

**HEAD TO HEAD AND TAIL TO TAIL 180° DOMAIN WALLS
IN $\text{PbTiO}_3/\text{PbTiO}_3$ FERROELECTRIC THIN FILMS: AN *AB INITIO*
STUDY**

JAMES SIMIYU SIFUNA

PhD

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STUDY**

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Degree of Doctor of Philosophy in Physics**

in

The School of Physics and Earth Sciences

of

The Technical University of Kenya

(November 2023)

DECLARATION

This thesis is my original work and has not been presented in any other institution for a degree award or other qualification.

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DEDICATION

To my beautiful wife IMELDA LINDA WAFULA, my loving daughter SHIZEL CHRISTINE & my son CHRISLANCE SIFUNA.

“Where there is family, there is love.”

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To God be the Glory ... The long wait has come to an end!

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ABSTRACT

Charged domain walls (DWs) in ferroelectric materials have gained a lot of interest for a decade now. Large conductivity has been reported at the DWs of insulating ferroelectric materials, and it has lots of applications in actuators, sensors and capacitors. In the prior studies, the origination of this conductivity at DWs and the stabilization procedures of the charged domains remain controversial. Plenty of studies have called for the employment of dopants, oxygen vacancies or other external potentials to screen the polarization discontinuity at the DWs. Unfortunately, these kind of computations in literature cannot be used to answer questions about; the intrinsic critical thickness for stabilizing the two-dimensional conducting layers for the screening of the polarization charges, the spatial extension of the hole and electron gases, or the size of the polarization that would result from the induction of such DWs in an ideal slab. This thesis seeks to elucidate the stabilization of 180° head to head (HH) and tail to tail (TT) DWs in an ideal slab. Once this stabilization is achieved, queries on the origin of the conductivity seen in at the DWs and the stabilization of such domains will be a thing of the past. The electronic and structural characteristics of charged domain walls (DWs) in PbTiO_3 thin films were determined using first-principles simulations as prescribed by the SIESTA method. At first, it was important to implement a strategy that would take into account the Hubbard (U) and spin-orbit coupling in the SIESTA method. This was important so as to accurately describe the physics of the DWs in this study. To benchmark the strategy implemented herein, calculations were performed on tetragonal IrO_2 . The lattice constants of IrO_2 were found to be in a perfect agreement to experimental results. A difference of the order of 1.5% on the lattice constants was seen in comparison to other well known methodologies like VASP and QUANTUM ESPRESSO. The band structures of IrO_2 generated by the implementation in here, VASP and QUANTUM ESPRESSO were identical. This gave the author confidence to use the implementation on the complex HH and TT domains. The polarization ($\tilde{P}_j^Z$) in the DWs under this study was computed using the effective Born charges. The polarization was then used to obtain the spatial extension of the hole and electron gases at the DWs. To understand better on how much charge was transferred from the free-surfaces to the DWs in order to screen the depolarizing fields, the author plotted the planar average of the free charge ($\bar{\rho}_{\text{free}}(z)$). This thesis demonstrates how the formation of two-dimensional electron and hole gases at the free surface and at the DWs may stabilize the highly energetic 180° head to head (HH) and tail to tail (TT) DWs in free-standing slabs. The walls' breadth, ≈ 7 unit cells for TT DW and ≈ 6 for HH DW, was found to be significantly more than what is seen when the domains are configured in their neutral state. With a perfect balance between the bound charges (divergence of polarization) and the screening charges, the distribution of the free charge was electrostatically associated with structural distortions. Examining the DWs in an intrinsic manner, the global charge neutrality expected, was observed. Also to note, was that at the interior of the domains, the polarization profile was astonishingly flat and was found to be $57.26 \mu\text{C}/\text{cm}^2$ for HH and $45.72 \mu\text{C}/\text{cm}^2$ for TT structures respectively. From a practical standpoint, this study provides an alternate explanation for the intriguing discovery of extremely high conductivities at the DWs between two insulating polar materials.

Key words: Domain walls, ferroelectricity, electronic reconstruction, PbTiO_3 .

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ACRONYMS & SYMBOLS USED IN THIS THESIS

$\text{\AA}$	Angstrom
μC	Microcoulomb
δ_w	Half width of the domain wall
δ^{2-}	Dipole moment
δ^+	Dipole moment
$\text{\AA}$	Thin film thickness
ε	Dielectric susceptibility
χ	Electric susceptibility
ϵ_0	Vacuum permittivity
Ψ	Wave function
2DEG	Two-dimensional electron gas
2DHG	Two-dimensional hole gas
ABO_3	Oxide perovskite
AlO_2	Aluminium (II) oxide
ASESMA	African school on electronic structure methods & applications
B1-WC	Hybrid functional
BaTiO_3 (BTO)	Barium titanate
BiFeO_3	Bismuth ferrite
CB	Conduction band
CBM	Conduction band minimum
CHPC	Center for high performance computing
DFT	Density functional theory
DFT+U	Density functional theory plus Hubbard U term
DFPT	Density functional perturbation theory
DOS	Density of states
DW	Domain wall
DWs	Domain walls

DZP	Double - ζ plus polarization
E	Electric field.
E_c	Coercive field
F	Helmholtz free energy
FE	Ferroelectrics
G	Gibbs free energy
GGA	Generalized gradient approximation
H	Hydrogen
HH	Head to head domain wall
HSE06	Heyd–Scuseria–Ernzerhof-2006
J	The total angular momentum
KNbO ₃	Potassium niobate
KS	Kohn-Sham
LaO	Lanthanum oxide
LaAlO ₃	Lanthanum aluminate
LDA	Local density approximation
LDA+ U	Local density approximation plus the Hubbard term (U)
LDA+ U +SOC	Local density approximation plus the Hubbard term (U) plus spin-orbit coupling
LDAs	Local density approximations
LGD	Landau-Ginzburg-Devonshire
LiNbO ₃	Lithium niobate
LR	Long range
MLWFs	Maximally localized Wannier functions
M.Sc	Master of Science
N	North
Nb	Niobium
O	Oxygen
P	Polarization

P_s	Spontaneous polarization
Pb	Lead
PBESol	PBE functional revised for solids
PbO	Lead oxide
PbTiO ₃	Lead (II) titanate
Pb(Zr _{0.2} Ti _{0.8})O ₃	Lead zirconate titanate
PDOS	Partial density of states
PZ	Perdew-Zunger
Quantum ESPRESSO	Quantum open-source package for research in electronic structure, simulation, and optimization.
S	South
Sc	Scandium
SCAN functional	Strongly constrained and appropriately normed
SIESTA	Spanish initiative for electronic simulations with thousands of atoms
SLs	Superlattices
SOC	Spin orbit coupling
SR	Short range
SrTiO ₃	Strontium titanate
T	Temperature
T_c	Critical temperature
Ti	Titanium
TiO ₂	Titanium oxide
TT	Tail to tail domain wall
U	Hubbard potential
UNICAN	University of Cantabria
VASP	Vienna <i>ab initio</i> simulation package
VB	Valence band
VBM	Valence band maximum

WO₃

Tungsten trioxide

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CHAPTER ONE

INTRODUCTION

To improve the performance of electronic gadgets, modern technology is always searching for smaller functional components. As devices like transistors continue to shrink in size from centimeters to tenths of nanometers, materials scientists are also heading to the *nano* world for novel traits that may change how a typical device functions. Ferroelectrics are a promising candidate class of materials in the *nano* world, that ought to be fully utilized.

Ferroelectrics easily provide a viable alternative to the traditional gate dielectrics used in transistors. Before delving into the discussion, it is important to define these materials. A ferroelectric material is one that exhibits a spontaneous reversible electrical polarization¹. Initially, this trait was only seen in few crystals but as time evolved, more ferroelectric materials were found with vast applications. For over a century now (Valasek, 1921), these materials have been employed in transducers, actuators and sensors both in industry and with a similar magnitude in the military. Also to note is that ferroelectric materials fall in the large class of materials known as multiferroics (*ferroelastics, ferroelectrics and ferromagnets*) (Spaldin, 2020).

To this date, plenty of works on ferroelectric thin films have been put forward in response to the drive toward downsizing and in conjunction with technological developments in film growth. As we go towards the *nano* world, a myriad of astounding new phenomena are being discovered, and their intriguing functional features are being revealed. The wonderful realm of nanotechnology allows for accurate film scaling that is almost atomic in scale. In this work, the behaviour of ferroelectrics (*oxide*) in the nanoscale regime were studied. PbTiO_3 , one of the most widely utilized and well-known ferroelectric material with a perovskite crystalline structure, is studied throughout in this work. This has been done with a proper benchmarking to other ferroelectrics in literature.

¹For simplicity, and all though this thesis, we will just call it polarization

1.1 Physics of Ferroelectrics

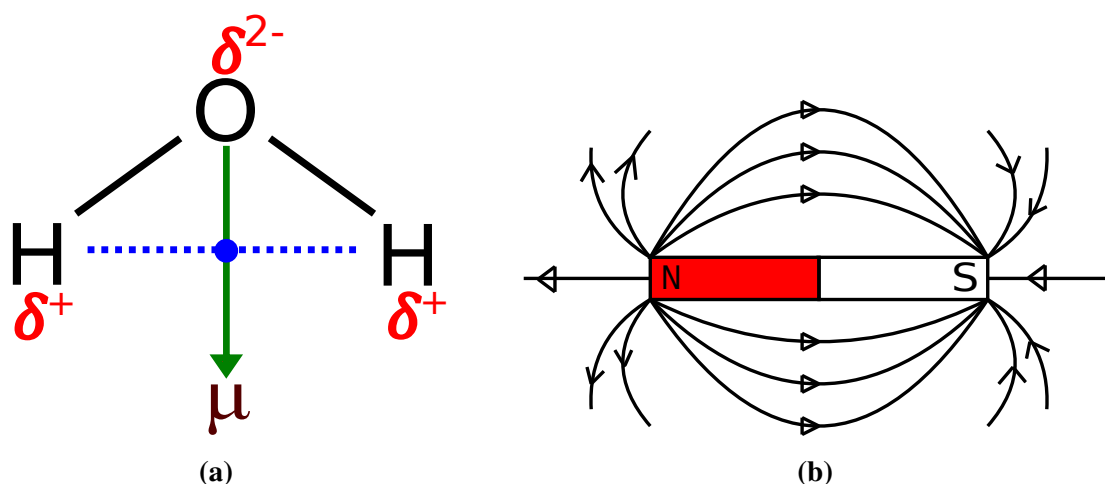


Figure 1.1: (a) A water molecule illustrating the net molecular dipole moment. (b) A bar magnet with a magnetic field around it. Both (a) and (b) fall in the broad family of materials known as multiferroics, if and only if, (a) is ferroelectric and (b) is ferromagnetic.

Ferroelectricity is a phenomenon that causes spontaneous electrical polarization and is present in some materials, not all. This implies that a material can exhibit electrical polarization/dipole moments if there isn't an applied external electric field. In any ferroelectric material, electric dipole moments that the molecules carry, spontaneously align to create a polarized material.

Please note that; ferroelectrics contain electric dipole moments unlike ferromagnets which have magnetic fields illustrated in Fig. 1.1. On a similar footing, it is essential to equally remember that dipole moments occur when there is separation of charges in a crystal. Variations in electronegativity can produce dipole moments between atoms in a covalent connection or between two ions in an ionic bond. In a particular crystal, a dipole moment practically grows with the difference in electronegativity. Noteworthy is the fact that the dipole moments determine the polarity of a molecule and that its magnitude is usually influenced by the charge gap between the charges. At this point, it is safe to introduce to you that any proper ferroelectric material, will have two very important signatures: (a) spontaneous polarization and (b) the said polarization must be switchable by an electric field. For any crystal to have spontaneous polarization, then it must have an electric dipole moment in a given unit volume which only occurs in non-centrosymmetric materials. Ma-

materials like BaTiO_3 , PbTiO_3 will always have polarization (spontaneous) with zero applied electric field (Junquera et al., 2007). When it comes to the polarization switchability in ferroelectrics, it implies that the polarization in a polar crystal must be able to adopt more than one orientation. To understand this better, let's employ a prototypical ferroelectric PbTiO_3 and consider its high symmetry centrosymmetric reference structure that occurs above curie temperature (*paraelectric structure*) as conveyed in Fig. 1.2(b). At the Curie

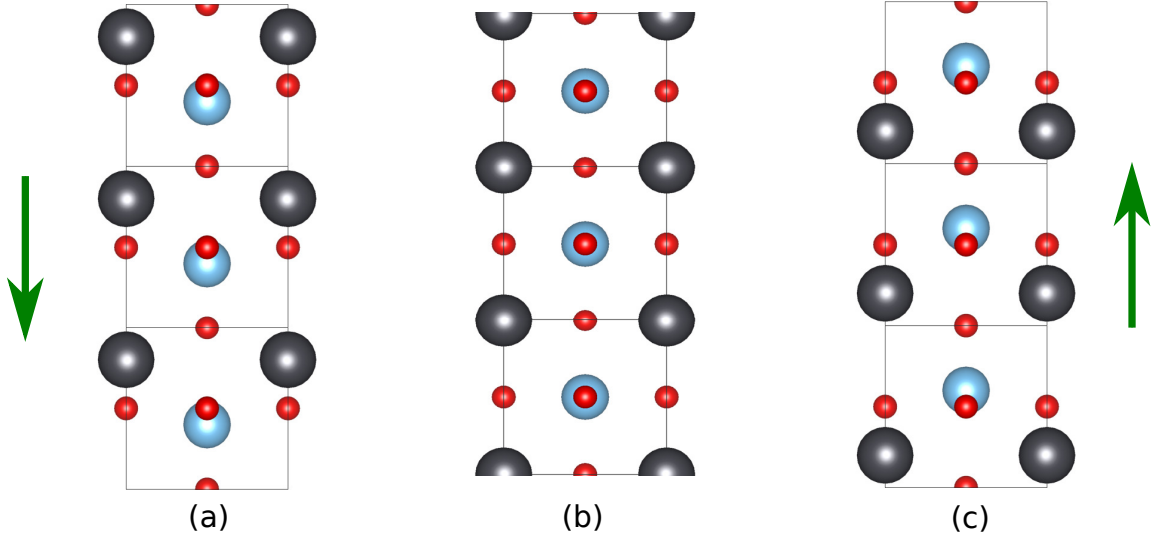


Figure 1.2: Prototypical ferroelectric PbTiO_3 in three possible phases, (a) tetragonal ferroelectric phase with polarization pointing down, (b) non-polar cubic configuration and (c) tetragonal ferroelectric phase with polarization pointing up. It is important to note that the polar mode PbTiO_3 , is associated with the change of the c/a ratio by ≈ 1.03 in the polarization direction. In such a ferroelectric, it is possible to switch from any of the three phases in a non-volatile manner. This has a great application in sensors and actuators.

temperature, symmetry lowering distortion takes place which in turn leads to a polar structure. If we consider the structure just below the Curie temperature (*tetragonal*), we see the titanium is pushed distant from the oxygen octahedron's core and yields net polarization. It is crucial to keep in mind that the ions might be displaced in more than one direction, resulting to a variety of polarization patterns, as depicted in Fig. 1.2(a) (*polarization point down*) and Fig. 1.2(c) (*polarization point up*).

1.1.1 Selected important observations in ferroelectrics

In this subsection key properties of ferroelectrics are discussed in a global fashion. The properties include but not limited to the following:

1.1.1.1 Hysteresis

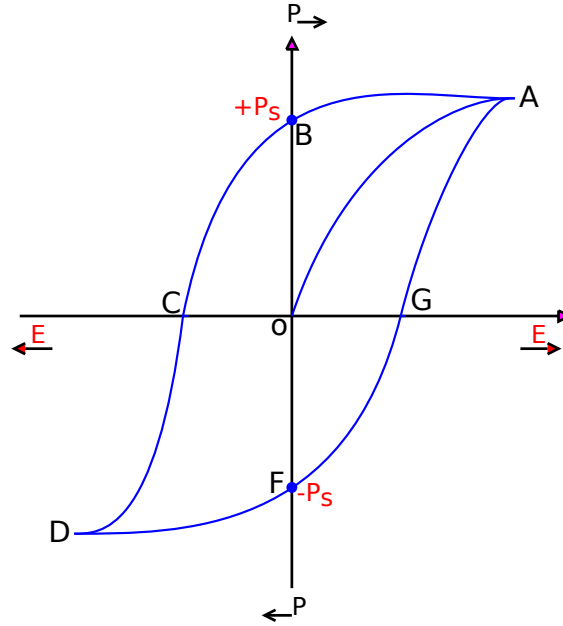


Figure 1.3: Polarization (P) variation with an applied electric field (E) in a typical ferroelectric.

A keen look on the hysteresis loop $OABCD FGA$ in Fig. 1.3, it is directly associated with the switchability capability of polarization seen in typical ferroelectrics. It is seen that, at zero electric field (point O), we have two values of spontaneous polarization ($+P_s$ and $-P_s$). This behaviour makes ferroelectrics play a role in data storage since the $+P_s$ and $-P_s$ can represent 1 and 0 in binary data storage respectively. It is expected that at extreme electric fields (*high and low*), a ferroelectric material will behave like a very normal dielectric that will have a large dielectric constant. In Fig. 1.3, point C shows the coercive field (E_c). At this point, polarization reversal takes place coupled with a large dielectric non-linearity. At point A and D in Fig. 1.3, we have saturated polarization, B and F hint at remnant polarization while C and G hint at coercive electric fields. The magnitudes in this case are directional dependent.

1.1.1.2 Coupling between polarization and strain

What this implies is that, in ferroelectrics, once polarization sets in, there is a change in shape as shown in Fig. 1.4. This usually occurs in the polarization's direction. This trait is novel and it makes ferroelectrics be applied in sensors (*where the change in electric field*

can be detected as a change in shape) and in actuators (in which the introduction of an electric field may modify the geometry). This trait is exhibited by all ferroelectrics.

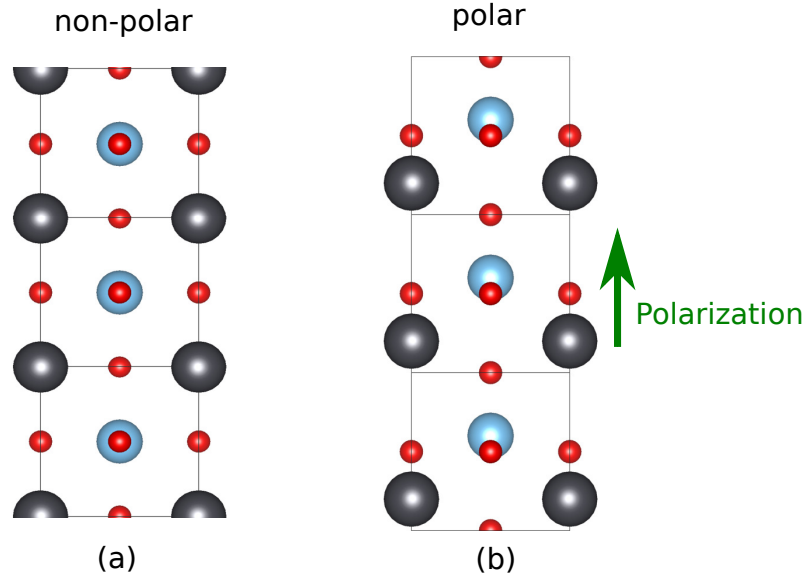


Figure 1.4: Polarization versus strain sketch. In (a), the system is non-polar while in (b) the system is polar, the strain is seen in the polarization's direction (*Tetragonality or the c/a ratio of the order of 1.03*).

1.1.1.3 Temperature dependence to polarization

Pyroelectricity in ferroelectrics is associated with the variation of polarization in relation to temperature. In such a depiction, a system is paraelectric when it is above the Curie temperature (T_c) and ferroelectric when it is below the Curie temperature. In other words, strong polarization is associated with lowering in temperature as shown in Fig. 1.5.

1.1.1.4 Dielectric response

Lastly, a constant called dielectric susceptibility (ϵ) illustrates how polarized a ferroelectric material is in relation to a given applied electric field (ΔE).

$$\epsilon = \frac{\Delta p}{\Delta E}, \quad (1.1)$$

where, Δp is the change in electric polarization. Most of the time, a material is non-polar (*paraelectric*) above the Curie temperature, as seen in the illustration in Fig. 1.6. When

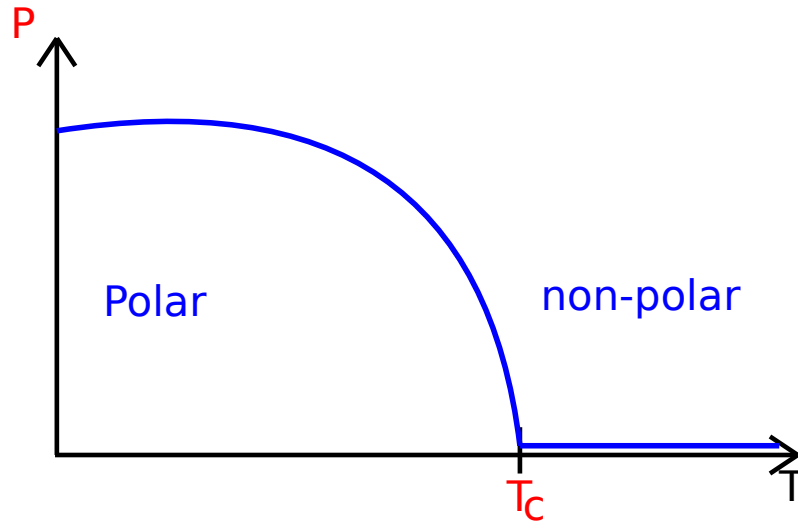


Figure 1.5: Polarization and temperature variation. A large polarization is seen at lower temperatures.

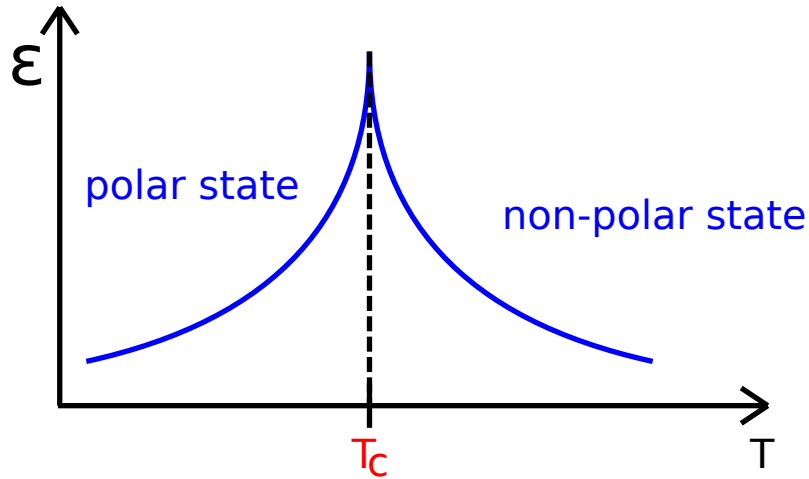


Figure 1.6: Variation of ϵ versus temperature in a ferroelectric.

an electric field is applied, some polarization could take place. As $T \rightarrow T_c$, the material is almost in the polar regime and a small electric field applied, will trigger a large change in polarization and thus a large ϵ . Below this Curie temperature, a material is already polar, this implies that applying an electric field doesn't cause substantive changes in the polarization and similarly a small ϵ is noted.

1.2 Milestones in the Ferroelectric Community

As summarized in Fig. 1.7, about a century ago, Valasek (Valasek, 1921) made the discovery that Rochelle salt had unpremeditated polarization that could be reversed in a strong

enough external electric field, resulting in a hysteretic loop that resembled that known for magnetization versus magnetic field in ferromagnets. This was the dawn on the history of ferroelectricity and the establishment of the ferroelectric community. Ferroelectricity at that time until 1940s remained an academic curiosity for a while, limited to weakly interesting hydrogen-bonded, water-soluble crystals (Ghosez & Junquera, 2022).

Early in the 1940s, the finding that barium titanate (BaTiO_3) was a potent ferroelectric, marked a significant turning point (Wul & Goldman, 1945). On the one hand, it served as a classic ferroelectric study material, due to the cubic perovskite ABO_3 structure's simplicity. Due to its stability and durability, ferroelectrics were able to be fully employed in a couple technological applications. Because of this, an electro-ceramic industry swiftly developed, focused on ferroelectricity as well as its other associated gigantic dielectric, piezoelectric, pyroelectric, or nonlinear optical features. Studies then progressed through time from ferroelectrics as a device to their incorporation into electronic chips; at a microscale (1990s) and at nanoscale (2000s).

Numerous ideas have been put out since the beginning, explaining the cause and principles of ferroelectricity. In the early 1950s, Devonshire (Devonshire, 1949, 1951, 1954) reported on ferroelectricity (*in perovskites*) based on a phenomenological and macroscopic thermodynamical approach², coming from a whole series of influential findings on Rochelle salt by Mueller (Mueller, 1940a,b). Later, a microscopic viewpoint was separately offered by Cochran (Cochran, 1959, 1960) and Anderson (Anderson, 1960). They proposed the conceptualization of soft-mode, providing a framework for the model of the displacive phase transitions, which rely on a potential conflict between short-range and long-range dipolar forces. Thereafter, an eight-site model of Comès, Lambert, and Guinier (Comès et al., 1968), which was more consistent with an order-disorder transition, eventually called into doubt the microscopic formalism. Lines (Lines, 1969) skillfully merged microscopic and macroscopic viewpoints in 1969. Since then, the anisotropic polarizability of oxygen (Migoni et al., 1976) plays a vital role in the so-called polarizability model (Bilz et al., 1987) still in use today. These notions were further refined from nonlin-

²Also known to many as the Landau-Ginzburg-Devonshire or LGD approach.

ear shell models in the 1970s and 1980s. At that time, it seemed as though ferroelectricity had already been covered in great detail.

First-principles density functional theory (DFT) was being developed independently and concurrently. DFT took considerable time to develop into a useful and manageable strategy since it relied on the foundational theorems of Hohenberg & Kohn (Hohenberg & Kohn, 1964) and Kohn & Sham (Kohn & Sham, 1965). The creation of pseudopotentials, the idea of effective techniques for sampling the Brillouin zone (Monkhorst & Pack, 1976), and the accurate determination of quantum Monte-Carlo data-sets for the homogeneous electron gas on which the ideal local density approximations (LDAs) (Ceperley & Alder, 1980) were fitted, were equally significant developments. Density functional-perturbation theory (DFPT) and Car-Parrinello technique were created almost at the same time. The majority of the ingredients needed to explore ferroelectric phase transitions and associated functional features were already on hand by the end of the 1980s. However, the computing power available at the time was essentially limited to only few atoms and similarly, electrons in any unit cell.

Despite a few earlier investigations, the publication by Cohen (Cohen, 1992), titled ‘Origin of Ferroelectricity in Perovskite Oxides’ in 1992 marked the beginning of the ongoing age of first-principles modeling in ferroelectrics. Since the publication of this seminal study, the symbiotic interaction between fundamental knowledge of ferroelectricity and associated phenomena and atomistic modeling in material science has continued to be mutually beneficial to this date. First-principles simulations have greatly aided advancements in ferroelectrics space, from the embryonic atomistic investigation of basic ferroelectric and piezoelectric properties of bulk compounds in the 1990s to multiferroics and nanostructures (thin films, superlattices) in the 2000s, and later, to more complex properties and mechanisms in domain walls (DWs)³. Conversely, the study of ferroelectrics was the catalyst for a series of theoretical innovations, many of which had an impact that went far beyond the ferroelectric community. Examples of these innovations include the famous and wide spread *modern* theory of polarization (Resta & Vanderbilt, 2007), finite-

³For simplicity and uniformity in this thesis, domain walls will be abbreviated as DWs, while a domain wall as DW.

field techniques, maximally localized Wannier functions (MLWFs) (Mostofi et al., 2008), sophisticated linear response schemes, and finally second-principles approaches (García-Fernández et al., 2016).

That said and done, you can see the kind of work done by a very small community of scientists around the world. This kind of work not only benefits the ferroelectric community, but also other scholars in different other spheres. Equally, the researcher hopes that you are now convinced as to why this research is sufficiently important in this technological era.

1.3 Why Ferroelectric Oxides in this Study?

As seen in Fig. 1.7, plenty of work has been put forward in the study of ferroelectrics. From early 1940s, plenty of efforts were put in finding new ferroelectrics. This wasn't biased on perovskites (PbTiO_3 , KNbO_3), but other material types were found: IV-VI semiconductors (GeTe), Polymers (PVDF), and V-VI-VII compounds (SbSI). As of today, over one hundred compounds are said to be ferroelectric, and surprisingly, most of them are non-perovskite and even non-oxide! Unfortunately, real device applications do borrow a lot from oxides and that dictates the reason for working with ferroelectric transition metal oxides in this thesis. Working with oxides in this thesis is in a two fold; (i) we won't run out of oxygen any time soon, (ii) their polarizability is just right (dielectric/ferroelectric). On the other hand, the transition metals are very abundant and their compounds with oxygen are also abundant. They are non-toxic and they are stable since they have already oxidized. From a standpoint of application, they are very desirable for this research. From a chemistry point of view: Oxygen & its compounds with transition metals occupy a perfect place in the periodic table in that the bonds with the transition metals are not too covalent and not too ionic. The author also chose Ti, a 3d element to be incorporated in this study. Transition elements have strong correlations: This means that the behaviour of an electron in a given soliton will explicitly influence the behaviour of the other electrons in that space. This is a rich tool box as you can see!

Every ferroelectric material has the fundamentally unique ability to have two, or even

more metastable polarization states, that may be switched between with the aid of an external electric field. Note that, a ferroelectric material is also termed *piezoelectric* and *pyroelectric* as discussed elaborately in Sec. 1.1.1. From a technological perspective, these fundamental characteristics are particularly enticing, and numerous paths have been established towards various applications, including Ferroelectric-Random-Access memory and non-volatile memories just to list but a few.

Ferroelectric oxides with the formula ABO_3 will be the main focus of this research. They are abundant, with $BaTiO_3$ (BTO) being the first to be identified in 1949. Perovskites are widely employed in real life applications and theoretical research due to their well known chemical structure. Many avenues towards a thorough understanding of ferroelectricity were provided by its relative structural simplicity. Due to perovskite compatibility with commercial substrates (Arnay et al., 2018), the ABO_3 structure provides for a wide range of various engineering structures from an experimental perspective. The perovskite oxide family is also big. A material can either be conductive or insulating but this is pegged on the type of the cations involved. The fact that ferroelectric oxides share characteristics like being centrosymmetric in their high symmetries and hence extremely symmetric, that is accompanied with symmetry lowering in the noncentrosymmetric phase is significant. For example, BTO, regarded as the parent ferroelectric system, goes through a number of structural phase transitions, remaining ferroelectric below 120°C while transitioning from cubic to the tetragonal phase at around 120°C , to orthorhombic phase at 0°C , and finally to rhombohedral phase at -90°C (Devonshire, 1949).

Ferroelectricity manifests in a perovskite structure as a deformation of the cubic cell. Of particular note is the Goldschmidt tolerance factor t (Goldschmidt, 1926), that relies solely on the chemical formula ABO_3 and the ionic radii, r_i , of each ion (A, B, O) to predict the stability of the perovskite structure as shown in Eq. (1.2),

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)}. \quad (1.2)$$

A very similar approach was also predicted by Bartel and co-workers (Bartel et al., 2019). A perfect cubic perovskite structure is only created for t values close to one. Usually, the

bond length between A and O determines the size of the oxygen octahedron when $t > 1$, as is the case for BaTiO_3 . A polar distortion will emerge as a result of B being too small. The B to O distance, on the other hand, will determine the cell size when $t < 1$ and hence, causing the oxygen octahedra to tilt and rotate, as in SrTiO_3 . All these minute features relating to the crystallographic fingerprints of ferroelectrics (perovskite) have been revealed courtesy of collaborative efforts between first-principles calculations and real world procedures like X-ray diffraction in materials science.

1.4 Domain Walls (DWs) in Ferroelectric Oxides

DWs in science have been in existence for a couple years now. The dividing line between two adjacent domains is what is referred to as a DW. This results in the extension of a DW in two spatial dimensions and one temporal dimension. Relevant instances include but not limited to: Magnetic domains, which are separated by a wall known as a DW and DWs in optics, referring to optical DWs. In this work, focus is given to DWs in ferroelectrics. In ferroelectrics, the boundary separating two domains with distinct polarization vectors is known as the DW (*This is exactly what we will focus on in this thesis*). In terms of a crystal structure, DW fall under the category of twin boundaries. However, the presence of electrical polarization necessitates taking charge neutrality into account. Please note that ferroelectric DWs are employed in capacitors and equally in adjustable capacitance due to their nonlinear nature. In sensors, they are also very critical as explained in Sec. 1.1.1 of this thesis.

1.5 Problem Statement

In chapter 2, plenty of mechanisms have been raised by the ferroelectric community, explaining the stabilization procedures and the idea of polarization screening of bound charges in the HH and TT 180° DWs.

Researchers have been swapping atoms on either one, both, or even a changeable faulty concentration solely at the tails of HH and TT DWs in superlattices or thin films. All these

procedures are pegged on a first principle formalization. Pending issues like;

1. What is the inherent critical thickness for stabilizing a two-dimensional conducting layers to screen the polarization charges at the DW?
2. What is the proportion, of these hole and electron gases in the HH and TT DW?
Lastly,
3. What will be the size of polarization that will emanate if these kind of DWs are simulated in a slab format?

still remain unanswered by all the previous computations in literature. In this study, the researcher questions whether this screening process may be carried out intrinsically by use of electronic reconstruction rather than via these crude extrinsic methods.

4. On the other hand, it was also important to perform a DFT+U+SOC calculation on PbTiO_3 . The SIESTA code missed this functionality at the time of starting this project. It was therefore necessary to come up with an appropriate functionality to perform this kind of calculation.

1.6 Main Objective

To employ a first principle approach to study HH and TT 180° PbTiO_3 DWs, in free standing slabs. Both the structural and the electronic properties will be studied in these two domains. The work also developed the DFT+U+SOC formalism in the SIESTA code to help study the physics at the DW accurately.

1.7 Specific Objectives

In a more specific way, the project sort to do the following:

1. Develop a strategy that clearly includes and treats the exchange J and Hubbard repulsion term U individually in the SIESTA code.
2. Calculate the polarization after the stabilization of the HH and TT DWs.

3. Calculate the amplitude, of the electron & hole gases formed at the DWs.
4. To estimate how much charge was transported to the DW from free surfaces in order to screen the depolarizing fields.

1.8 Justification

PbTiO_3 is a member of the significant class of cubic perovskite-based ferroelectric materials. PbTiO_3 only goes through one phase change, from the high symmetry paraelectric cubic phase to a tetragonally deformed ferroelectric phase, at a temperature of 765 K (*cubic* $\rightarrow$ *tetragonal*). It stays in this tetragonal phase until $T = 0$. There are six spontaneous polarization orientations in this state that are energetically comparable. On low-index lattice planes, the DWs separating these versions can be seen as twin borders. The two allowed types are twins on (100) planes with parallel polarizations of opposite orientation in the neighboring domains (180° DW) and twins on (101) planes with the polarizations on either side of the DW being nearly perpendicular to one another (90° DW). This kind of wisdom is essential in the community and may easily have a spill effect in industry too.

1.9 Significance

DWs, which are extremely thin sections that separate domains, are crucial to ferroelectrics' electrical, electromechanical, and optical capabilities.

Ferroelectric DWs are a brand-new category of interface that allows for real-time change of the position, density, and orientation of the walls thanks to the dynamic properties of ferroelectricity. With such traits, it is evident that ferroelectrics are good technological candidates for practical solution to mankind.

1.10 Scope and Limitations of this Study

This work constrains itself to 180° DWs illustrated in Fig. 2.2(b). The DW runs parallel to the tetragonal polarization axis in traditional 180° DWs in tetragonal ferroelectrics. The

polarization charge, which is defined as the dot product of the polarization times the unitary vector normal to the DW, disappears in this arrangement, leaving the DWs uncharged. It is also important to note that, since in this work we are mostly interested with eventual transfer of charge from the valence band at TT DW to the bottom of the conduction bands at HH DW, we are only concerned about a proper description of those VBM and CBM manifolds. This is a theoretical study and the characterization of these materials will be left out for future collaborations.

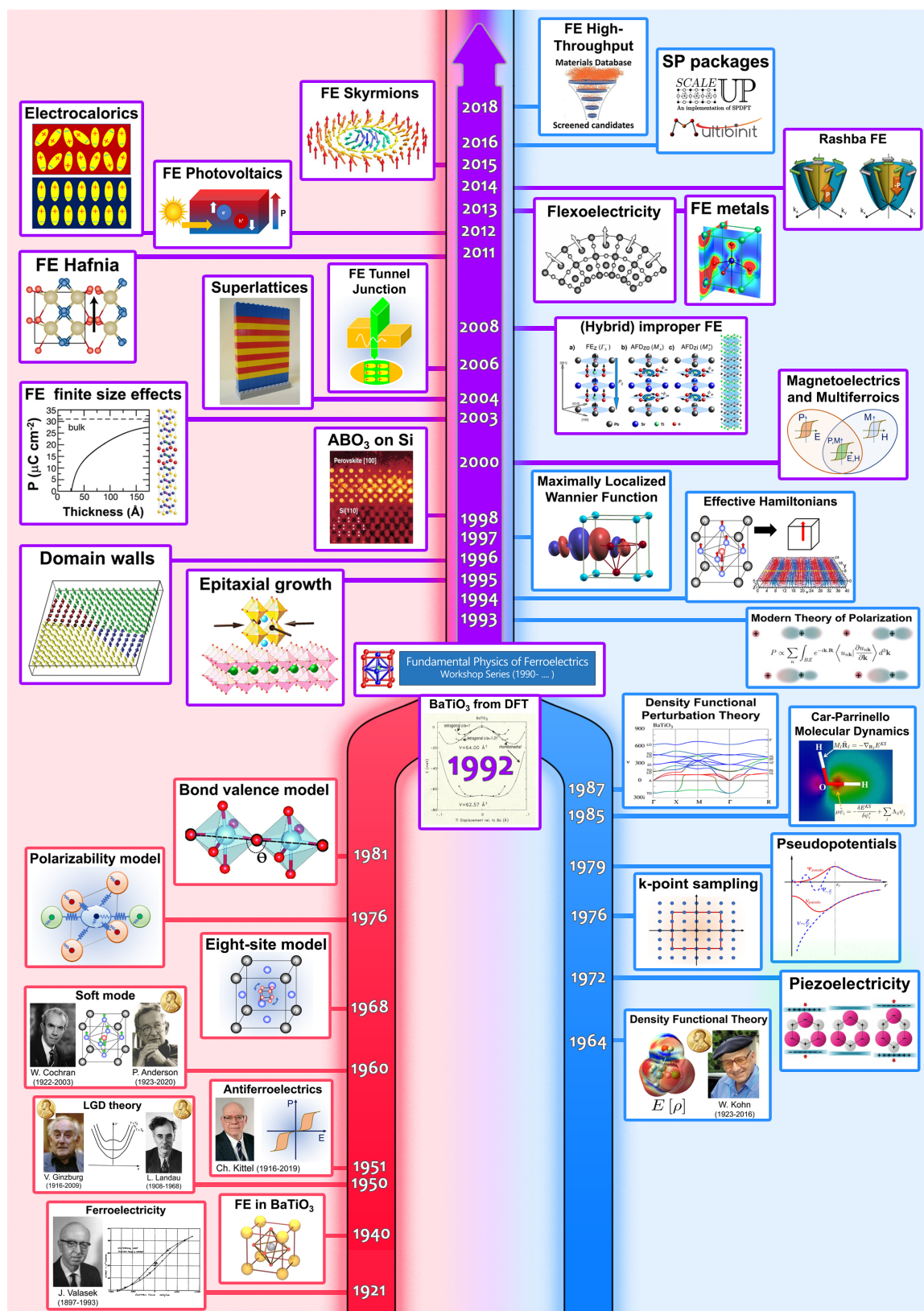


Figure 1.7: A time line of key selected breakthroughs in the ferroelectric community (red), the development of selected methodologies/approaches (blue) and combining them (Magenta). As seen in the image, a lot of work has been done on ferroelectrics for over a century now. The researcher inhere, obtained permission to use this image from Ghosez and Junquera (Ghosez & Junquera, 2022).

CHAPTER TWO

LITERATURE REVIEW

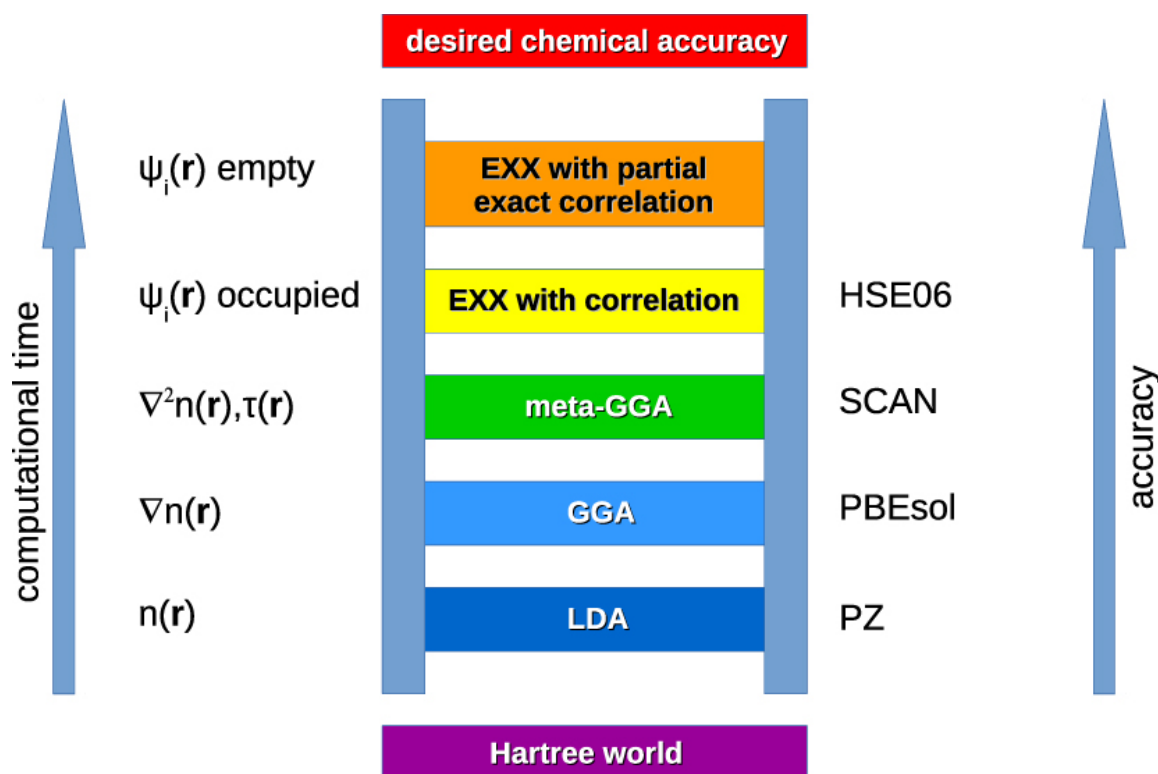


Figure 2.1: An image representation of the Jacob's ladder (Perdew & Zunger, 1981) used in Density Functional Theory studies retrieved from the work of Fritsch and Schorr (Fritsch & Schorr, 2020). This ladder shows two worlds; (i) the Hartree world that has independent electrons and (ii) the heaven having a chemical accuracy.

Computational methods in material science studies have been in existence for a while now. These methods have unravelled and explained accurately the most complicated science like that found in the earth's mantle (Wentzcovitch et al., 2023). It is wise to say that the computational methods in materials science now act as a bridge between theoretical and experimental studies. Density functional theory (DFT) (Hohenberg & Kohn, 1964; Kohn & Sham, 1965), is among these methods. DFT is so far the widely employed method in computational materials science. This thesis employs DFT too.

The ladder rungs seen in Fig. 2.1, ought to be implemented in an ideal code. As seen, DFT has equally evolved to a given accuracy since the functionals have kept on improving

as depicted by the rungs in Fig. 2.1. Today, theoretical scientists are targeting the chemical heaven (*perfectly matching theoretical predictions to experimental findings*) as far as simulations are concerned (Carchini et al., 2013), but they pay a price as far as the computing time is something to go by.

In DFT, attainment of a proper elucidation of the electronic structure is key in predicting further properties like formation energies among others. In correlated materials, the band gap problem has been, and still a big challenge as seen in Table. 3.1. The errors seen are usually a functional dependence problem. Many theories have been put forward to tackle this self interaction problem and thus the desired chemical accuracy being experienced in DFT. Local Density Approximation plus the Hubbard term (U) (LDA+ U) (Anisimov & Gunnarsson, 1991), Strongly constrained and appropriately normed (SCAN) functionals (Sokolovskiy et al., 2023), Heyd–Scuseria–Ernzerhof-2006 (HSE06) (Heyd & Scuseria, 2004), are just but a few functionals that many scholars have devoted time on. Many *ab initio* codes employing the plane wave basis sets, have most of these functionals implemented and thus it becomes a matter of pick and run. These codes comprise Quantum opEn-Source Package for Research in Electronic Structure, Simulation, and Optimization (QUANTUM ESPRESSO) (Giannozzi et al., 2009, 2017) among others. However, some codes, employing numerical atomic orbitals as basis sets, still lag behind with a number of these implementations. A good example is the SIESTA method (Soler et al., 2002), used in this work. At the beginning of this project, LDA+ U approach in the SIESTA code was well implemented. Unfortunately this LDA+ U approach could not be extended to systems that had a large spin-orbit effect in their Hamiltonians. In as much as we know that spin-orbit effect is an intrinsic property, most scholars using this code, neglected this effect due to the negligible contribution from the spin-orbit energy. We set out to avoid this kind of assumption by coming up with an implementation that will allow LDA+ U formalism be extended to systems with large spin-orbit coupling. In most cases, it is commonly referred to as the Local Density Approximation plus the Hubbard term (U) plus Spin-Orbit Coupling (LDA+ U +SOC) formalism. This was critical in this project since we wanted to take into account all the energy contributions in the Hamiltonian to be able to tell the physics

at the DWs accurately. Please note that DFT computations can benefit from two different forms of correction to increase precision without paying much for the computational time: DFT+U and SOC (spin-orbit coupling). While SOC corrects the spin-orbit interaction, DFT+U corrects the electronic interactions in strongly correlated systems.

2.1 Ferroelectrics: Physics of Domain Walls (DWs)

The amazing breakthroughs in ferroelectricity development over the last few decades as shown in Fig. 1.7, have enabled condensed matter scientists to broaden their studies beyond bulk materials to ultra thin films. In fact, methods that will be described in Chapter. 3, will make you understand how it is possible to have a proper growth of materials on various substrates. As a result, one may now begin thinking about boundary conditions, thickness dependency, strain states, domain barriers, and many other things that will lead to novel phenomena that are not seen in single crystals. This thesis gives special attention to DWs, which frequently contain traits that are not found in the domains themselves (Guyonnet et al., 2011; Farokhipoor et al., 2014; Catalan et al., 2012).

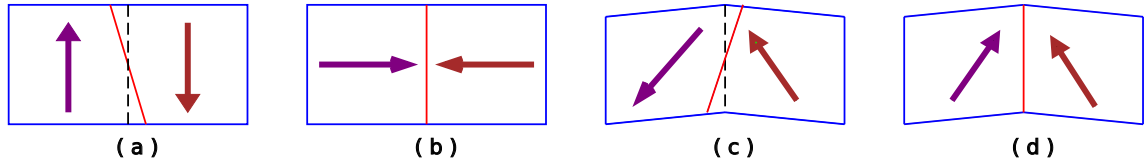


Figure 2.2: Here is a delineation of various charged DWs in a tetragonal polar system. The arrows indicate the direction of spontaneous polarization. Case by case; (a) 180° chargeless DW, while (b) 180° vehemently charged DW. On the other hand, (c) 90° weakly charged DW while (d) 90° strongly charged DW. Please note that (a) & (b) are non-ferroelastic while (c) & (d) are ferroelastic. The study in this work, focused on (b). (a), (c) and (d) are outside the purview of this work but they can be tackled in future. Hopefully they will yield interesting results.

Since they show distinct functional capabilities that differ from those reported in parent materials, DWs in oxide ferroelectric materials have accentuated in the recent past due to their novel applications as explained in Chapter. 1. DWs - scale interfaces are used to divide regions with various spontaneous electric polarization orientations (Catalan et al., 2012). The red line in Fig. 2.2 serves as an excellent example of this.

One of the novel properties that shocked the scientific community was the electronic conductivity observed at room temperature in BiFeO₃ ferroelectric DWs (Seidel et al., 2009). Around the same time, and following the work done in BiFeO₃, Guyonnet and co-workers (Guyonnet et al., 2011) demonstrated that 180° - DWs of Pb(Zr_xTi_{1-x})O₃ (PZTO) thin films were conducting as well. PZTO is a much simpler, purely tetragonal, ferroelectric perovskite indicating that this behaviour is more widespread than initially thought. In fact, a conductive DW exists in wide-bandgap single crystals that are millimeter thick such as LiNbO₃ (Schröder et al., 2012) or WO₃ (Kim et al., 2010) as well as thin films. Origination of the conductivity at DWs is controversial to this date. At first, it was attributed to some changes in structure exactly at the DWs that resulted in a polar discontinuity thus causing potential barrier in the electrostatic potential and an associated metalization (Seidel et al., 2009). Most recently, it has been proposed that *extrinsic* players like oxygen vacancies could be linked with such conductivity (Farokhipoor & Noheda, 2011; Guyonnet et al., 2011).

Fortunately, other players for metal like conductivity at the DWs have been reported by Bendnyakov and co-workers (Bednyakov et al., 2015, 2018). Sluka *et al.* (Sluka et al., 2013) observed that for a prototypical ferroelectric BaTiO₃ there was an increase of conductivity in charged DWs of the order of 10⁹ times that of the parent perovskite. This novel observation, was pegged to the fact that there was a stable but degenerate electron gas formed so as to screen the polarization divergence at the HH and TT DWs (Gureev et al., 2011). The walls were oriented in a parallel direction to the tetragonal polarization axis in tetragonal ferroelectrics for traditional 180° domains. (Pöykkö & Chadi, 1999; Meyer & Vanderbilt, 2002). The net polarization and the unit vector perpendicular to the DW are combined to form the polarization charge in this type of system configuration (*dot product*). A neutral configuration results from the polarization charge dissipating. It is important to note, that if the DWs are tilted like in Fig. 2.2(a) and Fig. 2.2(c), it would create bound charges due to polarization thus resulting in a significant and unfavorable electrostatic energy (Zhang et al., 2020).

In the most severe scenario like one seen in this thesis, where polarization is oriented

inline as the normal vector to the DW, HH or TT DWs develop. Positive bound charges are produced for HH DW, and negative bound charges are produced for HH DW.

It's possible that the physics of charged DWs differ greatly from those of the neutral configuration. Although this is not 100% true all the time since it depends on the critical thickness (Junquera & Ghosez, 2003a). In literature, a number of methods have been put out to substantiate on how the polarization bound charges at the DWs are screened, as well as their stabilization.

A keen look at the work done by Bednyakov and co-workers (Bednyakov et al., 2015), an examination of numerous elements governing the energetics and the magnitude of the charged DWs was proposed. A phenomenological model was utilized to explain the basic foundation for the development of charged DWs in appropriate ferroelectrics¹. A mixed electron/ion scenario seems to be the most promising one. This is accomplished by combining free equilibrium carriers that are produced from the ionized impurities' electronic reconstruction and redistribution during the development of the walls. Electronic reconstruction is the transfer of charge caused by a Zener-like breakdown between, the valence band (*its top*) and the conduction band (*its bottom*). Phase field simulations performed separately, also suggested the observation of this degenerate two-dimensional electron gas-2DEG (*Quasi*), which is confined as a result of the potential well created by the polarization charges (Sluka et al., 2013). By switching to the Landau model (L. Landau & Lifshitz, 1935), Gureev and associates (Gureev et al., 2011) were able to study charged DWs in isolation and commented on the polarization profile, the breadth and equally the energy of formation of the domains.

From a first-principles approach, Wu and Vanderbilt (X. Wu & Vanderbilt, 2006) proposed a regularly repeating chemical 'delta' doping in PbTiO_3 superlattices by using Nb- as donor or Sc- as acceptor atoms in the neighbouring columns in the periodic table to substitute Ti atoms at specific layers. For the same material Rahmanizadeh and co-workers (Rahmanizadeh et al., 2014) suggested the following; (i) a metallic like layer can form at the boundary wall with a geometry of a superlattice; (ii) in superlattice ge-

¹Note that we also have improper ferroelectrics.

ometry, polarons may appear but pegged to the positioning of electrons on a Ti ion; and (iii) also thin film geometries defects are present with different amounts of concentrations. In all of the prior first-principles simulations, it was assumed that either the atoms to perform the substitution existed at one or both domains of the HH and TT superlattices, or that the thin film geometry's tails had changing defect concentrations. These presumptions adequately account for the mentioned electric displacement and polarization inside the domain (Stengel, 2011). In the studies already mentioned, we see nothing about the intrinsic nature of the critical thickness to help stabilize the 2DEG/2DHG after screening of the polarization charges at the boundary wall in a free standing slab. Neither do we see anything on spatial extension of this two-dimension hole and electron gas nor the magnitude of the polarization that would be. This forms a bone of contention in this thesis. The concept of electronic reconstruction to aid in screening the polarization discontinuities has been investigated with similar problems by Stengel and co-workers (Stengel, 2011) and references therein.

A system similar to ours was also encountered by Aguado-Puente and co-workers (Yin et al., 2015); in this system, they had a ferroelectric (PbTiO_3)/dielectric (SrTiO_3) kind of a setup. Electronic reconstruction was used to perform the screening and the ferroelectric layers were able to stabilize on the out of plane *monodomain*. The critical thickness in this study was 16 unit cells. The researchers were equally able to develop a model of a 2DEG/2DHG that forms a frame work used in this study (Aguado-Puente et al., 2015).

The researcher herein is essentially curious on if the same results obtained by Agudo-Puente and co-workers in ferroelectric (PbTiO_3)/dielectric (SrTiO_3) set (Yin et al., 2015), hold when the dielectric is replaced by a ferroelectric. So in this case, we have ferroelectric (PbTiO_3)/ferroelectric (PbTiO_3). One thing that will for-sure happen is that we will have the size of the polarization charge doubling at the DW. With this in mind, and knowing that this research will deal with a very thin region separating domains of different polarization orientation, it is wise to say that this study will be very useful in the sensor technology sphere. This work will not deal with the actual product, but is constrained to the physics and properties of the DWs in the HH and TT forming 2DEG and 2DHG respectively. This

gives a head room for future collaborations and extensions of this novel work.

2.2 Origin of Ferroelectricity in some Materials

If we can get a grasp of the approach that was developed by Devonshire and was based on Ginzburg-Landau formalism, then we can advance our understanding of ferroelectricity. Thus, as addressed in the next subsections of this chapter, we get a full understanding of ferroelectricity from a phenomenological and macroscopic vantage point view.

2.2.1 From one phase to another

This is also referred to as the phenomenological approach. A phase transition is a complicated process that causes material's physical properties to change, such as from paramagnetic to ferromagnetic or from metal to insulator, or it can cause structural distortions in response to changes in temperature or pressure. This subsection seeks to clarify the factors that influence a material's decision to transition into a specific phase at a given pressure or temperature.

How relative stabilities change in various phases can be used to comprehend a phase transition if we use a thermodynamic method for a temperature-driven transition, which is the one we will now concentrate on. In every given pressure or temperature range, the phase with the lowest Gibbs free energy (G) is the one that is most stable.

$$\begin{aligned} G &= H - TS, \\ &= (U + PV) - TS, \end{aligned} \tag{2.1}$$

where H , T , P , U , S , V are enthalpy, temperature, pressure, internal energy, entropy and volume in that order. Since the structure has a lower symmetry and is more compact at low temperature, the enthalpy term controls the energy. With a greater temperature, the structure is not compact as such and frequently has a higher degree of symmetry, since the atoms are coupled more loosely, and thus entropy term mentioned takes a center stage.

Note that, for us to have a transition between two phases, then one phase's energy must outweigh the other.

2.2.1.1 Landau-Devonshire approach

In the mid 1930s, Lev Landau developed a model to represent the complex ideas of phase transitions in materials. The key argument for the Landau model (L. D. Landau, 1937) is that they expressed the Helmholtz free energy (F), being a polynomial expansion of a given order parameter that is close to a phase transition. The physical quantity, either macroscopic or microscopic, which is this order parameter, undergoes a transition from zero to a number that is not zero in value. In other words, the Helmholtz free energy (F) expansion must hold true for temperatures above and below the transition based on symmetry considerations. The highest symmetry phase is used to determine what terms are permitted in the expansion. The fact that the theory uses first-principle calculations or measurable parameters as its inputs lends itself to a *phenomenological approach*. It is crucial to note that a macroscopic model of this kind, as proposed by Landau, can only be as accurate as the input parameters. It is a very vital model also for the long-range interacting systems like ferroelectrics since it is predicated on the idea that the order parameter's fluctuations are minimal.

The Landau theory, was first applied by Devonshire in ferroelectrics in 1950s (Devonshire, 1949). Keep in mind that the Landau-Devonshire method works well for systems with uniform polarization in the bulk. Unfortunately, the systems under study in this thesis have domains and thus this model fails. This failure arises from the Landau theory's construction, that sees this order parameter disappearing uniformly everywhere above a given critical temperature. This said and done, the Landau theory is valid for displacive materials. When faced with such, it is necessary to employ Landau-Ginzburg theory which favours domains (spatial variation of polarization), and examine thin films with boundary conditions.

It seems appropriate to employ ferroelectric polarization primarily as an order parameter while concentrating on ferroelectric materials with the ABO_3 chemical structure. A

lattice distortion that is present during such a structural phase transition should also be considered as an order parameter in a post-primary way. However, for simplicity, it will be ignored for the remainder parts of this thesis. Due to the centrosymmetric nature of the paraelectric case, only even terms may be expanded. The orientation of the polarization should not affect the energy, which is the reason for,

$$F = \frac{\alpha}{2}P^2 + \frac{\gamma}{4}P^4 + \frac{\delta_w}{6}P^6, \quad (2.2)$$

where F and P are free energy and polarization respectively. α and γ are order parameters, while δ_w is domain width. The polarization state should be determined by,

$$\frac{\partial F}{\partial P} = E, \quad (2.3)$$

resulting in an expression for the electric field's relationship to polarization,

$$E = \alpha P + \gamma P^3 + \delta_w P^5. \quad (2.4)$$

The other coefficients in this theory (LGD) are presumed to be temperature independent, while α is assumed to linearly depend on temperature, changing sign at T_0 .

$$\alpha = \beta(T - T_0), \quad (2.5)$$

with $\beta > 0$ and T_0 the transition temperature. Either γ or δ must be positive in order for the ferroelectric phase to be stable. The temperature-dependent development of the order parameter is significantly altered by the sign of the coefficient γ , as we see in the subsections that follow:

1. A transition will be referred to as first order if γ is negative, and that δ is positive and equally considered.
2. A transition will be referred to as second order for positive γ , and that we disregard the δ term.

2.2.1.2 First order phase transition

In Eq. (2.2), this transition takes place if $\gamma < 0$ and δ is positive (Fernandez, 2017). The two criteria;

1. $F = 0$,
2. $\partial F / \partial P = 0$ (for $P \neq 0$),

define the Curie temperature (T_C). The abrupt emergence of polarization in a system occurs at this temperature. One habitual of a first order phase transition is a discontinuity in the order parameter. With $E = 0$, we therefore have:

$$F = 0 = \frac{\beta}{2}(T - T_0)P^2 + \frac{\gamma}{4}P^4 + \frac{\delta_w}{6}P^6, \quad (2.6)$$

and

$$\frac{\partial F}{\partial P} = 0 = \beta(T - T_0)P + \gamma P^3 + \delta_w P^5, \quad (2.7)$$

if solved, we obtain $T_C = T_0 + \frac{3\gamma^2}{16\delta\beta}$ which simply implies that $T_C > T_0$.

Checking at Fig. 2.3, a simulation of F against polarization is shown for different P :

1. When $T > T_C$, we have three wells that are different in nature appearing in F . Only one of them is a global minimum at $P = 0$.
2. When $T = T_C$, we see that three wells are present. Only one of them has $P = 0$.
3. When $T_0 < T < T_C$, we note that, in state where $P = 0$, it is the free energy's local minimum.
4. When $T = T_0$, we see two non-zero polarization outcomes - corresponding to the spontaneous ferroelectric polarization (P_s) being stable. Consequently, it is possible to examine the spontaneous polarization's temperature dependence from Eq. (2.7).

$$P_s^2(T) = \frac{-\gamma \pm \sqrt{\gamma^2 - 4\delta\beta(T - T_0)}}{2\delta}. \quad (2.8)$$

Usually, when we are at T_C , we see three polarization degenerate states. If a system will be in $P = 0$ or $P \neq 0$ state, that's T_C directional dependent. (i.e from a higher (T_C^+) or a lower (T_C^-)). On cooling at T_C , the system remains with $P = 0$, on further cooling, such a system jumps to either P_s^+ or P_s^- . This is the signature of the first transition.

$$P_s^+ = \sqrt{-\frac{3\gamma}{4\beta}} \quad ; \quad P_s^- = \sqrt{-\frac{3\gamma}{4\beta}}. \quad (2.9)$$

What happens if we heat at T_C ? The system, will take upon P_s^+ or P_s^- , but this is dependent to its history.

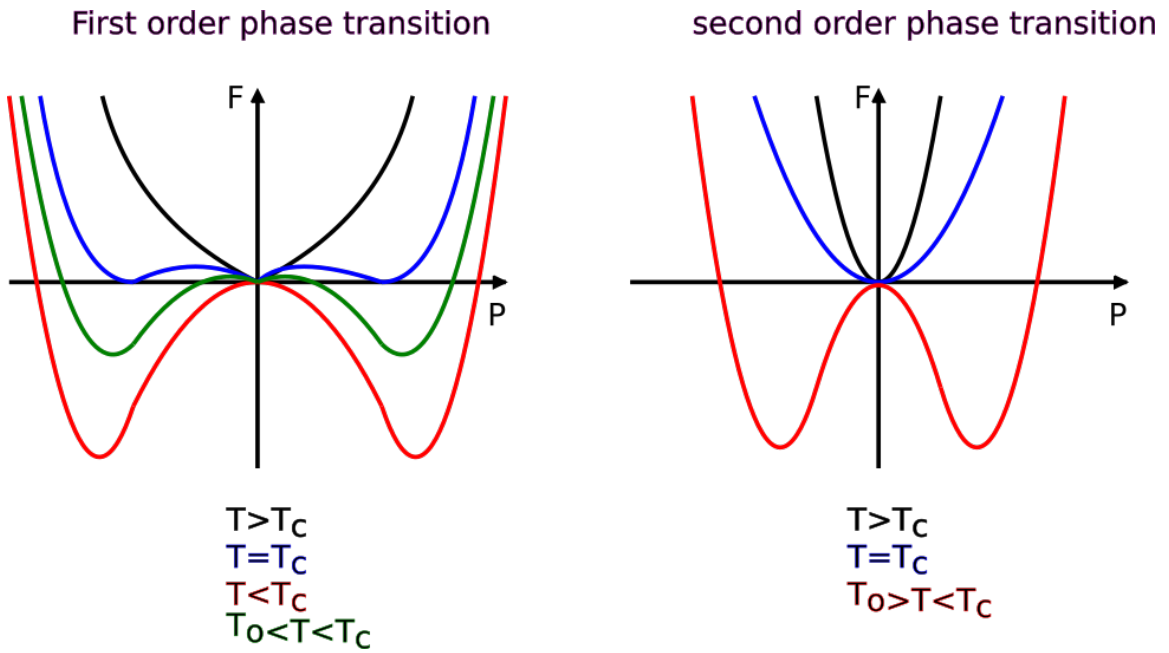


Figure 2.3: An example of the phase transition between first and second orders. The free energy across a certain phase transition for both kinds is displayed as a function of temperature and polarization.

2.2.1.3 Second order phase transition

Here, we can negate the higher order terms because γ is positive. We will then write $E = 0$:

$$\frac{\partial F}{\partial P} = 0 = \beta(T - T_0)P + \gamma P^3. \quad (2.10)$$

1. When $\alpha > 0$, this is straight since from Eq. (2.10), we only have one solution of polarization: $P = 0$.

2. When $\alpha < 0$, we find two solutions of polarization in Eq. (2.10)
3. When $\alpha = 0$, unsolicited polarization do appear when $T = T_0$. This the Curie temperature. Then, for a second order transition, $T_0 = T_C$. That means, the solution to Eq. (2.10) when $P \neq 0$ gives P_s .

$$P_s^2 = \frac{\beta}{\gamma}(T_C - T). \quad (2.11)$$

The free energy exhibits two minima at zero field and when $T < T_C$. These minima are associated by $P = \pm P_s$. Most of the time, the energy barrier between the wells determines the minimal electric field needed to flip all of the dipoles at once (Fernandez, 2017).

2.2.2 Hysteresis - A critical ferroelectric signature

A piezoelectric material becomes polarized when a specific amount of an electric field is exposed to it. If a crystal is already polarized, applying a field will cause this polarization to either increase or decrease, depending on the field's direction. The polarization P of a ferroelectric can be expressed as follows within the range of tiny E .

$$P = P_s + \epsilon_0 \chi E, \quad (2.12)$$

where P_s , χ , and ϵ_0 are spontaneous polarization, electric susceptibility and vacuum permittivity in that order.

If you recall the definition of ferroelectricity in Chapter 1, we said that a material portraying this trait must have a polarization that is switchable in the presence of an applied field. This behaviour causes the hysteresis we saw in Fig. 1.3. Such hysteretic behavior can be calculated mathematically by resolving the equation $dF/dP = E$ for P .

$$\left. \frac{dF_{LD}}{dP} \right|_{P \neq 0} = 2\alpha_1^* P_z + 4\alpha_{11}^* P_z^3 + 6\alpha_{111} P_z^5 = E. \quad (2.13)$$

The Helmholtz free energy (F) is asymmetrized by the electric field, favoring one state over the other and causing the hysteretical behavior indicated in Fig. 1.3. This polarization

loop demonstrates that the sample will change polarization for fields larger than the coercive field E_c , which is a threshold value. The additional polarization contribution resulting from the dielectric response occurs as the field strength increases. That means, the dipoles remain aligned, while the system on the other hand maintains its polarization even when the field goes to zero. The dipoles will abruptly change into the opposing polarization at the coercive value when the opposite field strength increases. This is, of course, a theoretical perspective that, because of the heterogeneity of the polarization, defects, domains, etc., differs from what actually occurs in real systems. The development and nucleation of zones with opposing polarizations represents a more plausible scenario for switching (Gao et al., 2011).

2.2.3 Tetragonality and polarization

Tetragonality taking place inline with the polarization axis in ferroelectric materials changes with polarization. This tetragonality, is defined as c/a when focusing on thin films with polarization P_z pointing away from the surface. Given that the expression for the out-of-plane strain S_z is

$$S_z = \frac{c_{film} - a_{film}}{a_{film}}. \quad (2.14)$$

where, c_{film} and a_{film} are the a and c lattice parameters in a tetragonal structure ($a = b \neq c$). Likewise, S_x , which is simply the in-plane misfit strain, is written as,

$$S_x = \frac{a_{sub} - a_0}{a_0}, \quad (2.15)$$

where a_0 is the theoretical lattice of the film. This follows that we can write: $c_{film} = a_{film} (S_z + 1)$ and after couple of manipulations, one gets:

$$\begin{aligned} \frac{c_{film}}{a_{film}} &= (1 - 2S_x) \left(1 - \frac{2c_{12}S_x}{c_{11}}\right) + \frac{g_{11}}{c_{11}} (1 - 2S_x) P_z^2, \\ &= (c/a)_{para} + cst \cdot P_z^2, \end{aligned} \quad (2.16)$$

The first part is analogous to c/a value of the paraelectric state that is also nonpolar. The lesson to be learned from this is that the c measurement provides a polarization value

indicator. Please note that the critical temperature of a ferroelectric can be obtained since the c lattice entirely depends on temperature.

2.2.4 Polarization according to the modern theory

This is a theory that makes it possible for us to accurately describe ferroelectricity in materials. Three individuals, Resta, King-Smith & Vanderbilt (King-Smith & Vanderbilt, 1993, 1994a; Resta, 1999, 1998), are the creators of this microscopic theory on polarization. They put out a beautiful definition of how a periodic solid's polarization can change. This somehow difficult issue was caused by the fact that; non-polar crystals would result in non-zero polarization in their bulk while computing the polarization, and that this value would be depended on the selected unit cell. The key was realizing that while polarization may be a *multi-valued* concept, polarization changes are simply *single-valued*. Note that we can not measure polarization itself, but only the difference between two polarization levels.

From a traditional perspective, we think of the charges as localized. According to quantum mechanics, typically, electrons are in Bloch states. They are also known as de-localized states in most of the cases. The genius of this formalism developed by the trio is that, it uses Wannier functions to maintain the conventional notion of localized charges. A Wannier function is just the sum of several Bloch functions that describe the charge density in a particular crystal across a certain Brillouin zone (Mostofi et al., 2008). The Wannier functions, are usually spatially confined and thus serve as a solid foundation for electronic calculations. Wannier functions, are frequently used to depict displacements of charge densities and to illustrate chemical bonds. As a result, while computing the polarization, it is important to consider two contributions: the ionic point-charge contribution and the Wannier contribution of the valence electrons.

According to this definition, the difference between the polarization of the polarized system and the polarization of the unpolarized system determines the ferroelectric spontaneous polarization². Note also that if cations keep on moving within a unit cell in a

²This is the real procedure of estimating polarization in any crystal.

centrosymmetric solid, the Wannier centers on the other hand also move, creating an admixture of the ionic and covalent states. The *effective charge*, Z^* , produced by this covalency is greater than the one, in a very pure ionic image. It is depicted in Eq. (2.17) using volume of a given unit cell (Ω), displacement (r) and the electronic charge (e).

$$Z_{ij}^* = \frac{\Omega}{e} \frac{\partial P_i}{\partial r_j}. \quad (2.17)$$

As a result, if a sub-lattice of a crystal is moved by d in the direction i , its polarization is impacted not only in that direction but also in the orthogonal direction. Therefore, the shifting of these effective charges ($\delta P_i = \frac{e}{\Omega} Z_{ij}^* \delta r_j$), leads to a change in polarization δP . In other words, the polarization brought on by an atomic displacement corresponds to the Born effective charge (Ghosez et al., 1998). The computed effective charges have a potential to exceed the ionic charges by a wide margin. While lead (Pb) has an ionic charge of +2 in PbTiO_3 , its effective charge is determined to be +3.9. It has been possible to dynamically examine polarization and subsequently ferroelectricity thanks to this combination of ionic charge and Wannier centers. The key signature of this model is pegged to the fact that polarization charges are the only variables that can be measured experimentally. To get a deep understanding on polarization and all that appertains to it, refer to the pioneer publications (King-Smith & Vanderbilt, 1993, 1994a; Resta, 1999, 1998) because they contain more information and a comprehensive mathematical analysis.

2.2.5 Depolarization field as the cause of 180° domains that are ferroelectric

2.2.5.1 What the depolarization field does

For a very long time, it has been supposed that a portion of a ferroelectric material's ferroelectric capabilities are lost as its thickness diminishes. This is attributed to the fact that bound charges at ferroelectric slabs surfaces produce an electric field called the *depolarization field* that destabilizes spontaneous polarization by pointing in the opposite direction. Free charges at the ferroelectric surfaces do screen out bound charges, lowering

this depolarization field. These free charges can act as carriers in the metallic electrodes, in addition to ions from the surrounding environment and mobile charges from the semi-conducting ferroelectric itself. Their screening ability, or how closely they can approach surfaces that are affected by the interface layer's dielectric constant, is represented by an effective screening length (λ_{eff}). It is prudent to say that at each interface, a potential drop is brought about. This causes a significant voltage drop across the given sample and that the voltage drop equals the total of the voltage drop at each interface due to short-circuit boundary circumstances (*but of opposite sign*).

As a result, the two interfaces are the sole factors affecting this voltage drop, which makes the film thickness irrelevant. Thus, for thinner samples, the electric field is stronger ($\Delta V = E \cdot t$). The depolarization field that we refer to throughout this thesis is not a stray field associated with the actual polydomain ground state, but rather, it is a field that would be produced by the uniform polarization in a PbTiO_3 , and has a finite screening length.

This field acts as a very important force for the formation of domains. Note that screening characteristics of an electrode, which are highly influenced by the caliber of an interface between the film and the electrode, as well as by interface chemistry (Stengel et al., 2009a), are reflected by the variable λ_{eff} . The depolarization field would be perfectly cancelled if the ideal metallic electrodes had $\lambda_{eff} = 0$. However, in practice, even for those structurally ideal metal to insulator interfaces, the screening charges do spread over a limited length λ_I , and that means, finite dielectric constant of an interface layer ϵ_I contributes to effective screening length via $\lambda_{eff} = \lambda_I/\epsilon_I$. Previous studies (Mehta et al., 1973; Stengel & Spaldin, 2006; Stengel et al., 2009b; Pacchioni & Valeri, 2011) are rich and have more specifics regarding this model.

First-principles calculations by Stengel and Spaldin (Stengel & Spaldin, 2006) emphasized the significance of contact chemistry in influencing the screening. For instance, despite SrRuO_3 being metallic with very strong ionic polarizability, its electronic traits have been found to be subpar and this leads to the so called *dead-layer* at the interface (Fernandez, 2017). On the other hand, Junquera and co-workers (Junquera & Ghosez, 2003b) demonstrated that BaTiO_3 in between SrRuO_3 electrodes loses ferroelectricity below 6 unit

cells as a result of dipoles presence at the interfaces that produce a strong depolarization field.

These findings suggest that, despite remarkable advancements in oxide interface growth quality, their screening properties are still inherently constrained. This raises significant issues for this thesis. By utilizing free charge carriers, the researcher attempts to address the screening threat in oxide interfaces as described in Chapter. 4 of this thesis.

Most calculations indicate that single elements like platinum or gold are frequently the best electrodes to utilize for screening. According to Sai and co-workers (Sai et al., 2005), platinum electrodes improve polarization in thin films of PbTiO_3 and BaTiO_3 when compared to oxide metallic electrodes. The significance of the chemical bonding at the metal oxide interface was theoretically shown by Stengel and others (Stengel et al., 2009a). It was discovered that anytime certain boundaries were polarizable, the ferroelectricity is increased. In experiments, strain, flaws, and even grain boundaries, do contribute to poor screening which in the long run results in depolarization fields, in addition to the interface chemistry. It is much correct to say that a system can easily become depolarized due to a high depolarization field.

Ferroelectrics can nevertheless manage to maintain their polarization, even when effective screening mechanism is absent. For instance, the system might ‘split’ into polarization-opposite domains, famously known as the Kittel domains, which are referred to as 180° domains in this case. S.K. Streiffer *et al.* (Streiffer et al., 2002) detected these domains in ultrathin films of PbTiO_3 using synchrotron X-ray diffraction in 2002.

Despite a significant remnant of polarization within each domain, a sample’s macroscopic characteristics are drastically changed when it forms domains. Thus, it is crucial to comprehend and manage the development of these domains. Literature hints that, scholars have employed many different mechanisms for screening the bound charges at the oxide interfaces; *electrodes* (Streiffer et al., 2002; Nagarajan et al., 2006; Takahashi et al., 2008), *dielectric spacers* (Lu et al., 2012; Lichtensteiger et al., 2014), and equally *ionic adsorbates* (Fong et al., 2006; Kolpak et al., 2007). As if that is not enough, switching of photochemical stripe domains was reported in the work of Takahashi and co-workers (Taka-

hashi et al., 2008), while Highland and company (Highland et al., 2010) investigated the possibility of polarization switching without domain formation in ultrathin films near the ferroelectric critical temperature T_C .

Complex systems like $\text{PbTiO}_3/\text{SrTiO}_3$ have been studied (Dawber et al., 2007; Zubko et al., 2012; Tang et al., 2015; Yadav et al., 2016) and they have proved useful in understanding the correlation between the nanoscale domains and electrical properties. Also to note is that construction of 180° DWs suppresses piezoelectric response and reduction of macroscopic polarization (Nagarajan et al., 2006). Many studies have also addressed the formation of 180° DWs and also studied the macroscopic and microscopic properties in them (Stephanovich et al., 2005; Luk'yanchuk et al., 2009; Prosandeev & Bellaiche, 2007; Aguado-Puente & Junquera, 2008).

In a similar spirit, this thesis set out to ascertain by use of density functional theory, the structural and electronic traits of such 180° DWs. The domain herein are that of free standing $\text{PbTiO}_3/\text{PbTiO}_3$ slabs.

The results of the literature search indicate that the previous computations cannot be used to answer questions about the intrinsic critical thickness for stabilizing the two-dimensional conducting layers for the screening of the polarization charges, the spatial extension of the hole and electron gases, or the size of the polarization that would result from the induction of such DWs in an ideal slab.

2.2.6 Formation of domain walls (DWs) in ferroelectrics

The size of ferroelectric domains, that is to say the lateral width, is in principle dictated by the famous *Kittel* law. This law was initially tailored for magnetism (L. D. Landau & Lifshitz, 1935; Kittel, 1946, 1949) and then extended to ferroelectricity (Kittel, 1972). As was already established, depending on their electrical boundary conditions, ferroelectric thin films can exhibit a variety of polarization states. Usually, in such systems, the type of mechanical boundary conditions are additionally significant. As an example, in this thesis, PbTiO_3 is grown on a SrTiO_3 substrate, what will happen is that the in-plane lattice parameter of SrTiO_3 will constrain the long axis of PbTiO_3 , and dictate the polarization

to be perpendicular to the surface. The functional characteristics of a film are affected by the electrical boundary conditions that cause depolarization and built-in fields, which also have a capability to determine if a sample is monodomain or polydomain. In the event of insufficient screening, the sample may develop 180° ferroelectric domains with opposing polarization, leaving the sample with a surface charge of zero overall and a vanishable depolarization field (at least away from the interfaces). On a length scale comparable to the domain width d_w , the fringing fields typically penetrate the film with an exponential decline.

In principle, this fields' associated electrostatic energy is related to the domain width as

$$F_P \sim P_s^2 d_w. \quad (2.18)$$

In principle, this suggests that small domains are preferred, yet small domains tend to have more energy-intensive DWs. The short-range interactions are changed when the polarization changes through the DW, which results in this energy cost. This energy is given as:

$$F_d = \sigma_{dw} \frac{t}{\rho}, \quad (2.19)$$

where t , σ_{dw} , and $1/\rho$ are the thickness of the film, the DW energy per unit area of the wall and representation of the DW density in that respective. It is wise to say that $\sigma_{dw} \sim P^3$ as proved by Mitsui and Furuichi (Mitsui & Furuichi, 1953). As a note, DWs have been reported to be larger in ferromagnets than they are in ferroelectrics (Schilling et al., 2006).

In such systems, the total energy is given as $F = F_P + F_d$. Interestingly, one is able to obtain the famous Kittel law, if F is minimized with respect to d_w :

$$d_w \sim \sqrt{t}. \quad (2.20)$$

This implies a very symbiotic relationship between a ferroelectric film and the domains. When the ferroelectric film's thickness is smaller, the domains too get smaller. The constant of proportionality in Eq. (2.20) is dependent on the properties of a material.

In order to prevent significant polarization changes, the electrostatic boundary condi-

tions should be maintained when comparing samples of the same material that are varied in thickness. Intriguingly, it has been demonstrated that this equation holds true to those ferroelectrics that have a thickness ranging over six orders of magnitude.

2.2.6.1 Depolarization versus built-in field

A film's polarization can be either be destabilized or enhanced by the nuances governing the metal-oxide contacts (Stengel et al., 2009a). There might be a built-in field in addition to the depolarization field. The latter results either directly from the asymmetry of the structure itself or, once more, from the chemistry at the interfaces. In the end, both of these fields have an impact on the intrinsic domain structure and polarization stability. One must recollect the well-known double well potential property of ferroelectrics in order to fully understand the various effects of ferroelectrics on polarization. This built-in field often favors one orientation of polarization and adjusts this polarization relative to the field loop in a common direction. The polarization loop, on the other hand, shrinks as a result of the depolarization field, which is always oriented in the opposite direction of the polarization. This minimizes the coercive fields.

CHAPTER THREE

FIRST-PRINCIPLES FORMALISM

3.1 Introduction

This research aims to theoretically investigate the screening properties in nanometric ferroelectric systems, where the interfaces between ferroelectric and ferroelectric materials are important. The combined intrinsic bulk properties of the materials making up the device and interface-specific properties give such systems their overall characteristics. The region of interest in the majority of the systems we are interested in, which often exhibit a planar geometry, is only a few nanometers thick, yet the system is expanded in the plane. Consider a typical ferroelectric thin film sample. The ferroelectric layer is only a few atomic monolayers thick, yet the device's surface area can reach 1 cm^2 and, in reality, can be expected to extend indefinitely in the plane given the in-plane to out-of-plane dimensions ratio. As we wish to run simulations with atomic precision to capture the nuanced physics of the interface in macroscopically huge systems, the situation is difficult. This Chapter will demonstrate how these challenges can be made simpler.

Condensed matter's explicit atomic nature must be taken into account at the atomic scale, where the classical continuum models of condensed matter are no longer applicable and the rules of quantum mechanics must be applied. First-principles methods are those that purely rely on electromagnetism and quantum mechanical equations, without employing any parameters that have been fitted to the outcomes of experiments. It is theoretically conceivable to use these techniques to research condensed matter system attributes in environments that are challenging or impossible to recreate in a laboratory, and they allow for the separation of distinct effects' diverse contributions. It is important to say that throughout this chapter, we employ atomic units, i.e. $e = \hbar = m_e = 1$. Unless it is stated otherwise, take it as that.

3.2 Theories Employed in this Work

The behavior of a material's fundamental atomic constituents, such as its nuclei and electrons, are studied in order to determine its properties at the nanometric scale. The predicted value of any physical quantity at this scale can potentially be determined according to quantum mechanics if one is aware of the wave function ψ for each particle in the system. Assuming a time-independent situation, we need to find the solution to the Schrödinger equation of the system as shown in Eq. (3.1).

$$H(\mathbf{R}, \mathbf{r})\psi(\mathbf{R}, \mathbf{r}) = E\psi(\mathbf{R}, \mathbf{r}), \quad (3.1)$$

where H is the Hamiltonian of the system, which is a function of the position of all nuclei, $\{\mathbf{R}\}$, and electrons, $\{\mathbf{r}\}$; and E is the total energy of the system. It is possible to write the Hamiltonian of a system of interacting nuclei and electrons as

$$\begin{aligned} H(\mathbf{R}, \mathbf{r}) &= T_N + T_e(\mathbf{r}) + V_{NN}(\mathbf{R}) + V_{ee}(\mathbf{r}) + V_{Ne}(\mathbf{R}, \mathbf{r}), \\ &= -\frac{1}{2} \sum_I \frac{1}{M_I} \frac{\partial^2}{\partial R_I^2} - \frac{1}{2} \sum_i \frac{\partial^2}{\partial r_i^2} + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{I, i} \frac{Z_I}{|\mathbf{R}_I - \mathbf{r}_i|}, \end{aligned} \quad (3.2)$$

where M_I is the mass of the nucleus, while Z_I and Z_J are nuclear nuclear Coulomb electrostatic interaction. In Eq. (3.2) the kinetic energy of nuclei and electrons are given by T_N and T_e respectively, while the nucleus-nucleus, electron-electron and nucleus-electron electrostatic interactions are given by V_{NN} , V_{ee} and V_{Ne} respectively. The latter can be thought as the “glue” of condensed matter systems since it is the only attractive interaction among all of them. Eq. (3.1) is difficult to solve except for the smallest molecules, despite the fact that solving it would yield all information about the system under study. To make this a problem that can be solved in real-world systems, a number of approximations must be made:

1. **Born-Oppenheimer approximation** enables the decoupling of electron and nuclei

motion.

2. **Density functional theory** replaces the electronic wave function with the electric charge density as the primary variable offering an effective way of solving electronic structure problem. Although this formalism is exact, the **exchange-correlation energy functional** needs to be approximated.
3. **Pseudopotentials** can be used to reduce the quantity of basis functions needed by eliminating a significant portion of chemically inert electrons and avoiding sharp oscillations of the wave functions at the core region.
4. **Periodic boundary conditions** enable the modeling of infinite periodic crystals, simplifying the issue to calculations on a simulation box that is repeated on a regular basis. Furthermore non-periodic systems can be studied within these boundary constraints using the **supercell** method.
5. A finite **sampling of reciprocal space** is typically used to calculate physical magnitudes that need integrations over the first Brillouin zone.
6. Our search for an unknown function becomes a search for a set of coefficients when one-electron wave functions are expanded into a linear combination of **basis functions**.

We will attempt to give a brief summary of how we use these approximations to solve our problem rather than providing a thorough explanation of how each one was derived because it would go beyond the scope of this thesis. In an effort to make clear their boundaries of applicability, we shall highlight their strong and weak characteristics.

3.3 Born-Oppenheimer Approximation

The Born-Oppenheimer or adiabatic approximation is the first one we employ to convert Eq. (3.1) into a problem that can be solved. The mass ratio between an electron and a proton is comparable to that of a newborn human and an adult elephant, taking into

account that nucleus mass is thousands of times greater than electron mass. Since the velocities of nuclei and electrons are typically in the order of 10^3 and 10^6 m/s respectively, we can expect that the kinetic energies of the electron to be significantly higher than those of the nuclei. As a result, the nuclei kinetic energy T_N in Eq. (3.2) can be regarded as a perturbation of an electronic Hamiltonian.

$$H_e(\mathbf{r}; \mathbf{R}) = T_e(\mathbf{r}) + V_{ee}(\mathbf{r}) + V_{Ne}(\mathbf{r}; \mathbf{R}) + V_{NN}(\mathbf{R}), \quad (3.3)$$

where nuclear positions are introduced as parameters and kept constant during the solution of the electronic problem by separating parameters and variables with a semicolon. Note that now in Eq. (3.3) $V_{NN}(\mathbf{R})$ is merely a constant and $V_{Ne}(\mathbf{R}, \mathbf{r})$ is the energy of the electrons in a fixed potential created by nuclei. Now, after solving the electronic Schrödinger Eq. (3.4) we obtain its eigenvalues E_e which functions as the potential energy for the nuclei whose movement can often be solved using classical mechanics.

$$H_e(\mathbf{r}; \mathbf{R})\Psi(\mathbf{r}) = E_e\Psi(\mathbf{r}). \quad (3.4)$$

The quantum description of the electronic characteristics for every given ionic position can be obtained from the solution of the electronic term of the Schrödinger equation. Furthermore, forces and stresses that can be employed for structural relaxation, molecular dynamics simulations, or phonon analysis can be acquired. The solution of the Schrödinger equation provides the quantum description of electronic properties for any given ionic positions. Moreover, forces and stresses can be obtained which can be used to perform structural relaxations, molecular dynamics simulations or phonon analysis. The Born-Oppenheimer approximation substantially simplifies the problem by decoupling the movement of the nuclei and the electrons while also enabling accurate and efficient characterization of both the electronic and structural features.

3.4 Density Functional Theory

The many body electronic wave function $\psi(\mathbf{r})$, a function of $3N_e$ coupled variables (where N_e is the number of electrons in the system), must be antisymmetric with respect to an interchange of any pair of electrons because electrons are fermions in order to solve Eq. (3.4) for a set of interacting particles. In the vast majority of instances, this task remains unattainable. The majority of quantum chemistry approaches to this problem produce the all-electron wave function from a combination of Slater determinants, which themselves are constructed from one-particle wave functions.

Density functional theory (DFT) which was born in the 1960's from the works of Hohenberg and Kohn (Hohenberg & Kohn, 1964) and Kohn and Sham (Kohn & Sham, 1965) provides an elegant and different solution to the electronic problem. Hohenberg and Kohn established in the first work that the ground state electronic density $\rho_0(\mathbf{r})$ determines the external potential $v_{ext}(\mathbf{r})$ in the electronic Hamiltonian, such as the electrostatic potential formed by the nuclei. It follows logically that the ground state electronic density defines the entire electronic Hamiltonian, as well as the ground state energy and wave function. As a result, it is possible to define an energy functional of the density, and minimizing of such a functional would yield the system's ground state density for a given external potential. We reformulate the problem of searching for the many-body Schrödinger equation solution in terms of the electronic density, which is a function of just three variables, using the ground-breaking work of Hohenberg and Kohn (Hohenberg & Kohn, 1964). The study by Hohenberg and Kohn, however, offers no guidance as to how to extract such properties from it, despite the fact that the ground state electronic charge density is in theory adequate to derive any attribute of a particular material.

At this point, the work by Kohn & Sham (Kohn & Sham, 1965) becomes important because it precisely offers a practical way to utilize the density functional theory. The approach involves using a fictitious system of non-interacting particles moving in an effective potential to replace the many-body problem of interacting electrons. The one-electron wave functions ($\psi_i(r)$), can be used to determine the electronic charge density of this auxiliary system as

$$\rho(\mathbf{r}) = \sum_i^{occ} |\psi_i(\mathbf{r})|^2. \quad (3.5)$$

The energy functional of the real system can be expressed in terms of the one-electron auxiliary functions and the electronic density as shown in Eq. (3.6) if the system is built so that the electronic charge density of non-interacting particles approximates the real one.

$$\begin{aligned} E_{KS}[\psi_i] = & -\frac{1}{2} \sum_i \langle \psi_i | \nabla^2 | \psi_i \rangle + \frac{1}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \\ & + E_{xc}[\rho(\mathbf{r})] + \int v_{ext}(\mathbf{r})\rho(\mathbf{r}) d\mathbf{r} + E_{NN}. \end{aligned} \quad (3.6)$$

The kinetic energy of a group of non interacting electrons is the first term in the equation. The second is the Coulomb electrostatic energy, often known as the Hartree term in the context of condensed matter quantum mechanics. The third term in the equation is the so-called exchange-correlation term, which includes any electron-electron interactions other than the standard Coulomb repulsion as well as the difference in kinetic energy between the real electrons and the non-interacting particles. The fourth term is the potential energy of the electrons due to the external potential, which is typically the potential formed by the nuclei and the final term is the electrostatic energy between nuclei.

The problem relating to electronic density changes into the variational problem over the set of one-electron functions. The minimization of the energy functional of Eq. (3.6) should give rise to the set of $\{\psi_i\}$ that would lead to the ground state electronic density using Eq. (3.5) for a real system of interacting electrons. The constraint for this minimization is orthonormalization of the one-electron wave functions using Eq. (3.7).

$$\langle \psi_i | \psi_j \rangle = \delta_{ij}, \quad (3.7)$$

This gives rise to the following Schrödinger-like equations

$$H_{eff}\psi_i(\mathbf{r}) = \left[-\frac{1}{2}\nabla^2 + v_{eff}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = E_i\psi_i(\mathbf{r}), \quad (3.8)$$

where the effective potential takes the form

$$v_{eff}(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{xc}(\mathbf{r}) + v_{ext}(\mathbf{r}). \quad (3.9)$$

The exchange-correlation potential is defined as

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})}. \quad (3.10)$$

The so-called Kohn and Sham equations, which consist of Eq. (3.5), Eq. (3.8) and Eq. (3.9), when solved give one-electron eigenstates whose electron density match the ground state density of the actual system. In practice this problem is solved self-consistently: starting with a trial set of $\{\psi_i(\mathbf{r})\}$ equations are solved for a trial density $\rho_{in}(\mathbf{r})$ and a new output density $\rho_{out}(\mathbf{r})$ is obtained. A comparison between the input and output densities is carried out creating a new input density as a mix between $\rho_{in}(\mathbf{r})$ and $\rho_{out}(\mathbf{r})$. The procedure is iterated until we achieve self consistency where $\rho_{out}(\mathbf{r}) = \rho_{in}(\mathbf{r})$.

Many features of the density functional theory should be emphasized at this stage. First, is that DFT is an *exact* theory, excluding the Born-Oppenheimer approximation, which is the foundation for the majority of theoretical condensed matter physics approaches. Every *ground state* physical property of the system might be deduced from the density computed using the one-electron wave functions obtained from the Kohn-Sham equations. This density is equivalent to the real ground state electronic density. This is valid as long as the energy functional of Eq. (3.6) is the exact one. Unfortunately, since the exchange-correlation term is unknown, approximations must be made in practice.

3.4.1 Exchange and correlation functional

Although DFT is exact as previously remarked, the form of universal exchange correlation energy functional to be used is in practice approximated since it is unknown.

$E_{xc}[\rho(r)]$ is in principle dependent on the charge density in every point of space. For the local density approximation (LDA) however, we could presume that this functional could be approximated by a function of the density at each point for slowly varying charge

densities such as those seen in metals. According to this approximation, the exchange and correlation energy at a particular site is that of a homogeneous electron gas, ϵ_{xc}^{hom} with the same electronic density as the system at that location,

$$E_{xc}^{LDA}[\rho(\mathbf{r})] = \int \epsilon_{xc}^{hom}(\rho(\mathbf{r}))\rho(\mathbf{r})d\mathbf{r}. \quad (3.11)$$

Quantum Monte carlo simulations (Ceperley & Alder, 1980) can be used to precisely calculate the exchange-correlation potential of an homogeneous gas. Functional terms can be added depending on the gradients of the charge density to improve this approximation known as generalized gradient approximation (GGA) where the exchange-correlation term is still a “semi-local” function and not a functional.

$$E_{xc}^{GGA}[\rho(\mathbf{r})] = \int \epsilon_{xc}(\rho(\mathbf{r})|\nabla^2\rho(\mathbf{r}), \dots)\rho(\mathbf{r})d\mathbf{r}. \quad (3.12)$$

A linear combination of the previous functionals (LDA or GGA) with the Hartree-Fock exact exchange calculated from the one-electron wave functions gives hybrid functionals. This hybrid functional as well as other functionals go beyond LDA and GGA in terms of precise approximations. These non local approximations are expensive and have great computational cost compared to local functions. Despite the cost, some of these hybrid functionals like the B1-WC (Bilc et al., 2008), have demonstrated good ground state electronic and atomic structure making them reasonable options to go beyond the LDA for some of the results of the present work.

The local LDA and GGA functionals are commonly employed owing to their efficient and remarkable performance, despite being crude approximations. LDA and GGA are surprisingly reliable especially for study of structural properties (see Table. 3.1) in many cases. Nevertheless, these approximations have notable errors the most serious being estimation of electronic band gap where values obtained are typically around 50% of the experimental gap. A practical application of the density functional theory is made possible by additional approximation to those needed to approximate the exchange-correlation functional. This enables highly effective yet accurate and reliable quantum simulations of con-

densified matter systems. For comparative studies and deep learning, see literature (Khein et al., 1995; Filippi et al., 1994; Z. Wu et al., 2004).

Table 3.1: Significant errors that are easily introduced while computing the structure, energetic and the electronic properties of materials by use of LDA & GGA approximation.

	LDA	GGA
Lattice Constants	$-1\% - -3\%$	$+1\%$
Bulk modulus	$+10\% - +40\%$	$-20\% - +10\%$
Cohesion energy	$+15\%$	-5%
Band gap	-50%	-50%

3.4.1.1 LDA+U+SOC on the Jacob’s ladder

A quick check on Table. 3.1, it is important that DFT calculations ought to be slightly improved to give better predictions. Previous research by Cococcioni and co-workers (Cococcioni & de Gironcoli, 2005) framed the Hubbard model as a correction to the self interaction error, which has been utilized to simulate Coulomb repulsion in transition metal oxide lattices. Effective Hubbard corrections can specifically rectify the erroneous curvature brought on by the self interaction error. This inaccurate curvature can be overcome by using quadratic DFT + U correction terms in electronic occupation. We briefly describe the Hubbard corrections in this section along with their contribution to the DFT energy. The Hubbard manifold’s definition, which is used when applying the correction, is crucial to understanding the adjustment we propose. The localized, atom-centered basis functions for the atom types (transition metals) to which the correction will be applied can be used to create this. This will only apply to the d and f electrons, as stated in Cococcioni and co-workers. We define a projector on local atomic orbitals centered on an atomic site i to get started.

$$\hat{P}_{m+m'}^i = |\phi_{m'}^i\rangle\langle\phi_m^i|. \quad (3.13)$$

The projector is constructed with the localized atomic orbitals, ϕ^i centered around site i for given magnetic quantum numbers m and m' . Site-centered atomic orbitals that are not orthonormal from site to site are employed in several techniques. We may get the occupation numbers by projecting the Kohn-Sham states $|\psi_{v\mathbf{k}\sigma}\rangle$ onto these localized orbitals.

These are provided for a site i as,

$$n_{mm'}^{i\sigma} = \sum_{\mathbf{k}} \sum_v^{N_{\mathbf{k}} \text{ Occ.}} \langle \psi_{v\mathbf{k}\sigma} | \hat{P}_{mm'}^i | \psi_{v\mathbf{k}\sigma} \rangle, \quad (3.14)$$

where the sum runs over the $\mathbf{k}$ -points in the first Brillouin zone, $N_{\mathbf{k}}$ and over occupied bands with index v , for spin index, σ . These occupation matrices are used to create the $\mathbf{n}^{i\sigma}$ occupation matrices for each unique site. From here, the total occupation of a given site (including spin) can be determined by the trace of the occupation matrices, $n^i = \sum_{\sigma} \text{Tr}[\mathbf{n}^{i\sigma}] = \sum_{\sigma m} n_{mm}^{i\sigma}$. The correction to the DFT energy follows simply in terms of these occupation matrices, is commonly referred to as E_U and is given as,

$$E_U = \frac{1}{2} \sum_{i\sigma} U^i \text{Tr}[(\mathbf{I} - \mathbf{n}^{i\sigma}) \mathbf{n}^{i\sigma}], \quad (3.15)$$

where strength of the correction on a given site is determined by the effective U parameter, U^i . The DFT energy as a function of electron occupation can roughly be represented as a parabola. Under this approximation, we can restore the piecewise linear behavior of the DFT energy as a function of occupation with the E_U correction above. This is achieved when a value of U^i counterbalances the spurious curvature from the regular GGA calculation, which is related to the second derivative of the total energy with respect to electronic occupation. The strength of the correction needed to do so is given by:

$$U^i = \frac{d^2 E}{d(n^i)^2} - \frac{d^2 E_{\circ}}{d(n^i)^2}, \quad (3.16)$$

where the first term is the second derivative of the interacting system's energy E in terms of electronic occupancy. By taking the second derivative of the energy of a non-interacting system, the changes that are not connected to electron-electron interactions must be subtracted out in the second term. For a certain site, this number may be thought of as the averaged coulombic repulsion less the Hund's exchange.

DFT computations can benefit from two different forms of correction to increase precision: DFT+ U and SOC (spin-orbit coupling). While SOC corrects the spin-orbit in-

teraction, DFT+U corrects the electronic interactions in strongly correlated systems. In this case, we perform a slight modification of Eq. (3.11) as will be discussed in detail in Sec. 5.1.1 of this thesis.

3.5 Pseudopotentials

The electrons in an atom can be divided into *core* and *valence* electrons based on how they contribute to the creation of bonds and chemical reactions. The inner core electrons are more intensely localized near the nucleus and have deeper energy levels. They are essentially insensitive to the chemical environment since their orbitals do not overlap those of nearby atoms. In reality, the majority of a condensed matter system's physical and chemical characteristics can be precisely characterized in terms of the valence electrons, and the primary function of core electrons is to screen the nucleus potential experienced by the former. Core electrons introduce an undesirable feature exclusion principle forces the orthogonality between core and valence wave functions besides unnecessarily increasing the number of electrons in the system (and thus the number of Kohn-Sham eigenfunctions to compute). This causes strong oscillations of the valence wave functions in the inner region of the electronic cloud. In order to accurately represent the strong oscillations of the wave functions, the description of valence states necessitates the use of a very large number of basis functions or very fine grids since most DFT methods make use of real space grids or expand the Kohn-Sham eigenfunctions in plane waves (see Sec. 3.8). Pseudopotentials were developed to address these issues. The pseudopotential approximation is executed in two steps: (i) frozen-core approximation where core electrons can be considered to be frozen into their isolated atom configuration and thus not affected by chemical environment, and then (ii) a screened and smoothed fictitious potential can be used to replace the frozen core electrons and the nucleus potential, the pseudopotential. Valence wave functions are then allowed to vary smoothly in the inner regions once the nucleus potential has been screened and core wave functions removed. In actuality, the development of a pseudopotential begins with an all-electron simulation of a single atom in a standard electronic configuration. The pseudopotential is then utilized to replace the nucleus potential

along with the core electrons, forcing the valence wave functions to match those of the all-electron atom in the outer area (in practice a cutoff radius is used). The pseudopotential is adjusted to replicate the eigenvalues as well as the valence wave functions of the reference all-electron simulation. There are two characteristics that a good pseudopotential should possess. A pseudopotential is generated for a reference electronic configuration, but in order for it to be effective, it must be *transferable* in order to reliably repeat the outcomes of an all-electron simulation in various chemical conditions. At the same time, it should be sufficiently *smooth* to minimize the amount of grid points and/or plane waves. These two characteristics, however, are in direct opposition to one another; the pseudopotential is more transferable and less smooth the more closely the pseudo-wave functions resemble the real ones. In the end, just like with any other estimate, it's important to strike a compromise between feasibility and reliability.

There can be significant overlap between core and valence charge densities when the distinction between core and valence states is not as stern as previously indicated. Although chemically inert, the so-called semi-core states introduce exchange-correlation interactions with valence electrons that must be taken into account either by incorporating these states in the valence set or by employing non-linear core corrections (Louie et al., 1982). Sometimes the division in core or valence states is not as strict as stated before and there is a significant overlap between core and valence charge densities. The so called semi-core states are chemically inert but introduce some exchange-correlation interactions with valence electrons that must be taken into account either including these states in the valence set or using non-linear core corrections (Louie et al., 1982). The number of electrons in the simulation is significantly reduced due to the pseudopotential approximation, and shorter basis sets can be employed while maintaining a decent representation of the valence wave functions, greatly reducing the number of variables in our problem.

3.6 The periodic boundary conditions

Born-von Karman periodic boundary conditions are frequently taken into account in the research of periodic solids. A periodic lattice is defined as an infinite recurrence of a partic-

ular unit cell in every direction within these boundary conditions. Each system observable, including the effective potential of course, must be periodic or, alternatively, it must be invariant with regard to a translation of a lattice vector $\mathbf{a}$,

$$v_{eff}(\mathbf{r}) = v_{eff}(\mathbf{r} + \mathbf{a}). \quad (3.17)$$

According to the Bloch theorem, for infinite periodic systems, the eigenfunctions of the the one-electron Hamiltonian in a periodic potential can be expressed as the product of the plane wave envelope function and the Bloch function $u_{n,k}(\mathbf{r})$, which has the same periodicity as the lattice (Ashcroft & Mermin, 1976).

$$\psi_{n,k}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n,k}(\mathbf{r}), \quad (3.18)$$

where

$$u_{n,k}(\mathbf{r}) = u_{n,k}(\mathbf{r} + \mathbf{a}). \quad (3.19)$$

Hence, a wave vector $\mathbf{k}$ inside the first Brillouin zone and a band index n can be used to categorize the one-electron Kohn-Sham wave functions (ψ_i in previous Sections, $\psi_{n,k}$ here).

A unit cell that repeats itself periodically along the three dimensions makes up the crystal. While there are important exceptions to this rule, and those are the main focus of this work, we shall see in a minute that the application of periodic boundary conditions does not preclude at all the study of those phenomena. This is despite the fact that the ideal fully periodic and infinite crystal does not exist in nature. For simulation of bulk crystalline materials, periodic boundary conditions are the natural choice and are also the boundary conditions implemented for the study of solid state systems in the majority of DFT-based approaches.

Despite periodic boundary conditions being specially suited for the study of bulk systems [Fig. 3.1(a)], they can also be used efficiently and reliably for simulation of more complex structures by employing the supercell technique (Payne et al., 1992). This method involves creating a simulation box that is periodically duplicated throughout all of space

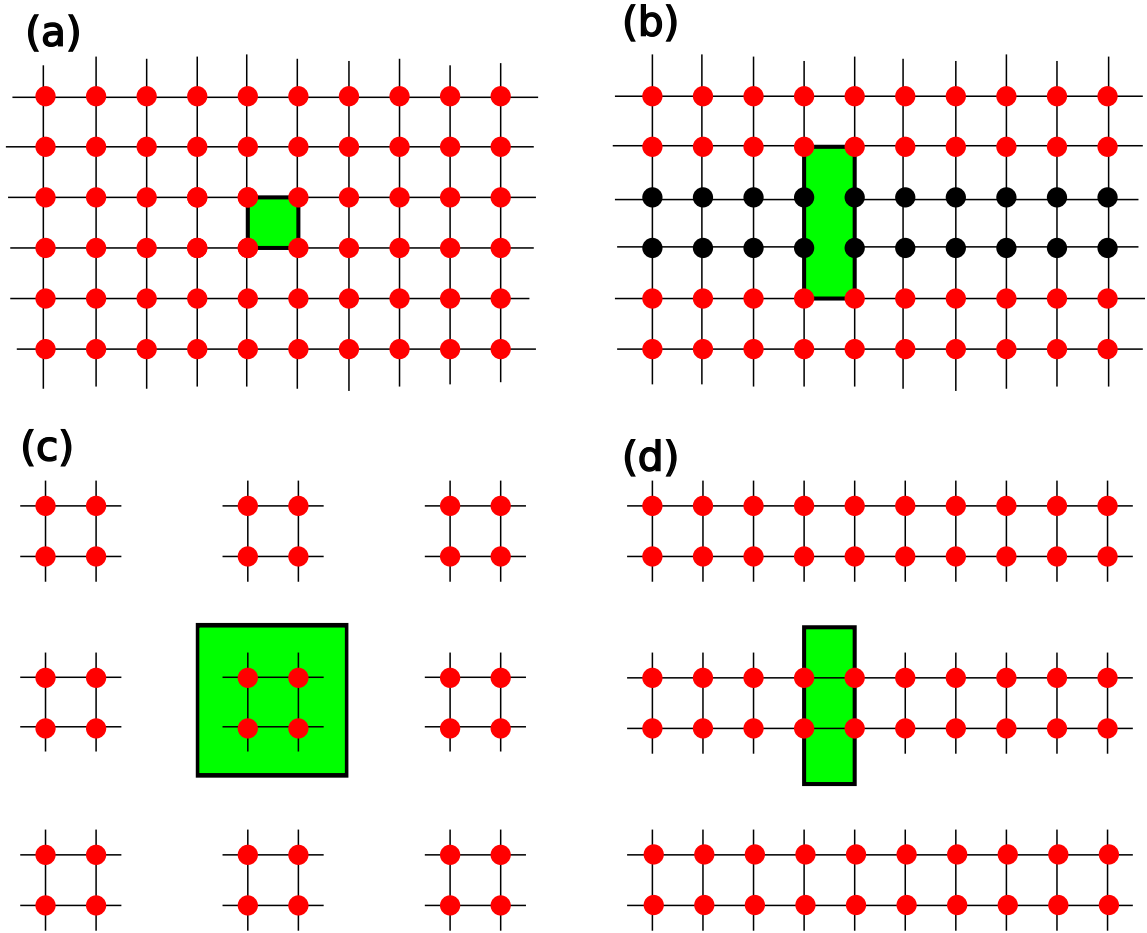


Figure 3.1: An illustration of appropriate supercells for the simulations under periodic boundary conditions; a bulk crystal (a), a superlattice (b), an isolated cluster (c) and a slab (d).

and contains more than just a basic unit cell of a specified material. Regular applications of this method include the simulation of:

- Complex structures within bulk crystals, like domains (of polarization, magnetic, elastic, etc.). Several combinations of the order parameter are permitted in this instance since the simulation box contains multiple unit cells of the material.
- Superlattices where supercells [Fig. 3.1(b)] can also be used for simulations. These are structures made up of alternating layers of different materials stacked periodically along a single axis.

One system that makes up the core topic of the current research, capacitors, could be viewed as an example of a superlattice. An actual thin film capacitor consists of an insulating layer sandwiched between two metallic electrodes that are quite thick (usually thought

to be semi-infinite). In reality, however, an infinite sequence of alternating metallic and insulating layers is what we are modelling owing to the periodic boundary conditions. This situation may be represented by Fig. 3.1(b) since the darker atoms belong to the metallic zone and the lighter ones to the insulator/ferroelectric. The metallic zone included in the simulation box should be thick enough to prevent interactions between the two regularly repeated interfaces in order to imitate the characteristics of a practical capacitor with semi-infinite electrodes. It is worth noting that for these particular systems, periodic boundary conditions have an impact on every measurable parameter of the system. In particular, the electrostatic potential must adhere to the periodicity of the supercell. This is equivalent to assuming short-circuit electrostatic boundary conditions between the electrodes thus crucial for the simulation of capacitors.

Recently, methods to calculate constrained electric field E (Souza et al., 2002, 2004) and electric displacement D (Stengel & Spaldin, 2007; Stengel et al., 2009b) under periodic boundary conditions have been developed. These methods allow for the removal of this restriction and the performance of simulations under virtually any electrostatic boundary condition.

- The object in vacuum can be embedded inside a large simulation box for zero-dimensional systems like molecules or nanoparticles to be simulated with this technique as well, as in Fig. 3.1(c).
- A vacuum region should be included in the simulation box when simulating slabs and surfaces [systems periodic only along two dimensions, see Fig. 3.1(d)] to prevent spurious interactions between periodic pictures.

Every time the supercell technique is employed, a thorough convergence analysis of the relationship between the system's attributes and the supercell size should be conducted.

3.7 Brillouin Zone Sampling and Electronic Temperature

As we saw in the section before, the periodic boundary conditions allow the one-particle Kohn-Sham equations eigenfunctions to be expressed as Bloch states, which are identified

by their quantum number $\mathbf{k}$ and band index n . Many condensed matter system physical characteristics depend not just on one specific eigenstate but rather on the integrated contribution of all of them. The electronic charge density, which is determined as the sum over bands of an integral over the first Brillouin zone, is the most obvious example.

$$\rho(\mathbf{r}) = \sum_n \int_{\mathbf{k} \in 1BZ} |\psi_{n,\mathbf{k}}(\mathbf{r})|^2 f_n(\mathbf{k}) d\mathbf{k}, \quad (3.20)$$

where $f_n(\mathbf{k})$ is the occupation function and 1BZ denotes the first Brillouin zone. The Aufbau rule is observed when filling energy levels at zero temperature, and as a result, $f_n(\mathbf{k})$ is a step function, with the occupancy of one-electron levels limited to two (assuming spin degeneracy) or zero electrons. The integral in Eq. (3.20) indicates a continuous sum over an infinite number of $\mathbf{k}$ -points in an infinite system, as those with which we are working. It goes without saying that such an infinite sum cannot be treated in reality. In order to calculate physical magnitudes that need integration over the first Brillouin zone, the conventional method is to replace the integral with a discrete sum over a finite number of $\mathbf{k}$ -points.

$$\rho(\mathbf{r}) = \sum_n \sum_{\mathbf{k} \in 1BZ} |\psi_{n,\mathbf{k}}(\mathbf{r})|^2 w_{\mathbf{k}} f_n(\mathbf{k}), \quad (3.21)$$

where $w_{\mathbf{k}}$ are the weight factors of $\mathbf{k}$ -points that depend on the way the sampling is performed. Fortunately, eigenfunctions change with $\mathbf{k}$ gradually, making it possible to represent the continuum of states accurately with a finite sample over a suitable grid of $\mathbf{k}$ -points. For efficient sampling of the Brillouin zone several schemes have been put forth (Baldereschi, 1973; Chadi & Cohen, 1973) but the Monkhorst and Pack (Monkhorst & Pack, 1976) is widely used. This method selects a certain number of divisions N_i along each reciprocal lattice vector of the simulation box, $\mathbf{b}_i$ is chosen. The sampled $\mathbf{k}$ -points are then calculated as

$$\mathbf{k} = q_1 \mathbf{b}_1 + q_2 \mathbf{b}_2 + q_3 \mathbf{b}_3, \quad (3.22)$$

where

$$q_i = \frac{2j - N_i - 1}{2N_i}, \quad j = 1, 2, \dots, N_i. \quad (3.23)$$

It is common practice to compare various computations made on various simulation boxes while studying a certain device (or supercells). It is strongly advised to make sure that the *density* (and not the total number) of $\mathbf{k}$ -points utilized for the discretization of the reciprocal space is the same in all calculations under those circumstances, and particularly in metallic systems.

Table 3.2: Convergence with respect to the Monkhorst-Pack mesh of structural parameters and energy difference between tetragonal and cubic phases of bulk PbTiO_3 . Δz_α is the off-center displacement of atom α in units of the lattice vector c . (For a $2 \times 2 \times 2$ Monkhorst-Pack mesh the cubic phase is found as ground state) (Aguado-Puente, 2011).

MP mesh	a (Å)	c (Å)	c/a	Δz_{Ti}	Δz_{O1}	Δz_{O2}	$\Delta(E_{\text{tetra}} - E_{\text{cubic}})$ (meV)
$2 \times 2 \times 2$	3.947	3.947	1.000	0.000	0.000	0.000	-
$4 \times 4 \times 4$	3.942	3.974	1.008	0.012	-0.015	-0.010	-3.41
$6 \times 6 \times 6$	3.938	3.997	1.015	0.016	-0.022	-0.015	-9.77
$8 \times 8 \times 8$	3.939	3.991	1.013	0.015	-0.020	-0.014	-10.86
Experiment	3.986	4.026	1.010	0.015	-0.023	-0.016	

The nature of our system and the attribute we are interested in will have a significant impact on how fine this sampling should be. In contrast to insulators, where the occupied states are strongly defined because of the band gap, metallic systems, where many features depend on a few states around the Fermi surface, call for finer grids. Ferroelectric perovskites require a fairly fine $\mathbf{k}$ -point mesh despite being insulators making them exceptional to this rule. For instance, the structural and energetic characteristics of bulk BaTiO_3 determined by various Monkhorst-Pack samplings are shown in Table. 3.2 demonstrating that converged results require a mesh of at least $6 \times 6 \times 6$ (King-Smith & Vanderbilt, 1994b).

In metallic systems a finite $\mathbf{k}$ -point sampling can lead to convergence problems as some states can cross the Fermi level during the course of the self-consistency process, leading to large oscillations of the electronic density. To avoid the use of huge samplings, mitigate the sensitivity with respect to the $\mathbf{k}$ -points, and improve convergence rate in metals, a smearing is often applied to the Fermi surface. This smearing introduces a smooth oc-

cupancy distribution in Eq. (3.21) where $f_n(\mathbf{k}) = f(E_{nk})$ substituting the step function that would correspond to an occupation function at zero temperature. A Gaussian distribution is a common option for the occupation function (Fu & Ho, 1983).

$$f_G(E_{n,k}) = \frac{1}{2} \operatorname{erfc} \left(\frac{E_{n,k} - E_F}{\sigma} \right), \quad (3.24)$$

where erfc is the complementary error function, or Fermi-Dirac distribution

$$f_{FD}(E_{n,k}) = \frac{1}{e^{(E_{n,k} - E_F)/\sigma} + 1}, \quad (3.25)$$

where the broadening energy parameter is given by σ . A smooth occupation function improves performance during the simulation of metallic systems by causing a partial population of the energy levels near the Fermi energy. The Kohn-Sham energy functional minimization only results in the ground state electronic density for a system of electrons at zero temperature, so when a finite electronic temperature is used to improve the stability of a simulation, it must be gradually decreased until convergence is achieved. The smearing parameter can be understood as a fictitious electronic temperature, where $T_e = \sigma/k_B$.

3.8 Basis Sets

Let's go back to the Kohn-Sham Eq. (3.5), Eq. (3.8) and Eq. (3.9). Eq. (3.8) consisting of a set of differential equations, the solutions to which are a set of functions $\psi_i(\mathbf{r})$. Expanding the solution as linear combinations of basis functions can substantially simplify this problem.

$$\psi_i(\mathbf{r}) = \sum_j c_{ij} \psi_j(\mathbf{r}), \quad (3.26)$$

where, c_{ij} are the basis functions. Eq. (3.8) is converted into a set of algebraic equations using this strategy, for which highly effective numerical techniques are available. In essence, what we just did was solve Eq. (3.8) for a set of coefficients (a 'few' complex numbers) instead of trying to solve it for a function at each point in space. This set of functions is what is known as a basis set. It is possible to use a variety of basis function types, each

with unique benefits and drawbacks. The majority of techniques use one of the following: atomic spheres, plane waves, or atomic orbitals.

3.8.1 Plane waves

The periodic boundary conditions and the Bloch theorem naturally lead to this basis. As products of plane waves with periodic functions may be used to represent the solutions to the Kohn-Sham equations, as we saw in Sec. 3.6, decomposing $\psi_{n,\mathbf{k}}$ in a Fourier expansion can help one comprehend solid physics in terms of the band structure. The expansion may be expressed as follows,

$$\psi_{n,\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{G}} C_{n,\mathbf{k},\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G})\mathbf{r}}, \quad (3.27)$$

where Ω is the volume of the simulation box and $\mathbf{G}$ is a reciprocal lattice vector. In theory, the previous sum involves an infinite number of plane waves, but in practice, a cutoff is put on the plane wave's maximum energy during the expansion.

The use of plane waves as basis functions offers various benefits. They are asymptotically complete, and more crucially, it is a straightforward to approach increasing the number of elements in the expansion without compromising the basis completeness. Due to their total lack of localization, they offer an impartial, homogenous, and isotropic depiction of the electronic structure of the system. Moreover, they provide the trivial use of fast Fourier transform methods for which highly effective subroutines are available, making it easier to create plane wave codes.

Of course, there are certain drawbacks to this approach. For instance, while being able to express all functions it is not especially well suited for any function. However, its homogeneity becomes a disadvantage in simulations of supercells with large vacuum zones since plane waves propagate over the whole space whether the material is present or absent near a point.

3.8.2 Atomic orbitals

This kind of basis set expands the one-electron eigenfunctions into a collection of functions focused on each atom in the system, capturing the essence of the atomic-like characteristics of solids and molecules. This enables extremely efficient expansions, requiring, in comparison, a far lower number of basis functions to get the same precision as a plane wave computation. The product of the spherical harmonic Y_{lm} and the radial function $R_{lm}(r)$ make up the localized functions centered at an atomic position $\mathbf{R}_I$,

$$\psi_{lm}(\mathbf{r}) = R_{lm}(|\mathbf{r} - \mathbf{R}_I|)Y_{lm}(\widehat{\mathbf{r} - \mathbf{R}_I}), \quad (3.28)$$

where $\widehat{\mathbf{r} - \mathbf{R}_I}$ is the direction vector. For the radial function, several options are available, including analytical and numerical functions. The most popular options for the former are Slater orbitals (te Velde et al., 2001) because of their resemblance to the real structure of the wave functions of an isolated atom, and Gaussian functions (Huzinaga, 1985) for their simplicity in implementation. On the other hand, numerical atomic orbitals (Artacho et al., 2005) are more flexible and can be tailored to each unique element and chemical environment (Junquera et al., 2001; Anglada et al., 2002), but they are more challenging to implement since they lack analytic integrals.

For us to construct order-N methods, whose computing cost scales linearly with the number of electrons in the system, atomic orbitals methods can make use of the localization principle. Atomic orbitals are useful instruments for the examination of bonding formation and hybridizations, in contrast to plane waves, which offer an intuitive image of band structure. They are significantly more effective since they are designed specifically to represent atomic wave functions; often, they only need a few dozens of basis functions to reach an accuracy that is similar to a computation with several hundreds of plane waves (Artacho et al., 2005).

Although being able to attain accuracy levels that are exactly similar to those of computations using plane waves, they are significantly harder to improve and there is no simple formula for doing so systematically. Atomic basis sets are enhanced by increasing their

radial and angular flexibility (Artacho et al., 1999). More than one alternative radial function for some chosen orbitals increases the radial flexibility of the basis functions. The ζ (Zeta) number of an orbital indicates how many radial functions it has. For example, radial flexibility is necessary to accurately reproduce the many ionization states of the atom, where the extension of the electronic cloud depends on the greater or smaller of the inter-electronic repulsion.

In order to polarize the most extended atomic valence orbitals and provide angular flexibility to the valence electrons, which will improve the description of bond formation and hybridization, an additional shell corresponding to the first unoccupied angular momentum channel is often introduced.

Double- ζ plus polarization, or DZP, is the common abbreviation for a basis set that includes, for example, two radial functions per atomic orbital plus polarization functions. Only testing can establish the proper size (ζZ) and polarization of a basis set.

It is clear that the fundamental disadvantage of using atomic orbitals as basis functions is a high cost in terms of human effort, which must be paid in order to benefit from its high efficiency.

3.8.3 Atomic spheres

The advantages of both earlier approaches are combined in this approach. This approach defines spheres centered at each atomic position. Plane waves are employed to describe the wave functions in the interstitial areas, whereas atomic-like orbitals are used to expand the wave functions inside these spheres. These basis sets can accurately describe the electronic structure of real solids with rapidly varying atomic-like functions close to the nuclei and smoothly varying functions between the atoms because they are asymptotically complete, like in the case of plane waves, but they converge more quickly as the number of basis functions increases. As a result of the usage of sharp functions in the atomic core areas, pseudopotentials are not required; instead, the frozen-core approximation is used to avoid computing the core levels.

Nevertheless, due to their challenging implementation and higher computing cost than the previously discussed approaches, their use is limited. However, because they explicitly include the core levels and do not rely on the use of pseudopotentials, the total energies acquired using these approaches are often extremely large, necessitating very converged simulations when calculating the energy differences between various phases.

3.9 Model of a Two-dimensional Electron Gas

As mentioned earlier, this work is build on the model proposed by P. Aguado-Puente and co-workers (Aguado-Puente et al., 2015). They showed that in the absence extrinsic screening mechanism, a monodomain phase can stabilize in a ferroelectric film by means of electronic reconstruction only. Our goal is to check whether our first-principles results for head-to-head and tail-to-tail in PbTiO_3 supports the model. One of the concepts they proposed is that if a two-dimensional electron gas or hole forms as a result of electronic reconstruction, then the free energy per unit volume of a ferroelectric thin film of thickness $\aleph$ is given as,

$$G = F + \frac{\sigma\Delta}{\aleph} + \frac{\sigma^2}{2g\aleph} + \frac{1}{2\epsilon_0}(\sigma - P)^2. \quad (3.29)$$

Here the first term F is the free energy from the bulk ferroelectric system with zero field and depends on P . The second and the third terms account for the energy cost of promoting electrons from the top of the valence band to the bottom of the conduction band. The second term corresponds to the cost of charge transfer across the gap, where σ is the surface density of free charge and Δ is the band gap (*experimental*) of the system in units of a voltage. The third term, takes into account the energy associated with filling of bands; in this case, conduction band with electrons while the valence band with holes. In this case, g is the lessened density of states. The last term is electrostatic energy of the remnant depolarising field and constitutes the driving force for the formation of a two-dimensional electron gas (2DEG). ϵ_0 in this case is the vacuum permittivity.

CHAPTER FOUR

COMPUTATIONAL METHODOLOGY

This section clearly describes, the technological aspects used in the simulation box. It also discusses how the specified objectives in Sec. (1.7) were executed.

4.1 Computational Details

The thesis profited from the SIESTA method's (Soler et al., 2002; García et al., 2020) inclination to numerical atomic orbital approach to simulate the selected DWs in free-standing slabs of PbTiO_3 . The local density approximation (LDA) (Ceperley & Alder, 1980) was employed to address the exchange and correlation facet within density functional theory (Hohenberg & Kohn, 1964; Kohn & Sham, 1965).

Using an onsite Hubbard term (U) in SIESTA as proposed by Dudarev (Dudarev et al., 1998), but now in a framework of numerical atomic orbitals, this research extended¹ DFT+ U technique to a situation of non-collinear magnetism and SOC. This was implemented by considering that both the exchange J parameter and the Hubbard repulsion term U were specified. To compute the occupancy numbers of localized orbitals that were part of the correlated shell, orthogonal and non-overlapping localized projectors were used (Gómez-Ortiz et al., 2023). This kind of implementation, leads to a more accurate band gap prediction.

Unfortunately, this course of action on Ti, was rejected. The rationale for the rejection was because; the Hubbard term (U) lessened the hybridization betwixt Ti $3d$ and O $2p$. This hybridization is the one responsible for the PbTiO_3 ferroelectric behaviour and, consequently, it causes conductive domains to arise in this simulation. To set the record straight regarding this decision, and by using a linearity approach in determining the Hubbard term (U) (Cococcioni & de Gironcoli, 2005). A Hubbard term (U) that reproduces

¹The researcher's LDA+ U +SOC implementation (Gómez-Ortiz et al., 2023) forms a bridge between Dudarev (Dudarev et al., 1998) and Cuadrado & co-workers scheme (Cuadrado & Cerdá, 2012).

the energy band gap of bulk PbTiO_3 and its polarization effects was calculated. None was found! As a matter of fact, the value of polarization fell sharply when U was more than 2 eV, and disappeared entirely when U exceeded 3 eV as manifested in Fig. 4.1(a). On the other hand, in Fig. 4.1(b), the band gap varied almost linearly with the U value and completely destroying the most important hybridization. However, remember that the

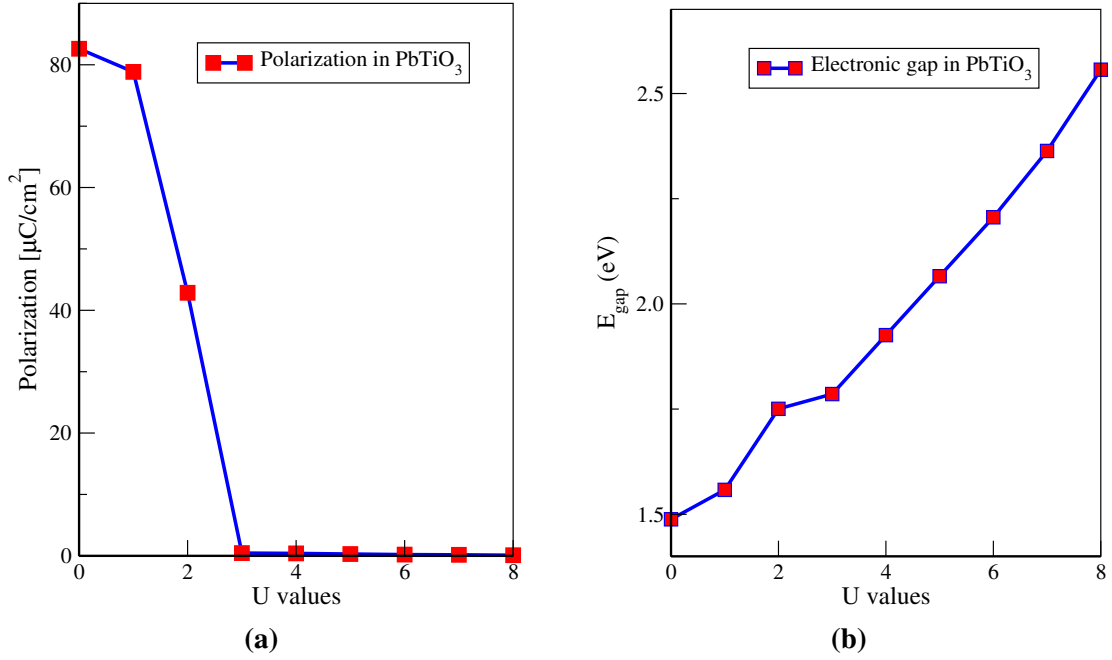


Figure 4.1: (a) The variation of polarization with Hubbard U values. It was for the above illustration that the intrinsic properties of the domains were dealt with in this study. (b) The change in the electronic band gap as a function of the U -term.

band-gap is drastically underestimated in plain LDA technique as shown in Table. 3.1 and discussed extensively by Chege *et al.* (Chege et al., 2020) and with a similar magnitude by Syed *et al.* (Zuhair Abbas Shah et al., 2023). The necessary thickness for the stability of conducting layers always has a significant association with the underestimating of the band-gap inside LDA; in this case, the two are proportional (Sifuna et al., 2020; Junquera & Ghosez, 2003b). In principle, such a system favours localization of the electrons at the interface, that would strongly depend on the value of the U -term (Rahmanizadeh et al., 2014).

In the Kleinman-Bylander fully non-local separable representation (Kleinman & Bylander, 1982), core electrons in this simulation were simply replaced with *ab initio* norm conserving pseudopotentials created using the Troullier-Martins method (Troullier & Mar-

tins, 1991). The substantial overlap between the semi-core and valence states demanded the inclusion of Ti $3s$ and $3p$ semi-core electrons along with Pb $5d$ electrons in the simulations as valence electrons. Scalar relativistically generated pseudopotentials for Ti and Pb were then produced. The cutoff radii and reference configuration for every angular momentum shell of the pseudopotentials utilized in this study are found in the researcher's earlier work (Sifuna et al., 2020) for Pb² and in the work of Junquera and co-workers (Junquera et al., 2003) for Ti and O.

In this thesis, the one-electron Kohn-Sham eigenstates, were expanded on the basis of the rigorously localized numerical atomic orbitals (Sankey & Niklewski, 1989; Artacho et al., 1999). The researcher used a robust selection of the basis set; a single- ζ (SZ) for the semi-core orbitals of Pb and Ti while a double- ζ plus polarization (DZP) for all valence states of every atom. Using variational optimization of the energy, and according to a previous study (Junquera et al., 2001), all those parameters that were able to define the shape and also the range of the basis functions were obtained for the case of Ti and O. Consequently, an additional optimization for Pb was carried out in PbTiO₃ (*bulk*), frozen in the Ti and that of O atomic orbitals to those initially optimized in the findings of Junquera and co-workers (Junquera et al., 2001). A plane-wave cutoff of 1200 Ry was employed using a charge density representation. The computation of electronic density, Hartree, exchange-correlation potentials and their related matrix elements was performed in a uniform real-space grid. In order to integrate the Brillouin zone, this work employed a Monkhorst-Pack sampling (Monkhorst & Pack, 1976) equivalent to $6 \times 6 \times 6$ in a perovskite unit cell with five atoms. For the one-particle Kohn-Sham (K-S) electronic eigenstates, a Fermi-Dirac smearing of 250 K (500 K) for the HH (TT) domain structures was employed.

A tetragonal (1×1) supercell shown in Fig. 4.2, was employed to simulate the domain structures in this thesis ([vacuum/(PbO-TiO₂)_{2n}-PbO/vacuum ($n = 16$)]). Simulations indicated the slabs falling back to the paraelectric (*centrosymmetric* structure when $n=12$ and the metallic gases do not stabilize as explained by the work of Aguado (Yin et al., 2015).

²The researcher's earlier work (Sifuna et al., 2020) is the published version of these findings in Physical Review B Journal.

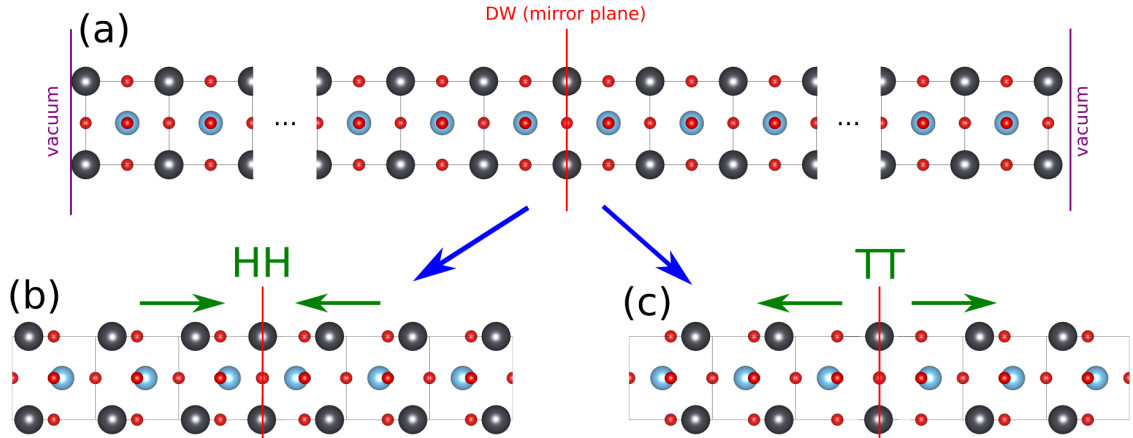


Figure 4.2: The simulation box used in this study. The paraelectric phase domains (a), head to head DW (b) while (c) depicts the DW in tail to tail (TT) configuration. Here, balls have been used to illustrate the atoms: the black ball is Pb, the blue ball is Ti, and the red ball is O. On the other hand, the arrows (in green) show the direction of the polarization, while the blue arrows show a deviation of HH and TT from the mother free standing slab.

Given that the only stable termination surface found using first principles is PbO (Meyer et al., 1999), this layer finished off both surfaces (*PbO termination*). The size of the vacuum used in this study was of the order of eight perovskite unit cells on both sides of the domains, and thus making a slab as shown in Fig. 4.2. In the out-of-plane direction, a dipole correction was introduced to prevent unwanted interaction between periodic duplicates of the slab. By doing this, the researcher also compelled the disappearance of the electric displacement field within the vacuum. The perpendicular component at the surface that was free remained continuous post electronic reconstruction, it precisely equals the surface charge density, in the PbTiO_3 domain. SrTiO_3 is a popular substrate for growing oxide heterostructures (Arnay et al., 2018). With a theoretical equilibrium lattice constant, $a_0 = 3.874 \text{ \AA}$, that was set as the in-plane lattice constant so as to mimic the influence of circumstances for mechanical boundaries arising from the strain induced by a divinator substrate. Under this compressive strain, the spontaneous polarization in confined bulk PbTiO_3 was equal to $P_S = 77.1 \mu\text{C}/\text{cm}^2$. An ideal structure was established as the starting point, consisting of $2n$ unit cells of PbTiO_3 stacked in the $[001]$ direction within a tetragonal paraelectric arrangement (i.e., without any layer exhibiting ramping) characterized by a tetragonality of $c/a = 1.0325$. Following this paraelectric arrangement, the

PbTiO₃ atoms underwent opposing displacements within the two sections of the slab structure. This pattern of displacement imitated the bulk tetragonal soft mode's displacement, scaled down to 62%. This represented the polarization value of a meta-stable monodomain PbTiO₃ slab, in reference to a study done by Aguado and co-workers (Aguado-Puente et al., 2015), where it was observed that the polarization charge could be screened by an electronic reconstruction, leading to the emergence of two-dimensional metallic layers at the surface. The mirror symmetry plane was the middle layer of PbO by design. No evidence from *ab initio* calculations showed that the energy of Pb-centered DW could be reduced by breaking the inversion symmetry as described by Meyer and Vanderbilt (Meyer & Vanderbilt, 2002). Beginning with this architecture, a conjugate gradient minimization was carried out until the largest force component on any atom was less than 0.04 eV/Å.

A non-self-consistent calculation was performed using a substantially denser sample of $150 \times 150 \times 5$ Monkhorst-Pack mesh in order to compute the density of states after the atomic structure had been relaxed, and the one-particle density matrix had converged.

In order to create the nomenclature, the researcher referred to the plane that was parallel to the interface as the (x, y) plane and the perpendicular direction as the z axis.

All this work was done with the aid of resources from the Center for High Performance Computing cluster (CHPC) in South Africa. The thesis employed the standard queue for parallel jobs with seventy-two cores assigned all through.

4.2 Highlights of Activities That Addressed the Set Objectives

1. The researcher came up with a method where the SIESTA code specifically included and treated the exchange J and the Hubbard repulsion term U parameters separately: Considering numerical atomic orbitals, this study extended DFT+U technique to a situation of spin-orbit coupling in a magnetic setup. The exchange J parameter was expressly provided and was considered independently from the Hubbard repulsion term U . The occupation numbers of the localized orbitals that make up the correlated shell were computed by projecting the K-S eigenfunctions onto a set of non-overlapping, orthogonal localized projectors. The study provided a clarification

for the precise formulation of forces, stresses and total energy and including Pulay adjustments. A simulations on a bulk solid, that included an atom with a significant spin-orbit coupling, was used to validate this implementation. These results were presented in the researcher's earlier work (Gómez-Ortiz et al., 2023).

2. Polarization ($\tilde{P}_j^Z$) was computed using the effective Born charges, re-normalized to take into account the finite electric field as shown in Eq. 4.1.

$$Z_{i,\alpha,\beta}^* = \frac{\Omega_0}{e} \left. \frac{\partial P_\alpha}{\partial u_{i,\beta}} \right|_{q=0}, \quad (4.1)$$

where e and Ω_0 , are the charge of an electron and the unit cell volume in that order.

3. This thesis utilized the polarization profile acquired above and fitted it to a functional form developed from Gureev *et al.* (Gureev et al., 2011) in order to compute this extension in matter space (*spatial magnitude*) of the electron or hole gases, δ_w .

$$P(z) = P_0 \tanh \left(\frac{z}{\delta_w} \right), \quad (4.2)$$

δ_w here, represents the normal DW half-width (i.e. we require a space four times as long as δ_w to transit from $-P_0$ to P_0).

4. The planar average of the free charge ($\bar{\rho}_{\text{free}}(z)$) was to be plotted to obtain the amount of charge that has been transferred from the free-surfaces to the DW in order to screen the depolarizing fields.

$$\bar{\rho}_{\text{free}}(z) = S^{-1} \int_S \rho_{\text{free}}(\mathbf{r}) dx dy, \quad (4.3)$$

where $\bar{\rho}_{\text{free}}(z)$ is the corresponding nanosmoothed version (Junquera et al., 2007) and S is the area of the interface unit cell. $\rho_{\text{free}}(\mathbf{r})$ for the electronic charge density

colonizing the bottom of the conduction band, has been calculated as

$$\rho_{\text{free}}^{\text{electrons}}(\mathbf{r}) = \sum_{E_{n\mathbf{k}} > E_0} w_{\mathbf{k}} f_{n\mathbf{k}} |\psi_{n\mathbf{k}}(\mathbf{r})|^2, \quad (4.4)$$

while the hole charge density for the valence band's highest portion was provided by

$$\rho_{\text{free}}^{\text{holes}}(\mathbf{r}) = \sum_{E_{n\mathbf{k}} < E_0} w_{\mathbf{k}} (1 - f_{n\mathbf{k}}) |\psi_{n\mathbf{k}}(\mathbf{r})|^2. \quad (4.5)$$

In the discrete Monkhorst-Pack mesh, $w_{\mathbf{k}}$ represents the weight of a single $\mathbf{k}$ point, $f_{n\mathbf{k}}$ represents the occupation numbers of the eigenstate $\psi_{n\mathbf{k}}$ with eigenvalue $E_{n\mathbf{k}}$, and E_0 represents the energy that corresponds to the centre of the gap between the valence and conduction bands.

CHAPTER FIVE

RESULTS AND DISCUSSION

In this section, the outcome of the specific objectives set in Sec. 1.7 are discussed.

5.1 LDA+U+SOC implementation in the SIESTA code

5.1.1 Magnetic collinearity

Bousquet and Spaldin (Bousquet & Spaldin, 2010) developed an approach a couple of years ago that was heavily borrowed in this subsection. This thesis extended their method to numerical atomic orbitals so as to be able to tackle density functional theory plus Hubbard potentials in the SIESTA code. This was inevitable because, at the start of this project, the code chosen to solve our problems was not able to perform a perfect self consistent calculation using density functional theory and Hubbard potentials on noncollinear magnets. Today, as the outcome of this work (Gómez-Ortiz et al., 2023), the code is well tailored for such problems in its latest version. In this part, the author will walk you through a step by step procedure of the theory implemented to tackle the problem in the SIESTA code.

5.1.1.1 The Hubbard's role to the possibility of self-consistency

The Hubbard Hamiltonian (E^{Hub}), introduced by Liechtenstein and co-workers (Liechtenstein et al., 1995) to represent coupled states, served as the starting point.

$$\begin{aligned} E^{\text{Hub}} \left[\{n_{mm'}^{I,\sigma}\} \right] = & \frac{1}{2} \sum_I \sum_{\sigma} \sum_{\{m\}} \{ \langle m, m'' | V_{\text{ee}} | m', m''' \rangle n_{mm'}^{I,\sigma} n_{m''m'''}^{I,-\sigma} \\ & + \langle m, m'' | V_{\text{ee}} | m', m''' \rangle \\ & - \langle m, m'' | V_{\text{ee}} | m''', m' \rangle \} n_{mm'}^{I,\sigma} n_{m''m'''}^{I,\sigma}. \end{aligned} \quad (5.1)$$

Where I brims over the atoms at $\mathbf{R}_I$ that contain correlated electron shells. m , on the other hand runs over specified L_z eigenstates, for a particular quantum number l , while σ denotes the electron's spin (Himmetoglu et al., 2014). The integrals on the wave functions of those correlated shells, or V_{ee} , were used to depict electron-electron interactions. Sec. 5.1.3 is devoted to a detailed explanation of how they are calculated in this thesis. It is very significant to notice that the Hubbard energy supplied in Eq. (5.1) lacks self-interaction.

The occupations $n_{mm'}^{I,\sigma}$ in SIESTA code are determined by projecting the K-S eigenfunctions to a collection of orthogonal (*in essence, one that do not overlap*) localized projectors $|\phi_m^I\rangle$, shown below;

$$\begin{aligned} n_{mm'}^{I,\sigma} &= \langle \phi_m^I | \hat{\rho}^\sigma | \phi_{m'}^I \rangle \\ &= \sum_{\mathbf{k}} \sum_i \langle \phi_m^I | \psi_{\mathbf{k}i}^\sigma \rangle f_{\mathbf{k}i}^\sigma \langle \psi_{\mathbf{k}i}^\sigma | \phi_{m'}^I \rangle, \end{aligned} \quad (5.2)$$

where $f_{\mathbf{k}i}^\sigma$ is the KS states' occupation, indicated by the $\mathbf{k}$ -point, spin σ indices and also the band i . This thesis moves a step ahead and defines the operator of the one particle density ($\hat{\rho}^\sigma$), as $\hat{\rho}^\sigma = \sum_{\mathbf{k}} \sum_i |\psi_{\mathbf{k}i}^\sigma\rangle f_{\mathbf{k}i}^\sigma \langle \psi_{\mathbf{k}i}^\sigma|$. In a more realistic fashion, the numerical atomic orbitals of the basis set may be used to compute these projectors, although with shorter ranges. Compared to the Mulliken charge projector algorithm used elsewhere (Han et al., 2006; Qu et al., 2022), such a computation is different. In the SIESTA method (Soler et al., 2002), the Bloch eigenstates are extended as a linear combination of atomic orbitals that are rigorously localized, ϕ_μ , as

$$\psi_{\mathbf{k}i}^\sigma(\mathbf{r}) = \sum_{\mu} e^{i\mathbf{k}\cdot\mathbf{R}_\mu} c_{\mu i}^\sigma(\mathbf{k}) \phi_\mu(\mathbf{r}), \quad (5.3)$$

where $\mu \equiv \{l m \zeta\}$. This ζ is an index that indicates all functions that have a similar angular dependence. This is determined by l and m . On the other hand, $c_{\mu i}^\sigma(\mathbf{k}) = \langle \phi^\mu | \psi_{\mathbf{k}i}^\sigma \rangle$, and ϕ^μ is the dual orbital related to ϕ_μ , $\langle \phi^\mu | \phi_\nu \rangle = \delta_{\mu\nu}$. The populations of Eq. (5.2) may thus be estimated by applying twice the projection operator to the region covered by the numerical atomic orbitals basis set as illustrated below.

$$\begin{aligned}
n_{mm'}^{I,\sigma} &= \langle \phi_m^I | \left(\sum_{\mu} |\phi_{\mu}\rangle \langle \phi_{\mu}^I| \right) | \hat{\rho}^{\sigma} | \left(\sum_{\nu} |\phi_{\nu}\rangle \langle \phi_{\nu}^I| \right) | \phi_{m'}^I \rangle \\
&= \sum_{\mu\nu} \langle \phi_m^I | \phi_{\mu} \rangle \langle \phi_{\mu}^I | \hat{\rho}^{\sigma} | \phi_{\nu} \rangle \langle \phi_{\nu}^I | \phi_{m'}^I \rangle \\
&= \sum_{\mu\nu} \langle \phi_m^I | \phi_{\mu} \rangle \rho_{\mu\nu}^{\sigma} \langle \phi_{\nu}^I | \phi_{m'}^I \rangle \\
&= \sum_{\mu\nu} S_{m\mu}^I \rho_{\mu\nu}^{\sigma} S_{\nu m'}^I,
\end{aligned} \tag{5.4}$$

where the duals of the numerical atomic orbitals are used to express the density matrix elements (Sánchez-Portal et al., 1995) ($\rho_{\mu\nu}^{\sigma} = \langle \phi_{\mu}^I | \hat{\rho}^{\sigma} | \phi_{\nu}^I \rangle$) and we have introduced the notation $S_{m\mu}^I = \langle \phi_m^I | \phi_{\mu} \rangle$ so as to show the basic overlap that occurs between these projectors that don't do computation on occupations and similarly, on the atomic orbitals of a given basis. At this point, it is possible to obtain an expression of the Hubbard energy. This is done by inserting Eq. (5.4) into Eq. (5.1), to obtain

$$E^{\text{Hub}} = \frac{1}{2} \sum_{\mu\nu} \sum_{\sigma} V_{\nu\mu}^{\text{Hub},\sigma} \rho_{\mu\nu}^{\sigma} = \frac{1}{2} \sum_{\sigma} \left(\hat{V}^{\text{Hub},\sigma} \hat{\rho}^{\sigma} \right), \tag{5.5}$$

where

$$\begin{aligned}
V_{\nu\mu}^{\text{Hub},\sigma} &= \sum_I \sum_{\{m\}} \left[\langle m, m'' | V_{\text{ee}} | m', m''' \rangle \left(n_{m''m'''}^{I,-\sigma} + n_{m''m'''}^{I,\sigma} \right) \right. \\
&\quad \left. - \langle m, m'' | V_{\text{ee}} | m''', m' \rangle n_{m''m'''}^{I,\sigma} \right] (S_{m\mu}^I S_{\nu m'}^I).
\end{aligned} \tag{5.6}$$

During a self consistent procedure, the potential in Eq. (5.6), is added to the famous DFT single particle potential. Please note that Eq. (5.6), may have some non-zero potential matrix elements, even between orbital pairs μ and ν that don't necessarily belong to a correlated subspace. If by any chance we have a basis set that is orthonormal with the projectors, it follows that, $\langle \phi_m^I | \phi_{\mu} \rangle = \delta_{m\mu}^I$, and $\langle \phi_{\nu} | \phi_{m'}^I \rangle = \delta_{\nu m'}^I$, and Eq. (5.6) would transmute to an expression shown in Eq. (3) of Bousquet and Spaldin's publication (Bous-

quet & Spaldin, 2010) which is shown as:

$$\begin{aligned} V_{m_2 m_1}^{\uparrow\uparrow} &= \sum_{3,4} J \delta_{1,2} n_{3,4}^{\uparrow\uparrow} - \frac{J}{2} \delta_{1,2} \\ &= J \delta_{1,2} \left(\sum_{3,4} n_{3,4}^{\uparrow\uparrow} \right) - \frac{J}{2} \delta_{1,2}. \end{aligned} \quad (5.7)$$

5.1.1.2 The self-consistent potential's double counting contribution

Together with these Hubbard contribution, it is also important to consider what is referred to as double counting energy term. Checking at this double counting energy term indicated in Eq. (13) of a similar work done by Bultmark and co-workers (Bultmark et al., 2009), it takes the form below in a fully localized limit;

$$E^{\text{dc}} = \frac{1}{4} \sum_I \left[2U^I n^I (n^I - 1) - 2J^I n^I \left(\frac{n^I}{2} - 1 \right) - J^I \mathbf{m}^I \cdot \mathbf{m}^I \right], \quad (5.8)$$

where

$$n^I = \sum_{\sigma} \sum_m n_{m\sigma}^{I\sigma}. \quad (5.9)$$

Let's assume a collinear spin, it will imply that $\mathbf{m}^I = (0, 0, m_z^I) = (0, 0, n^{I,\uparrow} - n^{I,\downarrow})$, so Eq. (5.8) reduces to

$$E^{\text{dc}} = \sum_I \left[\frac{U^I}{2} n^I (n^I - 1) - \frac{J^I}{2} [n^{I,\uparrow} (n^{I,\uparrow} - 1) + n^{I,\downarrow} (n^{I,\downarrow} - 1)] \right], \quad (5.10)$$

this now agrees with Eq. (5.11), which is Eq. (4) of the work done by Liechtenstein and co-workers (Liechtenstein et al., 1995),

$$E_{\text{dc}}[n^{\sigma}] = \frac{1}{2} U n (n - 1) - \frac{1}{2} J [n^{\uparrow} (n^{\uparrow} - 1) + n^{\downarrow} (n^{\downarrow} - 1)], \quad (5.11)$$

where, $n^\sigma = \text{Tr}(n_{\text{mm}}^\sigma)$ and that $n = n^\uparrow + n^\downarrow$.

Back to this work, replacing Eq. (5.9) into Eq. (5.10), and by use of functional derivatives, that are in respect to the density matrix, it is possible to arrive at the following,

$$\begin{aligned}
V_{\nu\mu}^{\text{dc},\sigma} &= \frac{\delta E^{\text{dc}}}{\delta \rho_{\mu\nu}^\sigma} \\
&= \sum_I \sum_m U^I (S_{m\mu}^I S_{\nu m}^I) \left(n^I - \frac{1}{2} \right) \\
&\quad - \sum_I J^I \left[\left(\sum_m (S_{m\mu}^I S_{\nu m}^I) \right) \left(\sum_{m'} \sum_{\mu'\nu'} \rho_{\mu'\nu'}^\sigma S_{m'\mu'}^I S_{\nu'm'}^I - \frac{1}{2} \right) \right]. \quad (5.12)
\end{aligned}$$

5.1.1.3 An energy-related contribution

It is easy to compute the effect on the total energy, by evaluating Eq. (5.1) and Eq. (5.8) for both Hubbard (U) & the duplex counting contributions in that order.

As an alternative, the energy related term may be expressed as, half trace of potential multiplied by the density matrix, with a few correction factors added as shown

$$\begin{aligned}
E^{\text{Hub}} - E^{\text{dc}} &= \frac{1}{2} \sum_{\sigma} [(V^{\text{Hub},\sigma} + V^{\text{dc},\sigma}) \rho^\sigma] \\
&\quad - \sum_I \frac{1}{4} (U^I - J^I) n^I. \quad (5.13)
\end{aligned}$$

5.1.2 Non collinear magnetism

5.1.2.1 Hubbard and the self-consistent potential's double counting effects

It is very possible to apply the prior formalization for collinear spins to the situation of noncollinear magnetism. In such a scenario, it is important to note that a complex (2×2) matrix shown in Eq. 5.14, is a density matrix that occurs between μ and ν atomic orbitals.

$$\rho_{\mu\nu} = \begin{pmatrix} \rho_{\mu\nu}^{\uparrow\uparrow} & \rho_{\mu\nu}^{\uparrow\downarrow} \\ \rho_{\mu\nu}^{\downarrow\uparrow} & \rho_{\mu\nu}^{\downarrow\downarrow} \end{pmatrix}. \quad (5.14)$$

That equally means, occupations that were instigated in Eq. (5.4), are equally complex (2×2) matrices,

$$n_{mm'}^I = \begin{pmatrix} n_{mm'}^{I,\uparrow\uparrow} & n_{mm'}^{I,\uparrow\downarrow} \\ n_{mm'}^{I,\downarrow\uparrow} & n_{mm'}^{I,\downarrow\downarrow} \end{pmatrix}. \quad (5.15)$$

A keen look at Eq. (5.15), shows that the sum of the correlated electrons (n^I) and the magnetic moment ($\mathbf{m}^I$) of each atom I is calculated as,

$$n^I = \sum_m \text{Tr} (\mathbb{1} n_{mm}^I) = \sum_m (n_{mm}^{I\uparrow\uparrow} + n_{mm}^{I\downarrow\downarrow}), \quad (5.16a)$$

$$m_x^I = \sum_m \text{Tr} (\sigma_x n_{mm}^I) = \sum_m (n_{mm}^{I\uparrow\downarrow} + n_{mm}^{I\downarrow\uparrow}), \quad (5.16b)$$

$$m_y^I = \sum_m \text{Tr} (\sigma_y n_{mm}^I) = \sum_m i (n_{mm}^{I\uparrow\downarrow} - n_{mm}^{I\downarrow\uparrow}), \quad (5.16c)$$

$$m_z^I = \sum_m \text{Tr} (\sigma_z n_{mm}^I) = \sum_m (n_{mm}^{I\uparrow\uparrow} - n_{mm}^{I\downarrow\downarrow}), \quad (5.16d)$$

where σ_x , σ_y , and σ_z are nothing but (2×2) Pauli matrices. The two-component spin space also contains the generalization of the DFT+U potential as,

$$V_{\nu\mu} = \begin{pmatrix} V_{\nu\mu}^{\uparrow\uparrow} & V_{\nu\mu}^{\uparrow\downarrow} \\ V_{\nu\mu}^{\downarrow\uparrow} & V_{\nu\mu}^{\downarrow\downarrow} \end{pmatrix}, \quad (5.17)$$

was presented earlier by Bousquet and Spaldin (Bousquet & Spaldin, 2010). It should be noted that every potential matrix component is a total of matching Hubbard and double counting contributions. Considering the energy in relation to the pertinent density matrix component as a functional derivative, each member of the (2×2) matrix may be calculated as,

$$V_{\nu\mu}^{\alpha\beta} = \frac{\delta E}{\delta \rho_{\mu\nu}^{\beta\alpha}}. \quad (5.18)$$

When it comes to the diagonal components, they are identical to those found in Eq. (5.6)

and Eq. (5.12) of Sec. 5.1.1, in that order, and may be summarised as,

$$V_{\nu\mu}^{\text{Hub},\uparrow\uparrow(\downarrow\downarrow)} = \sum_I \sum_{\{m\}} \left[\langle m, m'' | V_{\text{ee}} | m', m''' \rangle \left(n_{m''m'''}^{I,\downarrow\downarrow} + n_{m''m'''}^{I,\uparrow\uparrow} \right) - \langle m, m'' | V_{\text{ee}} | m''', m' \rangle n_{m''m'''}^{I,\uparrow\uparrow(\downarrow\downarrow)} \right] (S_{m\mu}^I S_{\nu m'}^I), \quad (5.19a)$$

$$V_{\nu\mu}^{\text{dc},\uparrow\uparrow(\downarrow\downarrow)} = \sum_I \sum_m U^I (S_{m\mu}^I S_{\nu m}^I) \left(n^I - \frac{1}{2} \right) - \sum_I J^I \left[\left(\sum_m (S_{m\mu}^I S_{\nu m}^I) \right) \left(\sum_{m'} \sum_{\mu'\nu'} \rho_{\mu'\nu'}^{\uparrow\uparrow(\downarrow\downarrow)} S_{m'\mu'}^I S_{\nu'm'}^I - \frac{1}{2} \right) \right]. \quad (5.19b)$$

When it comes to the off-diagonal terms, it is possible to follow the expressions proposed by the work of Bousquet and Spaldin (Bousquet & Spaldin, 2010),

$$V_{\nu\mu}^{\text{Hub},\uparrow\downarrow(\downarrow\uparrow)} = - \sum_I \sum_{\{m\}} \left[\langle m, m'' | V_{\text{ee}} | m''', m' \rangle n_{m''m'''}^{I,\uparrow\downarrow(\downarrow\uparrow)} \right] S_{m\mu}^I S_{\nu m'}^I. \quad (5.20a)$$

$$V_{\nu\mu}^{\text{dc},\uparrow\downarrow(\downarrow\uparrow)} = - \sum_I J^I \left[\left(\sum_m (S_{m\mu}^I S_{\nu m}^I) \right) \left(\sum_{m'} \sum_{\mu'\nu'} \rho_{\mu'\nu'}^{\uparrow\downarrow(\downarrow\uparrow)} S_{m'\mu'}^I S_{\nu'm'}^I \right) \right]. \quad (5.20b)$$

We must then compute self-consistently the Hubbard and also, the double counting matrix elements. Please note that the potential in Eq. (5.17) and the density matrix in Eq. (5.14) are in a way globally Hermitian ($\rho_{\mu\nu}^{\alpha\beta} = \rho_{\nu\mu}^{\beta\alpha*}$).

5.1.2.2 An energy-related contribution

We can compute the contribution to energy by following Eq. (5.13) but for the trace, it must be prolonged to a procreation of the (2×2) matrices as,

$$\begin{aligned}
E^{\text{Hub}} - E^{\text{dc}} = & \frac{1}{2} \sum_{\mu\nu} (\rho_{\mu\nu}^{\uparrow\uparrow} V_{\nu\mu}^{\uparrow\uparrow} + \rho_{\mu\nu}^{\uparrow\downarrow} V_{\nu\mu}^{\downarrow\uparrow} + \rho_{\mu\nu}^{\downarrow\uparrow} V_{\nu\mu}^{\uparrow\downarrow} + \rho_{\mu\nu}^{\downarrow\downarrow} V_{\nu\mu}^{\downarrow\downarrow}) \\
& - \sum_I \frac{1}{4} (U^I - J^I) n^I.
\end{aligned} \tag{5.21}$$

Checking at Eq.(5.21), one can see that $V_{\nu\mu}$ it is a summation of the Hubbard and the so called double counting benefaction.

5.1.3 Electron-electron interaction integrals

From the prior discussion, the integrals that relate to the electron-electron interaction,

$$\begin{aligned}
\langle m, m'' | V_{\text{ee}} | m', m''' \rangle = \\
\int d^3r \int d^3r' \psi_{lm}^*(\mathbf{r}) \psi_{lm''}^*(\mathbf{r}') \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \psi_{lm'}(\mathbf{r}) \psi_{lm'''}(\mathbf{r}'),
\end{aligned} \tag{5.22}$$

are still up in the air, and we will follow a recipe provided by Liechtenstein and co-workers (Liechtenstein et al., 1995) to bring them here. Let us assume that functions like ψ_{lm} found in Eq. (5.22) are in nature, atomic like d , or say f states. That implies, they can be put in black and white, as the product of a radial part and a *real* spherical harmonic, which can be demonstrated as, a linear combination of *complex* spherical harmonics.

It is possible that the Coulomb wave function here can be expanded in a basis of *complex* spherical harmonics as (Jackson, 1975),

$$\frac{e^2}{|\mathbf{r} - \mathbf{r}'|} = 4\pi e^2 \sum_{l=0}^{\infty} \sum_{m=-l}^l \frac{1}{2l+1} \frac{r_{<}^l}{r_{>}^{l+1}} Y_{lm}^*(\theta', \phi') Y_{lm}(\theta, \phi), \tag{5.23}$$

where $r_{<}$ and $r_{>}$ are the smaller and larger of $|\mathbf{r}|$ and $|\mathbf{r}'|$. Then, the product of a radial contribution and an angular contribution may be used to factorize the electron-electron interaction integrals.

$$\langle m, m'' | V_{ee} | m', m''' \rangle = \sum_k a_k(m, m', m'', m''') F^k, \quad (5.24)$$

where k and l are; an even integer in the range $0 \leq k \leq 2l$, and the angular momentum number of the localized manifold with $-l \leq m \leq l$ in that order.

5.1.3.1 The angular contribution

Recall Eq. (5.24), the a_k terms, depict the angular factors, and that they correspond to the product of 3 complex spherical harmonics also known as the Gaunt Coefficients.

$$a_k(m, m', m'', m''') = \frac{4\pi}{2k+1} \sum_{q=-k}^k \langle lm | Y_{kq} | lm' \rangle \langle lm'' | Y_{kq}^* | lm''' \rangle. \quad (5.25)$$

These can be broken down as a simple expression, involving only one normalization constant and two Wigner $3j$ symbols,

$$\begin{aligned} \langle lm | Y_{kq} | lm' \rangle &= \int_0^{2\pi} \int_0^\pi Y_{l,m}^*(\theta, \phi) Y_{k,q}(\theta, \phi) Y_{l,m'}(\theta, \phi) \sin \theta d\theta d\phi \\ &= \int_0^{2\pi} \int_0^\pi (-1)^m Y_{l,-m}(\theta, \phi) Y_{k,q}(\theta, \phi) Y_{l,m'}(\theta, \phi) \sin \theta d\theta d\phi \\ &= (-1)^m \sqrt{\frac{(2l+1) \times (2k+1) \times (2l+1)}{4\pi}} \begin{pmatrix} l & k & l \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l & k & l \\ -m & q & m' \end{pmatrix}. \end{aligned} \quad (5.26)$$

On the second product of the three spherical harmonics in Eq. (5.25), a similar equation is derived. The Gaunt integrals deviate from 0 if and only if $q + m' = m \Rightarrow q = m - m'$, and $-q + m''' = m'' \Rightarrow q = m''' - m''$ (Gómez-Ortiz et al., 2023). The $3-j$ symbols are given in terms of the famous Clebsch–Gordan coefficients by

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \equiv \frac{(-1)^{j_1-j_2-m_3}}{\sqrt{2j_3+1}} \langle j_1 m_1 j_2 m_2 | j_3 (-m_3) \rangle, \quad (5.27)$$

where these Clebsch–Gordan coefficients are easily obtained from a long existing and well

known Racah formula (Messiah, 1960).

As we end, note that Eq. (5.25) metamorphoses to the work of Liechtenstein and co-workers (Liechtenstein et al., 1995) as follows

$$\begin{aligned}
 a_k(m, m', m'', m''') &= \sum_{q=-k}^k (2l+1)^2 (-1)^{m+q+m''} \\
 &\times \begin{pmatrix} l & k & l \\ 0 & 0 & 0 \end{pmatrix}^2 \begin{pmatrix} l & k & l \\ -m & q & m' \end{pmatrix} \\
 &\times \begin{pmatrix} l & k & l \\ -m'' & -q & m''' \end{pmatrix}. \tag{5.28}
 \end{aligned}$$

5.1.3.2 The radial contribution

Note that the quantity F^k , found in Eq. (5.24) are Slater integrals that involve a radial part of the atomic wave function R_{nl} . On the other hand, n simply indicates the specific atomic shell that they do belong to. Usually, they obey the expression below (Himmetoglu et al., 2014),

$$F^k = e^2 \int d^3r \int d^3r' r^2 r'^2 R_{nl}^2(r) \frac{r_{<}^k}{r_{>}^{k+1}} R_{nl}^2(r'). \tag{5.29}$$

Considering the d electrons, we will only need F^0 , F^2 , and F^4 to compute V_{ee} matrix elements. On the other hand for f electrons, we will require F^6 . At this juncture, it is wise to say that if higher k values are selected, then the corresponding a_k vanish.

Practically, the Slater integrals seen in Eq. (5.29) are usually estimated from the Coulomb U and also the Stoner J parameters in the work of Liechtenstein and co-workers (Liechtenstein et al., 1995),

$$U = F^0, \tag{5.30a}$$

$$J = \frac{F^2 + F^4}{14}, \tag{5.30b}$$

while the ratio $\frac{F^4}{F^2} = 0.625$, is simply taken as a constant. The best approximation we can have for a d -electron system (Liechtenstein et al., 1995) (the ratio $\frac{F^4}{F^2}$ for all the $3d$ ions is between 0.62 and 0.63 (de Groot et al., 1990)). Consequently, if U and also J are used as parameters, then

$$F^0 = U, \quad (5.31a)$$

$$F^2 = \frac{14 \times J}{(1 + 0.625)}, \quad (5.31b)$$

$$F^4 = 0.625 \times F^2. \quad (5.31c)$$

In the same spirit but for f -orbitals, the ratio $\frac{F^4}{F^6}$ with respect to F^2 can be pegged to, $\frac{F^4}{F^6} \approx 0.67$ and $F^6/F^2 \approx 0.49$ (Vaugier, 2011). Consequently, U and also J parameters are to be given, then,

$$U = F^0, \quad (5.32a)$$

$$J = \frac{286F^2 + 195F^4 + 250F^6}{6435}, \quad (5.32b)$$

and if we write U and also J in terms of the Slater integrals, then

$$F^0 = U, \quad (5.33a)$$

$$F^2 = \frac{6435}{286 + 195 \times 0.67 + 250 \times 0.49} J, \quad (5.33b)$$

$$F^4 = 0.67 \times F^2, \quad (5.33c)$$

$$F^6 = 0.49 \times F^2. \quad (5.33d)$$

After accurately computing the electron-electron interaction integrals depicted in Eq. (5.24) using the expressions in Eq. (5.28) and also Eqs. (5.31a)-(5.31c), we can then transform back to a basis of the real spherical harmonics, that are similar to those used in expanding atomic orbitals.

Just to double check the implementation, we had to ascertain the following average

relationships that do in most cases, come from the properties of the Clebsh-Gordan coefficients (Anisimov et al., 1993; Amadon et al., 2017)

$$\begin{aligned}
U &= \frac{1}{(2l+1)^2} \sum_{m,m'} \langle m, m' | V_{ee} | m, m' \rangle = F^0 \\
U - J &= \frac{1}{2l(2l+1)} \sum_{m,m'} (\langle m, m' | V_{ee} | m, m' \rangle - \langle m, m' | V_{ee} | m', m \rangle). \quad (5.34)
\end{aligned}$$

5.1.4 The atomic forces and stresses

In principle, by directly differentiating energy in Eq. (5.21) with a regard to atomic locations, atomic forces and stresses are derived. Due to our basis set functions' explicit reliance on the ionic positions, the Pulay adjustments are automatically taken into account in the SIESTA code.

The force terms containing $\partial \rho_{\mu\nu} / \partial \mathbf{R}_K$ are essentially multiplied by, the corresponding potential matrix elements. Note that these kind of contribution, to the forces looks like $\sum_{\mu\nu} V_{\nu\mu} \partial \rho_{\mu\nu} / \partial \mathbf{R}_K$ and, thus computed by the orthogonality forces (Soler et al., 2002). The following list summarizes the forces that are expressly considered to come from the

Hubbard and also the double counting concepts discussed earlier.

$$\begin{aligned}
F^{\text{Hub}} = & -2 \sum_I \sum_{\mu\nu} \sum_{\{m\}} \left[\langle m, m'' | V_{ee} | m', m''' \rangle \left(n_{m''m'''}^{I,\uparrow\uparrow} + n_{m''m'''}^{I,\downarrow\downarrow} \right) \right. \\
& \left. - \langle m, m'' | V_{ee} | m''', m' \rangle n_{m''m'''}^{I,\uparrow\uparrow} \right] \frac{\partial S_{m\mu}^I}{\partial \mathbf{R}_K} S_{\nu m'}^I \rho_{\mu\nu}^{\uparrow\uparrow} \\
& -2 \sum_I \sum_{\mu\nu} \sum_{\{m\}} \left[\langle m, m'' | V_{ee} | m', m''' \rangle \left(n_{m''m'''}^{I,\uparrow\uparrow} + n_{m''m'''}^{I,\downarrow\downarrow} \right) \right. \\
& \left. - \langle m, m'' | V_{ee} | m''', m' \rangle n_{m''m'''}^{I,\downarrow\downarrow} \right] \frac{\partial S_{m\mu}^I}{\partial \mathbf{R}_K} S_{\nu m'}^I \rho_{\mu\nu}^{\downarrow\downarrow} \\
& + 2 \sum_I \sum_{\mu\nu} \sum_{\{m\}} \langle m, m'' | V_{ee} | m''', m' \rangle \frac{\partial S_{m\mu}^I}{\partial \mathbf{R}_K} S_{\nu m'}^I \left(n_{m''m'''}^{I,\uparrow\downarrow} \rho_{\mu\nu}^{\downarrow\uparrow} + n_{m''m'''}^{I,\downarrow\uparrow} \rho_{\mu\nu}^{\uparrow\downarrow} \right), \\
F^{\text{dc}} = & \sum_I \sum_{\mu\nu} \sum_m \rho_{\mu\nu}^{\uparrow\uparrow} \frac{\partial S_{m\mu}^I}{\partial \mathbf{R}_K} S_{\nu m}^I \left[(-U^I + J^I) + 2U^I n^I - 2J^I n^{I,\uparrow\uparrow} \right] \\
& + \sum_I \sum_{\mu\nu} \sum_m \rho_{\mu\nu}^{\downarrow\downarrow} \frac{\partial S_{m\mu}^I}{\partial \mathbf{R}_K} S_{\nu m}^I \left[(-U^I + J^I) + 2U^I n^I - 2J^I n^{I,\downarrow\downarrow} \right] \\
& - \sum_I \sum_{\mu\nu} \sum_m 2J^I \frac{\partial S_{m\mu}^I}{\partial \mathbf{R}_K} S_{\nu m}^I \left(\rho_{\mu\nu}^{\uparrow\downarrow} n^{I,\downarrow\uparrow} + \rho_{\mu\nu}^{\downarrow\uparrow} n^{I,\uparrow\downarrow} \right).
\end{aligned}$$

Using the same synergy, the energy is directly differentiated from the strain tensor to produce the stress tensor (Gómez-Ortiz et al., 2023).

They may be calculated numerically using the same procedure as the forces with minimal additional efforts (Soler et al., 2002).

5.1.5 A test run from the LDA+U+SOC implementation in the SIESTA code

After the implementation, it was wise to test our approach. The goal here was not to delve much into the science but to bench mark findings of our implementation to that of other well developed and known codes like VASP (Kresse & Furthmüller, 1996; Kresse & Furthmüller, 1996) and QUANTUM ESPRESSO (Giannozzi et al., 2009, 2017). The procedures used have been explained well in appx. A, for the SIESTA code and appx. B, for QUANTUM ESPRESSO and VASP codes. We computed the structural and electronic properties of IrO₂, a well known catalyst in water splitting. IrO₂, apart from being the known catalyst

that can produce O_2 in acidic conditions, it has also other fascinating traits (Ping et al., 2015). The internal parameter (u), lattice constants (a and c) from different methodologies are shown in Table. 5.1. One observation is that the difference in the lattice constant was of the order of 1.5% while that of the internal geometry varied by 0.13% despite the huge difference in the methodologies used. To note was that the implementation made herein at 0K was in a very good agreement with the experimental findings at 300K (McDaniel & Schneider, 1967).

Table 5.1: Internal parameter (u), lattice constants (a and c), of the optimized bulk IrO_2 in the rutile (tetragonal) structure. PW stands for Plane Waves. The lattice constants are in angstrom ($\text{\AA}$).

Method	Pseudopotential	Basis set	Functional	a	c	u
SIESTA	Norm-conserving	Local atomic orbitals	PBEsol	4.497	3.164	0.3085
			PBEsol+U	4.503	3.159	0.3081
			PBEsol+U+SOC	4.507	3.159	0.3081
QUANTUM ESPRESSO	Ultrasoft	PW	PBEsol+U+SOC	4.536	3.178	0.3082
VASP	PAW	PW	PBEsol+U+SOC	4.482	3.150	0.3083
QUANTUM-ESPRESSO (Ping et al., 2015)	Ultrasoft	PW	PBE	4.538	3.183	0.3083
CRYSTAL (Ping et al., 2015)	Core effective potentials	Local atomic orbitals	PBE	4.519	3.196	0.3087
Experiment (McDaniel & Schneider, 1967)				4.505	3.159	0.3077

The band structure of this system, estimated at the relaxed theoretical structure, is depicted in Fig. 5.1. The oxygen atoms would be O^{2-} according to formal oxidation states, but the iridium atoms should be thought of as Ir^{4+} . This indicates that five electrons are anticipated to occupy the Ir- d levels that are separated into three t_{2g} states and two e_g states by the strong crystal field that splits the distorted octahedral field. The Fermi level is anticipated to cross at the top of the t_{2g} band, making IrO_2 metallic, with the t_{2g} band only partially filled (five electrons for a maximum occupancy of six). This metallicity is obviously displayed in Fig. 5.1, which is well-concordant with earlier models (Kahk et al., 2014). The lifting of the degeneracy of the bands along the high-symmetry $Z - R - A$ path is the spin-orbit coupling's most significant consequence. It makes little difference in other directions. In order to produce a splitting of the bands at the Fermi energy and a spin-orbit Mott insulating state, the SOC in bulk IrO_2 is therefore insufficient (Kahk et al., 2014; Ping et al., 2015). The fact that the band structures generated by three distinct codes are essentially identical is the most significant finding for the purposes of this work.

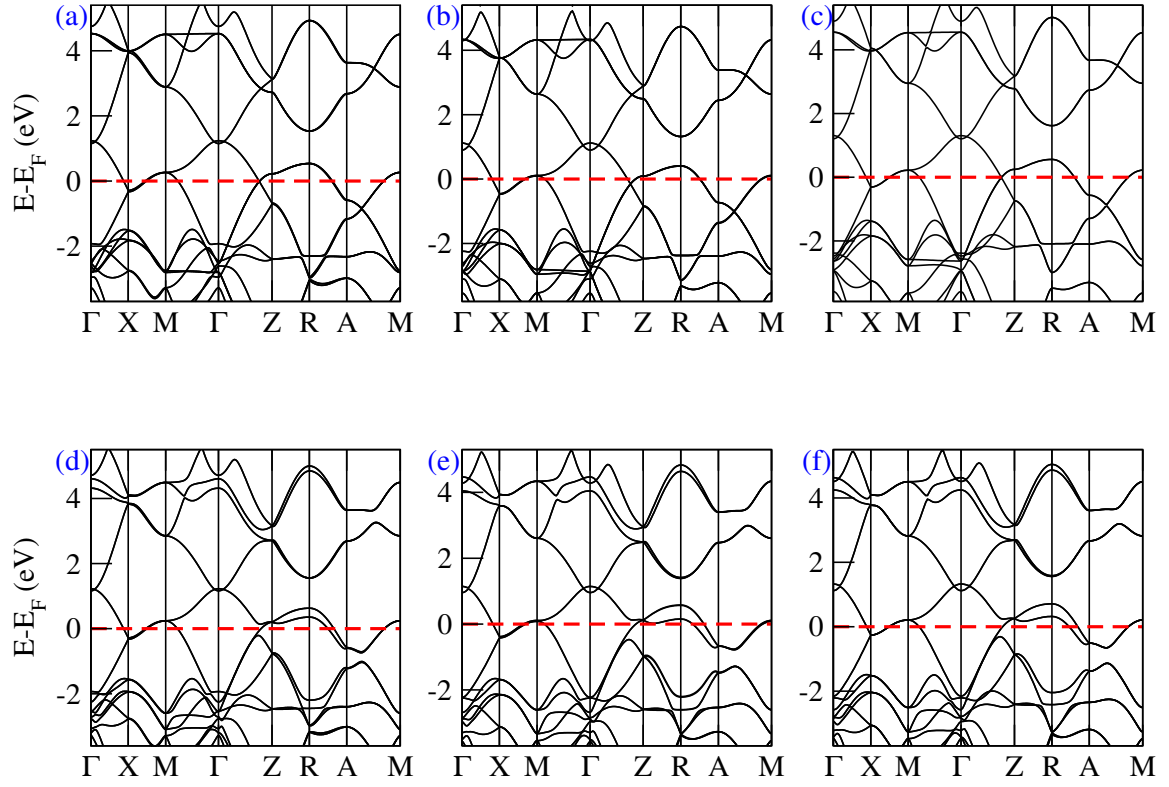


Figure 5.1: IrO₂ band structures in their hypothesized relaxed form. In SIESTA (a), VASP (b) and QUANTUM ESPRESSO (c), DFT+U bands are displayed. While the DFT+U+SOC band structures in SIESTA (d), VASP (e) and QUANTUM ESPRESSO (f) are plotted. The Fermi energy, E_F , which is thought to be an origin of energies, is shown by the horizontal red dashed lines.

The ABACUS code (Qu et al., 2022) yields outcomes that are quite comparable. Since the implementation passed all the tests subjected to it, we were now ready to use it on the science of DWs in this study.

5.2 Domains' Polarization Profiles

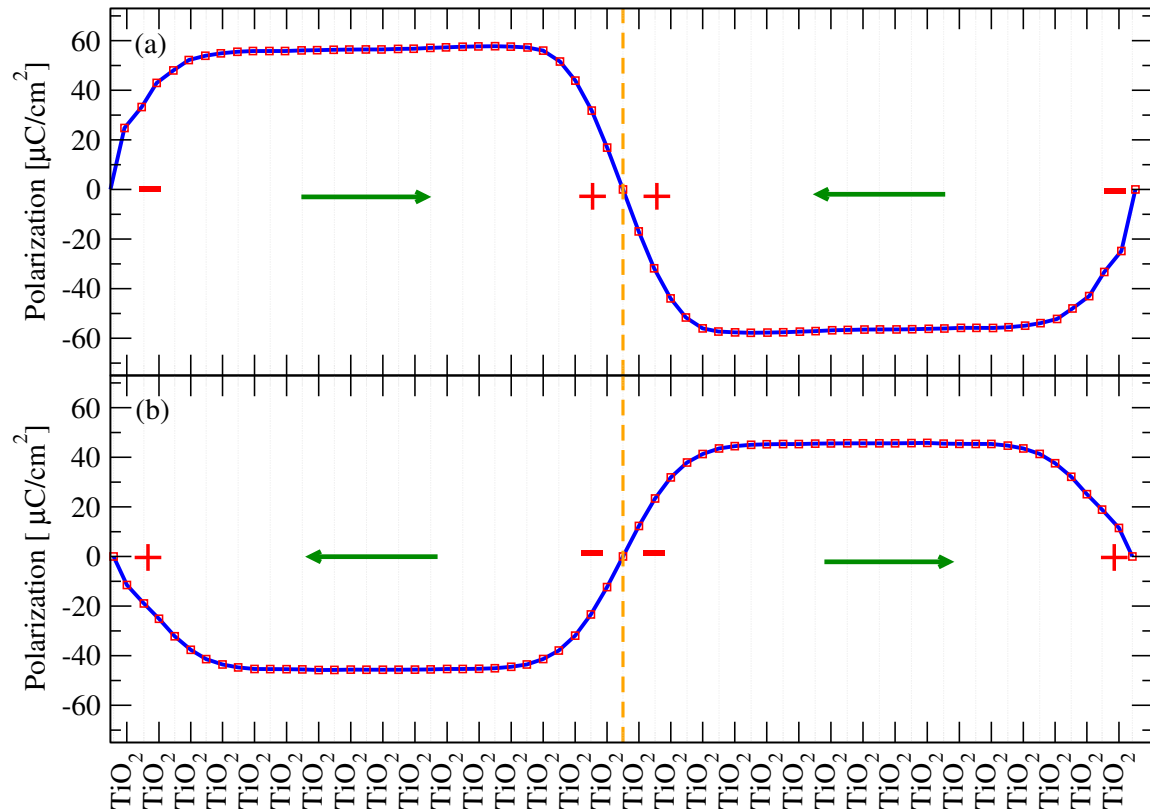


Figure 5.2: Local polarization profiles for 180° DWs in PbTiO₃, (a) HH and (b) TT. Based on ‘renormalized’ Born effective charges, red small squares show each layer’s polarization. The solid blue line serves as a visual cue. The DW is indicated by the vertically dashed orange line, and the PbO layers are indicated by vertically dotted grey lines. Checking at both HH and TT, in that order, the sprawling polarization values seen mid way the domain are $P_{\text{HH}} = 57.26 \mu\text{C}/\text{cm}^2$ and $P_{\text{TT}} = 45.72 \mu\text{C}/\text{cm}^2$. Arrows in green point the direction that the macroscopic polarization takes. The + and – signs are simply polarization induced charge densities.

These two polar configurations are essentially meta-stable upon relaxing of these slabs. Note that, it is the centrosymmetric unpolarized structure that is most stable phase. Agudo and co-workers (Yin et al., 2015), found a similar observation but in $\text{PbTiO}_3/\text{SrTiO}_3$ domains (*ferroelectric/paraelectric*). The energy differences with regard to the paraelectric (*centrosymmetric*) phase illustrated in Table. 5.2, demonstrate that the TT setup was energetically stable than the HH. The findings in Fig. 5.2 demonstrate the layer by layer characterization of polarization in; head-to-head Fig. 5.2(a), and tail-to-tail Fig. 5.2(b) in PbTiO_3 domain structures. This was determined from the Born charge method in which the dynamical bulk charges were re-normalized using a recipe proposed by Stengel and

co-workers (Stengel et al., 2011).

Throughout the interior of the domains, the polarization profile is astonishingly flat and is defined by a constant value equal to $57.26 \mu\text{C}/\text{cm}^2$ ($0.74 P_S$) for HH and $45.72 \mu\text{C}/\text{cm}^2$ ($0.59 P_S$) for TT structures in that order.

A spatial of polarization variation $P(z)$ was seen as a result of a localized, severe, and non-homogeneous atomic distortions. Since these patches that contain non-uniform polarizations span for roughly six unit-cells, we can easily calculate the DWs breadth as it was stated in one of the goals of this thesis. When this polarization profile is fit to a functional form found by Gureev *et al.* (Gureev et al., 2011), one can harvest more qualitative information,

$$P(z) = P_0 \times \tanh\left(\frac{z}{\delta_w}\right), \quad (5.35)$$

where, δ_w represents the half-width of the DW.

The specific results of fitting these profiles as shown in Fig. 5.2, to a scheme showed in Eq. (5.35), are contained in Table. 5.2. In contrast to the neutral configuration, where

Table 5.2: An outcome seen after fitting the effective polarization profiles for both HH and TT DWs (Fig. 5.2) to Eq. (5.35). The energy difference between the entire slab (162 atoms) and the most stable centrosymmetric unpolarized form is denoted as ΔE .

	$P_0 (\mu\text{C}/\text{cm}^2)$	$\delta_w (\text{\AA})$	$\Delta E (\text{eV})$
TT	45.72	6.87	1.160
HH	57.26	5.80	1.374

they were discovered as extremely narrow (*of the order of the lattice constant*) (Meyer & Vanderbilt, 2002), the DW widths are found to be bigger and thus inline with the findings of supporting conclusions of Gureev and co-workers (Gureev et al., 2011).

The walls of these 180° domains, which form a right angle with the polarization, produce polarization induced bound charges, that cause a localized buildup of a significant amount of electrostatic energy, which can easily destabilize the structure. This thesis suggests that the positive and negative polarization charges that are seen at the DWs in Fig. 5.2, have been filtered. This is pegged on the stability observed.

In this case, we expect a metallization to occur at the boundary walls and also at the surfaces. This is occasioned by the neutralization procedure done by the free carriers. This metallization is what leads to the genesis of two dimensional metallic layers. Unfortunately, this thesis doesn't take into account issues on defects or dopants as proposed by Wu and Vanderbilt (X. Wu & Vanderbilt, 2006), but we leave this as a head room for future studies. The telltale symptom of such a situation would be a sizable amount of free charge occupying the band edges, both at the DW and at the free surfaces of the slab.

5.3 Layer Resolved PDOS

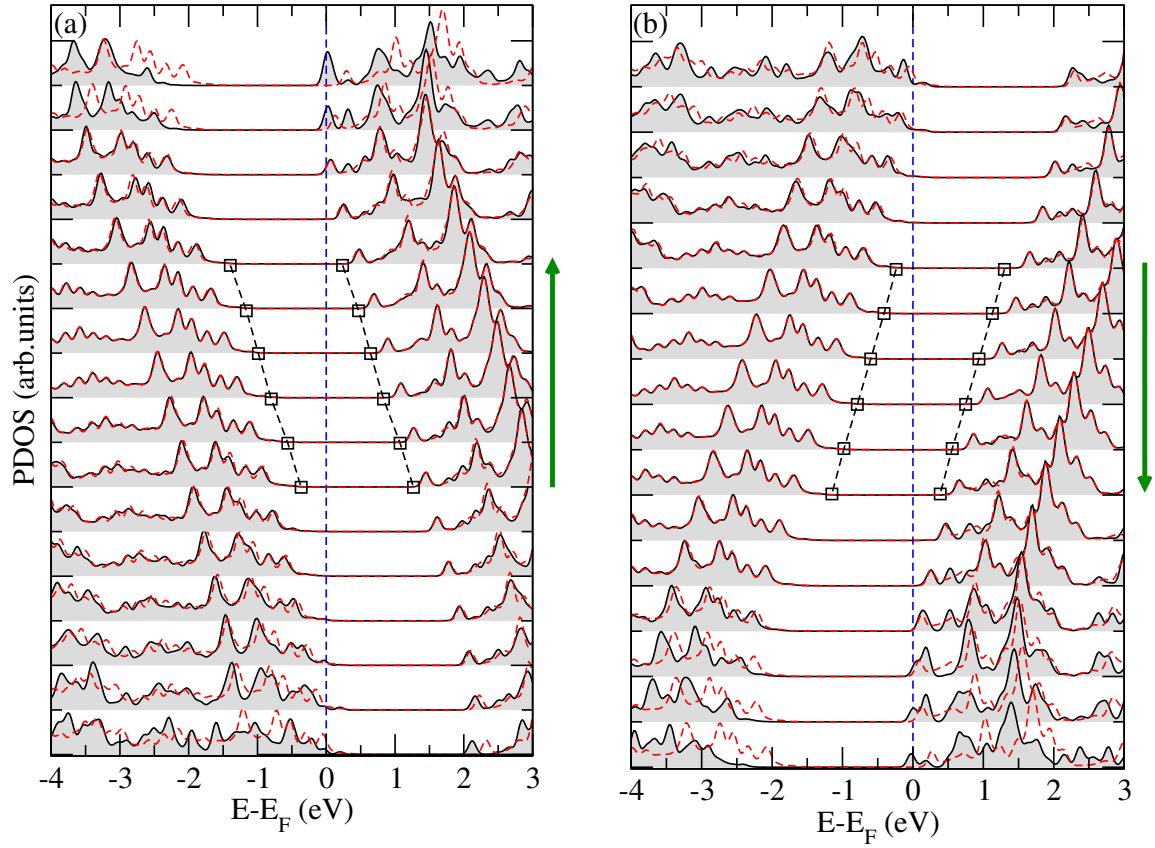


Figure 5.3: Layer by layer PDOS on the TiO_2 (a) HH and (b) TT 180° domains (solid black curves with gray shading). The top curve is at the DW, and the bottom curve is at the free surface. The $\text{Ti}(3s)$ peak and the bulk PDOS curves (red dashed), are in perfect alignment. The local band edges are depicted by the squares. The black dashed lines represent an interpolation of the computed band edges using a linear formula. The vertical blue dashed line indicates where the Fermi level is, which is at zero energy. The polarization direction is shown by the green arrow, and the only PDOS on display is on one half of the symmetric supercell.

Fig. 5.3 indicates a spatially resolved PDOS. This PDOS is for all atomic orbitals of Ti and O. That is to say, the TiO_2 layers in the system. An observation on Fig. 5.3, shows that the top layer is located near the DW, while the layer at the bottom is close to the free surface. Remember, and by design, we have a reflecting like symmetry plane at the DW. This explains why on the PDOS of only one domain is shown. As illustrated by the work of Stengel and others (Stengel, 2011), the equilibrium, distribution, and spreading of the electron gas is entirely determined by the electric displacement field's boundary values, which is really subject to asymmetric control.

The scope of this thesis does not include those asymmetric arrangements.

In this study, we superimpose the heterostructure PDOS on top of the bulk PDOS, which was calculated using an analogous k -point sample (dashed red lines). The unconstrained atomic structure (Fig. 5.2) has converged into a predictable pattern in an area of the HH or TT domains where the atomic distortions and out-of-plane strain were removed. A PbTiO_3 structure with five atoms per unit cell was employed in the periodic bulk computation. The PDOS for the identical TiO_2 atomic layer is then extracted. The strong peaks, which actually belong to $\text{Ti}(3s)$ semicore orbitals, were matched to superimpose the bulk PDOS at each layer.

These bands, almost at the Fermi level, are mostly $\text{O-}p$ (VB) and $\text{Ti-}t_{2g}$ (CB) in character.

A quick look at Fig. 5.3 shows that the Fermi level has been set to zero. The top of the valence band and the bottom of the conduction band are seen crossing the Fermi level which is a signature of metallization. There is a non-ending PDOS at the the bottom of the conduction band at the DW for the top three layers of TiO_2 , indicating an electronic population as is evident in Fig. 5.3(a). Also, checking at the top of the valence band, we see a non-ending PDOS around the Fermi level, of three TiO_2 layers which confirms that free electronic charge was transferred from the surface. In Fig. 5.3(b), a similar narrative is seen on the TT domains on the electrons and holes play opposite roles. What happens in this case, is that holes are produced at the top of the valence band layers at the DW, while electrons are populated at the bottom of the conduction band at the free surfaces.

As one advances away from the interface, the PDOS of the conduction and valence bands soon converge to the bulk curve and vanish at the Fermi level, proving that the system is locally insulating. Additionally, each layer's PDOS appears to be rigidly displaced in relation to the two layers directly below it, which is compatible with the existence of an internal residual depolarization field that keeps free charges electrostatically contained inside the metallic area of the domains. (Stengel et al., 2011) (see black dashed lines in Fig. 5.3). Because the bulk calculations were performed at zero external electric field while the slab calculations have a residual depolarizing field, the coincidence of the two

curves sufficiently far from the free surfaces and the DW suggests that the main influence on the layer-by-layer PDOS comes from the lattice distortions rather than from macroscopic depolarizing fields. As will be detailed in Sec. 5.4, this residual depolarizing field will be crucial in identifying the atomic orbitals involved in this very important electronic reconstruction.

5.4 The Relationship Between the Density of Free Carriers with the Polarization Profiles

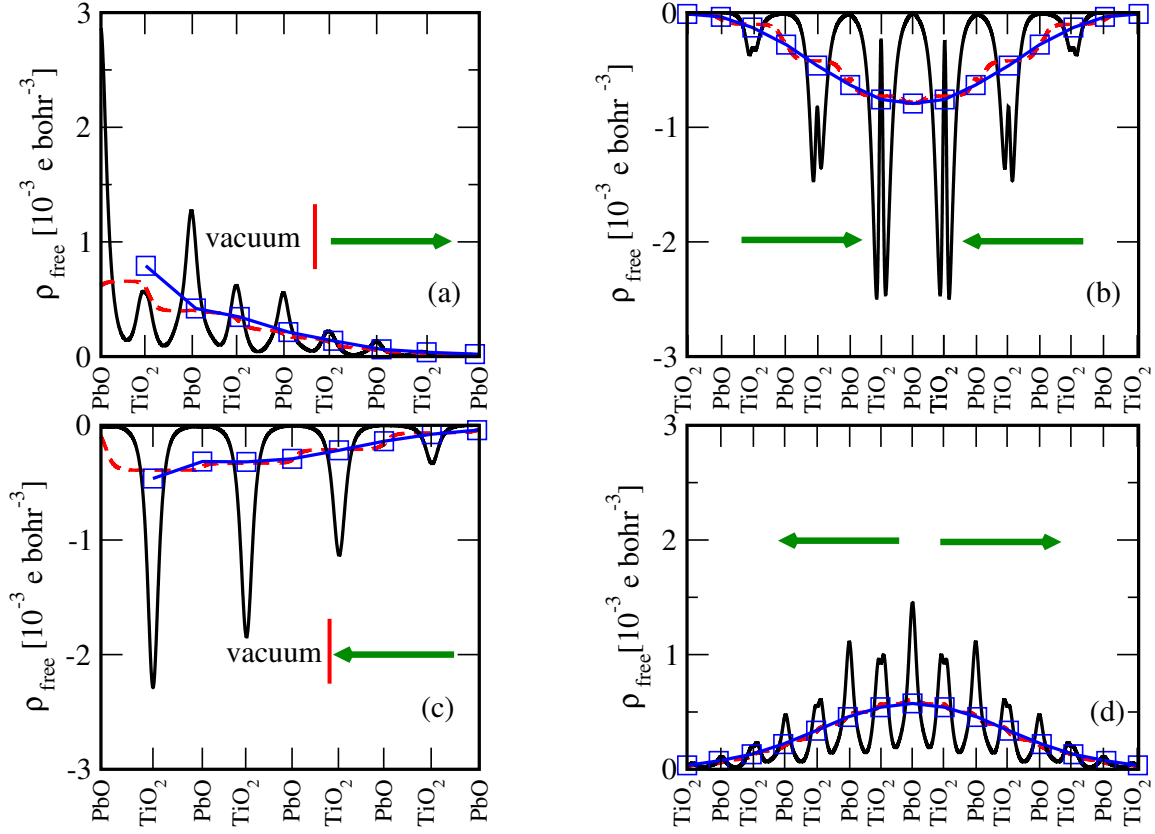


Figure 5.4: The resulting free charge for DW from HH and TT. The black curve seen, is the planar averaged $\bar{\rho}_{\text{free}}$, that was specified in Eq. (5.36). The dashed line in red represents the nanosmoothed average. The blue line indicates magnitude of bound charge profile, which was determined using finite difference derivative of (Fig. 5.2). Note that, at the surface and at the boundary wall, the sign of the bound charge is actually opposite to that of free charge. In the set up, for the HH system, (a) shows the charge density of the holes at the free surface and, (b) shows the charge density of the electrons at the DW. When it comes to the TT system, (c) depicts the electron charge density at the DW while (d) shows the charge density of the holes at the DW. The green arrows again, show the direction of polarization. Finally, note that electron gases have negative densities, while hole gases have densities that are positive.

For us to obtain the exact amount of charge moved to the DWs from the free surfaces to perform the screening of the depolarizing fields, we had to plot the planar average of the free charge $\bar{\rho}_{\text{free}}(z)$ in Fig. 5.4

$$\bar{\rho}_{\text{free}}(z) = \frac{1}{S} \int_S \rho_{\text{free}}(\mathbf{r}) \, dxdy, \quad (5.36)$$

in this case, S is an interface unit cell area and its analogous nanosmoothed version (Junquera et al., 2007), $\bar{\rho}_{\text{free}}(z)$. On the other hand, $\rho_{\text{free}}(\mathbf{r})$ has been calculated for that electronic charge density colonizing the conduction band as

$$\rho_{\text{free}}^{\text{electrons}}(\mathbf{r}) = \sum_{E_{n\mathbf{k}} > E_0} w_{\mathbf{k}} f_{n\mathbf{k}} |\psi_{n\mathbf{k}}(\mathbf{r})|^2, \quad (5.37)$$

while at the top of the valence band, we compute the hole charge density. This charge density is equal to

$$\rho_{\text{free}}^{\text{holes}}(\mathbf{r}) = \sum_{E_{n\mathbf{k}} < E_0} w_{\mathbf{k}} (1 - f_{n\mathbf{k}}) |\psi_{n\mathbf{k}}(\mathbf{r})|^2, \quad (5.38)$$

where $w_{\mathbf{k}}$, $f_{n\mathbf{k}}$ and E_0 are; weight of the special $\mathbf{k}$ point in the discrete Monkhorst-Pack mesh, occupation numbers of an eigenstate $\psi_{n\mathbf{k}}$ with eigenvalue $E_{n\mathbf{k}}$, and a value of energy equivalent to the center of the gap between the valence and conduction bands in that order. The results are show cased in Fig. 5.4.

At this point, the systems are not charge neutral both at the DW and at the free surfaces.

To quantify the free carriers per unit area, we simply integrate the profiles belonging to the nanosmoothed average free charge densities along the z direction. The free carriers here are σ_e (for electrons) and σ_h (for holes). There is an extra electron density at the DW filling the bottom of the conduction bands for the HH domains, amounting to $\sigma_e^{\text{HH}} = 1.033$ electrons as shown in Fig. 5.4(a). These electrons were removed from the free-surfaces, where $\sigma_h^{\text{HH}} = 0.517$ holes per surface unit cell is obtained by integrating the free hole charge shown in Fig. 5.4(b). Interestingly, and as required by the global charge neutrality, $\sigma_e^{\text{HH}} = 2\sigma_h^{\text{HH}}$. To make the charge neutrality easy to understand, note that we do have two free surfaces that are populated with holes and we only have one HH DW charged with electrons.

Shifting gears to the TT domains, the extra holes found at the DW shown in Fig. 5.4(c), equal $\sigma_h^{\text{TT}} = 0.827$. In order to fill the bottom of the conduction bands at the free surfaces, exactly twice as many more electrons are added. $\sigma_e^{\text{TT}} = 0.413$ as shown in Fig. 5.4(d).

After decomposing the electron and hole free charges into distinct orbital components,

as shown in Fig. 5.5, we may gain a better understanding of their origin.

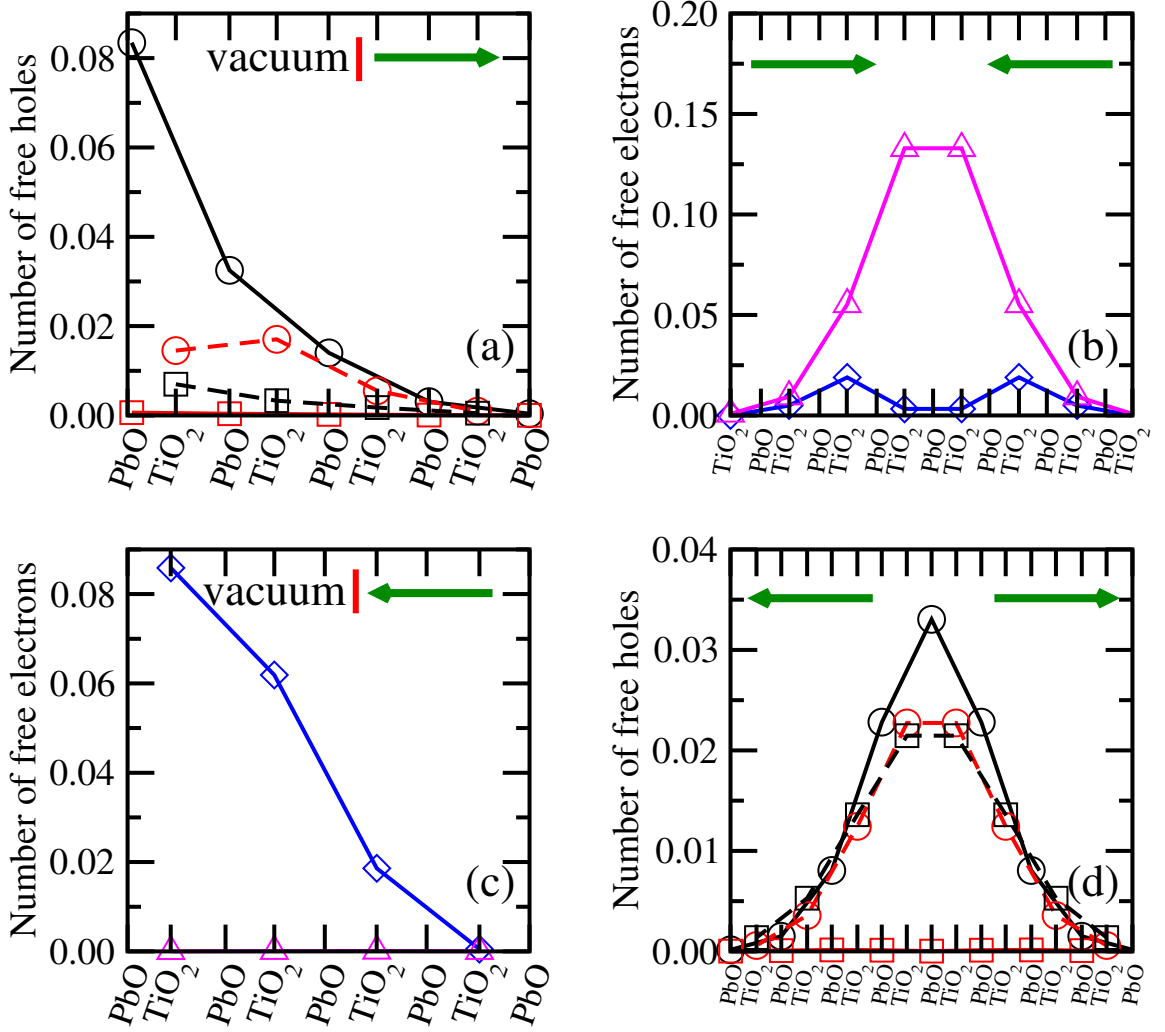


Figure 5.5: This is a representation of the free carrier densities in PbTiO₃ under this study. For the HH structure, (a) is the free surface while (b) shows the DW. On the TT structure, (c) is the free surface while (d) is the DW. Here, the black circles, represent the amount of free holes in the O orbitals that are responsible for the π -bonding. On the other hand, the red squares, are responsible for σ -bonding. The solid lines are utilized to depict O in the PbO layers, whereas the dashed lines demonstrate where the O is placed in the TiO₂ plane. On the other hand, the blue diamonds represent represent the amount of free electrons in the d_{xy} , while magenta triangles up, indicate the $d_{xz} + d_{yz}$ orbitals of Ti. The polarization direction is shown by the green arrows.

The d_{xy} orbitals, as per the current wisdom, are usually the first to be populated just like in the case of LaAlO₃/SrTiO₃ (Popović et al., 2008) or PbTiO₃/SrTiO₃ (Yin et al., 2015) interfaces, where two-dimensional electron gases were formed to screen the polar catastrophe at the interface. Similar circumstances may be observed in bulk polarized PbTiO₃ as well as on the free surface of our system in Fig. 5.5(c). Nonetheless, when considering

the metallic like states created at the DWs, it is seen that the HH electron gas (Fig. 5.5b) is mostly originating from d_{xz} and d_{yz} orbitals, while d_{xy} orbitals have relatively little charge. This is also seen in the doubled-peaks in Fig. 5.4b. Moving to the TT hole gas, the important contribution originates from the π -orbitals in the PbO plane and very small, but also important, contribution from both σ and π -bonded in TiO₂ planes. The remaining electric potential energy within the domains, which has a form like a $\vee$ for the HH and a $\wedge$ for the TT, with the peak placed near the DW in both cases, is responsible for the effects of localization, according to the facts herein. Those are the carriers' relative confinement potentials. Only the center of the subbands may be relocated, perfectly following the form of the potential. For the bands with majority weights on orbitals oriented parallel to the DW, the dispersion remains unaffected. The d_{xy} bands of Ti and the O- σ orbitals in this thesis are an exact example of this. However, due to the confinement potential, both the dispersion and the local center of mass of the bands for which the bulk of weights are on orbitals perpendicular to the domain wall are significantly changed. This narrows the available range of interactions. The hybridization is thus reduced and as a result, the matching bonding orbitals are activated. O- π in PbO layers increases energy, while the antibonding orbitals d_{xz} and d_{yz} simultaneously lose energy. As a result, these are the initial orbitals around the DW that are either filled with electrons as shown in Fig. 5.5(b) or that are emptied to form holes as seen in Fig. 5.5(d). We showed the mathematical differentiation of the polarization profiles shown in Fig. 5.2, in Fig. 5.4 in order to understand how electronic reconstruction in this situation is as a result of screening polarization at the DWs. As you can see, the bound charge profile, ρ_b , and the nanosmoothed free charge densities match perfectly. See the blue lines in Fig. 5.4 which are represented by the formula $\rho_b(z) = -dP/dz$. Therefore, keep in mind that any observed electronic reconstruction is driven by polarization discontinuity at the DW in this case, and that charge transfer from the DW to the free surface acts as a powerful screening mechanism to maintain monodomain configurations in the two domains.

CHAPTER SIX

CONCLUSION AND RECOMMENDATION

This thesis, specially customized the concept by Bousquet and Spaldin (Bousquet & Spaldin, 2010) to extended the DFT+U formalism in the SIESTA method to systems containing large SOC energies. In this scenario, the whole Kohn-Sham orbital space was mapped onto the correlated shell using non-overlapping orthogonal projectors, which were defined similarly to the basic atomic orbitals with shorter ranges. Expressions for the single-particle potential's inclusion in the self-consistent cycles for energy, forces, and stresses have been given. The LDA+U+SOC implementation in the SIESTA version 5.0 was supported by a real-world example (IrO_2) that is connected to some of our previous research. From the bench-marked results, the lattice constants of IrO_2 using the authors implementation agreed perfectly with experimentally determined lattice constants at 300k. On employing other simulation methods like VASP and QUANTUM ESPRESSO, the lattice constants had a discrepancy of $\approx 1.5\%$. Also to note was the fact that the band structures generated by the three distinct codes herein, were essentially identical. The implementation was successful in this case, and it actually extends with a large application benefiting researchers outside the ferroelectric community. In the ferroelectric community, we ought to be careful due to the hybridisation of the $O-2p$ and $Ti-3d$ in the case of PbTiO_3 that is responsible for polarization. Our implementation destroys this hybridization owing to the fact that it strives to improve the electronic band gap. If we were to employ our implementation in this case, it meant that we would have made the domains too large and thus making the calculations too expensive. As a matter of fact, experimental domains are usually larger than the DFT domains since they contain all the intrinsic factors like increased electronic bandgaps. In future, it is important to study all the key players in a material's Hamiltonian. The SIESTA code still needs a proper implementation to investigate electron-phonon interactions in crystals. This is very similar to what other codes like QUANTUM ESPRESSO and VASP can do. The main difference is that the electrostatic interactions in the men-

tioned codes are way too simplified in that approach (although there are many advantages to that simplification). This is essentially a tight-binding with a little bit of exciton physics attached.

On the other hand, in a flawless PbTiO_3 slab (free from vacancies and dopants), the 180° HH and TT charged domains became stable in an out-of-plane monodomain conformation. Calculations utilizing density-functional theory in this thesis demonstrate that this was made feasible by electrostatic screening provided by free carriers. Over a certain domain critical thickness, in this case $n = 16$ unit cells, an electronic reconstruction occurs, leading to the generation of quasi-two-dimensional electron and hole gases as charge is transported from the slab's free surface to the DW. The walls of these 180° domains, which form a right angle with the polarization, produce polarization-induced bound charges, that cause a localized buildup of a significant amount of electrostatic energy, which can easily destabilize the structure. Throughout the interior of the domains, the polarization profile is astonishingly flat and was defined by a constant value equal to $57.26 \mu\text{C}/\text{cm}^2$ ($0.74 P_S$) for HH and $45.72 \mu\text{C}/\text{cm}^2$ ($0.59 P_S$) for TT structures in that order. This thesis does not take into consideration problems with flaws, dopants, or any other external potentials and their effects on the polarization values. Nevertheless, we leave this as a headroom for future research and collaboration.

From the layer by layer PDOS, there is a non-ending PDOS near the bottom of the conduction band at the DW, suggesting an electronic population. Additionally, looking at the top of the valence band, we can detect three layers of TiO_2 that form a non-ending PDOS around the Fermi level, confirming the transfer of free electronic charge from the surface. In this case the domain wall is a mirror plane as discussed and only one half of the domain was shown. The DW, which measures around 6 unit cells for the HH and about 7 unit cells for the TT, were noticeably broader than the known width of neutral domains. It is expected that the size of the domain walls will definitely be altered if other screening mechanisms are employed in this study. Also, the width may be affected if a more complex scenario like domain slanting is considered. At this point, tilted DWs are still debatable but are a subject for further calculations in future.

The polarization profile, whose negative gradient matches the bound charge, has a specific electrostatic relationship with the density of free charge. The bottom of the conduction bands for the HH domains are occupied by an extra electron density at the DW, which corresponds to $\sigma_e^{\text{HH}} = 1.033$. These electrons were taken out of the free-surfaces, which now contain $\sigma_h^{\text{HH}} = 0.517$ holes per surface unit cell as calculated by integrating the free hole charge. Interestingly, $\sigma_e^{\text{HH}} = 2\sigma_h^{\text{HH}}$, as needed by the global charge neutrality. Noting that we do have two free surfaces that are filled with holes and only one HH DW charged with electrons helps to clarify the charge neutrality above. Moving on to the TT domains, the additional holes discovered at the DW equal $\sigma_h^{\text{TT}} = 0.827$. In order to fill the bottom of the conduction bands at the free surfaces, exactly twice as many more electrons are added. This thesis found that $\sigma_e^{\text{TT}} = 0.413$. The mismatch in formal polarization between the constituent materials is what causes the accumulation of free charges at the DW. In search of potential DWs where this scenario might occur, the bigger the polarization mismatch, the better. Since charge accumulation is a result of polarization discontinuity, what will happen to the charges if a different substrate is used in this study? The choice of a substrate will impact highly on the value of polarization and hence the charge accumulation. This can be done in future with little efforts.

As a general further work, these first-principles simulations obtained herein, could be used as a benchmark for second-principles calculations. This will be done in very large systems that take into account all of the necessary electronic and lattice degrees of freedom (García-Fernández et al., 2016). More difficult calculations, such as those involving slanting domains like those that emerge during domain switching or the conductivity at domain borders, can be taken on once the models (*electronic and atomistic*) for the second-principles calculations have been proven.

REFERENCES

- Aguado-Puente, P. (2011). *First-principles study of screening mechanisms of the depolarizing field in nanosized capacitors* (Ph. D. thesis). Universidad de Cantabria.
- Aguado-Puente, P., Bristowe, N. C., Yin, B., Shirasawa, R., Ghosez, P., Littlewood, P. B., & Artacho, E. (2015, Jul). Model of two-dimensional electron gas formation at ferroelectric interfaces. *Phys. Rev. B*, 92, 035438. Retrieved from <https://link.aps.org/doi/10.1103/PhysRevB.92.035438> doi: 10.1103/PhysRevB.92.035438
- Aguado-Puente, P., & Junquera, J. (2008, Apr). Ferromagneticlike closure domains in ferroelectric ultrathin films: First-principles simulations. *Phys. Rev. Lett.*, 100, 177601. Retrieved from <https://link.aps.org/doi/10.1103/PhysRevLett.100.177601> doi: 10.1103/PhysRevLett.100.177601
- Amadon, B., Applencourt, T., & Bruneval, F. (2017, Nov). Erratum: Screened coulomb interaction calculations: RPA implementation and applications to dynamical screening and self-consistency in uranium dioxide and cerium [phys. rev. b 89, 125110 (2014)]. *Phys. Rev. B*, 96, 199907. Retrieved from <https://link.aps.org/doi/10.1103/PhysRevB.96.199907> doi: 10.1103/PhysRevB.96.199907
- Anderson, P. (1960). Fizika dielektrikov. *Akad. Nauk SSSR, Moscow*, 476(2233), 290-96.
- Anglada, E., Soler, J. M., Junquera, J., & Artacho, E. (2002, nov). Systematic generation of finite-range atomic basis sets for linear-scaling calculations. *Physical Review B*, 66(20). Retrieved from <https://doi.org/10.1103/PhysRevB.66.205101> doi: 10.1103/PhysRevB.66.205101
- Anisimov, V. I., & Gunnarsson, O. (1991, Apr). Density-functional calculation of effective coulomb interactions in metals. *Phys. Rev. B*, 43, 7570–7574. Retrieved

- from <https://link.aps.org/doi/10.1103/PhysRevB.43.7570> doi: 10.1103/PhysRevB.43.7570
- Anisimov, V. I., Solovyev, I. V., Korotin, M. A., Czyżyk, M. T., & Sawatzky, G. A. (1993, Dec). Density-functional theory and NiO photoemission spectra. *Phys. Rev. B*, 48, 16929–16934. Retrieved from <https://link.aps.org/doi/10.1103/PhysRevB.48.16929> doi: 10.1103/PhysRevB.48.16929
- Arnay, I., Rubio-Zuazo, J., & Castro, G. R. (2018). Impact of cleaning methods on the structural properties and morphology of SrTiO₃ surface. *Applied Surface Science*, 427, 561-565. Retrieved from <https://www.sciencedirect.com/science/article/pii/S0169433217326223> doi: <https://doi.org/10.1016/j.apsusc.2017.09.025>
- Artacho, E., Gale, J. D., García, A., Junquera, J., Martin, R. M., Ordejón, P., ... Soler, J. M. (2005). *Electronic structure calculations with localized orbitals: The siesta method* (S. Yip, Ed.). Dordrecht: Springer Netherlands. Retrieved from https://doi.org/10.1007/978-1-4020-3286-8_6 doi: 10.1007/978-1-4020-3286-8_6
- Artacho, E., Sánchez-Portal, D., Ordejón, P., García, A., & Soler, J. M. (1999). Linear-scaling ab-initio calculations for large and complex systems. *Phys. Status Solidi (b)*, 215(1), 809-817. doi: 10.1002/(SICI)1521-3951(199909)215:1<809::AID-PSSB809>3.0.CO;2-0
- Ashcroft, N., & Mermin, N. (1976). *Solid State Physics*. Philadelphia: Saunders College.
- Baldereschi, A. (1973, Jun). Mean-value point in the brillouin zone. *Phys. Rev. B*, 7, 5212–5215. Retrieved from <https://link.aps.org/doi/10.1103/PhysRevB.7.5212> doi: 10.1103/PhysRevB.7.5212
- Bartel, C. J., Sutton, C., Goldsmith, B. R., Ouyang, R., Musgrave, C. B., Ghiringhelli, L. M., & Scheffler, M. (2019). New tolerance factor to predict the stability of perovskite oxides and halides. *Science Advances*, 5(2), eaav0693. Retrieved from <https://www>

.science.org/doi/abs/10.1126/sciadv.aav0693 doi: 10.1126/sciadv.aav0693

Bednyakov, P. S., Sluka, T., Tagantsev, A. K., Damjanovic, D., & Setter, N. (2015). Formation of charged ferroelectric domain walls with controlled periodicity. *Sci. Rep.*, 5(1), 15819. doi: 10.1038/srep15819

Bednyakov, P. S., Sturman, B. I., Sluka, T., Tagantsev, A. K., & Yudin, P. V. (2018, Nov 30). Physics and applications of charged domain walls. *npj Computational Materials*, 4(1), 1-11. Retrieved from <https://doi.org/10.1038/s41524-018-0121-8> doi: 10.1038/s41524-018-0121-8

Bilc, D. I., Orlando, R., Shaltaf, R., Rignanese, G.-M., Íñiguez, J., & Ghosez, P. (2008, Apr). Hybrid exchange-correlation functional for accurate prediction of the electronic and structural properties of ferroelectric oxides. *Phys. Rev. B*, 77, 165107. Retrieved from <https://link.aps.org/doi/10.1103/PhysRevB.77.165107> doi: 10.1103/PhysRevB.77.165107

Bilz, H., Benedek, G., & Busmann-Holder, A. (1987, Apr). Theory of ferroelectricity: The polarizability model. *Phys. Rev. B*, 35, 4840–4849. Retrieved from <https://link.aps.org/doi/10.1103/PhysRevB.35.4840> doi: 10.1103/PhysRevB.35.4840

Blöchl, P. E. (1994, Dec). Projector augmented-wave method. *Phys. Rev. B*, 50, 17953–17979. Retrieved from <https://link.aps.org/doi/10.1103/PhysRevB.50.17953> doi: 10.1103/PhysRevB.50.17953

Bousquet, E., & Spaldin, N. (2010, Dec). J dependence in the LSDA + U treatment of noncollinear magnets. *Phys. Rev. B*, 82, 220402. Retrieved from <https://link.aps.org/doi/10.1103/PhysRevB.82.220402> doi: 10.1103/PhysRevB.82.220402

Bultmark, F., Cricchio, F., Grånäs, O., & Nordström, L. (2009, Jul). Multipole decomposition of LDA + U energy and its application to actinide compounds. *Phys.*

- Rev. B*, 80, 035121. Retrieved from <https://link.aps.org/doi/10.1103/PhysRevB.80.035121> doi: 10.1103/PhysRevB.80.035121
- Carchini, G., Almora-Barrios, N., Revilla-López, G., Bellarosa, L., García-Muelas, R., García-Melchor, M., ... López, N. (2013, Sep 01). How theoretical simulations can address the structure and activity of nanoparticles. *Topics in Catalysis*, 56(13), 1262-1272. Retrieved from <https://doi.org/10.1007/s11244-013-0093-3> doi: 10.1007/s11244-013-0093-3
- Catalan, G., Seidel, J., Ramesh, R., & Scott, J. F. (2012, Feb). Domain wall nanoelectronics. *Rev. Mod. Phys.*, 84, 119–156. Retrieved from <https://link.aps.org/doi/10.1103/RevModPhys.84.119> doi: 10.1103/RevModPhys.84.119
- Ceperley, D. M., & Alder, B. J. (1980, Aug). Ground state of the electron gas by a stochastic method. *Phys. Rev. Lett.*, 45, 566–569. Retrieved from <https://link.aps.org/doi/10.1103/PhysRevLett.45.566> doi: 10.1103/PhysRevLett.45.566
- Chadi, D. J., & Cohen, M. L. (1973, Dec). Special points in the brillouin zone. *Phys. Rev. B*, 8, 5747–5753. Retrieved from <https://link.aps.org/doi/10.1103/PhysRevB.8.5747> doi: 10.1103/PhysRevB.8.5747
- Chege, S., Ning'i, P., Sifuna, J., & Amolo, G. O. (2020). Origin of band inversion in topological Bi₂Se₃. *AIP Advances*, 10(9), 095018. Retrieved from <https://doi.org/10.1063/5.0022525> doi: 10.1063/5.0022525
- Cochran, W. (1959, Nov). Crystal stability and the theory of ferroelectricity. *Phys. Rev. Lett.*, 3, 412–414. Retrieved from <https://link.aps.org/doi/10.1103/PhysRevLett.3.412> doi: 10.1103/PhysRevLett.3.412
- Cochran, W. (1960). Crystal stability and the theory of ferroelectricity. *Adv. Phys.*, 9, 387–423.
- Cococcioni, M., & de Gironcoli, S. (2005, Jan). Linear response approach to the calculation of the effective interaction parameters in the LDA + U method. *Phys.*

- Rev. B*, 71, 035105. Retrieved from <https://link.aps.org/doi/10.1103/PhysRevB.71.035105> doi: 10.1103/PhysRevB.71.035105
- Cohen, R. E. (1992). Origin of ferroelectricity in perovskite oxides. *Nature*, 358, 136-138.
- Comes, R., Lambert, M., & Guinier, A. (1968). The chain structure of BaTiO₃ and KNbO₃. *Solid State Communications*, 6(10), 715-719. Retrieved from <https://www.sciencedirect.com/science/article/pii/0038109868905711> doi: [https://doi.org/10.1016/0038-1098\(68\)90571-1](https://doi.org/10.1016/0038-1098(68)90571-1)
- Cuadrado, R., & Cerdá, J. I. (2012, jan). Fully relativistic pseudopotential formalism under an atomic orbital basis: spin-orbit splittings and magnetic anisotropies. *Journal of Physics: Condensed Matter*, 24(8), 086005. Retrieved from <https://dx.doi.org/10.1088/0953-8984/24/8/086005> doi: 10.1088/0953-8984/24/8/086005
- Cuadrado, R., Liu, K., Klemmer, T. J., & Chantrell, R. W. (2016). In-plane/out-of-plane disorder influence on the magnetic anisotropy of Fe_{1-y}Mn_yPt – L1₀ bulk alloy. *Appl. Phys. Lett.*, 108(12), 123102. Retrieved from <https://doi.org/10.1063/1.4944534> doi: 10.1063/1.4944534
- Dal Corso, A. (2014). Pseudopotentials periodic table: From H to Pu. *Computational Materials Science*, 95, 337-350. Retrieved from <https://www.sciencedirect.com/science/article/pii/S0927025614005187> doi: <https://doi.org/10.1016/j.commatsci.2014.07.043>
- Dawber, M., Stucki, N., Lichtensteiger, C., Gariglio, S., Ghosez, P., & Triscone, J.-M. (2007). Tailoring the properties of artificially layered ferroelectric superlattices. *Advanced Materials*, 19. Retrieved from <https://www.semanticscholar.org/paper/Tailoring-the-Properties-of-Artificially-Layered-Dawber-Stucki/99da8b37d2cacc17bab91e0a87ac6fb25c974089>
- de Groot, F. M. F., Fuggle, J. C., Thole, B. T., & Sawatzky, G. A. (1990, Sep). 2p X-ray absorption of 3d transition-metal compounds: An atomic multiplet description including

- the crystal field. *Phys. Rev. B*, 42, 5459–5468. Retrieved from <https://link.aps.org/doi/10.1103/PhysRevB.42.5459> doi: 10.1103/PhysRevB.42.5459
- Devonshire, A. F. (1949). Theory of barium titanate. part i. *Phil. Mag.*, 40, 1040-1063.
- Devonshire, A. F. (1951). Theory of barium titanate. part ii. *Phil. Mag.*, 42, 1065-1079.
- Devonshire, A. F. (1954). Theory of ferroelectrics. *Advances in physics*, 3(10), 85–130.
- Dudarev, S. L., Botton, G. A., Savrasov, S. Y., Humphreys, C. J., & Sutton, A. P. (1998, Jan). Electron-energy-loss spectra and the structural stability of nickel oxide: An LSDA+U study. *Phys. Rev. B*, 57, 1505–1509. Retrieved from <https://link.aps.org/doi/10.1103/PhysRevB.57.1505> doi: 10.1103/PhysRevB.57.1505
- Farokhipoor, S., Magén, C., Venkatesan, S., Íñiguez, J., Daumont, C. J. M., Rubi, D., ... Noheda, B. (2014, Nov 01). Artificial chemical and magnetic structure at the domain walls of an epitaxial oxide. *Nature*, 515(7527), 379-383. Retrieved from <https://doi.org/10.1038/nature13918> doi: 10.1038/nature13918
- Farokhipoor, S., & Noheda, B. (2011, Sep). Conduction through 71° domain walls in BiFeO₃ thin films. *Phys. Rev. Lett.*, 107, 127601. Retrieved from <https://link.aps.org/doi/10.1103/PhysRevLett.107.127601> doi: 10.1103/PhysRevLett.107.127601
- Fernandez, S. (2017). *Combining PbTiO₃ and SrTiO₃ toward 180° ferroelectric domains* (Ph. D. thesis). Université de Genève.
- Filippi, C., Singh, D. J., & Umrigar, C. J. (1994, Nov). All-electron local-density and generalized-gradient calculations of the structural properties of semiconductors. *Phys. Rev. B*, 50, 14947–14951. Retrieved from <https://link.aps.org/doi/10.1103/PhysRevB.50.14947> doi: 10.1103/PhysRevB.50.14947
- Fong, D. D., Kolpak, A. M., Eastman, J. A., Streiffer, S. K., Fuoss, P. H., Stephenson, G. B., ... Rappe, A. M. (2006, Mar). Stabilization of monodomain polarization in ultrathin PbTiO₃ Films. *Phys. Rev. Lett.*, 96, 127601. Retrieved from

<https://link.aps.org/doi/10.1103/PhysRevLett.96.127601> doi:
10.1103/PhysRevLett.96.127601

Fritsch, D., & Schorr, S. (2020, nov). Climbing jacob's ladder: A density functional theory case study for $\text{Ag}_2\text{ZnSnSe}_4$ and $\text{Cu}_2\text{ZnSnSe}_4$. *Journal of Physics: Energy*, 3(1), 015002. Retrieved from <https://dx.doi.org/10.1088/2515-7655/abc07b> doi: 10.1088/2515-7655/abc07b

Fu, C. L., & Ho, K. M. (1983, Nov). First-principles calculation of the equilibrium ground-state properties of transition metals: Applications to Nb and Mo. *Phys. Rev. B*, 28, 5480–5486. Retrieved from <https://link.aps.org/doi/10.1103/PhysRevB.28.5480> doi: 10.1103/PhysRevB.28.5480

Gao, P., Nelson, C. T., Jokisaari, J. R., Baek, S.-H., Bark, C. W., Zhang, Y., ... Pan, X. (2011, Dec 20). Revealing the role of defects in ferroelectric switching with atomic resolution. *Nature Communications*, 2(1), 591. Retrieved from <https://doi.org/10.1038/ncomms1600> doi: 10.1038/ncomms1600

García-Fernández, P., Wojdeł, J. C., Íñiguez, J., & Junquera, J. (2016, May). Second-principles method for materials simulations including electron and lattice degrees of freedom. *Phys. Rev. B*, 93, 195137. Retrieved from <https://link.aps.org/doi/10.1103/PhysRevB.93.195137> doi: 10.1103/PhysRevB.93.195137

García, A., Papior, N., Akhtar, A., Artacho, E., Blum, V., Bosoni, E., ... Junquera, J. (2020). SIESTA: Recent developments and applications. *The Journal of Chemical Physics*, 152(20), 204108. Retrieved from <https://doi.org/10.1063/5.0005077> doi: 10.1063/5.0005077

Ghosez, P., & Junquera, J. (2022). Modeling of ferroelectric oxide perovskites: From first to second principles. *Annual Review of Condensed Matter Physics*, 13(1), 325-364. Retrieved from <https://doi.org/10.1146/annurev-conmatphys-040220-045528> doi: 10.1146/annurev-conmatphys-040220-045528

- Ghosez, P., Michenaud, J.-P., & Gonze, X. (1998, Sep). Dynamical atomic charges: The case of ABO_3 compounds. *Phys. Rev. B*, 58, 6224–6240. Retrieved from <https://link.aps.org/doi/10.1103/PhysRevB.58.6224> doi: 10.1103/PhysRevB.58.6224
- Giannozzi, P., Andreussi, O., Brumme, T., Bunau, O., Nardelli, M. B., Calandra, M., ... Baroni, S. (2017, oct). Advanced capabilities for materials modelling with Quantum ESPRESSO. *J. Phys.: Condens. Matter*, 29(46), 465901. Retrieved from <https://dx.doi.org/10.1088/1361-648X/aa8f79> doi: 10.1088/1361-648X/aa8f79
- Giannozzi, P., Baroni, S., Bonini, N., Calandra, M., Car, R., Cavazzoni, C., ... Wentzcovitch, R. M. (2009, sep). QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials. *Journal of Physics: Condensed Matter*, 21(39), 395502. Retrieved from <https://dx.doi.org/10.1088/0953-8984/21/39/395502> doi: 10.1088/0953-8984/21/39/395502
- Goldschmidt, V. M. (1926). Die gesetze der krystallochemie. *Naturwissenschaften*, 14, 477–485.
- Gureev, M. Y., Tagantsev, A. K., & Setter, N. (2011, May). Head-to-head and tail-to-tail 180° domain walls in an isolated ferroelectric. *Phys. Rev. B*, 83, 184104. Retrieved from <https://link.aps.org/doi/10.1103/PhysRevB.83.184104> doi: 10.1103/PhysRevB.83.184104
- Guyonnet, J., Gaponenko, I., Gariglio, S., & Paruch, P. (2011). Conduction at domain walls in insulating $\text{Pb}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ thin films. *Adv. Mater.*, 23(45), 5377–5382. Retrieved from <https://onlinelibrary.wiley.com/doi/abs/10.1002/adma.201102254> doi: 10.1002/adma.201102254
- Gómez-Ortiz, F., Carral-Sainz, N., Sifuna, J., Monteseguro, V., Cuadrado, R., García-Fernández, P., & Junquera, J. (2023). Compatibility of DFT+U with non-collinear magnetism and spin-orbit coupling within a framework of numerical atomic orbitals. *Computer Physics Communications*, 286, 108684.

- Retrieved from <https://www.sciencedirect.com/science/article/pii/S0010465523000292> doi: <https://doi.org/10.1016/j.cpc.2023.108684>
- Han, M. J., Ozaki, T., & Yu, J. (2006, Jan). $O(n)$ LDA + U electronic structure calculation method based on the nonorthogonal pseudoatomic orbital basis. *Phys. Rev. B*, 73, 045110. Retrieved from <https://link.aps.org/doi/10.1103/PhysRevB.73.045110> doi: 10.1103/PhysRevB.73.045110
- Heyd, J., & Scuseria, G. E. (2004, Jul). Efficient hybrid density functional calculations in solids: Assessment of the Heyd–Scuseria–Ernzerhof screened Coulomb hybrid functional. *The Journal of Chemical Physics*, 121(3), 1187-1192. Retrieved from <https://doi.org/10.1063/1.1760074> doi: 10.1063/1.1760074
- Highland, M. J., Fister, T. T., Richard, M.-I., Fong, D. D., Fuoss, P. H., Thompson, C., ... Stephenson, G. B. (2010, Oct). Polarization switching without domain formation at the intrinsic coercive field in ultrathin ferroelectric PbTiO_3 . *Phys. Rev. Lett.*, 105, 167601. Retrieved from <https://link.aps.org/doi/10.1103/PhysRevLett.105.167601> doi: 10.1103/PhysRevLett.105.167601
- Himmetoglu, B., Floris, A., de Gironcoli, S., & Cococcioni, M. (2014). Hubbard-corrected DFT energy functionals: The LDA + U description of correlated systems. *Int. J. Quantum Chem.*, 114(1), 14-49. Retrieved from <https://onlinelibrary.wiley.com/doi/abs/10.1002/qua.24521> doi: <https://doi.org/10.1002/qua.24521>
- Hohenberg, P., & Kohn, W. (1964, Nov). Inhomogeneous electron gas. *Phys. Rev.*, 136, B864–B871. Retrieved from <https://link.aps.org/doi/10.1103/PhysRev.136.B864> doi: 10.1103/PhysRev.136.B864
- Huzinaga, S. (1985). *Gaussian basis sets for molecular calculations*. Amsterdam: Elsevier Sci. Publ. Co.,.
- Jackson, J. D. (1975). *Classical electrodynamics*. New York: John Wiley & Sons.

- Junquera, J., Cohen, M. H., & Rabe, K. M. (2007, may). Nanoscale smoothing and the analysis of interfacial charge and dipolar densities. *J. Phys.: Condens. Matter*, 19(21), 213203. doi: 10.1088/0953-8984/19/21/213203
- Junquera, J., & Ghosez, P. (2003a). Critical thickness for ferroelectricity in perovskite ultrathin films. *Nature (London)*, 422, 506–509.
- Junquera, J., & Ghosez, P. (2003b, Apr 01). Critical thickness for ferroelectricity in perovskite ultrathin films. *Nature*, 422(6931), 506-509. Retrieved from <https://doi.org/10.1038/nature01501> doi: 10.1038/nature01501
- Junquera, J., Paz, O., Sánchez-Portal, D., & Artacho, E. (2001, Nov). Numerical atomic orbitals for linear-scaling calculations. *Phys. Rev. B*, 64, 235111. Retrieved from <https://link.aps.org/doi/10.1103/PhysRevB.64.235111> doi: 10.1103/PhysRevB.64.235111
- Junquera, J., Zimmer, M., Ordejón, P., & Ghosez, P. (2003, Apr). First-principles calculation of the band offset at BaO/BaTiO₃ and SrO/SrTiO₃ interfaces. *Phys. Rev. B*, 67, 155327. Retrieved from <https://link.aps.org/doi/10.1103/PhysRevB.67.155327> doi: 10.1103/PhysRevB.67.155327
- Kahk, J. M., Poll, C. G., Oropeza, F. E., Ablett, J. M., Céolin, D., Rueff, J.-P., ... Payne, D. J. (2014, Mar). Understanding the electronic structure of IrO₂ using hard-X-ray photoelectron spectroscopy and density-functional theory. *Phys. Rev. Lett.*, 112, 117601. Retrieved from <https://link.aps.org/doi/10.1103/PhysRevLett.112.117601> doi: 10.1103/PhysRevLett.112.117601
- Khein, A., Singh, D. J., & Umrigar, C. J. (1995, Feb). All-electron study of gradient corrections to the local-density functional in metallic systems. *Phys. Rev. B*, 51, 4105–4109. Retrieved from <https://link.aps.org/doi/10.1103/PhysRevB.51.4105> doi: 10.1103/PhysRevB.51.4105

- Kim, Y., Alexe, M., & Salje, E. K. H. (2010). Nanoscale properties of thin twin walls and surface layers in piezoelectric WO_{3-x} . *Appl. Phys. Lett.*, 96(3), 032904. doi: 10.1063/1.3292587
- King-Smith, R. D., & Vanderbilt, D. (1993, Jan). Theory of polarization of crystalline solids. *Phys. Rev. B*, 47, 1651–1654. Retrieved from <https://link.aps.org/doi/10.1103/PhysRevB.47.1651> doi: 10.1103/PhysRevB.47.1651
- King-Smith, R. D., & Vanderbilt, D. (1994a, Mar). First-principles investigation of ferroelectricity in perovskite compounds. *Phys. Rev. B*, 49, 5828–5844. Retrieved from <https://link.aps.org/doi/10.1103/PhysRevB.49.5828> doi: 10.1103/PhysRevB.49.5828
- King-Smith, R. D., & Vanderbilt, D. (1994b, Mar). First-principles investigation of ferroelectricity in perovskite compounds. *Phys. Rev. B*, 49, 5828–5844. Retrieved from <https://link.aps.org/doi/10.1103/PhysRevB.49.5828> doi: 10.1103/PhysRevB.49.5828
- Kittel, C. (1946, Dec). Theory of the structure of ferromagnetic domains in films and small particles. *Phys. Rev.*, 70, 965–971. Retrieved from <https://link.aps.org/doi/10.1103/PhysRev.70.965> doi: 10.1103/PhysRev.70.965
- Kittel, C. (1949, Oct). Physical theory of ferromagnetic domains. *Rev. Mod. Phys.*, 21, 541–583. Retrieved from <https://link.aps.org/doi/10.1103/RevModPhys.21.541> doi: 10.1103/RevModPhys.21.541
- Kittel, C. (1972). Thickness of domain walls in ferroelectric and ferroelastic crystals. *Solid State Communications*, 10(1), 119–121. Retrieved from <https://www.sciencedirect.com/science/article/pii/0038109872903626> doi: [https://doi.org/10.1016/0038-1098\(72\)90362-6](https://doi.org/10.1016/0038-1098(72)90362-6)
- Kleinman, L., & Bylander, D. M. (1982, May). Efficacious form for model pseudopotentials. *Phys. Rev. Lett.*, 48, 1425–1428. Retrieved from <https://link.aps.org/doi/10.1103/PhysRevLett.48.1425> doi: 10.1103/PhysRevLett.48.1425

- Kohn, W., & Sham, L. J. (1965, Nov). Self-consistent equations including exchange and correlation effects. *Phys. Rev.*, *140*, A1133–A1138. Retrieved from <https://link.aps.org/doi/10.1103/PhysRev.140.A1133> doi: 10.1103/PhysRev.140.A1133
- Kolpak, A. M., Grinberg, I., & Rappe, A. M. (2007, Apr). Polarization effects on the surface chemistry of PbTiO₃-supported Pt films. *Phys. Rev. Lett.*, *98*, 166101. Retrieved from <https://link.aps.org/doi/10.1103/PhysRevLett.98.166101> doi: 10.1103/PhysRevLett.98.166101
- Kresse, G., & Furthmüller, J. (1996, Oct). Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B*, *54*, 11169–11186. Retrieved from <https://link.aps.org/doi/10.1103/PhysRevB.54.11169> doi: 10.1103/PhysRevB.54.11169
- Kresse, G., & Furthmüller, J. (1996). Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Comput. Mater. Sci.*, *6*(1), 15-50. Retrieved from <https://www.sciencedirect.com/science/article/pii/0927025696000080> doi: [https://doi.org/10.1016/0927-0256\(96\)00008-0](https://doi.org/10.1016/0927-0256(96)00008-0)
- Landau, L., & Lifshitz, E. (1935). Theory of the dispersion of magnetic permeability in ferromagnetic bodies. *Phys. Z. Sowjetunion*, *8*, 153.
- Landau, L. D. (1937). On the theory of phase transitions. I. *Phys. Z. Sowjet.*, *11*, 26. Retrieved from <http://cds.cern.ch/record/480039>
- Landau, L. D., & Lifshitz, E. (1935). On the theory of the dispersion of magnetic permeability in ferromagnetic bodies. *Phys. Z. Sowjet.*, *8*, 153. Retrieved from <http://cds.cern.ch/record/437299>
- Lichtensteiger, C., Fernandez-Pena, S., Weymann, C., Zubko, P., & Triscone, J.-M. (2014). Tuning of the depolarization field and nanodomain structure in ferroelectric thin films.

- Nano Letters*, 14(8), 4205-4211. Retrieved from <https://doi.org/10.1021/nl404734z> (PMID: 24983128) doi: 10.1021/nl404734z
- Liechtenstein, A. I., Anisimov, V. I., & Zaanen, J. (1995, Aug). Density-functional theory and strong interactions: Orbital ordering in Mott-Hubbard insulators. *Phys. Rev. B*, 52, R5467–R5470. Retrieved from <https://link.aps.org/doi/10.1103/PhysRevB.52.R5467> doi: 10.1103/PhysRevB.52.R5467
- Lines, M. E. (1969, Jan). Statistical theory for displacement ferroelectrics. *Phys. Rev.*, 177, 797–812. Retrieved from <https://link.aps.org/doi/10.1103/PhysRev.177.797> doi: 10.1103/PhysRev.177.797
- Louie, S. G., Froyen, S., & Cohen, M. L. (1982, Aug). Nonlinear ionic pseudopotentials in spin-density-functional calculations. *Phys. Rev. B*, 26, 1738–1742. Retrieved from <https://link.aps.org/doi/10.1103/PhysRevB.26.1738> doi: 10.1103/PhysRevB.26.1738
- Lu, H., Liu, X., Burton, J. D., Bark, C.-W., Wang, Y., Zhang, Y., ... Gruverman, A. (2012). Enhancement of ferroelectric polarization stability by interface engineering. *Advanced Materials*, 24(9), 1209-1216. Retrieved from <https://onlinelibrary.wiley.com/doi/abs/10.1002/adma.201104398> doi: <https://doi.org/10.1002/adma.201104398>
- Luk'yanchuk, I. A., Lahoche, L., & Sené, A. (2009, Apr). Universal properties of ferroelectric domains. *Phys. Rev. Lett.*, 102, 147601. Retrieved from <https://link.aps.org/doi/10.1103/PhysRevLett.102.147601> doi: 10.1103/PhysRevLett.102.147601
- McDaniel, C. L., & Schneider, S. J. (1967, March). Phase relations in the systems (TiO₂ – IrO₂) and (SnO₂ – IrO₂) in air. *J. Res. Natl. Bur. Stand. A Phys. Chem.*, 71A(2), 119–123. doi: 10.6028/jres.071A.016

- Mehta, R. R., Silverman, B. D., & Jacobs, J. T. (1973). Depolarization fields in thin ferroelectric films. *Journal of Applied Physics*, 44(8), 3379-3385. Retrieved from <https://doi.org/10.1063/1.1662770> doi: 10.1063/1.1662770
- Messiah, A. (1960). *Mécanique quantique*. Paris: Dunod.
- Meyer, B., Padilla, J., & Vanderbilt, D. (1999). Theory of PbTiO_3 , BaTiO_3 , and SrTiO_3 surfaces. *Faraday Discuss.*, 114, 395-405. Retrieved from <http://dx.doi.org/10.1039/A903029H> doi: 10.1039/A903029H
- Meyer, B., & Vanderbilt, D. (2002, Mar). Ab initio study of ferroelectric domain walls in PbTiO_3 . *Phys. Rev. B*, 65, 104111. Retrieved from <https://link.aps.org/doi/10.1103/PhysRevB.65.104111> doi: 10.1103/PhysRevB.65.104111
- Migoni, R., Bilz, H., & Bäuerle, D. (1976, Oct). Origin of raman scattering and ferroelectricity in oxidic perovskites. *Phys. Rev. Lett.*, 37, 1155–1158. Retrieved from <https://link.aps.org/doi/10.1103/PhysRevLett.37.1155> doi: 10.1103/PhysRevLett.37.1155
- Mitsui, T., & Furuichi, J. (1953, Apr). Domain structure of rochelle salt and KH_2PO_4 . *Phys. Rev.*, 90, 193–202. Retrieved from <https://link.aps.org/doi/10.1103/PhysRev.90.193> doi: 10.1103/PhysRev.90.193
- Monkhorst, H. J., & Pack, J. D. (1976, Jun). Special points for brillouin-zone integrations. *Phys. Rev. B*, 13, 5188–5192. Retrieved from <https://link.aps.org/doi/10.1103/PhysRevB.13.5188> doi: 10.1103/PhysRevB.13.5188
- Mostofi, A. A., Yates, J. R., Lee, Y.-S., Souza, I., Vanderbilt, D., & Marzari, N. (2008). Wannier90: A tool for obtaining maximally-localised wannier functions. *Computer Physics Communications*, 178(9), 685 - 699. Retrieved from <http://www.sciencedirect.com/science/article/pii/S0010465507004936> doi: <https://doi.org/10.1016/j.cpc.2007.11.016>

- Mueller, H. (1940a, Sep). Properties of rochelle salt. iii. *Phys. Rev.*, 58, 565–573.
Retrieved from <https://link.aps.org/doi/10.1103/PhysRev.58.565>
doi: 10.1103/PhysRev.58.565
- Mueller, H. (1940b, Nov). Properties of rochelle salt. iv. *Phys. Rev.*, 58, 805–811.
Retrieved from <https://link.aps.org/doi/10.1103/PhysRev.58.805>
doi: 10.1103/PhysRev.58.805
- Nagarajan, V., Junquera, J., He, J. Q., Jia, C. L., Waser, R., Lee, K., ... Rabe, K. M. (2006). Scaling of structure and electrical properties in ultrathin epitaxial ferroelectric heterostructures. *Journal of Applied Physics*, 100(5), 051609. Retrieved from <https://doi.org/10.1063/1.2337363> doi: 10.1063/1.2337363
- Pacchioni, G., & Valeri, S. (2011). *Oxide ultrathin films: Science and technology*. Wiley.
Retrieved from <https://books.google.com/books?id=Z35fXwAACAAJ>
- Payne, M. C., Teter, M. P., Allan, D. C., Arias, T. A., & Joannopoulos, J. D. (1992, Oct). Iterative minimization techniques for ab initio total-energy calculations: molecular dynamics and conjugate gradients. *Rev. Mod. Phys.*, 64, 1045–1097. Retrieved from <https://link.aps.org/doi/10.1103/RevModPhys.64.1045> doi: 10.1103/RevModPhys.64.1045
- Perdew, J. P., Ruzsinszky, A., Csonka, G. I., Vydrov, O. A., Scuseria, G. E., Constantin, L. A., ... Burke, K. (2008, Apr). Restoring the density-gradient expansion for exchange in solids and surfaces. *Phys. Rev. Lett.*, 100, 136406. Retrieved from <https://link.aps.org/doi/10.1103/PhysRevLett.100.136406> doi: 10.1103/PhysRevLett.100.136406
- Perdew, J. P., & Zunger, A. (1981, May). Self-interaction correction to density-functional approximations for many-electron systems. *Phys. Rev. B*, 23, 5048–5079. Retrieved from <https://link.aps.org/doi/10.1103/PhysRevB.23.5048> doi: 10.1103/PhysRevB.23.5048

- Ping, Y., Galli, G., & Goddard, W. A. (2015, May 28). Electronic structure of IrO₂: The role of the metal d orbitals. *J. Phys. Chem. C*, 119(21), 11570-11577. Retrieved from <https://doi.org/10.1021/acs.jpcc.5b00861> doi: 10.1021/acs.jpcc.5b00861
- Popović, Z. S., Satpathy, S., & Martin, R. M. (2008, Dec). Origin of the two-dimensional electron gas carrier density at the LaAlO₃ on SrTiO₃ Interface. *Phys. Rev. Lett.*, 101, 256801. Retrieved from <https://link.aps.org/doi/10.1103/PhysRevLett.101.256801> doi: 10.1103/PhysRevLett.101.256801
- Prosandeev, S., & Bellaiche, L. (2007, May). Asymmetric screening of the depolarizing field in a ferroelectric thin film. *Phys. Rev. B*, 75, 172109. Retrieved from <https://link.aps.org/doi/10.1103/PhysRevB.75.172109> doi: 10.1103/PhysRevB.75.172109
- Pöykkö, S., & Chadi, D. J. (1999). Ab initio study of 180° domain wall energy and structure in PbTiO₃. *Appl. Phys. Lett.*, 75(18), 2830-2832. doi: 10.1063/1.125164
- Qu, X., Xu, P., Jiang, H., He, L., & Ren, X. (2022). DFT + U within the framework of linear combination of numerical atomic orbitals. *J. Chem. Phys.*, 156, 234104. Retrieved from <https://doi.org/10.1063/5.0090122> doi: 10.1063/5.0090122
- Rahmanizadeh, K., Wortmann, D., Bihlmayer, G., & Blügel, S. (2014, Sep). Charge and orbital order at head-to-head domain walls in PbTiO₃. *Phys. Rev. B*, 90, 115104. Retrieved from <https://link.aps.org/doi/10.1103/PhysRevB.90.115104> doi: 10.1103/PhysRevB.90.115104
- Resta, R. (1998, mar). Quantum-mechanical position operator in extended systems. *Physical Review Letters*, 80(9), 1800–1803. Retrieved from <https://doi.org/10.1103/PhysRevLett.80.1800> doi: 10.1103/physrevlett.80.1800
- Resta, R. (1999). *Macroscopic polarization from electronic wavefunctions*. arXiv. Retrieved from <https://arxiv.org/abs/cond-mat/9903216> doi: 10.48550/ARXIV.COND-MAT/9903216

- Resta, R., & Vanderbilt, D. (2007). Physics of ferroelectrics: a modern perspective. In K. M. Rabe, C. H. Ahn, & J.-M. Triscone (Eds.), (Vol. 105, p. 31-68). Berlin: Topics of Applied Physics, Springer.
- Sai, N., Kolpak, A. M., & Rappe, A. M. (2005, Jul). Ferroelectricity in ultrathin perovskite films. *Phys. Rev. B*, 72, 020101. Retrieved from <https://link.aps.org/doi/10.1103/PhysRevB.72.020101> doi: 10.1103/PhysRevB.72.020101
- Sánchez-Portal, D., Artacho, E., & Soler, J. M. (1995). Projection of plane-wave calculations into atomic orbitals. *Solid State Commun.*, 95, 685-690. Retrieved from <https://www.sciencedirect.com/science/article/pii/003810989500341X> doi: [https://doi.org/10.1016/0038-1098\(95\)00341-X](https://doi.org/10.1016/0038-1098(95)00341-X)
- Sankey, O. F., & Niklewski, D. J. (1989, Aug). Ab initio multicenter tight-binding model for molecular-dynamics simulations and other applications in covalent systems. *Phys. Rev. B*, 40, 3979–3995. Retrieved from <https://link.aps.org/doi/10.1103/PhysRevB.40.3979> doi: 10.1103/PhysRevB.40.3979
- Schilling, A., Adams, T. B., Bowman, R. M., Gregg, J. M., Catalan, G., & Scott, J. F. (2006, Jul). Scaling of domain periodicity with thickness measured in BaTiO₃ single crystal lamellae and comparison with other ferroics. *Phys. Rev. B*, 74, 024115. Retrieved from <https://link.aps.org/doi/10.1103/PhysRevB.74.024115> doi: 10.1103/PhysRevB.74.024115
- Schröder, M., Haußmann, A., Thiessen, A., Soergel, E., Woike, T., & Eng, L. M. (2012). Conducting domain walls in lithium niobate single crystals. *Adv. Funct. Mater.*, 22(18), 3936-3944. doi: 10.1002/adfm.201201174
- Seidel, J., Martin, L. W., He, Q., Zhan, Q., Chu, Y.-H., Rother, A., ... Ramesh, R. (2009, Mar 01). Conduction at domain walls in oxide multiferroics. *Nature Materials*, 8(3), 229-234. Retrieved from <https://doi.org/10.1038/nmat2373> doi: 10.1038/nmat2373

- Sifuna, J., García-Fernández, P., Manyali, G. S., Amolo, G., & Junquera, J. (2020, May). First-principles study of two-dimensional electron and hole gases at the head-to-head and tail-to-tail 180° domain walls in PbTiO_3 ferroelectric thin films. *Phys. Rev. B*, *101*, 174114. Retrieved from <https://link.aps.org/doi/10.1103/PhysRevB.101.174114> doi: 10.1103/PhysRevB.101.174114
- Sluka, T., Tagantsev, A. K., Bednyakov, P., & Setter, N. (2013). Free-electron gas at charged domain walls in insulating BaTiO_3 . *Nat. Commun.*, *4*(1), 1808. doi: 10.1038/ncomms2839
- Sokolovskiy, V., Baigutlin, D., Miroshkina, O., & Buchelnikov, V. (2023). Meta-gga scan functional in the prediction of ground state properties of magnetic materials: Review of the current state. *Metals*, *13*(4). Retrieved from <https://www.mdpi.com/2075-4701/13/4/728> doi: 10.3390/met13040728
- Soler, J. M., Artacho, E., Gale, J. D., García, A., Junquera, J., Ordejón, P., & Sánchez-Portal, D. (2002, mar). The SIESTA method for ab initio order-n materials simulation. *J. Phys.: Condens. Matter*, *14*(11), 2745–2779. doi: 10.1088/0953-8984/14/11/302
- Souza, I., Íñiguez, J., & Vanderbilt, D. (2002, Aug). First-principles approach to insulators in finite electric fields. *Phys. Rev. Lett.*, *89*, 117602. Retrieved from <https://link.aps.org/doi/10.1103/PhysRevLett.89.117602> doi: 10.1103/PhysRevLett.89.117602
- Souza, I., Íñiguez, J., & Vanderbilt, D. (2004, Feb). Dynamics of berry-phase polarization in time-dependent electric fields. *Phys. Rev. B*, *69*, 085106. Retrieved from <https://link.aps.org/doi/10.1103/PhysRevB.69.085106> doi: 10.1103/PhysRevB.69.085106
- Spaldin, N. A. (2020). Multiferroics beyond electric-field control of magnetism. *Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences*, *476*(2233), 20190542. Retrieved from <https://royalsocietypublishing.org/doi/abs/10.1098/rspa.2019.0542> doi: 10.1098/rspa.2019.0542

- Stengel, M. (2011, Mar). First-principles modeling of electrostatically doped perovskite systems. *Phys. Rev. Lett.*, *106*, 136803. Retrieved from <https://link.aps.org/doi/10.1103/PhysRevLett.106.136803> doi: 10.1103/PhysRevLett.106.136803
- Stengel, M., Aguado-Puente, P., Spaldin, N. A., & Junquera, J. (2011, Jun). Band alignment at metal/ferroelectric interfaces: Insights and artifacts from first principles. *Phys. Rev. B*, *83*, 235112. Retrieved from <https://link.aps.org/doi/10.1103/PhysRevB.83.235112> doi: 10.1103/PhysRevB.83.235112
- Stengel, M., & Spaldin, N. A. (2006, Oct 01). Origin of the dielectric dead layer in nanoscale capacitors. *Nature*, *443*(7112), 679-682. Retrieved from <https://doi.org/10.1038/nature05148> doi: 10.1038/nature05148
- Stengel, M., & Spaldin, N. A. (2007, May). Ab initio theory of metal-insulator interfaces in a finite electric field. *Phys. Rev. B*, *75*, 205121. Retrieved from <https://link.aps.org/doi/10.1103/PhysRevB.75.205121> doi: 10.1103/PhysRevB.75.205121
- Stengel, M., Vanderbilt, D., & Spaldin, N. A. (2009a, May 01). Enhancement of ferroelectricity at metal-oxide interfaces. *Nature Materials*, *8*(5), 392-397. Retrieved from <https://doi.org/10.1038/nmat2429> doi: 10.1038/nmat2429
- Stengel, M., Vanderbilt, D., & Spaldin, N. A. (2009b, Dec). First-principles modeling of ferroelectric capacitors via constrained displacement field calculations. *Phys. Rev. B*, *80*, 224110. Retrieved from <https://link.aps.org/doi/10.1103/PhysRevB.80.224110> doi: 10.1103/PhysRevB.80.224110
- Stephanovich, V. A., Luk'yanchuk, I. A., & Karkut, M. G. (2005, Feb). Domain-enhanced interlayer coupling in ferroelectric/paraelectric superlattices. *Phys. Rev. Lett.*, *94*, 047601. Retrieved from <https://link.aps.org/doi/10.1103/PhysRevLett.94.047601> doi: 10.1103/PhysRevLett.94.047601

- Streiffer, S. K., Eastman, J. A., Fong, D. D., Thompson, C., Munkholm, A., Ramana Murty, M. V., ... Stephenson, G. B. (2002, Jul). Observation of nanoscale 180° stripe domains in ferroelectric PbTiO_3 thin films. *Phys. Rev. Lett.*, 89, 067601. Retrieved from <https://link.aps.org/doi/10.1103/PhysRevLett.89.067601> doi: 10.1103/PhysRevLett.89.067601
- Takahashi, R., Dahl, , Eberg, E., Grepstad, J. K., & Tybell, T. (2008). Ferroelectric stripe domains in PbTiO_3 thin films: Depolarization field and domain randomness. *Journal of Applied Physics*, 104(6), 064109. Retrieved from <https://doi.org/10.1063/1.2978225> doi: 10.1063/1.2978225
- Tang, Y. L., Zhu, Y. L., Ma, X. L., Borisevich, A. Y., Morozovska, A. N., Eliseev, E. A., ... Pennycook, S. J. (2015). Observation of a periodic array of flux-closure quadrants in strained ferroelectric PbTiO_3 films. *Science*, 348(6234), 547-551. Retrieved from <https://www.science.org/doi/abs/10.1126/science.1259869> doi: 10.1126/science.1259869
- te Velde, G., Bickelhaupt, F. M., Baerends, E. J., Fonseca Guerra, C., van Gisbergen, S. J. A., Snijders, J. G., & Ziegler, T. (2001). Chemistry with adf. *Journal of Computational Chemistry*, 22(9), 931-967. Retrieved from <https://onlinelibrary.wiley.com/doi/abs/10.1002/jcc.1056> doi: <https://doi.org/10.1002/jcc.1056>
- Troullier, N., & Martins, J. L. (1991, Jan). Efficient pseudopotentials for plane-wave calculations. *Phys. Rev. B*, 43, 1993-2006. Retrieved from <https://link.aps.org/doi/10.1103/PhysRevB.43.1993> doi: 10.1103/PhysRevB.43.1993
- Valasek, J. (1921, Apr). Piezo-electric and allied phenomena in rochelle salt. *Phys. Rev.*, 17, 475-481. Retrieved from <https://link.aps.org/doi/10.1103/PhysRev.17.475> doi: 10.1103/PhysRev.17.475

- Vanderbilt, D. (1990, Apr). Soft self-consistent pseudopotentials in a generalized eigenvalue formalism. *Phys. Rev. B*, *41*, 7892–7895. Retrieved from <https://link.aps.org/doi/10.1103/PhysRevB.41.7892> doi: 10.1103/PhysRevB.41.7892
- Vaugier, L. (2011). *Electronic structure of correlated materials from first principles : Hubbard interaction and Hund's exchange* (Ph. D. thesis). École Polytechnique.
- Wentzcovitch, R. M., Valencia-Cardona, J. J., Zhuang, J., Shukla, G., & Sarkar, K. (2023). The post-perovskite transition in Fe- and Al-bearing bridgmanite: Effects on seismic observables. *Journal of Geophysical Research: Solid Earth*, *128*(3), e2022JB025475. Retrieved from <https://agupubs.onlinelibrary.wiley.com/doi/abs/10.1029/2022JB025475> (e2022JB025475 2022JB025475) doi: <https://doi.org/10.1029/2022JB025475>
- Wu, X., & Vanderbilt, D. (2006, Jan). Theory of hypothetical ferroelectric superlattices incorporating head-to-head and tail-to-tail 180° domain walls. *Phys. Rev. B*, *73*, 020103. Retrieved from <https://link.aps.org/doi/10.1103/PhysRevB.73.020103> doi: 10.1103/PhysRevB.73.020103
- Wu, Z., Cohen, R. E., & Singh, D. J. (2004, Sep). Comparing the weighted density approximation with the LDA and GGA for ground-state properties of ferroelectric perovskites. *Phys. Rev. B*, *70*, 104112. Retrieved from <https://link.aps.org/doi/10.1103/PhysRevB.70.104112> doi: 10.1103/PhysRevB.70.104112
- Wul, B., & Goldman, L. (1945). Cr acad sci. *URSS*, *46*, 139.
- Yadav, A. K., Nelson, C. T., Hsu, S. L., Hong, Z., Clarkson, J. D., Schlepütz, C. M., ... Ramesh, R. (2016, Feb 01). Observation of polar vortices in oxide superlattices. *Nature*, *530*(7589), 198-201. Retrieved from <https://doi.org/10.1038/nature16463> doi: 10.1038/nature16463
- Yin, B., Aguado-Puente, P., Qu, S., & Artacho, E. (2015, Sep). Two-dimensional electron gas at the PbTiO₃/SrTiO₃ interface: An ab initio study. *Phys. Rev. B*, *92*,

115406. Retrieved from <https://link.aps.org/doi/10.1103/PhysRevB.92.115406> doi: 10.1103/PhysRevB.92.115406

Zhang, J., Wang, Y.-J., Liu, J., Xu, J., Wang, D., Wang, L., ... Bellaiche, L. (2020, Feb). Origin of sawtooth domain walls in ferroelectrics. *Phys. Rev. B*, *101*, 060103. Retrieved from <https://link.aps.org/doi/10.1103/PhysRevB.101.060103> doi: 10.1103/PhysRevB.101.060103

Zubko, P., Jecklin, N., Torres-Pardo, A., Aguado-Puente, P., Gloter, A., Lichtensteiger, C., ... Triscone, J.-M. (2012). Electrostatic coupling and local structural distortions at interfaces in ferroelectric/paraelectric superlattices. *Nano Letters*, *12*(6), 2846-2851. Retrieved from <https://doi.org/10.1021/nl3003717> (PMID: 22591200) doi: 10.1021/nl3003717

Zuhair Abbas Shah, S., Niaz, S., Nasir, T., Sifuna, J., & Ramay, S. M. (2023). A DFT computational design and exploration of direct band gap silver-thallium double perovskites. *Materials Science and Engineering: B*, *298*, 116846. Retrieved from <https://www.sciencedirect.com/science/article/pii/S0921510723005883> doi: <https://doi.org/10.1016/j.mseb.2023.116846>

Appendices

A IrO_2 calculation in SIESTA using the LDAU+U+SOC implementation

The generalized gradient approximation (GGA) to the density functional theory (DFT) (Hohenberg & Kohn, 1964; Kohn & Sham, 1965), addressed exchange and correlation. The functional employed was PBEsol (Perdew et al., 2008). Spin-orbit interaction was included using the off-site implementation (Cuadrado & Cerdá, 2012; Cuadrado et al., 2016) with $U = 2$ eV, while J was set at zero. In the Kleinman-Bylander (Kleinman & Bylander, 1982), completely non-local separable representation, core electrons were substituted with *ab initio* norm conserving pseudopotentials created using the Troullier-Martins method (Troullier & Martins, 1991). The reference configuration and cutoff radii for each angular momentum shell for the pseudopotentials utilized in this work are given in Table. A1.

Table A1: For the pseudopotentials employed in our investigation, the following parameters were used as a reference. All the units are in bohrs.

Reference		Ir	O
		$6s^2, 6p^0, 5d^7, 5f^0$	$2s^2, 2p^4, 3d^0, 4f^0$
Core radius	s	2.20	1.50
	p	2.80	1.60
	d	1.30	1.40
	f	2.00	1.15
Relativistic?		yes	yes
NLCC?		yes	yes
Matching radius NLCC		1,40	1.20

The basis's quality was set to be double- ζ -polarized. With an analogous plane-wave cutoff of 600 Ry in the representation of charge density, a consistent real-space grid was used to calculate the electronic density, Hartree, and exchange-correlation potentials as well as the associated matrix components linking the orbitals. We employed $8 \times 8 \times 12$

k-points Monkhorst-Pack (Monkhorst & Pack, 1976) sampling scheme for the Brillouin zone integrations. Experimental coordinates were derived from literature (Ping et al., 2015; McDaniel & Schneider, 1967) in the rutile (tetragonal) structure.

B Bench marking the LDAU+U+SOC implementation

After successfully implementing the LDA+U+SOC approach in the SIESTA code, and performing a calculation on IrO_2 , it was prudent that we benchmark the results with other well known and developed codes. The codes chosen were QUANTUM ESPRESSO and VASP.

B.1 Procedure employed in QUANTUM ESPRESSO

To make a more thorough comparison, we also ran simulations on bulk IrO_2 using the plane-wave based approach provided by the QUANTUM ESPRESSO program (Giannozzi et al., 2009, 2017). Ultrasoft pseudopotentials (Vanderbilt, 1990) taken from the PSLIBRARY (Dal Corso, 2014) were employed, with the same valence configuration discussed in appx. A. The remaining details remained the same as those covered in appx. A.

B.2 Procedure employed in VASP

Additionally, bulk IrO_2 simulations were performed using the VASP code (Kresse & Furthmüller, 1996; Kresse & Furthmüller, 1996). In this framework, the calculation employing the projector augmented-wave (PAW) method (Blöchl, 1994), kept the same valence electrons as in appx. A. With a mesh-cutoff of 500 eV, very convergent results were obtained. The calculation of the band structure and density of states also accounted for the spin-orbit coupling effect.

C Peer reviewed articles touching on this work

4. Fernando Gómez-Ortiz, Nayara Carral-Sainz, **James Sifuna**, Virginia Monteseguro, Ramón Cuadrado, Pablo García-Fernández & Javier Junquera. (2023). Compatibility of DFT+U with non-collinear magnetism and spin-orbit coupling within a framework of numerical atomic orbitals. *Computer Physics Communications*, 286, 108684.
3. Chege, S., Ning'i, P., **Sifuna, J.**, & Amolo, G. O. (2020). Origin of band inversion in topological Bi_2Se_3 . *AIP Advances*, 10(9), 095018.
2. **Sifuna, J.**, García-Fernández, P., Manyali, G. S., Amolo, G., & Junquera, J. (2020). First-principles study of two-dimensional electron and hole gases at the head-to-head and tail-to-tail 180° domain walls in PbTiO_3 ferroelectric thin films. *Physical Review B*, 101(17), 174114.
1. **Sifuna, J.**, García-Fernández, P., Manyali, G., Amolo, G., & Junquera, J. (2020). Comparison of band -fitting and Wannier-based model construction for WSe_2 . *MRS Advances*, 5(44), 2281-2290.

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E Code details and version

The code employed in the work was SIESTA version 4.1-b4.

The version to this code can be obtained from the GITLAB SIESTA link below.

<https://gitlab.com/siesta-project/siesta>

Then navigate the branches to obtain version 4.1-b4.

F Relaxed input files and the pseudopotentials used

Due to the large and long nature of the contents in the input files, they can not fit on this page. Please use the QR code below to download them together with the pseudopotentials and the constrain.f file used. This will go along way in helping reproducibility of these results.



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