring that these functions are orthonormal:

$$\frac{\delta E}{\delta \phi_i^*} = 0, \qquad (2-21)$$

$$\int d\mathbf{r} \phi_i^*(\mathbf{r}) \phi_j(\mathbf{r}) = \delta_{ij}$$
(2-22)

This leads to a set of Equations known as the Hartree-Fock Equations, which are a set of coupled integral-differential Equations (2-23 to 2-25).

$$\left[-\frac{\nabla^2}{2} + V_{\rm n}(\mathbf{r}) + V_{\rm H}(\mathbf{r})\right]\phi_{\rm i}(\mathbf{r}) + \int d\mathbf{r}' V_{\rm X}(\mathbf{r},\mathbf{r}')\phi_{\rm i}(\mathbf{r}') = \epsilon_{\rm i}\phi_{\rm i}(\mathbf{r}), \quad (2-23)$$

$$\mathbf{n}(\mathbf{r}) = \sum_{i} |\phi_i(\mathbf{r})|^2, \qquad (2-24)$$

$$\nabla^2 \mathbf{V}_{\mathrm{H}}(\mathbf{r}) = -4\pi \mathbf{n}(\mathbf{r}). \tag{2-25}$$

$$V_{\rm H}(\mathbf{r}) = \int d\mathbf{r}' \frac{\mathbf{n}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$
(2-26)

$$V_{X}(\mathbf{r},\mathbf{r}') = -\sum_{j} \frac{\phi_{j}^{*}(\mathbf{r}')\phi_{j}(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}$$
(2-27)

The Hartree-Fock Equations are typically solved iteratively using a self-consistent field (SCF) approach. In this procedure, an initial guess for the molecular orbitals is provided, and then the Equations are solved to obtain new orbitals. This process is

repeated until self-consistency is achieved, meaning the orbitals no longer change significantly between successive iterations.

2.3 Kohn-Sham (KS) Equations

Kohn-Sham Equations are the central idea of the density functional theory (DFT). The Kohn-Sham Equations are derived from a set of fundamental theorems in the DFT, including the Hohenberg-Kohn theorems and the Kohn-Sham theorem.²⁰ The Hohenberg-Kohn theorems establish that the external potential (Equation 2-13) is uniquely determined from the ground-state electron density, and conversely, the external potential uniquely determines the ground-state electron density.



Figure 2.2. Representation of a many-body electronic system in the DFT perspective.

- E is the energy of the ground state:
- $n(\mathbf{r}) \xrightarrow{\mathcal{F}} E \quad E = \mathcal{F}[n(\mathbf{r})]$ (2-26)
- E is the energy of an excited state:

$$\Psi(\mathbf{r}_{1}, \dots, \mathbf{r}_{N}) \xrightarrow{\mathcal{F}} E$$

$$E = \mathcal{F}[\Psi(\mathbf{r}_{1}, \dots, \mathbf{r}_{N})]$$
(2-27)



Figure 2.3. Correspondence between external potentials, ground state wave functions, and ground state densities for the case of degenerate ground states.

There is a unique one-to-one mapping between a ground-state wave function and its one-electron density, and the knowledge of $n(\mathbf{r})$ is sufficient to determine the ground-state energy (and other ground-state properties) of the molecular system. Therefore, the total energy of the system in their ground state is a functional of their electron density. From Equation (2-26 and 2-20), it can be concluded that:

$$\mathcal{F}[\mathbf{n}] = \int d\mathbf{r} \mathbf{n}(\mathbf{r}) \mathbf{V}_{\mathbf{n}}(\mathbf{r}) + \langle \Psi(\mathbf{n}) | \widehat{\mathbf{T}} + \widehat{\mathbf{W}} | \Psi(\mathbf{n}) \rangle \qquad (2-28)$$

The first term of the functional has an explicit dependence on the density, $n(\mathbf{r})$; however, the next two terms (kinetic and coulombic energy) at the end only have an implicit dependence on density. The idea of Kohn-Sham was to decompose these implicit terms into kinetic and coulomb energy of independent electrons as present

$$E = \mathcal{F}[n]$$

$$= \int d\mathbf{r}n(\mathbf{r})V_{n}(\mathbf{r}) - \sum_{i} \int d\mathbf{r}\phi_{i}^{*}(\mathbf{r}) \frac{\nabla^{2}}{2}\phi_{i}(\mathbf{r})$$

$$+ \frac{1}{2} \iint d\mathbf{r}d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}[n]$$
(2-29)

in Equation (2-23), along with an additional term that would account for the difference (Equation 2-29).

Here, the first three terms are total energy as independent electron approximation, and the last term is the exchange and correlation term. Collectively, the Kohn-Sham Equations are given by Equation (2-30 to 2-35).

Equation (2-30) is our standard single-particle Schrodinger Equation and can be solved as a standard eigenvalue problem. However, to solve this, we need to know the form of potentials in Equation (2-31). $V_{\rm H}(\mathbf{r})$, and $V_{\rm xc}(\mathbf{r})$ depend on the density, and the density depends on the unknown eigenfunctions, ϕ_i , through Equation (2-35). These Equations are, therefore, self-consistent and need to be solved iteratively.

$$\left[-\frac{1}{2}\nabla^2 + V_{\text{tot}}(\mathbf{r})\right]\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r}), \qquad (2-30)$$

$$V_{tot}(\mathbf{r}) = V_{n}(\mathbf{r}) + V_{H}(\mathbf{r}) + V_{xc}(\mathbf{r}), \qquad (2-31)$$

$$V_{n}(\mathbf{r}) = -\sum_{I} \frac{Z_{I}}{|\mathbf{r} - \mathbf{R}_{I}|'}$$
(2-32)

$$\nabla^2 \mathbf{V}_{\mathrm{H}}(\mathbf{r}) = -4\pi \mathbf{n}(\mathbf{r}), \qquad (2-33)$$

$$V_{\rm xc}(\mathbf{r}) = \frac{\delta E_{\rm xc}[n]}{\delta n}(\mathbf{r}), \qquad (2-34)$$

$$\mathbf{n}(\mathbf{r}) = \sum_{i} |\phi_{i}(\mathbf{r})|^{2}.$$
(2-35)

The practical way of solving these Kohn-Sham Equations involves starting with specifying nuclear coordinates in such a way that nuclear potential $V_n(\mathbf{r})$ could be easily calculated using Equation (2-32). This information is available in crystallographic data, which we can put in the POSCAR file for the Vienna *Ab initio* Simulation Package (VASP) software.^{17,21–23} Then, for the calculation of Hartree and exchange and correlation potential, an initial guess of density is taken, and this lets us construct our total potential $V_{tot}(\mathbf{r})$. With this information available to us, we can proceed to solve the Kohn-Sham Equations. The exact nature of the process is shown in Figure 2.4.



Figure 2.4. Schematic flow chart for finding self-consistent solutions of Kohn-Sham Equations.

2.4 Exchange and Correlation Functionals

While solving the Kohn-Sham Equations, exchange and correlation functions are required to account for the electron-electron interaction, as required by Equation (2-34).²⁴ John P. Perdew has related the progression of density functional approximations to a "Jacob's ladder," where each rung symbolizes a different level of complexity that increases as we climb higher.²⁵ At the bottom of this metaphorical ladder lies the Local Density Approximation (LDA),²⁴ which stands as the most rudimentary form of density functional. It exclusively computes the exchange and correlation energy based solely on the electron density. Generalized Gradient Approximation (GGA) is the next rung of this ladder,²⁶ which includes both the density and its gradient to solve for the exchange correlation energy density.²⁴ Hybrid functionals integrate a portion of non-local, exact exchange-energy density with a Generalized Gradient Approximation (GGA). Climbing further up the ladder, the highest rung introduces fully non-local functionals, which expand upon hybrid functionals by incorporating unoccupied Kohn-Sham orbitals and energies.



Figure 2.5. Jacob's ladder of exchange-correlation functionals.

As stated above, the LDA functionals only have a dependence on the local density and these functionals typically overestimate the strength of all bonds near to the equilibrium position.

$$E_{\rm XC}^{\rm LDA} = E_{\rm XC}^{\rm LDA}[n(\vec{r})]$$
(2-36)

GGAs, on the other hand, advance from LDAs by explicitly relying on both the density and its gradient (which signifies the rate of change of density in a local region). The gradient of density considers that a molecule's electron density is not spatially uniform, thereby, GGA functionals result in a more accurate description of system energies and equilibrium bond lengths. Some of the popular GGA functionals are PBE, BLYP, and OLYP.

$$\mathbf{E}_{\mathrm{XC}}^{\mathrm{GGA}} = \mathbf{E}_{\mathrm{XC}}^{\mathrm{GGA}}[\mathbf{n}(\vec{\mathbf{r}}), \, \vec{\nabla}\mathbf{n}(\vec{\mathbf{r}})] \tag{2-37}$$

2.5 Conclusion and Limitations of the DFT Methods

In conclusion, the development of Density Functional Theory (DFT) methods and the formulation of the Kohn-Sham Equations have revolutionized our understanding and computational modeling of electronic structure in modern applied quantum physics, materials chemistry and condensed matter physics. Here are some of the material properties which can be calculated with good accuracy using DFT:

- Equilibrium structures,
- Vibrational properties and vibrational spectra,
- Binding energies of molecules and cohesive energies of solids,
- Band structures of metals and semiconductors.
- Thermodynamics potentials and mechanical properties of solids.

While the DFT methods have become a highly successful and widely used method for predicting the properties of materials and molecules, it also has some limitations:

• The DFT method relies on approximations for the exchange-correlation functional (as present in Equation (2-34), which describes the electron-electron interactions. While many functionals exist, none are universally accurate across all systems and properties. The choice of functional can significantly impact the results obtained from the DFT calculations.

Chapter 3 Vienna *ab-initio* simulation package (VASP)

3.1 Introduction to VASP

The Vienna *Ab-initio* Simulation Package (VASP) stands as a cornerstone in the domain of computational materials science and quantum mechanics. Developed by the theoretical solid-state physics group at the University of Vienna, Austria, VASP has emerged as a powerful tool for accurately simulating the electronic structure and properties of materials from first principles.^{17,21–23}

At its core, VASP employs the DFT methods to describe the electronic structure of 3D bulk structure crystals, 2D slabs, nanomaterials, atoms and molecules. One of the distinguishing features of the VASP is its implementation of plane wave basis sets coupled with pseudopotentials or projector-augmented wave (PAW) methods.^{27,28} This combination enables accurate and efficient calculations, even for complex systems with large unit cells and a high number of atoms.

Furthermore, VASP offers a plethora of advanced functionalities and capabilities, including:

- Hybrid functionals: Combining the advantages of both standard DFT functionals and exact exchange-correlation functionals.²⁴
- Non-collinear magnetism: Allowing for the simulation of magnetic materials with complex magnetic structures.
- Vibrational properties and phonon spectra: Calculating phonon dispersion relations and vibrational spectra to study lattice dynamics.
- Molecular dynamics: Simulating the dynamical behavior of materials at finite temperatures.
- Transition state search: Identifying transition states and reaction pathways for chemical reactions.

The widespread adoption of VASP within the scientific community can be attributed to its robustness, accuracy, and versatility, making it an indispensable tool for researchers across various disciplines, including condensed matter physics, chemistry, materials science, and beyond.

<u>3.2</u> Input Files of VASP

To work with the VASP, we require knowledge of four basic standard input files which are required for all the various calculations possible through VASP, such as geometry optimization, single point calculations, electronic properties calculations, frequency calculations, etc. Users must provide these input files containing key parameters and settings. These input files serve as directives to the VASP, guiding the computational workflow and specifying the desired calculations. Here, we introduce the four fundamental input files utilized in the VASP simulations:

1. INCAR:

The INCAR file serves as the central control file in VASP simulations, containing a comprehensive list of computational parameters and settings. Users specify parameters such as electronic convergence criteria, type of calculations (e.g., optimization, electronic structure, and molecular dynamics), choice of exchange-correlation functional, and convergence thresholds for various iterative algorithms. Additionally, INCAR allows users to enable or disable specific features and functionalities within VASP, tailoring the calculation to the desired level of accuracy and computational efficiency. Some common tags used in the INCAR file are discussed below (there exist many more tags, but these are the most common and most used in this thesis work):

• **NELM:** NELM specifies the maximum number of electronic relaxation steps performed by VASP during a single electronic self-consistent field (SCF) cycle. NELM has a default value of 60. Increasing NELM can improve convergence, but it also increases computational cost. Users may choose values such as 80, 100, or even higher depending on the system and desired level of convergence.

- EDIFF: EDIFF sets the convergence criterion for the electronic energy during an SCF cycle. It determines the threshold below which the change in total energy between consecutive iterations must fall for the calculation to converge. EDIFF has a default value of 10⁻⁴.
- **ISTART:** ISTART specifies how the electronic structure calculation should be initialized. Users may choose values based on their specific requirements. Common alternatives include 0 (starting from scratch), 1 (read from WAVECAR), or 2 (read from CHGCAR).
- **ISPIN:** ISPIN determines whether spin polarization is included in the calculation. It specifies the number of spin channels, with ISPIN = 1 indicating non-magnetic calculations and ISPIN = 2 indicating spin-polarized calculations.
- ENCUT: ENCUT sets the plane wave energy cutoff (in eV) for the basis set used to expand the electronic wave functions.
- **NSW:** NSW specifies the maximum number of ionic steps in a molecular dynamics or geometry optimization calculation.
- **ISIF:** ISIF determines which degrees of freedom are allowed to relax during geometry optimization or molecular dynamics simulation. It enables the selective relaxation of atomic positions, cell shape, and cell volume to reach the equilibrium structure. Common alternatives include 0 (no relaxation), 1 (cell shape only), 2 (cell shape and volume), 3 (cell shape and atomic positions), 4 (cell shape, volume, and atomic positions), 5 (ionic strains), or 6 (constant volume).
- **ISYM:** ISYM specifies whether symmetry is used to speed up electronic structure calculations. It exploits the symmetry of the crystal lattice to reduce the computational effort required for electronic structure calculations. Users may choose between 0 (no symmetry), 1 (symmetry during self-consistency cycle), and 2 (symmetry for the entire calculation).
- **EDIFFG:** EDIFFG sets the convergence criterion for the ionic forces during a geometry optimization or molecular dynamics simulation. It ensures that

the forces acting on the atoms are minimized to achieve a relaxed atomic structure.

• **IBRION:** IBRION specifies the algorithm used for ionic relaxation in molecular dynamics or geometry optimization calculations. It determines the method employed to update atomic positions during structural relaxation, including conjugate gradient, quasi-Newton, or molecular dynamics algorithms. Users may choose between different algorithms for ionic relaxation. Common alternatives include 0 (no relaxation), 1 (conjugate gradient), 2 (quasi-Newton), or 3 (damped molecular dynamics).

2. POSCAR (POSCAR/CONTCAR):

The POSCAR file defines the crystal structure and atomic positions of the system under investigation. Users provide information regarding the lattice vectors, atomic species, and corresponding fractional coordinates or Cartesian coordinates of atoms. This file serves as the initial configuration for geometry optimizations, electronic structure calculations, and molecular dynamics simulations. Additionally, the CONTCAR file, generated during geometry optimization, stores the final relaxed atomic positions after convergence. Below is an example of a POSCAR file:

1	A1 B1	C3		
2	1.0			
3	3.94	43700000000006	0.0000000000000000	0.000000000000002
4	0.00	00000000000006	3.9443700000000006	0.000000000000002
5	0.00	000000000000000000000000000000000000000	0.0000000000000000	3.9443700000000006
6	ABC			
7	113			
8	direct			
9	0.00	000000000000000000000000000000000000000	0.0000000000000000	0.000000000000000 A3+
10	0.50	000000000000000000000000000000000000000	0.5000000000000000	0.500000000000000 B3+
11	0.00	000000000000000000000000000000000000000	0.5000000000000000	0.500000000000000 C2-
12	0.50	000000000000000000000000000000000000000	0.5000000000000000	0.000000000000000 C2-
13	0.50	000000000000000000000000000000000000000	0.0000000000000000	0.500000000000000 C2-

Figure 3.1. Format of basic POSCAR input file for VASP.

The first line contains a comment describing the material composition, in this case it is ABC₃. The second line specifies the universal scaling factor for the lattice vector (1.0 in this case). The next three lines define the lattice vectors of the unit cell in Cartesian coordinates. Following the lattice vectors, there is a line indicating the types of atoms present in the system, denoted by A, B, and C. The next line specifies

the number of these atoms present in the system. The next line specifies whether the atomic positions are present in direct (fractional) or Cartesian coordinates. Finally, the last section contains the fractional coordinates of the atoms present in the unit cell, along with their oxidation states.

3. **KPOINTS**:

The KPOINTS file specifies the k-point mesh used in Brillouin zone sampling for electronic structure calculations. K-points play a crucial role in accurately representing the electronic band structure and density of states of materials. Users define the grid of k-points along with optional parameters such as the Monkhorst-Pack scheme, which ensures an appropriate density of k-points in the Brillouin zone. The proper selection of k-points is essential for achieving convergence and obtaining reliable results for the electronic structure.

4. POTCAR:

The POTCAR file contains pseudopotential information for each atomic species present in the system. Pseudopotentials are used to describe the interaction between valence electrons and atomic nuclei, allowing for efficient and accurate calculations by reducing the computational burden associated with modeling core electrons. VASP provides a library of pre-generated pseudopotentials for a wide range of elements, each stored in the POTCAR file. Users select the appropriate pseudopotentials based on the elements present in their system.

3.3 Output Files Of VASP

VASP generates several output files during a calculation, each containing valuable information about the electronic structure, energy, and other properties of the simulated system. Here are explanations of some of the basic output files commonly produced by VASP:

1. **CONTCAR:** The CONTCAR file contains the final atomic positions and lattice vectors after relaxation, obtained from a geometry optimization or molecular dynamics simulation in VASP. The CONTCAR file follows the

same format as the POSCAR file. It typically contains information about the lattice vectors, atomic species, numbers of atoms, and atomic positions.

2. CHGCAR: The CHGCAR file in VASP contains information about the charge density of the system, which is a fundamental quantity in electronic structure calculations. The CHGCAR file is typically in a plain text format. It may be formatted similarly to the POSCAR or CONTCAR files, containing information about the lattice vectors, atomic species, numbers of atoms, and possibly atomic positions. Following this header information, the main body of the file consists of the charge density data arranged in a three-dimensional grid. In Figure 3.2 below, a general CHGCAR file and its visualization are shown.



Figure 3.2. (a) Format of basic CHGCAR input file for VASP (b) Visualization of a general CHGCAR using VESTA software.

3. **OUTCAR:** The OUTCAR file provides comprehensive information about the VASP calculation, including convergence details, iteration history, electronic structure, forces, stresses, and various other properties of the simulated system. The Free energies of the ion-electron systems for the materials are written at the end section of the OUTCAR file after performing calculations and minimizing the Hellmann-Feynman forces. Free energy without energy is also written.

These are some of the basic output files that are required while performing calculations in VASP software.

Chapter 4 Computational Details

4.1 Calculation of Electronic Properties of 3D and 2D LaMnO₃ Perovskite

For the calculations of equilibrium geometries, crystal lattice constants, and electronic properties, i.e., electronic band structure and total density of states (DOS) of both 3D and 2D monolayer of LaMnO₃ perovskite, the first principle-based density functional theory (DFT-D) method was employed. We have included Grimme's dispersion corrections for including the Van der Waals dispersion energy correction. To describe the exchange and correlation functionals accurately, we have utilized the Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation.^{29,30} Additionally, the method incorporates an all-electron core treatment approach to ensure comprehensive modeling of the electronic structure. These calculation methods were implemented in the Vienna ab-initio simulation package (VASP).^{17,31} This VASP code makes use of plane wave basis sets to express central quantities such as local potentials, electronic charge densities and one electron orbitals.^{31,32} To consider the weak Van der Waals interaction, the thirdorder correction of the Grimme's semi-empirical correction parameters were added in the DFT computation.³³ During the periodic DFT-D calculations, we performed spin-polarized calculations to obtain the equilibrium geometries and the electronic properties. This has been performed using the keyword "ISPIN" in the VASP code. The projector augmented wave potentials with Perdew-Burke-Ernzerhof (PAW_PBE) functional were used to describe the La, Mn, O, and H atoms.²⁹ A plane wave cut-off energy of 450 eV was used. Fermi-smearing with a Gaussian width of 0.05 eV is used to accelerate the relaxation process. Atomic positions were relaxed until the forces reached a threshold value of 0.01 eV/Å. A Hubbard potential correction of 5.0 eV is used for Mn d-orbitals, in all calculations.³⁴ For geometry optimization of 3D LaMnO₃ perovskite structure a k-point grid of 4 x 4 x 4 of Monkhorst pack was used. These k-points are used to carry out integrations in the first Brillouin zone of the sample. We cleaved a (001) plane from the 3D LaMnO₃ perovskite structure and computationally modeled a 2 x 2 supercell of the cleaved 2D surface. This 2D monolayer of LaMnO₃ was modeled to increase the surface area and the number of active sites on the surface. A vacuum slab of 15 Å was added to the 2D monolayer and there is no periodicity in the z-direction for the monolayer. For relaxation of the slab, atomic positions were relaxed until forces reached a threshold value of 0.02 eV/Å. For geometry optimization of 2D monolayer LaMnO₃ perovskite structure a k-point grid of 4 x 4 x 1 of Monkhorst pack was used.

4.2 Theoretical Calculations for the ORR

For the present investigation of the 2D monolayer slab of LaMnO₃ perovskite material, all the reaction intermediate steps of ORR are explored at the conditions respective to the computational hydrogen electrode (CHE) or the standard hydrogen electrode (SHE) model. Under the SHE conditions and pH = 0, and the electrode potential U = 0 versus SHE, the anodic reaction H⁺ + e⁻ $\rightarrow \frac{1}{2}$ H₂ is at equilibrium at 1 bar H₂ gas phase and temperature of 298 K. There are two mechanisms responsible for ORR, namely, associative, and dissociative mechanisms.

$$O_2 \rightarrow O_2^* \rightarrow 2O^* \rightarrow O^* + OH^* \rightarrow O^* + H_2O \text{ (or } H_2O_2) \rightarrow OH^* + H_2O$$

$$\rightarrow 2H_2O$$

$$O_2 \rightarrow O_2^* \rightarrow OOH^* \rightarrow O^* + H_2O \text{ (or } H_2O_2) \rightarrow OH^* + H_2O \rightarrow 2H_2O$$
(4-2)

Equation (4-1) represents the dissociative mechanism and Equation (4-2) represents the associative mechanism of the ORR. All the active sites of the catalyst, where the intermediate species are adsorbed during the reaction, are represented by * here. For the 4e⁻ transfer mechanism, the product is H₂O, while for the 2e⁻ transfer the product is H₂O₂. The adsorption energies (ΔE) presented in this study were determined by computing the energy difference between the energy of the monolayer with the adsorbed species [E_{monolayer+adsorbate}] and the energy of the catalytic monolayer [E_{monolayer}], along with the energy of the adsorbate in isolation [E_{adsorbate}]. This calculation utilizes the following Equation:

$$\Delta E = E_{\text{monolayer+adsorbate}} - E_{\text{monolayer}} - E_{\text{adsorbate}}$$
(4-3)

For an adsorbate to energetically bind to the catalyst the adsorption energy should be negative, indicating a favorable reaction between both the species. Therefore, negative adsorption energy is favorable for elementary reactions over the surface of the 2D monolayer of the catalyst. The value of ΔG in each reaction step is evaluated by the following Equation:

$$\Delta G = \Delta E - \Delta E_{ZPE} - T\Delta S \tag{4-4}$$

In Equation (4-4), ΔE is the adsorption energy obtained from the DFT-D calculations of the equilibrium structures, ΔE_{ZPE} is the zero-point energy and ΔS is the entropy correction.⁴ While calculating the free energies of all the reaction intermediates, we have performed frequency calculations in VASP to account for the T ΔS and ΔE_{ZPE} terms in the Equation (4-4). We have kept the temperature at 298.15 K to simulate room temperature conditions that are suitable for fuel cell operations. Another important parameter that reflects the energy barrier for a given electrochemical reaction, such as ORR, is the overpotential, η . To calculate this quantity, we have used the relationship $\eta = 1.23 - \min (\Delta G \text{ of ORR steps})/\text{eV}$. Here, ΔG_{\min} is the minimum of all the Gibbs free energies from the intermediate steps of the ORR, and 1.23 Vs SHE is the thermodynamic potential.

Chapter 5 Results and Discussion

5.1 Structural and Electronic Properties of the 3D Bulk Crystal structure LaMnO₃ Perovskite

The computed equilibrium lattice constants of the 3D bulk crystal structure of the LaMnO₃ perovskite material are a = b = c = 3.89 Å, $\alpha = \gamma = 90.0^{\circ}$ and $\beta = 89.99^{\circ}$. The equilibrium Mn-O and La-O bond distances are 1.94 Å and 2.75 Å, respectively, computed by using the GGA+U method as tabulated in Table 5.1. Figure 5.1a shows the equilibrium geometry of the LaMnO₃ perovskite. For the calculations of the electronic band structure and total DOS, a high symmetric k-vector path Γ -R-M-X-T-Z- Γ has been chosen, and plots have been obtained corresponding to this highly symmetric direction. A total number of eight electronic bands (which are sufficient to observe the electronic properties) around the Fermi level have been considered above and below the Fermi energy level (E_F) in the first Brillouin zone along the highly symmetric Γ -R-M-X-T-Z- Γ direction. The remarkable symmetry of this path aligns seamlessly with the inherent symmetry of the perovskite structure.

System	Lattice constants. (a, b, c in Å)	Angle (α, β, γ)	Space group symmetry	Bond type (Distance in Å)	Band gap (E g)
3D LaMnO ₃	a = b = c = 3.895	$\alpha = \gamma = 90.0^{\circ}$ and $\beta = 89.99^{\circ}$	Pm-3m	Mn-O = 1.948 La-O = 2.75	0.0 eV
2D LaMnO ₃	a = b = 7.41	$\alpha = \gamma = 90.0^{\circ}$	P1	Mn-O = 1.86 La-O = 2.65	0.0 eV

Table 5.1. The equilibrium lattice constants of the 3D and 2D LaMnO3 crystal structure.

It has been found that the LaMnO₃ perovskite has no electronic band gap, indicating it is metallic in nature, as there is almost negligible electronic density available at the

Fermi level. The equilibrium lattice constants and bond lengths exhibit close agreement with the findings reported earlier. The results are reported in Table 5.1. Both the electronic band structure and total DOS have been calculated (using the GGA+U method) with respect to the E_F meaning that both the band structure and DOS have been normalized and are depicted in Figure 5.2a-c.



Figure 5.1. (a) Equilibrium crystal structure of 3D LaMnO₃ perovskite material, (b) Top and Side view of equilibrium 2D monolayer structure of the LaMnO₃ perovskite.

The GGA+U calculation for the band structure of the LaMnO₃ has found that there is a significant overlap of the bands near the E_F , indicating the highly conducting properties of the material. From the DOS calculations, it can be concluded that near the E_F there are very few available electronic states for electrons to occupy, as represented in Figure 5.2a-c. Thus, the LaMnO₃ possesses a semi-metallic nature. We have compared the electronic properties of LaMnO₃ using the GGA+U method, where Hubbard's potential value (U) is set to 5.0 eV (for the Mn atom) with the calculations performed without Hubbard correction.



Figure 5.2. (a) Equilibrium crystal structure of 3D LaMnO₃ perovskite, (b) electronic band structure plot, the dotted lines represent the spin down states and solid lines represent the spin up states, (c) total density of states (DOS) of equilibrium LaMnO₃ perovskite. (Calculated with GGA+U method)



Figure 5.3. (a) Equilibrium crystal structure of 3D LaMnO₃ perovskite, (b) electronic band structure plot, the dotted lines represent the spin down states and solid lines represent the spin up states, (c) total density of states (DOS) of equilibrium LaMnO₃ perovskite (Calculated without GGA+U method)

The calculated electronic BAND structure and DOS without the Hubbard potential correction are plotted and shown in Figure 5.3a-c. These plots also confirm the semimetallic nature. However, the GGA+U calculations show a more accurate BAND structure plot and fewer crossovers of bands at the Fermi level. Because there is not much electronic density available at the Fermi level, the 3D LaMnO₃ perovskite can not be directly used as a catalyst. As there is no electronic density present near the Fermi level (E_F), so the 3D LaMnO₃ perovskite cannot be directly used as a catalyst for ORR applications, despite having an overlap of bands near the Fermi level. Therefore, extending our study in a new direction, we started with cleaving a (0 0 1) surface from the 3D LaMnO₃ crystal structure and computationally modeled a 2D monolayer 2 x 2 supercell of the LaMnO₃ with a vacuum slab of 15 Å in the zdirection, i.e., there is no symmetry along the z-axis for this 2D monolayer. The height of the 15 Å vacuum in the monolayer is kept avoiding any interactions among different layers of the 2D slab. Similar calculations for geometry optimization, equilibrium geometry, and electronic properties of the 2D monolayer LaMnO₃ were performed using the DFT-D method and incorporating GGA+U parameters. After obtaining the equilibrium geometry, obtained equilibrium lattice constants were found to be a = b = 7.41 Å, and $\alpha = \beta = 90.0^{\circ}$. The present DFT-D study found that this 2D monolayer of LaMnO₃ has a P1 layer group symmetry. We calculated the electronic band structure and total density of states of the 2D monolayer of LaMnO₃ perovskite and found an overlap of bands at the Fermi level and a significant increase in electron occupancy near the Fermi level. The electronic property calculations, i.e., the electronic band structure and total density of states, were plotted by selecting a highly symmetric k-vector path Γ -X-M- Γ . All the equilibrium constants, bond lengths, and symmetry are present in Table 5.1. The band structure and total density of states are plotted in Figure 5.4a-c.

5.2 Structural and Electronic Properties of 2D Monolayer of LaMnO₃ Perovskite

After obtaining the equilibrium geometry, the equilibrium lattice constants were found to be a = b = 7.41 Å, and $\alpha = \beta = 90.0^{\circ}$. The present DFT-D study found that this 2D monolayer of LaMnO₃ has a P1 layer group symmetry. We calculated the electronic band structure and total density of states of the 2D monolayer of the LaMnO₃ perovskite and found an overlap of bands at the Fermi level and a significant increase in electron occupancy near the Fermi level. The electronic property calculations, i.e., the electronic band structure and total density of states, were plotted by selecting a highly symmetric k-vector path Γ -X-M- Γ . All the equilibrium constants, bond lengths, and symmetry are reported in Table 5.1. The electronic band structure and total density of states are plotted in Figure 5.4a-c.



Figure 5.4. (a) Top view and side view of 2D monolayer structure of LaMnO₃ perovskite, (b) electronic band structure, (c) total density of states

5.3 Associative Mechanism of ORR

After the careful analysis of both the 3D and 2D electronic properties of the LaMnO₃ perovskite and confirming the conductive behavior of the 2D monolayer of LaMnO₃ perovskite, the DFT calculations are performed for all the intermediate species taking part in the ORR through two widely studied mechanisms: Associative and Dissociative. All the intermediate species for associative mechanism are carefully modeled using VESTA software, and the pathways are represented in Figure 5.5a-b.



Figure 5.5. Schematic representations of (a) Associative mechanism and (b) Dissociative mechanism of the O_2 reduction reaction pathway performed on the surface of the 2D monolayer of LaMnO₃.



Figure 5.6. Reaction pathway for the associative mechanism (a) 2D monolayer 2 x 2 supercell of LaMnO₃ perovskite (b) O_2^* adsorption on the 2D monolayer LaMnO₃ (c) OOH* intermediate formation after the addition of a pair of proton and electron (d) O* intermediate formation with removal of H₂O (e) formation of OH* intermediate with addition on another proton and electron pair.

The first step of ORR takes place with the adsorption of an oxygen molecule (O_2^*) on the surface of the 2D monolayer structure of LaMnO₃ perovskite at the Mn active site, as shown in Figure 5.5a. The equilibrium bond lengths of Mn–O and O–O are found to be 1.89 Å and 1.28 Å, respectively. The equilibrium geometry of the newly formed complex is shown in Figure 5.6b. The free energy, which is ΔG , for this complex [O₂_LaMnO₃] formed during the step was found to be -0.38 eV. In the next step, with the addition of H^+ and e^- , the H^+ ions form a bond with the O atom, leading to the formation of the complex [OOH_LaMnO₃], and it involves a change in the free energy of -0.44 eV. The equilibrium geometry of this complex is shown in Figure 5.6c. The bond lengths of Mn–O and O–O have been changed to 1.84 Å and 1.46 Å, respectively, which is a reduction in Mn–O bond length of about 0.05 Å and an expansion of the O–O bond length of about 0.18 Å, from the previous step. The newly formed O-H bond length is calculated to be 0.98 Å for this complex [OOH_LaMnO₃]. The equilibrium O–H bond length observed is consistent with the equilibrium O-H bond distance of the OH radical. The relative free energies of all the intermediate steps of the associative mechanism are shown in the potential energy surface diagram in Figure 5.7.



Figure 5.7. Relative free energy diagram or potential energy surface for the associative ORR mechanism in the 2D monolayer structure of LaMnO₃ perovskite.

Now again, the H⁺ ions coming through the proton exchange membrane present in the fuel cell and the e⁻ coming from the external circuitry again react with the activated O sites present in the complex [OOH_LaMnO₃] and with the removal of an H₂O molecule, the next intermediate species form with the change in free energy of -0.57 eV. This complex is [O LaMnO₃], and its equilibrium geometry is shown in Figure 5.6d. With the further addition of H+ and e-, the new complex formed is [OH_LaMnO₃] with a free energy change of -2.42 eV. The equilibrium geometry is shown in Figure 5.6e, and the equilibrium bond length of Mn–O is found to be 1.82 Å and that of O-H is found to be 0.97 Å. In the last step of this reaction mechanism, one more H₂O molecule was removed after the addition of one electron and one proton. The free energy change in this step was found to be -1.17 eV. The equilibrium geometries of all the reaction intermediates formed in the associative ORR pathway with their equilibrium structure parameters, such as lattice constants, angles, space group, and bond lengths, are listed in Table 5.2. The change in free energies ΔG and the relative free energies of all the intermediates involved in the associative mechanism are given in Table 5.3.

System	Lattice constants. (a and b in Å)	Angle. (α, β, and γ in degree)	Space group symmetry.	Band gap (eV)	Bond I Mn–O	engths (O– O	in Å) O–H
O2_LaMnO3	a = 7.38 b = 7.40	$\alpha = 89.75$ $\beta = 91.48$ $\gamma = 90.00$	P1	0.0	1.89	1.28	_
OOH_LaMnO ₃	a = 7.38 b = 7.41	$\alpha = 89.29$ $\beta = 91.31$ $\gamma = 90.00$	P1	0.0	1.84	1.46	0.98
O_LaMnO3	a = b = 7.33	$\alpha = 89.90$ $\beta = 91.91$ $\gamma = 90.00$	P1	0.0	1.57	_	_
OH_LaMnO3	a = 7.39 b = 3.41	$\alpha = 89.84$ $\beta = 92.86$ $\gamma = 90.00$	P1	0.0	1.82	_	0.97

 Table 5.2. Equilibrium lattice parameters and bond lengths of various intermediates of the associative ORR pathway on the surfaces of 2D LaMnO₃.

Table 5.3. Change in free energy ΔG (eV) of all reaction step intermediates of the oxygen reduction reaction (ORR) during the associative mechanism performed on the 2D LaMnO₃ perovskite.

ORR steps	ΔG (eV)	Systems	Relative free energy (eV)
$[LaMnO_3] \rightarrow [O_2_LaMnO_3]$	-0.38	O ₂ _LaMnO ₃	-0.38
$[O_2_LaMnO_3] \rightarrow [OOH_LaMnO_3]$	-0.44	OOH_LaMnO ₃	-0.83
$[OOH_LaMnO_3] \rightarrow [O_LaMnO_3]$	-0.57	O_LaMnO ₃	-1.40
$[O_LaMnO_3] \rightarrow [OH_LaMnO_3]$	-2.42	OH_LaMnO ₃	-3.82
$[OH_LaMnO_3] \rightarrow [LaMnO_3]$	-1.17	$LaMnO_3 + H_2O$	-4.99

5.3.1 Discussion of various Steps of the ORR Mechanisms

Step I. The GGA method was used to obtain the equilibrium structure of the 2D monolayer of La MnO_3 with O_2 being attached to the Mn active site of the monolayer.

The optimized structure is shown in Figure 5.6b, and the equilibrium bond lengths for Mn–O and La–O calculated are 1.87 Å and 2.74 Å, respectively and are reported in Table 3. The equilibrium structure of O₂_LaMnO₃ has *P1* symmetry with the equilibrium lattice constants a = 7.38 Å, b = 7.40 Å, and α = 81.75°, β = 91.48°. Figure 5.8a shows the electronic band structure and total density of states of both the spin-up and down states. For the calculations of the band structure, the GGA+U method has been employed and a high symmetric path $\Gamma - X - M - \Gamma$ has been chosen. From Figure 5.8a, it could be concluded that there is an overlap of the highest occupied valance band with the Fermi level pertaining to the semi-metallic nature of the complex, and correspondingly, there is increased electronic density of states at the Fermi level.

Step II. The next complex in the reaction is OOH_LaMnO₃ and its equilibrium geometry is shown in Figure 5.6c. The equilibrium lattice constants of this complex are calculated to be a = 7.38, b = 7.41 Å, and the angles α = 89.29°, β = 91.31° and it has *P1* symmetry. The equilibrium bond lengths for Mn–O, O–O and O–H calculated are 1.84 Å, 1.46 Å, 0.98 Å, respectively and are reported in Table 5.2. This complex also shows a semi metallic nature which can be concluded from Figure 5.8b which shows overlap of bands at the Fermi level and an increased electronic density. The highly symmetric k-path $\Gamma - X - M - \Gamma$ is used for band structure calculations. In this intermediate step, the free energy change ΔG for the formation of the complex is calculated to be -0.44 eV, and a relative free energy change is -0.83 eV.

Step III. Next the computational calculation is run for O_LaMNO₃ complex and resulted equilibrium lattice constants are a = b = 7.33 Å and angles, $\alpha = 89.90^{\circ}$, $\beta = 91.91^{\circ}$. The equilibrium geometry is shown in Figure 5.6(d). Here the calculated bond distance of Mn–O is 1.57 Å. In this step, the water molecule is removed, leading to a free energy change of -0.57 eV and a relative free energy change of -1.40 eV. The electronic band structure plot and total density of states are shown in Figure 5.8c and overlapping of band confirms that this complex is conducting in nature.

Step IV. The last complex that forms in this associative reaction mechanism before the removal of another water molecule and resulting in the same 2D monolayer catalyst LaMnO₃ perovskite is OH_LaMnO₃. The calculated equilibrium lattice constants are a = 7.39 Å, b = 7.41 Å, and α = 89.84°, β = 92.86° and the structure shows *P1* symmetry. The equilibrium bond lengths of Mn–O, and O–H calculated are 1.82 Å, 0.97 Å, respectively. The free energy change in this step is calculated to be -2.42 eV and the relative free energy change is calculated as -3.82 eV. The electronic band structure is calculated along the high symmetric path $\Gamma - X - M - \Gamma$ and is shown in Figure 5.8d.



Figure 5.8. Electronic structure properties i.e., Band structure and total DOS for (a) O₂_LaMnO₃ (b) OOH_LaMnO₃ (c) O_LaMnO₃ (d) OH_LaMnO₃ (e) 2O_LaMnO₃ (f) OH_O_LaMnO₃ reaction intermediates involved in both associative and dissociative mechanism. (In band structure plots the dotted and solid lines represent total spin down and up states, respectively. In total DOS plots, the blue and red lines represent total spin-down and spin-up densities).

5.4 Dissociative Mechanism of ORR

In this study, the dissociative mechanism of ORR is also studied and presented. The reaction intermediates and the reaction pathways are shown in Figure 5.9.



Figure 5.9. Reaction pathway for the dissociative mechanism (a) 2D monolayer 2 x 2 supercell of LaMnO₃ perovskite (b) O_2^* adsorption on the 2D monolayer LaMnO₃ (c) 2O* intermediate formation after the dissociation of adsorbed O_2^* on the surface of monolayer (d) OH_O* intermediate formation with addition of a proton and electron (e) O* intermediate after removal of H₂O (f) OH* intermediate with addition on another proton and electron pair.

The first step is the same for both the mechanisms. However, in the case of dissociative mechanism, the next step takes place with the O₂* getting dissociated and one oxygen atom getting adsorbed at the La active site leading to the formation of the 2O_LaMnO₃ complex. The free energy change in formation of this complex is calculated to be 2.41 eV and the relative free energy is found to be 2.02 eV. The equilibrium geometry of 2O_LaMnO₃ complex is shown in Figure 5.9(c). The calculated equilibrium lattice constants are a = 7.31 Å, b = 7.24 Å, and α = 89.85°, β = 89.74° with P1 symmetry. The calculated bond length of Mn–O is about 1.58 Å. The electronic band structure and total density of states are calculated and shown in Figure 5.8e.



Figure 5.10. Relative free energy diagram or potential energy surface for the dissociative ORR mechanism occurring at the surface of 2D monolayer structure of LaMnO3 perovskite.

The next step involves the addition of proton with the oxygen atom on the La active site leading to the formation of the OH_O_LaMnO₃. The free energy change is calculated to be -2.31 eV and the relative free is calculated to be -0.28 eV. The bond lengths of Mn–O, and O–H are calculated to be 1.78 Å, and 0.96 Å respectively. The electronic band structure and total density of states are calculated and shown in Figure 5.8f. All the further steps are same as followed in the associated mechanism and the relative free energy change for all the steps are plotted in Figure 5.10.

Table 5.4. Change in free energy ΔG (eV) of all reaction step intermediates of the oxygen reduction reaction
(ORR) during the dissociative mechanism performed on the 2D LaMnO3 perovskite.

ORR steps	ΔG (eV)	Systems	Relative free energy (eV)
$[LaMnO_3] \rightarrow [O_2_LaMnO_3]$	-0.38	O2_LaMnO3	-0.38
$[O_2_LaMnO_3] \rightarrow [2O_LaMnO_3]$	2.41	2O_LaMnO ₃	2.02
$[2O_LaMnO_3] \rightarrow [OH_O_LaMnO_3]$	-2.31	OH_O_LaMnO ₃	-0.28
$[OH_O_LaMnO_3] \rightarrow [O_LaMnO_3]$	-1.11	O_LaMnO ₃	-1.40
$[O_LaMnO_3] \rightarrow [OH_LaMnO_3]$	-2.41	OH_LaMnO ₃	-3.82
$[OH_LaMnO_3] \rightarrow [LaMnO_3]$	-1.16	$LaMnO_3 + H_2O$	-4.99

For all the reaction intermediates involved in dissociative mechanism, their corresponding equilibrium parameters such as lattice parameters, symmetry, bond lengths are mentioned in Table 5.5. The change in free energy and the relative free energy changes are mentioned in Table 5.4 for all the complexes involved.

Table 5.5. Equilibrium lattice parameters such as lattice constants, bond lengths, space group and equilibrium bond lengths of various intermediates of the dissociative pathway for ORR on the surfaces of 2D LaMnO₃.

System	Lattice constants. (a and b in Å)	Angle. (α, β, and γ in degree)	Space group symmetry	Band gap (eV)	Bond Mr	lengths (n–O O- O–H*	(in Å) -O
O2_LaMnO3	a = 7.38 b = 7.40	$\alpha = 89.75$ $\beta = 91.48$ $\gamma = 90.00$	P1	0.0	1.89	1.28	_
20_LaMnO3	a = 7.31 b = 7.24	$\alpha = 89.85$ $\beta = 89.74$ $\gamma = 90.00$	P1	0.0	1.58	_	-
OH_O_LaMnO ₃	a = 7.36 b = 7.41	$\alpha = 89.79$ $\beta = 89.79$ $\gamma = 90.00$	P1	0.0	1.78	_	0.96
O_LaMnO3	a = b = 7.33	$\alpha = 89.90$ $\beta = 91.91$ $\gamma = 90.00$	P1	0.0	1.57	_	_
OH_LaMnO3	a = 7.39 b = 7.41	$\alpha = 89.84$ $\beta = 92.86$ $\gamma = 90.00$	P1	0.0	1.82	_	0.97

5.5 Charge Density Plots and Charge Transfer During ORR

For both the associative and dissociative mechanisms to occur on the surface of the 2D monolayer of LaMnO₃ perovskite, there must be a significant charge transfer from the Mn active site to the adsorbing oxygen atom. In this study, Bader charge population analysis was performed for all the intermediate species. On the 2D monolayer of LaMnO₃ perovskite, +1.48 |e| charge was available, and after the

adsorption of O₂ molecule on surface of the monolayer, the charge was calculated to be +2.03 |e|. It can be concluded that a significant charge transfer for Mn active site to the adsorbing O atom has occurred. The calculated value of charge transfer is 0.55 |e|.



Figure 5.11. Charge density plots for all the intermediates forming during the dissociative mechanism of ORR occurring on the 2D monolayer of LaMnO₃ perovskite (Here Yellow contour represents the accumulation of charge, and Cyan contour show the depletion of charge in the region).



Figure 5.12. Charge density plots for all the intermediates forming during the associative mechanism of ORR occurring on the 2D monolayer of LaMnO₃ perovskite (Here Yellow contour represents the accumulation of charge, and Cyan contour show the depletion of charge in the region).

Figures 5.11 and 5.12 show the variation of charge density during the process of the ORR, both in dissociative and associative mechanisms. The yellow contour represents significant accumulation of charge and cyan contour represents the depletion of charge around the region. From the figure 5.11(a) it can be observed that

when O_2 molecule is getting adsorbed on the surface of the 2D monolayer, there is a significant charge accumulation around the adsorbing oxygen atom, which in turn has led to a stretch in oxygen-oxygen double bond. The value of bond length here is 1.28 Å, which is 0.07 Å more than that of oxygen-oxygen bond length in O_2 molecule.

5.6 Theoretical Over Potential

In any reaction, the rate determining step (RDS) is the elementary reaction with minimum reaction free energy (Equation 5-1). This minimum Gibbs free energy of all the steps of the ORR is used to calculate the value of over-potential in acidic media (Equation 5-2).³⁵

$$G^{ORR} = \min\{\Delta G \text{ of all ORR steps}\}$$
(5-1)

$$\eta^{\text{ORR}} = \frac{G^{\text{ORR}}}{e} - 1.23 \text{ V}$$
(5-2)

To attain optimal catalytic performance, it is essential that all the free energies of the ORR steps reach or surpass 4.92 eV, equivalent to 1.23 eV. In this study, we found that, the second step of the associative mechanism of ORR which involved addition of a proton to the adsorbed oxygen molecule on Mn active site on the surface of 2D monolayer of LaMnO₃ perovskite, could be the potential deciding factor for ORR. A higher G^{ORR} value corresponds to a lower overpotential, η^{ORR} , indicating improved catalytic activity. Equation (5-2) was employed to calculate the over-potential value, and the calculated value was found to be 0.85V. This value compared to the overpotential value of Pt(111) catalyst is higher by a magnitude of 0.4 V.³⁶

Chapter 6 Conclusion and Future Goal

This study has presented an in-depth analysis of LaMnO₃ perovskite material as an efficient electrocatalyst for ORR. The 3D LaMnO₃ perovskite was explored and its electronic properties: electrical band structure and total density of states were calculated. The GGA+U calculations showed an excellent semi-metallic behavior for the 3D structure. Further, the clever modeling of a 2 x 2 supercell of 2D monolayer LaMnO₃ perovskite by cleaving a (001) basal plane from the 3D LaMnO₃ structure was done. Mn atom was found to be the active site present on the surface of this 2D monolaver with Mn²⁺ oxidation state. This 2D monolayer showed excellent semimetallic behavior with overlapping of bands at the Fermi level as reported in the study. Then, a theoretical and computational study of the reaction kinetics of the ORR has been conducted by carefully modeling all the intermediate species present in both the well-studied mechanisms (associative and dissociative) and obtaining their equilibrium geometries. The entire O_2 reduction pathway was explored, and it can be concluded from the free energy calculations and the relative free energy plots that 2D La MnO_3 perovskite shows an excellent catalytic activity towards the associative mechanism rather than the dissociative mechanism. This is primarily due to the intermediate step, which involves the formation of the 2O_LaMnO3 complex in the dissociative mechanism after the dissociation of oxygen molecules at the surface of the 2D monolayer. The relative free energy change for $2O_LaMnO_3$ is positive and large, reaching 2.02 eV. This positive value of relative free energy makes this intermediate highly unstable and thermodynamically less favorable to form. Therefore, the associative mechanism will be thermodynamically favored over the dissociative mechanism. The calculated value of the overpotential for the associative mechanism in this O₂ reduction process was found to be 0.85 eV. This is a reasonable value of overpotential for practical fuel cell systems. However, for some systems with metal-based electrocatalysts, the reported values of overpotential are in the range of 0.7-1.0 eV.

The results reported in this study propose to explore similar lanthanum-based oxide double perovskites. The double perovskites have the structural formula AA'BB'O₆. One such example is La₂NiMnO₆. In depth computational study of these double perovskites, not only for the oxygen reduction but also for oxygen evolution reaction (OER) can be performed. These electrocatalysts can show good Bi-functional catalyst behavior and could have higher stability at high performing temperatures. The overpotential of these double perovskites can be calculated and could be compared with standard metal containing electrocatalysts. We have performed electronic properties calculations for La₂NiMnO₆ using similar computational methods described in Chapter 4 on computational details. Here the value of Hubbard correction for Ni atom was kept 6.0 eV.³⁷ The equilibrium structure obtained is shown in Figure 6.1. All the equilibrium lattice parameters, band gap and symmetry are reported in Table 6.2.



Figure 6.1. (a) Top view, (b) Side view of 3D La₂NiMnO₆ perovskite material.

We have also calculated the band structure and density of states for this 2D La_2NiMnO_6 perovskite material using the GGA+U method. The band gap of this La_2NiMnO_6 perovskite is calculated to be 1.46 eV, which is consistent with previous studies.³⁸ The band structure and density of states plots are shown in Figure 6.2a-b.

Table 6.1. The equilibrium lattice constants of the 3D and 2D La2NiMnO6 crystal structure.

System	Lattice constants. (a , b , c in Å)	Angle $(\boldsymbol{\alpha}, \boldsymbol{\beta}, \boldsymbol{\gamma})$	Space group symmetry	Band gap (E _g)	Reference
3D La ₂ NiMnO ₆	a = b = 5.58 c = 13.34	$\alpha = \beta =$ 90.0° and $\gamma = 120°$	R3	1.48 eV	This Work
3D La ₂ NiMnO ₆	a = b = 5.4 c = 13.2	$\begin{array}{l} \alpha = \beta \\ = 90.0^{\circ} \end{array}$		1.4 eV	38



Figure 6.2. (a) Electronic band structure, and (b) Total density of states of La2NiMnO6 double perovskite.

Finally, we propose that to model an electrode surface, a 2D monolayer from this 3D perovskite could be modelled such that it contains Mn and Ni as active sites on the surface for ORR and OER. All reaction intermediates for both ORR pathways (associative and dissociative) could be modelled, and their reaction free energies could be calculated along with transition states involved. Overpotential values from the rate limiting step could be calculated and compared to benchmark value for Pt(111) catalyst.

In the end, this study has provided a framework to explore various materials for O_2 reduction in fuel cell applications. The anodic reaction of HOR could also be analyzed in a similar framework and the reaction kinetics of both the reactions could be compared. This study has provided a step-by-step approach to analyze the catalytic activity of a material towards ORR, using computational methods.

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