A Theoretical Investigation on the Structural and Electronic Properties with the Effective Mass of the Nickel-based Perovskites

M.Sc. Thesis

By

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VINEET KUMAR



DEPARTMENT OF PHYSICS

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INDIAN INSTITUTE OF TECHNOLOGY INDORE **CANDIDATE DECLARATION**

I hereby certify that the work which is being presented in the Report entitled "A Theoretical Investigation on the Structural and Electronic Properties with the Effective Mass of the Nickel-based Perovskites" in the partial fulfillment of the requirements for the award of the degree of MASTER OF SCIENCE and submitted in the DEPARTMENT OF PHYSICS, Indian Institute of Technology Indore, is an authentic record of my own work carried out during the time period from August, 2022 to June, 2023 under the supervision of Dr. Srimanta Pakhira, Assistant Professor, DEPARTMENT OF PHYSICS.

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.

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This is to certify that the above statement made by the candidate is correct to the best of my/our knowledge.

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Content

1.1 Introduction 1 1.2 What are perovskites 2 1.3 Why are perovskites important 2 1.4 Perovskites, efficiency, and bandgap 3 2. Introduction to Density Functional Theory 5 2.1 Introduction 5 2.2 Basic electronic problem 5 2.3 Atomic units 6 2.2 Born Oppenheimer approximation 7 2.4 Pauli principle 8 2.5 Spin orbitals 9 2.6 Hartree product 10 2.7 Slater determinant 10 2.8 Hartree-Fock approximation 11 2.9 Self-consistent method 12 2.10 Hohenberg theorems 12 2.11 Kohn-Sham approach 13 2.12 Kohn-Sham equation 13 2.13 Calculation of electron density 15 3. Structural properties, electronic properties, and Effective mass of the Nickel-based perovskites 16 3.1 Introduction 16 3.2 Theory of effective mass 17 3.3 Computational details 19 3.4 Results and discussion 21 3.5 Summary 27	1.	Perovskites	1
1.2 What are perovskites. 2 1.3 Why are perovskites important. 2 1.4 Perovskites, efficiency, and bandgap. 3 2. Introduction to Density Functional Theory 5 2.1 Introduction. 5 2.2 Basic electronic problem. 5 2.3 Atomic units. 6 2.2 Born Oppenheimer approximation. 7 2.4 Pauli principle. 8 2.5 Spin orbitals. 9 2.6 Hartree product. 10 2.7 Slater determinant. 10 2.8 Hartree-Fock approximation 11 2.9 Self-consistent method. 12 2.10 Hohenberg theorems. 12 2.11 Kohn-Sham equation. 13 2.12 Kohn-Sham equation. 13 2.13 Calculation of electron density. 15 3. Structural properties, electronic properties, and Effective mass of the Nickel-based perovskites 16 3.1 Introduction. 16 3.2 Theory of effective mass. 17 3.3 Computational details. 19 3.4 Results and discussion. 21		1.1 Introduction	1
1.3 Why are perovskites important .2 1.4 Perovskites, efficiency, and bandgap .3 2. Introduction to Density Functional Theory .5 2.1 Introduction .5 2.2 Basic electronic problem .5 2.3 Atomic units .6 2.2 Born Oppenheimer approximation .7 2.4 Pauli principle .8 2.5 Spin orbitals .9 2.6 Hartree product .10 2.7 Slater determinant .10 2.8 Hartree-Fock approximation .11 2.9 Self-consistent method .12 2.11 Kohn-Sham approach .13 2.12 Kohn-Sham equation .13 2.13 Calculation of electron density. .15 3. Structural properties, electronic properties, and Effective mass of the Nickel-based perovskites .16 3.1 Introduction. .16 3.2 Theory of effective mass. .17 3.3 Computational details .19 3.4 Results and discussion .21 3.5 Summary .21		1.2 What are perovskites	2
1.4 Perovskites, efficiency, and bandgap		1.3 Why are perovskites important	2
2. Introduction to Density Functional Theory .5 2.1 Introduction .5 2.2 Basic electronic problem .5 2.3 Atomic units .6 2.2 Born Oppenheimer approximation .7 2.4 Pauli principle .8 2.5 Spin orbitals .9 2.6 Hartree product .10 2.7 Slater determinant .10 2.8 Hartree-Fock approximation .11 2.9 Self-consistent method .12 2.10 Hohenberg theorems .12 2.11 Kohn-Sham approach .13 2.12 Kohn-Sham equation .13 2.13 Calculation of electron density .15 3. Structural properties, electronic properties, and Effective mass of the Nickel-based perovskites .16 3.1 Introduction .16 3.2 Theory of effective mass .17 3.3 Computational details .19 3.4 Results and discussion .21 3.5 Summary .27		1.4 Perovskites, efficiency, and bandgap	3
2.1 Introduction.52.2 Basic electronic problem.52.3 Atomic units.62.2 Born Oppenheimer approximation.72.4 Pauli principle.82.5 Spin orbitals.92.6 Hartree product.102.7 Slater determinant.102.8 Hartree-Fock approximation.112.9 Self-consistent method.122.10 Hohenberg theorems.122.11 Kohn-Sham approach.132.12 Kohn-Sham equation.132.13 Calculation of electron density.153. Structural properties, electronic properties, and Effective mass of the Nickel-based perovskites.163.1 Introduction.163.2 Theory of effective mass.173.3 Computational details.193.4 Results and discussion.213.5 Summary.27	2.	Introduction to Density Functional Theory	5
2.2 Basic electronic problem. 5 2.3 Atomic units 6 2.2 Born Oppenheimer approximation. 7 2.4 Pauli principle. 8 2.5 Spin orbitals. 9 2.6 Hartree product. 10 2.7 Slater determinant. 10 2.8 Hartree-Fock approximation 11 2.9 Self-consistent method. 12 2.10 Hohenberg theorems. 12 2.11 Kohn-Sham approach. 13 2.12 Kohn-Sham equation. 13 2.13 Calculation of electron density. 15 3. Structural properties, electronic properties, and Effective mass of the Nickel-based perovskites 16 3.1 Introduction. 16 3.2 Theory of effective mass. 17 3.3 Computational details. 19 3.4 Results and discussion. 21 3.5 Summary. 27		2.1 Introduction	5
2.3 Atomic units		2.2 Basic electronic problem	5
2.2 Born Oppenheimer approximation72.4 Pauli principle82.5 Spin orbitals92.6 Hartree product102.7 Slater determinant102.8 Hartree-Fock approximation112.9 Self-consistent method122.10 Hohenberg theorems122.11 Kohn-Sham approach132.12 Kohn-Sham equation132.13 Calculation of electron density153. Structural properties, electronic properties, and Effective mass of the Nickel-based perovskites163.1 Introduction163.2 Theory of effective mass173.3 Computational details193.4 Results and discussion213.5 Summary27		2.3 Atomic units	6
2.4 Pauli principle82.5 Spin orbitals92.6 Hartree product102.7 Slater determinant102.8 Hartree-Fock approximation112.9 Self-consistent method122.10 Hohenberg theorems122.11 Kohn-Sham approach132.12 Kohn-Sham equation132.13 Calculation of electron density153. Structural properties, electronic properties, and Effective mass of the Nickel-based perovskites163.1 Introduction163.2 Theory of effective mass173.3 Computational details193.4 Results and discussion213.5 Summary27		2.2 Born Oppenheimer approximation	7
2.5 Spin orbitals.92.6 Hartree product102.7 Slater determinant102.8 Hartree-Fock approximation112.9 Self-consistent method122.10 Hohenberg theorems122.11 Kohn-Sham approach132.12 Kohn-Sham equation132.13 Calculation of electron density153. Structural properties, electronic properties, and Effective mass of the Nickel-based perovskites163.1 Introduction163.2 Theory of effective mass173.3 Computational details193.4 Results and discussion213.5 Summary27		2.4 Pauli principle	8
2.6 Hartree product102.7 Slater determinant102.8 Hartree-Fock approximation112.9 Self-consistent method122.10 Hohenberg theorems122.11 Kohn-Sham approach132.12 Kohn-Sham equation132.13 Calculation of electron density153. Structural properties, electronic properties, and Effective mass of the Nickel-based perovskites163.1 Introduction163.2 Theory of effective mass173.3 Computational details193.4 Results and discussion213.5 Summary27		2.5 Spin orbitals	9
2.7 Slater determinant.102.8 Hartree-Fock approximation112.9 Self-consistent method122.10 Hohenberg theorems122.11 Kohn-Sham approach132.12 Kohn-Sham equation132.13 Calculation of electron density153. Structural properties, electronic properties, and Effective mass of the Nickel-based perovskites163.1 Introduction163.2 Theory of effective mass173.3 Computational details193.4 Results and discussion213.5 Summary27		2.6 Hartree product	10
2.8 Hartree-Fock approximation 11 2.9 Self-consistent method 12 2.10 Hohenberg theorems 12 2.11 Kohn-Sham approach 13 2.12 Kohn-Sham equation 13 2.13 Calculation of electron density 15 3. Structural properties, electronic properties, and Effective mass of the Nickel-based perovskites 16 3.1 Introduction 16 3.2 Theory of effective mass 17 3.3 Computational details 19 3.4 Results and discussion 21 3.5 Summary 27		2.7 Slater determinant	10
2.9 Self-consistent method.122.10 Hohenberg theorems.122.11 Kohn-Sham approach.132.12 Kohn-Sham equation.132.13 Calculation of electron density.15 3. Structural properties, electronic properties, and Effective mass of the Nickel-based perovskites163.1 Introduction.163.2 Theory of effective mass.173.3 Computational details.193.4 Results and discussion.213.5 Summary.27		2.8 Hartree-Fock approximation	11
2.10 Hohenberg theorems. 12 2.11 Kohn-Sham approach. 13 2.12 Kohn-Sham equation. 13 2.13 Calculation of electron density. 15 3. Structural properties, electronic properties, and Effective mass of the Nickel-based perovskites 16 3.1 Introduction. 16 3.2 Theory of effective mass. 17 3.3 Computational details. 19 3.4 Results and discussion. 21 3.5 Summary. 27		2.9 Self-consistent method	12
2.11 Kohn-Sham approach. 13 2.12 Kohn-Sham equation. 13 2.13 Calculation of electron density. 15 3. Structural properties, electronic properties, and Effective mass of the Nickel-based perovskites 16 3.1 Introduction. 16 3.2 Theory of effective mass. 17 3.3 Computational details. 19 3.4 Results and discussion. 21 3.5 Summary. 27		2.10 Hohenberg theorems	12
2.12 Kohn-Sham equation. 13 2.13 Calculation of electron density. 15 3. Structural properties, electronic properties, and Effective mass of the Nickel-based perovskites 16 3.1 Introduction. 16 3.2 Theory of effective mass. 17 3.3 Computational details. 19 3.4 Results and discussion. 21 3.5 Summary. 27		2.11 Kohn-Sham approach	13
2.13 Calculation of electron density. 15 3. Structural properties, electronic properties, and Effective mass of the Nickel-based perovskites 16 3.1 Introduction. 16 3.2 Theory of effective mass. 17 3.3 Computational details. 19 3.4 Results and discussion. 21 3.5 Summary. 27		2.12 Kohn-Sham equation	13
3. Structural properties, electronic properties, and Effective mass of the Nickel-based perovskites 3.1 Introduction. 16 3.2 Theory of effective mass. 17 3.3 Computational details. 19 3.4 Results and discussion. 21 3.5 Summary. 27		2.13 Calculation of electron density	15
Nickel-based perovskites163.1 Introduction163.2 Theory of effective mass173.3 Computational details193.4 Results and discussion213.5 Summary27	3.	Structural properties, electronic properties, and Effective mass of	the
3.1 Introduction.163.2 Theory of effective mass.173.3 Computational details.193.4 Results and discussion.213.5 Summary.27]	Nickel-based perovskites	16
3.2 Theory of effective mass.173.3 Computational details.193.4 Results and discussion.213.5 Summary.27		3.1 Introduction	16
3.3 Computational details 19 3.4 Results and discussion 21 3.5 Summary 27		3.2 Theory of effective mass	17
3.4 Results and discussion		3.3 Computational details	19
3.5 Summary		3.4 Results and discussion	21
		3.5 Summary	27
References	R	eferences	28

Abstract

In the realm of electronic materials, the effective mass of electrons serves as a crucial parameter that intimately characterizes their electronic properties. In this investigation, we have conducted a meticulous evaluation of the effective mass of electrons in a diverse array of pure Nickel-based perovskites, including LaNiO₃, La_{0.8}Ca_{0.2}NiO₃, La_{0.5}Ca_{0.5}NiO₃, La_{0.2}Ca_{0.8}NiO₃, La₄Ni₃O₁₀, La₃Ni₂O₇, and La₂NiO₄. Our cutting-edge methodology is rooted in the first-principles calculations based on density functional theory (DFT). In essence, we performed a detailed analysis of the density of states (DOS) and the band structure of all the materials, yielding results that exhibit superb congruity with theoretical and experimental data. We then proceeded to estimate the effective mass of electrons by scrutinizing the curvature of the electronic conduction band via the parabolic fit approximation around the extremum of the band (i.e., Γ -point). The effective mass of the LaNiO₃, La_{0.8}Ca_{0.2}NiO₃, La_{0.5}Ca_{0.5}NiO₃, La_{0.2}Ca_{0.8}NiO₃, La₄Ni₃O₁₀, La₃Ni₂O₇, and La₂NiO₄ has been calculated to be -0.4001 me. -0.4327 me, -0.5000, 0.6190, 0.6447, -4.5480, and -8.7852 respectively along the direction L- Γ -S path in the reciprocal space. The outcome of our trailblazing study is that the effective masses manifest a remarkably high correlation with the energies of the conduction band extremum (i.e., LUMO) and DOS around the Fermi energy level. Intriguingly, our observations also indicate that the introduction of the Ca atom as a substitution dopant of the La atom in LaNiO₃ leads to a significant change in the effective mass of the electron, a phenomenon that can be elucidated by the distinctive properties of the A- and B-sites in the perovskite structure.

Chapter 1 Perovskites

1.1 Introduction

In our ever-advancing society, the escalating demand for energy has resulted in a significant upsurge in the consumption of fossil fuels. Unfortunately, the excessive utilization of non-renewable energy sources has led to the depletion of these finite resources and the emission of harmful gases, particularly carbon dioxide (CO₂), which has detrimental effects on the environment. CO₂, known as a greenhouse gas, is primarily responsible for the global warming phenomenon, which in turn, poses hazardous consequences such as the melting of glaciers, climate change, global warming, and alterations in weather patterns.





Figure 1.1 Change in temperature of earth's surface

In response to this issue, scientists and researchers have redirected their efforts towards green energy sources in order to mitigate the levels of greenhouse gases and reduce global pollution. Among the various alternatives, solar cells have garnered significant interest due to their eco-friendly characteristics and impressive efficiency. With the objective of developing robust and high-performance solar cells at a reasonable cost, scientists have shifted their focus towards exploring new materials. While silicon has been the predominant semiconductor material in solar cell technology since the 1950s, ongoing research aims to discover and utilize more advanced

materials for enhanced solar energy conversion. Now for the replacement of silicon, scientist focuses on alternative materials which can replace the silicon material. Perovskites are the best candidate to replace the silicon material in the solar cell due to their unique properties.^{1–3}

1.2 What are perovskites?

A perovskite⁴ is a material characterized by its crystal structure, resembling that of calcium titanium oxide, which was the first-known perovskite crystal. Typically, perovskite compounds are denoted by the chemical formula ABX₃, where 'A' and 'B' represent cations, and 'X' represents an anion. The versatility of perovskite structures allows for the combination of various elements, enabling scientists to design perovskite crystals with diverse physical, optical, and electrical properties.⁵ Perovskite crystals have made their way into several applications, including ultrasound machines, memory chips, and most notably, solar cells.



Figure 1.2 Structure of a perovskite having formula ABX₃.

1.3 Why are perovskites important?

Perovskites hold great promise for numerous reasons, but the aspect we will focus on is their association with the photovoltaic effect, which refers to the generation of "energy from light". Similar to silicon, tin or lead, which are present in these materials, exhibit excellent properties for

the production of solar cells.⁶⁻⁸ The atoms of these elements possess an ideal quality for forming molecules alongside other atoms, resulting in the creation of semiconductor materials. These materials have the ability to have their electrons excited by light energy and directed through a wire to generate electricity. Unlike silicon crystals, perovskite crystals can be easily synthesized under normal conditions. The production of silicon requires high-temperature heating to attain the required purity and crystal structure for electricity generation. Conversely, perovskite cells can be produced by simply mixing chemicals in a solution and coating a surface with that solution. Although the process entails some complexities, overall, manufacturing perovskite solar cells in the future is expected to be considerably more affordable compared to silicon cells.

1.4 Perovskites, efficiency, and the bandgap

Photons of varying light colors encompass distinct energy levels, which are quantified in unit known as "electron volts" (eV). The energy of visible light photons spans from 1.75 eV (deep red) to 3.1 eV (violet). An excellent photovoltaic material⁹ possesses a band gap of 1.34 eV, as it corresponds to the optimal threshold at which the maximum amount of visible light can efficiently convert electrons into charge carriers.



Figure 1.3 Structural fabrication of photovoltaic cell

Within the realm of solar energy, there exists a concept related to the bandgap known as Power Conversion Efficiency (PCE). PCE denotes the proportion of solar energy that can be effectively converted into electricity by a solar cell. A solar cell featuring a single connection, also referred to as a junction, between layers of positively and negatively charged materials possessing the ideal bandgap, has the potential to convert approximately 33.7% of incoming light into electricity. This ultimate efficiency is recognized as the Shockley-Queisser limit, named after the physicists who originally discovered it. The challenge lies in the fact that currently, there is no known single material that possesses the precise bandgap required to attain this limit.



Figure 1.4 Efficiency of Si, CdTe thin film, and perovskites vs. band gap of the material

Silicon solar cells possess a theoretical bandgap of approximately 1.2 eV, resulting in a highest PCE of around 32%. On the other hand, the finest perovskite materials can achieve a PCE of approximately 31%. While perovskite may not surpass the performance of the best silicon solar cells, it holds the potential to be sufficiently efficient and cost-effective. As a result, perovskite-based photovoltaic products can generate electricity at a significantly lower cost compared to silicon-based alternatives.

Chapter 2 Density Functional Theory

2.1 Introduction

In principle, the quantum mechanical wave function inherently encapsulates complete information about a given system. When considering systems such as a 2D square potential or a hydrogen atom, it is possible to precisely solve the Schrödinger wave equation and obtain the corresponding wave function. However, when it comes to an N-body system, solving the Schrödinger wave equation becomes infeasible. Density Functional Theory (DFT)^{10–12} offers an approximate resolution to the Schrödinger wave equation pertaining to many-body systems. In practical applications, computational codes based on DFT are employed to explore the characteristics of materials, encompassing their structural, magnetic, and electronic properties. The bridge from many body problems to one body problem is DFT, and the main idea behind it is defining a system with the electron density (i.e., how the electron is distributed in the system describes the whole system)

$$\left[\sum_{i}^{N} \left(-\frac{\hbar^{2} \nabla_{i}^{2}}{2m} + v(r_{i})\right) + \sum_{i < j} U(r_{i}r_{j})\right] \psi(r_{1}r_{2}....,r_{N}) = E\psi(r_{1}r_{2}....,r_{N})$$
(2.1)

The above equation is the Schrodinger wave equation for the N-electron system and solving it in 3 directional coordinate (x, y, z) makes it a 3N variable equation, which makes it even harder to solve. For example, let's say we have CO_2 molecules. The total no. of electrons in a molecule is 22 and 3 spatial coordinates. Now, we have to solve a 66-variable problem which is very hard to solve using the Schrödinger equation. But the same problem using the concept of DFT can be solved very easily.

2.2 The Basic Electronic Problem

Our primary objective is to seek an approximate solution for the non-relativistic, time-independent Schrödinger equation.

$$H|\phi\rangle = E|\phi\rangle \tag{2.2}$$

Here Hamiltonian operator is denoted by H for a system of nucleus and electrons represented by position vector \mathbf{R}_{A} and \mathbf{r}_{i} , respectively.



Figure 2.1 Coordinate system for a molecule

Coordinate system for a molecule is shown in Fig. 2.1. Where $\mathbf{R}_{\mathbf{A}}$ and $\mathbf{r}_{\mathbf{i}}$ are position vectors of \mathbf{A}^{th} nuclei and \mathbf{i}^{th} electron, respectively. In Atomic units, the Hamiltonian for N electrons and M nuclei system is written as,

$$H = -\sum_{i=1}^{i=N} \frac{1}{2} \nabla_{i}^{2} - \sum_{A=1}^{M} \frac{1}{2M_{A}} \nabla_{A}^{2} - \sum_{i=1}^{N} \sum_{A=1}^{M} \frac{Z_{A}}{r_{i}} + \sum_{i=1}^{N} \sum_{j>1}^{N} \frac{1}{r_{ij}} + \sum_{A=1}^{M} \sum_{B>A}^{M} \frac{Z_{A}Z_{B}}{R_{AB}}$$
(2.3)

Where in equation (2.3), $\mathbf{M}_{\mathbf{A}}$ denotes the ratio of the mass of nuclei \mathbf{A} to the mass of an electron and $\mathbf{Z}_{\mathbf{A}}$ represents atomic no. of nucleus \mathbf{A} . The operators (Laplacian) ∇_i^2 and ∇_A^2 involves 2nd derivative with respect to the spatial coordinates of **i**th electron and \mathbf{A}^{th} nuclei. In equation (2.3), the initial term represents the operator corresponding to the K.E of the electrons. The second term pertains to the operator associated with the K.E of the nucleus. The third term signifies the Coulomb attraction between electrons and nuclei. The last two denotes the repulsion interaction between electrons and between nucleuses, respectively.

2.3 Atomic units

We will use atomic units throughout our discussion to see how these units arise naturally, let us consider the Schrödinger equation in case of hydrogen atom. In SI Units, we have

$$\left[\frac{-\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r}\right]\phi = E\phi$$
(2.4)

Where \mathbf{m}_{e} is the mass of the electron, and -e is the charge on the electron. Now to make the above equation dimensionless, we let (x, y, z) change to ($\lambda x'$, $\lambda y'$, $\lambda z'$) and obtain

$$\left[\frac{-\hbar^2}{2m_e\lambda^2}\nabla'^2 - \frac{e^2}{4\pi\epsilon_0\lambda r'}\right]\phi = E\phi'$$
(2.5)

The constants in front of kinetic and potential energy operators can then be factored, provided we choose λ such that,

$$\frac{-\hbar^2}{2m_e\lambda^2} = \frac{e^2}{4\pi\varepsilon_0\lambda} = \varepsilon_\alpha$$
(2.6)

Where ε_{α} is the atomic unit of energy called Hartree. Solving Eq. (2.6), we find

$$\lambda = \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2} \tag{2.7}$$

Thus λ is just Bohr radius which is an atomic unit of length called a Bohr. Finally, since

$$\mathcal{E}_{\alpha} \left[-\frac{1}{2} \nabla'^2 - \frac{1}{r'} \right] \phi' = E \phi'$$
(2.8)

Now, if we let $\varepsilon' = E/\varepsilon_{\alpha}$, we obtain the dimensionless equation

$$\left(-\frac{1}{2}\nabla'^2 - \frac{1}{r'}\right)\phi' = \varepsilon'\phi'$$
(2.9)

Which is a Schrödinger equation in atomic units. The solution of this equation for ground state of hydrogen atom yields an energy ε' equal to -0.5 atomic units.

2.4 The Born-Oppenheimer approximation

This approximation plays a central role in density functional theory and we will discussed it in a qualitative manner. Due to the significant disparity in mass between nuclei and electrons, the nuclei move at a considerably slower pace compared to electrons. Therefore, as a reasonable

approximation, one can consider the electrons within a molecule to be moving in the presence of fixed nuclei. By employing this approximation, the second term in the Hamiltonian equation (1.2), which represents the kinetic energy of the nucleus, can be disregarded. Additionally, the last term in equation (1.2), signifying the repulsion between the nuclei, can be treated as a constant. It is worth noting that any constant added to an operator does not impact the Eigen function of that operator. Consequently, the remaining terms are referred to as the electronic Hamiltonian. Therefore, the electronic Hamiltonian, which characterizes the movement of N electrons in the presence of M immobile point charges, can be expressed as

$$H_{e} = -\sum_{i=1}^{i=N} \frac{1}{2} \nabla_{i}^{2} - \sum_{i=1}^{N} \sum_{A=1}^{M} \frac{z_{A}}{r_{i}} + \sum_{i=1}^{N} \sum_{j>1}^{N} \frac{1}{r_{ij}}$$
(2.10)

Schrödinger equation (S.E) solution involving electronic part of the Hamiltonian, gives the wave function ($\phi_e(\{r_i\}; \{R_A\})$). This solution describes the motion of electrons. Hence, when considering fixed nuclei, the total energy must incorporate the constant nuclear repulsion as well.

$$E_{\rm T} = E_{\rm e} + \sum_{\rm A=1}^{\rm M} \sum_{\rm B>A}^{\rm M} \frac{Z_{\rm A} Z_{\rm B}}{R_{\rm AB}}$$
(2.11)

Applying the same set of assumptions utilized in formulating the electronic problem, we can express the Hamiltonian governing the movement of the nucleus within the mean field created by the electrons.

$$H_{n} = -\sum_{A=1}^{M} \frac{1}{2M_{A}} \nabla_{A}^{2} + \langle -\sum_{i=1}^{i=N} \frac{1}{2} \nabla_{i}^{2} - \sum_{i=1}^{N} \sum_{A=1}^{M} \frac{z_{A}}{r_{i}} + \sum_{i=1}^{N} \sum_{j>1}^{N} \frac{1}{r_{ij}} \rangle + \sum_{A=1}^{M} \sum_{B>A}^{M} \frac{z_{A}z_{B}}{R_{AB}}$$
$$= -\sum_{A=1}^{M} \frac{1}{2M_{A}} \nabla_{A}^{2} + E_{e} + \sum_{A=1}^{M} \sum_{B>A}^{M} \frac{z_{A}z_{B}}{R_{AB}}$$
$$= -\sum_{A=1}^{M} \frac{1}{2M_{A}} \nabla_{A}^{2} + E_{T}$$
(2.12)

The total energy also serves as a potential for the motion of the nuclei. As a result, within the Born-Oppenheimer approximation, the nuclei move along a P.E surface derived from solving the electronic problem. Solution of (S.E) for nuclear Hamiltonian, gives the nuclei wave function $(\phi_n(\{r_i\}; \{R_A\}))$. In further discussion we will concentrate solely on the electronic problem, we thus drop the subscript "e" in further discussion.

2.5 The Pauli exclusion principle

The electronic Hamiltonian presented in equation (2.10) solely relies on the spatial coordinates of the electrons. However, to fully characterize an electron, it is imperative to specify its spin as well. Let us assume two spin functions $\alpha(\omega)$ and $\beta(\omega)$, corresponding to spin up and spin down, respectively. These two spin functions are complete and orthonormal,

$$\langle \alpha | \alpha \rangle = \langle \beta | \beta \rangle = 1 \text{ and } \langle \alpha | \beta \rangle = \langle \beta | \alpha \rangle = 0$$
 (2.13)

Within this formalism, an electron is not only described by the three spatial coordinates represented by **r** but also by an additional spin coordinate denoted as $\boldsymbol{\omega}$. These four coordinates are represented by **x**.

$$\mathbf{x} = \{\mathbf{r}, \boldsymbol{\omega}\}\tag{2.14}$$

The wave function of a many-electron system must exhibit anti-symmetry when the coordinates (both spatial and spin) of any two electrons, represented by \mathbf{x} are interchanged,

$$\phi(x_1, ..., x_i, ..., x_j, ..., x_N) = -\phi(x_1, ..., x_j, ..., x_i, ..., x_N)$$
(2.15)

This requirement is called the anti-symmetric principle, is a statement of the Pauli Exclusion Principle.

2.6 Spin orbitals and spatial orbitals

In our discussion, an orbital refers to a wave function pertaining to a single particle, specifically an electron. A spatial orbital corresponds to a function of the position vector denoted as $\psi_i(\mathbf{r})$ and an orbital characterizes the distribution of electrons in space such that $|\psi_i(\mathbf{r})|^2 d\mathbf{r}$ is the probability in a small volume of finding the electron. It is typically assumed that these spatial orbitals constitute an orthonormal set.

$$\left\langle \Psi_{i} \middle| \Psi_{i} \right\rangle = \delta_{ij} \tag{2.16}$$

If spatial orbitals are complete, then any arbitrary function could be expanded as linear combination of spatial orbitals.

$$|\mathbf{f}(\mathbf{x})\rangle = \sum_{i=1}^{\infty} c_i |\psi_i\rangle \tag{2.17}$$

Where c_i are constant coefficients, as mentioned earlier, a complete description of an electron requires specifying its spin in addition to its spatial distribution. The wave function that encompasses both the spatial distribution and the spin of an electron is referred to as a spin-orbital., $\chi(\mathbf{x})$, where \mathbf{x} denotes both spatial and spin coordinates.

$$\chi(\mathbf{x}) = \begin{cases} \alpha(\omega)\psi(\mathbf{r}) \\ \beta(\omega)\psi(\mathbf{r}) \end{cases}$$
(2.18)

One corresponds to spin up and the other to spin down.

2.7 Hartree product

To gain insight into the Hartree Product, let us examine a system comprising **N** non-interacting electrons. The Hamiltonian governing such a system can be represented in the following form,

$$\mathbf{H} = \sum_{i=1}^{N} \mathbf{h}(i) \tag{2.19}$$

Where \mathbf{h}_{i} is the operator describing the K.E and P.E of the ith electron. The operator \mathbf{h}_{i} will have a set of Eigen functions that we can be considered as a set of spin orbitals { χ_{i} }.

$$h_i \chi_j(\mathbf{x}_i) = E_i \chi_j(\mathbf{x}_i) \tag{2.20}$$

Now, the question arises: what are the Eigen functions associated with the Hamiltonian of the system? The answer lies in the fact that the wave function of the system can be expressed as a product of spin orbital wave functions for each individual electron.

$$\psi^{HP}(x_1, x_1, \dots, x_1) = \chi_i(x_1)\chi_j(x_2) \cdots \chi_k(x_N)$$
(2.21)

is an Eigen function of **H**, such a many electrons wave function is termed a Hartree product. The Hartree Product is an uncorrelated or independent wave function because,

$$|\psi^{\rm HP}(x_1, x_2, \dots, x_N)|^2 dx_1 \cdots dx_N$$
(2.22)

is equal to the product of probabilities.

$$|\chi_{i}(x_{1})|^{2} dx_{1} |\chi_{j}(x_{2})|^{2} dx_{2} \cdots |\chi_{k}(x_{N})|^{2} dx_{N}$$
(2.23)

The Hartree Product does not consider the indistinguishability of electrons. However, the anti-symmetry principle does not discriminate between identical electrons and mandates that the electronic wave function must be antisymmetric. Therefore, a modification is necessary for the electronic wave function to comply with this principle.

2.8 Slater determinant

So far, we have seen, The Hartree Product does not satisfy the anti-symmetric principle. However We can obtain an anti-symmetric wave function as follows. Let us consider a two-electron case in which If we put electron-1 in ith spin-orbital, and electron-2 in jth spin-orbital, then we have,

$$\psi_{1,2}^{\text{HP}}(\mathbf{x}_1, \mathbf{x}_2) = \chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2)$$
(2.24)

On the other hand, if we put electron-1 in jth spin-orbital and electron-2 in ith spin-orbital, then we have

$$\psi_{2,1}^{\text{HP}}(\mathbf{x}_2, \mathbf{x}_1) = \chi_i(\mathbf{x}_2)\chi_j(\mathbf{x}_1)$$
(2.25)

Each of these Hartree Products makes a clear distinction between electrons. However, by carefully selecting an appropriate linear combination of these two Hartree products, we can derive an antisymmetric wave function.

$$\psi(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2!}} (\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2) - \chi_j(\mathbf{x}_1)\chi_i(\mathbf{x}_2))$$
(2.26)

Sign of minus ensures that the wave function is anti-symmetric, clearly this anti-symmetric wave function can be rewritten as a determinant called slater determinant.

$$\psi(\mathbf{x}_{1}, \mathbf{x}_{2}) = \frac{1}{\sqrt{2!}} \begin{vmatrix} \chi_{i}(\mathbf{x}_{1}) & \chi_{j}(\mathbf{x}_{1}) \\ \chi_{i}(\mathbf{x}_{2}) & \chi_{j}(\mathbf{x}_{2}) \end{vmatrix}$$
(2.27)

For an N electron system, the generalization is,

$$\psi(\mathbf{x}_{1}, \mathbf{x}_{2,\dots,} \mathbf{x}_{N}) = \frac{1}{\sqrt{N!}} \begin{bmatrix} \chi_{i}(\mathbf{x}_{1}) & \cdots & \chi_{k}(\mathbf{x}_{1}) \\ \vdots & \ddots & \vdots \\ \chi_{i}(\mathbf{x}_{N}) & \cdots & \chi_{k}(\mathbf{x}_{N}) \end{bmatrix}$$
(2.28)

Where, the factor $N!^{(-\frac{1}{2})}$ is a Normalization Factor. The shorthand notation for a normalized slater determinant is more convenient which includes only diagonal elements of the determinant,

$$\psi(\mathbf{x}_1, \mathbf{x}_{2,\dots,} \mathbf{x}_N) = |\chi_1 \chi_2 \cdots \chi_k\rangle$$
(2.29)

2.9 Hartree-Fock approximation

The most elementary form of an antisymmetric wave function is a single Slater determinant appropriate for describing the ground state of an N-electron system,

$$|\psi_0\rangle = |\chi_1\chi_2\cdots\chi_N\rangle \tag{2.30}$$

and according to the variational principle, the optimal wave function within this functional form is the one that yields the lowest achievable energy.

$$E_0 = \left\langle \Psi_0 \middle| H \middle| \Psi_0 \right\rangle \tag{2.31}$$

Through the minimization of E_0 with respect to the selection of spin orbitals, an equation known as the Hartree-Fock (HF) equation can be derived. It takes the following form,

$$f(\mathbf{i})\chi(\mathbf{x}_1) = \mathbf{E}\chi(\mathbf{x}_1) \tag{2.32}$$

Where f(i) is an effective one-electron operator known HF operator, of the form,

$$f(i) = -\frac{1}{2}\nabla_{i}^{2} - \sum_{i=1}^{N} \frac{Z_{A}}{r_{i}} + v^{HF}(i)$$
(2.33)

 $v^{HF}(i)$ is the average potential experienced by the ith electron due to the presence of other electrons and is known as HF Potential. The HF potential is reliant on the spin orbitals of the remaining electrons, leading to the non-linearity of the HF equation, which necessitates an iterative solution process. The essence of the HF approximation lies in simplifying the complex many-electron problem into a single-electron problem, where repulsion between the electrons is treated in an averaged manner.

2.10 Self-consistent field method

The HF equation is solved using the Self-Consistent Field (SCF) method. Initially, an estimation of the spin orbitals is made, and the average field experienced by each electron is calculated. The eigenvalue equation is then solved using the updated set of spin orbitals. This iterative process continues until self-consistency is achieved. The resulting solution provides a set of orthonormal spin orbitals, with the lowest N energy levels known as occupied spin orbitals. The HF ground state wave function is represented by the Slater Determinant obtained by these orbitals, serving as

an approximate description of the system's ground state. The remaining spin orbitals in the set, referred to as virtual, unoccupied, or particle spin orbitals, complete the picture.

2.11 Hohenberg theorems

Hohenberg Kohn first theorem states that the using the electron density we can determine the ground state energy of the system because the ground state energy is unique functional of electron density.

Second theorem of Hohenberg-Kohn establishes that the ground state energy of a system can be determined through the application of the variational principle. When considering a specific external potential, by minimizing the energy of the system while varying the electron density, one can ultimately arrive at the energy corresponding to the ground state. In the context of DFT, this principle is known as the variational principle, and the electron density that achieves the minimum energy in the ground state is referred to as the true electron density. These theorems offer a very flexible and powerful means of finding the ground state energy and other properties, let's see how?

2.12 Kohn-Sham approach



Figure 2.2: DFT perspective

Earlier attempts to adopt electron density without the use of any wave function in the first principal calculation were not highly successful. The main reason is poorly written electronic K.E in terms of electron density. Kohn-sham used electron density as the main variable to solve the N electron problem. The biggest difference between the previous first-principal methods and this new approach is that, now the problem has changed from 3N dimensional to N separate 3 dimensional ones with the use of electron density. And assuming that there are no individual electrons but only

a three-dimensional electron density. The electron density is an observable quantity and does not depend on the no. of electrons, after it is constructed in a system. The important point is that the quantum mechanical system is now an electron density-independent problem. The skipped correlation energy in the Hartree-Fock method is accounted for by an approximation, thus all energy terms are present in DFT.

2.13 Kohn-Sham equation

Kohn-Sham¹⁰ proposed to work with a system of non-interacting electrons. The wave function and density of non-interacting electrons differ from those of interacting electrons, reflecting the impact of electron-electron interactions on their behavior. However, Kohn-Sham assumed that a system is created that has no interaction, but it has same electron density as that of interacting system. We know the many-body problem Schrödinger equation is written as, using eq. (2.1)

$$\left[\sum_{i}^{N}\left(-\frac{\hbar^{2}\nabla_{i}^{2}}{2m}+v(r_{i})\right)+\sum_{i< j}U(r_{i}r_{j})\right]\Psi_{e}(r_{1}r_{2}\ldots,r_{N})=E\psi_{e}(r_{1}r_{2}\ldots,r_{N})$$

Now due to assumption of non-interactive system we need to add some term to this equation to counter that assumption. Hence Kohn-Sham equation can be written as follows;

$$\begin{bmatrix} -\frac{\nabla^2}{2m} + v_{ext}(r) + v^{HF}(r) + v_{xc}(r) \end{bmatrix} \psi_n(r) = E_n \psi_n(r)$$
Exchange co-relation term
We use LDA or GGA approximation
$$\begin{bmatrix} 2.34 \end{bmatrix}$$

Now why do we need exchange-correlation term?

The addition term gives external potential, to force N non-interacting electrons system to have the same one-particle density of N interacting electrons system in that same external potential. The correlation energy is characterized as the disparity between the total precise energy and the combined contribution of the kinetic and exchange energies. How do we find the correlation term? We use some approximation to find out the exact form of the correlation term. There are methods like local density approximation (LDA),^{13,14} general gradient approximation(GGA)^{15,16} and many more.

2.14 Electron density calculation



Figure 2.3 Flow chart of density functional calculations.

Chapter 3

Structural Properties and Electronic Properties with the Effective Mass of the Nickel-based Perovskites

3.1 Introduction

LaNiO₃ is a highly promising material due to its wide range of applications such as metallic electrodes bottom in various fields of ferroelectric and superconductor devices.¹⁷ It belongs to the category of complex transition metal oxides, complex transition metal oxides fall under a class of materials suitable for alternative oxygen reduction reaction (ORR) catalysts in alkaline fuel cells and metal/air batteries due to their alkaline resistance. Perovskite structure compounds like LaNiO₃, when doped with small amounts of Mg and Fe on the B-site, have demonstrated enhanced catalytic activity.^{18,19}

At room temperature, LaNiO₃ adopts a rhombohedral structure, but it undergoes a phase transition to a cubic structure at higher temperatures. The degree of distortion from the cubic perovskite structure decreases as the size of the rare earth ion increases. Consequently, the larger La ion influences the less-distorted rhombohedral structure, preserving its metallic nature even at very low temperatures (down to 1.5 K) without exhibiting a metal-insulator transition. With its favourable electrical, structural, and morphological characteristics, LaNiO₃ exhibits metallic behaviour and Pauli's spin para-magnetism across a wide temperature range. These appealing properties render it a desirable material for diverse applications.

Numerous researchers have made efforts to fabricate high-quality epitaxial thin films of LaNiO₃ on perovskite substrates like SrTiO₃ or LaAlO₃.^{22–24} Furthermore, numerous studies have investigated the optical properties of LaNiO₃ experimentally.^{25–27} While some first-principles DFT calculations have been performed to study the electronic structures of LaNiO₃^{28–31}, despite its fundamental significance in physics and potential applications, theoretical investigations into the electronic structure of LaNiO₃ have not kept pace with experimental studies, highlighting a research gap that needs attention.^{32–37} In order to gain a deeper understanding of LaNiO₃ and elucidate its functional characteristics, a comprehensive investigation of its physical properties is crucial.²⁶

In this study, we have performed first-principles calculations based on DFT to calculate the effective mass of electrons for various pure Nickel-based perovskites, including LaNiO₃, La_{0.8}Ca_{0.2}NiO₃, La_{0.5}Ca_{0.5}NiO₃, La_{0.2}Ca_{0.8}NiO₃, La₄Ni₃O₁₀, La₃Ni₂O₇, and La₂NiO₄. We have calculated the DOS and electronic band structures for all the materials, and results obtained in this work are in good agreement with the previously reported data. We estimated the effective mass (m*) of electrons from the curvature of the electronic conduction band by a parabolic fit approximation near the extremum of the band (i.e., Γ -point). Our study shows that the effective masses are highly correlated with the energies of the conduction band extremum (i.e., LUMO) and the DOS near the Fermi energy level. Furthermore, doping of Ca atom as substitution dopant of La atom in LaNiO₃ shows a significant change in effective mass of the electron, which can be explained by the different surroundings of the A- and B-sites in the perovskites.

3.2 Theory of effective mass

Effective mass (m*) of an electron is a fundamental concept in solid-state physics that is crucial for understanding the electronic properties of materials. The concept of effective mass can be traced back to the early 20th century when it was introduced by Arnold Sommerfeld to describe the behaviour of electrons in metals. Effective mass is defined as the mass of a particle appears to have when it moves in a crystal lattice under the influence of an external force.

In solid-state physics, the effective mass of electrons in a crystal is one of the most important parameters that govern the electronic properties of materials. The effective mass of a carrier in a material is determined by the curvature of the band structure near the Fermi level. The Fermi level is the energy level at which the probability of finding an electron is 50%. The band structure of a material describes the allowed energies of electrons in the material as a function of their wave vector. The curvature of the band structure near the Fermi level determines the effective mass of carriers in the material.

 $LaNiO_3$ is a perovskite-type transition metal oxide that has been studied extensively in recent years due to its promising properties in catalysis, energy storage and electronic devices. The doping of $LaNiO_3$ with Ca has been shown to significantly alter its electronic properties, leading to change the conductivity and electrochemical performance.

The DOS is a fundamental concept in solid-state physics that describes the distribution of energy states available to electrons in a material. The DOS has been calculated using theoretical and computational method known as the DFT or DFT-D methods. The DOS near the Fermi level is of particular importance, as it determines the electronic properties of the material. The DOS near the Fermi level can be used to calculate the effective mass of carriers in the material.

The effective mass of an electron can be calculated using the curvature of the band structure near the Fermi level. The curvature can be obtained by calculating the second derivative of the energy dispersion with respect to wave vector. The effective mass is then given by the inverse of the second derivative:

$$m^* = rac{\hbar^2}{rac{d^2 E}{dk^2}}$$

Where m^* is the effective mass, \hbar is the reduced Planck constant, **E** is the energy, and **k** is the wave vector. The effective mass can also be obtained by measuring the carrier mobility in a material. The effective mass of a carrier is related to the DOS near the Fermi level through the following equation:

$$g(E) \equiv \frac{dn}{dE} = \frac{dn}{dk}\frac{dk}{dE} = \frac{1}{2\pi^2} (\frac{2m^*}{\hbar^2})^{\frac{3}{2}}E^{\frac{1}{2}}$$

This equation shows that the effective mass is proportional to the curvature of the energy dispersion and inversely proportional to the slope of the dispersion. Therefore, a high DOS near the Fermi level leads to a large curvature and a small effective mass.

The electronic properties of LaNiO₃ have garnered substantial attention in recent years and Ca-doped LaNiO₃. Our study has shown that the Ca doping leads to improved conductivity and electrochemical performance of the LaNiO₃. The effective mass of carriers in the Ca-doped LaNiO₃ has been investigated using theoretical and experimental methods. Density functional theory calculations have shown that the Ca doping leads to a significant reduction in the effective mass of carriers in LaNiO₃. The reduction in the effective mass can be attributed to the increased DOS near the Fermi level due to the Ca doping.

In this work, effective masses are obtained according to the following algorithm: Initially, the relaxation of the crystal structure is carried out using the Vienna Ab initio Simulation Package (VASP) suite code. Subsequently, the total density of states and the electronic band structure along the high-symmetry k-path, Γ -T-H-L- Γ -S-F-G, have been calculated at the equilibrium structures of the perovskites using the PBE method. To determine the effective mass of the electron, the conduction band minimum (i.e., LUMO band) is approximated to a parabolic fit along the L- Γ -S direction, near the extremum of the band (i.e., Γ -point). Finally, the second derivative of energy with respect to **k** (wave vector) is extracted to obtain the sought-after effective mass value.

Before closing this section, it is worth mentioning that other authors have used a different approach to determine the effective mass of electrons. The alternative approach begins with the computation of the Hessian matrix.³⁸ The Hessian matrix is a mathematical formulation that describes the curvature of the energy landscape of the material's electronic structure. It provides insights into the behavior of electrons in the valence and conduction bands. To obtain the Hessian matrix, a parabolic fitting of the energy of the frontier orbitals of the valence and conduction bands is performed. These frontier orbitals are usually the HOMO and the LUMO, respectively. The parabolic fitting captures the local behavior of the electronic structure around a specific k-point, which is denoted as \mathbf{k}_0 . The k-point selected for analysis corresponds to either the VBM or the CBM, depending on whether the focus is on the valence or conduction band. By choosing k_0 near these critical points, the analysis can provide valuable information about the behavior of charge carriers in the material. Once the Hessian matrix is obtained, it is diagonalized, leading to the determination of the principal axes of charge-carrier transport, known as eigenvectors, and their corresponding eigenvalues. The eigenvectors represent the directions along which charge carriers move most efficiently, while the eigenvalues quantify the curvature or stiffness of the energy landscape along these directions. From the eigenvalues of the Hessian matrix, the effective masses along the eigenvectors are derived. The effective mass corresponds to the inertia experienced by an electron moving through the crystal lattice and governs its response to external forces or fields. By examining the eigenvalues, researchers can identify the directions in which the effective mass is either low or high i.e., minimum or maximum, shedding light on the anisotropic nature of charge transport in the material.

3.3 Computational details

The electronic structure of a range of pure Nickel-based perovskites (including LaNiO₃, La_{0.8}Ca_{0.2}NiO₃, La_{0.5}Ca_{0.5}NiO₃, La_{0.2}Ca_{0.8}NiO₃, La₄Ni₃O₁₀, La₃Ni₂O₇, and La₂NiO₄) has been investigated through density functional theory calculations utilizing the state-of-the-art Vienna ab initio simulation package (VASP).^{39,40} To ensure the highest level of precision and reliability in the calculations, the Perdew-Burke-Ernzerhof (PBE)¹⁶ exchange-correlation functional and a projected augmented-wave (PAW) basis set with an energy cut-off about 600 eV have been employed. These advanced techniques have been shown to provide highly accurate and reliable results in previous studies of electronic structures of materials. While it is recognized that the use of a generalized gradient approximation (GGA) functional may underestimate band gaps in some materials, this is not an issue in the systems under investigation, which are not semiconductors. However, it is acknowledged that the relative values of band gaps among different crystals can still be compared when the same functional is used.⁴¹ Additionally, the topology of band structures around the valence band maximum (VBM) and conduction band minimum (CBM) is generally not strongly affected by the GGA approximation.⁴²⁻⁴⁴

Therefore, a GGA-level functional is deemed to be an appropriate for studying the effective carrier mass in the pure Nickel-based perovskites. These investigations can provide valuable insights into the electronic properties of the pure Nickel-based perovskites, which have potential applications in various technologies. For example, LaNiO₃ is of particular interest due to its potential use as a conductive oxide in solid oxide fuel cells, and La₂NiO₄ is a candidate for high-temperature superconductivity.¹⁷

Through the implementation of a rigorously converged 4x4x4 Gamma-centered k-point grid, the optimized unit cells of the pure LaNiO₃, La₄Ni₃O₁₀, La₃Ni₂O₇, and La₂NiO₄ perovskites exhibit exceptional agreement with experimental data.¹⁷ The calculated lattice parameters accurately capture the underlying physical characteristics of these systems. Interestingly, despite these laudable achievements, the band gaps of these structures are determined to be equal to zero. Taking a step further, the investigation delves into the effects of Ca doping in LaNiO₃. Specifically, the native Ni atom is substituted by a Ca atom, and the triclinic LaNiO₃ is investigated for three distinct doped unit cells of the chemical formula La_{0.8}Ca_{0.2}NiO₃, La_{0.5}Ca_{0.5}NiO₃, and

La_{0.2}Ca_{0.8}NiO₃. These doped unit cells are subjected to full relaxation, and the electronic structures are calculated through a Gamma 20 point-only approach.

To determine the effective masses of electrons within electronic bands, a fundamental equation of the form $m^* = \hbar^2/(d^2E/dk^2)$ is employed. This formula incorporates the reduced Planck constant (h/2 π) and the second derivative of the particle's energy E with respect to its wave vector k, denoted as d²E/dk². To extract the second derivative of the total energy³⁸, a Taylor series expansion is utilized to obtain a quadratic fit of the k points surrounding the valence band extremum (Γ -Point) regions. The explicit band energies are then calculated, which allows for an accurate determination of the d²E/dk² term. Through this intricate approach, the effective mass of electrons within the electronic bands can be obtained with utmost precision and reliability.

3.4 Results and discussion

Recent findings revealed that the studied systems namely LaNiO₃, La_{0.8}Ca_{0.2}NiO₃, La_{0.5}Ca_{0.5}NiO₃, La_{0.2}Ca_{0.8}NiO₃, La₄Ni₃O₁₀, La₃Ni₂O₇, and La₂NiO₄ are suitable for oxygen reduction reaction (ORR) catalysts. However, among them, LaNiO₃ demonstrated the highest catalytic activity for ORR,⁴⁵ surpassing the rest of the systems. Interestingly, the catalytic activity of the LaNiO₃ can be further enhanced by introducing Mg or Fe dopants at the site of Ni.^{18,19} This opens up new avenues for designing more efficient and effective ORR catalysts.

In this study, we have delved into the structural and electronic properties of pure Nickelbased perovskite-related structure oxides, including LaNiO₃, La_{0.8}Ca_{0.2}NiO₃, La_{0.5}Ca_{0.5}NiO₃, La_{0.2}Ca_{0.8}NiO₃, La₄Ni₃O₁₀, La₃Ni₂O₇, and La₂NiO₄. First, we performed the structural optimization of all the systems mentioned above, which shows that the calculated lattice parameters are in good agreement with the earlier reported experimental data.⁴⁶ On the basis of optimized geometries of all the systems, we find out the DOS as shown in the figures 3.1 to 3.7 given below and it shows that all the systems from LaNiO₃ to La₂NiO₄ have zero band gap, therefore all the systems are metallic. According to the crystal field theory Ni 3d state splits into t_{2g} and e_g levels, and t_{2g} is completely filled, while e_g one-quarter-filled¹⁷ with the electrons band suggests that Ni 3d e_g electrons contributing to the density of states near the Fermi energy level. Further, we have calculated the band structures of all the systems as shown in the figures 3.1 to 3.7 given below and the calculated band structures showed excellent agreement with the earlier reported ones.⁴⁶ Specifically, LaNiO₃ was found to follow the symmetry $R\overline{3}C$,¹⁷ while La_{0.8}Ca_{0.2}NiO₃, La_{0.5}Ca_{0.5}NiO₃, and La_{0.2}Ca_{0.8}NiO₃ exhibit *P1* symmetry. The electronic band structures of these perovskites were calculated along the K-path *Γ*-*T*-*H*-*L*-*Γ*-*S*-*F*-*G*, and the band gap was determined between the conduction band and the valence band at the high symmetry *Γ* point. On the other hand, La₄Ni₃O₁₀, and La₂NiO₄ follow the symmetry *I4/MMM*, while La₃Ni₂O₇ exhibits *CMCM*, and their electronic band structures were also calculated along the same K-path *Γ*-*T*-*H*-*L*-*Γ*-*S*-*F*-*G*. These results provide a comprehensive understanding of the electronic properties and structural characteristics of the studied Nickel-based perovskites, laying a solid foundation for their potential applications in various fields.

In order to gain a deeper understanding of the electronic structure of LaNiO₃, an important parameter for describing transport and electrical properties was explored: the effective mass of electrons. Specifically, the electronic band curvature was studied using this parameter along the path of *L*- Γ -*S* to calculate the effective mass. By analyzing the effective mass of electrons, we were able to gain further insights into the behavior of electrons within the material, allowing for a more comprehensive understanding of the electronic properties of LaNiO₃. These findings hold significant potential for advancing research in the fields of materials science and electrocatalysis, as well as facilitating the development of new and improved electronic devices.



Figure 3.1: (a) Relaxed crystal structure (b) band structure and (c) densisty of states of LaNiO₃



Figure 3.2: (a) Relaxed crystal structure (b) band structure and (c) densisty of states of La_{0.8}Ca_{0.2}NiO₃



Figure 3.3: (a) Relaxed crystal structure (b) band structure and (c) densisty of states of Ca_{0.5}La_{0.5}NiO₃



Figure 3.4: (a) Relaxed crystal structure (b) band structure and (c) densisty of states of Ca_{0.8}La_{0.2}NiO₃



Figure 3.5: (a) Relaxed crystal structure (b) band structure and (c) densisty of states of La₂NiO₄



Figure 3.6: (a) Relaxed crystal structure (b) band structure and (c) densisty of states of La₄Ni₃O₁₀



Figure 3.7: (a) Relaxed crystal structure (b) band structure and (c) densisty of states of La₃Ni₂O₆

We have employed the PBE-GGA method and plane wave basis sets in VASP to obtain the equilibrium geometry and electronic properties of all the systems studied in this work. These computational tools allowed us to accurately simulate the electronic properties of these materials, with results that were in good agreement with theoretical data. Our analysis of the electronic band properties of these perovskites revealed that they have significant potential as candidates for the ORR catalyst. This finding holds significant implications for the fields of materials science and electro-catalysis, as it points towards a promising avenue for the development of new and improved catalysts for a variety of applications. By leveraging the power of *ab initio* calculations, we were able to gain a deeper understanding of the electronic properties of these materials, paving the way for further research and development in this exciting field.

Table 3.1: Lattice parameters of	optimized geor	netry, symmet	ry, and band	gap of pure	Nickel-based		
perovskites							

System	Equilibrium lattice constants (Å)	Interfacial angle	Space group symmetry	Electronic band gap (Eg)
LaNiO ₃	a=5.48006 b=5.48006	$\alpha = \beta = 90$ and $\gamma = 120$	R3C	0
Lao.8Cao.2NiO3	c=13.04795 a=5.45275 b=5.45275	$\alpha = \beta = 90$ and $\gamma = 120$	P 1	0
La0.5Ca0.5NiO3	c=12.97475 a=5.40902 b=5.40902	$\alpha = \beta = 90$ and $\gamma = 120$	P 1	0
Lao.2Cao.8NiO3	c=12.83865 a=5.37723	$\alpha = \beta = 90$ and $\gamma = 120$	P 1	0
La2NiO4	b=5.37723 c=12.60572 a=3.81833	$\alpha = \beta = \gamma = 90$	I4/MMM	0
	b=3.81833 c=12.76716	∝-p-1->0		
La ₃ Ni ₂ O ₇	a=20.17904 b=5.49305 c=5.39415	$\alpha = \beta = \gamma = 90$	СМСМ	0
La4Ni3O10	a=3.83874 b=3.83874 c=27.75991	α= β= γ=90	I4/MMM	0

Effective mass of electron of all the systems is calculated near the Γ -Point along the direction *L*- Γ -*S*, and the average value of m* per system is ranging from -8.785 m_e to 0.644 m_e. The reason for calculating the effective mass near the Γ -Point can be clearly understood from the band structure of all the systems which shows that band extremum occurs at the Γ -Point. LaNiO₃, a perovskite material, displays an electron effective mass about -0.400 m_e, and its electronic and

magnetic properties make it a subject of significant scientific interest. Both the $La_{0.8}Ca_{0.2}NiO_3$ and La_{0.5}Ca_{0.5}NiO₃ are like solid solutions of LaNiO₃ and CaNiO₃, which demonstrate negative effective mass (-0.432 me and -0.5 me, respectively), resulting from the curvature of the band structure near the band extremum. La_{0.2}Ca_{0.8}NiO₃. Another solid solution of LaNiO₃ and CaNiO₃, has a positive effective mass of 0.644 me, and its intriguing properties, such as high electrical conductivity, make it a subject of intense research scrutiny. La₄Ni₃O₁₀ and La₃Ni₂O₇, members of the Ruddlesde-Popper⁴⁷ series of oxides, display negative effective masses (-8.785 m_e and -4.555 m_e , respectively) and experience metal-insulator transition, magnetism, and superconductivity⁴⁷, highlighting the impact of effective mass on these properties. La₂NiO₄, a member of the K₂NiF₄ structure family of oxides⁴⁸, has a positive effective mass of 0.619 m_e , with its exceptional properties, such as a metal-insulator transition and high electrical conductivity⁴⁸, position it as an object of scientific interest. The order of effective mass is an essential quantity that indicates the magnitude of the electron's mass in various systems, providing an indication of the electron's mobility and its response to external forces. The negative effective mass observed in some systems implies that the electron behaves as if it had a negative mass, and its acceleration is opposite to the direction of the applied force.

System	Effective mass	K-Path
LaNiO ₃	-0.4001 me	L-Γ-S
La0.8Ca0.2NiO3	-0.4327 me	L-T-S
La0.5Ca0.5NiO3	-0.5000 me	L-Γ-S
La0.2Ca0.8NiO3	0.6447 me	L-Γ-S
La2NiO4	0.6190 me	L-Γ-S
La3Ni2O7	-4.5553 me	L-T-S
La4Ni3O10	-8.7850 me	L-Γ-S

Table 3.2: effective mass of electron in o pure Nickel-based perovskites

3.5 Summary

We have employed first-principles based PBE GGA method to investigate the effective masses of electrons in a diverse range of pure Nickel-based perovskite-related structure oxides and found that the effective mass of electrons is strongly correlated with the energies of the CBM, band gap, and total density of states near the Fermi energy level. Additionally, we explored the impact of Ca

atom doping at the site of La atom in LaNiO₃ on the effective mass of electrons and observed that the substitutional Ca atom alters the total density of states near the Fermi energy level and the curvature of the bands, particularly the conduction band minimum near the gamma point, leading to a significant change in the effective masses of electrons. These results have unveiled a promising avenue for the discovery of novel materials that exhibit a diverse range of electronic properties.

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