FIRST-PRINCIPLES STUDIES OF THE EFFECTS OF TRANSITION METAL IMPURITIES ON THE ELECTRONIC STRUCTURE OF KNBO₃

by

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(Under the direction of William M. Dennis and Steven P. Lewis)

Abstract

The performance of KNbO₃, as a photorefractive crystal in the visible region, can be dramatically improved when impurities are incorporated into the host by doping. These materials lead to improvements in numerous technological applications such as optical data storage and phase conjugate mirrors. In this dissertation, KNbO₃ doped with various 3d transition metals *e.g.* Cr, Mn, Fe, Co and Ni, are investigated, with the long-term goal of extending the spectral range of the photorefractive KNbO₃ into the IR region. The electronic structure studies based on Density Functional Theory, described in this dissertation, has resulted in identifying definite trends in the impurity levels that could be explained in terms of crystal field and exchange field splitting. Different types of Fe impurity centers with coordinating and non-coordinating oxygen-vacancies have also been investigated. These results provide useful insights into the nature of the reduction center Fe³⁺ to Fe²⁺, which has been found to be a key contributor to a significantly enhanced photorefractive performance.

INDEX WORDS: photorefractive effect, DFT, crystal field splitting, exchange splitting

First-Principles Studies of the Effects of Transition Metal Impurities on the Electronic Structure of $\rm KNbO_3$

by

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Chapter 1

Introduction

Over the past three decades, the diverse range of tunable properties of ferroelectric materials has driven an intense scientific and technological research effort in this area (refer to [1] and the references therein). A prototypical example is the ferroelectric material $BaTiO_3$ which is used in dielectric capacitors in non-volatile computer memories. This application exploits material properties like switchable macroscopic spontaneous polarization, which is a key functional feature in this family of compounds. Other properties, like very large piezoelectric and pyroelectric responses, have also received a lot of attention, as they can be utilized for applications such as the transducers and actuators used in, for example, car crash detectors responsible for air-bag deployment.

Potassium niobate or KNbO₃, which exhibits the ABO₃ stoichiometry, belongs to a very important class of ferroelectrics called perovskites. The important properties of perovskites range from ferromagnetism, piezoelectricity, colossal magnetoresistance, and spin-dependent transport to high-temperature superconductivity and nonlinear optical phenomena [1–4]. The richness of these properties stems from both the great compositional diversity within the family of perovskites and the strong interplay amongst the elastic, electric, magnetic, and optical responses of these materials. Table.1.1 lists some of the applications of the extensive variety of pervoskite materials available [5]. Structurally, the ABO₃-type perovskite is paraelectric above the Curie temperature, $T_{\rm C}$, and the unit cell describes a high symmetry cubic phase where the A atoms are located at the corners of the cube, the B atom at the body center and the O atoms at the face centers as indicated in Fig.1.1(a). Thus the six O atoms are symmetrically arranged around a central B atom defining the vertices of a octahedron. The resulting oxygen cage, with B atom at its center, forms a network of BO₆ complexes with A atoms lying in the interstices which, in turn, are 12-fold coordinated to the neighboring O, as seen in Fig.1.1(b). It is to be noted here that these corner-sharing BO₆ units are predominately

Applications	Perovskite Materials
Multilayered Capacitors	BaTiO ₃
Second Harmonic Generator	KNbO_3
Piezoelectric Transducer	$Pb(Zr,Yi)O_3$
Electrooptic Modulator	$(\rm Pb,La)(Zr,Ti)O_3$
Dielectric Resonator	BaZrO_3
Thick Film Resistor	BaRuO_3
Elecrostrictive Actuator	$Pb(Mg,Nb)O_3$
Magnetic Bubble Memory	GdFeO_3
Laser Host	YAlO ₃
Ferromagnet	$(Ca,La)MnO_3$
Refractory Electrode	$LaCoO_3$

Table 1.1: Important applications of some perovskite materials.

responsible for the diverse functionality found in the perovskites. The environment of ideal perovskite dictates that given any two cations, the one with smaller size will occupy site B while the larger one is favored for the A site. Furthermore, the sum of their formal charges is +6, which balances exactly the negative charges due to the O²⁻ anions, rendering the unit cell electrically neutral. Thus, usually, A is an alkaline metal *e.g.* Li,



Figure 1.1: (a) A prototype cubic unit cell of the perovskite structure with formula unit ABO_3 and the origin centered on the B-site cation. (b) A-site cations at the centers of the BO_6 octahedral units. [001] direction points out of the page.

Na or K with oxidation state +1, an alkaline earth metal *e.g.* Mg, Ca, Ba with oxidation state +2 or a rare earth element *e.g.* La (oxidation state +3). The corresponding B site is occupied by transition metals with oxidation states +5, +4 or +3, respectively. Below $T_{\rm C}$, several perovskites *e.g.* BaTiO₃, PbTiO₃, PbZrO₃, KNbO₃ and NaNbO₃ exhibit one or more ferroelectric or antiferroelectric structural phase transitions, while materials like SrTiO₃ and KTaO₃ undergo no such changes and remain nonpolar throughout. Finding the origin of these phase transitions forms a crucial part of the perovskite related scientific literature. As per one approach motivated by the size of the ions, the ionic radii $r_{\rm A}$, $r_{\rm B}$ and $r_{\rm O}$ of the participating atoms, A, B and O respectively are such that the tolerance factor, *t*, first introduced by Goldschmidt [6], and defined to be $t = \frac{r_{\rm A} + r_{\rm O}}{\sqrt{2}(r_{\rm B} + r_{\rm O})}$, ideally equals to one. In other words, if the sizes of the constituent ions are optimal, there is no strain in the structure. Distortions tend to occur as the cations allocated to sites A and B are inappropriately sized to fit into the ideal perovskite. This imposes increasing strain on the structure. Under such circumstances the tolerance factor deviates from one. The perovskite structure is relieved of such strain by structural modifications like displacement of A and/or B cations, tilting or rotation of the octahedral units, or a suitable combination of these modifications that changes the six B-O bond lengths nonuniformly. B-site cation displacement is more common and calls for small shifts of the B atom from its ideal position towards one of the surrounding O atoms. This off-centered movement gives rise to a permanent dipole moment leading to ferroelectric effects. All these different types of distortions are aimed at producing a structure that is energetically more favorable. In an alternative but equivalent view, displacive ferroelectric transitions are attributed to the presence of "soft-modes" [7, 8]. This concept is based on the assumption that the crystal gets unstable against particular normal modes of vibration of the lattice. Then in the symmetric cubic phase, there exists a certain unstable or soft phonon mode, whose frequency decreases as the temperature approaches $T_{\rm C}$ and becomes zero at $T_{\rm C}$. This implies that the free energy is minimized at some finite amplitude of the soft mode at this temperature, rather tun at zero amplitude, producing a structure of lower symmetry with a finite dipole moment. However, for some materials, many results, inconsistent with the soft-mode theory, have been explained on the basis of an alternate theory based on the "order-disorder" model. According to this theory, some ions or group of ions which were disordered in the high temperature paraelectric phase, are ordered in the low temperature ferroelectric phase, again producing a nonzero dipole moment in the unit cell [9–12]. Despite decades of research, there is still controversy regarding the nature of the origin of the ferroelectric transitions with contradictory evidence in support of both these competing theories of order-disorder and soft-mode behavior.

 $KNbO_3$, noteworthy among the perovskites, is usually grown by the Czochralski method [13]. Upon cooling from the growth temperature 1050 °C to room temperature, the three subsequent ferroelectric phase transitions are observed as follows: from

paraelectric cubic to tetragonal at 450 °C, from tetragonal to orthorhombic at 225 °C and finally from orthorhombic to the rhombohedral ground state below -10 °C [14, 15]. The unit cells of these different phases are shown in Fig. 1.2.

Of the three ferroelectric phases of KNbO₃, the room-temperature orthorhombic phase has probably attracted most attention from experimental as well as theoretical researchers because of its suitability to a wide range of practical applications. A vast amount of data related to the nature of the Nb atom shift in this phase has been extracted from neutron scattering [16] and Raman scattering [17–19] experiments, X-ray absorption fine-structure (EXAFS) measurements of the local Nb environments [20], as well as time-resolved Raman experiments [21, 22].

Ab initio methods were also used for in-depth analysis at the microscopic level. Density Functional Theory (DFT), based on Kohn Sham principles, is an extremely powerful firstprinciples tool that can be used to investigate the electronic ground-state properties of solids and molecules. By treating the systems at the quantum level, the DFT approach allows one to calculate and predict properties accurately, thus providing insights that can guide experimental characterization and synthesis of existing and new materials. In the simplest application of first-principles based techniques, the calculation of total energy, atomic forces and unit-cell stresses were used to determine the equilibrium geometry [1] and the relevant structural parameters, *i.e.*, lattice constants, atomic positions and bulk moduli of the various phases of KNbO₃. It is important to note here that the calculations of ferroelectric distortive transitions in KNbO₃ involve very small energy differences and are sensitive to the numerical approximations [23], so that careful testing is required. Other fruitful areas of research include lattice dynamics, calculations of Born effective charges and spontaneous polarization, the piezoelectric response and linear dielectric constants in KNbO₃ [24–32].

The small magnitude non-linear effects in this crystal became significant and observable after the invention of laser. The orthorhombic KNbO_3 (point group is mm^2), being



Figure 1.2: Unit cells of the different phases of KNbO_3 . (Not drawn to scale: The size of the spheres used to represent different atoms do not correspond to the ionic radii of the atoms. The distortions are exaggerated manyfold for clarity.)

non centrosymmetric, was found to be an ideal candidate for displaying second-order nonlinear effects. The absence of center of a inversion, combined with a large value of spontaneous electric polarization at room temperatures and high packing density of polarizable NbO₆ units was found to yield large values of electro-optic coefficients [33, 34] and nonlinear optical susceptibilities [35, 36]. The three independent elements of the dielectric tensor were evaluated at the room temperature [37, 38]. These anisotropic refractive indices, yielding phase matching abilities, were exploited to make pure crystals good frequency converters.

Additionally, it was found that the second-order, non-linear opto-electric effect combines with the photoconductive properties in certain perovskites, including KNbO₃, to yield the very interesting phenomenon of photorefractivity. Photorefractivity is a lightinduced, reversible non-linear phenomenon that changes the refractive index of a material locally in response to a spatially modulated light intensity. It has been exploited effectively in high-tech applications including real-time holographic optical data storage, photorefractive solitons, optically induced waveguides, optical computing, information processing and optical neural networks [33]. The photorefractive properties were discovered in the late 60s, primarily in doped and undoped inorganic crystals e.g. LiNbO₃, BaTiO₃, Bi₁₂SiO₂₀ and KNbO₃ [33], although recently some semiconductors and organic polymers are also found to exhibit photorefractivity [39, 40]. The main characteristic feature of such effects is that relatively low light powers can induce large material changes, optical sources being for example helium-neon, diode or small argon lasers. This high sensitivity comes at the expense of relatively slow response times which can vary from milliseconds to hours [33].

Photorefactive materials are photoconductive and electro-optic [41]. Photoconductivity means that light of adequate wavelength can excite charge carriers, either electrons or holes, from localized photoactive centers such as donors or acceptors, into conduction or valence band. The electro-optic or Pockels effect is a non linear material response where the local refractive index varies in accordance with the local electric field applied to the material. The combination of the carrier-trap dynamics and the electro-optic process enables suitable materials to display photorefactive effects. When two coherent beams are incident and cross in a photorefractive material producing an interference pattern of alternate dark and light fringes, as shown in Fig. 1.3(a), more charge carriers are preferentially photoexcited in the brighter regions than in the darker ones (Fig.1.3(b)). In the Figures 1.3(a) and (b), H and L represent the high and low light intensity regions and electron concentrations respectively. For simplicity only electrons are considered. The mobile electrons in the conduction band, respond to this concentration gradient by diffusing from a high density to a low density region. The diffusion current, being proportional to the gradient of the electron density, is 90° out of phase with respect to the latter as shown in Fig.1.3(c). In the darker regions, some electrons that have migrated from brighter regions, as well as locally excited electrons, will get captured by deep trapping centers thereby reducing their density. This leads to a progressive accumulation of electrons in darker regions leaving behind a higher density of uncompensated, immobile, positively charged donors (Fig.1.3(d)). Such a spatially modulated charge density creates a spatially modulated electric space-charge field that is 90° out of phase with the spatial charge distribution (Fig.1.3(e)). The space-charge field, by means of the linear electro-optic or Pockels effect, modulates the refractive index of the material locally. Therefore, in this class of materials, a periodic optical standing wave can give rise to a periodically modulated index of refraction, resulting in an optical volume grating that is out of phase with respect to the interference pattern created by the incident beams, as shown in Fig.1.3(f). This phase difference is responsible for an irreversible energy transfer between the two beams. Several theoretical approaches modeling this effect have been developed, with the band transport model [42–44] being currently the most widely used.

A remarkable property of photorefractive materials, as detailed above, is their ability to transfer energy between beams interacting in the volume of the material [33], and



Figure 1.3: Different processes involved in the photorefractive effect.

this phenomenon is referred to as two-beam coupling or two-wave mixing. This process has emerged to be a very promising area of research, as a weak information bearing signal can be amplified by transferring energy form an intense pump beam, an effect that is maximized when the phase shift between the interference pattern and grating is $\frac{\pi}{2}$. The two-beam coupling forms the basis of important nonlinear phenomena, for example, self-pumped phase conjugation and mutually-pumped phase conjugation used effectively in optical devices like photorefractive phase conjugate mirrors. These mirrors have the ability to compensate dynamically for the phase disturbing aberrations that arise in laser cavities, enabling solid-state lasers to operate at higher intensities.

KNbO₃, an important member of the family of ferroelectric photorefractives, is the material of choice in many nonlinear applications because of its large effective electro-optic coefficients and its stability over a wide temperature range (-50° C to 220° C) [45]. Impurities and defects unavoidably present in the real material of $KNbO_3$, with ionization energies smaller than the band gap (3.3 eV), provide the charge centers for photoexcitation. These levels can be introduced and influenced by intentional doping of the crystal melt of KNbO₃ [45]. The dopants affected the different photorefractive performance parameters, such as, carrier mobility, trapping time, effective trap density, electro-optic coefficient and others. Fe-doped crystals have been the subject of extensive experimental investigation with the aim of enhancing the photorefractive response to visible light [46-48]. A comprehensive collection of data of the fundamental physical parameters governing the photorefractive performance of Fe-doped $KNbO_3$ at visible wavelengths has been reported [49]. Many authors claim that $KNbO_3$: Fe is one of the most efficient photorefravtives in the visible range. Other impurities like Cu, Co, Mn, Ni and Rh have also been studied, with promising results [50–56]. Significant improvements have been reported in two-beam coupling gain and self-pumped phase conjugate reflectivities when the $KNbO_3$ host is doped with Mn, Cu, Co and Ni [57, 58]. Additionally, it has been found that the extension of the spectral response of KNbO₃ into the near infrared can be achieved through doping [59, 60], for example, Ni-doping has extended the spectral response to 830 nm [60]. All these improvements in the samples doped with Fe, Mn and Ni are achieved at the expense of introducing a long response time of several seconds for two-beam coupling at a moderate intensity level. This problem is overcome by doping with rubidium, reducing the response time to the milliseconds range, but at the expense of very low two-beam coupling gain coefficients [61,62]. Thus, the possibility of controlling various photorefractive performance parameters of KNbO₃ via doping has led to a search of newer dopants that would generate properties tailored to IR applications.

Additionally, the effect of a reductive treatment on crystals of Fe-doped KNbO₃ has been found to be particularly important. Reducing KNbO₃:Fe crystals, converts a fraction of the Fe^{3+} dopants into Fe^{2+} , where the valence state is reduced by one unit charge. As pointed out in [49], this leads to electrons donated by Fe^{2+} being the main photoexcited charge carriers and Fe^{3+} acting as traps to the photo excited conduction electrons. The resulting donor-acceptor combination facilitates the build-up of the space charge field, which is at the core of the photorefractive effect. Under visible irradiation, reduced KNbO₃:Fe shows a significant improvement of photorefractive sensitivity and speed, for example, faster two-beam coupling and phase conjugation, that could be used advantageously in areas such as optical computing [63]. Various Fe-defect centers have been identified experimentally [64–66]. They are of the following types (i) Fe^{3+} - V_O, where a Fe^{3+} ion replaces a Nb^{5+} ion and a charge compensating oxygen-vacancy V_O , is created in the first coordination shell of the impurity, (ii) an isolated Fe^{3+} substituting a niobium ion and (iii) Fe_K^{3+} - V_K , where the Fe^{3+} replaces a K^+ ion and an associated vacancy is located in the first coordination shell of the K atoms. As a result of the electron paramagnetic resonance (EPR), optical absorption and electrical conductivity measurements conducted in the investigations reported in [67], it has been found that Fe^{2+} - V centers play a very important role as the main photorefractive centers when they are formed by

electro-reduction of Fe^{3+} - V complexes. Whether the Fe substitutional impurity at the Nb-site or the K-site is responsible for Fe^{2+} formation remains an open question.

A first-principles based theoretical model would be an effective tool in gaining a detailed understanding of the mechanisms involving the formation and stabilization of different impurities and associated vacancies. It is also essential from the crystal growth and reduction perspective, to have insights into how the impurities are coordinated by charge-compensating defects (e.g., oxygen vacancies). The ultimate aim for such a study would be to find the "ideal impurity candidate(s)" tailored to optimize the photorefractive performance of KNbO₃ beyond the visible range. The Density Functional Theory (DFT)based model proposed and developed in this dissertation, is a first step towards unravelling an extremely complicated multi-step process like photorefractivity, which involves several dynamical processes on multiple time scales. An attempt is made to understand, from band structures and density of states (DOS) and projected density of states (pDOS) calculations, explained in detail in the later chapters, various impurity level trends in doped KNbO₃ that would provide guidance in the synthesis of new enhanced materials.

The remainder of this dissertation is organized as follows: Chapter 2 provides an overview of the DFT formalism, which is the tool used in the work presented in the later chapters. Chapter 3 describes the DFT-based code used and the parameters for the present DFT calculations. It also details convergence tests, along with other preliminary considerations. The calculations related to bulk KNbO₃ are also discussed in this chapter. Chapter 4 describes the model and the electronic-related results when pure KNbO₃ is doped with a series of 3*d* transition metal impurities *i.e.*, Ti, V, Cr, Mn, Fe, Co and Ni. Chapter 5 describes an investigation of the effects of the position of the charge-compensating oxygen vacancy in systems with an Fe³⁺ impurity. Finally, Chapter 6 provides conclusions and discusses future directions for this research program.

Chapter 2

First Principles Total-energy Methodology

2.1 Background

Our modern visualization of materials of any form (condensed, liquid, gaseous, homogeneous, heterogeneous or others), in the microscopic realm, as an ensemble of atomic nuclei and electrons interacting via electrostatic forces, was firmly established in the early 20th century. It was understood that the matter, at such a small spatial scale, does not obey the classical laws of Newtonian mechanics and electromagnetism. Building blocks for the new field of quantum mechanics were laid by the idea of *quanta* of energy introduced by Planck (originally proposed in 1900) and Bohr's postulates [68] of nonradiating orbits in atoms. This was propelled further by the Schrödinger equation [69] published in 1926 that soon extended to multi-electron and eventually to multi-atom systems such as molecules and solids.

Detailed analysis of complex many-body systems requires computer simulations that can be of either classical or quantum-mechanical nature. The former is a semi-empirical approach that takes advantage of the already available experimental data to parameterize the force of interaction between the atoms to reproduce data like equilibrium geometries, bulk moduli, vibrational frequencies and others. In situations where *a priori* knowledge of the material is not available we have to resort to the second option of first-principles, or *ab initio*, methods within the quantum-mechanical framework. In non-relativistic cases, this amounts to solving the time-independent Schrödinger equation associated with the system, in compliance with certain assumptions. To understand its salient features let us consider the Hamiltonian of a system of N electrons subjected to an external potential of P nuclei, represented as [70]

$$\hat{H} = -\sum_{i=1}^{N} \frac{\hbar^2}{2m_e} \nabla_i^2 + \frac{e^2}{2} \sum_{i=1}^{N} \sum_{j\neq i}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - e^2 \sum_{i=1}^{N} \sum_{I=1}^{P} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} - \sum_{I=1}^{P} \frac{\hbar^2}{2M_I} \nabla_I^2 + \frac{e^2}{2} \sum_{I=1}^{P} \sum_{J\neq I}^{P} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} + V_{\text{EXT}} ,$$
(2.1)

where i, j run over electrons, I, J over nuclei and ∇^2 is the Laplacian operator. The symbols e and m_e denote the charge and the mass of an electron, M_I the mass of the nucleus and Z_I the atomic number of the I^{th} nucleus. Furthermore, $\mathbf{R} = \{\mathbf{R}_I\}$, where $I = 1, \dots, P$ and $\mathbf{r} = \{\mathbf{r}_i\}$, where $i = 1, \dots, N$ denote a set of nuclear and electronic coordinates (including spin) respectively. The terms on the right hand side of the equality in (2.1), from left to right, are the electronic kinetic energy, the internal potential energy due to the electron-electron two-body Coulomb repulsive interaction, the electron-nuclear Coulomb energy, the nuclear kinetic energy, the potential energy due to the nuclei interacting among themselves and finally the term that includes other external fields like static electric or magnetic or electromagnetic fields of laser-atom interaction when present and is assumed to be zero in this discussion. In principle, access to all the information regarding

the properties of a system, both physical and chemical, can be obtained by solving the stationary version of Schrödinger equation,

$$\hat{H}\Psi_n^{\text{total}}(\boldsymbol{r},\boldsymbol{R}) = \xi_n \Psi_n^{\text{total}}(\boldsymbol{r},\boldsymbol{R})$$
(2.2)

where \hat{H} is given in (2.1), ξ_n are the different energy eigenvalues and Ψ_n^{total} are the corresponding many-body eigenfunctions, which must be antisymmetric with respect to exchange of electronic coordinates in **r** and symmetric or antisymmetric (depending on nuclear spin) with respect to exchange of nuclear coordinates **R** [70].

This is a difficult problem virtually impossible to solve without resorting to approximations except for a very limited number of trivially simple systems. Complete analytical solutions, within the full quantum-mechanical framework, are available only for cases such as the hydrogenoid atoms or the H_2^+ molecule. Exact numerical solutions are limited to homogeneous electron gas, atoms with a small number of electrons and for a few small molecules. Among several other contributing factors, the primary sources of this intractability are (1) that the computational effort required to solve for all Ψ_n^{total} scales exponentially with exponent¹ 3(N + P), with N, P being large; (2) that the Coulomb potential is a two-body interaction. As a result, the presence of an electron in one region of space affects how the electrons in some other region behave. In other words, electrons cannot be treated as independent entities, thus precluding the separation of the Schrödinger equation into (N + P) single-body problems. Furthermore, the interactions are too strong to be treated perturbatively.

Certain well controlled assumptions play effective roles in making Equation (2.2) amenable to numerical solutions without loosing the key physics behind the many-body, multi-component systems. First is the Born-Oppenheimer approximation [71]. It pro-

¹The coefficient 3 is due to the three spatial degrees of freedom of each particle and the exponential scaling factor arises from the correlated Coulomb interaction of each particle with the other N-1 particles.

poses that the nuclear motion can be completely decoupled from the electronic motion if we consider the former in the time scale of the electrons. With the forces on the particles being the same, and the electrons being much lighter compared to the massive nucleus (the mass of a proton is 1836 times the mass of an electron), a classical picture suggests that the electronic velocity is much larger, about two orders of magnitude faster, compared to that of the nucleus. In fact, the nucleus is rendered stationary in the Born-Oppenheimer picture. This enables us to neglect the kinetic energy of the nuclei completely. The potential energy, due to internuclear interaction, E_{ii} given by the last term in (2.1), becomes constant (since all the nuclear positions, \mathbf{R}_I 's, are assumed to be fixed in space) and doesn't contribute to the electronic description, but, can be added later to yield the the total energy of the system. Consequently we can decouple the total wave function into electronic and nuclear (*i.e.*, vibrational, rotational) components ($\Psi^{\text{total}} = \Theta^{\text{nuclear}} \times \Phi^{\text{electronic}}$). As Kohanoff [70] points out, the composite solution of Equation (2.2) can be of the form

$$\Psi^{\text{total}}(\boldsymbol{R}, \boldsymbol{r}, t) = \sum_{n} \Theta_{n}(\boldsymbol{R}, t) \Phi_{n}(\boldsymbol{r}, \boldsymbol{R}), \qquad (2.3)$$

where $\Theta_n(\mathbf{R}, t)$ represents the time evolved eigenstate of the nuclear subsystem when the electrons are in one of the adiabatic eigenstates, $\Phi_n(\mathbf{r}, \mathbf{R})$ for a fixed nuclear configuration given by \mathbf{R} . The function $\Phi_n(\mathbf{r}, \mathbf{R})$ satisfies the time independent Schrödinger equation

$$\hat{h}_e \Phi_n(\boldsymbol{r}, \boldsymbol{R}) = \epsilon_n(\boldsymbol{R}) \Phi_n(\boldsymbol{r}, \boldsymbol{R}), \qquad (2.4)$$

where $\epsilon_n(\mathbf{R})$ defines the different nuclear potential energy surfaces. The electronic Hamiltonian operator \hat{h}_e is given by

$$\hat{h}_e = \hat{T} + \hat{V}_{\rm ee} + \hat{V}_{\rm ext}, \qquad (2.5)$$

where the operators on the right hand side are as follows: \hat{T} represents the electronic kinetic energy operator, \hat{V}_{ee} the electron-electron interaction and \hat{V}_{ext} refers to the interaction of electrons with external fields (a generalization of electron-nuclear interactions). It is interesting to note how this partial differential equation now depends on variable \boldsymbol{r} only, with the 3P nuclear coordinates embedded in \boldsymbol{R} behaving as a parameter. Adopting Hartree units ($\hbar = m_e = e = \frac{4\pi}{\epsilon_0} = 1$), the operators in Eq (2.5), are explicitly of the form

$$\hat{T} = -\frac{1}{2} \sum_{i=1}^{N} \nabla_{i}^{2}; \quad \hat{V}_{ee} = \frac{1}{2} \sum_{i=1}^{N} \sum_{j \neq i}^{N} \frac{1}{|\mathbf{r}_{i} - \mathbf{r}_{j}|} = \sum_{i < j}^{N} \frac{1}{|\mathbf{r}_{i} - \mathbf{r}_{j}|};$$

$$\hat{V}_{ext} = -\sum_{i=1}^{N} \sum_{I=1}^{P} \frac{Z_{I}}{|\mathbf{r}_{i} - \mathbf{R}_{I}|} = \sum_{i=1}^{N} v_{ext}(\mathbf{r}_{i})$$
(2.6)

It is to be emphasized that the $\Phi_n(\mathbf{r}, \mathbf{R})$ describes the electronic behavior corresponding to a static external potential due to a particular frozen-in nuclear configuration. When allowance has to be made for motion of the nucleus, the electrons can be thought of as following the nuclear dynamics instantaneously and relaxing to the ground state of the electronic hamiltonian corresponding to the new nuclear configuration. Henceforth, for all future references, $\Phi_n(\mathbf{r_1}, \mathbf{r_2}, \dots, \mathbf{r_N})$ is regarded as the many body electronic wave function², where the condensed coordinate \mathbf{r}_i represents a set of both position and spin values for N electrons $\{\mathbf{r}_i, \sigma_i\}^3$.

One needs to remember two important features while trying to solve for Φ_n . The fact that the electrons are fermions requires that their wave functions must be antisymmetric (i.e., the wave function must change sign when two electrons are interchanged) as given by,

$$\Phi_n(\boldsymbol{r_1}, \boldsymbol{r_2}, ..\boldsymbol{r_a}...\boldsymbol{r_b},, \boldsymbol{r_N}) = -\Phi_n(\boldsymbol{r_1}, \boldsymbol{r_2}, ..\boldsymbol{r_b}...\boldsymbol{r_a},, \boldsymbol{r_N})$$
(2.7)

 $^{{}^{2}\}boldsymbol{R}$ is dropped for brevity.

³ σ_i refers to the spin which is neglected for all our calculations unless otherwise specified.

This phenomenon is often referred to as exchange and must be captured correctly in the eigenstate solution of the many-body system. Further, Coulomb interaction between electrons results in their motions being correlated. Thus, our aim is to find suitable approximations that enable us to detangle this formidable mathematical problem without compromising the essential physics and chemistry. This effort is worthwhile as the knowledge about the electronic eigenstates give access to a wealth of information.For example, the electronic ground state yields information about atomic structure, the relative stability of different structures, elastic properties, polarizabilities and dielectric properties, molecular and lattice vibrations and so on. The excited states, on the other hand, determine the electronic transport and optical properties.

Now, with $|\Phi\rangle$ representing the N-electron state, the expectation value of the electronic Hamiltonian \hat{h}_e in Eqn. (2.5) yields energy as

$$E = \frac{\langle \Phi | \hat{h}_e | \Phi \rangle}{\langle \Phi | \Phi \rangle} \equiv \langle \hat{h}_e \rangle = \langle \Phi | \hat{T} + \hat{V}_{ee} + \hat{V}_{ext} | \Phi \rangle$$
(2.8)

$$= \int_{1} \int_{2} \cdots \int_{N} d^{3}r_{1} d^{3}r_{2} \cdots d^{3}r_{N} \Phi^{*} \left(-\frac{1}{2} \sum_{i=1}^{N} \nabla_{i}^{2} + \sum_{i$$

The last term in Eqn (2.9) can be rewritten as

$$\langle \Phi | \hat{V}_{\text{ext}} | \Phi \rangle = \int v_{ext}(\mathbf{r}) \rho(\mathbf{r}) d^3 r$$
 (2.10)

where $\rho(\mathbf{r})$ refers to the electron density of an eigenstate Φ . Such simplification is not possible for the other two terms in (2.9). Thus we write

$$E = \langle \hat{T} \rangle + \langle \hat{V}_{ee} \rangle + \langle \hat{V}_{ext} \rangle$$

$$E = \langle \hat{T} \rangle + \langle \hat{V}_{ee} \rangle + \int v_{ext}(\mathbf{r}) \rho(\mathbf{r}) d^3 r$$

$$E = \langle \hat{T} \rangle + \langle \hat{V}_{ee} \rangle + V_{ext}[\rho]$$
(2.11)

where $[\rho]$ denotes a density functional⁴. If sensible approximations would allow us to model kinetic energy (T) and internal (*i.e.*, electron-electron) energy (V_{ee}) as explicitly dependent only on density, in the form of density functionals, then electronic density could be looked upon as the fundamental variable of the many-body problem. This concept would vastly simplify the mathematical intractability of the problem. Then, one could map a 3N-dimensional ($N \approx 10^{23}$) problem onto a 3-dimensional space (density is a function of 3 coordinates i.e., 3 Cartesian directions only) without loss of generality. This scheme is referred to as density functional theory, since it expresses each term in the energy as a functional of the density and is discussed in greater detail in the next section.

2.2 Modern Density Functional Theory

Early on there were some heuristic attempts to express the kinetic and internal energies as functionals of electronic density only. One of the most well known of such schemes, proposed by Thomas [72] and Fermi [73] independently, is often regarded as the precursor to the modern density functional theory (see A.1). The Thomas-Fermi approach falls short of the goal of providing a useful description of electron in matter, as it neglected both exchange and correlation and treated kinetic energy as a local functional of density⁵. As a result the theory suffers from many problems the most critical among them being its failure to explain the bonding between atoms and hence the formation of molecules and solids. There were other attempts failing to improve the Thomas-Fermi results significantly. It was not before three decades thereafter that modern density functional theory, could be placed on firm mathematical ground with help of two theorems by Hohenberg and Kohn [74].

 $^{^{4}\}mathrm{A}$ functional is a mapping that takes a function to a number and is represented in terms of square brackets []

⁵Thomas-Fermi theory works reasonably well when the electronic density is smooth as in alkali metals.



Figure 2.1: First Hohenberg-Kohn Theorem visualized.

2.2.1 Hohenberg-Kohn Theorems and Kohn-Sham Ansatz

Hohenberg-Kohn First Theorem (HK1): *The external potential of a system of interacting particles is unambiguously determined by the ground-state electronic density, apart from a trivial additive constant.*

Corollary: Since the hamiltonian is fully determined, except for a constant shift in energy, it follows that the many-body wavefunctions for all the states (ground and excited) can be obtained. *Therefore, all properties of the system are completely determined given only the ground-state density.*

The proof of the theorem is given in A.3. A schematic representation of HK1, following Martin [75], is shown in Fig 2.1, where the ground state wave function Φ_0 , corresponding to the ground-state density $\rho_0(\mathbf{r})$, is the state with the lowest energy that obeys the symmetries of the particles and all the conservation laws.

Hohenberg-Kohn Second Theorem (HK2): For any given external potential, a functional of energy in terms of the particle density can be defined.

Corollary: The ground-state energy may be obtained variationally from the global minimum of the energy functional. The density that minimizes the total energy functional is the exact ground state density.

The proof of this theorem is given in A.4.

The HK theorems allow us to write

$$E_{\rm HK}[\rho] = \langle \Phi[\rho] | \hat{h}_e | \Phi[\rho] \rangle$$

= $\langle \Phi[\rho] | \hat{T} + \hat{V}_{\rm ee} | \Phi[\rho] \rangle + \int v_{\rm ext}(\boldsymbol{r}) \rho(\boldsymbol{r}) d^3 r$
= $F_{\rm HK}[\rho] + \int v_{\rm ext}(\boldsymbol{r}) \rho(\boldsymbol{r}) d^3 r$
 $\geq E[\rho_0] = E_0 = \langle \Phi[\rho_0] | \hat{h}_e | \Phi[\rho_0] \rangle$ (2.12)

where ρ is some nonnegative density normalized to N, ρ_0 is the ground state density and $F_{\rm HK}[\rho] = \langle \Phi[\rho] | \hat{T} + \hat{V}_{\rm ee} | \Phi[\rho] \rangle$ is a universal functional that is same for all electron systems and does not depend on the external potential explicitly but only on electron density. Thus the goal of expressing energy as a functional of electronic density, mentioned in the previous section, has been achieved in principle⁶. The insightful guidance of the HK theorems allows us to represent the total energy of a system of N correlated electrons as an explicit electron-density functional (2.21). But we still lack the feasible methodology for calculating the universal functional $F_{HK}[\rho]$ that has contributions from both the kinetic energy T and electron-electron interaction, V_{ee} . The recipe for explicitly constructing the functional was provided by Kohn-Sham ansatz [78].

Kohn and Sham took an important step in attempting to solve the many-body electron problem by replacing the difficult real system, with all its intractable challenges by a reference fictitious system of non-interacting electrons yielding the same ground state density as the real system. In a seminal paper in 1965, they made use of the fact that the wave function of a system of N non-interacting electrons can be conveniently expressed as a Slater determinant (SD) of the one-electron orbitals $\{\phi_i(\boldsymbol{r_i})\}^7$. The kinetic energy of such a system can be easily computed. Then, the non-interacting equivalent reference

⁶One important point to be considered here is that there is no way to ensure that the electron density referred to in the above formulation is not unphysical *i.e.*, it might fail to generate wave functions that are anti-symmetric, a primary requirement for fermions like electrons. Levy and Lieb [76, 77] addressed this issue with a constrained variational search strategy. $^{7}\Phi_{\mathrm{SD}}(\boldsymbol{r}) = \frac{1}{\sqrt{N!}} \mathrm{SD} \left[\phi_{1}(\boldsymbol{r_{1}}) \phi_{2}(\boldsymbol{r_{2}}) \cdots \phi_{N}(\boldsymbol{r_{N}}) \right]$

system of density $\rho(\mathbf{r})$ is described by the Hamiltonian,

$$\hat{h}_{\rm KS} = \sum_{i=1}^{N} \left[-\frac{\hbar^2}{2m} \,\nabla_i^2 + v_{\rm R}(\boldsymbol{r}_i) \right], \qquad (2.13)$$

where N is the total number of electrons that interact only with the reference potential $v_{\rm R}$ (includes interactions with all the nuclei and possibly other external fields) and not among themselves. The corresponding energy functional is

$$E_{\rm KS}[\rho(\boldsymbol{r})] = T_{\rm R}[\rho(\boldsymbol{r})] + \int \rho(\boldsymbol{r}) v_{\rm R}(\boldsymbol{r}) d^3 r , \qquad (2.14)$$

where the density of the auxiliary system is constructed from the independent one electron orbitals $\{\phi_i\}$,

$$\rho(\boldsymbol{r}) = \sum_{i=1}^{N} |\phi_i(\boldsymbol{r})|^2, \qquad (2.15)$$

and the independent-particle kinetic energy T_R is given by

$$T_{\rm R} = -\frac{1}{2} \sum_{i=1}^{N} \langle \phi_i | \nabla^2 | \phi_i \rangle \tag{2.16}$$

The Kohn-Sham ansatz demands that such an auxiliary system be chosen carefully so that its ground-state electron density coincides with that of the real system, ρ_0 . Then, the HK theorems ensure that the ground-state energies are same i.e.,

$$E_{\rm KS}[\rho] \ge E_{\rm KS}[\rho_0] = E_0 ,$$
 (2.17)

the equality being valid only for $\rho = \rho_0$, where $E_{\rm KS}[\rho_0]$ equals the ground state energy E_0 of the real system. This means that the functional derivative of $E_{\rm KS}[\rho]$ must vanish for the corresponding ground-state density. Applying variational principle and rules of functional derivation to (2.14), subjected to the constraint that the density yields the

correct number of electrons, we get⁸

$$\frac{\delta}{\delta\rho(\boldsymbol{r})} \left[E_{\rm KS}[\tilde{\rho}] - \mu_{\rm R} \int \rho(\boldsymbol{r}) d\boldsymbol{r} \right]_{\rho=\rho_0} = 0 , \text{ or,}$$
(2.18)

$$\frac{\delta T_{\rm R}}{\delta \rho(\mathbf{r})} + v_{\rm R} = \mu_{\rm R} , \qquad (2.19)$$

where $\mu_{\rm R}$, the Lagrangian multiplier of the constraint, is interpreted to be the chemical potential of the reference system.

In an attempt to cast (2.12) in a comparable form to (2.19), it cannot be emphasized enough that the exact many-body kinetic energy, T, is not the kinetic energy of the reference KS system as it omits correlation effects. The idea of a non-interacting kinetic energy $T_{\rm R}$, on the other hand, is a useful one, as it permits us to model T as the sum of two managable pieces: non-interacting kinetic energy $T_{\rm R}$ accounting exactly for the most important part of the kinetic energy and the interaction contributions considered separately in the exchange-correlation term (See below and Exchange and Correlation section on page 26).

Similarly a useful strategy is to express the V_{ee} term in (2.12) as a sum of two contributions. The first one, referred to as Hartree energy, is a significant component of V_{ee} . It is the long-range classical electrostatic energy calculated by assuming that each electron interacts with the mean electronic charge without disturbing it. Mathematically, the Hartree term is exactly given by

$$E_{\text{Hartree}}[\rho] = \frac{1}{2} \int \int d^3r d^3r' \frac{\rho(\boldsymbol{r})\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} . \qquad (2.20)$$

This mean-field approach not only ignores the effect of electron-electron repulsion but also incurs the error of unphysical self-interaction. The self-interaction error arises be-

 $^{8 \}frac{\delta F[f]}{\delta f(x)}$ is referred to as a functional derivative, distinguished from a partial derivative.

cause of the fact that the mean charge density is obtained by summing over all the electrons including the test electron itself. This, together with the missing kinetic energy correlation contribution, is accounted for in the second contribution known as the exchange-correlation $(E_{\rm xc})$. Therefore, the terms of the HK energy functional (2.12) that make the most important contribution to the energy are exact and computable, while all the ignorance about the complex interacting system is grouped together and assigned to $E_{\rm xc}$ which generally makes a much smaller contribution to the energy. $E_{\rm xc}$ can be reasonably approximated as a local or nearly local functional of density. Thus, the HK energy functional of (2.12) is usually rewritten, within the Kohn-Sham framework, in the form

$$E[\rho] = T_{\rm R} + \int v_{\rm ext}(\boldsymbol{r})\rho(\boldsymbol{r})d^3r + E_{\rm Hartree}[\rho] + E_{\rm XC}[\rho] . \qquad (2.21)$$

As in (2.18), applying the variational principle to (2.21) the following is obtained:

$$\frac{\delta}{\delta\rho(\boldsymbol{r})} \left[E[\rho] - \mu_{\rm R} \int \rho(\boldsymbol{r}) d\boldsymbol{r} \right]_{\rho=\rho_0} = 0 \quad \text{or}, \qquad (2.22)$$

$$\frac{\delta T_{\rm R}}{\delta \rho(\boldsymbol{r})} + v_{\rm ext}(\boldsymbol{r}) + \int \frac{\rho(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} d\boldsymbol{r}' + v_{\rm XC} = \mu . \qquad (2.23)$$

Here, μ is the chemical potential of the real system, and $v_{\rm xc} = \frac{\delta E_{\rm xc}}{\delta \rho(\mathbf{r})}$ is a multiplicative potential capturing the effects of exchange and correlation as described above. Since there is no charge flow between real and auxiliary systems, equating $\mu_{\rm R}$ in (2.19) to μ in (2.22), we get

$$v_{\rm R} = v_{\rm ext}(\boldsymbol{r}) + \int \frac{\rho(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} d\boldsymbol{r}' + v_{\rm XC} . \qquad (2.24)$$
Thus, the total energy of a multi-electron system, characterized by an electron density $\rho = \sum_{i}^{N} |\phi_i|^2$, following (2.21), is given by

$$E[\rho] = -\frac{\hbar^2}{2m} \sum_{i} \langle \phi_i | \nabla_i^2 | \phi_i \rangle + \int d\boldsymbol{r} \rho(\boldsymbol{r}) v_{\text{ext}}(\boldsymbol{r}) + \frac{e^2}{2} \int \int d\boldsymbol{r} d\boldsymbol{r}' \frac{\rho(\boldsymbol{r})\rho(\boldsymbol{r'})}{|\boldsymbol{r} - \boldsymbol{r'}|} + E_{\text{XC}}[\rho] , \quad (2.25)$$

It is important to note here that the ion-ion interaction E_{ii} , given by the last term in (2.1), should be added to (2.25) for a complete picture. E_{ii} , which is merely a sum over Coulomb pair repulsions, is a constant for a given ionic configuration. Then (2.25) is directly minimized with respect to the single electron KS orbitals, $\{\phi_i\}$, to yield the ground-state electron density and energy of the interacting system. This minimization problem, by Raleigh-Ritz theorem [79], is equivalent to solving an eigenvalue problem of the form (2.26). It is a set of coupled non-linear Schrödinger-like Kohn-Sham equations given by:

$$\left[-\frac{1}{2}\nabla^2 + v_{\text{ext}}(\boldsymbol{r}) + \int \frac{\rho(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} d\boldsymbol{r}' + v_{\text{XC}}(\boldsymbol{r})\right] \phi_i(\boldsymbol{r}) = \epsilon_{i(\text{KS})} \phi_i(\boldsymbol{r})$$
(2.26)

where $\epsilon_{i(\text{KS})}$, the Kohn-Sham eigenvalues, corresponds to the Lagrange multiplier used in the corresponding minimization problem. Thus, the KS equations describe the behavior of non-interacting electrons in an effective reference potential v_{R} . This system of equations are required to be solved iteratively for self-consistency because v_{R} is constructed from the density which we are solving for. In the process, the density used to construct v_{R} and solve the equations (2.26) coincides with the new density constructed from the solved set of orbitals using (2.15).

The KS eigenvalues, $\epsilon_{i(\text{KS})}$, should not be interpreted as one-electron excitation energies of the interacting many body system. Rather they are the excitation energies of the fictitious non-interacting system used to deduce the ground-state electronic density. However, it turns out that KS eigenvalues and the true many-body energy spectrum often

have much in common qualitatively, if not quantitatively. Therefore, much can be learned about the true excitation spectrum by examining the KS energy spectrum provided one is looking at trends and not making quantitative predictions.

Exchange and Correlation

The KS approach is an exact theory provided the exact exchange-correlation functional $E_{\rm xc}$ were known. It is interesting to note that given an exact $v_{\rm xc}$, the exact Kohn-Sham functional $E_{\rm KS}$ can be constructed which yields the exact ground-state energy and hence the exact ground-state density of the real system. But in practice KS theory is an approximate one as an exact $E_{\rm XC}$ is unknown. Instead, comparatively simple approximations have been made that have proven quite successful for accurately describing an array of diverse systems. This simplification reduces the computational costs as well as allows for accurate, efficient predictions of material properties. A satisfactory description of a realistic condensed matter system depends on essentially how good the approximations are. To understand the phenomena of exchange and correlation within the limited scope of this dissertation, an implicit definition of $E_{\rm XC}$ as in (2.27) is very helpful. In terms of the Honenberg-Kohn functional $F_{\rm HK}$ (see (2.21)), $E_{\rm XC}$ can be expressed as,

$$E_{\rm XC}[\rho] = F_{\rm HK}[\rho] - (T_{\rm R}[\rho]) + E_{\rm Hartree}[\rho]), \qquad (2.27)$$

or in a more revealing form

$$E_{\rm XC}[\rho] = \langle \hat{T} \rangle - T_{\rm R}[\rho] + \langle \hat{V}_{\rm ee} \rangle - E_{\rm Hartree}[\rho] ; \qquad (2.28)$$

i.e., E_{XC} is simply the sum of errors made in using non-interacting kinetic energy and treating the electron-electron interaction in the classical mean-field approach.

The exchange-correlation energy, $E_{\rm XC}$, is the sum of two terms, exchange energy (E_{ex}) and correlation energy E_c. The exchange phenomenon takes into account the behavior of two electrons, with like spins σ , in the vicinity of each other. According to the Pauli Exclusion Principle, the many-body wave function for a system of electrons must be antisymmetric with respect to swapping the particle labels for any pair of electrons. This places a condition on the allowed many-body wave functions that they must vanish when two electrons of the same spin state have the same spatial coordinates. No such constraint exists for the electrons of the opposite spin states. Therefore, the Pauli principle alone guarantees that the like-spin electrons will stay farther apart, on average, than oppositespin electrons. Since the Coulomb interaction between the electrons is repulsive, this exchange effect due to Pauli principle means that like-spin states tend to be lower in energy than opposite-spin states. This energetic difference is referred to as "exchange energy" even though it is ultimately electrostatic in nature. Assuming wave functions to be orthonormal, the exchange energy can be expressed as [80],

$$E_{\rm ex} = -\frac{e^2}{2} \sum_{\sigma} \int \int d\boldsymbol{r} d\boldsymbol{r}' \frac{\delta_{\sigma\sigma'} |\sum_i \phi_i^{\sigma*}(\boldsymbol{r}) \phi_i^{\sigma}(\boldsymbol{r'})|^2}{|\boldsymbol{r} - \boldsymbol{r'}|} .$$
(2.29)

Calculations reveal that the non-zero $E_{\rm XC}$ for a single-electron system is equal to $|E_{\rm Hartree}|$, which cancels the spurious self-interaction term in $E_{\rm Hartree}$. An alternative way of interpreting $E_{\rm XC}$ that provides useful insight takes into account the fact that the presence of an electron at a point \mathbf{r} in space will cause the charge density from all of the remaining electrons with same spin to have hole or lack of charge in the vicinity of \mathbf{r} . This explicit interaction of each electron with its corresponding exchange hole [75] is manifest when $E_{\rm XC}$ is expressed as

$$E_{\rm ex} = \frac{e^2}{2} \int \rho(\mathbf{r}) \int \frac{\rho_{\rm ex}(\mathbf{r'})}{|\mathbf{r} - \mathbf{r'}|} d\mathbf{r} d\mathbf{r'}$$
(2.30)

Apart from the quantum mechanical repulsion associated with like-spins of the electrons, as described above, there is a classical repulsion as well due to their electric charge. Intuitively, correlation can be thought of as an instantaneous interaction when an electrons pushes away other electrons, due to Coulomb repulsion, as it moves around. This tendency for electrons to stay apart diminishes the repulsion energy. A complete analysis of correlation is beyond the scope of this dissertation and can be found in [70].

Exchange and correlation can be combined yielding $E_{\rm XC}$ given by,

$$E_{\rm XC}[\rho] = e^2 \int \rho(\boldsymbol{r}) \epsilon_{\rm XC}([\rho], \boldsymbol{r}) d\boldsymbol{r} = e^2 \int \rho(\boldsymbol{r}) \int \frac{\tilde{\rho}_{\rm XC}(\boldsymbol{r}, \boldsymbol{r'})}{|\boldsymbol{r} - \boldsymbol{r'}|} d\boldsymbol{r} d\boldsymbol{r'} , \qquad (2.31)$$

where the exchange-correlation hole density $\tilde{\rho}_{\rm XC}$ comes about in a manner similar to (2.30). The details of $\tilde{\rho}_{\rm XC}$ can be found in references [75,81].

The most widely used approximate exchange-correlation functionals used in solid-state calculations are the Local Density Approximation (LDA) [82] and the Generalized Gradient Approximation (GGA) [83–85]. In LDA, the exchange-correlation energy per electron at a point \boldsymbol{r} , $\epsilon_{\rm XC}$, in the inhomogeneous electron gas is equal to $\epsilon_{\rm XC}^{\rm HEG}$ in a homogeneous electron gas (HEG) that has the same density as the local density in inhomogeneous gas at \boldsymbol{r} . Mathematically,

$$E_{\rm XC}[\rho] = e^2 \int \rho(\boldsymbol{r}) \epsilon_{\rm XC}^{\rm HEG}[\rho(\boldsymbol{r})] d\boldsymbol{r}$$
(2.32)

The latter can be computed with great accuracy using quantum Monte-Carlo simulation [75,82,86]. Even though LDA is assumed to be purely local while the true $E_{\rm XC}$ is not, the results compare well with the experiments. The discrepancies that do remain are found to follow systematic trends. For example, LDA typically overestimates binding energies and underestimates bond lengths. Consequently lattice constants are typically too short by about 1% - 2% while bulk moduli are too large by about 30% compared to experimental findings [87]. The effects of nearby inhomogenity on the electron density around each

electron that has been ignored in LDA, is partially addressed in GGA which incorporates the local density gradient as in

$$E_{\rm XC}[\rho] = e^2 \int \rho(\boldsymbol{r}) \epsilon_{\rm XC}[\rho(\boldsymbol{r}), \nabla \rho(\boldsymbol{r})] d\boldsymbol{r}$$
(2.33)

It has been demonstrated that GGA gives good atomic ground-state energies [88, 89]. Some examples of GGA functionals used by the physics community are those due to Perdew, Burke and Ernzerhof (PBE) [83], to Becke (B88) [84] and to Perdew-Wang (PW-91) [85]. As with LDA, the errors due to GGA are found to be systematic, *i.e.*, the bond lengths are somewhat overestimated.

2.2.2 Practical implementation of Kohn-Sham Methods

So far we have made some headway in unravelling the mathematically intractable problem of N correlated electrons by mapping onto an equivalent problem of N independent electrons moving in an effective reference potential $v_{\rm R}$, provided we can find a suitable approximation for the exchange-correlation term $v_{\rm XC}$. In addition, however, we need the following computational tools to successfully implement KS approach in real systems.

Plane Wave Basis: In order to take a step forward we need to choose a basis set. For crystalline solids, the present area of focus, one natural choice is plane waves. This is because, in such solids with a periodic potential $v(\mathbf{r}) = v(\mathbf{r} + \mathbf{R})$ for all \mathbf{R} in the Bravais lattice, the electrons are represented by Bloch states $\phi_{n\mathbf{k}}$ [90]. Furthermore, $\phi_{n\mathbf{k}}$ can be written as a product of a function $u_{n\mathbf{k}}$ that has the same periodicity as the potential and a purely imaginary phase factor arising from translational symmetry:

$$\phi_{n\,\boldsymbol{k}}(\boldsymbol{r}) = e^{i\boldsymbol{k}\cdot\boldsymbol{r}} u_{n\,\boldsymbol{k}}(\boldsymbol{r}) \tag{2.34}$$

where $u_{n k}(\mathbf{r}) = u_{n k}(\mathbf{r} + \mathbf{R})$ that can be expanded naturally into Fourier series. For the present purpose, the KS eigenstates satisfying (2.26) must have the Bloch form. We can identify the quantum state label *i* used previously being replaced by *n* \mathbf{k} used to label Bloch functions where *n* is the band index and \mathbf{k} is a wave vector in the first Brillouin Zone (BZ). An alternative, equivalent form of Bloch's theorem that provides useful insight, is:

$$\phi_{n\,\boldsymbol{k}}(\boldsymbol{r}+\boldsymbol{R}) = e^{i\boldsymbol{k}\cdot\boldsymbol{R}}\phi_{n\,\boldsymbol{k}}(\boldsymbol{r}) \tag{2.35}$$

This representation emphasizes the fact that the values of an electron eigenfunction of two unit cells, linked by lattice vector \mathbf{R} , differ only by a phase factor $e^{i\mathbf{k}\cdot\mathbf{r}}$. It is to be noted that the corresponding probability densities are same, since a phase factor has unit modulus. The Bloch's theorem permits the calculation of the properties of an infinite, periodic solid by considering only a single unit cell. Therefore, in crystalline solids, the otherwise prohibitively expensive computational load is made tractable and efficient by exploiting lattice periodicity with the help of Bloch's theorem.

Since the functions $u_{n k}$ are periodic, they can be expanded in a Fourier series as,

$$u_{n\,\boldsymbol{k}}(\boldsymbol{r}) = \sum_{\boldsymbol{G}} C_{n\,\boldsymbol{k}}(\boldsymbol{G}) e^{i\boldsymbol{G}\cdot\boldsymbol{r}}$$
(2.36)

where $C_{n \mathbf{k}}(\mathbf{G})$ is the expansion coefficient corresponding to the plane wave $e^{i\mathbf{G}\cdot\mathbf{R}}$ and the \mathbf{G} are reciprocal lattice vectors defined through $\mathbf{G}\cdot\mathbf{R} = 2\pi n$, where n is an integer. Thus the full Bloch functions also can be written as a discrete plane-wave expansion:

$$\psi_{n\,\boldsymbol{k}}(\boldsymbol{r}) = \sum_{\boldsymbol{G}} C_{n\,\boldsymbol{k}+\boldsymbol{G}} \, e^{i(\boldsymbol{k}+\boldsymbol{G})\cdot\boldsymbol{r}} \tag{2.37}$$

Except for G = 0, all the reciprocal lattice vectors lie outside the first BZ and an infinite number of them are required to describe the electron orbitals with infinite precision. However, in practice it has been found that, for large enough $|\mathbf{G}|$, the contribution of the plane waves decreases exponentially with the increasing kinetic energy $\left|\frac{\hbar^2(\mathbf{k}+\mathbf{G})}{2m}\right|^2$, and the series in (2.37) can be truncated after a finite number of terms without loosing important information. A finite basis set optimizes computational resources as well. A cutoff energy, $E_{\rm cut}$, is chosen such that only plane waves with kinetic energy less than some $E_{\rm cut}$ are included in the process and the size of the basis set for a given calculation is set as:

$$\left|\frac{\hbar^2(\boldsymbol{k} + \boldsymbol{G}_{\max})}{2m}\right|^2 \le E_{\text{cut}}$$
(2.38)

For the case $\mathbf{k} = 0$, (2.38) describes a sphere of radius, G_{max} , given by

$$|\boldsymbol{G}| \le G_{\max} = \sqrt{\frac{2mE_{\text{cut}}}{\hbar^2}} = 2\sqrt{E_{\text{cut}}[Ry]}$$
(2.39)

For Bloch functions corresponding to different k-points in the Brillouin zone, different number of plane-wave basis functions survive the truncation of (2.38). A cutoff energy suitable for the problem at hand is deduced by performing convergence tests of some benchmark quantity as a function of increasing $E_{\rm cut}$.

Representation of one-electron orbitals in terms of plane waves has the advantage of being complete (in principle this basis spans the associated Hilbert space completely) and mathematically desirable because of its simplicity. The calculation of energy and its derivatives like forces and stresses is analytic and simple in this representation compared to localized basis sets.

Brillouin Zone Sampling: Thus far we know that for a complete description, Bloch's theorem allows us to consider a single unit cell rather than the infinite crystal. But this description introduces the wave-vector parameter, \boldsymbol{k} , restricted to the first BZ. In principle, however, there are infinitely many k-points in the BZ for an infinite crystal. At this point, replacing one infinite quantity, the number of electrons, with another, the

number of k-points, may not seem to be an improvement. A way out of this problem is the important observation that it is not required to consider each of the k points individually. The wave functions, at k-points that are sufficiently close, are very similar. Therefore, the wave functions over a small portion of the BZ can be represented by a wave function at a particular k-point. Several methods have been devised to find special sets of k-points that will optimally sample the BZ (for example, the Monkhorst-Pack grid [91] used in this work). In this light, any function f that needs to be integrated over the BZ, e.g. the electron density, can be expressed as

$$f(\boldsymbol{r}) = \frac{\Omega}{(2\pi)^3} \int_{BZ} F(\boldsymbol{k}) d\boldsymbol{k} = \sum_j w_j F(\boldsymbol{k}_j) , \qquad (2.40)$$

where $F(\mathbf{k})$ is the Fourier transform of $f(\mathbf{r})$, Ω is the real space cell volume and w_j s are the weighing factors that sum up to one. The number of k-points can be further reduced by appealing to the point group symmetry of the lattice. In that case,

$$f(\mathbf{r}) = \sum_{j=1}^{P(n_j)} w'_j F(\mathbf{k}_j) , \qquad (2.41)$$

where $P(n_j)$ is the symmetry-dependent number of points in the irreducible wedge of the Brillouin zone. The weighing factors, w'_j , are now given by the the ratio of the order of the little group of the k-point to the full group of the crystal.

Pseudopotentials: Calculations involving all electrons in the atoms, including both core and valence electrons, are very difficult to carry out using a plane-wave basis. This is because the strong peaks of the tightly bound core states near the nucleus and the highly oscillatory nature of the valence states in the core region, required by orthogonalization constraint, impose stringent demands on the plane wave basis. These sharp features require plane waves of very short wavelengths for a faithful representation, and therefore a very high $E_{\rm cut}$ must be used to achieve adequate convergence. Therefore, a lot of effort

is wasted by using plane waves to describe the highly localized core states that are rather inert to their chemical environment and do not contribute to the material properties that we are interested in. On the other hand, it is desirable to retain the plane wave basis for the reasons already mentioned. Remembering that information about valence states in the core region is not strictly necessary and that valence electrons are solely responsible for chemical bonding, the nucleus and the core electrons can be replaced by point-like "pseudo-ion", whose interaction with valence electrons is described by a screened pseudo potential, without loss of crucial information. This pseudopotential is carefully constructed such that its scattering properties for the valence electrons are the same as the all-electron potential and it must mimic core-valence interactions reliably over a wide range of conditions. In other words, the corresponding pseudo wave-function, Ψ_{pseudo} , is an eigenstate of a pseudo hamiltonian with the same eigenvalues as Ψ_{AE}^{9} . The smooth pseudo wavefunction, different from the true wave function, has no nodes inside some cutoff radius r_c (see Fig. 2.2 (a) and (b)). Beyond r_c it decays exactly like as all-electron function. As a result of this smoothness, many fewer plane waves are required in the Fourier expansion.

There are two main recipes for constructing a pseudopotential, the norm-conserving approach and the ultrasoft approach. The norm-conserving pseudopotential [70, 92] requires, among other things, that the norm of the true and the pseudo-wavefunction inside the pseudized core region ($r \leq r_c$) should coincide. This ensures a high degree of accuracy and transferability from one system to another at the expense of the pseudopotential being fairly hard. In ultrasoft pseudopotentials [93, 94], the norm-conserving condition is relaxed, resulting in much smoother but still highly transferable potentials where the plane-wave cutoff is reduced considerably. Once the pseudopotential is obtained, its implementation in the KS equations is quite straightforward. The $v_{\text{ext}}(\mathbf{r})$ or the ionic potential in (2.26) is now replaced by the pseudo potential $v_{\text{ps}}(\mathbf{r})$ while all other terms remain

 $^{^9\}mathrm{AE}$ refers to all-electron case





(a) A schematic representation of pseudopotential and pseudo wave function

(b) Oxygen pseudo wavefunction

Figure 2.2: Pseudopotential and pseudo wave function.

unaltered. All calculations in this dissertation were carried out using ultrasoft pseudo potentials. For a more in depth discussion of pseudo potentials see [70].

Ground State Solution: Until now, theoretically, the intractable task of determining $\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$, for $N \approx 10^{23}$, has been reduced to evaluating $\phi_{n,\mathbf{k}}(\mathbf{r})$ for a discrete set of points $\{k\}$ in the first BZ and for a number of bands that is of the order of the number of electrons per unit cell. To obtain the ground-state energy of a strongly many-electron system in practice there are two possible approaches. The first one is to consider the total energy $E[\{\phi_i\}]$ as a functional of KS wave functions $\{\phi_i\}$ or the potential [95]. This strategy then calls for minimization techniques like conjugate gradient method (see A.5) to be applied directly on (2.25). The basic idea is to take a single-particle trial wave function and minimize the contribution of this state to the total energy (i.e., by varying the plane wave coefficients), while obeying the orthogonality condition to all other states. The second and most widely used approach is to replace the nonlinear minimization problem by an eigenvalue problem. For solid-state applications, expansion of electron wave

functions in terms of plane waves of the form (2.37) cast the KS differential equations of the form (2.26) into a particularly simple eigenvalue problem:

$$\sum_{\mathbf{G'}} \left[\frac{\hbar^2}{2m} |\mathbf{k} + \mathbf{G}|^2 \delta_{\mathbf{GG'}} + \tilde{V}_{\mathrm{ex}}(\mathbf{G} - \mathbf{G'}) + \tilde{V}_{\mathrm{H}}(\mathbf{G} - \mathbf{G'}) + \tilde{V}_{\mathrm{XC}}(\mathbf{G} - \mathbf{G'}) \right] \times C_{n \, \mathbf{k} + \mathbf{G'}} = \epsilon_n(\mathbf{k}) C_{n \, \mathbf{k} + \mathbf{G}} , \qquad (2.42)$$

where \tilde{V} refers to the Fourier transform of the respective potential. For each k-point included in the BZ sampling, there are N_{pw} such equations coupled through the self-consistent electron density:

$$\rho(\mathbf{r}) = \sum_{\mathbf{k} \in \mathbf{BZ}} w_{\mathbf{k}} \sum_{n=1}^{N_{\mathbf{k}}} f_n^{(\mathbf{k})} |\phi_{n(\mathbf{k})}(\mathbf{r})|^2 , \qquad (2.43)$$

where $N_{\mathbf{k}}$ is the number of electronic states occupied at each \mathbf{k} point, $f_n^{(\mathbf{k})}$ is the occupation number of the KS state $n\mathbf{k}$, weighted by factors $w_{\mathbf{k}}$. There are many ways to approach the solution of the set of equations in (2.42). The most standard approach calls for matrix diagonalization applying techniques such as block Davidson diagonalization [96], the size of the matrix being determined by the choice of the cut-off energy E_{cut} . In this method, working with a reduced basis helps to extract only the lowest lying eigenvalues important to us. Solution by diagonalization scales as N^3 where N is the number of electrons in a unit cell. The flow chart on page 37 illustrates such a scheme. It is to be noted that several details have been omitted in the flowchart for brevity.

As seen in the flowchart, the process starts with an initial guess for electron density, usually a superposition of atomic electron densities. Then the KS reference potential $v_{\rm R}$ is calculated. It is convenient to calculate several pieces of $v_{\rm R}$ in reciprocal space; for example, the kinetic energy is diagonal in reciprocal space, and the Hartree potential, which is a convolution in real space becomes merely a product in reciprocal space. On the other hand, $v_{\rm ext}$ and $v_{\rm XC}$ are more naturally calculated in real space. The transformation of wave functions and electron density back and forth between real space and reciprocal space is handled very efficiently by Fast Fourier Transform algorithm which has a computational cost of $N_{\rm FFT}\log N_{\rm FFT}$, where $N_{\rm FFT}$ is the total number of points in the FFT grid. The KS equations are then solved to obtain the single-particle eigenvalues and wave functions for a given configuration of nuclei. Subsequently a new electron density is calculated from the wave functions. After this, one or more self-consistent conditions are checked. Self-consistent condition(s) may include change of total energy or electron density from the previous iteration. Specifically, extensive time and effort goes into starting off with a good initial guess as well as mixing old and new particle densities prior to the next iteration. Additionally for completeness of the picture, spin should also be included. If self-consistency is not achieved, the current electron density is mixed with that from the previous cycle to obtain a new electron density. The mixing algorithm is chosen to optimize the SCF convergence. A new iteration starts with the newly obtained density. Such a cycle is referred to as one electronic iteration. After several such electronic iterations self-consistency is reached. Then quantities like total energy, atomic forces, unit-cell stress, electronic band structures, etc can be calculated for this particular atomic arrangement. If forces and stresses are not below a specified tolerance, the atoms are moved according to a quasi-Newton relaxation algorithm, and electronic iterations are initiated as before. This cycle is known as an atomic iteration. Each atomic iteration encompasses several electronic iterations. After multiple atomic iterations the equilibrium configuration is achieved, and the calculation has ended.



Figure 2.3: Basic scheme for solving Kohn-Sham Equations Iteratively.

Chapter 3

Computational Details

3.1 Software and Hardware

The *ab initio* electronic-structure calculations and modeling in this thesis, using plane waves and pseudopotentials within the density functional theory framework, were performed using a computer code package known as Quantum ESPRESSO (QE) [97], which stands for opEn Source Package for Research in Electronic Structure, Simulation, and Optimization. The QE-based simulations, presented in this dissertation, run on a cluster which currently comprises five 4-CPU 3GHz, 64-bit Intel core 2 Quad (Apple Computers) nodes with either 32GB or 48 GB of RAM respectively. The nodes are connected by gigabit ethernet connections. This facility also allows for 3 TB of local data storage.

Keeping in mind that the primary job of a DFT code is to calculate the energy and the relevant properties of a system in its ground state, this integrated suite of codes is built around core executibles such as pw.x that is concerned with geometrical optimization of atomic configurations and evaluation of the self-consistent potential (*i.e.*, the reference potential v_R as defined in (2.24)) and charge density and hence the total energy for a relaxed structure in the ground electronic state. Once v_R is determined, the self-consistent Hamiltonian of the system is known, and pw.x is used to solve the KS equations non-self-

consistently to obtain KS eigenvalues in various situations, for example, along a specified path in the BZ, as in band structure calculations, or on a denser grid of k-points for density of states (DOS) and projected density of states (pDOS) calculations. QE also includes several post-processing tools, such as ph.x for phonon calculations, pp.x for data analysis and plotting charge density and wave functions as well as data extraction for density of states and atomic-projection calculations using dos.x and projwfc.x respectively. Omitting the details, the schematic representation in Fig. 3.1 shows the basic architectural organization of the code relevant to the runs.

In QE, the user can specify the calculations to be performed on a system defined by its characteristic properties and constraints, through an interface called the "input file". Page 41 provides a very simple overview of the input file [98]. As seen in the sample input file, it consists of several sections, or "namelists", defined between the "&" and "\" characters together with some mandatory and optional "cards" mentioned at the end. Namelists are a standard input construct in Fortran 90. There are recommended default settings for all the parameters used for building up different namelists; however the user may also specify the value of an input variable when the default value is inadequate. The "cards" are specific to the QE code and are always required to specify a system under study [99]. Both of these can be fine-tuned by the user according to the area of focus. Only the important parameters that were changed during the runs will be discussed. It is to be noted here that systematic convergence testing is absolutely essential in choosing certain parameters of the input file to achieve a balance between computational efficiency and accuracy.



An input file has the following structure:

```
& CONTROL
  Control the flux of calculation and the amount of I/O
  on the disk and screen.
/
&SYSTEM
This section specifies with the unit cell of the system under
 consideration.
1
&ELECTRONS
This block control the algorithms used to obtain self-consistent
solution of the KS equations for electrons.
1
[ &IONS
 This section is optional and used for geometric optimization.
  It is ignored otherwise.
 / ]
[ &CELL
  The section, ignored otherwisee, is used when unit cell volume
  and shape needs to be optimized.
 / ]
The following are the mandatory "cards" to be included in the input file.
```

```
ATOMIC_SPECIES
```

Names of different atomic species, their atomic masses and the corresponding pseudo potential files.

```
ATOMIC_POSITIONS
```

Positions of different atoms in the unit cell.

K_POINTS

Coordinates and weights of k-points for BZ integration can be chosen in a number of ways.

Before describing the computational details, it is helpful to know that the systems investigated in this work mainly include pure orthorhombic KNbO₃ as well as KNbO₃ with substitutional impurities at the Nb and K sites. The impurities focussed upon in this dissertation, titanium (Ti), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co) nickel (Ni) and silver (Ag), are either experimentally observed or potentially relevant. Now, QE invokes three-dimensional periodic boundary conditions. Under such circumstances, the distance between the dopant and its periodic image, in a 10-atom conventional unit cell of pure KNbO₃, is such that their effects are not entirely localized, and the substitutional impurity does not behave like an isolated point defect as desired. This can be mitigated if we move to larger unit cells or supercells so that there is a reduced interaction between a given dopant and it neighboring periodic images. However, one also has to take into account the increased computational load that this strategy imposes. Calculations reveal that a $2 \times 2 \times 2$ supercell with 80 atoms is an optimal candidate for unit cell given our computational resources. So for all the calculations presented here, unless otherwise specified, a $2 \times 2 \times 2$ supercell has been used.

The first input parameter of relevance is CALCULATION. It determines the type of task to be performed. The options scf (self-consistent field), relax (structural optimization), nscf (non-scf) and bands were used for the analysis of different systems studied in this dissertation. For a SCF or total-energy calculation, the KS equations are solved iteratively as described previously in Fig. 2.3. A self-consistent value for the total energy is obtained after several electronic iterations whenever the difference in energy from two consecutive steps is less than the threshold value specified by the input variable CONV_THR, which was set to either 1.0×10^{-8} Ry or 1.0×10^{-6} Ry in this work, depending on the size of the unit cell under study.

Following a total energy calculation for a specific ionic configuration, the forces on each atom and the stress tensor for the unit cell can be computed. Those quantities can be used to determine the lowest energy crystal structure. A system is considered to be geometrically optimized if both the following conditions are met simultaneously: the total energy change between two scf steps is less than the specified tolerance value of ETOT_CONV_THR, which was set at 0.5×10^{-4} Ry here, and all the components of force are less than the FORC_CONV_THR value of 0.5×10^{-3} Ry/Bohr. If these structural convergence criteria are not met, the atoms are moved in a direction determined by the forces. Such atomic iterations, interleaved with electronic iterations, are repeated until the ground-state structure with vanishing forces is obtained. During the structural optimization, all atoms are allowed to relax to their equilibrium positions, within the constraints of the system symmetries. During this structural relaxation, some selected atom (or symmetrically equivalent atoms) are held fixed in space. The cell volume or shape remains constant during all our runs, as it would be for real systems with impurity concentration of 1-2 % ¹. The specific algorithm used for ionic minimization can be specified by ION_DYNAMICS tag. We have used the Broyden-Fletcher-Goldfarb-Shanno method, which is a qausi-Newton approach [100–103].

Another computational parameter of importance is ECUTWFC, which is the kinetic energy cutoff for the wave functions and is expressed in Ry. An advantage of using ultrasoft over norm-conserving pseudopotentials is that one can work with a lower cutoff. This is desirable from the computational perspective because it retains high accuracy at reduced computational cost. An input variable that goes hand in hand with ECUTWFC is ECUTRHO, which is the kinetic energy cutoff for charge density and potential which is usually set at 4 to 12 times ECUTWFC. Mandatory convergence testing reveals that the optional cutoff for the material studied here is higher than the highest recommended cutoffs of its individual constituent elements. The well-converged plane wave basis energy cutoff and charge cutoff used in this work are 50 Ry and 600 Ry respectively.

To simulate the ion-core interaction with valence electrons, we have used ultrasoft pseudopotentials supplied in the Quantum Espresso package [97] as well as the pseudopo-

¹The theoretical concentration used in the work presented here is 6.25% as discussed later on page 59.

tential vault [104]. The Vanderbilt recipe [94] was followed for all the elements except for K where the RRKJUS parameterization [105] was the only option available. The valence and the semi-core states that were explicitly treated as valence include the K-3s -3p and -4s; Nb-3s -3p, -3d, -4s and -4p; O-2s and -2p states. Hence, the K atom is treated with 9 electrons, Nb with 13 electrons and O with 6 electrons. The valence states of the different impurities at the A- and B- sites of KNbO₃ are given in Table 3.1. Ultrasoft pseudopotentails have the advantage of being able to use a smaller cutoff energy, which is desirable for computational efficiencies. Additionally, relaxing the norm-conserving condition in ultrasoft pseudopotentials helps in more effectively pseudizing the 3-d wave functions of the third row transition elements, which constitute the majority of the impurities studied. The exchange-correlation effects were implemented following Perdew-Burke-Ernzerhof parametrization for the Generalized Gradient Approximation [83] (chapter 4) and the Perdew-Zunger parametrization [106] for the Local Density Approximations (chapter 5).

The k-points required for sampling the BZ of a given crystal structure are generated using the K_POINTS card. For the structural optimization related calculations, all the kpoints are obtained with the **automatic** option. Under such circumstances it is sufficient to specify the Monkhorst-Pack [91] sampling grid only. Additionally, It must be ensured that the total energy of a system is satisfactorily converged with respect to the number of k-points determined by the dimension of the grid. Pure KNbO₃ is an insulator. The requirement of supercell in real space, corresponding to a smaller Brillouin zone (BZ) in reciprocal space, makes the calculations on a relatively smaller k-points grid reliable as far as accuracy is concerned. The 3d transition elements, treated as impurities in KNbO₃:Im (Im: impurity), on the other hand, imparts a small but non-negligible metallic character (*i.e.*, partially filled bands) to the pristine host material. Metals require denser grids compared to the insulators to capture the details of the Fermi surface [92] accurately.

Impurity	Total Number	Reference
Atom	of Valence	Pseudopotential
	Electrons	Configuration
Ti	12	$3s^23p^64s^23d^1$
V	13	$3s^23p^64s^23d^34p^0$
Cr	14	$3s^23p^64s^14p^03d^5$
Mn	15	$3s^23p^64s^24p^03d^5$
Fe	16	$3s^23p^63d^{6.5}4s^14p^0$
Со	9	$4s^13d^8$
Ni	10	$4s^{1}3d^{9}$
Ag	11	$6s^16p^{0.5}5d^{9.5}$

Table 3.1: Important pseudopotential parameters for different atoms used later as substitutional impurities in $KNbO_3$: Core charges and reference configurations

It was found that good convergence was achieved with a $4 \times 4 \times 4$ Monkhorst-Pack BZ sampling grid for the structural relaxation calculations with $2 \times 2 \times 2$ supercell.

The final set of option tags is related to the occupation of bands by electrons. For the ground state in non-magnetic insulators and semiconductors, the bands are filled with two electrons of opposite spins, at each k-point, from the lowest energy up until all the electrons are used up. Under such circumstances the top of the highest filled band is referred to as the Fermi level, following which there is a gap of forbidden energies and finally empty energy levels. For all our calculations involving bulk KNbO₃, an insulator, the input variable OCCUPATIONS was set at fixed. This option reliably recreates the "band gap" picture. In metals, on the other hand, the spins of the electrons become more important, and we need to switch to spin-polarized calculations. This is effected in Quantum Espresso by setting NSPIN to a value of 2, *i.e.*, a spin-polarized calculation which effectively doubles the number of k-points considered as compared to the non-spinpolarized case in insulators. As a result the calculations take significantly longer. In deciding the appropriate value for the variable OCCUPATIONS in metal-like situations, it is to be noted that metals are characterized by the absence of a band gap at the Fermi level. Thus occupied and unoccupied levels are arbitrarily close in energy. Evaluating quantities like charge density involves summation over the user-specified discrete set of k- points. As the electron occupancies jump from one to zero (a step function in the summation) in a given band, as k-points are scanned from to another, the highest occupied bands can exit or enter the sum as the eigenvalues and hence the Fermi level, adjusts from one electronic iteration to the next. This leads to an unphysical, macroscopic charge redistribution or "charge sloshing" due to microscopic energy changes. So when dopants like Ti, V, Cr, Mn, Fe, Co, Ni, Ag and Cu are included in the host material, this unstable situation hinders the convergence. Slower convergence and additional k-points makes the calculations computationally more expensive. If the step function is replaced with a smoother function, *i.e.*, a continuous distribution function, faster convergence can be achieved with minimal sacrifice in accuracy. Physically this would amount to allowing part of an electron in one band and the remainder in another. This partial electron occupancy is referred to as "electron smearing". While conceptually this is unphysical, it is a computationally practical solution to an otherwise significantly slow convergence problem. The parameter OCCUPATIONS is then set at "smearing" while the Gaussian scheme is chosen for the SMEARING tag. The smearing width is controlled by the DEGAUSS variable, which was set to 0.02 Ry in this work.

The majority of our calculations focussed on adding substitutional impurities to a $2 \times 2 \times 2$ supercell of the host material. A convenient strategy for testing convergence in such a scenario is to start with a $1 \times 1 \times 1$ unit cell of the pure material where the atoms are arranged in their experimentally verified positions. Then the impurity atom is added under the charge neutrality conditions specified in Section 4.2. ECUTWFC convergence is tested in this sample structure. This is followed by a subsequent convergence test with different combinations of k-point grid and smearing width using the converged value of ECUTWFC found in the previous step. It is to be noted here that k-point and ECUTWFC convergences are independent of each other.

Band structure calculations are central to the work presented here. This requires calculation of energy eigenvalues at user specified k-points along a certain path in the BZ, usually along high symmetry directions. This calls for non-scf calculations and is invoked by the **bands** option for CALCULATION input variable. These non-scf calculations can only be done after the scf potential of the system under consideration has been obtained. Now the K_POINTS card no longer uses the automatic option, and all the k-points are entered manually.

Other non-scf calculations relevant to this work include density of states (DOS) and the projected density of states (pDOS) calculations. Unlike quantities such as charge density that are derived from scf calculations by integrating over the entire BZ, calculation of DOS demands integration over different constant energy surfaces, $E(\mathbf{k})$, inside the BZ,

as seen in (A.17). This type of calculation requires a much denser k-point grid than is needed for self-consistency, in order to make the best approximation for the constantenergy surfaces. This is taken care of by using the "automatic" option for K_POINTS set at $8\times8\times8$. With nscf chosen as the task to be performed by the input variable CALCULATION, the linear interpolation tetrahedra method is used in conjunction with OCCUPATIONS to approximate the different constant-energy surfaces. Suitable post-processing tools like dos.x and projwfc.x are used subsequently to extract the desired information.

3.2 Preliminary Calculations

In this section, preliminary calculations on pure KNbO₃ are presented. This is of importance because the comparison between the readily available experimental data on pure KNbO₃, and the theoretical data from this work, helps to determine the suitability of the different pseudopotentials used henceforth. Additionally, the relaxed unit cell of undoped KNbO₃ from this work can be used to set the initial atomic configuration in the supercells used as basic unit cells in the subsequent chapters and obtained by expanding the pure conventional orthorhombic unit cell two fold along the $\langle 100 \rangle$, $\langle 010 \rangle$ and $\langle 001 \rangle$ directions. These atomic positions are subsequently relaxed to their optimum values.

KNbO₃ has a high symmetry cubic phase (space group Pm3m) and is paraelectric in nature at temperatures above 435 °C. In this phase KNbO₃ K and Nb atoms are located at the corner and body center respectively, and the O atoms are located at the face centers of the unit cell. As the temperature is lowered, zone center and zone boundary distortions along $\langle 100 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$ directions produces three successive phase transitions: tetragonal (P4mm) below 435 °C, orthorhombic (Amm2) below 235 °C and rhombohedral (R3m) below -10 °C. Each of these reduced-symmetry phases is ferroelectric, with the Nb atom at the body center is displaced with respect to the O octahedral cage surrounding it. This yields a non-zero spontaneous electric polarization that can be reversed with the application of external electric fields. The unit cells of these different phases are shown in Fig. 1.2, and their relevant structural parameters, including the lattice constants as well as the magnitude and direction of the displacements of the different atoms, calculated in this work, are reported in Table 3.2. The Δ symbols in Table 3.2, refer to the net displacement expressed in terms of lattice coordinates of the associated atom from its corresponding position in the cubic aristotype, along the direction specified in the subscript of Δ . In the experiments, the assumption that the center of mass cannot move during a phase transition fixes the displacements of Nb atom(s) in terms of the other atoms. This is incorporated in the present theoretical calculations by keeping the Nb atom /atoms in each unit cell fixed in position during structural relaxation. Hence the Δ (Nb) are reported to be zero. The three oxygen atoms at the face centers of the high symmetry cubic unit cell, which are equivalent in the cubic phase, are distinguished as O_I, O_{II} and O_{III}, as they will not be identical in the subsequent lower symmetry phases. The data for the orthorhombic phase which is important to our work, is reported separately in Table 3.3.

The conventional unit cell of the orthorhombic phase has 10 atoms (two KNbO₃ formula units) and is denoted as the $1 \times 1 \times 1$ base cell in upcoming discussions of larger super cells. The lattice coordinates of the atoms in this cell are given as:

- K at $[0, 0, \Delta_z(K)]$ and $[0, 0.5, 0.5 + \Delta_z(K)]$
- Nb at $[0.5, 0, 0.5 + \Delta_z(Nb)]$ and $[0.5, 0.5, \Delta_z(Nb)]$
- O_{I} at $[0, 0, 0.5 + \Delta_{z}(O_{I})]$ and $[0, 0.5, \Delta_{z}(O_{I})]$

$$O_{\text{II}} \text{ at } [0.5, 0.25 + \Delta_y(O_{\text{II}}), 0.25 + \Delta_z(O_{\text{II}})] \text{ and } [0.5, 0.75 + \Delta_y(O_{\text{II}}), 0.75 + \Delta_z(O_{\text{II}})]$$
$$O_{\text{III}} \text{ at } [0.5, 0.75 - \Delta_y(O_{\text{II}}), 0.25 + \Delta_z(O_{\text{II}})] \text{ and } [0.5, 0.25 - \Delta_y(O_{\text{II}}), 0.75 + \Delta_z(O_{\text{II}})]$$

This room temperature phase is a result of zone boundary distortions of the high symmetry cubic unit cell, leading to cell doubling. Following the notation used by Hewat [14], the three optimized lattice vectors for the pure orthorhombic $1 \times 1 \times 1$ KNbO₃ cell, computed here using the DFT-based QE code, are a = 3.942Å along $\langle 010 \rangle$, b = 5.614Å along $\langle \overline{1}01 \rangle$ and c = 5.619Å along $\langle 101 \rangle$, where vectors are written relative to the high symmetry cubic phase (see Table 3.3). The spontaneous polarization is along the positive $\langle 010 \rangle$ direction. By comparing theoretical and experimental results in Table 3.3, it can be seen that our calculations reproduced the relative magnitudes of the displacement of O_I and O_{II} atoms, along the z direction, fairly well with the y displacement of O_{II} being reduced in magnitude compared to the experimental estimates [14]. However it is to be noted that the magnitude of this displacement is itself very small, as pointed out by Postnikov and Bostel [107].

The model for the undoped host material, KNbO₃, used in the calculations presented here, is obtained by expanding the pure, orthorhombic, conventional $1 \times 1 \times 1$ unit cell twofold along the $\langle 100 \rangle$, $\langle 010 \rangle$ and $\langle 001 \rangle$ directions and therefore is referred to as a $2 \times 2 \times 2$ supercell. The calculated band structure, total density of states and projected density of states of a pure $2 \times 2 \times 2$ KNbO₃ supercell are displayed in Fig. 3.2(a) and (b) respectively. These calculations used lattice constants a = 7.88 Å, b = 11.23 Å and c = 11.24 Å. Band structure calculations involve solving KS equations for every k-point chosen by the user along some path in the first BZ of the crystal using the scf potential already determined. Here, the k-points are chosen so as to include several high symmetry points. The path followed in this calculation starts from Γ and then goes to X to R to Y to Z and finally to S. It is indicted in the x-axis of the Fig. 3.2a(i). It is to be noted that only the special high symmetry k-points are indicated in the plot axis, although a total of 51 points were used for the actual calculation.

Since pure $KNbO_3$ is a non-magnetic insulator, it was possible to carry out non-spinpolarized calculations. This was also verified by spin-polarized test calculations yielding identical spin-up and spin-down KS eigenvalue distributions. It can be seen from Fig. 3.2a that the top of the valence band has been chosen as the zero of energy. This is

Dhaaa	Structural Parameters	Structural Parameters [14]
P hase	(Theoretical)	(Experimental)
cubic	$a=4.025~{\rm \AA}$	$a=4.000~{\rm \AA}$
	$a=3.956~{\rm \AA}$	$a=3.997~{\rm \AA}$
	c/a = 1.0118	c/a = 1.0165
Tetragonal	$\Delta_z(\mathbf{K}) = 0.01176$	$\Delta_z({\rm K}) = 0.023 \pm 10$
	$\Delta({\rm Nb}) = 0.0$	$\Delta(\rm Nb) = 0.0$
	$\Delta_z(\mathcal{O}_{\mathcal{I}}) = 0.029$	$\Delta_z(\mathrm{O_I}) = 0.040 \pm 3$
	$\Delta_z(\mathcal{O}_{\mathrm{II}}) = 0.031$	$\Delta_z(\mathcal{O}_{\mathrm{II}}) = 0.042 \pm 3$
	$\Delta_z(\mathcal{O}_{\mathrm{III}}) = \Delta_z(\mathcal{O}_{\mathrm{II}})$	$\Delta_z(\mathcal{O}_{\mathrm{III}}) = \Delta_z(\mathcal{O}_{\mathrm{II}})$
Rhombohedral	$a=3.970~{\rm \AA}$	$a=4.016~{\rm \AA}$
	$\Delta_z(\mathbf{K}) = 0.0080$	$\Delta_z(\mathbf{K}) = 0.0112 \pm 25$
	$\Delta(\rm Nb) = 0.0$	$\Delta(\rm Nb) = 0.0$
	$\Delta_x(\mathrm{O_I}) = 0.0180$	$\Delta_x(\mathrm{O_I}) = 0.0295 \pm 5$
	$\Delta_z(\mathcal{O}_{\mathrm{II}}) = 0.0198$	$\Delta_z(\mathrm{O_{II}}) = 0.0308 \pm 7$

Table 3.2: Comparison of the experimental and the theoretical (present work) structural parameters of the cubic, tetragonal and rhombohedral phases of KNbO_3 .

also the location of the Fermi level, E_F . Therefore, the valence band here is completely full, accommodating all 640 valence electrons, two per level, while the conduction band is empty. Combining the k-resolved band structure information in reciprocal space, (Fig. 3.2a(i)), with the DOS plots which portrays the distribution of all electronic states with energy in the unit cell (Fig.3.2a(ii)), helps one to gain comprehensive knowledge about the different eigenstates of KNbO₃ and its occupancies. It can also be noted that the band structure is very similar to BaTiO₃ [108], which undergoes the same sequence of phase transitions as KNbO₃. The band gap values reported in the literature are usually with respect to a $1\times1\times1$ system. In a separate band structure calculation in a $1\times1\times1$ cell, the difference between the top of the valence band (VB) and the bottom of the conduction band (CB) is found to be 1.77 eV as compared to the theoretical value of 1.4 eV in Ref. [109]. Experimentaly measured values are 3.79 eV (determined from Faraday

ח	Structural Parameters	Structural Parameters [14]
Phase	(Theoretical)	(Experimental)
	$a=3.950~{\rm \AA}$	$a=3.971~{\rm \AA}$
	b/a = 1.424	b/a = 1.435
	c/a = 1.426	c/a = 1.441
	$\Delta_z({\rm K}) = 0.009$	$\Delta_z(\mathbf{K}) = 0.017 \pm 1$
Orthorhombic	$\Delta_z(\mathrm{Nb}) = 0.0$	$\Delta_z(\mathrm{Nb}) = 0.0$
	$\Delta_z(\mathcal{O}_{\mathrm{I}}) = 0.025$	$\Delta_z(\mathcal{O}_{\mathcal{I}}) = 0.021 \pm 2$
	$\Delta_z(\mathcal{O}_{\mathrm{II}}) = 0.022$	$\Delta_z(\mathrm{O_{II}}) = 0.035 \pm 2$
	$\Delta_y(\mathcal{O}_{\mathrm{II}}) = -0.0003$	$\Delta_y(\mathrm{O_{II}}) = 0.004 \pm 2$

Table 3.3: Comparison of the experimental and the theoretical (present work) structural parameters of the orthorhombic phase of $KNbO_3$.

rotation at 77K [110]) and approximately 3.3 eV, as extrapolated to 0 K from the high temperature cubic phase [15]. This discrepancy between the calculated and experimental values of the band gap can be attributed to the fact that Kohn-Sham DFT is known to significantly underestimate band gap energies, up to 50%, due to self interaction error and the absence of a derivative discontinuity in the exchange-correlation potential [82].

A projection analysis onto different pseudized atomic wave functions is shown in Fig. 3.2b. It should be noted that the bottom of the CB mostly comprises niobium-4d states while the top of the VB gets its features from the oxygen 2p states. The VB section from -2 eV to about -3 eV exhibits strong hybridization between the oxygen-2p and niobium-4d orbitals, a characteristic feature of the perovskites. The contribution of the alkali metal cation, potassium, is negligible; potassium 3p states do not hybridize significantly with the oxygen-2p states. If the present calculation window is extended to include all the lower lying eigenvalues, it would be possible to see many almost flat bands corresponding to the semi-core states of the different atoms deep in the VB. This flatness in energy reveals the atomic-like nature of these states and verifies that they do not directly participate in bonding.



(a) (i) Band Structure (ii) Total density of states of the $2 \times 2 \times 2$ KNbO₃ supercell.



(b) (i) Potassium (ii) Niobium and (iii) Oxygen Projected Density of States

Figure 3.2: Band strucure, density of states and projected density of states of the $2 \times 2 \times 2$ supercell of pure KNbO₃.

Chapter 4

Trends in $KNbO_3$ Electronic Structure with Various 3d Transition Metal Dopant Species

4.1 Background

Dopants: Photorefractives are electro-optic and photoconductive materials as seen in chapter 1. In response to an inhomogeneous illumination pattern of adequate wavelength and intensity incident on such a material, the electrons (holes) are photo-excited from localized photoactive centers, like donors (acceptors) in the band gap, to the conduction band (valence band) of the material. In these extended states, the diffusion or drift (in the presence of an external field) causes the quasi-free charge carriers to move towards darker regions where, they are eventually trapped by the empty localized trap levels, re-excited and re-trapped again. This leads to charge carriers being progressively accumulated in the darker regions leaving, behind uncompensated oppositely charged brighter regions. Consequently, a separation of charges, and hence a spatially modulated space charge field, develops that lags behind the incident interference fringes by a phase difference.

Finally, crystals with the linear electrooptic properties respond to this field in the form of a modulated refractive index pattern. Thus, the presence of localized defect-states in the band gap is crucial to the formation of the space-charge field which is at the core of photorefractive properties. This has been confirmed when hydrothermally grown, almost perfect Bi₁₂SiO₂ crystals were found to be devoid of any photochromic and photorefractive properties [111, 112]. On the other hand, crystals containing defects, grown using the same raw chemicals, exhibited photorefractive effects. The formal definition of point defects classify them as any point like deviation from perfect crystalline order that breaks the translational symmetry of a crystal. Point defects can be of the following types: (i) intrinsic, produced during the growth process such as Schottky defects (vacancies), Frenkel defects (vacancy-interstitial pairs), and antisite defects, (ii) extrinsic, arising from substitutional or interstitial impurities or (iii) a combination of both, as in the work presented here.

In a real material, the photorefractive process is an immensely complicated phenomenon that involves interplay of different dynamical subsystems at multiple time scales. The mathematical model trying to describe the actual photorefractive process has to consider the coexistence of many factors, including multiple valence states of single (or more) dopants, shallow and deep traps, electron-hole competition to name a few. One has to resort to considerable simplifications to obtain even a solvable analytical model. This theoretical work investigates the effect on the electronic structure of the photorefractive material KNbO₃ when doped with a +3 valence, 3d transition-metal as a function of dopant species *i.e.*, Cr, Mn, Fe, Co and Ni. This study can be regarded as a first step towards unraveling the complex, multiple-mechanism dynamics in real photorefractive samples. Better theoretical understanding of photorefractive models will contribute towards the eventual aim of deducing "ideal" donor-acceptor combinations to maximize several important photorefractive performance parameters such as beam-coupling coefficient.

4.2 Setting Up the Theoretical Model

A- or B-site substitution: The photorefractive effect in nominally undoped KNbO₃ is caused by iron impurities that occur in the niobium pentoxide component used during the growth of the pure crystals [49]. The usual way to modify the pure host materials for enhanced photorefractive performance is to dope them with transition metals such as Fe. There are two possible ways of incorporating Fe, substitutionally into the host lattice: A-site substitution (*i.e.*, substituting for a K atom) and B-site substitution (*i.e.*, substituting for a Nb atom). Data from Electron paramagnetic resonance (EPR) experiments [64–66] show that the angular variation of Fe³⁺ lines can be well explained by a model in which Fe⁺³ substitutes for a Nb⁺⁵ ion. One can also arrive at the same conclusion of most likely candidate for substitution by comparing the ionic radii of the different species involved. As indicated in Table 4.1 the radii of Fe³⁺ and Nb⁵⁺ are comparable. The choice of B-site substitution, followed in the present work, is also based on the optimum size of the unit cell that plays a major role in determining the computational load. This is explained in detail in the following Supercells section.

Supercells: The methodology described in Chapter 2 required a periodic structure. Therefore, instead of modeling a single and isolated defect, the calculations in this work, must model a periodic array of defects. Doping, on the other hand, should introduce localized effects ideally, so that the intrinsic properties of the bulk, sufficiently away from the dopant, do not change appreciably. So doping in KNbO₃ cannot be simulated with desired effects in the conventional 10-atom orthohrombic unit cell as impurities would interact strongly with their periodic images. Hence, bigger unit cells or supercells are required. To illustrate the situation, let us consider a 10 atom (*i.e.*, 2 formula units) orthorhombic unit cell with dimensions a, b and c along directions $\langle 100 \rangle$, $\langle 010 \rangle$, and $\langle 001 \rangle$, respectively, such that c > b > a. If such a conventional unit cell, or a $1 \times 1 \times 1$ supercell as we may call it, is doped by replacing a Nb atom with an Fe atom, the distance

Element	Valence State	Ionic Radius (Å) [113]
К	1+	1.51
Nb	5+	0.64
Ti	3+	0.67
V	3+	0.64
Cr	3+	0.62
Mn	3+	0.65
Fe	3+	0.65
Со	3+	0.61
Ni	3+	0.60

Table 4.1: Comparison of the ionic radii of K, Nb and the different 3d transition metals used as substitutional impurities.

between the dopant and its nearest neighbor is a. If now the unit cell is doubled along $\langle 100 \rangle$ direction to accommodate 20 atoms (*i.e.*, 4 formula units), at the expense of the computational load being quadrupled, the shortest distance between the Fe impurity and its periodic image increases to b, as indicated in Fig.4.1a. Subsequent calculations with this $2 \times 1 \times 1$ super cell showed that the doping effects were highly non-localized. Hence a bigger unit cell is necessary to ensure sufficiently reduced interaction between the impurity and its periodic images. It is to be noted that the computation becomes expensive with

the system size. In an effort to maintain a balance between computational efficiency and doping concentration, a $2 \times 2 \times 2$ super cell (Fig.4.1b) with 80 atoms (*i.e.*, 16 formula units) is chosen as the structural model for the investigations of defects and impurities in this chapter. The resulting distance between a defect and its nearest periodic neighbor is now 2b. This corresponds to a theoretical doping concentration of 6.25%, still well above the experimentally realized dopant concentration of ≈ 0.1 %, but the best that is presently computationally feasible.

Charge Compensation: In a perfectly ionic KNbO₃ crystal, the atoms are in the ionic states K^{1+} , Nb⁵⁺ and O²⁻, and thus the question of charge neutrality upon doping with impurity ions needs to be addressed. Iron can exist in a +2 , +3 or +4 stable oxidation states. EPR experiments [47, 114] have verified stable Fe⁺³ in KNbO₃. Fe⁺² has also been observed in n-type KNbO₃ [48, 114]. Though there is no direct experimental data regarding the thermodynamic stability of Fe⁺⁴, its presence has been observed in SrTiO₃ and BaTiO₃. For the work presented here and in the following chapters, Fe is forced into a +3 oxidation state by removing an oxygen.

Theoretical calculations indicate that an energetically favorable way to maintain charge neutrality if one of the Nb⁵⁺ ions is replaced by a Fe³⁺ ion is to remove one O²⁻ ion near the impurity, thereby resulting in a impurity-vacancy complex $Fe_{Nb}^{"}$ - $V_{O}^{"}$ (Kröger-Vink notation is used to represent the defect pair). The oxygen vacancy was chosen to lie in the first coordination shell of the iron substitutional impurity. The model presented here, then, for a KNbO₃ crystal with a Fe_{Nb}["] - $V_{O}^{"}$ defect pair consists of a 2×2×2 supercell with one Nb atom replaced by Fe and one coordinating O atom removed, yielding 79 atoms per supercell.



(a) A collection of $2 \times 1 \times 1$ supercells with one Fe-O vacancy pair/cell are shown. Four such cells are indicated with blue outlines. The distance between a Fe atom and its nearest neighbors is b.



(b) A collection of $2 \times 2 \times 2$ supercells with one Fe-O vacancy pair/cell are shown. Two such cells are indicated with blue outlines. The distance between a Fe atom and its nearest neighbors is 2a.

Figure 4.1: Schematic representation of $2 \times 1 \times 1$ and $2 \times 2 \times 2$ super cells.
4.3 Expected Doping Trends

The *d* electrons of transition metals play a very important role in determining the material properties of pure and doped KNbO₃. The 4*d* orbitals of Nb mix with the oxygen 2p orbitals to form the highest lying valence bands of KNbO₃ as seen in Fig. 3.2. For an isolated transition-metal impurity, the band picture is inappropriate, and instead the impurity is viewed as an isolated ion in the fixed crystal field of the surrounding lattice. It is then appropriate to consider competing effects on the atomic energy levels of the impurity. In this model, the impurity is not perfectly isolated, but rather exists as a periodic array of widely spaced impurities. Therefore, residual band-like behavior is expected, but the atomic nature of the impurity bands should still be recognizable.For 3*d* impurities, the main competing effects that need to be considered in understanding trends in impurity energy levels, are crystal-field splitting and exchange splitting of the atomic 3*d*-derived states.

4.3.1 Crystal Field Splitting

In an independent-electron picture, the d orbitals of a transition metal ion, in free space, are five-fold degenerate and can accommodate a maximum of ten electrons due to spin degeneracy. When the transition-metal atom is placed at the center of a perfect octahedron with O^{2-} ions at the vertices, valence d electrons experience different repulsive forces depending on the shape of the orbitals they occupy. The d_{z^2} and $d_{x^2-y^2}$ orbitals have lobes that point directly towards the negative point charges on the O^{2-} anion as seen in Fig. 4.2. So the electrons in those states experience a strong Coulombic repulsion. For the d_{xy} , d_{yz} or d_{xz} orbitals, however, the O^{2-} ions lie on the nodal planes, so that electrons in these orbitals naturally stay away from the anions. As a result, these states are energetically lower compared to d_{z^2} or $d_{x^2-y^2}$. Thus the five degenerate levels split due to the octahedral field into two sets: the higher lying doubly degenerate e_g states



Figure 4.2: Schematic representation of splitting of *d*-orbitals of the transition metal ion in octahedral crystal field. The geometry of the three t_{2g} and e_g states are also shown on the right. For each orbital, the transition metal atom is at the center (not shown) surrounded by oxygen atom (shown as grey dots) located at the corners of the octahedra.

 $(d_{z^2} \text{ and } d_{x^2-y^2})$ and the lower lying triply degenerate t_{2g} s states (d_{xy}, d_{yz} and d_{xz}). The designations e_g and t_{2g} are traditional and derive from a symmetry analysis. This phenomenon is referred to as crystal-field splitting and the amount of splitting is denoted by Δ_{cf} . This parameter is found to decrease along the 3d row of the periodic table, going from left to right [115].

4.3.2 Exchange Splitting

We need to consider another phenomenon that breaks the degeneracy of the 3d states. In the absence of all electron-electron interactions, each orbital of a five-fold spin degenerate d state, accommodates two electrons, one spin-up and one spin-down; hence, a maximum of ten electrons can be accommodated each contributing the same energy. If Coulomb repulsion is then turned on, it becomes energetically more costly to have two electrons in the same d orbital than in different orbitals. The exchange interaction provides a symmetry constraint preventing electrons of like spins from achieving this high energy arrangement. Electrons of opposite spins have no such constraint. Therefore, the exchange interaction gives rise to an energetic preference for filling single-particle states of like spin (say, spin up) before beginning to fill states of the opposite spin (say, spin down). This energetic difference between spin-up and spin-down states is referred to as exchange splitting. When exchange splitting is taken into consideration, spin-degenerate d levels (the octahedron crystal field effect being neglected for the time being) split into two separate sets of five-fold degenerate spin orbitals. One spin-up electron can be placed in each of the lower-lying five levels while each of the higher lying five levels can accommodate one spin-down electron. All the lower lying spin-up states are filled up before filling up the energetically higher spin-down states. The energy difference between the spin-up and spin-down levels defines the exchange splitting energy Δ_{ex} which is interpreted as the energy required to flip the spin of an electron. Moving across the 3d row of the periodic table from Cr to Ni, it is known that Δ_{ex} first increases from Cr to Fe and then decreases from Fe to Ni [116].

4.3.3 Core Charge, $Z_{\rm eff}$

The atomic number of an element, Z, refers to its total nuclear charge in units of e. For the present purpose of examining impurity trends across the 3d row, however, it is more useful to define a core charge, $Z_{\text{eff}} = Z - 18$, where the 18 electrons that make up the closed-shell argon-like core are combined with the nucleus. In this admittedly oversimplified picture, the closed-shell core electrons maximally screen the nucleus, and the valence electrons feel a core charge of Z_{eff} . How is then increasing Z_{eff} expected to affect the energy of the 3d states when going across the 3d row? Following a Bohr-model argument, the energy of the 3d state (ignoring electron-electron interactions) should be proportional to $-Z_{\text{eff}}^2$. Therefore, as we move right across the 3d row from Cr, the valence electrons encounter an increasingly attractive core: Z_{eff} increases from 6 in Cr^{3+} to 7 in Mn^{4+} , 8 in Fe^{3+} , 8 in Co^{3+} and 9 in Ni^{3+} . Thus a higher value of Z_{eff} , equivalent to a more attractive core, more strongly pulls down the center of the 3*d*-derived levels of the transition metal impurity as we progress from Cr to the right. In the KS eigenvalue picture presented here, this trend with increasing Z_{eff} is reflected in a tighter binding, or downward migration, of the *d*-derived impurity energy levels from the conduction band of the host material through the band gap and eventually into the valence band as the impurity species go from the left end of the 3*d* row to the right end.

4.4 Results

In this study, we consider KNbO₃ with various 3*d* transition metals substitutional impurities on the Nb-site. The impurities are chosen considering the following: firstly, the size, or the ionic radius of the impurity should be comparable to the Nb⁵⁺ ion that it replaces (refer to Table 4.1) to avoid excessive strain in the doped crystals. Secondly, only impurities that exhibit a stable +3 oxidation state are considered in this work. To restore charge balance when a +3 impurity ion substitute for a Nb⁵⁺ ion, a nearest neighbor oxygen atom is removed to make a neutral vacancy, $V_{O}^{"}$.

The impurities chosen for this work are the transition metals Ti^{3+} , V^{3+} , Cr^{3+} , Mn^{3+} , Fe^{3+} , Co^{3+} and Ni^{3+} . All calculations are spin polarized in contrast to the pure host study as shown in Fig. 3.2. The calculated electronic properties such as band structure and the projected density of states (pDOS) of the KNbO₃ crystal with different impurities are presented in Figs. 4.3 - 4.6. The data related to the substitutional impurities Ti and V are presented in Fig. 4.3. Fig. 4.4 includes results related to Cr^{3+} , Mn^{3+} and Fe^{3+} impurities and Fig. 4.5 displays the characteristic features of Co^{3+} and Ni^{3+} impurities. Fe^{3+} has been included in Fig. 4.5 for the sake of continuity. For comparing the important features of impurity doping and identifying trends, the band structures and total DOS of spin-up

and spin-down states, for all impurities, from Cr to Ni, are presented in the Fig. 4.6. It is also to be noted that, for the sake of clarity, the bands contributed by the pure host is faded in the background and only the impurity levels are highlighted and labelled. The zero of energy, in all these plots, is adjusted with the top of the valence band of the pure host KNbO₃, and the Fermi level, E_F , is denoted by a red dashed line.

Before presenting the results related to each dopant type, a few remarks, in general, about the impurity levels appearing in the band gap of the doped structure are in order: if theoretical impurity concentrations were comparable to those of experiments, the impurity bands would have been quite flat, corresponding to highly localized states and signifying minimum dopant-dopant interaction. In the present study, a fair amount of residual dispersion in some of the impurity bands, owing to comparatively high theoretical doping concentration, is observed. Additionally, the O-octahedron surrounding the impurity is imperfect. Not only is it distorted by virtue of the orthorhombic symmetry of the crystal lattice, but it also contains the charge-compensating oxygen vacancy. As a result the crystal-field split levels are not sets of precisely doubly or triply degenerate levels but groups of two and three very closely lying levels that are not perfectly degenerate¹.

KNbO₃:**Ti** and **KNbO**₃:**V**: The band structures of KNbO₃:Ti and KNbO₃:V crystals resemble that of the undoped pure host with spin-up and down states being indistinguishable and no impurity levels in the band gap. These systems differ from pure KNbO₃ in that the Fermi level, E_F , in these doped systems, pass through the conduction band (CB) (as seen in Fig. 4.3). It is found that the valence band (VB), in KNbO₃:Ti, is completely full with one electron in the CB. It is to be noted that the Ti dopant, at a Nb⁵⁺-site, was forced into a +3 oxidation state by removing an oxygen atom. The two electrons thus released in the process, was expected to bind to the dopant atom thereby rendering it a +3 oxidation state. The calculations imply that an oxidation state of +4 is more

¹It is to be noted that the band structures, total DOS and the complete pDOS corresponding to the individual substitutional impurity systems are presented in Appendix B.

favorable for Ti atom than an oxidation state of +3 and the extra electron that did not bind to Ti is now free in the CB. A similar situation prevails in KNbO₃:V where none of the two electrons released by oxygen-vacancy bound to the dopant. The vanadium substitutional impurity, thus, remains in a +5 oxidation star while the two free electrons are accommodated in the CB.

 $KNbO_3:Cr:$ A set of three t_{2g} -derived levels can be identified in the gap near the edge



Figure 4.3: Spin-up (\uparrow) and spin-down (\downarrow) band structures and projected DOS of KNbO₃:X³⁺ where X = Ti and V. In each case the impurity substitutes for a Nb⁵⁺ ion, with a charge-compensating oxygen vacancy in the coordinating octahedron.

of the conduction band in the spin-up configuration as shown in the Cr-labelled column in the Fig. 4.4. The e_g -derived levels are higher up in the conduction band beyond our calculation window. The location of the Fermi level is such that all the three t_{2g} -derived levels are fully occupied. The corresponding pDOS plots indicate these impurity levels are entirely contributed by impurity Cr-*d* states. The band structure for the spin-down configuration (Fig. 4.4) shows that the impurity bands are higher up in the CB and do not appear in the band gap. As a result, the total magnetization, M, predicted by the firstprinciples calculations in this chapter, is $3\mu_B$ /cell. The spin density is localized around the impurity and corresponds to the difference in occupied \uparrow and \downarrow impurity 3d states. **KNbO**₃:**Mn**: For spin-up states of Mn-doped KNbO₃, we can see, in Fig. 4.4 a flat e_g -derived level in the middle of the forbidden energy gap. The group of three t_{2g} -derived levels lie lower in the gap, below close to the top of the valence band. All the four impurity levels are fully occupied and are derived from Mn-*d* orbitals without any involvement of Nb-*d* states. Additionally, spin-down configuration in Fig. 4.4 shows that, like Cr, there are no impurity levels in the band gap. Here, M is 4 μ_B /cell.

KNbO₃:**Fe**: For the iron impurity, as seen in the rightmost panel of Fig. 4.4, the spin-up t_{2g} states have left the band gap and are now within the valence band, preventing them from being identified separately. The spin-up pair of e_g -derived levels have fully emerged from the conduction band and are now entirely visible in the band gap. These five levels are fully occupied as can be verified from their position below the Fermi level. For the spin-down eigenstates, we can identify the group of three t_{2g} -derived states at the edge of the conduction band. But these levels are unoccupied. As a result, the predicted magnetization, M, is 5 μ_B /cell.

KNbO₃:**Co**: The calculated electronic structure of KNbO₃:Co is shown in Fig. 4.5. Here, as in KNbO₃:Fe, the three spin-up t_{2g} -derived levels are in the valence band now and are fully occupied. One of the e_g -derived levels is below the E_F and hence occupied. The other e_g level is empty. Fig. 4.5, corresponding to spin-down states, indicates that the group of three t_{2g} -derived levels, in this case is partially occupied yielding a total magnetization of 2 μ_B .

KNbO₃:**Ni**: For the spin-up states (Fig. 4.5), the group of three t_{2g} -derived levels are full as they form a part of the valence band. One e_g -derived level, below E_F , is occupied while the other e_g level is empty. The corresponding spin-down states look similar as seen in Fig. 4.5, the difference being that only the t_{2g} -derived levels are full while both the e_g -derived levels lie able the Fermi level and M is 1.05 μ_B /cell.







In each case the impurity substitutes for a Nb^{5+} ion, with a charge-compensating oxygen vacancy in the coordinating Figure 4.5: Spin-up (\uparrow) and spin-down (\downarrow) band structures and projected DOS of KNbO₃:X³⁺ where X = Fe, Co and Ni. octahedron.



Figure 4.6: Comparison of the band structures and projected DOS of KNbO_3 doped with various 3*d* transition impurities in their \uparrow and \downarrow configurations.

4.5 Discussion

Before comparing the electronic structures of KNbO₃ doped with various 3*d* transition elements, it is important to note that competition between Δ_{cf} and Δ_{ex} results in two situations. When $\Delta_{cf} < \Delta_{ex}$ the exchange splitting dominates. In this case the ten degenerate spin-orbitals split into two sets of five spin-orbitals, with the ones corresponding to spin-up lower in energy than those corresponding to spin-down by Δ_{ex} . The weaker crystal-field effect then causes each of these 5-fold degenerate levels to split into t_{2g} and e_g derived states as shown in Fig. 4.7a.It is less costly, energetically, to occupy the $t_{2g\uparrow}$ and $e_{g\uparrow}$ levels before filling the set of $t_{2g\downarrow}$ and $e_{g\downarrow}$ levels. For example, if there are six d electrons (d^6), the states are filled up as shown in Fig. 4.7a, maximizing the spin as required by Hund's rule. This is referred to as the high-spin state.

In the second case, when the magnitude of the exchange splitting is reduced such that $\Delta_{cf} > \Delta_{ex}$, the crystal field splitting is the primary effect and exchange splitting is secondary. Here the *d* orbitals are first split into three t_{2g} orbitals and two e_g orbitals. At this point, the spin degeneracy is not broken, so each orbital can accommodate two electrons. The comparatively small exchange splitting leaves the $t_{2g\uparrow}$ and $t_{2g\downarrow}$ spin-orbitals all lower in energy than the $e_{g\uparrow}$ and $e_{g\downarrow}$ spin-orbitals, once spin-degeneracy is broken. This case is illustrated in Fig. 4.7b. For example, the order of filling of a d^5 system in this case, is such that both spin-up and spin-down t_{2g} levels are filled while all e_g levels remain unoccupied. This situation corresponds to a so-called low-spin state.

In an attempt to understand the trends with varying impurity species, Cr^{3+} , Mn^{3+} and Fe^{3+} are considered first because Δ_{ex} is expected to increase with this progression. Then the progression Fe^{3+} , Co^{3+} and Ni^{3+} is followed where Δ_{ex} is expected to decrease. It is known that the effect of an increasingly attractive core (higher value of Z_{eff}), as one moves right from Cr, causes more defect levels to appear in the band gap progressively. This is confirmed in Fig. 4.6 for the spin-up states of the first three dopants. Additionally, as



 $\Delta_{ex} > \Delta_{cf}$

(a) High-Spin State in a d^6 system

 $\Delta_{cf} > \Delta_{ex}$ (b) Low-Spin State in a d^5 system

Figure 4.7: Interplay between Δ_{cf} and Δ_{ex} .

per our prediction, Δ_{cf} decreases and Δ_{ex} increases progressively till Fe. So, the primary effect here is due to exchange splitting and the crystal field effects becomes secondary. Referring to Fig. 4.7a, it becomes clear that the higher value for exchange splitting is the reason for the defect levels corresponding to the spin-down states to lie well above energy gap beyond the calculation window. Therefore, in Cr and Mn they are not visible but a sufficiently high Z_{eff} in Fe pulls them down, binding the *d* levels more tightly and we can finally identify the t_{2g} group hanging at the conduction band edge in Fe spin down configuration. Following Fig. 4.7a, we can expect an order of filing where the spin up $t_{2g} - e_g$ derived defect levels are occupied before the corresponding spin-down ones. This is exactly what we see if we compare the band structures (\uparrow and \downarrow) of Cr, Mn and Fe as shown in Fig. 4.6 and also take into consideration the position of the Fermi levels, E_F , in each case. But the higher energy \downarrow states in Cr, Mn and Fe are unoccupied as expected.

For Co and Ni, the effect of higher Z_{eff} , pulling down the center of the *d*-derived impurity levels, is evident in the spin-down states. In contrast with the instances of Cr, Mn or Fe, Δ_{ex} for Co and Ni, decreases together with Δ_{cf} . Now, Δ_{ex} , decreases at a relatively faster rate than Δ_{cf} so that the exchange splitting effect can be regarded as a perturbation on the crystal field effect. The order of filling, as seen previously in Fig.4.7b, is now different from that of Cr, Mn and Fe and the t_{2g} states for \uparrow and \downarrow configurations are filled prior to the corresponding e_g levels, as verified in Fig. 4.6.

The Kohn-Sham spectra, derived from DFT-calculations, can be used to predict trends in the energies of the impurity levels as a function of the position in the third row of the periodic table. The electron and hole excitations that involve the various impurity levels in the different doped species are summarized in Table 4.2. This data can be used to provide guidance to crystal growers interested in extending the spectral sensitivity of doped KNbO₃ into the infra-red (IR) region. It is to be noted that an electron transition would excite an electron from a filled impurity level into the conduction band while a hole transition would be possible if an electron is excited from a filled valence band into an impurity level. A scaling factor, defined as the ratio of the experimental band gap of pure KNbO₃ to the DFT-derived Kohn-Sham theoretical band gap of the same obtained in this work, is used to scale all the energies of the different impurity levels obtained here from DFT calculations and are finally used for excitation predictions.

It is evident from Table 4.2 that, KNbO₃, doped with different 3*d* transition metals, show electron or hole excitations in the visible range. For example, in KNbO₃:Fe, an electron excited from the $e_{g\uparrow}^{H}$ to the conduction band would cause an emission in the visible range. This roughly corresponds to the experimental finding in Ref [67] that has reported a visible emission of 2.5 eV in Fe-doped KNbO₃ samples. Based on Table 4.2, it appears that KNbO₃:Cr is the most likely candidate for IR-sensitive photorefractive effects as it has a shallow, filled $t_{2g\uparrow}$ impurity band, at approximately, 0.4 eV below the conduction band .

Ni	h	N/A		IR, Visible (0.9 - 2.0) eV	N/A	Visible (2.4 eV)	Visible (1.8 - 2.8) eV
Co	h	N/A		Visible (1.9 - 2.6) eV	IR, Visible (0.9 - 1.6) eV	N/A	N/A
	в	N/A	Visible (2.6 eV)	N/A	IR, Visible (1.3 - 2.1) eV	N/A	
Fe	е	N/A	N/A	IR, Visible (0.80 - 2.2) eV	V N	V /N1	
${ m Mn}$	в	Visible (2.8 eV)	IR (1.3 eV)		N/A		
Cr	в	IR (1.4 - 0.4) eV		N/A^*			
Bands		$\mathrm{t}_{2g\uparrow}$	$\mathrm{e}_{g\uparrow}^{L}$	${ m e}_{g\uparrow}^{H}$	$\mathrm{t}_{2g\downarrow}$	$\mathbf{e}_{g\downarrow}^{L}$	$\mathrm{e}_{g\downarrow}^{H}$

* N/A means unavailability of the impurity level due to one of the following reasons: (1) part of conduction band (2) part of valence band (3) empty for e excitation and (4) full for h excitation. Superscripts L and H refer to the energetically lower and higher-lying impurity bands of the same type. Table 4.2: Prediction of e and h excitations from the Kohn-Sham spectra of different doped crystals of KNbO₃.

Chapter 5

Study of the Electronic Structures of KNbO₃ Doped with Different Types of Fe-centers

5.1 Background

It has been observed experimentally [67, 117–119] that when Fe-doped KNbO₃ crystals undergo reduction to add an electron to the Fe³⁺ ion, there is a significant improvement in the photorefractive figures of merit, for example, an increased gain coefficient and a reduced response speed. Furthermore, investigations based on EPR, optical absorption spectroscopy, electric conductivity and beam coupling studies [64–66] have identified the following primary types of impurity centers in Fe-doped KNbO₃ samples:

(i) $Fe_{Nb}^{3+}-V_O$, where a Fe^{3+} ion substitutes for a Nb^{5+} ion and a charge compensating oxygen-vacancy, V_O , is created in the first coordination shell of Fe_{Nb}^{3+} .

(ii) Fe_{Nb}^{3+} , where an isolated Fe^{3+} ion, without any coordinating vacancy, replaces a Nb⁵⁺ ion.

(iii) $Fe_K^{3+}-V_K$, where a Fe^{3+} ion occupies a K-site forming a nearest-neighbor K-vacancy.

Reference [64] shows that, in the reduced Fe-doped KNbO₃ crystals, an unspecified center, of the form Fe³⁺ - V, is primarily responsible for its enhanced photorefractive performance. The Fe³⁺ ion, in this generic defect-vacancy complex, is identified to be the dominant impurity center for reduction *i.e.*, a fraction of the Fe³⁺ ions readily reduce to Fe²⁺ state, thereby increasing the effective number of electron-donor centers and consequently changing the conductivity of the crystal from p- to n- type. The presence of this donor-trap (Fe²⁺-Fe³⁺) site facilitates the build-up of a space-charge field, which manifests as faster response time and higher two-beam coupling gain. The Fe³⁺ ion can substitute for a Nb⁵⁺ or a K⁺ ion. However, the experiments could not conclusively distinguish between Fe³⁺_{Nb} - V_O and Fe³⁺_K - V_K centers as the source of Fe²⁺ donors, although the results in the reference [67] seem to support Fe³⁺_K - V_K as the principal photorefractive center.

5.2 Theoretical Models

Ideally, all three different types of centers ought to be considered theoretically. Modeling the $\operatorname{Fe}_{Nb}^{3+}$ - V_O and $\operatorname{Fe}_{Nb}^{3+}$ centers sufficiently accurately is computationally feasible within DFT. However, molding the $\operatorname{Fe}_{K}^{3+}$ - V_K center with comparable accuracy turns out to be computationally intractable at present for reasons described below. Therefore, the conclusions drawn from the pewswnt theoretical investigation are based on DFT calculations for the first two types of impurity centers alone.

The Fe_{Nb}^{3+} - V_O complex is modeled using a 2×2×2 KNbO₃ supercell. This large unit cell ensures sufficiently small interactions between the defect-vacancy complex and its periodic images. One of the sixteen Nb-sites, in the supercell, is substituted with a Fe atom. Whether it adopts the Fe³⁺ oxidation state depends on whether that state is energetically favorable. To make a likely outcome, an oxygen vacancy, in the first nearest neighbor shell of Fe_{Nb}, is introduced. This would allow a +3 ion to form on a nominally +5 site, without incurring the cost of non-neutral charge. A charge-neutral unit cell is essential for calculations based on a periodic system, in order to avoid unphysical infinite Coulomb energy that would otherwise result.

The isolated Fe_{Nb}^{3+} center is modeled in a similar way as above, substituting a Nb⁵⁺ ion with a Fe³⁺ ion. The only difference is the position of the charge-compensating vacancy, which needs to be far away from the Fe-impurity to ensure minimum influence on the impurity which then can be considered to be isolated. Constrained by the size of the 2×2×2 supercell, the oxygen-vacancy is chosen to be located in the second coordination shell of Fe_{Nb}. It is a reasonable approximation that this non-coordinating vacancy will leave the impurity isolated since KNbO₃ has a high dielectric constant. These considerations indicate that, attempting to model Fe_K^{3+} - V_K complexes, suitably charge-compensated by additional vacancies and guaranteeing sufficiently small interactions between periodic images, would require even larger unit cells and consequently greater computational resources.

Within Quantum Espresso (QE), the DFT-based tool used for theoretical investigations in this dissertation, there is an option of adding an extra electron to a unit cell. To make calculations feasible under the cumulative effect of the charged unit cell, QE adds an uniform jellium compensating background charge. In the context of the work presented in this section, additional calculations were carried out in which an electron was added to the Fe_{Nb}^{3+} - V_O and isolated Fe_{Nb}^{3+} systems. It was assumed that if this extra electron binds to any of the Fe-centers, thereby reducing it to +2 state, it would be able to identify the preferred Fe-center candidate for reduction.

Four types of impurity centers in KNbO₃ were modeled: a Fe_{Nb}^{3+} - V_O complex, an isolated Fe_{Nb}^{3+} , a (Fe_{Nb}^{3+} - V_O) + e complex and an isolated Fe_{Nb}^{3+} + e. The calculations in the following sections were performed using DFT in the local density approximation. In an attempt to understand the local environment of the various defect centers at a microscopic level, electronic properties such as band structures, total DOS and projected DOS are calculated and compared. To account for the metallic nature of the substitutional impurity Fe, spin polarized calculations are carried out. The results corresponding to the spin-up (\uparrow) and spin-down (\uparrow) configurations are presented separately.

5.3 Results

5.3.1 Fe $_{\rm Nb}^{3+}$ - V $_{\rm O}$ and Fe $_{\rm Nb}^{3+}$ centers:

The band structures, total density of states (DOS) and projected density of states (pDOS) corresponding to a $\operatorname{Fe}_{Nb}^{3+}$ - V_O and an isolated $\operatorname{Fe}_{Nb}^{3+}$ center in Fe-doped KNbO₃, are shown in Figs. 5.1 and 5.2. The vacancy in the surrounding O-octahedra coordinates with the impurity Fe_{Nb} in the first case, while it is non-coordinating in the second arrangement. The first column of Fig. 5.1 contains two plots related to the spin-up (\uparrow) and spin-down (\downarrow) states of Fe_{Nb}³⁺ - V_O, while the second column contains the same for the Fe_{Nb}³⁺. Each of the plots in Fig. 5.1 consists of three subplots that share a common ordinate energy expressed in eV. It is to be noted that the zero of the energy is adjusted to the position of the top of the valence band in the pure host. The subplots are as follows:

(i) The left pane represents the k-resolved band structure of the two Fe-centers, currently discussed, along the path $\Gamma \to X \to R \to Y \to Z \to S$, in the first BZ corresponding to the unit cell under consideration.

(ii) The middle pane shows the total DOS of the same system. The scale, indicated at the top of the plot, is over the range 0 to 2400 states/eV.

(iii) The right pane shows the pDOS and highlights the presence of the impurity levels in the valence band, conduction band and band gap. The scale, in this pane, ranges from 0 to 240 states/eV. The Fermi energy, E_F , denoted by a red dotted line, runs through all the subplots.

Comparison of the band structure plots of host $KNbO_3$ containing Fe_{Nb}^{3+} - V_O and $\mathrm{Fe}_{\mathrm{Nb}}^{3+}$ centers indicate that the two share most of the broad features, differing only in some small details. In the spin-up states, two impurity bands can be identified in the band gaps of the respective modeled systems. These are e_g -derived bands arising from the octahedral crystal-field splitting of the impurity 3d levels. The remaining three lowerlying t_{2g} -derived bands are already within the valence band and cannot be distinguished clearly. The origin and the distribution of $t_{2g}-e_g$ levels have been described in detail in Chapter 4. The states within the band gap are occupied and almost entirely composed of iron 3d orbitals, with slight niobium 4d participation in both instances. Another notable feature of these impurity bands, in both cases, is the fairly high amount of dispersion in the upper e_g band. Ideally, a truly isolated impurity band would be flat. However, the dispersion of this impurity band can be attributed to the high doping concentration of this model, which is 6.25%. Thus the interaction between the dopant and its images was not entirely mitigated. A closer look at the spin-up impurity bands reveals that the splitting between the two e_g bands is larger in the Fe_{Nb}^{3+} - V_O system than in Fe_{Nb}^{3+} . Another notable feature is the relative flatness in the lower e_g band and the corresponding sharp peak in the DOS and pDOS plots in the case of Fe_{Nb} center with a coordinating oxygen-vacancy. Fairly high residual dispersion in the corresponding e_g state, manifested as wriggles, with reduced peak in DOS and pDOS plots, characterize the non-coordinating system.

For the \downarrow states in both models, a group of three t_{2g} -derived bands appear at the conduction band edge. None of these bands are filled. A closer examination of the DOS results indicate that the general features of the spin-down impurity states in both systems are similar, with the exception of a second peak appearing around 2.5 eV in the Fe³⁺_{Nb} - V_O system, which is absent in the Fe³⁺_{Nb} system. This peak corresponds to a flat e_g-derived band. The higher energy e_g-derived band is outside the calculated energy range, and for the Fe³⁺_{Nb} system the spin-down e_g impurity bands are both outside the energy range.

Fig. 5.2 shows pDOS plots showing detailed contributions of the s, p and d orbitals of each of the K, Nb, O and Fe atoms, to the conduction and valence bands as well as the impurity bands for the Fe_{Nb}^{3+} - V_O and the Fe_{Nb}^{3+} systems. Each subplot, corresponding to an atom type, shows the pDOS due to the different orbitals involved, in both the spin-up and down configurations. It is to be noted that the scales of pDOS due to various atoms, are different, ranging from 4 states/eV for K to 40 states/eV for Nb and O and finally 240 states/eV for Fe. Since these plots are oriented differently from the band structure plots, it is to be noted that the region to the left of E_F denotes the valence band and that to the right is the conduction band. The contribution of the K atoms in the energy window displayed, as observed from the pDOS plots, are found to be in both these systems. It was seen in Fig. 3.2, in the pure host, that oxygen p states are solely responsible for forming the top of the valence band (VB) while the bottom of the conduction band (CB) is mainly due to Nb d orbitals. In presence of the impurity Fe^{3+} , the contributions from Fe d is superimposed on these features. The result is that, in the spin-up configuration, the bottom of the CB is primarily due to Nb d as in pure KNbO₃ while the Fe d character dominates the VB top. In the spin-down configuration, the CB bottom is primarily due to Fe d states while the O p contribution is predominant in the VB top. In other words, the Fe d assumes a key role, depending on the position of the impurity bands and competes with or dominates over the background host pDOS distribution. Further, the impurity bands are observed to be entirely made up of Fe d states in both spin-up and down cases, as expected. It should also be noted that differences are present in the details of the impurity-state features that are not significant enough to affect any dynamics in the real material appreciably. In the pDOS corresponding to Fe_{Nb}^{3+} - V_O , a sharp peak, corresponding to the localized, lower-lying e_g band, near the VB, is noted in the spin up scenario while this feature is broader and higher in energy in Fe_{Nb}^{3+} -related pDOS. This corroborates the data obtained from the band picture where the same e_g is dispersive.

The shape and amount of dispersion of the higher e_g band is approximately the same in both the the vacancy-coordinated and non-coordinated cases of Fe_{Nb}^{3+} - V_O and Fe_{Nb}^{3+} .

5.3.2 (Fe³⁺_{Nb} - V_O) + e and (Fe³⁺_{Nb}) + e centers:

To contrast with the Fe³⁺ centers, Fe²⁺ complexes with coordinating and non-coordinating vacancies were also studied. The results pertaining to this models are presented in Figs 5.3 and 5.4. An important difference to be noted, with respect to the Fe³⁺ model, is the position of the Fermi level E_F . To accommodate the extra electron, E_F now runs through the bottom of the conduction band. The results in Fig. 5.3, corresponding to the $(Fe_{Nb}^{3+} - V_O) + e$ and $(Fe_{Nb}^{3+}) + e$ models, indicate that, the general distribution and shape of energy levels in \uparrow and \downarrow states remain largely the same as in the $Fe_{Nb}^{3+} - V_O$ and Fe_{Nb}^{3+} cases, presented in the previous section. As mentioned before, two spin-up e_g -derived impurity bands appear in the forbidden energy gap, while the corresponding group of three t_{2g} bands are further down in the valence band. The lower-lying e_g in $(Fe_{Nb}^{3+}) + e$ is more dispersive than the $(Fe_{Nb}^{3+} - V_O) + e$ case, a feature also noted in Fe³⁺ model without the extra electron. The impurity levels are mostly made up of Fe 3*d* orbitals. For \downarrow states, the group of three t_{2g} , levels, now partially filled, can be identified at the edge of the conduction band. It can be inferred from these features that the extra electron added to the models here does not really bind to Fe³⁺ ion and remains a free conduction electron.

The pDOS results for the $(Fe_{Nb}^{3+} - V_O) + e$ and $(Fe_{Nb}^{3+}) + e$ systems are presented in Fig. 5.4. Within the range of this calculation, the potassium involvement is found to be negligible irrespective of whether the oxygen vacancy, V_O , is coordinating or not. As seen before in Fig. 5.2, O p and Nb d play an important role in the shape of the valence band top and conduction band bottom, respectively, only when the Fe d-derived impurity states are far far off from the respective regions. The details of the localized impurity levels, made up of Fe d states, does not differ significantly except for the observation that



Figure 5.1: Comparison of band structures, DOS and projected DOS of KNbO₃ containing Fe_{Nb}^{3+} - V_O and isolated Fe_{Nb}^{3+} impurity systems for spin-up (\uparrow) and spin-down (\downarrow) polarizations.

the trend of peak heights in the spin-up and spin-down states in the $(Fe_{Nb}^{3+} - V_O) + e$ system are opposite to that found in the $Fe_{Nb}^{3+} - V_O$ model earlier.

Electron densities were also calculated and plotted for all the four complexes considered i.e., $\text{Fe}_{\text{Nb}}^{3+}$ - V_{O} , $(\text{Fe}_{\text{Nb}}^{3+} - V_{\text{O}}) + e$, $\text{Fe}_{\text{Nb}}^{3+}$ and $(\text{Fe}_{\text{Nb}}^{3+}) + e$. Two dimensional plots, as shown in Figs. 5.5 and 5.6, depict the distribution of electron densities around the impurity Fe ion and the coordinating and the non-coordinating oxygen vacancies respectively. Charges of the impurity and the vacancy, in all the four systems considered, were evaluated by



Figure 5.2: Comparison of the projected DOS of K, Nb, O and Fe of KNbO₃ containing Fe_{Nb}^{3+} - V_O and isolated Fe_{Nb}^{3+} impurity systems for spin-up (\uparrow) and spin-down (\downarrow) polarizations.



Figure 5.3: Comparison of band structures, DOS and projected DOS of KNbO₃ containing $(Fe_{Nb}^{3+} - V_O) + e$ and isolated $(Fe_{Nb}^{3+}) + e$ impurity systems for spin-up (\uparrow) and spin-down (\downarrow) polarizations.



Figure 5.4: Comparison of the projected DOS of K, Nb, O and Fe of KNbO₃ containing $(Fe_{Nb}^{3+} - V_O) + e$ and isolated $(Fe_{Nb}^{3+}) + e$ impurity systems for spin-up (\uparrow) and spin-down (\downarrow) polarizations.

integrating over a sphere of radius 0.875 Å centered around Fe_{Nb} and V_O . It was found that:

(i) For the Fe_{Nb}^{3+} - V_O system: charge of the impurity was 13.027 and the the charge of the coordinating vacancy was 0.082.

(ii) For the $(Fe_{Nb}^{3+} - V_O) + e$ system: charge of the impurity was 13.065 and the the charge of the coordinating vacancy was 0.086.

(iii) For the Fe_{Nb}^{3+} system: charge of the impurity was 12.981 and the charge of the non-coordinating vacancy was 0.073.

(iv) For the $(Fe_{Nb}^{3+}) + e$ system: charge of the impurity was 13.016 and the charge of the non-coordinating vacancy was 0.077.

The importance of these calculations will be discussed in the Section 5.4.

5.4 Discussion

The following inferences could be drawn from the theoretical calculations presented in this chapter:

(i) No significant difference in the electronic structure of the Fe_{Nb}^{3+} -V_O and the isolated Fe_{Nb}^{3+} systems could be identified. It has been found experimentally [67] that the reduction of the Fe³⁺-ions in an oxygen deficient atmosphere causes a dramatic decrease of the Fe^{3+} - V concentration, by about a factor of 30, while concentration of Fe_{Nb}^{3+} remains unaffected. Given the similarities in the electronic and energetic properties of Fe_{Nb}^{3+} -V_O and Fe_{Nb}^{3+} revealed by these calculations there is no reason that the former would behave differently than the latter. under reducing conditions. Thus, it can be argued that the concentration of Fe_{Nb}^{3+} - V_O is likely to remain unaltered as well. This indirectly points towards the likelihood of Fe_{K}^{3+} - V_K centers playing a dominant role as electron traps, thereby reducing the charge state of the Fe ion, at a K-site, from +3 to +2.

(ii) The band structures, DOS and pDOS corresponding to Fe_{Nb}^{3+} - V_O and $(Fe_{Nb}^{3+} - V_O) + e_{Nb}^{3+}$



Figure 5.5: Plots indicating the electron distribution around Fe ion and the coordinating oxygen-vacancy, V_O , in Fe³⁺_{Nb} - V_O and (Fe³⁺_{Nb} - V_O) + e systems.

centers are strikingly similar. This shows that the extra electron that was added to the unit cell, does not bind to Fe^{3+} ion, but rather remains a free conduction electron. Furthermore, the electron density plots in the Fig. 5.5a do not indicate any additional charge build-up around Fe_{Nb} as compared to that seen in the Fig. 5.5c. It is to be noted that the nominal charge of Fe is 16, as verified from the corresponding pseudo potential file and the charge of the impurity Fe^{3+} ion, was found to be 13.027 and 13.065 in $\text{Fe}_{\text{Nb}}^{3+} - \text{V}_{\text{O}}$ and $(\text{Fe}_{\text{Nb}}^{3+} - \text{V}_{\text{O}}) + e$ models respectively. Charge evaluation around V_{O} , ideally expected to be zero, also indicate that the external electron did not bind to $\text{Fe}^{3+} - \text{V}_{\text{O}}$ complex. The



(c) $(re_{Nb}) + e$ model (d) $(re_{Nb}) + e$ model

Figure 5.6: Plots indicating the electron distribution around Fe ion and the noncoordinating oxygen-vacancy, V_O , in Fe_{Nb}^{3+} and $(Fe_{Nb}^{3+}) + e$ systems.

minor deviation of the calculated charges form the expected nominal charges is due to the contribution from the bonding electrons. Additionally, the non-preference of the added electron to bind to the impurity ion is also reflected in the isolated Fe_{Nb}^{3+} and $(Fe_{Nb}^{3+}) + e$ systems that provides additional evidence to the claim in (i) above that $Fe_{Nb}^{3+} - V_O$ and the isolated Fe_{Nb}^{3+} systems behave in the same way. Therefore, in this study, $Fe_{Nb}^{3+} - V_O$ did not exhibit any preference for reduction, indicating that $Fe_{Nb}^{3+} - V_O$ might not be readily reducible in the real sample. Therefore it can be concluded that Fe^{2+} donors are probably primarily obtained from K-site Fe substitutional impurities.

Therefore, the theoretical investigations presented in this section indicate the likelihood of a different Fe^{3+} - V center acting as the dominant impurity candidate for reduction, *e.g.*, the $\text{Fe}^{3+}_{\text{K}}$ - V_K site proposed in Ref [67]. It will be fruitful in future first-principles based calculations on KNbO₃ crystals to examine these $\text{Fe}^{3+}_{\text{K}}$ - V_K centers, however at present these calculations were deemed computationally prohibitive.

Chapter 6

Conclusions and Future Directions

6.1 Conclusions

In the investigations described in this dissertation, first-principles-based Density Functional Theory was used as a tool to study doped KNbO₃, a technologically important photorefractive crystal. The effects of Nb-site substitution of pure KNbO₃, by a series of 3d transition metals in the +3 oxidation state, *e.g.*, Cr, Mn, Fe, Co and Ni were studied. Qualitative trends in defect level energies with the positions of the dopants across the 3drow of the periodic table were identified. These trends could be interpreted in terms of crystal field and exchange splitting. By examining these results based on KS eigenvalues, electron and hole excitation systematics for doped KNbO₃ were predicted without making any quantitative claim. KNbO₃:Cr was found to be the most likely candidate for infrared-sensitive photorefractive applications.

A number of Fe-vacancy complexes were also studied in an effort to determine the dominant source of the Fe²⁺ ions in reduced iron-doped KNbO₃ that causes enhanced photorefractive performance. No evidence, in terms of electronic structure properties e.g., band structure, DOS and pDOS, were found that would support the possibility of Fe³⁺_{Nb} - V_O center being more readily reducible to Fe²⁺ than the isolated Fe³⁺ center. This

implicitly provides evidence for the Fe_K^{3+} - V_K center as the dominant reducing center as reported in the experimental work of Basun and co-workers [67].

6.2 Future Work

6.2.1 Ag Co-doping:

It has been shown that co-doping KNbO₃ with Ag enhances linear absorption, photocurrent and photo refractive beam coupling efficiency of the crystal [118,119]. For theoretical understanding of the processes that control the figures of merit microscopically, the DFTbased model for Fe_{Nb}^{3+} - V₀ center, described in detail in Chapters 4 and 5, has been modified, where, now, in addition to a coordinating oxygen vacancy, a next nearest neighbor K⁺ ion, belonging to the second coordination shell of Fe_{Nb} is replaced with Ag⁺ ion. Preliminary band structure data, as obtained in this ongoing work, is shown in Fig. 6.1. The impurity levels, in the bandgap, contributed mostly by iron *d* states are not influenced by the silver co-dopant. This behavior is expected as the Ag ion is sufficiently distant from Fe_{Nb}. The top of the valence band shows significant Ag participation, a feature that needs to be studied in detail. DOS and pDOS calculations for the silver co-doped KNbO₃:Fe with Ag⁺ ion replacing a nearest neighbor K⁺ in the first coordination shell of Fe_{Nb}, are a part of an ongoing investigation. Additionally, copper co-doped KNbO₃:Fe with nearest neighbor and the next nearest neighbor K-vacancies are also being investigated.

6.2.2 Direct Fe²⁺ Modeling:

The enhanced photorefractive performance of reduced Fe-doped KNbO₃ demands additional investigation. Explicit modeling of the Fe²⁺ - V_O defect-vacancy complex, to verify the approximate results of the subsection 5.3.2, would be a step forward. Another worthwhile effort would be the investigation of systems containing Fe_K^{2+} - V_K where the Fe²⁺



(a) Band structure and total DOS of Ag co-doped KNbO₃:Fe in spin-up (\uparrow) configuration.



(b) Band structure and total DOS of Ag co-doped KNbO₃:Fe in spin-down (\downarrow) configuration. Figure 6.1: Band structures and total DOS of KNbO₃:Fe:Ag.

ion now occupies a K-site and the vacancy is created by removing a K atom in the first coordination shell. These calculations would require larger supercells to incorporate charge compensation and reduced interaction between dopant center and its images. This would require the use of more powerful computational resources. Appendices

Appendix A

Miscellaneous

A.1 Thomas Fermi Model

Thomas Fermi model takes advantage of the fact for an ideal, homogeneous, non-interacting, classically repulsive gas, the dependence of electronic density to the Fermi energy is explicitly known [120]. Therefore,

$$T[\Phi] \approx T_{TF}[n] = C_F \int d^3r \, n^{5/3}(\boldsymbol{r}) \tag{A.1}$$

where $C_F = \frac{3}{10} (3\pi^2)^{\frac{2}{3}} = 2.871$ in Hartree units. The approximate internal potential energy of the electrons, completely ignoring electron correlation and exchange, is the classical Coulomb interaction energy of electron density $n(\mathbf{r})$ acting with itself and is given by

$$V_{ee}[\Phi] \approx J[n] = \frac{1}{2} \int \int d^3 r_1 d^3 r_2 \frac{n(\mathbf{r_1})n(\mathbf{r_2})}{|\mathbf{r_1} - \mathbf{r_2}|}$$
 (A.2)

Therefore the total energy E, as in (2.11), can be expressed as a pure functional of the electronic density

$$E \approx E_{TF}[n] = C_F \int d^3r \, n^{5/3}(\mathbf{r}) + \frac{1}{2} \int \int d^3r_1 d^3r_2 \, \frac{n(\mathbf{r_1})n(\mathbf{r_2})}{|\mathbf{r_1} - \mathbf{r_2}|} + \int d^3r \, v(\mathbf{r})n(\mathbf{r})$$
(A.3)

Exchange (Thomas-Fermi-Dirac model) and correlation [121] can also be included in this model. The crude approximations in the Thomas-Ferm model fail to incorporate the crucial quantum mechanical effects related to exchange and correlation leading to anomalous quantitative predictions in areas such as shell structure in atoms and Friedel oscillations in solids. The cause of such inaccuracies rests mostly on the fully local treatment of kinetic energy.

A.2 Hamiltonian Variational Principle

An important stepping stone in understanding DFT is the Variational principle. The ground state energy of a system, E_{gs} , is given by the expectation of the Hamiltonian as

$$E_{gs} = \min_{\psi} \frac{\langle \Psi | \hat{H} \Psi \rangle}{\langle \Psi | \Psi \rangle} \tag{A.4}$$

where the minimization is over all the variables of Ψ . Following variational principle, any guess or trial solution for the ground state energy $E_{trial} \geq E_{gs}$, the equality sign being valid only when the trial is the exact solution. Let us represent a normalized trial wave function Ψ_{trial} in terms of coefficients c_i as

$$|\Psi_{trial}\rangle = \sum_{i} c_{i}|\Psi_{trial}\rangle$$

$$\langle \Psi_{trial}|\Psi_{trial}\rangle = \sum_{i} |c_{i}|^{2} = 1$$
(A.5)
$$E_{trial} = \langle \Psi_{trial} | \hat{H} | \Psi_{trial} \rangle$$

$$= \langle \sum_{i} c_{i} \Psi_{i} | \hat{H} | \sum_{j} c_{j} \Psi_{j} \rangle$$

$$= \sum_{i} \sum_{j} \langle c_{i} \Psi_{n} | E_{j} | c_{i} \Psi_{j} \rangle$$

$$= \sum_{i} \sum_{j} c_{i}^{*} c_{j} E_{j} \langle \Psi_{i} | \Psi_{j} \rangle$$

$$= \sum_{i} |c_{i}|^{2} E_{i}$$

$$= |c_{0}|^{2} E_{0} + |c_{1}|^{2} E_{1} + |c_{2}|^{2} E_{2} \cdots + |c_{n}|^{2} E_{n}$$
(A.6)

 $\{E_i\}$ being an ordered set of solutions such that $E_0 < E_1 < E_2 \cdots < E_n$. For E_{trial} to be the lowest ground state energy E_{gs} the contribution from the higher order terms should be zero or $|c_0|^2 = 1$.

A.3 Proof of Hohenberg-Kohn Theorem 1

Let us assume that two external potentials $v_{ext}^{(1)}(\mathbf{r})$ and $v_{ext}^{(2)}(\mathbf{r})$ that differ by no more than an additive constant, yield two different ground states $\Phi_0^{(1)}$ and $\Phi_0^{(2)}$ with corresponding eigenvalues $E_0^{(1)}$ and $E_0^{(2)}$ respectively, the ground state electron density $n_0(\mathbf{r})$ being the same in both the instances. Following variational principle in A.2, we can write the following inequality

$$E_{0}^{(1)} = \langle \Phi_{0}^{(1)} | \hat{H}^{(1)} | \Phi_{0}^{(1)} \rangle < \langle \Phi_{0}^{(2)} | \hat{H}^{(1)} | \Phi_{0}^{(2)} \rangle$$

$$\langle \Phi_{0}^{(2)} | \hat{H}^{(1)} | \Phi_{0}^{(2)} \rangle = \langle \Phi_{0}^{(2)} | (\hat{H}^{(1)} - \hat{H}^{(2)} + \hat{H}^{(2)} | \Phi_{0}^{(2)} \rangle$$

$$= E_{0}^{(2)} + \langle \Phi_{0}^{(2)} | \hat{H}^{(1)} - \hat{H}^{(2)} | \Phi_{0}^{(2)} \rangle$$

$$= E_{0}^{(2)} + \int d^{3}r \left[v_{ext}^{(1)}(\boldsymbol{r}) - v_{ext}^{(2)}(\boldsymbol{r}) \right] n_{0}(\boldsymbol{r})$$
(A.7)

Therefore we can write

$$E_0^{(1)} < E_0^{(2)} + \int d^3 r \left[v_{ext}^{(1)}(\boldsymbol{r}) - v_{ext}^{(2)}(\boldsymbol{r}) \right] n_0(\boldsymbol{r})$$
(A.8)

Treating $E_0^{(2)}$ in exactly the same way we get

$$E_0^{(2)} < E_0^{(1)} + \int d^3r \left[v_{ext}^{(2)}(\boldsymbol{r}) - v_{ext}^{(1)}(\boldsymbol{r}) \right] n_0(\boldsymbol{r})$$
(A.9)

Adding (A.8) and (A.9) we get

$$E_0^{(1)} + E_0^{(2)} < E_0^{(1)} + E_0^{(2)}$$
 (A.10)

Clearly (A.10) is a contradiction leading to the conclusion that, for systems without degenerate states¹, two external potentials that differ from each other by no more than an additive constant will always give rise to an unique ground state electron density.

A.4 Proof of Hohenberg-Kohn Theorem 2

$$E_{HK}[n] = T[n] + E_{int}[n] + \int d^3r \ v_{ext}(\mathbf{r})n(\mathbf{r}) + E_{II}$$

$$\equiv F_{HK}[n] + \int d^3r \ v_{ext}(\mathbf{r})n(\mathbf{r}) + E_{II}$$
(A.11)

where

$$F_{HK}[n] = T[n] + E_{int}[n]$$
 (A.12)

¹Later, this was found to be valid for degenerate states as seen in [70].

A.5 Steepest Descent and Conjugate Gradient

The simplest multivariate optimization technique which is quite inefficient is that of steepest descent. It is is stable, easy to implement and each iteration is computationally cheap. Given a differentiable scalar function $f(\boldsymbol{x})$, steepest descent iteratively slides down the guess towards lower values of f by taking steps in the direction of the negative gradient $-\nabla f$. The negated gradient is the direction in which \boldsymbol{x} would need to move to decrease f the fastest. For the present purposes, the local gradient of the functional with respect to Kohn-Sham orbitals, are used. It approaches the minimum in a zigzag way where the new downhill search direction, always orthogonal to the previous, is stopped once a uphill is encountered. Therefore, this algorithm uses information about the current sampling point and neglects previous choices leading to its major drawback of slow convergence.

The philosophy of the Conjugate Gradient [122–124] method is to avoid this problem by "learning from experience", remembering the directions already explored. Here each minimization step is carried out along a direction that is conjugated to all the previous search directions. If \mathbf{g}^m is the steepest descents vector associated with iteration m, then the conjugate gradients directions, \mathbf{d}^m , is given by

$$\mathbf{d}^m = \mathbf{g}^m + \gamma^m \mathbf{d}^{m-1}$$

where

$$\gamma^m = \frac{\mathbf{g}^m \cdot \mathbf{g}^m}{\mathbf{g}^{m-1} \cdot \mathbf{g}^{m-1}}$$

and $\gamma^1 = 0$.

It is to be noted here that, given the number of plane waves involved in a calculation is typically of the order $\sim 10^5$, each iteration of a conjugate gradients minimizer could take a long time. A preconditioning scheme is used to address this issue.

A.6 Density of States

As shown in [75], and [120] given a general energy dispersion relation $E(\mathbf{k})$, the density of states per unit energy range per unit volume or just the density of states for convenience, can be quantitatively expressed as,

$$D(E) = \sum_{n} D_n(E) \tag{A.13}$$

where $D_n(E)dE$ is the number of allowed k points in the k-space of primitive cell, for the *n*th band, in the energy range E and E + dE, calculated as shown below,

$$D_n(E)dE = \frac{2}{V} \times \left(\frac{L}{2\pi}\right)^3 \int_{shell} d\mathbf{k} \times \begin{cases} 1, & \text{if } E \le E_n(\mathbf{k}) \le E + dE. \\ 0, & \text{otherwise.} \end{cases}$$
(A.14)

where the integral is extended over the volume of the shell in \mathbf{k} space bounded by two surfaces, $S_n(E)$ and $S_n(E + dE)$ on which the energy is constant at E and E + dErespectively. The factor 2 arises as each level specified by n and \mathbf{k} can accommodate 2 electrons and V is the volume of the cell. The volume integral can be converted into a surface integral by considering that the element of volume between the two constant energy surfaces, at a particular point \mathbf{k} , is a right cylinder of base dS and altitude $\delta k(\mathbf{k})$ so that

$$D_n(E)dE = \left(\frac{1}{4\pi^3}\right) \int_{S_n(E)} d\mathbf{k}$$
(A.15)

where $\delta k(\mathbf{k})$ is the perpendicular distance between the constant energy surfaces concerned and will carry from one point on the surface to another. Thus the difference in energy between the two surfaces, dE, can be alternatively expressed in terms of the the k gradient of $E_{n(\mathbf{k})}$, $\nabla E_n(\mathbf{k})$, which is a vector normal to the surface $S_n(E)$ with a magnitude equal to the rate of change of $E_{n(\mathbf{k})}$ in the normal direction. Therefore,

$$\delta k(\mathbf{k}) = \frac{dE}{|\nabla E_n(\mathbf{k})|} \tag{A.16}$$

or, the density of states per unit volume per unit energy, for a given n is,

$$D_n(E) = \frac{1}{4\pi^3} \int_{S_n(E)} \frac{dS}{|\nabla E_n(\mathbf{k})|}$$
(A.17)

Appendix B

Band structure, DOS and projected DOS of $KNbO_3$ doped with various 3d transition metals



(a) Band structure and total DOS of $\rm Ti^{3+}\mathchar`-doped\ KNbO_3$ in spin-up (\uparrow) configuration.



(b) Band structure and total DOS of Ti^{3+} -doped KNbO₃ in spin-down (\downarrow) configuration. Figure B.1: Band structures and total DOS of KNbO₃:Ti.



(a) Projected DOS of K and Nb in \uparrow and \downarrow configurations of Ti³⁺-doped KNbO₃.



(b) Projected DOS of O and Ti in \uparrow and \downarrow configurations of Ti³⁺-doped KNbO₃. Figure B.2: Projected DOS of KNbO₃:Ti.



(a) Band structure and total DOS of V³⁺-doped KNbO₃ in spin-up (\uparrow) configuration.



(b) Band structure and total DOS of V^{3+} -doped KNbO₃ in spin-down (\downarrow) configuration. Figure B.3: Band structures and total DOS of KNbO₃:V.



(a) Projected DOS of K and Nb in \uparrow and \downarrow configurations of V³⁺-doped KNbO₃.



(b) Projected DOS of O and V in \uparrow and \downarrow configurations of V³⁺-doped KNbO₃. Figure B.4: Projected DOS of KNbO₃:V.



(a) Band structure and total DOS of Cr^{3+} -doped KNbO₃ in spin-up (\uparrow) configuration.



(b) Band structure and total DOS of Cr^{3+} -doped KNbO₃ in spin-down (\downarrow) configuration. Figure B.5: Band structures and total DOS of KNbO₃:Cr.



(a) Projected DOS of K and Nb in \uparrow and \downarrow configurations of Cr³⁺-doped KNbO₃.



(b) Projected DOS of O and Cr in \uparrow and \downarrow configurations of Cr³⁺-doped KNbO₃. Figure B.6: Projected DOS of KNbO₃:Cr.



(a) Band structure and total DOS of Mn^{3+} -doped KNbO₃ in spin-up (\uparrow) configuration.



(b) Band structure and total DOS of Mn^{3+} -doped KNbO₃ in spin-down (\downarrow) configuration. Figure B.7: Band structures and total DOS of KNbO₃:Mn.



(a) Projected DOS of K and Nb in \uparrow and \downarrow configurations of Mn³⁺-doped KNbO₃.



(b) Projected DOS of O and Mn in \uparrow and \downarrow configurations of Mn³⁺-doped KNbO₃. Figure B.8: Projected DOS of KNbO₃:Mn.



(a) Band structure and total DOS of Fe^{3+} -doped KNbO₃ in spin-up (\uparrow) configuration.



(b) Band structure and total DOS of Fe^{3+} -doped KNbO₃ in spin-down (\downarrow) configuration. Figure B.9: Band structures and total DOS of KNbO₃:Fe.



(a) Projected DOS of K and Nb in \uparrow and \downarrow configurations of Fe³⁺-doped KNbO₃.



(b) Projected DOS of O and Fe in \uparrow and \downarrow configurations of Fe³⁺-doped KNbO₃. Figure B.10: Projected DOS of KNbO₃:Fe.



(a) Band structure and total DOS of Co^{3+} -doped KNbO₃ in spin-up (\uparrow) configuration.



(b) Band structure and total DOS of Co^{3+} -doped KNbO₃ in spin-down (\downarrow) configuration. Figure B.11: Band structures and total DOS of KNbO₃:Co.



(a) Projected DOS of K and Nb in \uparrow and \downarrow configurations of Co³⁺-doped KNbO₃.



(b) Projected DOS of O and Mn in \uparrow and \downarrow configurations of Co³⁺-doped KNbO₃. Figure B.12: Projected DOS of KNbO₃:Co.



(a) Band structure and total DOS of Ni^{3+} -doped $KNbO_3$ in spin-up (\uparrow) configuration.



(b) Band structure and total DOS of Ni^{3+} -doped $KNbO_3$ in spin-down (\downarrow) configuration. Figure B.13: Band structures and total DOS of $KNbO_3$:Ni.



(a) Projected DOS of K and Nb in \uparrow and \downarrow configurations of Ni³⁺-doped KNbO₃.



(b) Projected DOS of O and Ni in \uparrow and \downarrow configurations of Ni³⁺-doped KNbO₃. Figure B.14: Projected DOS of KNbO₃:Ni.

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