Development of computational methods for electronic structural characterization of strongly correlated materials: from different ab-initio perspectives

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Development of computational methods for electronic structural characterization of strongly correlated materials: from different ab-initio perspectives

Uthpala Kaushal Herath

Dissertation submitted to the
Eberly Collage of Arts and Sciences
at West Virginia University
in partial fulfillment of requirements
for the degree of

Doctor of Philosophy
in
Physics

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2022

Keywords:
Electronic Structure, Density Functional Theory, Strongly Correlated Materials,
Dynamical Mean Field Theory, Materials Science, Many Body Physics

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Abstract

Development of computational methods for electronic structural characterization of strongly correlated materials: from different ab-initio perspectives

Uthpala Herath

The electronic correlations in materials drive a variety of fascinating phenomena from magnetism to metal-to-insulator transitions (MIT), which are due to the coupling between electron spin, charge, ionic displacements, and orbital ordering. Although Density Functional Theory (DFT) successfully describes the electronic structure of weakly interacting material systems, being a static mean-field approach, it fails to predict the properties of Strongly Correlated Materials (SCM) that include transition and rare earth metals where there is a prominent electron localization as in the case of d and f orbitals due to the nature of their spatial confinement.

Dynamical Mean Field Theory (DMFT) is a Green’s function based method that has shown success in treating SCM. This dissertation focuses on the development of a user-friendly, open-source Python/Fortran framework, “DMFTwDFT” combining DFT and DMFT to characterize properties of both weakly and strongly correlated materials. The DFT Kohn-Sham orbitals are projected onto Maximally Localized Wannier Functions (MLWF) which essentially maps the Hubbard model to a local impurity model which we solve numerically using quantum Monte Carlo methods to capture both itinerant and localized nature of electrons. Additionally, we provide a library mode for computing the DMFT density matrix which can be linked and internally called from any DFT package allowing developers of other DFT codes to interface with our package and achieve full charge-self-consistency within DFT+DMFT.

We then study the stability and diffusion of oxygen vacancies in the correlated material LaNiO$_3$. By treating Ni-d as correlated orbitals along with a Ni-O hybridization manifold, we show that certain configurations undergo a MIT based on the environment of their vacancies. We also compute the transition path energy of a single oxygen vacancy through means of the nudged elastic band (NEB) method. We show that the diffusion energy profile calculated through DFT+U differs from that of DMFT, due to correlation effects that are not quite well captured with static mean-field theories.

Additionally, DMFTwDFT was utilized to study strongly correlated alloys and materials useful for neuromorphic computing applications.
Acknowledgements

First and foremost, I am thankful to my parents and my brother who have been there for me since day one of my journey. I would also like to remember my late uncle who recently passed away due to COVID-19 and everything he has done to support us.

I would like to thank my research advisor, Prof. Aldo Romero for his guidance and help throughout the course of my Ph.D. Thank you for believing in me and giving me an opportunity to prosper in your group.

I would also like say thanks to my collaborators Prof. Hyowon Park and Dr. Vijay Singh at UIC for their invaluable support in the DMFTwDFT project. I also appreciate the support from Prof. Javier Junquera of University of Cantabria on the Siesta+DMFTwDFT full charge self-consistency implementation.

To the rest of my Ph.D. committee, Prof. Matthew Johnson and Prof. Tudor Stanescu, I offer my gratitude for your support and valuable lessons related to my dissertation.

My current and past group mates have been a tremendous help throughout the years. I would never have made it without your help. Thank you Sobhit, Adam, Pedram, Vivi, Reese, Guillermo, Zac, Logan, Andres, Arturo and Soumya.

I would like to thank Viola, Sherry, Beena, and Miranda for all the departmental administrative support they have provided.

The WVU HPC clusters- Spruce Knob and Thorny Flat along with XSEDE facilities-Bridges2 and Stampede2 have been paramount for the calculations done in my dissertation. I offer my thanks to their administration for allowing me access to them.

I am grateful to all my Sri Lankan friends in Morgantown who became my family away from home. Life would have been difficult without your love and support throughout the years. I will miss you all dearly!

I offer my sincere gratitude to all my professors at the Department of Physics and Astronomy at WVU and the Faculty of Science at University of Peradeniya for their insightful guidance through my physics journey from bachelors to Ph.D.

I would like to say thanks to my close friends Navid, Saeed, Paul and Pete for being there
for me in both good and bad times. A thanks goes to Ashok for being a great roommate and tolerating me for three years.

Morgantown has given me the opportunity of meeting some amazing people including Alex, Kara, Jessica, Meera, CJ, Mike, Sanket, Neeraj, Ashish, Teresa and the list goes on. Thank you for being warm and friendly and making my stay in town memorable.

Finally, I would like to thank Katharine, Hank and Elli for being there for me as long as they could, until they couldn’t anymore. I will never forget the amazing moments we shared together and the support you gave me throughout the last two years.
To all the Ph.D. students out there seeking the light at the end of the tunnel.
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<td>CTQMC</td>
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Chapter 1

Introduction

With the advent of computational technology, we are today able to solve materials science problems within a time span of only hours or days—a significant improvement from the archaic computers that would have taken the same calculations months to complete. Computational materials science is at the forefront of technology today which work hand-in-hand with experimentalists to either provide a theoretical model of experimental outcomes, or to provide first-principles based blueprints for their next fabrication.

Among popular electronic structure methods, Density Functional Theory (DFT) [1, 2] is one of the most widely used as it provides a nice computational efficiency. DFT essentially solves the many body Schrödinger equation from first-principles using approximations. Designed to be an exact theory, DFT becomes “less exact” due to the inability of XC functionals to address exchange and correlation effects accurately. As a result, DFT performs fairly well for many materials systems, but fails to address the physics in a class of materials known as “strongly correlated materials” due to the presence of strong electron-electron interactions which must be treated independently. Methods such as Hartree-Fock [3] address the exchange, but still does not correct the correlations. This calls for the need of so called beyond-DFT methods.

Dynamical Mean Field Theory (DMFT) [4–16] is a beyond-DFT method which has been very successful in addressing strongly correlated material properties, where standard DFT fails. The simplest mathematical definition of correlation could be written as:
\[ < n(r) n(r') > \neq < n(r) > < n(r') > . \] (1.1)

This essentially means that the movement of one electron is influenced by the presence of another. Correlated materials are mostly found in the \(d\) and \(f\) block of the periodic table. These effects are due to the spatial geometry of the orbitals of such materials which create rise to an interplay between their itinerant and localized behaviour. The electronic correlations in materials drive a variety of fascinating phenomena from superconductivity to Mott transitions, which are due to the coupling between electron’s spin, charge, ionic displacements and orbital ordering. These lead to astonishing \textit{emergent} phenomena solely arising from the collective communication between them- a behaviour the American physicist Philip Anderson’s described as \textit{“More is different”} \cite{17}. Such properties allow using correlated materials in a wide range of intriguing novel applications including spintronics, high \(T_c\) superconductors and smart windows. Therefore, it is imperative to develop proper tools to facilitate scientists to study them without the need of extensive theoretical or computational expertise.

This dissertation is organized as follows. It consists of three parts, namely, Theoretical background, Method development of electronic structure frameworks and Applications.

In Chapter 2, I give an introduction to many body electronic structure methods mostly focusing on Density Functional Theory (DFT). This chapter concludes with the notion that beyond-DFT methods are required to properly understand properties of strongly correlated materials. Chapter 3 follows a discussion on methods to treat strong correlations in materials primarily engaging in Green’s functions formulation and DMFT. This concludes the theoretical background section.

In the Method development section I start with Chapter 4, which is on the electronic structure pre and post-processing tool PyProcar where I am a pioneering main developer. PyProcar is a widely popular code among multiple DFT communities given its ease of use and rich features. Next, I discuss the DMFTwDFT framework in Chapter 5 which is a tool used to perform DFT+DMFT calculations using a variety of DFT codes. In Chapter 6 I discuss one of my main contributions to the MECHELASTIC code, which is a tool used to perform mechanical and elastic analysis of materials. Specifically, I implemented the Equation of State (EOS) module for this code.
In the Applications section, I discuss my work done using the aforementioned tools and frameworks. Chapter 7 discusses our study on the stability and diffusion of oxygen vacancies in the correlated nickelate perovskite LaNiO$_3$ using DMFT. Chapter 8 and Chapter 9 are on-going projects. The former is an investigation on using Virtual Crystal Approximation (VCA) in combination with DMFT to study strongly correlated alloys aiming to replace the computationally expensive supercell approach. The latter aims to generate machine learning models for atomic force fields for potential applications in neuromorphic computing devices.

Finally, I conclude the dissertation with an outlook and summary chapter.
Part I

Theoretical background
Chapter 2

Ab-initio electronic structure theory

This chapter provides the theoretical background of electronic structure calculations in order to understand the research performed in this dissertation. It begins with a discussion on the quantum many-body problem and the Density Functional Theory (DFT) method used to solve it. Afterwards, it discusses about the shortcomings of DFT which is a segway into the next chapter on strongly correlated materials.

2.1 The many body problem

Complexities in physics arise as the number of interactions between objects increase. Prior to the quantum many-body problem, a more general $n$-body problem was prevalent with macroscopic objects such as planets in the gravitational interaction realm. Although Newtonian Mechanics was able to conveniently address the two-body problem, the three-body problem brought in complexities which made it a difficult problem to solve.

In microscopic atomic environments where quantum effects dominate, this problem becomes even more complex due to additional degrees of freedom coming from interactions between electrons and nuclei, both among themselves and each other. In an atom there exists a positively charged nucleus and a negatively charged electron cloud shielding the nuclei so that the net charge of an atom amount to zero. Baryonic matter consists of a large collection of such atoms. The Avogadro constant, $6.023 \times 10^{23}$, gives the amount of atoms
in a mole of a substance suggesting how large these collective atomic environments are. A diagram showing the many-body particle interactions is shown in Fig. 2.1. Through methodologies that can aid in solving the many body problem and understanding these interactions between particles, we could predict a plethora of information about materials and their emergent properties.

Figure 2.1: A schematic depicting the interactions between ions and electrons, both among themselves and between each other. $R_I$ and $r_i$ represent the position vectors of the ions and electrons, respectively.

The starting point to decipher the quantum many body problem can be thought to be the many body Schrödinger equation which was formulated by the Austrian-Irish physicist Erwin Schrödinger in 1926 [18]. This takes the form of a wave equation, but as the quantum nature of particles tell us that they behave both as a particle and a wave at the same time, the equation is applicable. Even with the advent of state-of-the-art computational technology, this equation is impossible to solve as the number of constituents become large. Therefore, in order to arrive at practical solutions to this equation, it is decorated with various approximations which we will discuss throughout this chapter. To start off, the time-independent, non-relativistic $^1$ form of the fundamental many body Schrödinger’s equation is shown in Eq. (2.1).

\[ \text{Refer to Klein-Gordon and Dirac equations for relativistic case.} \]
where, $\psi$ is the wave function and $E$ is the total energy of the system and $\hat{H}$ is the Hamiltonian of this multi atomic system is given by,

$$\hat{H} = \hat{T}_{\text{ion}} + \hat{T}_e + \hat{V}_{\text{ion-ion}} + \hat{V}_{\text{ion-e}} + \hat{V}_{\text{e-e}}.$$  

More specifically, Eq. (2.2) can be expanded as shown below,

$$\hat{H} = - \sum_{l=1}^{N} \frac{\hbar^2}{2M_l} \nabla^2_{R_l} - \frac{\hbar^2}{2m_e} \sum_{i=1}^{n} \nabla^2_{r_i}$$

$$\hat{T}_{\text{ion}} + \hat{T}_e + \sum_{l=1}^{N} \sum_{j=1}^{N} \frac{Z_l Z_j e^2}{|R_l - R_j|} - \sum_{l=1}^{N} \sum_{j=1}^{n} \frac{Z_l e^2}{|R_l - r_j|} + \frac{1}{2} \sum_{i=1}^{n} \sum_{j=1}^{n} \frac{e^2}{|r_i - r_j|} \equiv \hat{V}_{\text{ion-ion}} + \hat{V}_{\text{ion-e}} + \hat{V}_{\text{e-e}}.$$  

where, $R_l$ and $r_i$ denote the positions of ions and electrons, $M_l$ and $m_e$ denote the mass of ions and electrons, $Z$ denotes the atomic number of the ions and $e$ denotes the charge of an electron. The terms on the first line of the Eq. (2.3) represents the kinetic energy of ions and electrons, respectively. The terms on the second line describes the Coulomb potential energy of ion-ion, ion-electron and electron-electron interactions, respectively. Since this provides an overly complex equation to solve we start introducing approximations to simplify it.

Our first approximation lies with the assumption that ions are much heavier than electrons ($M_l \gg m_e$) meaning ions are stationary with respect to the dynamics of the electrons.
This allows us to decouple the ionic and electronic degrees of freedom in the wave function letting us treat ions and electrons separately. This is the so-called Born-Oppenheimer approximation [19]. This reduces Eq. (2.2) to Eq. (2.4) shown below.

\[
\hat{H} = \hat{T}_e + \hat{V}_{\text{ext}} + \hat{V}_{\text{e-i}}.
\]  

(2.4)

Since we assumed stationary ions, \(\hat{T}_{\text{ion}}\) has been dropped. The ion-ion interaction \(\hat{V}_{\text{ion-ion}}\) reduces to a constant and can also be dropped. We have replaced the \(\hat{V}_{\text{ion-e}}\) term in Eq. (2.2) as an external potential acting on the electrons due to the ions i.e.

\[
\hat{V}_{\text{ext}} = -\sum_{I=1}^{N} \sum_{j=1}^{n} \frac{Z_I e^2}{|\mathbf{R}_I - \mathbf{r}_j|}.
\]

(2.5)

This leaves us with a much simpler form of the Schrödinger equation Eq. (2.6) with the new Hamiltonian formulated above. The ionic contribution now appears as a static external potential in the Hamiltonian and the electronic wavefunction depends only parametrically on the ionic coordinates.

\[
\hat{H}\psi(\{r_i\}) = E\psi(\{r_i\}).
\]

(2.6)

Although we have made simplifications, this is still a hard problem to solve for two main reasons.

1. The wavefunction contains 3N degrees of freedom. In realistic systems N is a very large number (\(\sim 10^{23}\)) making the solution intractable.

E.g.- In a Pb nanocluster there are 82 electrons per atom and the nano cluster contains a 1000 atoms. This becomes a \(82,000 \times 3 = 246,000\) dimensional problem. Such
Ab-initio electronic structure theory

problems are difficult to solve numerically with our current computing technology. This is known as the \textit{curse of dimensionality} \footnote{The definition of \textit{curse of dimensionality} differs slightly from field to field.}.

2. The electron-electron Coulomb interaction $\hat{V}_{e-e}$, results in correlation effects between electrons which adds an additional layer of complexity to the problem.

Thus, the many-body wavefunction is a complicated mathematical object that requires approximations in order to be solved. In the next sections we will discuss about several methods physicists came up with throughout history to achieve that whilst attempting to retain the physics as much as possible.

\section*{2.2 The Variational Principle}

The Variational Principle is an approximation method used to find the ground state energy of a system. It states that the ground state energy $E_0$ of a system is always less than or equal to the expectation value of the Hamiltonian $H$ calculated with the trial wavefunction $\psi$, i.e.

$$E_0 \leq \langle \psi | \hat{H} | \psi \rangle = \int \psi^* \hat{H} \psi \, dr \quad (2.7)$$

This is used as a fundamental property in the approximation methods we discuss next.

\section*{2.3 Hartree and Hartree-Fock}

\subsection*{2.3.1 Hartree approximation}

The Hartree approximation \footnote{\cite{10.1088/1361-648x/34/2/3157}} which assumes independent electrons and turns the many-electron wave function into a product of single-particle wave functions as shown in Eq. (2.8)
known as the Hartree product.

\[ \psi(r_1, r_2, \ldots, r_N) = \psi_1(r_1) \ldots \psi_N(r_N) \quad (2.8) \]

Each of these single particle wavefunctions \( \psi_i(r) \) satisfies a one-electron Schrödinger equation form, Eq. (2.9) with an effective averaged mean-field Coulomb potential \( V(r) \) arising from the other electrons. Thus, Hartree introduced the idea of a “self-consistent field” in which the final potential field as computed from the charge distribution to be self-consistent with its initial guess. This could be used along with the Variational principle Eq. (2.7) discussed in Sec. 2.2 to approach an approximate solution to the Schrödinger equation.

\[ -\frac{\hbar^2}{2m} \nabla^2 \psi_i(r) + V(r)\psi_i(r) = \epsilon_i \psi_i(r) \quad (2.9) \]

where, \( V(r) \) is the effective potential each individual electron feels coming from both ion-electron interaction and the mean field from the other \( N-1 \) electrons. i.e.

\[ V(r) = -Ze^2 \sum \frac{1}{|r - R|} - e \int dr' \rho(r') \frac{1}{|r - r'|}. \quad (2.10) \]

The second term in Eq. (2.10) contains a charge density term, \( \rho(r') = \sum_i |\psi(r')|^2 \) which represents a smeared electron cloud stemming from the other \( N-1 \) electrons. However, there is a major fundamental problem with the Hartree approximation in which Pauli’s exclusion principle fails. Pauli’s exclusion principle requires the many body wavefunction to be antisymmetric for the interchange of any two fermions (electrons) i.e.

\[ \psi(r_1, r_2, \ldots, r_i, r_j, \ldots, r_N) = -\psi(r_1, r_2, \ldots, r_j, r_i, \ldots r_N). \quad (2.11) \]
The failure to address this in Hartree’s method rendered it to be quite inaccurate.

2.3.2 Hartree-Fock Theory

Slater [21] and Fock [3] recognized that imposing the antisymmetric conditions to Eq. (2.9) would make it satisfy the exchange condition. This was achieved by employing Slater determinant of the form,

\[
\psi(r_1, r_2, \ldots, r_N) = \frac{1}{\sqrt{N!}} \left| \begin{array}{cccc}
\varphi_1(r_1) & \varphi_2(r_1) & \cdots & \varphi_N(r_1) \\
\varphi_1(r_2) & \varphi_2(r_2) & \cdots & \varphi_N(r_2) \\
\vdots & \vdots & \ddots & \vdots \\
\varphi_1(r_N) & \varphi_2(r_N) & \cdots & \varphi_N(r_N) 
\end{array} \right|
\]

(2.12)

to replace Eq. (2.8) and ultimately modify Eq. (2.9) to become,

\[
-\frac{\hbar^2}{2m} \nabla^2 \psi_i(r) + V(r)\psi_i(r) - \sum_j \int dr' \frac{\psi_j^*(r') \psi_i^*(r') \psi_j(r)}{|r - r'|} = \epsilon_i \psi_i(r)
\]

(2.13)

These equations are known as the single-particle Hartree-Fock equations [3]. The last term on the left hand side of Eq. (2.13) is the exchange term that satisfies the antisymmetry property which was lacking in Hartree’s original equation Eq. (2.9).

Although Hartree-Fock is able to deal with exchange, it still neglects the electron-electron correlation effects. This leads to erroneous results such as predicting jellium to be insulating rather than metallic. These failures brought the need for a more improved methodology to incorporate both the exchange and correlation effects and Density Functional Theory (DFT) [1, 2] became the answer.

\(^3\)Improved post-Hartree methods such as configuration interaction (CI) address the correlation effects up to a certain extent.
The concept of Density Functional Theory (DFT) is to replace the N-body wavefunction in the Schrödinger equation with the electron density \( n(r) \) given by,

\[
n(r) = N \int d^3r_2 \cdots \int d^3r_N |\Psi (r, r_2, \cdots, r_N)|^2.
\] (2.14)

Considering the electron density reduces the dimensionality of the problem from 3N to 3, significantly reducing the computational cost. The pioneering idea of using the electron density as a functional \(^4\) of energy to solve the many body Schrödinger equation emerged in the 1920’s from Thomas \([22]\) and Fermi \([23]\) with the Thomas-Fermi model Eq. (2.15).

\[
\frac{5}{3} C_k n(r)^{\frac{3}{2}} + e^2 \int dr' \frac{n(r')}{|r - r'|} + V_{\text{ext}} (r) + \lambda = 0
\] (2.15)

where, \( C_k = \frac{3\hbar^2 (3\pi^2)^{\frac{3}{2}}}{10m_e} \), \( V_{\text{ext}} \) is the external potential and \( \lambda \) is the Lagrange multiplier related to the constraint of constant particle number. Their assumption was that the electrons form a homogeneous electron gas satisfying Fermi-Dirac statistics and that the kinetic energy was a functional of the electron density \( n(r) \). However, this too neglected both exchange and correlation terms similar to Hartree’s equation Eq. (2.9). Later, Dirac came up with a term to incorporate exchange \([24]\) although it didn’t make any significant improvements.

Once Density Functional Theory (DFT) was introduced by Hohenberg and Kohn in 1964 \([25]\), it became quite popular as it managed to address both exchange and correlation \(^5\)

\(^4\)A functional is a function of a function.

\(^5\)Correlations were addressed to a certain extent.
As of today, it is well established and is employed in a wide range of fields ranging from materials science to biology. DFT is based on two theorems which is discussed in the following sub-section.

2.4.1 Hohenberg-Kohn Theorems

DFT is a ground state theory based on the following two simple theorems as obtained from Ref. [26]:

Theorem I:
For any system of interacting particles in an external potential $V_{\text{ext}}(r)$, the potential $V_{\text{ext}}(r)$, is determined uniquely, except for a constant, by the ground state particle density $n_0(r)$.

Theorem II:
A universal functional for the energy $E[n(r)]$ in terms of the density $n(r)$ can be defined, valid for any external potential $V_{\text{ext}}(r)$. For any particular $V_{\text{ext}}(r)$, the exact ground state energy of the system is the global minimum value of this functional, and the density $n(r)$ that minimizes the functional is the exact ground state density $n_0(r)$ (Fig. 2.2).

In other words, Theorem I says provided the charge density, the Hamiltonian of the system can be uniquely determined, therefore allowing the determination of wavefunction and other material properties. Theorem II essentially follows the Variational Principle (Eq. (2.7)) minimizing the total energy with respect to the charge density. The ground state energy is thus $E_0 = E[n_0(r)]$. However, it is important to note that this is valid only for the ground state and not any excited states.

With these two theorems we can write the expectation value of the Born-Oppenheimer approximated Schrödinger equation Hamiltonian Eq. (2.4) in the following form:
Figure 2.2: The energy $E[n(r)]$ as a functional of electron density $n(r)$.

\[
E = \left\langle \psi \left| \hat{T}_e + \hat{V}_{e-e} + \hat{V}_{\text{ext}} \right| \psi \right\rangle
\]  

(2.16)

or,

\[
E = \left\langle \psi \left| \hat{T}_e + \hat{V}_{e-e} \right| \psi \right\rangle + \left\langle \psi \left| \hat{V}_{\text{ext}} \right| \psi \right\rangle - \int V_{\text{ext}}n(r) dr.
\]  

(2.17)

Eq. (2.17) can be written in terms of electron density $n(r)$ as,

\[
E[n(r)] = F[n(r)] + \int V_{\text{ext}}n(r) dr.
\]  

(2.18)

$F[n(r)]$ is a functional of electron density $n(r)$ related to the kinetic and potential energy of electrons. $V_{\text{ext}}$ is the external potential which encodes information of the material since it has ionic contributions. The form of $F[n(r)]$ as a functional of electron density $n(r)$ is
unknown due to the complex correlation effects between electrons. In 1965, Kohn and Sham proposed a methodology to solve approximately this equation [27]. In the next subsection we expand on this method.

2.4.2 Kohn-Sham formalism

The method proposed by Kohn and Sham [27] to solve the many body Schrödinger equation involved the introduction of a fictitious system of N non-interacting electrons, similar to the approach by Hartree Eq. (2.8) and Eq. (2.9), to be described by a single-determinant fictitious wavefunction of N orbitals known as Kohn-Sham orbitals $\phi_i$. These non-interacting electrons move within an effective Kohn-Sham potential, $V_{KS}$. These equations can be written as,

\[
\begin{aligned}
\left[ -\frac{\hbar^2}{2m} \nabla^2 + v_{KS}(r) \right] \phi_i(r) &= \epsilon_i \phi_i(r) \\
\hat{H}_{KS} &= \epsilon_i \phi_i(r)
\end{aligned}
\]  

(2.19)
The first term in the Kohn-Sham Hamiltonian $\hat{H}_{KS}$ in Eq. (2.19) is the fictitious kinetic energy of the non-interacting electrons. The second term is the effective Kohn-Sham potential $v_{KS}$ which can be broken down as,

$$v_{KS}(\mathbf{r}) = v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) + v_{XC}(\mathbf{r}).$$  \hspace{1cm} (2.20)

Here, $v_{ext}(\mathbf{r})$ is the external potential, $v_H(\mathbf{r})$ is the Hartree potential which is the classical Coulomb electron-electron interaction given by,

$$v_H(\mathbf{r}) = \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'$$ \hspace{1cm} (2.21)

and the exchange-correlation potential $v_{XC}$ is given by,

$$v_{XC} = \frac{\delta E_{XC}[n(\mathbf{r})]}{\delta n(\mathbf{r})}.$$ \hspace{1cm} (2.22)

This is shown in Fig. 2.3. The electron density $n(\mathbf{r})$ for these equations are given by,

$$n(\mathbf{r}) = \sum_{i=1}^{N} |\varphi_i(\mathbf{r})|^2$$ \hspace{1cm} (2.23)

The number of Kohn-Sham states $\phi_i$ in Eq. (2.19) correspond to the number of electrons in the system. This is a fixed number given by the summation of the electron density,

$$N_e = \int_V \sum_{i=1}^{N_e} |\varphi_i(\mathbf{r})|^2 d^3 \mathbf{r}.$$ \hspace{1cm} (2.24)

The exchange-correlation potential, $v_{XC}$, is a correction term that attempts to compensate for the information lost when mapping the interacting many body Schrödinger equation to
the fictitious Kohn-Sham equations. This includes both exchange and correlation effects. The Kohn-Sham equations become exact if the exchange-correlation term is known exactly and the Kohn-Sham orbitals $\phi$ will yield the exact ground state wavefunctions, but that is not the case. There are many approximations to the exchange-correlation term targeting higher accuracy to the exact form which we will discuss in Sec. 2.4.3.

### 2.4.2.1 Solving the Kohn-Sham equations

The Kohn-Sham equations, Eq. (2.19) are solved self-consistently in an iterative manner as shown in Fig. 2.4.

As the terms in the Kohn-Sham potential $v_{KS}$ rely on the electron density $n(r)$, and the Kohn-Sham orbital $\phi$ is required to calculate $n(r)$ we must initialize the calculation with a trial electron density. Afterwards, the Kohn-Sham potential $v_{KS}$ is calculated using this electron density (Eq. (2.20), Eq. (2.21), Eq. (2.22)). With this $v_{KS}$ the Kohn-Sham equations Eq. (2.20) are then diagonalized to obtain the Kohn-Sham orbitals $\phi_i$ and their corresponding eigen value $\epsilon_i$ for each electron in the system. Using $\phi_i$ the new electron density $n^{\text{new}}(r)$ can be calculated with Eq. (2.23). If this new electron density differs with the initial electron density by a pre-defined tolerance amount, then the self-consistent cycle is converged. The electron density $n(r)$ corresponds to the ground state electron density. Otherwise, this electron density is fed into the loop as the new initial electron density and the cycle is repeated until convergence is reached. In practice, there are many minimization schemes such as linear mixing, Davidson and RMM-DIIS.

Once we have the ground state quantities, we have access to calculating a wide range of properties including forces, phonons, magnetism etc. With this converged electron density $n(r)$, the total energy of the ground state can be calculated by,
Guess a trial electron density
\[
n(r) = n^{new}(r)
\]
Calculate Kohn-Sham potential
\[
v_{KS}
\]
Solve Kohn-Sham equations to obtain \( \phi_i \) and \( \epsilon_i \)
Calculate new electron density
\[
n^{new}(r)
\]
\[\text{NO} \]
\[
n^{new}(r) = n(r) ?
\]
\[\text{YES} \]
DFT SCF cycle complete

Figure 2.4: The Kohn-Sham self-consistency cycle.

\[
E[n(r)] = T[n(r)] + \int d\mathbf{r} v_{ext}(\mathbf{r}) + \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}[n(r)]
\]  \hspace{1cm} (2.25)

where, \( T[n(r)] \) is the fictitious Kohn-Sham kinetic energy,

\[
T[n(r)] = -\frac{\hbar^2}{2m} \sum_i^N \langle \phi_i | \nabla^2 | \phi_i \rangle .
\]  \hspace{1cm} (2.26)
The $\phi_i$ are the Kohn-Sham orbitals corresponding to the solutions to the Kohn-Sham equation which provided the converged electron density. We should note that these Kohn-Sham orbitals are not eigen functions of the original interacting electron problem, but are mathematical quantities representing an auxiliary non-interacting single particle problem. In Chapter 3 we will discuss about methods where the interactions are taken into account exactly.

2.4.3 The exchange-correlation functional

The compensation exchange-correlation $E_{XC}$ term plays a significant role in the accuracy of the DFT calculation. This term manages both the exchange and electron-electron correlation effects that are neglected in the fictitious Kohn-Sham non-interacting formalism. It also accounts for the difference between the kinetic energy in the interacting electron kinetic energy and the fictitious Kohn-Sham system. The exchange is due to the anti-symmetric behaviour of the fermions, in which an “exchange energy” is required to interchange two electrons with the same spin while satisfying Pauli’s Exclusion Principle. Exchange is accounted for in the Hartree-Fock method as it is contained in the Slater determinants. Correlations on the other hand, are interactions between electrons and are not addressed properly in either Hartree-Fock or the Kohn-Sham formalism. As the exact form of $E_{XC}$ is still not known, there exists a variety of approximations each with different accuracies and computational costs. Next, we will elaborate on some of these approximations.

2.4.3.1 Local Density Approximation (LDA)

The Local Density Approximation (LDA) is the simplest approximation for the XC functional [28]. LDA approximates exchange-correlation energy density in a homogeneous uniform gas $\epsilon_{XC}[n(r)]$ to only depend on the local electron density $n(r)$. This is given by,
LDA works well for solids that have a relatively uniform electron density. It tends to overestimate chemical bonding strength making overestimations in elastic constants and underestimating lattice parameters and bandgaps [29].

2.4.3.2 Generalized Gradient Approximation (GGA)

In GGA, $E_{XC}$ depends on both the local density and its gradient $\nabla n(r)$ [30] and is given by,

$$E_{XC}^{\text{GGA}} = \int n(r) \epsilon_{XC}[n(r), \nabla n(r)] dr.$$  \hspace{1cm} (2.28)

There are many forms of GGA, but the most popular one is Perdew, Burke and Ernzerhof (PBE). It overestimates lattice parameters and underestimates elastic constants. However, it does a better job predicting experimental data compared to LDA.

Further improvements have been made by adding higher order derivatives such in the case of meta-GGA functionals [31] such as SCAN [32].

2.4.3.3 Hybrid Functionals

This exchange-correlation approximation combines multiple approximations such as LDA, GGA and Hartree-Fock together with different ratios. For example, HSE06 [33] contains 0.25 of HF exact exchange, 0.75 of GGA exchange and correlation energy from GGA, i.e.
\[ E^{\text{HSE}}_{XC} = 0.25E^{\text{HF}}_X + 0.75E^{\text{GGA}}_X + E^{\text{GGA}}_C. \]  

\[ (2.29) \]

2.4.4 Limitations of DFT

DFT is widely popular as it addresses the curse of dimensionality issue along with decent fixes to exchange-correlation interaction compared to previous electronic structure methods. It also delivers a good balance between accuracy and computational scaling with respect to the number of electrons in the system, \( O(N^3) \). As we have discussed previously, DFT through the Kohn-Sham formalism only approximates the exchange and correlations between particles. In materials where these effects are negligibly, the so called weakly-correlated materials DFT tends to perform rather well. However, when it comes to explaining certain properties of strongly correlated materials (SCM) such as the metal-to-insulator transition, DFT fails drastically. Therefore, we must resort to more accurate methodologies when dealing with such systems. We will discuss such methods in the next chapter. DFT is an exact theory, given we have exact XC functionals, which we do not possess as of now. Therefore, we are limited to it being a ground state method based on the Hohenberg and Kohn theorems. As such, DFT fails to capture ionization energies, electron affinities, optical spectra and excitation energies. These could be addressed with methodologies such as GW approximation [34, 35] and Bethe-Salpeter equation (BSE). However, it is out of the scope of this thesis so the reader is referred to literature for further information on these topics.
Chapter 3

Strongly Correlated Materials and methods to treat them

In this chapter we explain what strongly correlated materials (SCM) are and how they differ from weakly correlated materials. We then formulate the Dynamical Mean Field Theory (DMFT) method used to study these materials which will be the primary methodology used for the studies done in the subsequent chapters of this dissertation.

3.1 Introduction

The electronic correlations in materials drive a variety of fascinating phenomena from magnetism to superconductivity, which are due to the coupling between electron's spin, charge, ionic displacements and orbital ordering. Although DFT is a very successful theory in describing the electronic structure of weakly interacting material systems, it fails to predict the properties of a class of materials known as Strongly Correlated Materials (SCM) that include transition and rare earth metals where there is a prominent electron local-
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ization as in the case of $d$ and $f$ orbitals due to the nature of their spatial confinement (Fig. 3.1 (a)). They lead to a wide variety of astonishing phenomena in materials including magnetism, high-temperature superconductivity, colossal magnetoresistance, heavy fermion systems, metal to insulator transitions (Mott insulator) and thermomagnetism, all which have a profound impact on novel applications. These correlated electrons cannot be studied under mean field approaches since their interactions on each other are too prominent to be treated independently [36]. An example depicting the failure of DFT is shown in Fig. 3.1 where DFT incorrectly predicts the ground state of CeSF to be metallic [37].

Conventional band theories predict certain strongly correlated materials to be conductive, while experimentally they show insulating behavior (E.g. NiO). This discrepancy in band theory was noticed by Sir Nevil Mott, who realized that electron-electron interactions cannot be neglected as they result in the existence of a bandgap in these falsely predicted conductors which were later introduced as Mott insulators [39].
The reason for strong correlations is due to the interplay between orbital overlap and Coulomb repulsion. The former is related to kinetic energy of electrons and represents a metal in its extreme and the latter represents the potential energy and represents an insulator in its extreme. This is visualized in Fig. 3.2. SCM’s lay between this metal and insulating region. The underlying mechanism is discussed in detail in Sec. 3.2 where we introduce the Hubbard Model [40–44]. Many body models based on low-energy Hamiltonians such as the Hubbard model has the ability to capture the effect of electronic correlations whereas the high-energy ones used previously fail in that aspect.

![Figure 3.2: The itinerant and localized behaviour of electrons in a lattice. U is the onsite Coulomb repulsion and t is the hopping amplitude related to the kinetic energy of the electrons. This is discussed in detail in Sec. 3.2.](image)

3.2 The Hubbard Model

In Chapter 2 we discussed methods on solving the many body Schrödinger equation, Eq. (2.1). The methodologies discussed there were less accurate when it comes to properly addressing the correlation effects. The Hubbard Model [40–44] is a low-energy Hamiltonian capable of addressing the correlations. It describes the competition between the itinerant and localized character of electrons which is an important aspect of SCM. A pictorial representation of the single-orbital Hubbard Model is shown in Fig. 3.3. In realistic materials, the multi-band version of the Hubbard model is used which describe the valence electrons of correlated orbitals close to the Fermi energy. Each lattice site can at most contain two electrons with
opposite spins so that Pauli’s Exclusion Principle is followed.

![A schematic of the single-orbital Hubbard model for electrons in a square lattice. Each circle is a lattice site. The arrows represent an electron and their spin. Electrons can hop to neighboring sites with a hopping amplitude \( t \) and be subject to an onsite Coulomb repulsion \( U \).](image)

The simplest form of the Hubbard model is the single-orbital Hubbard Hamiltonian which is given in second quantization by,

\[
H = \sum_{\langle i,j \rangle \sigma} t_{ij} \left( c_{i\sigma}^\dagger c_{j\sigma} + \text{h.c.} \right) - \mu \sum_{i\sigma} n_{i\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow}.
\] (3.1)

The first term of Eq. (3.1) represents the kinetic energy of the electrons through the hopping amplitude \( t_{ij} \) representing a hopping from site \( j \rightarrow i \). The creation operator \( c_{i\sigma}^\dagger \) creates an electron with spin \( \sigma \) at site \( i \). Likewise, the annihilation operator \( c_{i\sigma} \) destroys an electron with spin \( \sigma \) at site \( i \). In most cases, only nearest-neighbor hoppings are considered \(^1\).

\(^1\)High \( T_c \) superconductors require next-nearest-neighbor hoppings to be considered.
second term represents the chemical potential $\mu$ of the system which measures how much energy changes in the system when the density of the system changes. The last term relates to the Coulomb interaction $U$ which penalizes two electrons with opposite spins occupying the same site. It goes through all the lattice sites and adds energy $U$ if the site is doubly occupied. $n_{i\uparrow} = c_{i\uparrow}^\dagger c_{i\uparrow}$ is the spin-density operator of site $i$ for spin $\uparrow$ and $n_i = n_{i\uparrow} + n_{i\downarrow}$ is the total density operator and the occupation of site $i$ for the wavefunction $\Phi$ is given by $n_i = \langle \Phi | \hat{n}_i | \Phi \rangle$.

The system’s insulating character develops when electrons do not have sufficient energy to overcome the Coulomb repulsion on neighboring sites, i.e. when $t \ll U$. DFT does a good job predicting electronic properties when $U \ll t$, while for large $U$ values, DFT significantly fails, and cannot capture the physics of Mott insulators as we do not have exact XC functionals capable of doing so.

The multi-orbital Hubbard model is required to explain the physics in real materials such as $d$ and $f$ materials. To expand the single-orbital Hubbard model to multi-orbital, the following two additions are required

1. A term for the degree of freedom to transition between orbitals

2. A term for the interaction between orbitals

Thus, the multi-orbital Hubbard model is given by,

$$H = - \sum_{\langle i,j \rangle} t_{i\alpha j\beta} \left( c_{i\alpha \sigma}^\dagger c_{j\beta \sigma} + \text{h.c.} \right) - \mu \sum_{i\alpha \sigma} n_{i\alpha \sigma} + \sum_i H_{U,i}$$

(3.2)

with,
\[ H_{U,i} = \frac{1}{2} \sum_{\alpha \beta \gamma \delta \sigma \sigma'} U_{\alpha \beta \gamma \delta} c_{i \alpha \sigma}^{\dagger} c_{i \beta \sigma}^{\dagger} c_{i \delta \sigma} c_{i \gamma \sigma}, \]

and \( \alpha, \beta, \gamma, \delta \) being orbital indices given by their magnetic angular momentum quantum number, \( l \). \( H_{U,i} \) is the local interaction acting on site \( i \) and \( U_{\alpha \beta \gamma \delta} \) is the interaction tensor which is parametrized by Slater integrals.

### 3.3 DFT+U

An immediate implication of the Hubbard Model is to add a *Hubbard Correction* term \( U \) to the DFT energy functional to address the correlation effects as the XC term does not completely fix the problem. Some XC functionals tend to over-delocalize valence electrons and over-stabilize metallic ground states [45]. This is because these XC doesn’t completely cancel out the self-interaction term coming from the Hartree potential, therefore a remnant of it induces added self-interaction leading to excessive delocalization of the wave function [46]. This could be overcome with hybrid XC potentials as they include a linear combination of XC contribution with HF exact exchange free from any self-interactions. However, this is at the expense of heavy computational cost and even so it does not capture the dynamics of strong correlations.

This is a rather straightforward approach to account for the underestimated electronic correlations by simply adding a numerical parameter \( U \) which is either formulated from first principles or empirically by tuning the \( U \) value in agreement with experimental results of a system’s physical properties [47]. Without the \( U \) correction, the plain DFT results predict band gaps, total energies, magnetic and mechanical properties inaccurately. With this \( U \) correction inspired by the Hubbard model, the DFT+U method [48] improves the results for SCM in calculating their ground state. The DFT+U energy functional can be
split into three parts; a functional describing the non-correlated states with standard DFT, a functional Hubbard term describing the correlations and a double counting correction term. This is written as below.

$$E^{\text{LDA+U}}[\rho] = E^{\text{LDA}}[\rho] + E^{\text{Hub}}[n^{i\sigma}] - E^{\text{DC}}[n^{i\sigma}]$$ (3.3)

with,

$$E^{\text{Hub}}[n^{i\sigma}] = \frac{1}{2} \sum_{mm'\sigma} U_{mm'} n_{m\sigma} n_{m'\sigma} + \sum_{m>m'\sigma} (U_{mm'} - J_{mm'}) n_{m\sigma} n_{m'\sigma}$$ (3.4)

where, $U_{mm'} = \langle mm' | V_{\text{Coulomb}} | mm' \rangle$ and $J_{mm'} = \langle mm' | V_{\text{Coulomb}} | m'm \rangle$ are matrix elements of the screened Coulomb interaction in the local orbital basis. We have suppressed the $i$ index by only focusing on a single site.

The second term of Eq. (3.3) contains the Hubbard correction to address strong correlations. This contains the on-site Coulomb interaction term $U$ and the exchange term $J$. The values of $U$ and $J$ can be determined from first principles through methods such as constrained Random Phase Approximation (cRPA) which computes the effective interactions among correlated electrons [49–51] and linear response [45]. This correction can fairly easily be added to LDA and GGA without a significant cost in computational expense.

Because of the added Hubbard term, the correlated states will contain a double counting term which must be subtracted from the standard DFT total energy. There are multiple types of double counting corrections such as the Fully Localized Limit (FLL) and Around Mean-Field (AMF) method [47].

DFT+U performs much better than standard DFT in correlated materials, however, the
Hubbard correction here is only a mean field quantity that compliments the XC functional and does not address correlations exactly. Also as DFT+U is a zeroth-order approximation of the self energy, thus has no frequency dependence or imaginary part of self energy. This corresponds to a constant shift of Kohn-Sham energies and excludes band renormalization and effective mass enhancement effects. As the self energy is purely real here, electrons have infinite lifetime. A divergence of the imaginary part of the self-energy at Fermi level is present in metal-insulator transitions, which DFT+U does not capture [52, 53]. A gap is opened at this transition due to quasiparticle excitation being suppressed leading to zero lifetimes. The concepts of quasiparticle lifetimes and self-energy is discussed in detail in Sec. 3.4. In the next section we will discuss about Dynamical Mean Field Theory (DMFT) [4–16] which is an exact treatment for studying the dynamical correlations in materials.

### 3.4 Dynamical Mean Field Theory (DMFT)

As we saw in the Hubbard model Eq. (3.1) the interplay between the itinerant and localized behaviour of electrons is not a trivial task. Exact solutions to the Hubbard model exist for the one-dimensional system [54] but for realistic cases we need better methods to solve it. In 1989 Metzner and Vollhardt pioneered the groundwork for DMFT with their work on the limit of the infinite dimensional Hubbard model [15]. Later in 1992, Georges and Kotliar formulated the theory on mapping the Hubbard model onto an effective impurity model which is determined self-consistently [16]. DMFT is a very successful non-perturbative, effective many particle, single site theory \(^2\) to solve the Hubbard model [4–16]. However, it is not a *first principles* method such as DFT as it requires an input from an electronic structure code. DMFT is used along with DFT to improve the DFT results that miss the

\(^2\)In contrast to DFT which is an effective many single particle theory.
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Strong correlation effects. DMFT becomes an exact theory in infinite dimensions. Unlike in static mean-field theories such as DFT and DFT+U, DMFT treats a frequency dependant \textit{dynamical} mean-field which captures quantum fluctuation essential to describe correlated phenomena such as metal-to-insulator transitions.

In DMFT, the interacting solid is mapped onto a local interacting impurity problem, where the impurity is an interacting single site coupled to an effective non-interacting bath representing the residual lattice through a hybridization function as depicted in Fig. 3.4. This impurity is described by its one-particle Green’s function which is used to calculate the hybridization that provides the self-energy of the interactions. This bath is determined in a self-consistent manner.

The electrons move from the bath (reservoir) and occupy the impurity site and return back to the bath as shown in Fig. 3.5.

A key approximation in DMFT is to treat the interactions as local quantities. That is to
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Figure 3.5: The electrons hop from the bath to the impurity site and back to the bath. At most two electrons with opposite spins can occupy the site at any given time. The hybridization $V_\nu$ is the quantum mechanical amplitude that specifies the probability of a state flipping between two different configurations. Retrieved from Ref. [10].

drop the $k$ dependence when obtaining the self-consistency conditions. With that we have the self-energy equivalence condition,

$$\Sigma_{lattice}(k, \omega) \approx \Sigma_{imp}(\omega) \quad (3.5)$$

which essentially says the lattice self-energy is equal to the self-energy of the local effective impurity. The approximation becomes exact when,

1. Non-interacting limit ($U=0$) : When there are no interaction in the lattice, the self-energy becomes zero, i.e. $\Sigma(k, \omega) = 0$.

2. Localized atomic limit ($t_{ij}=0$) : When the overlap between atoms is minor, atoms act as individual quantities.

3. Infinite dimensional lattice ($d \to \infty$) : The self-energy becomes local when the lattice has infinite dimensions.
Through this locality in DMFT, by dropping the $k$ dependence the spatial dependence disappears and only the temporal dependence remains. This is what gives it a *dynamical* mean field as opposed to the static mean-field found in more primitive methodologies.

To keep this dissertation from becoming exceedingly lengthy we refer the reader to well compiled literature for derivations of DMFT equations [8, 12] and stick to the pragmatic aspects of the theory essential to comprehend the subsequent chapters. We first introduce Green’s functions which is a key concept in DMFT and then revisit the formulation of the DMFT method.

### 3.4.1 Summary of Green’s functions in DMFT

Named after the British mathematician George Green, Green’s functions are an important mathematical tool to study the response of an inhomogeneous linear differential operator. Green’s functions are used in a wide range of fields including quantum field theory and condensed matter physics. They are also called “the propagator” as it is related to the probability amplitude of measuring a field at one point given that it is sourced at a different point as it travels through an interacting medium. This is illustrated in Fig. 3.6.

![Figure 3.6: The particle motion in the lattice.](image)

In the scope of this dissertation, Green’s functions are used to characterize the propagation of particles through a lattice. DMFT is formulated using the single-particle Green’s function
$G(k, z)$ which are complex analytic functions defined in the complete complex plane $z$ excluding the real axis poles. There are many different flavors of Green’s functions which we will discuss in the following sections.

The probability amplitude of a particle (electron) with spin $\sigma'$ put into an interacting system at position and time $(r', t')$ let it propagate and located at a later position and time $(r, t)$ with spin $\sigma$ is given by the \textit{retarded} Green’s function,

$$G^R(r\sigma t', r'\sigma' t') = -i\theta(t - t') \langle \{ \Psi_{\sigma}(rt), \Psi_{\sigma'}(r't') \} \rangle. \quad (3.6)$$

Here, $\Psi_{\sigma'}(r', t')$ and $\Psi_{\sigma}(r, t)$ are field operators that creates an electron with spin $\sigma'$ at position and time $(r', t')$ and annihilates an electron with spin $\sigma$ at position and time $(r, t)$, respectively. The expectation value of this formula is taken with respect to the ground state of the system, $|\psi_0\rangle$. $\theta$ is the Heaviside step function that guarantees the causality condition $t > t'$. The time evolution of the field operator is given in the Heisenberg picture by,

$$\Psi_{\sigma}(rt) = e^{\frac{i}{\hbar} Ht'} \Psi_{\sigma}(r)e^{-\frac{i}{\hbar} Ht}. \quad (3.7)$$

Essentially, the particle is excited from its ground state, propagated to time $t$ and measured how much of the original state is left in this final state. Through lengthy mathematical steps which I skip here $^3$, the \textit{non-interacting} retarded Green’s function, $G_0$, could be obtained in terms of crystal momentum $k$ and frequency $\omega$.

$$G_0^R(k, \sigma, \omega) = \frac{1}{\omega - \xi_{k,\sigma} + i\eta} \quad (3.8)$$

---

$^3$Readers are referred to Ref. [55–59] for additional details.
Here, $\xi_k$ is the band dispersion and $\eta'$ is an infinitesimal shift of the domain of the real frequencies slightly upwards into the complex plane in order to define a meaningful Fourier transform.

The non-interacting Green’s function and the interacting Green’s function are related through the so called self-energy $\Sigma(k, \omega)$ which is given by the Dyson Equation which reads,

$$G(k, \omega)^{-1} = G_0(k, \omega)^{-1} - \Sigma(k, \omega) \quad (3.9)$$

The goal of DMFT is essentially to calculate this self-energy $\Sigma(k, \omega)$ as it recovers the interactions of the system. Green’s functions are popular objects in quantum physics as they directly correspond to spectra obtained from experimental methods such as Angular Resolved Photo Emission Spectroscopy (ARPES)\(^4\) and Scanning Tunneling Microscopy (STM). For non-interacting systems the DMFT DOS (spectral function) is the same as DFT DOS.

The $k$-resolved spectral function of a system $A(k, \omega)$ is given by,

$$A(k, \omega) = \frac{i}{2\pi} \text{Tr} \left[ G(k, \omega) - G^\dagger(k, \omega) \right]. \quad (3.10)$$

As the trace is taken over orbitals, Eq. (3.10) can be reduced to Eq. (3.11) shown below for single-orbital systems.

\(^4\)See Appendix B for a detailed description.
$A(k,\omega) = -\frac{1}{\pi} \Im \{G(k,\omega)\}$  \hspace{1cm} (3.11)

The lifetime of excitations is proportional to the inverse of frequency-width of peaks in the spectral function. In a non-interacting system, the particles have infinite lifetime, thus, results in delta function peaks in their spectral function as depicted in Fig. 3.7.

![Figure 3.7: Schematic view of angular-resolved photoemission spectra (ARPES) for normal (left) and correlated electron materials (right). Retrieved from Ref. [60].](image)

By summing the momenta, $k$, over the 1st Brillouin zone, the DMFT Density of States (DOS) can be obtained as,

$A(\omega) = \sum_k A(k,\omega).$  \hspace{1cm} (3.12)

By discretizing the frequency axis, one obtains the so called Matsubara Green's functions on the Matsubara axis $z = i\omega_n$ where the Matsubara frequency $\omega_n$ is defined by,
\[ \omega_n = \frac{2n\pi}{\beta} : \text{for bosons} \]  
(3.13)

\[ \omega_n = (2n + 1)\pi \beta : \text{for fermions} \]  
(3.14)

with \( \beta = \frac{\hbar}{k_B T} \) and \( n \in \mathbb{Z} \). These are easier to compute than their continuous real axis counterparts. We are interested in the fermionic Matsubara frequencies, as in this research we limit our study to electrons which are fermions. The Matsubara Green’s function \( G(k, i\omega_n) \) embeds finite temperature \( T \) which manifests the quantum fluctuations of electrons. However, inorder to compare outcomes with real experiments, the Green’s functions need to be in the real axis and this can be obtain through means of analytic continuation i.e. \( G(k, i\omega_n) \rightarrow G(k, \omega) \).

In the next section, we continue onto formulate the DMFT procedure.

### 3.4.2 The DMFT workflow

As discussed previously, we employ the Hubbard model to calculate the self-energy of the lattice with embeds the interactions between electrons. This is done by mapping the Hubbard model onto an impurity model with an interacting single site coupled to a self-consistently determined effective non-interacting bath representing the residual lattice through a hybridization function as pictured in Fig. 3.4.

We start with the interacting lattice Greens’s function \( G(k, i\omega_n) \) in the Matsubara formalism given by,

\[ G(k, i\omega_n) = \frac{1}{i\omega_n - \epsilon_k + \mu - \Sigma(i\omega_n)}. \]  
(3.15)
Here, $\mu$ is the chemical potential and $\epsilon_k$ is the dispersion (eigen energies) of the non-interacting system. We have also suppressed orbital and spin indices for simplicity. Note that we have imposed the non-locality of the self-energy $\Sigma(k, i\omega_n)$ in Eq. (3.15) i.e. $\Sigma(k, i\omega_n) \rightarrow \Sigma(i\omega_n)$. In practice, this is provided through an initial guess as we shall see later. The local Green’s function can be obtained by summing the lattice Green’s function over the Brillouin zone.

$$G_{\text{loc}}(i\omega_n) = \sum_k G(k, i\omega_n) = \sum_k \frac{1}{i\omega_n - \epsilon_k + \mu - \Sigma(i\omega_n)}$$

(3.16)

The mapping of the (local) lattice model onto the impurity model demands their Green’s functions to be equivalent. i.e.,

$$G_{\text{loc}}(i\omega_n) \equiv G_{\text{imp}}(i\omega_n).$$

(3.17)

As we shall see later, this is what governs the self-consistency condition. Through Dyson’s equation discussed in Eq. (3.9), we obtain the bath Green’s function $G_0(i\omega_n)$,

$$G_0(i\omega_n) = \left[G_{\text{loc}}^{-1}(i\omega_n) + \Sigma(i\omega_n)\right]^{-1}$$

(3.18)

$G_0(i\omega_n)$ is the effective Weiss field which we see in static mean-field theory (E.g. Ising model), but the key difference is that here, the Weiss field is dynamic, hence the term dynamical mean field. It is the local Green’s function with locally removed interactions. Equivalently, it defines the non-interacting part of the impurity model i.e. $G_{0,\text{imp}}(i\omega_n) = G_0(i\omega_n)$ and is the exact bare Green’s function of the impurity model. The effective Weiss field
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can be described through the *hybridization* function $\Delta(i\omega_n)$ which provides communication between the impurity site and the effective bath, i.e.,

$$G^{-1}_0(i\omega_n) = i\omega_n + \mu - \Delta(i\omega_n). \quad (3.19)$$

This hybridization comes from impurity model used which is the Anderson impurity model (AIM) [61] whose Hamiltonian is given by,

$$H_{\text{AIM}} = \sum_{l\sigma} \epsilon_l a^\dagger_l a_l + \sum_{l\sigma} \left( V_l a^\dagger_{l\sigma} c_{\alpha\sigma} + V_l^* a_{l\sigma} c^\dagger_{\alpha\sigma} \right) + \epsilon_\alpha \sum_{\sigma} c^\dagger_{\alpha\sigma} c_{\alpha\sigma} + U n_{\alpha\uparrow} n_{\alpha\downarrow} \quad (3.20)$$

The first term of Eq. (3.20) represents the non-interacting bath sites with bath electron energies $\epsilon_l$, the second term represents the coupling between the bath and the interacting impurity site through a coupling constant $V_l$. The last term describes the interacting impurity site with impurity orbital energy $\epsilon_\alpha$. The $H_{\text{imp}}$ term mimics the interaction term $U$ of the lattice Hubbard model. The hybridization function $\Delta(i\omega_n)$ is defined by,

$$\Delta(i\omega_n) = \sum_l \frac{|V_l|^2}{i\omega_n - \epsilon_l}. \quad (3.21)$$

However, the exact form of the hybridization function for the lattice is not known and does not allow us to calculate the bath Green’s function $G^{-1}_0(i\omega_n)$ via Eq. (3.19). But we can instead use the initial self-energy $\Sigma(i\omega_n)$ and local Green’s function $G_{\text{loc}}(i\omega_n)$ in Eq. (3.18) to calculate $G^{-1}_0(i\omega_n)$. By using this bath Green’s function $G^{-1}_0(i\omega_n)$ as an input to an impurity solver, the interacting impurity Green’s function $G_{\text{imp}}(i\omega_n)$ can be calculated using the effective action of the impurity Hamiltonian. This is the heart of the DMFT
problem. Many methods are available to solve this impurity problem including CTQMC [62, 63], exact diagonalization. In this dissertation, the former was used.

Once the interacting impurity Green’s function $G_{\text{imp}}(i\omega_n)$ is obtained from the impurity solver, it can be used again in Dyson’s equation to calculate the impurity self-energy $\Sigma_{\text{imp}}(i\omega_n)$ with,

$$\Sigma_{\text{imp}}(i\omega_n) = G^{-1}_0(i\omega_n) - G^{-1}_{\text{imp}}(i\omega_n).$$

(3.22)

This impurity self-energy $\Sigma_{\text{imp}}(i\omega_n)$ is then inserted into Eq. (3.16) to obtain the new local Green’s function $G_{\text{loc}}(i\omega_n)$ to continue further iterations of the cycle. The DMFT convergence criteria yields:

$$G_{\text{loc}}(i\omega_n) = G_{\text{imp}}(i\omega_n).$$

(3.23)

Eq. (3.23) further yields that all calculated impurity quantities are equivalent to their local counterparts. In the case of self-energy, for each iteration, this can be stated as,

$$\Sigma_{\text{loc}}(i\omega_n) = G^{-1}_0(i\omega_n) - G^{-1}_{\text{loc}}(i\omega_n)$$

$$\Sigma_{\text{imp}}(i\omega_n) = G^{-1}_0(i\omega_n) - G^{-1}_{\text{imp}}(i\omega_n).$$

(3.24)

Thus, if $\Sigma_{\text{loc}}(i\omega_n) = \Sigma_{\text{imp}}(i\omega_n)$, then DMFT convergence is reached.

This essentially means that given the interacting Green’s function of local and impurity quantities are equal, the self-energy of the system will be converged. Note that the lattice self-energy becomes exact in the limit of infinite dimensions.
The above procedure is illustrated in Fig. 3.8 and is summarized as follows:

1. Guess an initial self-energy $\Sigma(i\omega_n)$.

2. Compute the local Green’s function $G_{loc}(i\omega_n)$ from Eq. (3.16).

3. Compute the bath Green’s function $G_0(i\omega_n)$ from Eq. (3.18).

4. Using the above bath Greens function $G_0(i\omega_n)$ as input, run impurity solver to obtain the interacting impurity Green’s function $G_{imp}(i\omega_n)$.

5. Compute the new self-energy $\Sigma_{imp}(i\omega_n)$ using Dyson’s equation from Eq. (3.22).

6. Use this new self-energy $\Sigma_{imp}(i\omega_n)$ in Eq. (3.16) to obtain the new $G_{loc}(i\omega_n)$.

7. If $G_{loc}^{new}(i\omega_n) = G_{imp}(i\omega_n)$, then DMFT convergence is reached. If not, go back to step 3 and repeat until convergence is reached.  

Once converged, the interacting Greens function $G(i\omega_n)$ i.e. either $G_{imp}(i\omega_n)$ or $G_{loc}(i\omega_n)$ as they are both equal once converged, can be used to calculate observables such as the spectral function $A(k,\omega)$ from Eq. (3.11). As these frequencies must be on the real axis, an analytic continuation is required to convert $i\omega_n \rightarrow \omega$. In the next section we discuss how DFT and DMFT can be combined to perform DFT+DMFT calculations.

### 3.5 DFT+DMFT

The benefit of combining DFT+DMFT brings the ability to treat high energy Hamiltonians for weakly correlated orbitals with DFT and the strong correlations with DMFT through low energy Hamiltonians, thus, bridging both scales together. Throughout the years DFT+DMFT has shown wide success in studying correlated materials [7, 12, 64].
Figure 3.8: The DMFT self-consistency cycle. Starting from an initial guess for the self-energy \( \Sigma(i\omega_n) \) the local lattice Green’s function is obtained. Next, the bath Green’s function calculated with Dyson’s equation. Solving the impurity model, gives the impurity Green’s function and a new self-energy is calculated via the Dyson equation. The whole procedure is iterated until convergence is reached.
To interface DFT and DMFT, the DFT Kohn-Sham wave functions must be projected onto a localized basis set and Maximally Localized Wannier Functions (MLWF) \cite{65, 66} are a popular choice. This is discussed in detail in Chapter 5.2.2.

Once an initial DFT calculation is performed, the correlated Wannier subspace is constructed to represent the low energy Hubbard Hamiltonian. This Hubbard model is solved using DMFT as described in the previous section. Often times, “One-Shot” DMFT calculations are performed where the calculation is terminated once DMFT convergence is reached. However, one may use the converged Green’s functions to calculate the DMFT charge density which is fed back into the DFT charge density to obtain a total DFT+DMFT charge density leading to a full charge self-consistent DFT+DMFT loop. This is illustrated in Fig. 3.9. The formulation of the DFT+DMFT method and additional details are discussed in detail in Chapter 5.

![Figure 3.9: The full charge self-consistent DFT+DMFT workflow. Retrieved from Ref. [67].](image)
Part II

Method development of electronic structure frameworks
4 PyProcar

This chapter focuses on the electronic structure pre/post processing tool, PyProcar. PyProcar has gained wide popularity across multiple DFT communities and has a variety of features beneficial to studying both weakly and strongly correlated materials including projected band structures and DOS, spin textures, Fermi surfaces etc. This chapter is based on the published article, Herath, U. et al., PyProcar: A Python library for electronic structure pre/post-processing, Comput. Phys. Commun. 251 107080 (2020).

4.1 Introduction

Density Functional Theory (DFT) [25, 28] is one of the most widely used methodologies for electronic structure calculations in materials science. Its very good quality/computational-cost ratio, together with the emergence of high performance computing, has reshaped the field of computational materials research. Decades efforts in developing DFT for simulation programs have led to highly efficient DFT codes which include, among others, Abinit [68],
VASP [69, 70], Siesta [71] or Quantum Espresso [72, 73], which are capable of exploring remarkable material properties. Thorough calculations with these DFT codes have already been done for a wide range of compounds and the accumulated data can be publicly accessed from databases such as Materials Project [74], AFLOW [75], Materiae [76]. This new approach to materials has had a large impact into condensed matter physics developing new paradigms such as the quantum materials [77]. However, countless possibilities of exploring novel materials still exist and thus the necessity of efficient and reliable DFT pre- and post-processing tools.

As computational capabilities increase, the size and complexity of the systems under study increase as well, hindering the analysis and the capability of abstraction on key aspects of these systems. As physicists, we encountered this problem and realized that we require a tool designed to gain insight from our calculations but spending less time on coding. In particular, we have three requirements for such a tool: (i) the generation of a graphical representation of the quantity of interest -surface states, spin-texture, orbital projection, etc.- should take only a single line of input. This approach also enables the scripting of similar analysis, a must for high throughput calculations. (ii) We also realized the need of producing high-quality graphics, ideally using a vector format, suitable for further post-processing. (iii) Finally, there are several issues preventing a straightforward analysis of electronic structure results, e.g., the size of output data files generated by DFT codes can be extremely large, thus making the post-processing of data very slow by excessive memory usage. In such a case, the post-processing tool, not the researcher, should be capable of taking care of large data files in a smart way and enabling the user to extract essential information while ignoring less interesting information from a large data file.

This paper focuses on the presentation of PyProcar, a robust, open source Python library used for pre- and post-processing of the electronic structure data coming from DFT cal-
PyProcar is capable of performing a multitude of tasks including plotting spin non-polarized and spin/atom/orbital projected band structures and Fermi surfaces - both in 2D and 3D, Fermi velocity plots, unfolding bands of a super cell, comparing band structures from multiple DFT calculations and generating a $k$-path for a given crystal structure. Our code has matured throughout the last decade and currently has over forty users who are members of the PyProcar forum [78]. To retrieve a reliable number of users of an open source code is a difficult task due to inconsistencies in keeping track of downloads or installations, nevertheless, according to Google BigQuery [79] PyProcar has been downloaded almost 9000 times and PyPI Download Stats [80] counts more than 100 installations of PyProcar per month based on the download analytics from the Python Packaging Index (PyPI) [81]. Even though, PyProcar is written to parse the PROCAR file from the VASP package (and from a fork of Abinit, which will be included in the next main production version), due to its object-oriented approach, PyProcar can be easily adapted to handle the output from other DFT codes.

In Section 4.2 we will briefly explain some basic aspects of PyProcar. Then in Section 4.3 we present some examples illustrating the capabilities of the PyProcar code for analysis of electronic structure.

4.2 Library Overview

4.2.1 Electronic structure projection

The projection of the Kohn-Sham states over atomic orbitals and spins can give a large amount of information about the calculated system. However, such amount of information needs to be post-processed to extract the physical insight. In the VASP code, this information is written into the PROCAR file when LORBIT = 11 or 12 (to include phase projections of the wave functions) in the INCAR, which arranges the information of projec-
tions in blocks, as seen in Fig. 4.1 This block is repeated if calculations are spin polarized and for noncollinear spin calculations, three more blocks are present which correspond to \( S_x, S_y \) and \( S_z \) spin directions. There also exist a special format of PROCAR file that includes the phases of the wave function, as described in Fig. 4.2, which is an important quantity required for band unfolding. The direction of the atomic orbitals \( (p_x, p_y, p_z, \text{etc.}) \) is defined with respect to the Cartesian coordinates \( x, y \) and \( z \).

The site projected wave function in the PROCAR file is calculated by projecting the Kohn-Sham wave functions onto spherical harmonics that are non-zero within spheres of a Wigner-Seitz radius around each ion by:

\[
| \langle Y_{lm}^{\alpha} | \phi_{nk} \rangle |^2 \tag{4.1}
\]

where, \( Y_{lm}^{\alpha} \) are the spherical harmonics centered at ion index \( \alpha \) with angular moment \( l \) and magnetic quantum number \( m \), and \( \phi_{nk} \) are the Kohn-Sham wave functions. In general, for a non-collinear electronic structure calculation the same equation is generalized to:

\[
\frac{1}{2} \sum_{\mu,\nu=1}^{2} \sigma^i_{\mu,\nu} < \psi_{\mu,n,k} | Y_{lm}^{\alpha} > < Y_{lm}^{\alpha} | \psi_{\nu,n,k} > \tag{4.2}
\]

where, \( \sigma^i \) are the Pauli matrices with \( i = x, y, z \), \( \mu \) and \( \nu \) spin directions, and the spinor/spin polarized wavefunction \( \phi_{nk} \) is now defined as

\[
\phi_{nk} = \begin{bmatrix} \psi_{nk}^{\uparrow} \\ \psi_{nk}^{\downarrow} \end{bmatrix} \tag{4.3}
\]

This projection is performed for every \( k \)-point used in the DFT calculation, for every energy band and every atom of the crystal. Files can be stored as the absolute value of the
projections, as it is usually needed for the band analysis or by also including the complex nature of the projections, which are used for the electron band folding. The raw data written on the PROCAR file captures most of the material details, essential to investigate interesting materials properties. But on the downside, these files are often too big to be analyzed without additional computational support. For instance, a polarized calculation involving 10 atoms, with 100 bands and 100 \( k \)-points gives almost \( 10^6 \) entries in the PROCAR file, and the file size grows with the number of atoms as \( O(n^2) \). Therefore, it is essential to reduce the PROCAR file size in an efficient way without losing the key information stored in the file. The PyProcar parser can be used to manipulate, reduce, filter, and comprehend the information stored in the PROCAR file.

4.2.2 PyProcar Design

PyProcar is an object-oriented code, and despite its name, only the file-related classes (mostly the parsing) are related to the VASP’s PROCAR and OUTCAR. The OUTCAR gives a summary of the calculation including information about the electronic steps, eigenvalues, Fermi energy, forces on the atoms, etc. PyProcar code parses the OUTCAR file and stores the Fermi energy, which is later used to shift the Fermi level to zero in band structure plots. The reciprocal lattice vectors are also parsed from OUTCAR. PyProcar is currently capable of parsing the outputs from a recent version of Abinit and given the code’s flexibility, the extension to other codes is trivial. Once the data is stored in memory, PyProcar can be used regardless of the employed DFT code. PyProcar consists of several classes and functions, as mentioned below. The functions provide a high-level interaction with the user, allowing the relevant task to get done with minimum instructions. For convenience, and to allow an easy scripting, all these functions are fully decoupled. Also, the manipulation of the data can be saved/exported as a new file on the disk.
Figure 4.1: Example of the PROCAR file structure for a spin non-polarized calculation. For spin polarized or noncollinear calculations there are additional blocks for each spin component. The PROCAR stores the real projections of the Kohn-Sham orbitals over the atomic orbitals in different blocks for each spin direction \((x,y,z)\), the total spin for each \(k\)-point in the Brillouin zone and for each electron band.

The low level work is carried by classes, each handling one specific task or sub-task, they are fairly complex and no interaction with the user is expected unless a new feature is needed. By design, the classes are as loosely connected as possible. Each class uses the `logging` module to provide a user-defined level of verbosity, which is very useful for debugging.

Fig. 4.3 displays an overview of the PyProcar library. PyProcar can be used to generate files required for DFT calculations such as a suitable KPOINTS file for both self-consistent and non self-consistent DFT calculations. The structures can be generated manually, or
Figure 4.2: Example of the PROCAR file structure for a spin non-polarized calculation with a phase factor. This includes an additional block containing real and complex projections of the Kohn-Sham orbitals over the atomic orbitals.

From one of many databases publicly available such as Materials Project [74], AFLOW [75], etc. Once the DFT calculation is complete, PyProcar uses the VASP generated outputs, PROCAR and OUTCAR, for further post-processing.

The core classes within PyProcar consist of Procparser, Utilsproc and Procarselect which parses the PROCAR data and stores them in organized arrays for later calculations or analysis. These core classes are explained briefly below.

1. **Utilsproc**: This class contains modules to parse the OUTCAR file from a DFT calculation. It reads and stores the Fermi energy and the reciprocal lattice vectors. The Fermi energy is used to shift the Fermi level to zero in band structure calculations.
Figure 4.3: A structural overview of the PyProcar library

The availability of the reciprocal lattice vectors enable `Utilsprocar` to convert the $k$-mesh grid between direct and Cartesian coordinates. The Fermi energy and reciprocal lattice vector could also be provided manually through command line inputs.

2. **ProcarParser**: As the name suggests, this class contains modules required to parse the `PROCAR` file. It reads information related to bands, $k$-points and orbitals, and saves the data in the memory. It is designed to be somewhat resilient to errors derived from the fixed-format of the `PROCAR` file (i.e., missing blank spaces, use of *** characters as an index, etc.)

3. **ProcarSelect** After the `PROCAR` file is parsed and stored in memory, this class manipulates the required orbital(s), atom(s) and or spin information separately.
4.2.3 Installation

The latest stable version of PyProcar, version 4.0.0 at the time of writing this paper, can be installed using the Python Packaging Index (pip) using the following command:

```
$ pip install pyprocar
```

The project’s GitHub repository is located at [https://github.com/romerogroup/pyprocar](https://github.com/romerogroup/pyprocar). An easy to follow documentation with examples can be found at [https://romerogroup.github.io/pyprocar/](https://romerogroup.github.io/pyprocar/). PyProcar is supported by both Python 2.x and 3.x.

4.3 Examples: MgB$_2$, BiSb, TaSb, and SrVO$_3$

4.3.1 The MgB$_2$, BiSb, TaSb and SrVO$_3$ crystal structures

In this section, we choose four example systems, namely MgB$_2$, BiSb, TaSb, and SrVO$_3$, to illustrate the capabilities of the PyProcar code. Fig. 4.4 shows the crystal structure of these systems. The DFT calculations were performed using the Vienna Ab Initio Simulation Package (VASP) version 5.4.4. Similar calculations can be performed using the forthcoming version of Abinit, version 9.x, where the keyword `prtprocar` needs to be added in the input. The examples are available in the github repository.

For the strongly correlated cubic perovskite SrVO$_3$ (crystal symmetry $Pm\overline{3}m$ and lattice constant 3.84 Å), the plain and projected band structures were evaluated within the generalized gradient approximation (GGA) using PBE functional [82]. An $8 \times 8 \times 8$ Monkhorst-Pack [83] $k$-mesh and an energy cutoff of 600 eV were required for electron wavefunction convergence. We considered 10 valence electrons of Sr ($3s^23p^64s^2$), 5 valence electrons of V ($3d^34s^2$) and 6 valence electrons of O ($2s^22p^4$) in the PAW pseudopotential.

The superconducting material MgB$_2$ of the crystal symmetry $P6/mmm$ and lattice param-
eters 3.07 Å and 3.53 Å for $a$ and $c$, respectively, was used to showcase the Fermi surface plotting and band unfolding capabilities of PyProcar. For the former, we used a $10 \times 10 \times 10$ Monkhort-Pack grid with an energy cut-off of 700 eV within the GGA with the PBE exchange-correlation function. The latter was done with a $5 \times 5 \times 5$ Monkhort-Pack grid with an energy cut-off of 500 eV within the GGA with the PBESol exchange-correlation function [84]. Both of these calculations were done with 2 valence electrons of Mg (3s$^2$) and 3 valence electrons of B (2s$^2$2p$^1$) in the PAW pseudopotential.

To demonstrate the 2D spin texture plotting capability of PyProcar we use the Rashba semiconductor BiSb monolayer which belongs to the space group $P3m1$ with lattice parameters $a = b = 4.26$ Å. The calculation, which included spin-orbit coupling (SOC) was performed with a $k$-mesh grid of $10 \times 10 \times 1$ and an energy cut-off of 650 eV with PBE using 15 valence electrons of Bi (5d$^{10}$6s$^2$6p$^3$) and 5 valence electrons of Sb (5s$^2$5p$^3$) in the PAW pseudopotential.

PyProcar can also be used to investigate the band degeneracy and Dirac/Weyl points in topological materials. We use the material TaSb belonging to the space group $P\bar{6}m2$ with lattice parameters $a = b = 3.58$ Å, $c = 3.81$ Å to demonstrate this feature. An energy cut-off of 600 eV and $k$-mesh grid of $10 \times 10 \times 10$ along with PBE and SOC were used for the calculation considering 5 valence electrons of Ta (5d$^3$6s$^2$) and 5 valence electrons of Sb (5s$^2$5p$^3$) in the PAW pseudopotential.

4.3.2 Generating a $k$-path

In order to plot a band structure, one must define a set of $k$-points following a desired $k$-path in momentum space. A common option is to employ the AFLOW software framework [75], the SeeK-path module in Materials Cloud [85] or the Bilbao Crystallographic Server [86–88] to generate the $k$-path. However, PyProcar’s $k$-path generation utility enables a the user to
Figure 4.4: (a) Crystal structure of a phase of BiSb with rhombohedral symmetry, the primitive cell is enclosed by red lines. (b) Hexagonal lattice of MgB$_2$. (c) First Brillouin zone of a hexagonal lattice. (d) Cubic lattice of SrVO$_3$. (e) Hexagonal lattice of TaSb

automatically generate a suitable and sufficient $k$-path given the crystal structure, typically read from the **POSCAR** file. The $k$-path is then automatically written to a **KPOINTS** file. The $k$-path generation utility within PyProcar is based on the Python library **seekpath** developed by Himuma *et al.* [89]. The red line in Fig. 4.4 (c) depicts such a $k$-path of a hexagonal lattice generated using the algorithms of **seekpath**.

General format:

```python
pyprocar.kpath(infile, grid_size, with_time_reversal, recipe, threshold, symprec, angle_tolerance)
```
Usage:

```python
pyprocar.kpath(‘POSCAR’ , 40 , True , ‘hpkot ’ , 1e−07 , 1e−05 , −1.0)
```

More details regarding these parameters can be found in Ref. [90].

### 4.3.3 Repair

This utility is used to repair the ill-formatting of the PROCAR file due to the erroneous file handling in Fortran, particularly in a VASP calculation. This prevents issues arising from the lack of white space between a number and a negative sign, for instance 0.000000-0.5000000. Typically, pyprocar.repair() is recommended to be applied before using any other utility.

Usage:

```python
pyprocar.repair(‘PROCAR’ , ‘PROCAR-repaired’)
```

### 4.3.4 k-mesh generator

This utility can be used to generate a 2D k-mesh centered at a given k-point and in a given k-plane. The mesh is then automatically written to a KPOINTS file. This is particularly useful in computing 2D spin-textures and plotting 2D Fermi surfaces. For example, the following command creates a 2D k_x-k_y mesh centered at the Γ point (k_z=0) ranging from coordinates (-0.5, -0.5, 0.0) to (0.5, 0.5, 0.0) with 5 grids in the x direction and 7 grids in the y direction:

General format:

```python
pyprocar.generate2dkmesh(x1 , y1 , x2 , y2 , z , num_grids_x , num_grids_y)
```

Usage:
4.3.5 Band structure

PyProcar goes beyond the conventional plain band structure to plot the projected bands that carry even more information, which will be described shortly. The projected bands are color coded in an informative manner to portray fine details. PyProcar is capable of labeling the \( k \)-path names automatically, however, the user can manually input them as desired. This will be showcased in the next section.

1. No projection

This is the most basic type of band structure. No projection information is contained here. See Fig. 4.5 (a) for a plain band structure of SrVO\(_3\). In order to use the plain mode one sets `mode='plain'`. `elimit` sets the energy window limits. `outcar` specifies the OUTCAR file. For Abinit calculations, `abinit_output` is used instead. `color` lets the user use any color available in the matplotlib [91] package.

Usage:

```python
pyprocar.bandsplot('PROCAR-repaired', outcar='OUTCAR', elimit=[-2,2], mode='plain', color='blue')
```

2. Spin projection

For collinear spin polarized and noncollinear spin calculations of DFT codes, PyProcar is able to plot the bands of each spin channel or direction separately. An example for a collinear spin polarized calculation is given in Fig. 4.5 (b) where blue corresponds to spin down channel and red to spin up channel. For this case setting `spin=0` plots the unpolarized spin density and `spin=1` plots the spin channels separately.
Figure 4.5: (a) plain band structure (b) collinear spin projected (c) V atom projected (d) $e_g$ orbital projected band structure of SrVO$_3$. In the projected plots, the color intensity corresponds to the degree of contribution of that particular orbital, spin or atom type.

Usage:

```python
pyprocar.bandplot('PROCAR_repaired', outcar='OUTCAR', e limit=[-5,5], kticks=[0,39,79,119,159], knames=['G', 'X', 'M', 'G', 'R'], cmap='seismic', mode='parametric', spin=1)
```

For noncollinear spin calculations, spin=1,2,3 corresponds to spins oriented in $S_x$, $S_y$ and $S_z$ directions respectively. Setting `spin='st'` plots the spin texture perpendicular
in the plane \((k_x,k_y)\) to each \((k_x,k_y)\) vector. This is useful for Rashba-like states in surfaces. For parametric plots such as spin, atom and orbitals, the user should set `mode='parametric'`. `knames` and `kticks` corresponds to the labels and the number of grid points between the high symmetry points in the \(k\)-path used for the band structure calculation. At the end of this section we explain how to retrieve this automatically. \LaTeX entries, such as \(\Gamma\) also can be used. `cmap` refers to the matplotlib color map used for the parametric plotting and can be modified by using the same color maps used in matplotlib. If spin-up and spin-down bands are to be plot separately, one may use the `pyprocar.filter()` function to create two PROCAR’s for each case and plot them individually. Refer to the user manual for more information.

3. Atom projection

The projection of atoms onto bands can provide information such as which atoms contribute to the electronic states near the Fermi level. PyProcar counts each row of ions in the PROCAR file, starting from zero. In the example of a five atom SrVO\(_3\), the indexes of `atoms` for Sr, V and the three O atoms would be 1,2 and 3,4,5 respectively. It is also possible to include more than one type of atom. See Fig. 4.5 (c) for an example of V atom projected bands in SrVO\(_3\).

Usage:

```python
pyprocar.bandplot('PROCAR_repaired', outcar='OUTCAR', elim=[-5,5], kticks=[0,39,79,119,159], knames=['G', 'X', 'M', 'G', 'R'], cmap='seismic', mode='parametric', atoms=[1])
```

4. Orbital projection

The projection of atomic orbitals onto bands is also useful to identify the contribution
of orbitals to bands. For instance, to identify correlated \( d \) or \( f \) orbitals in a strongly correlated material near the Fermi level. It is possible to include more than one type of orbital projection. Fig. 4.5 (d) displays an orbital projected band structure of \( \text{SrVO}_3 \). The mapping of the index of orbitals to be used in \textbf{orbitals} is as follows (this is the same order from the PROCAR file, see Fig. 4.2).

\[
\begin{array}{cccccccccccccccc}
\text{s} & \text{p}_x & \text{p}_y & \text{p}_z & \text{d}_{xy} & \text{d}_{yz} & \text{d}_{zx} & \text{d}_{x^2-y^2} & \text{d}_{3z^2-r^2} & \text{f}_{xy} & \text{f}_{xz} & \text{f}_{yz} & \text{f}_{z^2} & \text{f}_{x^2-y^2} & \text{f}_{y^2} \\
0 & 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 & 10 & 11 & 12 & 13 & 14 & 15
\end{array}
\]

Usage: To project all five \( d \)-orbitals:

```python
pyprocar.bandsplot('PROCAR_repaired', outcar='OUTCAR', elimit=[-5,5], kticks=[0,39,79,119,159], knames=['G', 'X', 'M', 'G', 'R'], cmap='seismic', mode='parametric', orbitals=[4,5,6,7,8])
```

If a KPOINTS file from a VASP calculation is present, PyProcar automatically retrieves \texttt{kticks} and \texttt{knames} and labels the band structure plots accordingly for any of the above cases and also for the \texttt{bandscompare()} function in section ??.. For example:

```python
pyprocar.bandsplot('PROCAR_repaired', outcar='OUTCAR', mode='plain', kpointsfile='KPOINTS')
```

One or many of the above can be combined together to allow the user to probe into more specific queries such as a collinear spin projection of a certain orbital of a certain atom.

Different modes of band structures are useful for obtaining information for different cases. The four modes available within PyProcar are \texttt{plain}, \texttt{scatter}, \texttt{parametric} and \texttt{atomic}. The \texttt{plain} bands contain no projection information. The \texttt{scatter} mode creates a scatter plot of points. The \texttt{parametric} mode interpolates between points to create bands which are also projectable. Finally, the \texttt{atomic} mode is useful to plot energy levels for atoms.
These projected band structures play a vital role in revealing the physics of a system. For instance, the $V^{4+}$ projected bands displayed in Fig. 4.5 (c) correctly captures the contribution from the V-3$d$ electrons with O-2$p$ states from -6 eV to -1 eV. Furthermore, in Fig. 4.5 (d) where $e_g$ states are projected, one can clearly notice the octahedral crystal field splitting in SrVO$_3$ where $t_{2g}$ states exist below $e_g$ states, as expected.

4.3.6 3D Fermi surface

PyProcar’s 3D Fermi surface utility is able to generate Fermi surface plots projected over spin, atoms and orbitals or a combination of one or many of each. This utility is also capable of projecting external properties that are provided on a mesh grid in momentum space. This feature is useful when one wants to project properties that are not provided in a PROCAR file such as Fermi velocity, electron-phonon coupling and electron effective mass. We divide this section into three sub sections, plain Fermi surface, projection of properties from PROCAR and projection of properties from external file.

1. Plain Fermi surface

The ProcarParser class provides eigenvalues on a momentum space mesh grid. In all of the 3D Fermi surface functions in PyProcar the eigenvalues are interpolated using Fourier transform. This type of interpolation is suitable for eigenvalues as they are periodic in nature. The points in the mesh grid is generated in reduced space and some of the points sampled by VASP might not be in the first Brillouin Zone (BZ). The points outside of the first BZ can be returned to the first BZ using the reciprocal lattice vectors. As transforming the points to the first BZ will cause the distortion in the shape of the iso-surface, it is better to add the points missing from the first BZ then remove the points lying in the second BZ. In order to identify these points, we first create the boundaries of the first BZ by creating the Wigner-Seitz cell from
the reciprocal lattice vectors. The BZ is a convex hull created by the points located at the corner of the BZ. To figure out if a point is inside the first BZ or outside the following procedure is performed on each point. A point is added to the collection of the points on the BZ corners and a new convex hull is created, if the convex hull is the same as the original BZ, the point is located inside, and if the BZ is different, the point is located outside of the first BZ. Since this operation can be slow in a scripting language like Python, we use data parallelism. This task is offloaded to a number of worker processes, which can be defined by the user. After obtaining enough points we use Lewiner marching cubes algorithm provided by scikit-image package[92]. This function provides vertices and faces required to create the Fermi surface. The last step that is needed is to transform the coordinates of the vertices from the reduced coordinates to the Cartesian coordinates. To visualize the Fermi surface, we have provided four different plotting packages, mayavi[93], matplotlib[94], plotly[95] and ipyvolume [96] which can be chosen by the user. The figures shown here are produced using mayavi.

Usage:

```python
pyprocar.fermi3D(procar, outcar, bands, scale=1, mode='plain', st=False, **kwargs)
```

The main arguments in this function are **procar**, **outcar**, **bands**, **scale**, **mode** and **st**, where **procar** and **outcar** are the names of the input PROCAR and OUTCAR files respectively, **bands** is an array of the bands that are desired to be plotted. Note if **bands** = -1, the function will try to plot all the bands provided in the PROCAR file. The k-mesh will be interpolated by a factor of **scale** in each direction. The **st** tag controls the spin-texture plotting, and **mode** determines the type of projection of colors. There are additional keyword arguments that can be accessed in the
help section of this function, such as `face_color`, `cmap`, `atoms`, `orbitals`, `energy`, `transparent`, `nprocess` etc. Fig. 4.6 shows the Fermi surface of MgB$_2$ generated using `plain` mode of this function.

![Fermi surface of MgB$_2$](image)

**Figure 4.6:** (a) Plain 3D Fermi surface of MgB$_2$, (b) Plain 3D Fermi surface of MgB$_2$ with `face_colors` specified. Note that the face colors have to be provided in tuples of (r,g,b) normalized to 1.

### 2. Surface coloring based on properties from PROCAR

Similar to the `bandsplot` section one can choose to project the contribution of different properties provided in the PROCAR file, such as atom, orbital and spin contributions. The projection can be represented by different color mapping schemes chosen by the user. The projection is not restricted to only one property at a time, so it can be chosen from all the provided properties. For example, one might want to see the contribution of the orbitals $p_x$, $p_y$, $p_z$ from specific atoms, this function will parse the desired contributions and projects the sum of contributions on each face. To do so, we perform an interpolation on the data provided by the DFT package and evaluate the function at the center of each face created in the previous section. To use this
functionality one has to change the **mode** from ‘plain’ to ‘parametric’ and choose the atoms, orbitals, spin that are desired to be projected. As an example, we project the different contribution of different p orbitals of Boron atom in Fig. 4.7. The results show the middle cylinder is mostly comprised of p_x and p_y orbitals while the bands closer to the edges of BZ are p_z orbitals. This is in agreement with the calculations performed using the SIESTA DFT package [97].

![Projection of p_z orbitals of Boron atoms on Fermi surface of MgB_2](image)

![Projection of p_x, p_y orbitals of Boron atoms on Fermi surface of MgB_2](image)

**Figure 4.7:** (a) The projection of p_z orbitals of Boron atoms on Fermi surface of MgB_2 (b) Projection of p_x, p_y orbitals of Boron atoms on Fermi surface of MgB_2

For noncolinear calculations, this function is able to plot arrows in the direction of the spinors provided in the PROCAR file. To turn this functionality on the one can set `st=True` to turn the spin-texture ON. The user can choose between coloring all the arrows originated from one band with a specific color, or project the contribution of that arrow in a specific Cartesian direction. We plot two examples to demonstrate this functionality in Fig. 4.8, the spin-texture of BiSb at 0.60 eV above the Fermi level and the spin-texture of SrVO_3. To better represent the spin-texture we use the key
argument `transparent=True` which changes the opacity of the Fermi surface to zero.

![Image](a) ![Image](b)

Figure 4.8: (a) The spin-texture of BiSb calculated above the Fermi-level at $E = E_F + 0.60 \text{eV}$. One can clearly notice Rashba-type spin-splitting of conduction band electrons by analysing spin-texture at $\mathbf{k}$ and $-\mathbf{k}$ wave vectors. (b) Spin texture of SrVO$_3$.

3. **Surface coloring based on properties obtained from an external file**

Similar to the previous section, this function is able to read an external file, containing information about a scalar or a vector field in BZ and project the field on the Fermi surface. This file does not need to have the same mesh grid as the PROCAR file as long as the mesh sampling is fine enough. This function performs an interpolation on the provided data and evaluates functions at the center of each face on the Fermi surface. The external file should have the following format.

```
band = <band number>
<kx1> <ky1> <kz1> <color1>
<kx2> <ky2> <kz2> <color2>
<kx3> <ky3> <kz3> <color3>
... 
```
band = <band number>
...

The function matches information about the first band present in the file to the first band requested to be plotted, second band present in the file to the second band requested to be plotted, and so on. As an example, we have plotted the Fermi velocity of MgB$_2$ calculated by numerically evaluating the energy gradient from the PROCAR file in Fig. 4.9. Of course, one can acquire more accurate Fermi velocity by means of the Wannier interpolation method [65], however the following plot shows close enough accuracy for an example designed to represent the capabilities of this functional mode.

Figure 4.9: Fermi velocity of MgB$_2$ projected on the Fermi surface.
4.3.7 Handling big files: filtering the selected data and reducing the memory requirement for post-processing

A simpler version of a PROCAR file containing only a subset of information from the original dataset can be generated with this utility. This feature is very useful when there are many bands in the PROCAR file (e.g. in heterostructures or supercells calculations) making the file size enormously large for post-processing while only bands near the Fermi-level are needed for analysis. In this case, one can filter data of selected bands near the Fermi-level. This considerably reduces the file size and makes the post-processing of data faster. For instance, in graphene/MoS$_2$ (5:4) heterostructures [98, 99] the size of a VASP generated PROCAR file is 1.49 GB (98 atoms, 584 electrons, 804 bands in total, 63 $k$-points, and spin-orbit coupling included). However, by filtering only 30 bands above and below the Fermi-level (i.e. band indexes 554–614), the file size reduces to 108 MB and data processing becomes much faster. In the same way, one could use the filter utility to filter the PROCAR file to extract information regarding particular spins, atoms, or orbitals in a relatively smaller PROCAR-new file.

The following example extracts information of bands ranging from index 50 to 70 from a PROCAR-repaired file (Fermi-level is near band #60) while ignoring all other bands located far from the Fermi-level, and stores resulting dataset in a new file named PROCAR-repaired-band50-70. Now the new PROCAR-repaired-band50-70 file can be used for further post-processing of data at relatively low memory requirements.

Usage:

```python
pyprocar.filter('PROCAR-repaired', 'PROCAR-repaired-band50-70', bands=[50, 70])
```
### 4.3.8 2D spin-texture

This module can be utilized to visualize the constant energy surface spin textures in a given system. This feature is particularly useful in identifying Rashba and Dresselhaus type spin-splitting effects, analyzing the topology of Fermi surface, and examining Lifshitz transitions, as demonstrated in Refs. [99–105]. To plot 2D spin texture, we require a 2D $k$-grid centered a certain special $k$-point in Brillouin zone near which we want to examine the spin-texture in $k$-space (see section 4.3.4 regarding generation of 2D $k$-mesh).

**Usage:** To plot $S_x$ spin component at a constant energy surface $E = E_F + 0.60\,eV$ (spin=1, 2, 3 for $S_x$, $S_y$, $S_z$, respectively)

```python
pyprocar.fermi2D('PROCAR-repaired', outcar='OUTCAR', st=True, energy=0.60,
noarrow=True, spin=1)
```

For example, in Fig. 4.10 we plot $S_x$, $S_y$, and $S_z$ spin projections on the 2D spin texture of BiSb monolayer, which is a Rashba semiconductor (Rashba spin-splitting takes place the $\Gamma$ point of BZ), computed in a $k_x - k_y$ mesh centered at the $\Gamma$ point. Fig. 4.10(a) shows spin-texture calculated above Fermi-energy ($E_F$) at constant energy value $E = E_F + 0.60\,eV$ (conduction bands), and Fig. 4.10(a) shows the spin-texture calculated below Fermi surface at constant energy value $E = E_F - 0.90\,eV$ (valence bands). One can notice linear in $k$ Rashba spin-splitting effects in Fig. 4.10(a), and additional warping effects in Fig. 4.10(b) appearing due to the higher order $k^3$ terms in lower energy valence bands.

One could also plot spin texture using arrows instead of a heat map, as shown in Fig. 4.11. This can be done by setting tag: `noarrow=False`.

To set maximum and minimum energy values for color map, one could use `vmin` and `vmax` tags. For example, `vmin=-0.5, vmax=0.5` in Fig. 4.10 and Fig. 4.11.
Figure 4.10: Spin texture in BiSb monolayer, calculated at a constant energy surface, above and below the Fermi-level, respectively, at (a) $E = E_F + 0.60 \, eV$, and (b) $E = E_F - 0.90 \, eV$ in a $k_x$-$k_y$ plane centered at the $\Gamma$ point [103]. Color depicts the spin projection. 2D spin texture plots reveal the presence of a Rashba type spin-splitting (linear in $k$) of electronic bands near the $\Gamma$ point in BiSb monolayer. Warping effects arising due to the $k^3$ terms in the lower energy valence bands can also be noticed in Fig. 4.10(b).

4.3.9 Identification of Weyl points

Weyl points appear in the momentum space when two spin non-degenerate electronic bands (one valence and one conduction) linearly cross or touch each other near the Fermi-level forming a topologically non-trivial gapless point in the energy-momentum space. Depending upon the dispersion of valence and conduction bands, Weyl points can be categorized into two types: (i) Type-I, when Weyl cone is not titled and the crossing bands have opposite Fermi-velocity [106–108], and (ii) type-II, when Weyl cone is titled such that Weyl points appear at the touching point of an electron and a hole pocket. In the later case, the crossing bands have unidirectional Fermi-velocity with different magnitudes. When such band crossing occurs between spin degenerate bands, thus formed gapless...
Figure 4.11: Projection of $S_x$ spin component shown using arrows instead of heat map as in Fig. 4.10. Spin texture computed at a constant energy surface (a) $E = E_F + 0.60\, eV$, and (b) $E = E_F - 0.90\, eV$. All other details are same as in Fig. 4.10.

points are referred as Dirac points. Analogous to Weyl points, Dirac points can also be classified into two type-I and type-II categories.

We can use the PyProcar code to check the spin degeneracy of electronic bands near the crossing points and determine the type of gapless point by analyzing the dispersion of bands in the vicinity of the crossing point. Fig. 4.12 shows the spin projected bandstructure of TaSb, which is a topological metal hosting both type-I and type-II Weyl points. For more details regarding the topological properties of TaSb and other similar topological metals, we refer the reader to Refs. [108, 109].

4.3.10 Concatenating multiple calculations

Multiple PROCAR files from multiple DFT calculations can be combined with this utility. For instance, performing DFT calculations for MgB$_2$ supercells are very computationally expensive to do in a single run. This utility is particularly useful in such cases of large systems, where one can split the bandstructure calculations along different high-symmetry directions in BZ, and then concatenate the PROCAR files for each separate $k$-paths, and finally plot the full bandstructure in a single plot. The following command concatenates the PROCAR files obtained from three separate bandstructure
Figure 4.12: Projection of one of the spin components ($S_x$) on the bandstructure of TaSb near the type-I (a) and type-II (b) Weyl points [109]. Spin non-degenerate bands with linear dispersion forming a gapless point near the Fermi-level can be observed. Color depicts the spin projection on electronic bands. Direct coordinates of $k_1$, $k_2$, $k_3$, and $k_4$ are (0.5, -0.25, 0.0421), (0.430, -0.215, 0.0421), (-0.040, -0.040, 0.357), and (0.000, 0.000, 0.357), respectively.

calculations done along $\Gamma$-K, K-M, and M-$\Gamma$ $k$-path in hexagonal Brillouin zone.

Usage:

```python
pyprocar.cat(['PROCAR_G-K', 'PROCAR_K-M', 'PROCAR_M-G'], 'PROCAR_merged')
```

To concatenate PROCAR’s generated from Abinit assuming the files are all in the same directory, use the following command:

Usage:

```python
pyprocar.mergeabinit('PROCAR_merged')
```

### 4.3.11 Band Unfolding

Often times, we need to perform DFT calculations for a supercell geometry rather than the primitive cell. In such cases the band structure becomes quite sophisticated due to the folding of the BZ, and
it is difficult to compare the band structure of supercell with that of the primitive cell. The purpose of the band unfolding scheme [110–113] is to represent the bands within the primitive cell BZ. By calculating the unfolding weight function [113] and plotting the fat bands with the line width proportional to the weight, the unfolded bands can be highlighted. Here we use a $2 \times 2 \times 2$ MgB$_2$ supercell as an example to show the unfolding of band structure. In the bulk structure, where the primitive cell translation symmetry is preserved, the unfolded band is exactly the same as calculated from primitive cell structure. In a structure with a B atom replaced by Al, the translation symmetry can be seen as approximated, and we can still get an unfolded band, with some band smearing out. By comparing these two, we can clearly see the shifting and smearing of the band. The ASE library [114] was employed to perform atomic and cell manipulations required for the unfolding.

Figure 4.13: Band structure unfolded into primitive cell BZ of $2 \times 2 \times 2$ supercell (a) MgB$_2$ bulk structure, and (b) MgB$_2$ with one B atom replaced by Al in a $2 \times 2 \times 2$ supercell. The gray lines show the original bands. The width of the blue line denotes the weight of the unfolding.

Usage: First, calculate the band structure in the primitive cell BZ. The PROCAR should be produced with the phase factor included, by setting LORBIT=12 in VASP. Then the unfold module can be used to plot the unfolded band.

```python
import numpy as np
pyprocar.unfold(
    fname='PROCAR',
    poscar='POSCAR',
)```
PyProcar is a user friendly, open source Python library that can be easily used for a variety of DFT pre- and post-processing calculations. We have demonstrated its capability through providing examples for each functionality through a set of four materials with unique characteristics. PyProcar’s main specialty lies in its ability to project spin, orbitals and atoms in band structures and 2D and 3D Fermi and constant energy surfaces without involving lengthy, complex syntax. The code is freely available to download at https://github.com/romerogroup/pyprocar, and via pip. A standalone version of the library, procar.py is located in the github repository. An easy to follow user manual is available at https://romerogroup.github.io/pyprocar/. The PROCAR format is easy to implement in any DFT code, rendering PyProcar accessible across a wide range of DFT codes. We hope this tool will be useful to computational materials scientists in exploring state-of-the-art novel material which would in turn immensely impact the materials community.
Chapter 5

The DMFTwDFT Framework

In this chapter we present our open-source computational framework combining DMFT with various DFT codes interfaced through the Wannier90 package. This work was done in collaboration with Dr. Hyowon Park at University of Illinois Chicago. Dynamical Mean Field Theory (DMFT) is a successful method to compute the electronic structure of strongly correlated materials. The correlated subspace is expanded as a linear combination of Wannier functions introduced in the DMFT approach as local orbitals. In particular, we provide a library mode for computing the DMFT density matrix to facilitate the full charge self-consistent interface with other DFT codes. To validate the accuracy of this implementation, we computed the density of states and the band structure of well-known solid-state correlated materials, namely LaNiO$_3$, SrVO$_3$, and NiO. The obtained results are benchmarked to those obtained from other DFT+DMFT implementations. This chapter is based on the published article, Singh, V., Herath, U. et al., DMFTwDFT: An open-source code combining Dynamical Mean Field Theory with various density functional theory packages, Comput. Phys. Commun. 107778 (2020).
5.1 Introduction

One of the challenging tasks in modern material science is the theoretical design of novel materials with exceptional properties established only from their atomic species and positions based on first-principle methodologies. While DFT, a workhorse of the electronic structure calculation, is the most-used methodology to describe material properties, it has several drawbacks in the description of strongly correlated materials. This problem is mainly due to the lack of accuracy in describing strongly correlated materials because DFT relies on a crudely approximated exchange-correlation functional neglecting significant many-body fluctuations. Therefore, the existing approximations cannot capture correctly strong correlations present in localized orbitals or dispersionless bands. Examples of significant failures in DFT are the incorrect prediction of metallic state in strongly correlated Mott insulators observed in many transition metal oxides, and severe underestimation of the electronic effective mass in heavy fermions [115–117].

DMFT has been one of the most successful methods treating many-body fluctuations, by including strong but local correlations beyond the static DFT exchange-correlation functional [118, 119]. The heart of DMFT is to solve a single-site Anderson impurity problem embedded in an electronic bath determined self-consistently as the original lattice is approximated to a quantum impurity problem. There are several impurity solvers such as exact diagonalization (ED) [120], Configuration interaction (CI) [121], density-matrix renormalization group (DMRG) [122], and Quantum Monte Carlo (QMC) [41, 123], which can provide a non-perturbatively solution of the many-body problem. We use the QMC method because it can also provide a numerically exact solution without the user’s need of discretization or truncations of the problem. Among QMC methods, continuous-time QMC (CTQMC) [62] has been frequently used in that respect. Several free-licensed CTQMC packages [63, 124–126] are currently available and our DMFTwDFT code is interfaced to one of the CTQMC codes [63] included in the EDMFTF package [127].

In the last a few decades, great progress has been made in developing computational algorithms or packages for solving the DMFT equations [124, 128, 129] and combining DMFT with other electronic structure methods such as DFT or GW. Examples of available DFT+DMFT or GW+DMFT packages include EDMFTF [127], TRIQS/DFTTools [130], D-core [131], AMULET [132], LMTO+DMFT [133],
The DMFTwDFT Framework

Questaal [134], DMFT-abinit [4] and ComDMFT [125]. These implementations of DMFT in combination with DFT usually require the construction of local orbitals to define a correlation subspace for solving the DMFT equations. One choice is to obtain the correlated orbitals which are exactly centered at the ion sites and highly localized, so called projectors. Local atomic orbitals which are exactly centered at the ion sites and highly localized, so called projectors. They are constructed from the atomic solution and projected to the wide energy window of Kohn-Sham (KS) one-particle states to ensure the locality of orbitals. These orbitals are frequently used in all-electron DFT codes where different flavors of approximations are introduced as in LMTO, LAPW, and so on [135]. The other popular choice of localized orbitals is the Maximally Localized Wannier functions (MLWFs) [66, 136, 137]. Wannier functions can be used to construct both the hybridization and correlation subspace from the given energy window of the DFT band structure. The correlated subspace can be understood as a quantum-numbered real-space region where correlated electrons are mostly hosted. For example, a sub-manifold of the 3d shell of a transition-metal ion in a solid serves as the so-called “correlated subspace”. Also, for each site, these correlated orbitals with the local interaction U couples to other uncorrelated orbitals via hybridization. Therefore, the subspace including both correlated orbitals and uncorrelated orbitals in which the correlated orbitals are hybridized is called as the “hybridization subspace”. Thus, in practice, Wannier orbitals are a good representation for both correlated as well as hybridization subspace. Currently, the interface to Wannier90 package has been implemented in various DFT codes including VASP [69, 70, 138], Quantum Espresso [139], Siesta [140], Abinit [141–143], ELK [144], Wien2k [145], and so on. Our code is interfaced with VASP, Quantum Espresso and Siesta. The required overlap matrices are obtained from the DFT code and the localization of the Wannier function is performed by Wannier90.

While DMFT has been a powerful method for studying the electronic structure of strongly correlated materials, the full implementation of DFT+DMFT sometimes requires the combination of a DMFT implementation with licensed DFT codes. This has been a bottleneck of the wide-applicability of the DFT+DMFT methodology. In this paper, we provide a DMFT package interfaced to the Wannier90 code for its efficient extension to various free-licensed DFT codes. Our DMFTwDFT package can 1) use the Wannier orbitals for constructing the hybridization and correlation subspaces to perform DMFT loops by taking advantage of the Wannier90 interface between various DFT codes,
2) provide the library mode to link the module for computing a DMFT density matrix and updating a charge density within the DFT loops without modifying any DFT source codes significantly, and 3) provide a flexible Python-based interface that do not rely much on extensive user experience or specific parameters to perform DFT+DMFT calculations of strongly correlated materials. The outputs of our DMFTwDFT package currently include band structures, density of states, and total energies.

Since our DMFT implementation is interfaced to efficient plane-wave DFT codes, one can also study a rather large size of supercells such as correlated materials with defects in which the effect of defects can be investigated directly. A much simpler and computationally less expensive approach such as Virtual Crystal Approximation (VCA) [146] can be also adopted within our implementation to understand disorder systems. Research performed using this method is presented in Chapter 8. Forces and the Fermi surface calculations will be available in the future release of the code. Source codes are currently located at the GitHub repository, https://github.com/DMFTwDFT-project/DMFTwDFT which also includes a documentation with examples.

5.2 Theoretical formulation

In this section, we explain the methodology used for implementing our code.

5.2.1 Implementation of DFT+DMFT

The formal derivation of electronic structure methods including DFT and DMFT can be achieved by constructing an effective Free energy functional, \( \Gamma \), which depends on the choice of variables to write the energy functional [118, 119]. For example, the variable of choice that parametrize the Free energy minimization in DFT is the electronic charge density \( \rho_r \) [1] and the corresponding \( \Gamma^{DFT} \) is given by

\[
\Gamma^{DFT}[\hat{\rho}, \hat{V}^{Hxc}] = - \text{Tr} \left( \ln \left( (i\omega_n + \mu) \hat{1} - \hat{H}^{KS} \right) \right) + \Phi^{DFT}[\hat{\rho}] - \text{Tr} \left( \hat{V}^{Hxc} \hat{\rho} \right), \tag{5.1}
\]

where, \( \omega_n \) is the Matsubara frequency for fermions, \( \mu \) is the chemical potential, \( \hat{1} \) is the unit matrix,
Φ^{DFT}[\rho] is the DFT interaction energy, and \( \hat{H}^{KS} = -\frac{\hbar^2}{2m} \nabla^2 + \hat{V}^{ext} + \hat{V}^{Hxc} \) is the Kohn-Sham (KS) Hamiltonian operator, where \( \hat{V}^{ext} \) is the ionic potential operator and \( \hat{V}^{Hxc} \) is the Hartree-exchange-correlation (Hxc) potential operator. Since the exact form of the functional \( \Phi^{DFT}[\rho] \) is not known, it is usually approximated by using the local density approximation\[147, 148\] or the general gradient approximation\[149\]. The stationary value of \( \Gamma \) with respect to the selected variable can provide the Free energy within the electronic structure methods.

In DFT, minimizing the functional \( \Gamma^{DFT} \) with respect to \( \rho(\mathbf{r}) \) and \( V^{Hxc}(\mathbf{r}) \) leads to the self-consistent equation, also known as the KS equation.

In DMFT, the variable of choice is the dynamical Green’s function \( G^{cor}(i\omega_n) \). The effective many-body potential conjugate to \( G^{cor}(i\omega_n) \) is the dynamical self-energy \( \Sigma(i\omega_n) \). The main idea of DFT+DMFT is to treat \textit{strong} correlations of localized orbitals using the DMFT functional in terms of \( G^{cor}(i\omega_n) \) and \( \Sigma(i\omega_n) \) within a “correlated subspace” defined from the DFT band structure, and then to subtract a double-counting term of correlations for which both DFT and DMFT functionals are accounted. As a result, the DFT+DMFT functional \( \Gamma \) can be constructed using four operators (\( \hat{\rho}, \hat{V}^{Hxc}, \hat{G}^{cor}, \) and \( \hat{\Sigma} \)):

\[
\begin{align*}
\Gamma \left[ \hat{\rho}, \hat{V}^{Hxc}, \hat{G}^{cor}, \hat{\Sigma} \right] &= -\text{Tr} \left( \ln (i\omega_n + \mu) \hat{1} - \hat{H}^{KS} \right) \\
&\quad - \hat{\rho}^\dagger \left( \hat{\Sigma} - \hat{V}^{DC} \hat{P}^{cor} \right) \hat{P}^{cor} + \Phi^{DFT}[\rho] - \text{Tr} \left( \hat{V}^{Hxc} \hat{\rho} \right) \\
&\quad + \Phi \left( \hat{G}^{cor} \right) - \text{Tr} \left( \hat{\Sigma} \hat{G}^{cor} \right) - E^{DC} \left\{ \hat{G}^{cor} \right\} + \text{Tr} \left( \hat{V}^{DC} \hat{G}^{cor} \right),
\end{align*}
\]

where \( \hat{V}^{DC} \) is the double-counting (DC) potential operator, \( E^{DC} \) is the DC energy, and \( \hat{P}^{cor} (\hat{P}^{cor})^\dagger \) is a projection operator defined to downfold (upfold) between the correlated subspace and the hybridization subspace. The DMFT interaction energy, \( \Phi[G^{cor}] \) is the Luttinger-Ward functional summing all vacuum-to-vacuum Feynman diagrams which are local \[150–152\].

The stationary solution of the Free energy functional \( \Gamma \) within DFT+DMFT is obtained by extremizing \( \Gamma \) with respect to \( G^{cor}(i\omega_n) \) and \( \Sigma(i\omega_n) \), which lead to:
\[
\hat{\Sigma} = \frac{\delta \Phi[\hat{G}^{\text{cor}}]}{\delta \hat{G}^{\text{cor}}}, \quad (5.3)
\]
\[
\hat{G}^{\text{cor}} = \hat{P}^{\text{cor}} \hat{G}^{\text{hyb}} \hat{P}^{\text{cor}}\dagger, \quad (5.4)
\]

where \(\hat{G}^{\text{hyb}} = [(i\omega_n + \mu)\mathbb{1} - \hat{H}^{\text{KS}} - \hat{P}^{\text{cor}} (\hat{\Sigma} - \hat{V}^{\text{DC}}) \hat{P}^{\text{cor}}]^{-1}\) is the Green’s function operator defined within the energy window where \(\Sigma(i\omega_n)\) is hybridized (upfolded).

Although the many-body functional \(\Phi[\hat{G}^{\text{cor}}]\) in Eq. (5.29) needs to be evaluated only within the correlated subspace, computing the exact and non-perturbative \(\Phi[\hat{G}^{\text{cor}}]\) is still a formidable task. Nevertheless, it is approximated to a solution of an effective impurity problem within DMFT, i.e., \(\Phi[\hat{G}^{\text{cor}}] \approx \Phi[\hat{G}^{\text{imp}}]\) by assuming that the correlated Green’s function of a lattice is approximated to the impurity one, i.e., \(\hat{G}^{\text{cor}} \approx \hat{G}^{\text{imp}}\). Therefore, the numerically exact solution can be obtained by solving an impurity problem hybridized to an effective electronic bath \(\hat{\Delta}(i\omega_n)\) using the QMC method. As a result, \(\Sigma(i\omega_n) = \Sigma^{\text{imp}}(i\omega_n)\) from Eq. (5.3) and the DMFT self-consistent condition ensures that the hybridization function operator \(\hat{\Delta}(i\omega_n) = (i\omega_n + \mu)\mathbb{1} - \hat{\epsilon}^{\text{imp}} - \hat{\Sigma}(i\omega_n) - [\hat{G}^{\text{cor}}(i\omega_n)]^{-1}\) where \(\hat{\epsilon}^{\text{imp}}\) is the matrix representing the impurity levels of correlated orbitals.

The DMFT self-consistent condition is completed by computing new \(\hat{G}^{\text{cor}}\) from the obtained \(\Sigma(i\omega_n)\) using Eq. (5.4) and by iterating the calculation until both \(\hat{G}^{\text{cor}}\) and \(\Sigma(i\omega_n)\) are converged. This part is the so-called non-charge self-consistent DMFT. The charge-self-consistency in DFT+DMFT has been discussed later in section 2.3. Solving Eq. (5.4) requires the construction of a projection operator, \(\hat{P}^{\text{cor}}\) to define the correlated subspace. To achieve this, one needs to adopt the localized orbital \(\phi^\tau_m\) having the orbital character \(m\) of the correlated atom centered at \(\tau\) in an unit cell, namely \(\hat{P}^{\text{cor}} = \sum_{m\tau} \phi^\tau_m \langle \phi^\tau_m |\) and choose the energy window where these correlated orbitals will be hybridized. In this way, orbitals within the hybridization window do not mix with states outside this energy window. Eq. (5.4) can be represented as a matrix equation using the KS wavefunction basis. \(\hat{H}^{\text{KS}}\) can be diagonalized within these KS basis while \(\hat{\Sigma}\) is in general a non-diagonal matrix with complex numbers. Therefore, computing \(\hat{G}^{\text{hyb}}\) requires the inversion of a non-Hermitian matrix with complex numbers and can be achieved by solving the generalized eigenvalue problem of the Hamiltonian in the KS basis at each momentum \(\mathbf{k}\) and frequency \(\omega_n\):
\[
\sum_j \left[ \epsilon^k_i \delta_{ij} + \Sigma_{ij}^{k\omega_n} \right] C_{jl,k\omega_n}^R = C_{il,k\omega_n}^R \epsilon^k_n, \quad (5.5)
\]

where \( \epsilon^k_i \) is the KS eigenvalue at the band index \( i \) and the momentum \( k \). \( \epsilon^k_n \) is the complex
eigenvalue and \( C_{il,k\omega_n}^R \) is the right (left) eigenfunction of the above matrix equation. \( \Sigma_{ij}^{k\omega_n} \) is the
DMFT self-energy upfolded to the KS space (\( |\psi^k_i\rangle \)):

\[
\Sigma_{ij}^{k\omega_n} = \sum_{mn\tau} \langle \psi^k_i | \phi^\tau_m \rangle (\Sigma_{mn}^{\tau} (i\omega_n) - V^{DC}) \langle \phi^\tau_n | \psi^k_j \rangle. \quad (5.6)
\]

One can note that the self-energy matrix element can be \( k \)-dependent in the KS basis although they are purely local in the correlated orbital basis. Finally, \( \hat{G}^{\text{cor}} \) (Eq. (5.4)) in the local orbital
basis can be represented using these obtained eigenvalues and eigenfunctions:

\[
G_{mn}^{\text{cor}} (i\omega_n) = \frac{1}{N_k} \sum_{k,ijl} \langle \phi^\tau_m | \psi^k_i \rangle C_{il,k\omega_n}^R \left(C_{jl,k\omega_n}^L \right)^* \langle \psi^k_j | \phi^\tau_n \rangle \frac{1}{i\omega_n + \mu - \epsilon^k_n} . \quad (5.7)
\]

5.2.2 Construction of the hybridization and correlation subspace: Wannier orbitals

Since the implementation of DFT+DMFT requires the construction of the correlated subspace where
the self-energy \( \Sigma \) is defined, one needs to construct the localized orbital \( \phi^R_m \) centered at each cor-
related atom. Here, the locality of the correlated orbital matters since \( \Sigma \) is approximated as a
local quantity within DMFT, i.e., \( \Sigma(k, \omega) \simeq \Sigma(\omega) \) and the non-locality of the Coulomb interaction
should be minimized. \textit{One choice of such orbitals is so called “projectors” as we mentioned earlier.}
Those projectors are exactly centered at correlated atoms and highly localized by definition. Usually
projectors require the construction of a quite large hybridization window as these highly localized
orbitals are hybridized with KS \textit{one-particle states} in a rather wide energy window.

Wannier functions have been also frequently used as the choice of correlated orbitals. They are
constructed from the unitary transform of the KS \textit{one-particle states} and can represent the isolated
DFT band structure within the hybridization window exactly. In this way, not only the correlated orbitals but also other orbitals strongly hybridized with those correlated orbitals are also constructed. However, the choice of the Wannier function is not unique and there have been several methods to achieve the locality of Wannier functions. They include MLWFs, selectively localized Wannier functions, symmetry-adapted Wannier functions, and so on [66, 136, 137]. However, it is important to note that once the calculated Wannier function is converged and the obtained Wannier band structure is in agreement with the DFT band structure, we believe that the obtained MLWF will be sufficient enough to capture the physics of correlated subspace. It has also been found that spreads of Wannier orbitals such as d or f characters are much more localized than other s or p orbitals, therefore we generally treat them as correlated orbitals. Here, we show some examples of DFT+DMFT using MLWFs to construct localized orbitals within the hybridization window.

The MLWF $|\tilde{\phi}_R^n\rangle$ can be constructed from the KS orbital $|\psi^k_i\rangle$ by performing the Unitary transform $U^k$ which minimize the sum of all Wannier orbital spreads:

$$|\tilde{\phi}_R^n\rangle = \frac{1}{\sqrt{N_k}} \sum_{ik} e^{-i\mathbf{k} \cdot \mathbf{R}_i} |\psi^k_i\rangle \cdot U^k_{in}. \quad (5.8)$$

And the KS Hamiltonian can be represented using the basis of the MLWF $|\tilde{\phi}_R^n\rangle$ as:

$$\tilde{\epsilon}_{mn}(\mathbf{R}_i - \mathbf{R}_j) = \langle \tilde{\phi}^R_m | \hat{H}^{KS} | \tilde{\phi}^R_n \rangle = \frac{1}{N_k} \sum_{ik} e^{i\mathbf{k} \cdot (\mathbf{R}_i - \mathbf{R}_j)} \tilde{\epsilon}_{mn}^k \quad (5.9)$$

$$\tilde{\epsilon}_{mn}^k = \sum_i (U^k_{im})^* \epsilon_i^{k\tau} U^k_{in} \quad (5.10)$$

where $\tilde{\epsilon}_{mn}^k$ is the Wannier Hamiltonian matrix elements at the momentum $\mathbf{k}$ and $m, n$ are dual indices $(\tau, \alpha)$ in which $\tau$ labels correspond to an atomic site in the unit cell and $\alpha$ labels to the orbital character of the corresponding site. One can note that the $\mathbf{k}$–point mesh representing the Wannier Hamiltonian can be much denser than the DFT $\mathbf{k}$–point mesh by adopting the band-structure interpolation scheme [136].

Since Wannier orbitals can represent not only the correlated orbitals but also all other orbitals in
the energy window where the correlated orbitals are hybridized, Eq. (5.5) can be solved using the Wannier orbital basis at each momentum $k$ and frequency $\omega_n$:

$$\sum_n \left[ \epsilon_{mn}^k + \Sigma_{mn} (i\omega_n) - V^{DC} \right] C_{nl,k\omega_n}^R = C_{ml,k\omega_n}^R \epsilon_{n\omega}^k. \tag{5.11}$$

Here, the size of the matrix for the eigenvalue problem becomes exactly the number of Wannier orbitals specified in an unit cell. Moreover, $\Sigma$ can be also a diagonal matrix ($\Sigma_{mn} \approx \Sigma_m \delta_{mn}$) as the local axis for the Wannier orbital can be rotated to minimize the off-diagonal term of the hybridization function $\Delta (i\omega_n)$ and CTQMC can solve the impurity problem for this diagonal $\Delta (i\omega_n)$ matrix. Finally, the correlated Green’s function in the Wannier basis is given by

$$G^{\text{cor}}_{mn} (i\omega_n) = \frac{1}{N_k} \sum_{kl} C_{nl,k\omega_n}^R \left( C_{ml,k\omega_n}^L \right)^* \frac{1}{i\omega_n + \mu - \epsilon_{l\omega}}, \tag{5.12}$$

In principle, the off-diagonal term of the self-energy can be important in some cases. For example, the inter-orbital mixing due to the low-symmetry structure can generate the off-diagonal component in the orbital basis (e.g. transition metal ions in a distorted octahedral cage) and the non-collinear magnetism due to the spin-orbit coupling can produce the off-diagonal term in the spin-orbit coupled basis (e.g. irridates). Moreover, the inter-site correlation can also occur in some cases such as the dimerized structure of VO$_2$ in which the off-diagonal self-energy should be explicitly treated by adopting the cluster expansion of DMFT to employ a multi-site cluster within the impurity problem rather than a single-site [5, 153, 154]. While solving the DMFT equations, the CTQMC impurity solver can suffer from the minus-sign problem if the off-diagonal hybridization term is present. As mentioned above, we avoid the inter-orbital mixing problem in the multi-orbital case by rotating the local axis of the Wannier function and minimizing the off-diagonal component of the hybridization function (refer to Appendix A in Ref. [155]).

While our DMFT formalism focuses on the local on-site Coulomb interaction, this is usually acceptable in real materials since the local interaction term is much larger than the non-local term due
to the screening effect. However, the non-local screened interaction diagrams can be also computed explicitly using the GW formalism while the local diagrams are included within DMFT. This is the so-called GW+DMFT methodology in which the non-local part of the two-particle interaction can be computed within the GW level and the local part can be treated by adopting the extended DMFT formalism [156–158]. Unlike GW, the screened on-site interaction parameters in our DFT+DMFT implementation can be usually given as free parameters or already used values from literatures, however these parameters can be still computed from first-principles based on the linear-response method [159, 160].

5.2.3 Charge-self-consistency in DFT+DMFT

The charge density $\rho(r)$ in DFT+DMFT can be obtained when the Free energy functional $\Gamma$ in Eq. (5.29) is minimized by extremizing this functional with respect to the density functional potential $V^{Hxc}(r)$. As a result, the equation for the charge density $\rho(r)$ is obtained to be:

$$
\rho(r) = T \sum_{\omega_n} \langle r \mid \hat{G} \mid r \rangle e^{i\omega_n 0^+}
$$

(5.13)

where $T$ is temperature and the Green’s function operator $\hat{G} = [(i\omega_n + \mu) \hat{1} - \hat{H}^{KS} - \hat{P}_{cor}^\dagger (\Sigma - \hat{V}^{DC}) \hat{P}_{cor}]^{-1}$. The full charge-self-consistency is achieved when both $\rho$ and $G$ are converged after DFT+DMFT loops. $\rho(r)$ in Eq. 5.13 can be computed by representing $\hat{G}$ using KS orbitals:

$$
\rho(r) = \frac{T}{N_k} \sum_{ij\kappa,\omega_n} \langle r \mid \psi_i^\kappa \rangle \langle \psi_i^\kappa \mid \hat{G} \mid \psi_j^\kappa \rangle \langle \psi_j^\kappa \mid r \rangle e^{i\omega_n 0^+}
$$

(5.14)

$$
= \frac{1}{N_k} \sum_{ij\kappa} \psi_i^\kappa(r) \left( \psi_j^\kappa(r) \right)^* n_{ij}^\kappa
$$

where $n_{ij}^\kappa$ is the DMFT occupancy matrix element in the KS orbital basis:
\[
\begin{align*}
\langle \psi_k^i | \hat{G} | \psi_k^j \rangle &= \sum_{\omega_n} \langle \psi_k^i | \hat{G} | \psi_k^j \rangle e^{i\omega_n 0^+}, \\
\langle \psi_k^i | \hat{G} | \psi_k^j \rangle &= \sum_{mnl} U_{im}^k C_{m,kl}^R \left( \tau_{jn}^k C_{nl,k}^L \right)^*,
\end{align*}
\]

(5.15)  

(5.16)

One can note that the DMFT occupancy matrix, \( n_k \), contains non-diagonal matrix elements in the Kohn-Sham basis and it becomes a diagonal matrix whose elements are DFT Fermi functions (DFT occupation matrix) when dynamical self-energies are zero. Since DMFT self-energies are hybridized with DFT bands only within the hybridization window \( W \), the DMFT occupation matrix can be given by: Eq. (5.17).

\[
\begin{align*}
n_{ij}^k &= \begin{cases} 
n_{ij} & \text{if } (\epsilon_{ik}, \epsilon_{jk}) \in W, \\
\delta_{ij} & \text{otherwise.}
\end{cases}
\end{align*}
\]

(5.17)

Namely, \( n_k \) is a non-diagonal matrix \( \pi_k \) when both \( \epsilon_{ik} \) and \( \epsilon_{jk} \) are located inside the energy window \( W \) while \( n_k \) is a DFT Fermi function outside the window \( W \).

Since \( \pi_k \) is not only a non-diagonal but also Hermitian matrix in the KS basis, it can be also decomposed in terms of eigenvalues \( \omega^k_\lambda \) and eigenfunctions \( v^k_\lambda \) as:

\[
\pi_{ij}^k = \sum_\lambda v^k_{i\lambda} \omega^k_\lambda \left( v^k_{j\lambda} \right)^*
\]

(5.18)

where the eigenvalue index \( \lambda \) runs over the number of bands in the window \( W \). Therefore, the DMFT occupation matrix can be diagonalized by rotating a KS one-particle states \( |\psi^k_i\rangle \) to a new DMFT wavefunction \( |\psi^k_\lambda\rangle \) using the unitary transform whose matrix row is the eigenfunction \( v^k_\lambda \):

\[
\langle r | \psi^k_\lambda \rangle = \sum_i \langle r | \psi^k_i \rangle \cdot v^k_{i\lambda}
\]

(5.19)
Now, $w^k_\lambda$ will be the diagonal elements of the DMFT occupation matrix in this rotated KS basis and the sum over band indices $i,j$ in Eq. (5.14) can be simplified to the sum over a new index $\lambda$. As a result, the DFT+DMFT charge density $\rho(r)$ can be constructed as:

$$
\rho(r) = \begin{cases} 
\frac{1}{N_k} \sum_{\lambda,k} |\psi^k_{\lambda}(r)|^2 w^k_\lambda, & \text{if } (\epsilon_{ik}, \epsilon_{jk}) \in W, \\
\frac{1}{N_k} \sum_{i,k} |\psi^k_i(r)|^2 f^k_i, & \text{otherwise.}
\end{cases}
$$  (5.20)

Eq. (5.20) implies that $\rho(r)$ in DFT+DMFT can be computed using the existing modules for computing $\rho(r)$ in a DFT package without much modifications. The major modifications within the hybridization window include 1) the change of DFT Fermi function $f^k_i$ to the DMFT occupation function $w^k_\lambda$ and 2) the unitary transform of $|\psi^k_i\rangle$ to $|\psi^k_{\lambda}\rangle$.

To facilitate the implementation of the charge calculation in a DFT package, our DMFTwDFT package provides a library mode such that any DFT codes can call the Fortran subroutine to obtain the necessary information to update charge density within DFT+DMFT. Specifically, one can pass the $k$–points information within DFT to the subroutine $\text{Compute}_\text{DMFT}$ and can obtain the DMFT weight $w^k_\lambda$ and the Unitary matrix $v^k$ at each $k$–point for computing the charge density $\rho(r)$. Details about the structure of this subroutine are provided in the following section.

Total number of valence electrons, $N_{tot}$ can be computed by integrating $\rho(r)$ over the space, or equivalently from the trace of the occupation matrix $n^k$: 
\[ N_{\text{tot}} = \int dr \rho(r) = \frac{1}{N_k} \sum_{ik} n_{ii}^k \]
\[ = \frac{T}{N_k} \sum_{k\omega_n} e^{i\omega_n 0^+} \frac{1}{i\omega_n + \mu - \epsilon_i^{k\omega_n}} \]
\[ = \frac{T}{N_k} \sum_{k\omega_n} \left( \frac{1}{i\omega_n + \mu - \epsilon_i^{k\omega_n}} - \frac{1}{i\omega_n + \mu - \epsilon_i^{k\omega_\infty}} \right) \]
\[ + \frac{1}{N_k} \sum_{kl} f(\epsilon_l^{k\omega_\infty} - \mu) \] (5.21)

where \( \epsilon_i^{k\omega_\infty} \) is the eigenvalue of Eq. (5.11) evaluated at \( \omega \to \infty \) and \( f(\epsilon) \) is the Fermi function. Here, the high-frequency \( \omega_n \) summation can be done analytically when \( \omega_n \to \omega_\infty \). The chemical potential \( \mu \) can be determined by imposing the condition that the total number of valence electrons \( (N_{\text{tot}}) \) obtained from DFT+DMFT should be fixed during the self-consistent loop and equal to the number of valence electrons in a material usually given in DFT.

### 5.2.4 Total energy and double counting correction

Once the charge-self-consistent DFT+DMFT loop is converged, the functional \( \Gamma \) in Eq. (5.29) evaluated at the stationary point (self-consistently determined DFT+DMFT solution) delivers the electronic Free energy of a given material within DFT+DMFT. The total energy \( E \) within DFT+DMFT can be obtained from the Free energy functional in the zero temperature limit as follows:

\[ E = E^{DFT}[\rho] + \frac{1}{N_k} \sum_{ik} \epsilon_i^k \cdot (n_{ii}^k - f_i^k) + E^{POT} - E^{DC} \] (5.22)

where \( E^{DFT}[\rho] \) is the DFT energy evaluated using the charge density \( \rho \) obtained within DFT+DMFT, \( \epsilon_i^k \) is the DFT KS eigenvalue, \( n_{ii}^k \) is the diagonal element of the DMFT occupancy matrix \( n^k \) (Eq. (5.17)), and \( f_i^k \) is the Fermi function (DFT occupancy matrix) with the KS band \( i \) and the momentum \( k \).

The potential energy \( E^{POT} \) is the Luttinger-Ward functional \( \Phi \) evaluated using the DMFT Green’s function \( G^{cor} \) and can be given from the Migdal-Galistkii formula[161]:
E_{pot} = \frac{1}{2} \text{Tr} [\Sigma \cdot G^\text{cor}] = \frac{1}{2} \sum_{\omega_n} [\Sigma(i\omega_n) \cdot G^\text{cor}(i\omega_n)]. \quad (5.23)

A frequently used expression of $E^{DC}$ is the fully localized limit (FLL) form which has been adopted mostly in DFT+U calculations [162].

\[ E^{DC} = U^2 \cdot N_d \cdot (N_d - 1) - J^4 \cdot N_d \cdot (N_d - 2) \quad (5.24) \]
\[ V^{DC} = \frac{\partial E^{DC}}{\partial N_d} = U \cdot (N_d - \frac{1}{2}) - J^2 \cdot (N_d - 1) \quad (5.25) \]

where $V^{DC}$ is the DC potential, $U$ is the on-site Hubbard interaction, $J$ is the Hund’s coupling, and $N_d$ is the occupancy of correlated orbitals within the correlation subspace which is obtained from the result of self-consistent DFT+DMFT or DFT+U calculations.

While the DC energy correction needs to be subtracted from the DFT+DMFT functional, the calculation of the exact $E^{DC}$ and $V^{DC}$ values can be difficult and the different choices of the DC energy can often produce quantitatively distinct physical results by modifying the hybridization between the correlated orbital and non-correlated orbitals. Therefore, the accuracy of DFT+DMFT can be limited by how one can choose the proper form of the DC energy term. Indeed, previous studies showed that the smaller DC energy than the conventional FLL form can often produce consistent results of the metal-insulator transition boundary, the d-p spectra, and energetics compared to experiments [163–169]. In this paper, we adopt the following modified forms of the DC correction from the conventional FLL form.

Here, we provide three different types of $E^{DC}$ functions. A modified $E^{DC}$ form (DC_type=1) is given by

\[ E^{DC} = \frac{(U - \alpha)}{2} \cdot N_d \cdot (N_d - 1) - J^4 \cdot N_d \cdot (N_d - 2) \quad (5.26) \]

where the Hubbard $U$ used in Eq. (5.24) becomes smaller by $\alpha$ so that the $E^{DC}$ value is reduced.
Here, the value for the parameter $\alpha$ can be chosen by users. $\alpha = 0$ (default setting) recovers the FLL form in Eq. (5.24). Another modified form (DC_type=2) is given by

$$E^{DC} = \frac{U}{2} \cdot (N_d - \alpha) \cdot (N_d - \alpha - 1) - \frac{J}{4} \cdot (N_d - \alpha) \cdot (N_d - \alpha - 2)$$

where $N_d$ used in Eq. (5.24) gets smaller by $\alpha$ so that the $E^{DC}$ value is reduced. Also, $\alpha = 0$ setting recovers the FLL form. The other modified $V^{DC}$ form (DC_type=3) is given by

$$V^{DC} = \frac{U}{2} \cdot N_d^0 \cdot (N_d^0 - 1) - \frac{J}{4} \cdot N_d^0 \cdot (N_d^0 - 2)$$

where $N_d^0$ is the nominal occupancy of the correlated orbital. Also, this nominal $V^{DC}$ potential is known to be close to an exact $V^{DC}$ form [170].

To show how different choices of DC formula and $\alpha$ values can affect the electronic structure, we have shown the DMFT density of states of LaNiO$_3$ at different DC types and $\alpha$ values in Fig. 5.1. Note that the detailed electronic structure of LaNiO$_3$ has been discussed in a later section. We observed that DC types 1 and 2 have similar effects as the O-2p DOS is pushed away from the Ni-3d DOS which leads to a weaker p-d hybridization when we increase the $\alpha$ value. On the other hand, we found that the DC type 3 is independent of the $\alpha$ value although the resulting DOS is similar to the DC type 1 DOS with $\alpha = 0.2$

Further, an atomic force calculation within DFT+DMFT can be performed by taking an explicit derivative of the total energy in Eq. (5.22) or the Free energy with respect to the atomic position. Some implementations of atomic force calculations in DFT+DMFT are already present [171, 172].

5.3 Features of DMFTwDFT

In this section, we provide the most important features of our DMFTwDFT code including the overall structure of the code, the parallelized nature, the library mode, the interface to different DFT codes, and the automated scripts.
Figure 5.1: Comparing the calculated DMFT partial density of Ni-3d and O-2p states of LaNiO$_3$ for different DC formula (a) DC_type = 1, (b) DC_type = 2, and (c) DC_type = 3 (inset). Note, DC_type = 3 is independent on $\alpha$.

5.3.1 Overall structure

Here, we describe the overall structure of our DMFTwDFT code in Fig. 5.2. The overall DFT+DMFT loop is performed by a Python script (RUNDMFT.py). The DMFT loop in Fig. 5.2 is performed by the main executable of the DMFTwDFT program (dmft.x). First, the local Green’s function $G^{\text{cor}}(i\omega_n)$ (G_loc.out) and the hybridization function $\Delta(i\omega_n)$ (Delta.out) are computed using inputs of a DMFT self-energy $\Sigma(i\omega_n)$ (sig.inp) and a Wannier-based Hamiltonian (see Eq. (5.11) and Eq. (5.12)). The Wannier Hamiltonian can be obtained from DFT interfaced with the wannier90 code [137] or from tight-binding parameters provided by users. The outputs of dmft.x including $\Delta(i\omega_n)$ (Delta.out), impurity energy levels (Ed.out), and the chemical potential (DMFT_mu.out)
are used as inputs of a DMFT impurity solver. Our code is currently interfaced with the CTQMC impurity solver. The DMFT self-energy obtained from CTQMC is used as the input of dmft.x for the next DMFT loop.

![Diagram](image)

**Figure 5.2**: The overall structure of the DMFTwDFT code.

The charge-self-consistency in DFT+DMFT is achieved by updating the charge density from the DMFT Green’s function within the DFT loop in Figure 5.2. Our code provides the library mode for passing the necessary information from the DMFT calculation to a DFT code, where the DMFT occupation matrix (Eq. (5.20)) is included, and a new charge density and Wannier functions are obtained within the DFT loop. It is important to note that the main component of our code is interfaced to the MLWF, which is an independent basis set from a DFT-specific basis set used in obtaining the Bloch states. Thus, our code can also be interfaced straightforwardly to any electronic structure code, as long as the DFT implementation is able to obtain MLWFs. Currently, the VASP (with the full DFT+DMFT loop) and Siesta codes (the DMFT loop only) are interfaced with our program. The detailed procedure of the full charge-self-consistent DFT+DMFT calculation is as follows.
1. First, a complete DFT self-consistent calculation is performed from the given atomic structure without any spin-polarization and the solution of the DFT KS equation is obtained.

2. The Wannier functions are constructed to represent the localized orbitals within the hybridization energy window. The KS Hamiltonian ($\hat{H}^{KS}$) in the basis of the Wannier function is obtained. In order to find the appropriate hybridization window (Wannier energy window), one may employ a projected band structure or density of states plot to identify the energy range of the hybridization subspace. One such method to achieve this is through PyProcar [173], a code developed in the group of one of the authors.

3. Next, the DMFT loop in Figure 5.2 is performed using the dmft.x executable. The inputs of dmft.x are the Wannier Hamiltonian ($\hat{H}^{KS}$) obtained from the Wannier90 outputs, the self-energy $\Sigma(i\omega_n)$, and the DC potential $V^{DC}$. Both $\Sigma(i\omega_n)$ and $V^{DC}$ can be given as an initial guess or obtained from the previous DFT+DMFT loop. The outputs of dmft.x are the chemical potential $\mu$, the impurity energy level $\epsilon_{imp}$, the hybridization function $\Delta(i\omega_n)$, and the Green’s function $G^{cor}(i\omega_n)$.

4. A quantum impurity problem coupled to $\Delta(i\omega_n)$ is solved using a CTQMC impurity solver to obtain $\Sigma(i\omega_n)$. The new $\Sigma$ is mixed with the old $\Sigma$ and used as input of dmft.x for the next DMFT step. The $V^{DC}$ potential is also updated.

5. While the DMFT loop is converging, one can achieve the full charge-self-consistent DFT+DMFT result by updating $\rho(r)$ from the DMFT occupancy matrix $n^k$ (Eq. (5.14)). For the new charge update, a DFT code should be modified by linking our library mode to the DFT package and implement Eq. (5.20).

6. Once the new $\rho(r)$ is obtained, one can go back to Step 1 and a new KS equation can be solved. The Wannier functions are computed again to generate the new $\hat{H}^{KS}$. For a better convergence of $\rho(r)$, one can iterate $\rho(r)$ using the new $\hat{H}^{KS}$ while the DMFT self energy is fixed until the DFT loop (see Figure 5.2) is converged.

7. The full charge-self-consistent DFT+DMFT solution is achieved when both DFT and DMFT loops are converged. While the DFT+DMFT loops are converging, the information about the occupancy of correlated orbitals, the total energy, and both the Green’s function and the
The self energy at each iteration are stored. The convergence can be checked by monitoring the change of these variables.

8. After the DFT+DMFT loop is converged, one can perform the post-processing to obtain the band-structure and the density of states (see Sec. 5.3.5).

The source files can be found in the /src directory of our package in the github repository. After the compilation of the source codes, executable files (dmft.x, ctqmc, wannier90.x, modified DFT code) and Python scripts (RUNDMFT.py) can be copied to the /bin directory and the path to this bin directory should be added to the path to environmental variables ($PATH and $PYTHONPATH).

As an example, in the run_example directory of our package we have also kept the result of LaNiO$_3$ for both non-charge self consistent and charge self consistent DMFT calculation. By comparing these results, we did not find any significant change in the band structure of LaNiO$_3$.

5.3.2 Parallelization

Our DMFTwDFT code has been implemented by adopting efficient parallelization using message passing interface (MPI). A bottleneck in running the dmft.x executable is solving the eigenvalue problem of the general complex matrix given in Eq. (5.11) for a dense $k$–point mesh and large Matsubara $\omega_n$ points. Our code adopts the $k$–point parallelization so that calculations with different $k$–points can be distributed to different cores. Moreover, our code is also compatible with the VASP $k$–point parallel scheme (INCAR tag:KPAR) and the charge update calculation can be also performed using the $k$–point parallelization.

5.3.3 Library mode

As we explained in the Method section, implementing a fully charge self-consistent solution of DFT+DMFT requires the modification of the DFT package so that $\rho(\mathbf{r})$ can be updated using Eq. (5.20) from eigenvalues $w^k$ and eigenfunctions $v^k$ of the DMFT occupation matrix $\mathbf{n}^k$ obtained within our DMFTwDFT code. This can be easily achieved by employing our library mode. A schematic of our library mode is given in Figure 5.3. It is clear from the schematic that any DFT code can be linked to our library mode and call the Fortran subroutine $\text{Compute\_DMFT}$. 


from dmft_lib.F90 to obtain the outputs of \(w^k\) (DMFT_eval) and \(v^k\) (DMFT_evec) of \(\pi^k\). These outputs are used for modifying the DFT occupation (the Fermi function) and the KS one-particle states to the DMFT occupation \(w^k\) and the DMFT wavefunction \(\psi^k\) to compute new charge density. The structure and details of input and output parameters used in this subroutine are given as follows:

```fortran
subroutine Compute_DMFT(n_kpts_loc, n_wann, kpt_dft, wght_dft, band_win_loc,
                         DMFT_eval, DMFT_evec)
  integer, intent(in) :: n_kpts_loc, n_wann
  real(kind=dp), intent(in) :: kpt_dft(3, n_kpts_loc)
  real(kind=dp), intent(in) :: wght_dft(n_kpts_loc)
  integer, intent(out) :: band_win_loc(2, n_kpts_loc)
  real(kind=dp), intent(out) :: DMFT_eval(n_wann, n_kpts_loc)
  complex(kind=dp), intent(out) :: DMFT_evec(n_wann, n_kpts_loc)
```

Here, n_kpts_loc is a variable to represent the number of \(k\)–points in DFT (It can be either \(k\)–points in irreducible Brillouin zone (IBZ) or full BZ). n_wann is the number of wannier orbitals.
in an unit cell (the size of the Wannier Hamiltonian). kpt_dft is the list of \( k \)–points with fractional coordinates. wght_dft is the weight of each \( k \)–point in BZ. The sum of weights should be one. band_win_loc is the range of the band index (minimum and maximum values) for the Wannier subspace \( W \) at each \( k \)–point. This will be needed for computing charge density within the subspace. DMFT_eval is the eigenvalue \( (w_k^\lambda) \) of the DMFT occupancy matrix \( n^k \). And DMFT_evec is the eigenvector \( (v_k^\lambda) \) of \( n^k \).

5.3.4 Interfacing with various DFT codes

Due to the object oriented nature of the DMFTwDFT code it is possible to interface our library to a variety of DFT codes. Modern DFT codes are interfaced with the Wannier90 package. An initial DFT+wannier90 calculation is all it takes to feed inputs to the DMFT loop. However, for full charge self-consistent DFT+DMFT calculations the DFT codes must be modified to sum the DFT and DMFT charge densities, as the total charge density. Our DMFTwDFT library mode mentioned in the features section renders this possibility. Currently we have the full charge DFT+DMFT self-consistent calculation interfaced to VASP [155] and the self-consistent DMFT calculation interfaced to Siesta.

5.3.4.1 VASP

The Vienna Ab initio Simulation Package (VASP)[174], is a package for performing first principles electronic structure calculations using either Vanderbilt pseudopotentials[175], or the projector augmented wave (PAW) method[176]. This code uses a plane wave basis set for the KS orbitals, which has several advantages while performing the electronic structure calculations. The basic methodology employed in VASP is DFT, but it also allows use of post-DFT corrections such as hybrid functionals mixing DFT and Hartree–Fock exchange, many-body perturbation theory (the GW method) and dynamical electronic correlations within the random phase approximation (RPA). VASP uses fast iterative techniques for the diagonalization of the DFT Hamiltonian and allows to perform total-energy calculations and structural optimizations for systems with thousands of atoms. Also, ab-initio molecular dynamics simulations for ensembles with a few hundred atoms extending over several tens of picosecond is possible using this code. It also has an interface with Wannier90.
The DMFTwDFT Framework code. More details on the DMFT implementation and how was interfaced with VASP (v5.4.4), using the projector augmented wave method, can be found in Ref. [155].

5.3.4.2 Siesta

Siesta [140] is a DFT code based in Spain to perform electronic structure calculations and ab-initio molecular dynamics based on localized basis sets and with a large global community. Unlike VASP, this code uses numerical atomic orbitals as the basis set for the KS orbitals. It also supports interfacing with wannier90 which enables the implementation of our DMFT code to it. As VASP is a commercial code, it was decided to pursue developments with free license codes and Siesta was our first choice. Currently, we have interfaced our DMFTwDFT code with latest Siesta code (Siesta version 4 or greater) to perform self-consistent DMFT calculations. We have checked our implementation by performing DMFT calculation on SrVO$_3$. For SrVO$_3$, we have used Troullier-Martins norm-conserving pseudopotentials scheme as implemented in the Siesta code [177]. Exchange and correlation functional was approximated using generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE)[149], with a plane wave energy cutoff of 600 Ry and a $8 \times 8 \times 8$ k-point mesh. We selected the multiple-zeta basis set, split and fixed the orbital confining cut-off to 0.02 Ry. The split norm used was 0.15. Geometry optimizations were performed using the conjugate gradient algorithm until all residual forces were smaller than 0.001 eV/Å.

The convergence procedure is very similar to the VASP case. Once the calculation is complete, one can perform the post-processing similarly to VASP+DMFT. Obtained DMFT projected density of states using Siesta interface for SrVO$_3$ is shown in Figure 5.4a. In addition, we have compared the imaginary part of the self energy for V-3d $e_g$ and $t_{2g}$ states as a function of Matsubara frequency obtained by both VASP and Siesta DMFT interface. A comparison is shown in Figure 5.4b. Our results clearly revealed a similar trend for the self-energy on both electronic structure codes. Thus, the obtained correlation is very similar in both Siesta and VASP. In the next section, we discuss our full charge self-consistent DFT+DMFT implementation within Siesta.
5.3.4.3 Full charge self-consistency implementation

Here we summarize the formulation to implement DFT+DMFT full charge self-consistency using the DMFTwDFT code to the DFT program Siesta \[71\]. For a full derivation please refer to Ref. \[7\].

For example purposes we will assume a DFT+DMFT calculation performed for the correlated material \(SrVO_3\) using 512 k-points, 28 bands and 14 Wannier bands for the V-d orbitals and O-p orbitals. The Siesta input file \(SrV03.fdf\) should contain the following block to allow the Wannier90 calculation.

\[
\begin{align*}
\text{Siesta2Wannier90.WriteMmn} & \quad \text{.true.} \\
\text{Siesta2Wannier90.WriteAmn} & \quad \text{.true.}
\end{align*}
\]
A Siesta+DMFT calculation can be launched easily through the DMFTwDFT program as follows:

```
$DMFT.py -dft siesta -structurename SrVO3 -dmft
```

DMFTwDFT automatically generates a `SrVO3.win` file for the Wannier90 calculation based on these inputs. The subdirectory `subroutine_dmft` contains some of the outputs from a Siesta+DMFT calculation with a single DFT step and multiple DMFT steps. To develop a Siesta+DMFTwDFT interface for full DFT+DMFT charge self-consistency, the DFT charge density must be updated from the DMFT charge density. The formalism to achieve this is explained briefly below.

The total DFT+DMFT charge density $\rho(r)$ can be given by

$$\rho(r) = \sum_{i \in W} \rho_{i}^{DFT}(r) + \sum_{i,j \in W} \rho_{ij}^{DMFT}(r)$$  \hspace{1cm} (5.29)

where, $\rho(r)^{DMFT}$ is the charge density within the DMFT subspace, $W$ is the energy window for constructing Wannier functions, and $i,j$ are the band indices. The DMFT charge density $\rho(r)^{DMFT}$ for the correlated subspace can represented using DFT KS wavefunctions as follows:

$$\rho_{ij}^{DMFT}(\vec{r}) = \frac{1}{N_{K}} \sum_{\vec{k}} n_{\vec{k}ij} \langle \psi_{i\vec{k}}^{KS} | \vec{r} \rangle \langle \vec{r} | \psi_{j\vec{k}}^{KS} \rangle$$  \hspace{1cm} (5.30)

where, $n_{\vec{k}ij}$ is the DMFT occupancy matrix in the KS basis (calculated in `dmft.F90` as the 3-d array, $n$) and $|\psi_{i\vec{k}}^{KS}\rangle$ is the KS wavefunction at momentum $\vec{k}$ and band $i$.

Following Eq. (43) of Ref. [71], at every sampled $\vec{k}$-point the eigenfunctions of the Hamiltonian are written as,
\[ \psi_{i\vec{k}}^{KS}(\vec{r}) = \langle \vec{r} | \psi_{i\vec{k}}^{KS} \rangle = \sum_{\mu'} e^{i\vec{k} \cdot \vec{R}_{\mu'}} \phi_{\mu'}(\vec{r}) c_{\mu' i}(\vec{k}) \] (5.31)

where, the sum in \( \mu' \) extends to all basis orbitals in space (each of them centered in an atom at position \( \vec{R}_{\mu'} \)), \( i \) labels the different bands, and \( c_{\mu' i} \equiv c_{\mu i} \).

Inserting Eq. (5.31) into Eq. (5.30),

\[
\rho_{ij}^{DMFT}(\vec{r}) = \frac{1}{N_{\vec{k}}} \sum_{\vec{k}} n_{\vec{k}ij} \left( \sum_{\mu'} e^{-i\vec{k} \cdot \vec{R}_{\mu'}} \phi_{\mu'}(\vec{r}) c_{\mu' j}(\vec{k}) \right) \left( \sum_{\mu'} e^{i\vec{k} \cdot \vec{R}_{\mu'}} \phi_{\mu'}(\vec{r}) c_{\mu' i}(\vec{k}) \right)
\]

\[
= \sum_{\mu'} \sum_{\mu} \phi_{\mu'}^*(\vec{r}) \phi_{\mu}(\vec{r}) \left( \frac{1}{N_{\vec{k}}} \sum_{\vec{k}} n_{\vec{k}ij} e^{i\vec{k} \cdot (\vec{R}_{\mu'} - \vec{R}_{\mu})} c_{\mu' j}(\vec{k}) c_{\mu' i}(\vec{k}) \right)
\]

\[
= \sum_{\mu'} \sum_{\mu} \phi_{\mu'}^*(\vec{r}) \phi_{\mu}(\vec{r}) \rho_{\mu' \mu' i j},
\]

where we have defined the “density matrix” \( \rho_{\mu' \mu' i j} \) as

\[
\rho_{\mu' \mu' i j} = \frac{1}{N_{\vec{k}}} \sum_{\vec{k}} n_{\vec{k}ij} e^{i\vec{k} \cdot (\vec{R}_{\mu'} - \vec{R}_{\mu})} c_{\mu' j}(\vec{k}) c_{\mu' i}(\vec{k}),
\] (5.32)

and \( c_{\mu' i} \equiv c_{\mu' i}^* \).

The sum over band indices \( i, j \) in Eq. (5.30) can be simplified to the sum over one index because the DMFT occupancy matrix \( n_{\vec{k}ij} \) is Hermitian and so can be written in terms of eigenvalues \( w_{\vec{k}\lambda} \) and eigenfunctions \( \phi_{\lambda} \) as

\[
n_{\vec{k}ij} = \sum_{\lambda} U_{k\lambda i}^{DMFT} \cdot w_{\vec{k}\lambda} \cdot U_{kj\lambda}^{*DMFT}
\] (5.33)

where, \( U_{k\lambda i}^{DMFT} \) are unitary matrices whose rows are \( \phi_{\lambda} \)'s. \( n_{\vec{k}ij} \) is calculated in \texttt{dmft.F90}. These matrices need to be updated at every self-consistent step.
The following section discusses the Fortran subroutines to perform the calculations relating to the above formulation.

1. **test_dmft.F90**
   This mimics a subroutine in Siesta which calculates the DFT charge density. Inputs from Siesta namely kgrid, k-mesh weights, number of wannier bands, number of kpoints and charge density grid dimensions are passed into the subroutine dmft() from here. For now we have included sample values which should be replaced by corresponding values obtained from Siesta. Once the DMFT charge density is passed back here it can be added to the DFT charge density as portrayed in Eq. (5.29).

2. **dmft.F90**
   This subroutine is meant to calculate the DMFT charge density using Eq. (5.30) and Eq. (5.33). So far we have computed the DMFT occupancy matrix, $n_{ki\lambda}$ in here. What we have to achieve now is to calculate the DMFT charge density $\rho(r)^{DMFT}$ using this occupancy matrix $n_{ki\lambda}$ and the Siesta Kohn-Sham wave functions as depicted in equations Eq. (5.30) - Eq. (5.33). Using the above we can then obtain the full DFT+DMFT charge density which is used as the starting charge density for the DFT calculation. This subroutine calls `Compute_DMFT()` from the dmft library (libdmft.a) to compute the DMFT weight $w_{ki\lambda}$ and Unitary matrix $U_{ki\lambda}^{DMFT}$ at each k-point. The variables of the dmft() subroutine is as follows:

<table>
<thead>
<tr>
<th>Variable</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td><code>integer n_kpts</code></td>
<td>The number of k-points in DFT</td>
</tr>
<tr>
<td><code>integer n_wann</code></td>
<td>The number of Wannier orbitals</td>
</tr>
<tr>
<td><code>real kpt_dft(3, n_kpts)</code></td>
<td>List of k-points in DFT using fractional coordinates</td>
</tr>
<tr>
<td><code>real wght_dft(n_kpts)</code></td>
<td>List of k-point weights. The sum should be one.</td>
</tr>
<tr>
<td><code>integer Nx</code></td>
<td>Number of grid points in x direction for charge density grid</td>
</tr>
</tbody>
</table>

The variables of the dmft() subroutine is as follows:
integer Ny : Number of grid points in y direction for charge density grid

integer Nz : Number of grid points in z direction for charge density grid

INTERMEDIATE:

These variables are calculated from Compute_DMFT() using the above inputs and are then used to calculate the DMFT charge density:

integer band_win(2, n_kpts) : Band range of the Wannier subspace at each k-point

real DMFT_eval(n_wann, n_kpts) : Eigenvalues \( W_{k, \lambda} \) of the DMFT occupancy matrix \( n_{k, i, j} \)

complex DMFT_evec(n_wann, n_wann, n_kpts) : DMFT eigenvectors of the Unitary matrix

U_{k, i, \lambda}

complex DMFT_evec_k(n_wann, n_wann) : Unitary matrix \( U_{k, i, \lambda} \) at a given k-point

complex DMFT_evec_T(n_wann, n_wann) : Transpose Conjugate of the Unitary matrix \( U_{k, i, \lambda} \) at a given k-point

complex n(n_wann, n_wann, n_kpts) : DMFT Occupancy Matrix \( n_{k, i, j} \)

OUTPUT:

real DMFT_chg(Nx, Ny, Nz) : DMFT charge density \( \rho_{i, j} \), where \( i, j \) is in the Wannier window
3. libdmft.a -

This contains the subroutine `Compute_DMFT()` which is called from dmft.F90 and calculates the DMFT Unitary matrix that is used in dmft.F90 to calculate the Occupancy matrix needed for the DMFT charge density calculation.

5.3.4.4 Quantum Espresso

Similar to VASP, Quantum Espresso [139] is also a plane-wave basis DFT code from Italy. DMFTwDFT is interfaced to Quantum Espresso both natively and through the Aiida workchain toolkit. So far we have only implemented Quantum Espresso to perform One-shot DMFT calculations, although the full charge self consistency through the library mode interfaced will be available in a future release of the code.

5.3.5 Automated scripts

We have created a set of Python scripts to automate the complete DFT+DMFT calculation and the post-processing procedure. The functionality of the scripts are described below.

5.3.5.1 DMFT.py

This script performs the DFT+DMFT calculation. Running DMFT.py -h displays a help message providing instructions. The calculation has the following options:

- `-dft`:
  The choice of DFT code. Currently, VASP and Siesta are supported.

- `-relax`:
  This flag turns on DFT convergence testing. If the forces are not converged a convergence calculation is attempted and if it fails the user is asked to modify convergence parameters. This is useful for vacancy and defect calculations where a force convergence is required after the vacancy or defect is created in order to obtain a relaxed structure to perform DFT+DMFT calculation. Currently supported for VASP. This uses PyChemia [178] to check for convergence. The relaxation occurs inside a “DFT_relax” directory.
The DMFTwDFT Framework

- **-structurename:**
  DFT codes such as Siesta uses input files that contain the name of the system e.g. SrVO$_3$.fdf. Therefore when performing DFT+DMFT calculations with Siesta this flag is required.

- **-dmft:**
  This flag performs the DMFT calculation using the results from the DFT calculation if a previous DMFT calculation in the same directory is incomplete.

- **-hf:**
  This flag performs the Hartree-Fock (HF) calculation to the correlated orbitals specified in INPUT.py if a previous HF calculation in the same directory is incomplete.

- **-force:**
  This flag forces a DMFT or HF calculation even if a previous calculation has been completed. The option to check for completeness is helpful when running many DMFT/HF jobs on a cluster.

- **-kmeshtol:**
  This controls the tolerance of two k-points belonging to the the same shell in the wannier90 calculation.

The calculations are performed in an automatically generated “DMFT” or “HF” directory where the script was run from. E.g.:

```
$DMFT.py -dft vasp -relax -dmft
$DMFT.py -dft siesta -structurename SrVO3 -dmft
```

### 5.3.5.2 postDMFT.py

This script performs analytical continuation, density of states and band structure calculations on the DMFT/HF data. Once the DMFT/HF calculations are complete, this script should be initiated within the “DMFT” or “HF” directories. Running postDMFT.py -h displays a help message providing instructions. The calculations has the following options:
• ac:
  This function performs the Analytic Continuation to obtain the Self Energies on the real axis.
  It has the option `-siglistindx` to specify the last number of Self Energy files to average for
  the calculation.

• dos:
  This function performs the partial density of states of the correlated orbitals. It has the
  following options:
  
  – `emin` : Minimum energy value for interpolation
  – `emax` : Maximum energy value for interpolation
  – `rom` : Number of Matsubara Frequency ($\omega$) points
  – `broaden` : Broadening of the dos
  – `show` : Display the density of states
  – `elim` : The energy range to plot

• bands:
  This function performs the DMFT band structure calculations. It has the following options:
  
  – `emin` : Minimum energy value for interpolation
  – `emax` : Maximum energy value for interpolation
  – `rom` : Number of Matsubara Frequency ($\omega$) points
  – `kpband` : Number of k-points for band structure calculation
  – `kn` : A list of labels for k-points
  – `kp` : A list of k-points corresponding to the the k-point labels
  – `plotplain` : Flag to plot a plain band structure
  – `plotpartial` : Flag to plot a projected band structure
  – `wo` : List of Wannier orbitals to project onto the band structure
  – `vlim` : Spectral intensity range
  – `show` : Display the bands
The projected bands are especially helpful in determining the contribution to bands from different orbitals.

The calculations are stored in directories ac, dos and bands, respectively. The following are some example commands to perform post-processing, e.g.:

```bash
$postDMFT.py ac -siglistindx 4
$postDMFT.py dos -show
$postDMFT.py bands -plotplain
$postDMFT.py bands -plotpartial -wo 4 5 6
```

### 5.4 Examples

In this section, we illustrate the capabilities of our DMFTwDFT code by describing electronic structure of three different correlated systems: (1) SrVO$_3$, a paramagnetic $d-$orbital system; (ii) LaNiO$_3$, a paramagnetic system with a $p-d$ covalent bonding; (iii) NiO, a charge-transfer insulator.

#### 5.4.1 SrVO$_3$

SrVO$_3$ forms a perovksite crystal structure with an ideal cubic Pm$\bar{3}$m symmetry, containing one V ion in the unit cell [179]. In the cell, V-ion is coordinated by 6 oxygens and forms an undistorted VO$_6$ octahedra (see Figure 5.5). Due to the cubic symmetry, the $d$ orbitals split into two sets of three $t_{2g}$ and two $e_g$ orbitals. The expected electronic configuration for V-ion is $3d^1$ following from the formal oxidation V$^{4+}$. One $d$ electron partially occupied in the $t_{2g}$ shell can exhibit the correlation effect. Therefore, SrVO$_3$ has been the subject of many experimental and theoretical investigations using DFT+DMFT [180–182] as a benchmark material for strong correlation physics.

Previous electronic-structure studies show that SrVO$_3$ exhibits pronounced lower and upper Hubbard bands, which cannot be explained by conventional DFT [183–185]. Here, we perform the DFT+DMFT calculation of SrVO$_3$ using our DMFTwDFT package interfaced with VASP. To prepare the necessary input for our DMFT run, we begin by performing DFT calculations of SrVO$_3$ using the VASP code [138, 176] with the PBE exchange and correlation functional [149]. The plane-
The DFT band-structure plotted using our recently implemented DFT pre/post-processing software PyProcar [173], is shown in Figure 5.6. V-3d(t$_{2g}$) states are located near the Fermi energy between -1.0 eV and 1.0 eV and V-3d(e$_g$) bands are between 1.0 eV and 5.0 eV. Oxygen 2p states are below -2.0 eV and mixed with some of V-e$_g$ bands. While many DFT+DMFT calculations of SrVO$_3$ used the V-t$_{2g}$ orbitals as correlated orbitals and chose the Wannier energy window between -1.0 eV and 1.0 eV [187], we use the wider energy window of [-8.0:5.0] eV from the Fermi energy to ensure the highly localized nature of V-d orbitals. Therefore, we construct the MLWFs of V-3d and O-2p orbitals using the Wannier90 code [66, 136] interfaced to VASP and converge the gauge-dependent spread of Wannier orbitals in 1000 steps. We compared the original band structure obtained from VASP with our Wannier-interpolated band structure and a good agreement was obtained.

Our DMFTwDFT code can perform the DMFT calculations of SrVO$_3$ by copying required DFT and Wannier90 output files from the DFT run directory using the python script “Copy_input.py”. In the case of SrVO$_3$, we treat V as a correlated site and V-3d (t$_{2g}$ and e$_g$) orbitals as the correlated orbitals. We used CTQMC [62] as the DMFT impurity solver using the local Coulomb repulsion
Figure 5.6: The V 3d orbital projected band structure of SrVO$_3$ (red). The energy range that encloses these projected orbitals is used to construct the Wannier window for the DMFT calculation.

U = 5.0 eV, a Hund’s exchange coupling J=1.0 eV [188], and temperature as low as 0.01 eV $\approx 110$K. To avoid the double counting of the Coulomb interaction, we also used the modified DC correction, DC_type = 1 (Eq. (5.26)) with $\alpha = 0.2$ for SrVO$_3$ DMFT calculation [155]. Our results are not sensitive to the choice of different DC corrections as the t$_{2g}$ orbitals are rather separated from other orbitals. We have used $20 \times 20 \times 20$ k-points while doing the DMFT calculations. After DFT+DMFT calculations are converged, we used our post-processing script as we discussed earlier and calculated the $k$-resolved spectral function $A(k, \omega)$ (Fig. 5.7) and density of states $A(\omega)$ (Fig. 5.8a) for SrVO$_3$.

In Figure 5.7, we present the DMFT band structure $A(k, \omega)$ plotted following a $k$-path in the BZ for the energy $\omega$ between -5.0 and 5.0 eV. Comparison of our DMFT bands to DFT bands shows that V-t$_{2g}$ bands near the Fermi energy are renormalized and slightly incoherent due to the broadening of the self-energy while e$_g$ and oxygen p bands are very similar to DFT bands. This is also consistent with the fact that the imaginary part of $\Sigma(i\omega_n)$ for both t$_{2g}$ and e$_g$ orbitals are very small at $\omega_n = 0$ but the t$_{2g}$ orbital has the larger $\Sigma(i\omega_n)$ than the e$_g$ orbital as $\omega_n$ increases. Our calculated mass renormalization factor for t$_{2g}$ states is 1.7, which is slightly smaller than the experimental mass renormalization factor that ranges from 1.8-2[189–191]. This is a measure of the reduction in quasiparticle weight that can be easily inferred from the slope of the Matsubara-axis
self-energy at $\omega = 0$ [$Z \approx 1/(1-\text{Im}(\Sigma(i\omega_n)/\omega_n))$]. The reciprocal of Z can be considered as a mass renormalization factor. The overall DMFT spectra $A(\omega)$ for SrVO$_3$ (Fig.5.8a) exhibits noticeable changes of the local spectral function compared to the DFT DOS (Fig.5.8b). Namely, a narrowing of the $t_{2g}$ quasi-particle (QP) bands close to the Fermi level occurs and the QP spectral weights move to lower and upper Hubbard bands, whose positions are dependent on the choice of the Hubbard U [192].

5.4.2 LaNiO$_3$

LaNiO$_3$ is the only known paramagnetic and metallic compound among the rare-earth nickelate series down to very lowest temperatures [193, 194]. In spite of the metallic state, LaNiO$_3$ resides on very close to the Mott insulator phase boundary, and moreover various experimental probes including Angle-resolved Photoemission Spectroscopy (ARPES) [195], optical conductivity [196, 197], and thermo-dynamical measurements [198] show that LaNiO$_3$ is still correlated. Moreover, recent discovery for superconductivity in the infinite-layer rare-earth nickelate has also resurged the correlation effects in nickelates [199, 200]. LaNiO$_3$ has a rhombodedral symmetry, described by R3c space group. The crystal structure of LaNiO$_3$ is shown in Figure 5.9.

Several DFT calculations have been performed to study the electronic and lattice properties of
Figure 5.8: The projected density of states of SrVO$_3$ for the correlated V 3d-$e_g$ and 3d-$t_{2g}$ orbitals obtained using (a) DMFT and (b) DFT calculations.
LaNiO$_3$. Guo et al [201] found the A1g Raman mode, whose frequency is sensitive to the electronic band structure method, is a useful signature to characterize the octahedral rotations in rhombohedral LaNiO$_3$. The authors also found that DFT with local spin density approximation (LSDA) accurately reproduces the delocalized nature of the valence states in LaNiO$_3$ and gives the best agreement with the available experimental data [202] for the electronic structure. Surprisingly, they have found that NiO$_6$ rotation angle $\theta$, the order parameter characterizing the structural phase transition in LaNiO$_3$, is highly sensitive to the exchange correlation (XC) functional. Even calculations with the same functional but different pseudopotentials (e.g., the LSDA calculations performed with the VASP and Quantum espresso codes) yield $\theta$ values with obvious differences. Therefore, the authors suggest that an accurate and comprehensive study of various theoretical approximations for the description of octahedra rotation angles in rhombohedral perovskite oxides is needed which remains a mystery until now. This implies an accurate calculation of the forces is indeed necessary to obtained the accurate structure of LaNiO$_3$, which remain the next target of the current project. Calculation of the forces using DMFT will be available with the next release of DMFTwDFT code.

Nevertheless, recently, Nowadnik, et al[203] performed DFT+DMFT calculations in LaNiO$_3$ using the early version of our DMFTwDFT code and quantified the electronic correlation strength by comparing with ARPES measurements. Their results established that the LaNiO$_3$ is indeed a
moderately correlated Fermi liquid. Obtained DFT+DMFT spectral-function of LaNiO$_3$ along the momentum space cut ($\pi/2a_{pc}$, $k_y$, $0.7\pi/a_{pc}$) which is in good agreement with existing ARPES data as shown in Figure 5.10 (Copyright for the Figure 5.10 is provided by the American Physical Society and Scientific Publishing and Remittance Integration services (SciPris)). In both experiment (left side) and DFT + DMFT (right side), there is a shallow band crossing the Fermi level with a band bottom at 50 meV and a Fermi level crossing at $k_y = -0.2\pi/a_{pc}$. This band is substantially renormalized by electron correlations relative to the rhombohedral DFT band structure. By considering the frequency derivative of the electron self-energy obtained by the DMFT, authors have also calculated the theoretical mass renormalization for LaNiO$_3$, which is 3.5. This implies, $m_{DMFT}^* = 3.5 \times m_{band}^*$, where $m_{band}^*$ is the electron effective mass calculated from DFT and $m_{DMFT}^*$ is the mass approximated from the DMFT spectral function. This is in a good agreement with the soft X-ray ARPES mass renormalization value which is 3. In the following, for completeness, we discuss the full DFT+DMFT spectral function along the high-symmetry points of the BZ and density of states of LaNiO$_3$ obtained using our DMFTwDFT code.

Similar to the SrVO$_3$ case, we first perform DFT calculations using the VASP code [138] by consider the bulk LaNiO$_3$ in a rhombohedral crystal structure (space group R$\bar{3}$c, $a^-a^-a^-$ in Glazer notation) [201]. As we mentioned earlier, by comparing different DFT functionals Guo et al. reach to a conclusion that the LDA functional is the best functional for LaNiO$_3$ [201]. Thus, to treat exchange-correlation in LaNiO$_3$ we have also employed LDA functional and core electrons were defined within the PAW methodology [176] as implemented in the VASP code. We have used a 600 eV plane-wave cutoff and, for structural relaxations, a force convergence tolerance of 2 meV/A. We used $8 \times 8 \times 8$ $k$–points meshes. The obtained DFT band-structure along the high symmetry points in BZ is shown in Figure 5.11.

From the DFT band structure, we construct the Ni 3d and O 2p MLWFs using the Wannier90 [66, 136] code over the $\sim11$ eV range ($[-8:3.2]$eV from the Fermi energy) spanned by the p-d manifold as the hybridization window and treated Ni d orbitals as the correlated orbitals. The obtained Wannier interpolated band-structure is shown in Figure 5.12 which is in good agreement with the DFT band structure as shown in Figure 5.11. In LaNiO$_3$, the nominal configuration is Ni d$^7$ with fully filled
t_{2g} (Figure 5.12a) band and quarter filled e_g band (Figure 5.12b). Our results clearly revealed that Ni 3d t_{2g} bands are completely filled at energy between -2.0 eV and 0.0 eV, and e_g bands are partially filled in the range of -1.0 eV and 3.0 eV. Different from the SrVO_3 band structure, oxygen 2p states are much closer to the Fermi energy and e_g bands are covalently mixed with O p states. Therefore, including all Ni d and O p orbitals in the hybridization window will be important for a better description of LaNiO_3.

DMFT calculations were performed such that the correlated subspace is treated using the Hubbard interaction strength U=5eV and the Hund’s interaction J=1eV. For the double-counting correction
Figure 5.11: Ni-3d orbital projected DFT band structure of LaNiO$_3$ (orange). The energy range that encloses these projected orbitals is used to construct the Wannier window for the DMFT calculation.

Figure 5.12: Wannier-interpolated band structure with (a) Ni-3d($e_g$) and (b) Ni-3d($t_{2g}$) states of LaNiO$_3$. The zero energy is the Fermi level.

required in DFT+DMFT, we use the parametrization of $U$ as $U - \alpha$ (DC_type = 1 and $\alpha = 0.2$), which was found to correctly reproduce the pressure phase diagram of the RNiO$_3$ [164]. The DMFT impurity problem is solved using the CTQMC method [62] with the temperature set to 0.01 eV $\approx$ 110 K. Using our post processing scripts, we obtained the Ni-3d projected DOS (see Figure 5.13a) and k–resolve spectral function along the high-symmetry direction of the BZ (see Figure 5.14) for LaNiO$_3$. Both results clearly reveal that moderate correlation is associated with the renormalized Ni-$e_g$ manifold near the Fermi energy while $t_{2g}$ state is almost filled and broader than the DFT
DOS, Figure 5.13b.

Figure 5.13: The projected density of states of LaNiO$_2$ for the correlated Ni 3d-$e_g$ and 3d-$t_{2g}$ orbitals obtained by (a) DMFT and (b) DFT calculations.

5.4.3 NiO

Crystal structure of NiO adopts a cubic rock-salt (B1) structure with octahedral Ni$^{+2}$ and O$^{-2}$ sites as shown in Figure 5.15. NiO has been extensively studied experimentally and theoretically. It is a strongly correlated charge-transfer insulator with a large insulating gap of 4.3 eV and antiferromagnetic (AFM) ordering temperature ($T_N$) of $\approx 523$K [204–206]. Conventional band theories cannot explain this large gap and predicted wrongly NiO to be metallic [207]. Spin-polarized DFT calculations using local spin density approximation (LSDA) found the AFM insulating state but obtained local magnetic moment at Ni sites are considerably smaller than the experimental values [208]. There has been several studies which made an effort to go beyond DFT including self-
Figure 5.14: The DFT (green) and DFT+DMFT (red) bandstructures of LaNiO$_3$.

Figure 5.15: Crystal structure of NiO. Ni and O atoms are in gray and red color, respectively. Rocksalt crystal of NiO, visualized as NiO$_6$ octahedral networks.
interaction-corrected density functional theory (SIC-DFT) [209], the LDA+U method [210], and
the GW approximation [211, 212]. These methods represent some corrections of the single-particle
Kohn-Sham potential and provide the improvements over the L(S)DA results for the values of the
energy gap and local moments. It is important to note that in these methods the self-energy is
static and hence does not take dynamical correlation effects into account adequately. Also, different
GW schemes give quite different results regarding the value of the insulating gap and the relative
position of the energy bands [211–214].

Figure 5.16: Compared the projected density of states of NiO obtained by Wannier (a) and DMFT
calculation for $U = 5$ eV (b) and 10 eV (c).

Experimentally, it has been found that both the local magnetic moment and the energy band gap for
NiO are essentially unchanged even above the Neel temperature [215]. Also, in other experiments,
it has been found that long range magnetic order do not has significance influence on the valence band photo emission spectra [216] and the electron density distributions [217]. Therefore, the role of magnetism and correlation is still not clear in NiO. To resolve the above controversy, Ren et al [218] has employed the LDA+DMFT approach and concluded that a large insulating gap in NiO is due to the strong electronic correlations in the paramagnetic state. They also suggest that AFM long-range order has no significant influence on the electronic structure of NiO. Recently, using ab-initio LQSGW + DMFT, Kang et al [219] claimed that they have resolved the long standing controversy of two-peak structure in the valence band photoemission spectra of NiO [205, 220]. They suggest that, the two peak structure is driven by the concerted effect of AFM ordering and inter-site electron hopping. Surprisingly, the two peak structure has also been obtained by Ren et al [218] where authors used LDA+DMFT approach for T = 1160 K and U = 8 eV, J = 1 eV. Thus, although considerable progress was made in the theoretical understanding of NiO from first principles, several important issues are still open. This is certainly not the goal of the present manuscript. However, in the following we will discuss our DFT+DMFT results for NiO and compare with other existing DMFT results and experiments.

Figure 5.17: (a) NiO DFT fatbands, (b) Ni-3d and O-2p projected Wannier interpolated band structure, (c) a DMFT momentum-resolve spectral function along the high symmetry direction of the BZ obtained using U=10eV and J=1eV, and (d) the spectral function of NiO compared with the ARPES data (green dots) obtained by Shen et al[221].

To prepare the required input for our DMFT run, we first performed the first principles DFT cal-
calculations followed by DMFT calculations. First principles DFT calculations of NiO were performed using VASP code [138]. We have used PAW pseudopotentials[176], and PBEsol[222] exchange and correlation functional for NiO, which as per our knowledge is not tested before. In practice, while PBEsol provides better crystal cell parameters than PBE[223], it is not clear that all properties are improved overall. Here we use PBEsol to demonstrate that DMFT is less sensible to the exchange correlation details and provide quite similar results than those obtained from LDA and PBE. The plane wave energy cutoff was chosen 600 eV for NiO. $6 \times 6 \times 6$ Monkhorst-pack k-point grids[186] were used for reciprocal space integration. After obtaining the self-consistent ground state, we perform a self-consistent calculation on uniform grid of k-points without changing the potential.

Figure 5.18: Imaginary part of the Ni self energy of NiO for Ni-3d $e_g$ and $t_{2g}$ states as a function of Matsubara frequencies obtained using U=10 eV and J=1 eV.

Obtained DFT density of states clearly revealed that NiO is metal with Ni-3d($e_g$) state and O-2p states are strongly mixed due to the nature of the charge-transfer insulator (refer Figure 5.16a). Ni-3d($t_{2g}$) states are fully filled, and Ni-3d($e_g$) and O-2p states are widely formed between -8 eV and 2 eV (refer Figure 5.16a). We also construct MLWFs as we did for other examples. Projections onto atom centred Ni-3d and O-2p function are used to construct the initial guess, and further Wannier90 is used to obtained the MLWFs[66, 136]. To obtained the correct energy window of [-8.0 - 3.0]eV for wannier-function, we compared the original band structure obtained from DFT calculation with our Wannier-interpolated band structure as shown in Figure 5.17a and b, respectively. In the case of
NiO, we treat Ni as a correlated site and Ni-3d ($t_{2g}$ and $e_g$) orbitals as the correlated orbitals. The Coulomb interaction $U=5.0$ eV as well as $10.0$ eV and a Hund’s exchange coupling $J=1.0$ eV are used. Previously, suggested value of Hubbard U on Ni-3d orbital vary in the range of 4-10 eV.[219, 224, 225] We have used the FLL double counting correction (DC_type =1 and $\alpha = 0.0$). Temperature as low as $0.03$ eV $\approx 300K$ are used and set of $24 \times 24 \times 24$ k-points have been used for the DMFT calculations.

Using the post-processing tools, we have calculated the DMFT density of states as well as k-resolved spectral function $A(k, \omega)$ for NiO. Interestingly, our DMFT results clearly revealed that including the strong correlation leads to an insulating state in NiO as shown in Figure 5.16b and c. As $U$ increases, the insulating gap gets larger and Ni 3d states below the Fermi energy are strongly hybridized with O-2p orbitals. As a result, both $e_g$ and $t_{2g}$ orbitals exhibit longer tails below the Fermi energy and the separation between O-2p and Ni-3d states has been reduced at $U=10$eV (see Figure 5.16c). Compared to the experimental spectra (see Figure 5.19), $U=10$eV produces better agreements with experiments than $U=5$eV. Moreover, a divergent nature of the self-energy ($\Sigma(i\omega_n) \sim 1/(i\omega_n - \omega_0)$) for Ni 3d-$e_g$ states for low Matsubara frequency clearly indicate that the $e_g$ state develops a Mott gap while $t_{2g}$ states behaves as a band insulator due to much smaller $\Sigma(i\omega_n)$ (refer to Figure 5.18).

In Figure 5.17c and d, we also present the k–resolved DMFT spectra for NiO along the high symmetry direction of BZ. In Figure 5.17c, dispersionless Ni $t_{2g}$ bands are located near -2eV and the mixture of Ni $e_g$ and O bands are dispersing slightly above -2eV. Below -4eV, the bands are mostly O-2p characters while they are also strongly mixed with $t_{2g}$ and $e_g$ bands, therefore those mixed bands are strongly incoherent. We have also compared our obtained DMFT band structure with the experimental band structure along the $\Gamma$ - $X$ direction in Figure 5.17d. The obtained result is in very good agreement with the experimental result [221].

We also compared our DMFT density of the states with existing experimental data [205, 220] as well as theoretical results obtained using other DMFT codes in Figure 5.19. We compared our $U=10$eV result, which is in good agreement with experimental results. In Figure 5.19(b-d), we also presented total density of states of NiO obtained by other equally important DMFT tools.
including WIEN2k+EDMFT [127], LQSCGW + DMFT [125], and LDA+DMFT [125]. Note that the presented DMFT spectra of LQSCGW + DMFT and LDA +DMFT was taken from the example directory of ComDMFT [125]. Surprisingly, we observed different DMFT tools at the same U and J values give slight variations of energy-band gaps for NiO. However, the overall features of peak positions are in good agreement with experiment. Namely, a small bump with the Ni $e_g$ and O-2p mixture below the Fermi energy, the $t_{2g}$ peak at around -2eV, and the O-2p peak below the $t_{2g}$ state are all consistent in different codes. The peak positions are also comparable to experimental data.

Figure 5.19: Compared the total density of states of NiO obtained by DMFTwDFT code (this work) with existing experimental PES as well as with other DFT+DMFT codes such as WIEN2k+EDMFT and ComDMFT[125] (LQSCGW + DMFT and LDA+DMFT).
5.5 Conclusions

We have implemented a computational package (DMFTwDFT) combining the DMFT methodology to different DFT codes to improve our theoretical description of strongly correlated materials. Our package can perform a charge-self-consistent DFT+DMFT calculation adopting Wannier functions as localized orbitals, which are constructed from the Wannier90 package interfaced to many DFT codes. Our current implementation has been interfaced with different DFT codes including VASP, Quantum Espresso and Siesta. We also provide a library mode to link our package to different DFT codes without much modifications.

We applied our package to compute the band structure and the density of states of different strongly correlated materials, namely SrVO$_3$, LaNiO$_3$, and NiO. Results of SrVO$_3$ obtained from both VASP+DMFT and Siesta+DMFT are in good agreement showing the moderate mass enhancement of t$_{2g}$ orbitals near the Fermi energy. Both SrVO$_3$ and LaNiO$_3$ are correlated metallic systems and the quasi-particle band renormalizations near the Fermi energy are captured properly by DMFT, consistently with experiments. Moreover, our NiO calculation shows that Ni e$_g$ orbital develops a Mott gap near the Fermi energy (the divergence of the self-energy) and band structures below the Fermi energy are consistent with ARPES measurements. Calculations of NiO with different DFT+DMFT codes with the same $U$ and $J$ parameters also exhibit the similar density of states compared to our results.
Implementation of the Equation of State module in MechElastic

6.1 Introduction

Investigating elastic and mechanical properties of a material is essential in modern materials design and characterization. The success of Density Functional Theory (DFT) [226–229] has enabled us to conveniently predict properties of materials from first-principles which has expedited the discover and design of novel functional materials for a set of desired applications. A variety of modern DFT codes
Implementation of the Equation of State module in MechElastic

including ABINIT [68, 142, 143, 230], VASP [231, 232], SIESTA [71], Quantum Espresso [72, 73], exciting [233], WIEN2k [234], CASTEP [235], ELK [236], CRYSTAL [237, 238] allow the calculation of the elastic tensor which has led to the creation of vast databases containing the elastic constants of materials [74, 239–244]. Additionally, several tools have also been developed to carry out further analysis of this data such as ELATE [245, 246], AELAS [247], ElaStic [248], and ELAM [249].

With the emergence of high-throughput electronic structure calculation, the need for tools that facilitate the automation of the elastic and mechanical analysis of bulk as well as of 2D materials is rapidly increasing. Moreover, access to the full elastic tensor enables one to determine numerous other important elastic, mechanical, and thermodynamic properties of materials vital for the screening of materials in the process of materials discovery and design [241, 250–252].

To address such requirements, we develop the MechElastic package, a robust open-source Python library, that can facilitate the analysis of the elastic and mechanical properties of bulk and 2D materials in a manual way as well as in a high-throughput manner. The MechElastic package reads the DFT calculated elastic tensor data obtained from various DFT codes (current implementation supports the output generated from the VASP [231, 232], ABINIT [68, 142, 143, 230], and Quantum Espresso [72, 73] codes, stores the elastic tensor following the Voigt notation [250], and carries out the calculation of several important elastic moduli and mechanical parameters as per user’s requirement. This package can also perform the Born-Huang mechanical stability tests [253] for all crystal classes. Furthermore, elastic wave velocities, hardness, Debye temperature, and melting temperatures can be estimated using this package. One can also use this package to plot the equation of state (EOS) curves and investigate the structural phase transitions in the spirit of the Murnaghan, Birch, Birch-Murnaghan, and Vinet EOS models [254–260].

With MechElastic’s interface with the ELATE software [246], it is possible to analyze the three-dimensional spatial distribution of linear compressibility, shear modulus, Young’s modulus, and Poisson’s ratio, and make the desired plots offline, i.e., without requiring access to the website of ELATE [245].

In this dissertation, we will only focus on the Equation of State (EOS) module implemented by the
author in the MechElastic package.

6.2 Equation of State Analysis

An Equation of State (EOS) is a thermodynamic relation between the state variables such as temperature (T), volume (V), pressure (P), internal energy, and/or specific heat, etc. It helps us to describe the state of a system under given physical conditions. For instance, it could be used to study a certain property of a material such as its density, under varying pressure or temperature or any other physical variable. The EOS’s are used in a wide range of fields ranging from Geo-Physics to Materials Science Other than predicting thermodynamical properties, EOS can be used to gain insight into the nature of solid-state and molecular theories [261].

The EOS models considered here are for the isothermal processes, where T is kept constant while P and V could be varying. Experimentally, these values can be obtained through x-ray diffraction (XRD), Diamond Anvil Cells (DAC), or shock experiments. However, the pressure range obtainable by such experimental techniques is limited and therefore, it calls for theoretical methods to extend the range for environments in extreme conditions such as planetary interiors.

MechElastic’s EOS class contains methods to plot ‘Energy vs. Volume’ and ‘Pressure vs. Volume’ curves from energy, pressure and volume data obtained from either calculations or experiments using several fitting models including Vinet, Birch, Murnaghan, and Birch-Murnaghan [261–269]. As calculations are sensitive to the type of the EOS model, outcomes from multiple models should be carefully examined [270]. MechElastic employs a central-difference scheme to calculate the pressure from the ‘Energy vs. Volume’ data, and similarly an integration scheme to calculate the energy from ‘Pressure vs. Volume’ data. This is especially helpful for studying the phase diagrams of materials to investigate the existence of phase boundaries.

To the best of our knowledge, currently there is no universal EOS model that is applicable to all types of solids and accurate over the whole range of pressure, especially, when a solid undergoes several structural phase transitions within the region of interest [271]. Therefore, we have included several EOS models in the MechElastic package whose accuracy can be evaluate by the mean-squared error (MSE) of the fitting. These models are briefly described below.
Figure 6.1: The fitted equation of state (EOS) plots for (a) Energy vs. Volume and (b) Pressure vs. Volume data obtained by differentiating the energy with a central difference scheme using different EOS models. Here, the material under investigation is $T_d$-MoTe$_2$ for which ‘Energy vs. Volume’ data was computed using the VASP code (numerical details are given in Ref. [272]).
6.2.1 Vinet EOS

The Vinet EOS model is based on the empirical interatomic potentials and is formulated as follows [261, 267]:

\[
E(\eta) = E_0 + \frac{2B_0 V_0}{(B'_0 - 1)^2} \times \left(2 - (5 + 3B'_0(\eta - 1) - 3\eta) e^{-3(B'_0 - 1)(\eta - 1)/2}\right) 
\]  

(6.1)

where, \(\eta = (V/V_0)^{1/3}\). \(V_0\), \(E_0\), \(B_0\), and \(B'_0\) denote the equilibrium volume, total energy, bulk modulus and its pressure derivative at zero pressure, respectively.

Vinet model performs better at high pressure and high compressibility (upto 40 %) since it includes non-linear pressure contributions as opposed to the Birch and Murnaghan EOS models [261]. However, it is not suitable for solids with significant structural flexibility, such as bond-bending in materials such as feldspars.

6.2.2 Birch EOS

The Birch EOS model is an empirical model as written below [273]:

\[
E(V) = E_0 + \frac{9}{8} B_0 V_0 \left[(V_0/V)^{2/3} - 1\right]^2 + \frac{9}{16} B_0 V_0 (B'_0 - 4) \times \left[(V_0/V)^{2/3} - 1\right]^3 + \sum_{n=4}^{N} \gamma_n \left[(V_0/V)^{2/3} - 1\right]^n 
\]

(6.2)

where, \(E_0\), \(V_0\), \(B_0\) and \(B'_0\) are the equilibrium energy, volume, bulk modulus and pressure derivative of the bulk modulus, respectively. \(n\) denotes the order of the fit.

For experimental high pressure data, Birch model fares better than the Murnagahn model, but underperforms the Vinet model [261, 265].

6.2.3 Murnaghan EOS

The Murnaghan EOS model is given as below [274]:
\[ E_T(V) = E_T(V_0) + \frac{B_0 V}{B'_0} \left[ \frac{(V_0/V)^{B'_0}}{B'_0 - 1} + 1 \right] - \frac{V_0 B_0}{B'_0 - 1} \quad (6.3) \]

where, \( V \) is the volume, and \( B_0 \) and \( B'_0 \) denote the bulk modulus and its pressure derivative at the equilibrium volume \( V_0 \).

While results from the Murnaghan model agree well with the data obtained at low pressures and low compressions (upto 10 %), they deviate from the high pressure ones [261]. The Murnaghan EOS is based on the empirical data and it does not include non-linear pressure contributions. When deriving the Murnaghan EOS, it is assumed that the bulk modulus is a linear function of pressure, \( i.e., K = K_0 + P K'_0 \) [264].

### 6.2.4 Birch-Murnaghan EOS

This model is based on the pressure expansion of the bulk modulus and finite strain theory, and consequently, it is valid only at moderate compression [270]. This model assumes Eulerian strains under hydrostatic compression. This EOS is continuously differentiable and higher-order terms of the Taylor expansion are negligible. The Birch-Murnaghan EOS model is the most used EOS model in Earth physics. The model for the second order is shown below.

\[ E(\eta) = E_0 + \frac{9B_0 V_0}{16} (\eta^2 - 1)^2 \left( 6 + B'_0 (\eta^2 - 1) - 4\eta^2 \right) \quad (6.4) \]

where, \( \eta = (V/V_0)^{1/3} \) and \( V_0, B_0, B'_0 \) and \( E_0 \) the total energy at zero pressure are the fitting parameters. \( B_0, B'_0 \) are the bulk modulus at zero pressure and its pressure derivative, respectively.

An improvement of the Birch-Murnaghan model from other models is the inclusion of the third-order strain components [263].

Initially, a text file with two columns containing volume and energy or volume and pressure, respectively, should be passed into MechElastic. With this, an initial second order parabolic numpy [275] polyfit is performed to obtain the initial fitting parameters, \( E_0 \) or \( P_0 \), \( B_0 \), \( B'_0 \) and \( V_0 \). Afterwards,
a more accurate fitting for the energy or pressure is performed using the least square method in scipy [276] against each EOS model. A central-difference scheme is used to obtain the pressure from this fitted energy. If pressure is to be obtained from energy, an integrating scheme is used instead. Finally, a plot of ‘Energy vs. Volume’ and ‘Pressure vs. Volume’ is obtained, as shown in Fig. 6.1, comparing the values obtained from the different EOS models with the originally provided raw data. With these plots, an analysis of the phase boundaries could be performed. A range of initial and final values for the volume can be set with the vlim parameter and if not given, the minimum and maximum would be calculated from the provided dataset. A desired model can be provided with the model parameter and if not specified, the calculation would be performed against all the available models.

<table>
<thead>
<tr>
<th>Fitting coefficients [E0 (eV), B0 (GPa), Bp (GPa), V0 (Anstroms^3)] along with Mean Squared Error (MSE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vinet : [-67.074 0.259 8.232 297.941]</td>
</tr>
<tr>
<td>Vinet (MSE) : 8.377e-06</td>
</tr>
<tr>
<td>Birch : [-67.075 0.251 8.939 298.112]</td>
</tr>
<tr>
<td>Birch (MSE) : 6.999e-06</td>
</tr>
<tr>
<td>Murnaghan : [-67.074 0.278 6.698 297.574]</td>
</tr>
<tr>
<td>Murnaghan (MSE) : 1.385e-05</td>
</tr>
<tr>
<td>Birch-Murnaghan : [-67.076 0.128 -28.930 301.014]</td>
</tr>
<tr>
<td>Birch-Murnaghan (MSE) : 4.219e-07</td>
</tr>
</tbody>
</table>

Based on MSE Birch-Murnaghan is the best EOS model for this dataset

Figure 6.2: The output of an EOS analysis with MechElastic. MechElastic also prints the best EOS model to use for the provided dataset. The EOS fitting was performed for the Td-MoTe2 dataset, as shown in Figure 6.1.

In addition to the fitting, MechElastic also performs a regression analysis for fitting using the Mean-Squared Error (MSE) of the residuals. This allows users to decide the best EOS model to use for their dataset. A sample output of the EOS analysis is shown in Fig. 6.2, which displays the fitting coefficients, E0, B0, Bp, and V0 along with the Mean-Squared Error (MSE) of the residuals for each EOS model.
Implementation of the Equation of State module in MechElastic

Usage:

```python
from mechelastic import EOS
eos_object = EOS()

eos_object.plot_eos('energyvsvolume.dat', eostype='energy', natoms=1, au=False)
```

*energyvsvolume.dat* is a text file with volume as the first column and energy as the second. *eostype* is set to *energy* for this case. If pressure and volume data is provided, *eostype* is set to *pressure* instead. *natoms* is the number of atoms in the structure and is used to output the quantities per atom. Setting *au=True* sets the units in Ha while it is in eV when False.

### 6.2.5 Enthalpy Curves

Enthalpy \((H)\) is defined as the sum of a system’s internal energy \((U)\) and the product of its pressure \((P)\) and volume \((V)\), \(i.e.,\)

\[
H = U + PV. \tag{6.5}
\]

It is a measure of a system’s capacity to do non-mechanical work and the ability to release heat. MechElastic’s EOS analysing tool is equipped with a function to calculate the ‘Enthalpy vs. Pressure’ curves provided the energy. Pressure is calculated from the ‘Energy vs. Volume’ data using a central-difference scheme, similar to the one mentioned in the previous section. MechElastic first automatically detects the suitable EOS model for the fitting for each phase, and then it calculates the pressure for corresponding energy values. The *plot_enthalpy_curves* method implemented within MechElastic plots the ‘Enthalpy vs. Pressure’ curves for multiple datasets of different phases and determines the phase-transition pressure by identifying the intersection points among the curves. The volume ranges are to be set individually for each phase, using the *vlim_list* option. This is a list that contains elements of the minimum and maximum value of volume for each phase. Care must be given while selecting the volume ranges, as different models are sensitive to different volume ranges for each phase, and it may produce erroneous results if *vlim_list* exceeds the valid volume range. If not provided MechElastic will determine the best volume ranges based on the
input data.

The ‘Enthalpy vs. Pressure’ curves for five different phases of bismuth are plotted in Figure 6.3. The data used in these calculations were obtained using the VASP code with the PBE exchange-correlation functional. An energy cutoff of 350 eV was employed together with k-grids of size $6 \times 6 \times 12$, $5 \times 5 \times 10$, $12 \times 12 \times 12$, $14 \times 14 \times 14$, and $10 \times 10 \times 4$ for phases $C2/m$, $I4/mcm$, $Im\bar{3}m$, $Pm\bar{3}m$, and $R\bar{3}m$, respectively. Additionally, the phase-transition pressures and their corresponding enthalpies were calculated for all the intersections among the ‘Enthalpy vs. Pressure’ curves for different phases. This is particularly helpful in identifying phase boundaries and the potential phase transitions. The output of this calculation is shown in Figure 6.4. The transition paths are ordered with ascending enthalpy. This means that the first transition is energetically the most favorable one and the last transition is the least favorable. This is further elucidated in Figure 6.5, where a network plot is presented with a color bar depicting the relative energetics of different phase transition paths. Furthermore, the enthalpy differences with respect to a certain phase can be plotted with `deltaH_index=<phase_index>`, where `phase_index` is the index of the file corresponding to the baseline phase.

**Usage:**

```python
from mechelastic import EOS
eos_object = EOS()
inf files = ['R−3m', 'Pm−3m', 'Im−3m', 'I4_mcm', 'C2_m']
natoms = [6, 1, 2, 9, 4]
eos_object.plot_enthalpy_curves(infiles, natoms, au=False)
# set au=True to convert units from eV to Ha.
```

6.3 Conclusion

In this chapter we focused on the Equation of State (EOS) module in MechElastic. We discussed its features including obtaining Energy vs. Volume, Pressure vs. Volume, and Enthalpy vs. Pressure curves through an automated process using a variety of EOS models such as Vinet, Murnaghan, Birch, and Birch-Murnaghan. We also showed the automatic phase transition detec-
Figure 6.3: Enthalpy variation with pressure for five different phases of Bi as calculated using the `plot_enthalpy_curves` function.

Figure 6.4: Possible phase transitions of Bi as calculated using the `plot_enthalpy_curves` function.

The top most transition has the lowest enthalpy, hence it is energetically the most favorable phase transition.
Figure 6.5: A network plot of the phase transition paths for different phases of Bi. The color of the arrows represents the relative enthalpy for different phase transitions.

A distinctive feature which could be beneficial for detecting potential phase transitions in high-throughput material calculations.
Part III

Applications
Chapter 7

Stability and diffusion of oxygen vacancies in LaNiO$_3$: a DMFT study

This chapter focuses our study of the stability and diffusion of oxygen vacancies in the correlated rare-earth nickelate perovskite LaNiO$_3$. Here, we noticed that introducing oxygen vacancies drive a metal-to-insulator transition based on the geometry of the vacancy environment, which is also consistent with experiments. We also calculated the energy barrier of oxygen vacancy diffusion and noticed the difference of the energy barrier profile between DFT+U and DMFT. This chapter is based on the article being submitted to Phys. Rev. B. titled, Herath U. et al., Stability and diffusion of oxygen vacancies in LaNiO$_3$: a DMFT study.

7.1 Introduction

The metal to insulator transition (MIT) is an intriguing phenomena in material science which is still not quite well understood [277, 278]. As the name suggests, in a typical MIT there is an abrupt change in the material conductivity as it undergoes a transition from a metallic state to an insulating state. The MIT in a material can be externally stimulated through various means including strain,
doping, and vacancy creation. This transition could be highly useful in a wide range of applications such as switching devices, Field Effect Transistors (FETs) and photonics [279]. As switches operate as states of either binary 1’s or 0’s, this could be manifested as either a metallic or insulating state in a material. By controlling external stimuli, this switch can be turned on or off [280]. As the transition can be made to have hysteresis, it could also be used to contain memory, hence the application in non-volatile switching devices which can find use in fields such as neuromorphic computing [281].

As the transition is affected by numerous degrees of freedom, it is difficult to pinpoint the exact mechanism that is responsible for the transition and requires a deeper theoretical understanding of the phenomena. In general, materials that display MIT reside in a critical quantum point in phase diagrams and with a slight change to their atomic environment, could undergo a metal-to-insulator phase transition. Though many classes of materials exhibit the MIT behavior, rare-earth nickelates (RNiO$_3$) stand out as they are more sensitive to undergo MIT through external stimuli [282, 283]. However, the origins of this transition in these materials are elusive and still require gaps in knowledge to be filled. They can be tunable using external parameters including strain, doping, electric field and temperature. At a critical temperature $T_{MI}$, RNiO$_3$ compounds exhibit an electronic MIT, which also involves a structural transition from $Pbnm$ to monoclinic $P2_1/n$ symmetry [284–286]. Another reason to study oxygen vacancies in materials lies in the fact that unlike pure theoretical calculations, experiments performed in labs will most likely have defects such as vacancies and theoretical studies would have to account for these in order to reproduce experimental observations accurately. Therefore, it is important to gain a clear understanding about such defects in materials in order to control their effects. Among rare-earth nickelates, LaNiO$_3$ portrays remarkable characteristics. This was the only known rare-earth nickelate that is a paramagnetic metal not exhibiting MIT at any temperature in bulk form [287]. However, recent experiments have shown that using single crystal LaNiO$_3$ instead of powdered or polycrystalline samples bring out it to be highly conductive and having magnetic ordering under high oxygen pressures. Beyond the well known paramagnetic phase of LaNiO$_3$ they observed AFM configuration with an ordering temperature of $T_N=157$ K [288]. Additional studies have shown that LaNiO$_3$ thin films and creating defects in LaNiO$_3$ result in MIT in room temperature [289]. Defects could be introduced through multiple means such as lattice distortion, doping or creating vacancies. Through oxygen vacancies,
excess electrons are released into the environment and based on whether the material is p-type or n-type oxide it may drive a metal-to-insulator transition by reducing the hole concentration or a insulator-to-metal transition by increasing the electron concentration, respectively, at a quantum critical point. As rare-earth metals are becoming a center of attention for renewable energy applications, investigating the effect of oxygen vacancies on their electronic properties would be a timely study.

Nickelates consist of a NiO$_6^{3-}$ octahedra linked at their corners with R$^{3+}$ cations, in our case La$^{+3}$, which can be deformed through external stimuli which affect the conductivity among other properties (Fig. 7.1). Due to the rotations of the octahedra, the Ni-O-Ni bond lengths vary from their original 180° bond angle. The phase transitions occur primarily due to the interaction between the Ni-3d and O-2p electrons which is further elucidated from their density of state (DOS) plots which display strong hybridization between these orbitals [284]. Applications of LaNiO$_3$ include ferro-electric capacitors and non-volatile memory [290]. Although there have been studies of oxygen vacancies performed using DFT and DFT+U, using DMFT to investigate them are rare.

Although, Density Functional Theory (DFT) [2, 291] is successful in treating weakly correlated materials, due to the interplay between d and f electrons, a more accurate theory is required to properly capture the physics in such materials. This is because the exchange-correlational term (XC) used in Kohn-Sham DFT uses an static approximation to compensate for the correlation effects arising from these localized orbitals. As an alternative, Dynamical Mean Field Theory (DMFT) [6, 8] is a method which is now gaining popularity due to its success for studying strongly correlated materials. Effects of oxygen vacancies have been studied using DMFT previously, albeit in rare occasions, in materials such as SrTiO$_3$ and several RNiO$_3$ [292–295], however our study focuses on a more intricate and systematic approach to generate and investigate the effects of vacancies. Using DMFT to probe for the MIT would shed more light on its elusive behaviour as it captures the dynamics of the electronic correlations which goes beyond the static limitation of DFT or DFT+U methods.

In addition to the general electronic properties study of oxygen vacancies in LaNiO$_3$, we also perform Nudged Elastic Band (NEB) calculation to investigate the energy barrier of a single oxygen vacancy
diffusion as there is no such study that has done prior to our study. Energy barrier studies are used in a variety of fields, for instance, to study the energy barrier of Li ion diffusion in battery materials which lead to igniting fire in mobile phone, automobile etc. batteries [296]. By gaining sufficient knowledge on the diffusion of Li, such troubles could be avoided. In the scope of this work, oxygen vacancy in diffusion could be use in applications related to ultra-fast switching devices. In this paper, we discuss the MIT of LaNiO$_3$ studies with DFT, DFT+U and DFT+DMFT using our DMFTwDFT code [297]. Recently, Liao et al. studied the LaNiO$_{2.5}$ system using DFT+DMFT and interestingly, the authors revealed that in LaNiO$_{2.5}$, the Ni octahedron site develops a Mott insulating state with strong correlations as the Ni d-$e_g$ orbital is half-filled, while the Ni square-planar site with apical oxygen vacancies becomes a band insulator.[294] However, compared to such previous studies done to study the effects of oxygen vacancies in LaNiO$_3$ [294, 295], we use a slightly different method to generate the oxygen vacancies which is based on Site Occupation Disorder (SOD) [298] such that the complete vacancy configurational space is addressed.

This chapter is organized as follows. We first discuss the computational methodology followed to generate the vacancies and perform the DFT+DMFT calculations for vacancies and vacancy diffusion. Then we discuss the results focusing on stability of each vacancy case and the emergence of metal to insulator transitions. Finally, we discuss about the NEB energy barriers for both symmetry conserved and non-symmetry conserved DMFT calculations for different double counting mechanisms.

7.2 Methodology

7.2.1 Oxygen vacancy generation using the site occupation disorder (SOD) method

The number of all possible vacancy configurations in a supercell increases exponentially with the number of created vacancies. Calculating the energetics of such supercell configurations is a highly computationally expensive task, even if it could be technically possible. In order to mitigate this issue, we employed the site occupation disorder method as available through the SOD package [298]. This method reduces the number of site-occupancy configurations by utilizing the crystal symmetry
Stability and diffusion of oxygen vacancies in LaNiO$_3$: a DMFT study

of the lattice. The equivalence between configurations is gauged through *isometric transformations* which are geometric operations including translations, rotations, reflections etc. that keep all the distances and angles constant within the transformed object. Through this transformation, we obtain a *reduced configurational space* containing a significantly smaller sets of configurations compared to those with the total independent configurations.

For this study, we used the primitive 10-atom cell of LaNiO$_3$ with the $R\bar{3}c$ symmetry group in a paramagnetic structure, then generated the pristine supercell of La$_6$Ni$_6$O$_{18}$, which can accommodate different oxygen vacancies. We calculated there to be 1, 8, 28, 100, and 256 different ways of creating the oxygen vacancies for 1, 2, 3, 4 and 5 vacancies, respectively, as summarized in Table 7.1. We realized that using the SOD method significantly reduces the configurational space. In this work we limit our electronic structure calculations to 1, 2 and 3 vacancies as the configurational space beyond that rises drastically deeming the calculations to be computationally very expensive to study through DMFT. Fig. 7.1 and Fig. 7.2 show the pristine and vacancy configurations for 1 and 2 vacancies, respectively. The dotted circles represent the generated oxygen vacancy.

Table 7.1: The number of symmetrically possible combinations for different number of vacancies as calculated with the SOD package.

<table>
<thead>
<tr>
<th>Vacancies</th>
<th>Supercell Combinations</th>
<th>Inequivalent Combinations</th>
<th>Formula</th>
<th>Reduced Formula</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
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<td>La$_6$Ni$<em>6$O$</em>{18}$</td>
<td>LaNiO$_3$</td>
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<td>1</td>
<td>1</td>
<td>La$_6$Ni$<em>6$O$</em>{17}$</td>
<td>LaNiO$_2$.83</td>
</tr>
<tr>
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<td>18</td>
<td>1</td>
<td>La$_6$Ni$<em>6$O$</em>{16}$</td>
<td>LaNiO$_2$.66</td>
</tr>
<tr>
<td>2</td>
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<td>8</td>
<td>La$_6$Ni$<em>6$O$</em>{15}$</td>
<td>LaNiO$_2$.5</td>
</tr>
<tr>
<td>3</td>
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<td>28</td>
<td>La$_6$Ni$<em>6$O$</em>{14}$</td>
<td>LaNiO$_2$.33</td>
</tr>
<tr>
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<td>La$_6$Ni$<em>6$O$</em>{13}$</td>
<td>LaNiO$_2$.16</td>
</tr>
<tr>
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<td>252</td>
<td>La$_6$Ni$<em>6$O$</em>{12}$</td>
<td></td>
</tr>
</tbody>
</table>

**7.2.2 DFT+DMFT calculation**

We used the Vienna Ab-initio simulation package (VASP) [69] to perform the DFT calculations in a combination of our in-house DMFTwDFT framework [297] to perform the DMFT calculations.
Figure 7.1: (a) Primitive unit cell of LaNiO$_3$ (b) A single oxygen vacancy of LaNiO$_{2.83}$ is displayed with the dotted circle. La, Ni and O are displayed in green, gray and red, respectively.

For the DFT calculation, we used the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional within the PAW method and a k-point mesh of $8 \times 8 \times 8$ for the pristine structure and $5 \times 5 \times 5$ for all the vacancy structures for the summation over the Gamma centered k-mesh with an energy cut-off of 692 eV. A Gaussian smearing of 0.2 eV was used. The Hubbard parameter was set to $U = 5$ eV and Hund’s coupling was set to $J=1$ eV as obtained from [299] for both DFT+U and DMFT calculations. Although bulk LaNiO$_3$ is known to mostly be paramagnetic, some studies suggest four magnetic configurations namely NM, FM, AFM-I and AFM-II [300] as depicted in Fig. 7.4. Therefore, we have considered the structural relaxation using each of these configurations.

Initially, the structural relaxation (both cell and atoms) was performed on the La$_6$Ni$_6$O$_{18-x}$ ($x = 0, 1, 2, 3$) supercell configurations using DFT and DFT+U such that the force convergence criteria was satisfied at $1 \times 10^{-3}$ eV/ per atom. The conjugate gradient algorithm was used for the relaxation.

The Kohn-Sham wave functions resulting from the DFT calculation were projected onto Maximally
Localized Wannier Functions (MLWF) through the Wannier90 package \cite{301} to construct the correlated subspace for DMFT calculations. From the DFT+U projected DOS, we noticed that there is a strong Ni-d, O-p hybridization within the energy range of -8 eV to 3.5 eV with respect to the Fermi energy level. Therefore, both Ni-d and O-p orbitals were considered in the hybridized Wanner subspace while the Ni-d orbitals are treated as correlated orbitals using DMFT. We used a double counting term $\alpha = 0.2$ eV in the modified Fully localized limit (FLL) limit methods, dc_type = 1, dc_type = 2 and dc_type = 3 as implemented in the DMFTwDFT code \cite{297}. The choice of $\alpha$ is motivated by previous work performed on LaNiO$_3$ by Park et al. \cite{7,67}. More explanations about different double-counting formula are given below.

In pristine LaNiO$_3$, the nominal configuration of Ni-d is $d^7$ with $t_{2g}$ fully filled and $e_g$ bands partially
Figure 7.3: A single configuration of a triple vacancy structures of LaNiO$_{2.5}$. The oxygen vacancy is shown in orange dotted circles. La, Ni and O are represented in green, gray and red, respectively.

filled. The crystal field splitting in a NiO$_6$ octahedron separates the energy level between $e_g$ and $t_{2g}$ orbitals. This is not the case in the vacancy induced cases as the NiO$_6$ octahedron is distorted resulting in a breaking of the symmetry. In principle, all Ni-d orbitals can be non-degenerate under the low-symmetry structure. However, we performed DMFT calculations for both the Ni-d degenerate and non-degenerate cases. The Wannierization was done using a Wannier k-mesh of $24 \times 24 \times 24$. The Wannier Hamiltonian was then mapped onto an impurity model which was solved using the hybridization expansion version of the numerically exact continuous time QMC (CTQMC) method implemented by Haule et al. [302]. We set the temperature for the calculation to be 0.01 eV. 100 one-shot DMFT iterations were run to obtain a decent self-energy convergence, i.e. when the local/lattice self-energy, $\Sigma^{cor}(i\omega)$ approaches the impurity self-energy, $\Sigma^{imp}(i\omega)$. The effective DFT+DMFT energy functional $\Gamma$ can be formulated using the four operators ($\hat{\rho}$, $\hat{V}^{Hxc}$, $\hat{G}^{cor}$, and $\hat{\Sigma}$) as shown in Eq.(2) of Ref. [297]. Here, $\hat{V}$ is the double-counting potential operator along with
Figure 7.4: The magnetic configurations of LaNiO\(_3\). (a) NM, (b) FM, (c) AFM-I and (d) AFM-II used for the initial structural relaxation. Yellow and blue arrows represent spin up and spin down, respectively.

\(E^{DC}\), the double counting energy.

Once the self-consistency conditions are reached, the DFT+DMFT total energy is calculated as Eq. (7.1) from the Free energy functional, \(\Gamma\) in the zero temperature limit.

\[
E = E^{DFT}[\rho] + \frac{1}{N_k} \sum_{i,k} \epsilon_i^k \cdot (n_{ii}^k - f_i^k) + E^{POT} - E^{DC}
\]  

(7.1)

Here, \(E^{DFT}[\rho]\) is the DFT energy calculated with the DFT charge density, \(\epsilon_i^k\) is the DFT KS eigenvalue, \(n_{ii}^k\) is the diagonal of the DMFT occupancy matrix \(n^k\), and \(f_i^k\) is the Fermi function (DFT occupancy matrix) with the KS band \(i\) and the momentum \(k\).

The potential energy \(E^{POT}\) is evaluated through the Luttinger-Ward functional, \(\Phi[G^{cor}]\) is given by the Migdal-Galistkii formula [303].
Here, $E_{\text{pot}}$ is calculated using the Migdal-Galisky formula and one can also obtain it using the direct sampling of CTQMC. We find that both methods produce very similar results.

The double-counting energy term in Eq. (7.1) can be evaluated through multiple means which are implemented in the DMFTwDFT framework. The fully localized limit (FLL) is used widely in DFT+U calculations and is given by,

$$E^{\text{DC}} = \frac{U^2}{2} \cdot N_d \cdot (N_d - 1) - \frac{J}{4} \cdot N_d \cdot (N_d - 2)$$

Previous studies have shown that the conventional double-counting energy is overestimated for the metal-insulator boundary, d-p spectra and energetic compared to experiments [304–310]. Therefore, we have introduced a fine tuning parameter $\alpha$ to improve this through multiple dc types.

- $\text{dc\textunderscore type}=1$:

$$E^{\text{DC}} = \frac{(U - \alpha)}{2} \cdot N_d \cdot (N_d - 1) - \frac{J}{4} \cdot N_d \cdot (N_d - 2)$$

- $\text{dc\textunderscore type}=2$:

$$E^{\text{DC}} = \frac{U}{2} \cdot (N_d - \alpha) \cdot (N_d - \alpha - 1) - \frac{J}{4} \cdot (N_d - \alpha) \cdot (N_d - \alpha - 2)$$

In Eq. (7.4), $E^{\text{DC}}$ is reduced by the lowering of $U$ by $\alpha$ term and in Eq. (7.5) $E^{\text{DC}}$ is reduced by the lowering of $N_d$ by $\alpha$. Setting $\alpha = 0$ recovers the original FLL term in Eq. (7.3). Additionally, we have implemented $\text{dc\textunderscore type}=3$ which uses the nominal occupancy of the correlated orbital, $N_0^d$ [309]. The double-counting potential for this case is given by,

$$V^{\text{DC}} = \frac{U}{2} \cdot N_0^d \cdot (N_0^d - 1) - \frac{J}{4} \cdot N_0^d \cdot (N_0^d - 2)$$

For DMFT post-processing, the self-energies were analytically continued onto the real axis using the maximum entropy method [311] which is essentially $\Sigma(i\omega) \rightarrow \Sigma(\omega)$. This is necessary since CTQMC
samples the self-energy on the imaginary axis. This self-energy was then used to perform further post-processing including calculating the spectral function $A(\omega)$ and DMFT density of states. The spectral function is given in Eq. (B.19).

$$A(\omega) = -\frac{1}{\pi} \ln G(\omega)$$  \hspace{1cm}(7.7)

Here, $G(\omega)$ is the local Green’s function. To obtain the DMFT band structure the Eq. (7.8) was used.

$$A(k, \omega) = -\frac{1}{\pi} \frac{\text{Im } \Sigma(\omega)}{(\omega - \epsilon_k - \text{Re } \Sigma(\omega))^2 + (\text{Im } \Sigma(\omega))^2}$$  \hspace{1cm}(7.8)

Additionally, we calculated the mass renormalization $(m^*/m_0)$ by calculating the inverse of quasi-particle residue $Z$ given by,

$$Z^{-1} = 1 - \left( \frac{\partial \text{Re } \Sigma(\omega)}{\partial \omega} \right)_{\omega=0} = \frac{m^*}{m_0}$$  \hspace{1cm}(7.9)

### 7.2.3 Nudged Elastic Band calculations for single oxygen vacancy diffusion

The NEB method is a popular method for calculating the minimum energy pathways of kinetic processes. In this work we have used NEB through VTST tools [312–314] along with DiSPy [315] to study the energetics involved in oxygen vacancy diffusion for a single oxygen vacancy. A wrapper developed by Romero Group, NEBgen (https://github.com/uthpalaherath/NEBgen) was used to automate the complete process to generate symmetrically unique paths for the single oxygen vacancy system through Distortion Symmetry Method with DiSPy and then run the NEB with VTST Tools. Although, linear interpolation between an initial and final structure (image) provides a decent estimate for the minimum energy pathway, the Distortion Symmetry Method takes into account symmetry-adapted perturbations to systematically lower the initial path symmetry, enabling the exploration of other low-energy pathways that may exist. VTST uses VTST scripts to perform a linear interpolation between the first and last image and performs the NEB calculation with
VASP once the Distortion Symmetry Method is applied to the images with DiSPy. However, with the preliminary calculations we performed, we realized that due to the lower symmetry (P1) of the vacancy structure, the distortion paths generated by DiSPy and VTST were identical. Therefore, we only performed NEB calculations using the linear interpolated path using VTST tools. The following setup for NEB calculations were used. A NEB climbing image algorithm with 7 intermediate images and a spring constant of 5.0 was used. The Force optimizer used was \textit{quick-min} (IOPT=3) with a EDIFFG=-0.05 and 1000 NSW steps. We obtained a NEB force convergence to the order of 1 eV/Å. The NEB was performed with DFT+U. The resulting images (structures) of the NEB path were then used to perform DMFT calculations to obtain the DMFT total energy which was used to generate the DMFT energy profile for the vacancy diffusion.

7.3 Results and Discussion

7.3.1 Structural relaxation

Following the introduction of oxygen vacancies, we performed a structural relaxation as discussed in Sec. 8.2. The relaxations were performed with NM, FM, AFM-I and AFM-II magnetic ordering imposed with an initial magnetic moment of 2 $\mu_B$ on each Ni atom [300]. We also noticed that using a higher initial magnetic moment such as 5 $\mu_B$ resulted in the same ground states.

The total energies of these ground states are shown in Table 7.2. For the single vacancy structure, the AFM-II and FM ordering was found to be the ground state of DFT and DFT+U, respectively. For the double vacancy, the AFM-I state was found to be the lowest energy while with DFT+U it was found to be in FM, similar to the DFT+U ground state of the single vacancy. For the triple vacancy, it was found that the AFM-II phase was the ground state with both DFT and DFT+U. For double and triple vacancies, the total energies were averaged over their number of possible configurations i.e. 8 and 28, respectively. These outcomes are consistent with several experimental and computational studies [294, 316, 317]. Although the magnetic moments after the relation was much lower than their initial value of 2 $\mu_B$, we did not see any consistent pattern of these magnetic moments based on the proximity of their atom to the vacancy site. In the presence of oxygen defects, the possible geometries for the Ni-O bonding environment are shown in Fig. 7.5. For the pristine structure, all
the Ni atoms form a NiO6 octahedra with equal Ni-O bond lengths. Based on the total energies, it was evident that the most stable cases for the oxygen vacant structures were ones that had the most number of square-planar Ni-O geometries (Fig. 7.5(d)). In fact, for the double vacancy case, out of the 8 possible configurations, only one had a square-planar geometry and this configuration had the lowest total energy. For the triple vacancy case, there were 28 possible configurations and the three with the highest number of square-planar geometries (two square-planar (Fig. 7.5(d)) each, along with two octahedra (Fig. 7.5(a)) and two half-octahedra (Fig. 7.5(b)), had the lowest three total energies. The next stable configurations consisted of at most one square-planar geometry with a mixture of octahedra and half-octahedra environments. With this, we could anticipate that the higher number of square-planar geometries in oxygen vacant structures lead to higher stability. This outcome is in consistent with studies done by Refs. [294, 295]. Additionally, configurations containing more quarter-octahedra Fig. 7.5(c) and trigonal-planar Fig. 7.5(e) type geometries have higher ground state energies.

Figure 7.5: The possible Ni-O coordination geometries in LaNiO3. The Ni and oxygen ion are displayed in grey and red, respectively. The coordination numbers for each geometry are given by CN.

For the DMFT calculations following the structural relaxation, we used the optimized NM structures in each case assuming a paramagnetic (PM) configuration to include the dynamical correlation effect. As a final note, we record that the energy difference between the lowest energy state and the highest energy state was $\sim 2.20$ eV, meaning the states are energetically achievable with relatively low energy excitations.
Table 7.2: The total energy of different magnetic configurations for single, double and triple oxygen vacancies with respect to their ground state. The total energy for double and triple vacancies are averaged over their number of different configurations. The initial magnetic moment used for the relaxation was 5 $\mu$B. The U and J values for DFT+U are 5 eV and 1 eV, respectively.

<table>
<thead>
<tr>
<th>Ordering</th>
<th>$\Delta E_{TOT}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1vac</td>
</tr>
<tr>
<td>DFT</td>
<td>DFT+U</td>
</tr>
<tr>
<td>NM</td>
<td>0.0130</td>
</tr>
<tr>
<td>FM</td>
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</tr>
<tr>
<td>AFM-I</td>
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</tr>
<tr>
<td>AFM-II</td>
<td>0</td>
</tr>
</tbody>
</table>

7.3.2 Goldschmidt tolerance factor

The Goldschmidt tolerance factor (t), of a perovskite is given by Eq. (7.10), and is a measure of the stability and distortion of a perovskite [318].

$$t = \frac{r_A + r_O}{\sqrt{2} (r_B + r_O)},$$  \hspace{1cm} (7.10)

where $r_A$, $r_B$, $r_O$ is the radius of the A cation, B cation and oxygen atom, respectively. If t=1 it means the atoms fit perfectly in the given structure. If t>1 it means that the A cation is too large and if t<0.8 it means it is too small to fit in. In both these cases, this mis-fitting causes distortion in the structure in the form of octahedral rotations. Bulk LaNiO$_3$ has a tolerance factor, t=0.97 [319] signalling a decent stability. The Ni-O bond increases when Ni$^{3+}$ goes towards a Ni$^{2+}$ oxidation state decreasing the tolerance factor. The Shannon’s radii, which measures ionic radii for different coordination numbers (CN), for Ni$^{3+}$ and Ni$^{2+}$ are shown in Table 7.3 [320]. Additionally, the larger Ni-O bond narrows the bandwidth of conduction and valence bands. This creates a stronger coulomb repulsion and possibly can lead to a large Mott-Hubbard splitting.
Table 7.3: The Shannon ionic radii of $\text{Ni}^{+2}$ and $\text{Ni}^{+3}$ ions.

<table>
<thead>
<tr>
<th>Ion</th>
<th>CN</th>
<th>Ionic radius (nm)</th>
</tr>
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<tbody>
<tr>
<td>$\text{Ni}^{+2}$</td>
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<td>0.55</td>
</tr>
<tr>
<td></td>
<td>4-SP</td>
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</tr>
<tr>
<td></td>
<td>5</td>
<td>0.63</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>0.69</td>
</tr>
<tr>
<td>$\text{Ni}^{+3}$</td>
<td>6*</td>
<td>0.60</td>
</tr>
</tbody>
</table>

*High-spin state Ref: [320]*

Table 7.4: Calculated value of crystal tolerance factors and bond length between La-O and Ni-O for each vacancy case with DFT and DFT+U is shown. The tolerance factors are only defined for full octahedra environments.

<table>
<thead>
<tr>
<th>Structure</th>
<th>DFT</th>
<th>DFT+U</th>
</tr>
</thead>
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<tr>
<td></td>
<td>$d_{\text{La-O}}$ (Å)</td>
<td>$d_{\text{Ni-O}}$ (Å)</td>
</tr>
<tr>
<td>Pristine</td>
<td>2.58</td>
<td>1.95*</td>
</tr>
<tr>
<td>1vac</td>
<td>2.53</td>
<td>1.97*</td>
</tr>
<tr>
<td>2vac</td>
<td>2.57</td>
<td>1.97b</td>
</tr>
<tr>
<td>3vac</td>
<td>2.60</td>
<td>2.11*</td>
</tr>
</tbody>
</table>

*octahedra  
)b half-octahedra  
)c plane
Our calculations for the tolerance factor for different vacancy cases is summarized in Table 7.4. The ground state magnetic configurations were considered for each vacancy case as calculated in Table 7.2. As in some structures, the octahedra environment is modified, we have included the tolerance factor only for cases where a octahedra is preserved as this is required for its definition. For better accuracy, the values here are averaged over multiple bond lengths of La-O and Ni-O. Our calculated values for the pristine LaNiO$_3$ Ni-O bond length, 1.95 Å and 1.96 Å with DFT and DFT+U, respectively, are consistent with the experimental value of 1.933 Å obtained from neutron diffraction experiments [317]. We also noticed that for the double vacancy case, DFT+U does not result in any configurations with a planar geometry, however, DFT does. The tolerance factor calculated to be 0.93 for both DFT and DFT+U for the pristine LaNiO$_3$ is also similar to the value found by [319].

For the triple vacancy case which corresponds to LaNiO$_{2.5}$ the calculated Ni-O bond length for the full octahedra environment, 2.11 Å, 2.16 Å and the Ni-O bond length for the planar environment, 1.83 Å, 1.84 Å is consistent with their corresponding experimental values obtained by Ref. [316] which are 2.12 Å and 1.91 Å, respectively. According to Table 7.4, we notice that DFT predicts a rather stable tolerance factor with increased number of vacancies, except for the triple vacancy case where it becomes 0.87. On the contrary, tolerance factors calculated by DFT+U show a lowering of values up to the triple vacancy case where the tolerance factor becomes 0.79. This discrepancy between DFT and DFT+U values could possibly be attributed to effects arising from correlations coupled with environment changes due to the creation of vacancies.

### 7.3.3 DMFT density of states

As expected the pristine LaNiO$_3$ was found to be metallic as seen in its spectral function and DMFT DOS depicted by Fig. 7.6. Since the Ni-O octahedral symmetry is conserved in this case, we preserved the Ni-$e_g$ and Ni-$t_{2g}$ degeneracy in the DMFT calculation.

However, due to the breaking of symmetry of the NiO$_6$ octahedra as oxygen vacancies are introduced, the cubic symmetry within Ni-$d$ $e_g$ and $t_{2g}$ manifolds is broken. Therefore, we also performed the calculations using full broken symmetry, i.e. breaking both the Ni atomic and orbital degeneracy. Fig. 7.7 shows the DMFT DOS of the single oxygen vacancy case with broken degeneracy. There is only one symmetrically inequivalent configuration for this case. The Wannier functions for the single
vacancy case compared to the pristine is illustrated in Fig. 1 in the SM. This system is metallic which is the expected behaviour as the oxygen deficiency in LaNiO$_{2.83}$ is not sufficient to drive a metal to insulator transition. Based on work done by Ref. [289, 294] the transition occurs at LaNiO$_{2.5}$. Ni-3 and Ni-6 atoms consist of a half-octahedra environment due to the creation of the vacancy while the rest retain their full-octahedra environments, albeit with slightly different Ni-O bond lengths in contrast to the pristine case.

The breaking of the octahedra environment due to the introduction of an oxygen vacancy has multiple effects on the DOS. Although Ni-1, Ni-2, Ni-4, Ni-5 have their octahedra geometry intact, their Ni-O bond lengths have changed slightly which appears to be the reason why Fig. 7.7 shows slight degeneracy breaking in their DOS. However, in Ni-3 and Ni-6 where the octahedra environment is completely broken and resembles the half-octahedra geometry, the degeneracy breaking is much more evident. Additionally, we see that in this case the peaks of almost all orbitals shift their position above the Fermi level. Moreover, we noticed that in the octahedra preserved cases, Ni d-$e_g$
shows conducting behavior as these orbitals cross the Fermi level, whereas in the octahedra broken environments the DOS shows insulating behavior. Therefore, we may be able to use the stability of the octahedra environment as an indicator of the metallic/insulating behavior of the DOS of those atomic environments.

Figure 7.7: The DMFT PDOS of the symmetry broken Ni-d orbitals for a single oxygen vacancy. The octahedra environment of Ni-1, Ni-2, Ni-4 and Ni-5 are preserved while it is broke in Ni-3 and Ni-6. The latter shows insulating behavior while the former shows metallic given the Ni d-\(e_g\) orbitals cross the Fermi level.

The density of states for all of the 8 configurations of the double vacancy case (LaNiO\(_{2.66}\)) was found to be metallic for \(U=5\) eV. This also is in agreement with previous work [289, 294]. Increasing the \(U\) value may induce a MIT due to the increase of Coulomb repulsion, however since the \(U\) value reported for LaNiO\(_3\) was 5 eV, we only investigated the effects keeping it constant.

However, the DMFT DOS for the triple vacancy case is a bit more interesting as the metallic/insulating behavior varies with the configuration. Our DFT calculations showed all the configurations to be metallic which is possibly due to the failure in the XC functionals to account for correlation effects properly. Using DFT+DMFT, however, 57.1% of the configurations showed metallic behavior.
while the rest were insulating. The lowest energy configuration for both DFT+U and DMFT was insulating, agreeing with previous studies. For the metallic configurations we were interested in calculating the effective mass enhancement \((m^*/m)\). The reason this is calculated only for the metallic case is because quasi-particle residue is not defined for insulators. The calculated values are shown in Fig. 7.8. The DMFT calculations were performed with broken d orbital and Ni atom degeneracy. The x-axis corresponds to the configuration and the y-axis corresponds to the effective mass enhancement. (a), (b), (c), (d) and (e) correspond to octahedra, half-octahedra, quarter-octahedra, square-planar and trigonal-planar, respectively, as shown in Fig. 7.5. In some configurations not all geometries were found, which is the reason for the configuration axis to be different.

Figure 7.8: The effective mass enhancement \((m^*/m)\) of Ni d orbitals for the 3 vacancy configurations that showed metallic behavior from their total DMFT DOS. The x-axis corresponds to the configuration and the y-axis corresponds to the effective mass enhancement. (a), (b), (c), (d) and (e) correspond to octahedra, half-octahedra, quarter-octahedra, square-planar and trigonal-planar, respectively, as shown in Fig. 7.5. Here, we performed the DMFT calculations with broken d orbital and Ni atom degeneracy. Note that the effective mass enhancement of only those d-orbitals are shown, which shows a metallic solution. In some configurations not all geometries were found, which is the reason for the configuration axis to be different for each of the geometry environments.
From Fig. 7.8 we see that the octahedra environment is the most prevalent among the metallic configurations, while the trigonal-planar had only 4 metallic configurations. We also noticed that the Ni $d-x^2 - y^2$ showed high effective mass enhancements in most of these metallic configurations closely followed by Ni $d-z^2$.

To explore along this avenue further, we also plot the imaginary part of the self-energy, $\text{Im} \Sigma(i\omega)$ along with the corresponding DOS for an insulating configuration from of the triple vacancy structures.

![Image of DOS and Imaginary Part of Self-Energy](image)

Figure 7.9: The DMFT DOS (top) and imaginary part of self-energy (bottom) for an insulating configuration for the triple vacancy structure. The plots are done for each available Ni-O manifold for the configuration.

Fig. 7.9(top) shows a wide band-gap DOS and Fig. 7.9(bottom) shows the $\text{Im} \Sigma(i\omega)$ for the Ni orbitals. At $\omega = 0$ traces of strong correlations leading to a Mott insulating behavior are seen in the $e_g$ orbitals of Ni-octahedra, $e_g$, $xz$, $yz$ orbitals in the Ni-half octahedra and all the orbitals in the Ni-quarter octahedra environments. In the former, $t_{2g}$ orbitals behave as a band insulator while in the second only the $xy$ orbital retains this band insulating nature.
7.3.4 Effect of correlations on single oxygen vacancy diffusion

In this section we discuss the Nudged Elastic Bands (NEB) [312, 314] calculations performed to calculate the energy barrier of a single oxygen vacancy diffusion in LaNiO$_3$. Although, vacancy diffusion could have been studied for a higher number of vacancies, for this study we only limited it to a single vacancy case as increasing the number of vacancies renders a very complex diffusion problem. We use DFT+U for the initial step of the NEB calculation. As the lowest energy for a single oxygen vacancy takes the FM magnetic configuration as we showed in Table 7.2 for DFT+U we use that here for both the initial and final states of the NEB path.

Our initial methodology intended to use DiSPy [315] to generate a path for the NEB calculation based on irreducible distortion symmetry, however, we noticed that the linear interpolated path between the end-points created by VTST Tools [313] is identical to the path generated by DiSPy due to the lack of symmetry in the oxygen vacant structure.

Next we performed the Nudged Elastic Band calculation with VTST Tools [313] along the generated path as outlined in Sec. 8.2. Once the NEB energy profile using DFT+U was obtained, we used the intermediate structures along the path to perform the subsequent DFT+DMFT calculation. The parameters used for the DFT+DMFT calculation was the same as in the previous section. The DMFT calculation here was done by keeping the Ni d orbital symmetry preserved. The resulting energy profile consisting of both DFT+U and DFT+DMFT energies is shown in Fig. 7.10 along with key intermediate images as insets. The calculated energy barrier with DFT+U was found to be $\sim 0.75$ eV. The DMFT energy barrier was found to be 0.6 eV per atom and 0.58 eV per atom, calculated from the Migdal-Galistkii and CTQMC sampling methods, respectively using dc_type 1. Malashevich et al. performed a NEB calculation for single oxygen vacancy diffusion using LDA for a 79-atom supercell and found the energy barrier height to be 1.24 eV [295]. In our study, the higher energy of the barrier height obtained with DMFT is possibly due to the extra energy required for the quantum fluctuations of electrons which are captured by DMFT unlike static mean field theories. However, if we used DMFT forces for the NEB instead of performing DMFT calculations with the images retrieved from the DFT+U NEB, this energy may have been lowered.
We used two different methods to calculate the DMFT total energy, namely, Migdal-Galistkii [303] and CTQMC sampling, which seems to have similar energy profiles, except, the former method has a higher energy end state. The magenta circle in the inset represents the migration of the oxygen vacancy throughout the energy profile.

![DFT+U vs. DMFT energy barrier for single OV diffusion in LaNiO\textsubscript{3}](image)

**Figure 7.10:** Minimized NEB for a single oxygen vacancy diffusion in LaNiO\textsubscript{3} calculated with DFT+U and degenerate DMFT using dc\_type 1.

However, one limitation of this case is the fact that we have performed the DMFT calculations imposing the $e_g$ and $t_{2g}$ degeneracy. To explore if this is the case we extended our DFT+DMFT calculations along the NEB path with broken degeneracy, that is to say all the d orbitals have broken symmetry for each of the 6 Ni atoms, which are also considered to be degenerate. The resulting DOS for each intermediate image is shown in Fig. 7.11 for the image #5 in the energy profile.

Here we notice that for Ni-2, Ni-4 and Ni-5 atoms there is a gap opening. This is in contrast with
Figure 7.11: The DMFT PDOS of the LaNiO$_3$ NEB by breaking the degeneracy of d orbitals for each Ni atom. The DOS here are shown for image #5. dc$_{\text{type}}$ 1 was used for the DMFT calculation.

the degenerate DMFT calculations performed previously. Although, we do not display it here, some configurations display complete metallic behavior for all the atoms and their orbitals. However, we are more interested in the collective conductive properties which dictate the macroscopic properties. Therefore, we sum the contributions of each orbital for all the Ni atoms and plot the total DOS for each of the images as shown in Fig. 7.12 using both DFT+U and DMFT NEB results.

Here, we don’t notice obvious gap openings as we did for individual Ni atoms, previously. However, we do note that the conductivity appears to differ for each image along the NEB path also depending on DFT+U and DMFT DOS variations. We notice that all the DFT+U DOS are lower than the DMFT DOS except for image #3, which DMFT predicts to be rather insulating. This makes it evident that the system changes conductivity along the vacancy diffusion path.

The outcomes of DMFT calculations depend significantly on the double counting method used. For the NEB DMFT calculations thus far in this section, we have been using the dc$_{\text{type}}$ 1 as available through the DMFTwDFT framework and calculated by Eq. (7.4). Next we calculated the DMFT
Figure 7.12: The DMFT total DOS of all d orbitals of each Ni atoms for non-degenerate DMFT calculation for the NEB path. \texttt{dc\_type 1} was used for the DMFT calculation.

NEB for the non-degenerate case using different double counting methods. The resulting energy profile comparison is shown in Fig. 7.13. The CTQMC sampling DMFT energy was used for this case.

There seems to be drastic differences between the preserving degeneracy (Fig. 7.10) and breaking it (Fig. 7.13). In general the non-degenerate curve for \texttt{dc\_type 3} calculated with ctqmc sampling is lower in energy. It is lower in energy than the degenerate DMFT curve for the whole profile, but with respect to DFT+U, it is only lower until image #6. Between the initial state and the 4th image, the non-degenerate DMFT curve has negative energies suggesting the diffusion in this region to occur.
Stability and diffusion of oxygen vacancies in LaNiO$_3$: a DMFT study

Figure 7.13: The NEB based on double counting type used for the DMFT calculation. The energies are obtained from non-degenerate DMFT calculations and only considering the ctqmc sampling energies. The dc_type 1, dc_type 2 and dc_type 3 are represented in blue, red and yellow curves, respectively.

spontaneously. The reason for the non-degenerate DMFT curve to be lower in energy might be due to the fact that when the symmetry is broken it gives rise to higher degrees of freedom lowering the energy. There appears to be two peaks along this path, the first being around image #4 with a height of $\sim 0.8$ eV and the second being around image #7 with a height of $\sim 1.0$ eV with respect to the lowest point of the profile. These values are lower than that of the degenerate DMFT value, 1.4 eV.

The energy for dc_type 1 and dc_type 2 are calculated within DMFT using Eq. (7.4) and Eq. (7.5), respectively. Fig. 7.13 shows that dc_type 1 and dc_type 2 are almost identical and has a higher
energy than that of \texttt{dc\_type 3} along the NEB path at any point. \texttt{dc\_type 1} and \texttt{dc\_type 2} energy profiles do not result in negative energies as much as \texttt{dc\_type 3} does. This suggests that the initial and final states of the path calculated with \texttt{dc\_type 3} is unlikely.

Therefore, we can discard \texttt{dc\_type 3} for this calculation and only focus on \texttt{dc\_type 1} and \texttt{dc\_type 2}. Comparing with the DFT+U profile, the profile of \texttt{dc\_type 1} and \texttt{dc\_type 2} has its highest peak around image #4 of around \(\sim 0.52\) eV and a secondary peak at image #7 of \(\sim 0.35\) eV, whereas the DFT+U profile has its primary peak which is the highest around image #5 of 0.74 eV and the lower secondary peak between images #7 and #8 of 0.3 eV which is lower than the DMFT values. A summary of the comparison of barrier height’s of the primary peaks of DFT+U and DMFT energy profiles with Ni-d orbital degeneracy breaking is presented in Table 7.5.

Further, we decomposed the DMFT total energy to potential energy and kinetic energy terms as shown in Fig. 7.14. In the images where potential energy dominates, the electrons are more localized. The DMFT kinetic energy (KE) and DMFT potential energy (PE) displayed here are independent of the double counting method used. Therefore, this plot could be used to isolate the effects of the double counting type. The total energy is calculated as a function of KE and PE along with an added term for double counting correction and from the figure we can see how this changes the energy profile with the dc type used. This further establishes that effects of \texttt{dc\_type 1} and \texttt{dc\_type 2} are almost identical, but \texttt{dc\_type 3} is significantly different. For the barrier height changes with respect to double counting type, please refer to the SM.

Additionally, the variation of KE and PE along the diffusion path is a signature of changes to the itinerant and localization behavior throughout the diffusion process.

7.4 Conclusions

Introducing oxygen vacancies in LaNiO\(_3\) transforms the system from metal to insulator at sufficient U and based on the vacancy configuration. We noted that for single and double vacancy, all configurations resulted in metallic behavior which is consistent with previous studies. However, for triple vacancy case, we noticed that the metallic/insulating behavior varies depending on the configuration. Based on the coordination geometry of the vacancy structures, the stability of the system can
Figure 7.14: The total DMFT energy decomposition for the NEB path. dc_type 1 and dc_type 2 are displayed here in solid and dotted lines, respectively.

Table 7.5: The barrier height’s of the primary peaks of DFT+U and DMFT energy profiles for broken Ni orbital degeneracy. The DMFT total energy is computing using Migdal-Galistkii and CTQMC sampling methods. Note, we use the dc_type 1 and dc_type 2.

<table>
<thead>
<tr>
<th>DFT+U</th>
<th>Barrier Height (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DMFT (MG)</td>
</tr>
<tr>
<td>0.75</td>
<td>0.40</td>
</tr>
</tbody>
</table>
be gauged.

We also performed NEB for a single oxygen vacancy diffusion and realized that the DMFT energy profile is much higher in energy than that of DFT+U when enforcing $e_g$ and $t_{2g}$ degeneracy. This is mostly due to the quantum fluctuations arising from the correlation effects that is not well addressed within DFT+U. Once the degeneracy was broken, the barrier heights were lowered significantly, more-so than that of DFT+U. This was a possible cause of increasing the degrees of freedom as degeneracy is broken. We demonstrated the effect of double counting types to the energy profile and realized `dc_type 3` did not show realistic outcomes regarding its energy profile. We also noticed that along the vacancy diffusion path, the conductivity of the system changes in addition to the localized/itinerant behaviour displayed from the KE/PE profiles. This could be used as applications in switching devices. Although, vacancy diffusion could have been studied for a higher number of vacancies, for this study we only limited it to a single vacancy case as increasing the number of vacancies renders a very complex diffusion problem.
A DMFT study of strongly correlated alloys

This chapter focuses our on-going study of strongly correlated alloys. We use two different methods, namely Virtual Crystal Approximation (VCA) and Site Occupation Disorder (SOD) in combination with DFT+DMFT to study the correlated alloy \( \text{Nd}_{1-x}\text{La}_x\text{NiO}_3 \). A main goal of the study was to verify if the VCA method could be used in place of the computationally expensive supercell method to study alloys. Following this verification, we continue to use the method to study additional systems of correlated alloys. It is in preparation to be submitted to Phys. Rev. B.

8.1 Introduction

Throughout history, alloying has been used by humans to improve materials including their strength and conductivity. For instance, the alloying of bronze predates back to 3000 BC [321]. In modern times, alloyed materials are used in a wide range of applications ranging from the automobile industry to thermo-electrics [322]. Additionally, real materials perfect periodicity is hard to achieve thus
A DMFT study of strongly correlated alloys requires a better understanding in implementing methods to study disordered systems in theoretical calculations [323].

In correlated materials, the metal-to-insulator transition is a phenomena that can be driven by various external stimuli. This leads to potential applications in electrode devices, thermal sensors, switches and gas sensors [324]. Recent studies have shown that doping elements into these materials have successfully instigated these phase transitions. More specifically, rare-earth nickelate perovskites (RNiO$_3$) are known for exhibiting metal-to-insulator transitions driven by external stimuli. For instance, Sanchez et al. carried out electrical resistivity measurements showing doping Eu in correlated LaNiO$_3$ opens a band gap as the Eu concentration increases [325].

There are two major bottlenecks in studying doping effects in correlated materials. (1). In order to study doping, the most popular method is the supercell approach which is computationally very expensive. (2). Correlated materials require beyond-DFT methods to be studied properly as the XC functional in DFT does not properly address the correlation effects. The combined bottleneck effect of these to factors motivate a proper method to study doping in such materials without requiring heavy computation.

In this study we investigate the usage of Virtual Crystal Approximation (VCA) in a combination with DFT+DMFT to study correlated materials. To verify the accuracy of the method, we compare the results to a modified supercell method, Site Occupation Disorder (SOD) [298] which uses symmetry to reduce the configurational space of supercells required. The material we base this study on is Nd doped LaNiO$_3$, i.e. $Nd_{1-x}La_xNiO_3$ by varying $x=0.0$ to $x=1.0$.

### 8.2 Methodology

We used the Vienna Ab-initio simulation package (VASP) [69] to perform the DFT calculations in a combination of our in-house DMFTwDFT framework [297] to perform the DMFT calculations. Here we discuss the two different approaches used to study the doping effects in $Nd_{1-x}La_xNiO_3$.

In both cases, once the structures were generated an atomic relaxation was performed DFT such that the force convergence criteria was satisfied at $1 \times 10^{-3}$ eV/ per atom. The conjugate gradient
algorithm was used for the relaxation.

For the DFT calculation, we used the Perdue-Burke-Ernzerhof (PBE) exchange-correlation functional within the PAW method and a k-point mesh of $7 \times 7 \times 7$ for VCA and $7 \times 7 \times 1$ for SOD for the summation over the Gamma centered k-mesh with an energy cut-off of 692 eV. A Gaussian smearing of 0.2 eV was used. The Hubbard parameter was set to $U = 5$ eV and Hund’s coupling was set to $J = 1$ eV as obtained from [299] for both DFT+U and DMFT calculations.

The Kohn-Sham wave functions resulting from the DFT calculation were projected onto Maximally Localized Wannier Functions (MLWF) through the Wannier90 package [301] to construct the correlated subspace for DMFT calculations. From the DFT+U projected DOS, we noticed that there is a strong Ni-d, O-p hybridization within the energy range of -8 eV to 3.5 eV with respect to the Fermi energy level. Therefore, both Ni-d and O-p orbitals are considered in the hybridized Wannier subspace while the Ni-d orbitals are treated as correlated orbitals using DMFT. We used a double counting term $\alpha = 0.2$ eV in the modified FLL limit methods, dc_type = 1 as implemented in the DMFTwDFT code [297].

In pristine LaNiO$_3$, the nominal configuration of Ni-d is $d^7$ with $t_{2g}$ fully filled and $e_g$ bands partially filled. The crystal field splitting in a NiO$_6$ octahedron separates the energy level between $e_g$ and $t_{2g}$ orbitals. This is not the case in the vacancy induced cases as the NiO$_6$ octahedron is distorted resulting in a breaking of the symmetry. In principle, all Ni-d orbitals can be non-degenerate under the low-symmetry structure. However, we performed DMFT calculations for both the Ni-d degenerate and non-degenerate cases. The Wannierization was done using a Wannier k-mesh of $24 \times 24 \times 24$. The Wannier Hamiltonian was then mapped onto an impurity model which was solved using the hybridization expansion version of the numerically exact continuous time QMC (CTQMC) method implemented by Haule et al. [302]. We set the temperature for the calculation to be 0.01 eV. 100 one-shot DMFT iterations were run to obtain a decent self-energy convergence, i.e. when the local/lattice self-energy, $\Sigma^{cor}(i\omega)$ approaches the impurity self-energy, $\Sigma^{imp}(i\omega)$. The effective DFT+DMFT energy functional $\Gamma$ can be formulated using the four operators ($\hat{\rho}$, $\hat{V}^{Hxc}$, $\hat{G}^{cor}$, and $\hat{\Sigma}$) as shown in Eq.(2) of Ref. [297]. Here, $\hat{V}$ is the double-counting potential operator along with $E^{DC}$, the double counting energy. Once DMFT convergence is reached, we calculate the spectral
function $A(\omega)$.

### 8.2.1 Virtual Crystal Approximation

The Virtual Crystal Approximation (VCA) [146] is a method to study alloying in materials by creating a pseudo atom or a “ghost” atom that comprises characteristics coming from multiple atoms. In this work, we discuss our methodology to employ Virtual Crystal Approximation (VCA) with DMFT to study strongly correlated alloys and disordered systems for investigating the realistic defect physics in correlated materials, that can be naturally occurring via doping or through intrinsic (point) defects. Even though it has been used with DFT, VCA within DMFT has not yet been studied widely. We have performed DFT+DMFT calculations for $Nd_{1-x}La_xNiO_3$ using our in-house DMFTwDFT code, where we doped the La atom with different concentrations of Nd.

For VCA+DMFT calculations, the electronic structure calculations were performed with VASP and DMFTwDFT along with wannier90. To verify if the VCA method does the projection onto the correlated space correctly, we initially compare the DFT band structures with the wannier90 bands.

### 8.2.2 Site Occupation Disorder

To compare our VCA results with the more precise supercell method, we use the modified supercell method SOD which reduces the number of site-occupancy configurations by utilizing the crystal symmetry of the lattice. The equivalence between configurations is gauged through isometric transformations which are geometric operations including translations, rotations, reflections etc. that keep all the distances and angles constant within the transformed object. Through this transformation, we obtain a reduced configurational space containing a significantly smaller sets of configurations compared to those with the total independent configurations.

For SOD+DMFT calculations, we created a reduced configurational space of inequivalent 6 supercells out of a 66 super configurational space to mimic 16% Nd doping i.e. $Nd_{0.16}La_{0.84}NiO_3$. Similar to VCA+DMFT, we performed DMFTwDFT calculations for all these structures and averaged the Green’s function $G_{imp}(\omega)$ to obtain an averaged spectral function contributing from all the
supercells.

The complete workflow is illustrated in Fig. 8.1.

Figure 8.1: A schematic diagram displaying the workflow of the VCA and SOD methodology for performing DMFT calculations on strongly correlated alloys.

8.3 Results and Discussion

With VCA, we initially performed DFT calculations followed by wannier90 projection to confirm whether the localization was done properly. This is shown in Fig. 8.2.

The exact overlap of DFT and wannier90 bands verifies that the projection was done properly. We saw that this was the case for the complete range of doping in \( Nd_{1-x}La_xNiO_3 \). This allows us to perform the VCA+DMFT calculations knowing the correlated subspace is properly generated.

Following successful convergence in both VCA+DMFT and SOD+DMFT methods, we compared their spectral functions. The latter required an averaging of the Green’s function as there were multiple supercell calculations performed. The results are shown in Fig. 8.3.

As we see here, the spectral function from the two different method are considerably similar. With
A DMFT study of strongly correlated alloys

Figure 8.2: Comparison of DFT bands with wannier90 bands for Nd$_{0.16}$La$_{0.84}$NiO$_3$ using VCA.

Figure 8.3: The DMFT spectral function of Nd$_{0.16}$La$_{0.84}$NiO$_3$ obtained from VCA+DMFT and SOD+DMFT.
this we can conclude that the two different approaches result in identical outcomes, hence we could replace the supercell method with the more computationally friendly VCA method.

As such, we used VCA+DMFT to study the complete range of stoichiometries for $Nd_{1-x}La_xNiO_3$. The non-degenerate DMFT spectral function this is shown in Fig. 8.4.

From Fig. 8.4 we notice that the doping does not drive a metal to insulator transition, however, it does affect the conductivity. Additionally, the degeneracy of Ni d-$e_g$ orbitals hold while that of the Ni d-$t_{2g}$ is broken. Moreover, we notice that the peaks shift based on the doping percentage which is an interesting observation.

8.4 Conclusions

In this study we verified that the VCA+DMFT method can replace the more computationally expensive supercell method by performing DFT+DMFT calculations on Nd doped LaNiO$_3$. We further noticed that the doping does not drive any metal-to-insulator transition for any doping percentage. To complete this study, we must perform calculations for a variety of strongly correlated alloys which is currently in process.
Figure 8.4: The non-degenerate spectral function for $Nd_{1-x}La_xNiO_3$ with $x$ varying from 0.0 to 1.0 from left to right and downwards.
Chapter 9

Application of DMFT to Neuromorphic Computing devices

This chapter focuses on our on-going project using DMFT for studying devices useful for neuromorphic computing done in collaboration with Dr. Subramanian Sankaranarayanan at Argonne National Laboratory. The goal of the project is to use machine learning methods to train atomic force fields for strongly correlated materials. I performed the DMFT calculations for the materials used to feed the machine learning model.

9.1 Introduction

To overcome limitations in technology, new paradigms must be explored. More recently, neuromorphic computing emulating the neural behavior and response of the human brain has been gaining attention to overcome such limitations [326–328]. We study the potential use of strongly correlated rare-earth nickelates with Metal-to-insulator transitions for neuromorphic applications. These materials that display interesting phenomena such as magnetism, charge and orbital ordering, thermally and doping-induced metal-insulator transitions, are sensitive to a broad set of external stimuli, for
instance, subtle manipulation of the electronic orbital occupancy due to non-degeneracy in the energy levels of the Ni-O framework. The filling-controlled Mott transition is unique in that it is not temperature-constrained unlike thermally-driven phase transitions [329–333]. We forge a deep learning force field by training a neural network with energy, charges, and forces obtained from DMFT through our DMFTwDFT framework. The configurational space is generated from known crystal phases, ab initio molecular dynamics with exchange correlation functionals corrected with the Hubbard model, disordered phases with different concentrations of oxygen vacancies, non-symmetrical positions, and induced strain at grain interfaces or contact with a substrate. Strategies to train the model with a reduced number of training examples are obtained from active learning methods, and new structures for improving the learning process are generated by using machine learning autoencoders. This classical potential is validated through electronic structure methods. Different types of external stimuli are simulated with the developed machine learning potential. Selected configurations are again analyzed with more accurate theories to provide an accurate electronic description and to study how the orbitals and charges are rearranged under different conditions. The outcomes of the project provide a clear understanding of the effect of different external stimuli over the metal to insulator transition of rare earth nickelates and how we can control this transition. This knowledge benefits experimental groups who are designing neurons within novel artificial intelligence devices based on this phenomenon. Controlling the response to external stimuli provides the most considerable plasticity of the designed device. As a starting point for this study, we selected several nickelates RNiO$_3$ (R= La, Sm, Gd, Lu, Nd, Y, Ho) and their alloyed variants for the calculation. Due to the electronic occupation in each of the rare earth considered, it is expected that the classical potential should be different for each case, which means that the training process cannot be generalized to all compounds.

9.2 Methodology

For neuromorphic applications, we performed DMFT total energy calculations using our in-house DMFTwDFT framework for various strongly correlated rare-earth nickelates (RNiO$_3$). Various configurations are generated for each RNiO$_3$, mimicking a Boltzmann distribution under a Debye model at a finite temperature, and the calculated DMFT energies will be used to train an atomic
interaction potential based on artificial neural networks (ANN). Thus far we have carried out DMFT calculations for SmNiO$_3$, and the results demonstrated that we require at least 600 configurations to produce a fair description of the potential energy surface. For the materials SmNiO$_3$ and GdNiO$_3$, we generated 200 configurations with 80 atoms in the unit cells, mimicking Boltzmann distribution for 300K, 500K and 700K temperatures. This gives a total of 600 configurations per each system. For each configuration, we ran DMFT calculations through DMFTwDFT to obtain the total energy. As the purpose of the study is to generate a machine learning potential that is accurate enough to reproduce the different local atomic configurations, we also require configurations under three other conditions: varying the number of oxygen vacancies, proton diffusion, and effect of the substrate, which is simulated by applying different strains on the ab-plane (two compressed and two expansions, reflecting different substrates, close to those used in experiments, but they usually range between 1-3%).

The workflow is illustrated in Fig. 9.1.

![Figure 9.1: The workflow of the methodology to generate force fields using DMFT total energies.](image-url)
9.3 Results and Discussion

As preliminary testing for our neuromorphic computing project we have carried out DMFT calculations to obtain total energies for SmNiO$_3$ and GdNiO$_3$ for a population of 150 and 300 structures mimicking a molecular dynamics simulation at finite temperatures. Using the SmNiO$_3$ DMFT total energy data, we have been able to generate an Active Learning force field based on neural networks and the corresponding correlation plots are shown in Fig. 9.2. The first two graphs correspond to correlation plots generated when the network is trained using 300 configurations (a) and tested for 150 configurations (b), which results in lower value of testing error (3.8meV/atom). However, for the new 150 configurations, the network catastrophically failed with testing error of 1527 meV/atom (Fig. 9.2c). Retraining the network including these new 150 configurations reduces the testing error to 117 meV/atom (Fig. 9.2d). Further including 300 new configurations and retraining the network, reduces the validation error to 26 meV/atom (Fig. 9.2e). This demonstrates that a minimum 600 configurations per system are necessary to correctly describe the potential energy surface of SmNiO$_3$.

We also performed nudged energy band calculations with DFT, DFT+U and DMFT to study the energy profile of a single oxygen vacancy in SmNiO$_3$. The results of this is shown in Fig. 9.3. We note that the energy barrier calculated from DMFT is the highest measuring around 0.032 eV/atom while DFT provides the lowest. This is possibly due to the correlation effects captured in DMFT.

9.4 Conclusion

As this is an ongoing research, we only have preliminary results at the time of writing this dissertation. Our preliminary data showed that the machine learning model trained for SmNiO$_3$ has considerable accuracy and requires more data for both training and validation. We are currently performing DMFT calculations for other rare-earth nickelates including GdNiO$_3$ to obtain a force fields that support a wider range of materials.
Figure 9.2: Correlation plots for SmNiO$_3$ (a) Training using 300 configurations and corresponding testing plots for (b) 150 and (c) new 150 configurations. Testing plots for the network retrained by additionally considering (d) 150 and (e) 300 new configurations.
Figure 9.3: The energy profile of a single oxygen vacancy diffusion in SmNiO$_3$ calculated with NEB using DFT, DFT+U and DMFT.
Part IV

Conclusion
Summary and outlook

In this dissertation, we covered multiple research projects performed for both weakly and strongly correlated materials, mostly focusing on the latter. It was a mixture of both code development work and their applications.

In Chapter 4, we discussed the features of our electronic structure pre and post-processing tool, PyProcar. Currently, it is one of the most popular tools used in the global DFT community with over 150 users registered in the user forum due to its user-friendly nature and rich features. As such, it is gaining momentum and new features are added to it frequently both by the original developers and the user community.

We then explored the features of the DMFTwDFT framework which is also gaining popularity among users interested in studying strongly correlated materials. It was featured in a workshop organized by Oxford University in 2020 and another organized by the Simons Foundation in 2021. Similar to PyProcar, this is also being improved and new features are being added to cater to a wide range of studies performed on correlated systems.

In Chapter 6, we discussed the Equation of State (EOS) module implemented in the MechElastic code and how it could be useful to scientists studying properties such as phase transitions in extreme
conditions. MechElastic hosts a much wider range of features which we did not entertain in this dissertation, but an interested reader is referred to its literature [334].

Next, we discussed about the application side of the methods developed. In Chapter 7 we presented our research on the stability and diffusion of oxygen vacancies in correlated LaNiO$_3$. We showed how the creation of vacancies drive a metal-insulator transition and the differences in DFT+U and DMFT energetics of single oxygen vacancy diffusion. We noticed how correlations can come into play which affect the energy profile. This is a useful study as the MIT in such materials can be used to tailor switching devices and properties in energy storage devices.

We then discussed our on-going work on the proof of concept for replacing computationally expensive supercell calculations of strongly correlated alloys with the more efficient VCA method. Using Nd doped LaNiO$_3$ we showed that the DMFT spectral function from both the VCA and supercell method are almost identical. We then performed a stoichiometric study of the range of Nd$_{1-x}$La$_x$NiO$_3$ and noticed that the Ni d-$e_g$ orbitals preserved degeneracy while Ni d-$t_{2g}$ did not. We concluded that further studies must be performed on a class of correlated alloys to establish additional verification of the method.

Finally, in Chapter 9 we discussed our current progress in the on-going work to generate atomic force fields for correlated materials to study materials useful for neuromorphic computing applications. Our preliminary calculations show that the force field generated for SmNiO$_3$ performs fairly decently. We are currently training the machine learning model with additional correlated rare-earth nickelates including GdNiO$_3$.

Throughout, this dissertation, we have discussed multiple methods both viable to study weakly and strongly correlated materials. One major goal of such code development work was to create user-friendly frameworks that facilitate scientists from different backgrounds to perform electronic structure calculations without advanced technical expertise. To that end we have been successful, judging by the shear number of active users involved in these codes.

Additionally, we also contributed to research done in rare-earth nickelate perovskites to expand its
class of materials studied through proper means by treating correlations more accurately through methods such as DMFT.

Although, DMFT performs quite well, it is computationally expensive compared to standard mean-field methods such as DFT. However, with the advancement of computational technology including quantum computing, this may not be much of an issue in the near future.
Appendix A

MechElastic Elastic Tensor

Enhancements

A.1 Pressure dependence of elastic constants in VASP

Unlike in several other DFT codes such as ABINIT, in VASP the elastic tensor components need to be adjusted for any residual pressure on the cell while performing elastic constants analysis for the case of non-zero hydrostatic pressure [335, 336].

To overcome this issue, hydrostatic pressure (P) is subtracted from the diagonal components ($C_{ii}$) and added to $C_{12}$, $C_{13}$, $C_{23}$, $C_{21}$, $C_{31}$ and $C_{32}$. This is elaborated in the following matrix representation.
\[
\begin{bmatrix}
C_{11} - P & C_{12} + P & C_{13} + P & C_{14} & C_{15} & C_{16} \\
C_{21} + P & C_{22} - P & C_{23} + P & C_{24} & C_{25} & C_{26} \\
C_{31} + P & C_{32} + P & C_{33} - P & C_{34} & C_{35} & C_{36} \\
C_{41} & C_{42} & C_{43} & C_{44} - P & C_{45} & C_{46} \\
C_{51} & C_{52} & C_{53} & C_{54} & C_{55} - P & C_{56} \\
C_{61} & C_{62} & C_{63} & C_{64} & C_{65} & C_{66} - P
\end{bmatrix}
\] (A.1)

By default the pressure correction is enabled if MechElastic detects a non-zero pressure in VASP’s output. However, it could be disabled with the flag `adjust_pressure=False`. 
Angular Resolved Photo-Emission Spectroscopy (ARPES)

B.1 Introduction

Angular Resolved Photo-Emission Spectroscopy (ARPES) is an experimental technique capable of mapping 3-dimensional momentum space and energy in the form of a band structure. ARPES provides experimental observations to theory demonstrating Fermionic quasi-particle behaviour of electrons described by the single-particle spectral function or single-particle Green’s function [337, 338]. By providing energy-momentum maps, ARPES can reveal a plethora of information of a material from electron velocities to Fermi surface geometries; deciphering elusive behaviour of materials including superconductivity and Mott insulators, as depicted in Fig. B.1.

ARPES is based on the underlying theory of the photoelectric effect experimentally observed by Hertz [339] and later formulated by Einstein [340], as a manifestation of the quantum nature of light. In the photoelectric effect, an incident photon’s energy is absorbed by an electron, which, given sufficient energy, escapes from the material. As a spectroscopic tool, ARPES is able to resolve the kinematic information of the photoemission process deducing the binding energy $E_B$ and the
Angular Resolved Photo-Emission Spectroscopy (ARPES)

Figure B.1: Representation of microscopic interactions and their unique signatures in an ARPES spectrum. For independent electrons ARPES provides the band structure of the system. Electron-phonon coupling leads to a “kink” in the band structure broadening the peak width. Electron-electron interactions lead to an energy dependent peak width and renormalization of band velocity. In the presence of spin-orbit coupling spin-degenerate bands can occur. The interplay between such interactions give rise to intriguing physical phenomena such as superconductivity and Mott insulators. Retrieved from Ref. [338].
crystal momentum $\hbar k$ of an electron in a material prior to its escape from the material surface. As shown in Fig. B.2, photons of energy $h\nu$ are absorbed into the material which photoemits electrons into free space where a detector can be used to determine their kinetic energies and emission angles, which provides information of the material from which they came.

Figure B.2: Photons of energy $h\nu$ excite electrons into free space where their kinetic energies and emission angles are used to obtain information of the material they came from. Retrieved from Ref. [338].

The maximum kinetic energy in which these photoelectrons are emitted from the solid is given by,

$$E_{\text{kin}} = h\nu - \phi$$  \hspace{1cm} (B.1)  

where, $\nu$ is the photon frequency, $h$ is Plank’s constant and $\phi$ is the work function of the material which is a measure of the minimum energy required to remove an electron from it. In the following sections, we discuss the theoretical background of ARPES.
B.2 Kinematics of photoemission

If a beam of monochromatic photos of an energy higher than the work function $\phi$ is incident on a material, electrons absorb the photon energy and gain sufficient energy to escape the material surface. By measuring the kinetic energy and momentum of these escaped electrons, one can probe properties of the material that these electrons came from. This information is then used to construct the energy-momentum dispersion relationship which can provide many characteristics of a material.

The momentum of this escaped electron in free space is given by,

$$\vec{K} = \sqrt{\frac{2mE_{\text{kin}}}{\hbar}}$$

where, $m$ is the mass of the electron and $E_{\text{kin}}$ is the kinetic energy of the electron. By taking the surface parallel and perpendicular components of the momentum we can write,

$$\vec{K}_\parallel = \vec{K}_x + \vec{K}_y$$

and

$$\vec{K}_\perp = \vec{K}_z.$$

$K_x$, $K_y$ and $K_z$ components can be written as,

$$K_x = \frac{\sqrt{2mE_{\text{kin}} \sin \theta \cos \varphi}}{\hbar},$$

and

$$K_y = \frac{\sqrt{2mE_{\text{kin}} \sin \theta \sin \varphi}}{\hbar},$$
\[ K_z = \frac{\sqrt{2mE_{\text{kin}}}}{\hbar} \cos \theta. \] (B.7)

\[ E_{\text{kin}}(k) \] represents the dispersion relationship of electrons in free space, however, what we are interested in is the dispersion relationship of electrons inside the material, \( E(k) \).

Due to the translational symmetry in the x-y plane and the absence of a potential in the plane, the electron’s parallel component of the momentum is conserved, i.e.,

\[ k_\parallel = K_\parallel = \left( \frac{2m}{\hbar^2} E_{\text{kin}} \right)^{\frac{1}{2}} \sin(\theta). \] (B.8)

With \( E_B \) as the binding energy, since \( E_{\text{kin}} = E_B + h\nu - \phi \), we have

\[ k_\parallel = K_\parallel = \left( \frac{2m}{\hbar^2} [E_B + h\nu - \phi] \right)^{\frac{1}{2}} \sin(\theta). \] (B.9)

The perpendicular component could be written with an additional surface potential term, \( V_0 \) whose gradient is perpendicular to the surface,

\[ k_\perp = \left( \frac{2m}{\hbar^2} (E_{\text{kin}} + V_0) \right)^{\frac{1}{2}} \cos(\theta). \] (B.10)

In 2D materials such as cuprates where there is no electron coupling between crystallographic planes, \( k_\perp \) is zero. \( V_0 \) can be determined using experimental techniques such as the periodicity of the 3D Fermi surface.

The total photoemission intensity of the optical excitation of electrons is given by,

\[ I(E, K, h\nu) \propto \sum_{i,f} \frac{2\pi}{\hbar} \left| \langle \Psi_f^N | H_{\text{int}} | \Psi_i^N \rangle \right|^2 \times \delta (E_f^N - E_i^N - h\nu) \times \delta (k_i - \mathbf{G} - K) \] (B.11)
where, \( \langle \Psi_f^N | H_{\text{int}} | \Psi_i^N \rangle \) is the transition probability of an electron being optically excited from the ground state \( \Psi_i^N \) to a final state, \( \Psi_f^N \). \( G \) is a reciprocal lattice vector. The transition probability is proportional to Fermi’s golden rule given by,

\[
w_{fi} = \frac{2\pi}{\hbar} \left| \langle \Psi_f^N | H_{\text{int}} | \Psi_i^N \rangle \right|^2 \delta (E_f^N - E_i^N - h\nu).
\]  

(E.12)

\( E_i^N = E_i^{N-1} - E_B^k \) are the initial energies for a system of \( N \) electrons while \( E_f^N = E_f^{N-1} + E_{\text{kin}} \) corresponds to its final state. The perturbation Hamiltonian of the system is given by,

\[
H_{\text{int}} = \frac{1}{2m} \left( \frac{e}{c} \mathbf{A} \right)^2 - e\Phi - \frac{p^2}{2m}
\]

\[
\approx \frac{e}{2mc} (\mathbf{A} \cdot \mathbf{p} + \mathbf{p} \cdot \mathbf{A}) \approx \frac{e}{mc} \mathbf{A} \cdot \mathbf{p}.
\]  

(E.13)

Eq. (E.13) treats the electron-photon interaction as a perturbation. \( \mathbf{A} \) is the electromagnetic vector potential, \( \mathbf{p} \) is the electron momentum operator and \( \Phi \) is the electromagnetic scalar potential, where we have enforced the Weyl gauge i.e. \( \Phi = 0 \). Assuming a linear optical regime let’s us drop the \( \mathbf{A}^2 \) terms. In the ultra-violet regime, we are allowed to use the dipole approximation, i.e. \( \nabla \cdot \mathbf{A} = 0 \).

As a simplification, the photoemission process can be broken into three steps as illustrated in Fig. B.3.

1. Optical excitation of the electron in the bulk material through interaction with the incoming photon.

2. Travel of excited electron to the surface with a probability proportional to its mean free path.

3. Escape of photo-electron into vacuum after transmission through the surface potential barrier.

The electron can only escape to vacuum if it has sufficient energy compared to the work function and binding energy, i.e.,

\[
\frac{\hbar^2 k^2}{2m} \geq |E_B| + \phi.
\]  

(E.14)
This approximation is known as the *three-step model* and is often preferred in photoemission studies due to its simplicity. Another approximation, the *sudden approximation* is used to overcome the complications of interactions between the photo-electron and the system it left behind. In other words, the photo-electron is instantaneously removed from the system. For such instantaneous systems, we can write the initial and final state vectors as,

\[
\begin{align*}
|\Psi_N f\rangle &= A |\phi_k f\rangle \otimes |\Psi_{N-1} f\rangle, \\
|\Psi_N i\rangle &= A |\phi_k i\rangle \otimes |\Psi_{N-1} i\rangle
\end{align*}
\]  

(B.15)

where \(A\) is an antisymmetry operator enforcing the Pauli Exclusion principle. \(|\phi_k i\rangle\) and \(|\phi_k f\rangle\) are wave functions of the electron before and after absorbing a photon where the momentum \(k\) is conserved. Their eigen values (energies) are \(\epsilon_i\) and \(\epsilon_f\). \(|\Psi_{N-1} i\rangle\) and \(|\Psi_{N-1} f\rangle\) are the initial and final state wave functions of the remaining \((N - 1)\) electron system. The transition probability can now be written.
Angular Resolved Photo-Emission Spectroscopy (ARPES) in the following form:

\[
w_{f,i} = \frac{2\pi}{\hbar} \left| \langle \Psi_f^N | H_{\text{int}} | \Psi_f^N \rangle \right|^2 \propto \left| \langle \phi_k^f | H_{\text{int}} | \phi_k^f \rangle \langle \Psi_{m-1}^N | \Psi_{m-1}^N \rangle \right|^2 (B.16)
\]

where we have changed the index \(f\) in \(\Psi_{m-1}^N\) to \(m\) as \(\Psi_{m-1}^N\) to represent the excited state of the remaining \((N-1)\) system following the photo-excitation. The non-interacting approximation gives \(\Psi_{m-1}^N|\Psi_{m-1}^N\rangle\), therefore we have,

\[
w_{f,i} \propto \left| \langle \phi_k^f | H_{\text{int}} | \phi_k^f \rangle \right|^2. (B.17)
\]

The total photoemission intensity is given as a summation over all the interacting states in the system with the outgoing kinetic energies, \(E_{\text{kin}}\) and momenta \(k\) as,

\[
I(k, E_{\text{kin}}) = \sum_{f,i} w_{f,i} \propto \sum_{f,i} \left| \langle \phi_k^f | H_{\text{int}} | \phi_k^f \rangle \right|^2 \sum_m \left| \langle \Psi_{m-1}^N | \Psi_{m-1}^N \rangle \right|^2 \delta \left( E_{\text{kin}} + E_{m-1}^N - E_i^N - h\nu \right). (B.18)
\]

For non-interacting particles, \(\sum_m \left| \langle \Psi_{m-1}^N | \Psi_{m-1}^N \rangle \right|^2 = 1\) for a single \(m\) thus the spectral function would provide a series of delta function peaks at a given momentum and energy as shown in Fig. B.4(b).

However, for strongly correlated systems \(\Psi_{m-1}^N \neq \Psi_{m-1}^N\) the delta function peaks would be replaced by convolution between delta functions and interacting states taking a form of a main line and satellites based on the number of excited states \(m\) created in the process as seen in Fig. B.4(c).

**B.3 Green’s functions formalism**

The single particle spectral functions are described by the Green’s function formalism [341, 342]. The electron-photon interaction is given by the total spectral function,
Figure B.4: (a) The geometry of the ARPES experiment where a photoelectron emitted from a sample is resolved through a detector. (b) The spectral function for a non-interacting electron system. (c) The spectral function for an interacting electron system, i.e. Fermi liquid. The ground-state momentum distribution function \( n(k) \) is also shown here. Retrieved from Ref. [337].

\[
A(k, \omega) = -\frac{1}{\pi} \text{Im} G(k, \omega).
\]  
(B.19)

Here, \( G(k, \omega) \) is the single particle Green’s function given as,

\[
G(k, \omega) = \frac{1}{\omega - \varepsilon_k - \Sigma(k, \omega)}
\]  
(B.20)

where, \( \Sigma(k, \omega) \) is the self-energy of the system and \( \varepsilon_k \) is the band energy. \( \omega \) represents the energy of the system previously given as \( E_{\text{kin}} - h\nu \). The self-energy can be separated into real and imaginary components, i.e. \( \Sigma(k, \omega) = \Sigma'(k, \omega) + i\Sigma''(k, \omega) \) thus we can rewrite Eq. (B.19) as,

\[
A(k, \omega) = -\frac{1}{\pi} \frac{\Sigma''(k, \omega)}{[\omega - \varepsilon_k - \Sigma'(k, \omega)]^2 + [\Sigma''(k, \omega)]^2}.
\]  
(B.21)

\( A(k, \omega) \) takes a Lorentzian form. The self-energy can be modeled theoretically and extracted from experiment.
B.4 Experimental procedure

Prior to ARPES, photoemission data were not angle resolved. In 1964 Gobeli et al. \[343\] demonstrated the possibility of mapping the complete band structure through photoemission studies. Early ARPES setups required probing through all $\theta$ and $\phi$ angles to map the full band structure. Modern ARPES uses 2-D detector arrays with energy and momentum channels such that only one angle of the sample is required to be varied to map the band structure. State-of-the-art *time of flight* detectors are able to detect all 3 dimensions at once so that none of the angles require changing \[344\].

The ARPES data reduction workflow is illustrated in Fig. B.5.

![Figure B.5: The workflow of the ARPES procedure. Retrieved from Ref. [338].](image)

The raw camera images undergo a series of image processing procedures to remove pixel-to-pixel efficiency variations \[345\]. Additionally, the detector nonlinearity is corrected such that the recorded intensity is proportional to the true electron counts. In the following section, we discuss the different parts of the ARPES process.

ARPES analyzers are tasked with collecting the outgoing electrons with angle and energy resolution and bin them with their corresponding momentum and kinetic energy. They consist of three parts:

1. Electron lens - sorts electrons according to their ejection angle
Angular Resolved Photo-Emission Spectroscopy (ARPES)

2. Hemispherical energy analyzer - sorts electrons by their kinetic energy

3. MCP detector - Records the above two quantities for each photo-electron

A schematic diagram illustrating this setup is shown in Fig. B.6. In modern devices, an energy resolution of 1 meV and angular resolution of 0.1° can be achieved through UV lasers [346]. The sample is placed in front of the electron lens with a beam of monochromatic light being incident on it. Popular light sources used in modern ARPES experiments are highlighted in Fig. B.7. Once the electrons are ejected from the sample, they travel through vacuum and enter the lens. Here they are binned according to their ejection angle. They then travel through the hemispherical analyzer where they are now binned by both their kinetic energy and angle. The hemispherical analyzer consists of two metal hemispheres each subjected to a different voltage, thus forming an electric field between the two. This electric field separates the electrons based on their energy. Finally, they are counted by the 2D micro channel plate (MCP) detector. The detector houses a charge-coupled-device (CCD) camera.

Figure B.6: (a) Schematic setup of the ARPES experiment. The protruding section is the electron lens which is attached to the hemispherical energy analyzer. (b) Diagram showing the inside of hemispherical energy analyzer. The 2D MCP detector records the electron counts. Retrieved from Ref. [347].
Figure B.7: Light sources used for ARPES experiments. Retrieved from Ref. [338].
Appendix C

List of Publications

C.1 Published


C.2 In progress

List of Presentations

1. Uthpala Herath, Pedram Tavadze, He Xu, Eric Bousquet, Sobhit Singh, Reese Boucher, Logan
Lang, Freddy Farah, Francisco Muñoz and Aldo H Romero
A tutorial on PyProcar: A Python library for electronic structure pre/post-processing
Rutgers University, June 25th, 2021 (INVITED VIRTUAL TALK)

2. Uthpala Herath, Pedram Tavadze, He Xu, Eric Bousquet, Sobhit Singh, Reese Boucher, Logan
Lang, Freddy Farah, Francisco Muñoz and Aldo H Romero
Recent Developments in PyProcar: A Python library for electronic structure pre/post-processing
APS March Meeting, Mar 15-19, 2021 (VIRTUAL TALK)

3. Uthpala Herath, Vijay Singh, Benny Wah, Xingyu Liao, Hyowon Park and Aldo H. Romero
DMFTwDFT: An open-source code combining Dynamical Mean Field Theory with various
Density Functional Theory packages
APS Mid Atlantic Section Meeting, December 4-6, 2020 (VIRTUAL TALK)

4. Uthpala Herath, Pedram Tavadze, Xu He, Eric Bousquet, Sobhit Singh, Francisco Muñoz,
and Aldo H. Romero
PyProcar: A Python library for electronic structure pre/post-processing
Carolina Science Symposium, Nov 12-13, 2020 (VIRTUAL TALK)
5. Uthpala Herath, Pedram Tavadze, Xu He, Eric Bousquet, Sobhit Singh, Francisco Muñoz, and Aldo H. Romero

*PyProcar: A Python library for electronic structure pre/post-processing*

Electronic Structure Workshop, June, 2020, University of California, Merced (VIRTUAL TALK)

6. Uthpala Herath, Hyowon Park and Aldo H. Romero

*An ab-initio DFT+DMFT study of the effect of oxygen vacancies on structural, electronic and magnetic properties of rare-earth nickelate perovskites (RNO3)*

APS March Meeting, March 4-8, 2019, Boston, MA (TALK)

7. Uthpala Herath, Hyowon Park and Aldo H. Romero

*Development of computational methods for the characterization of novel strongly correlated materials*

International Summer School on Computational Quantum Materials, June 2018, Sherbrooke, Québec, Canada (POSTER)
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