



POLITECNICO
MILANO 1863

DIPARTIMENTO DI FISICA

Doctoral Programme in Physics

A combined *ab initio* and high-throughput approach to ferroic materials exploration

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2026 - Cycle XXXVIII

Summary

Density Functional Theory (DFT) has been, for over three decades, the standard computational method for predicting materials properties from first principles. Traditionally, DFT has flourished within a “calculation-first”, system-by-system framework. Over time, however, this perspective has been complemented by data-oriented, high-throughput strategies, enabling systematic exploration. This paradigm shift has led to the development of extended, standardised materials databases and, more recently, has fostered the integration into computational materials science of Artificial Intelligence techniques, that allow the identification of patterns and trends hardly detectable on a case-by-case basis.

The present research advances materials characterisation by combining the power and accuracy of DFT – embedded where appropriate into automated workflows – with the scalability of high-throughput frameworks. Two families of ferroic systems (displaying at least one emergent property related to magnetic, electric, or mechanical order) are selected as areas of interest, reflecting the intertwining of the theoretical and experimental research lines behind this project.

The first part of the work addresses the rapidly developing field of two-dimensional (2D) magnetism. For decades, the existence of long-range magnetic order in strictly 2D systems was considered unlikely on fundamental thermodynamic grounds. This view changed in the late 2010s, when experiments reported stable magnetism in monolayers of FePS₃, CrI₃ and CrGeTe₃. Since then, many additional compounds have been identified, exhibiting a rich variety of magnetic textures, with potential relevance for spintronic technologies. A central task in understanding these materials is the evaluation of exchange parameters, which collectively determine the nature of the magnetic ordering. These parameters are commonly extracted from DFT using approaches such as the “four-state method”, which maps total energies of selected spin configurations onto a Heisenberg-like model Hamiltonian. This technique, however, is typically laborious and multi-step, since each parameter in the model requires four separate DFT calculations, performed in as many independent simulation cells, that also vary depending on the parameter.

To overcome this limitation, I designed AMaRaNTA (Automating Magnetic paRAmeters iN a Tensorial Approach), a Python-based computational workflow that automates the four-state method for 2D magnets. Starting solely from a crystal structure file, AMaRaNTA automatically generates the required simulation cells, submits and monitors calculations on high-performance computing facilities, retrieves total energies, and ultimately extracts exchange parameters. In its current implementation, the code returns the nearest-neighbour exchange tensor, along with scalar parameters for second- and

third-nearest-neighbour interactions and single-ion anisotropy. These form a minimal yet comprehensive set to capture the mechanisms stabilising diverse magnetic textures in 2D materials.

The functionality of AMaRaNTA was validated on a compact dataset of around 30 compounds. The workflow successfully reproduces expected features of well-established 2D magnets, including chromium trihalides (CrX_3 , $\text{X} = \text{Cl, Br, I}$) and transition-metal dihalides (NiX_2 , VX_2 , MnX_2). It also captures the unusually strong antiferromagnetic interactions reported for VPS_3 (at the nearest-neighbour level), as well as for NiPS_3 and NiPSe_3 (at the third-nearest-neighbour level). Beyond this, the screening also predicts previously unreported features in selected systems, including antiferromagnetism in NiF_4Te_2 , sizeable Kitaev-like magnetism in MnBi_2Te_4 , and antisymmetric Dzyaloshinskii–Moriya interactions in VF_4 and VAgP_2Se_6 . Altogether, AMaRaNTA provides a robust, systematic and reproducible strategy for extracting exchange parameters in 2D magnets, with clear potential for a large-scale, high-throughput exploration.

The second half of the thesis is devoted to piezoelectric materials. These systems, in which electric and mechanical degrees of freedom are strongly coupled, have a long history of industrial and technological applications. Today, most such devices rely on lead-based compounds, whose toxicity, however, raises significant human health concerns; research is therefore increasingly directed towards the development of lead-free alternative materials. A prominent example is the sodium–potassium niobate solid solution $\text{K}_{1-x}\text{Na}_x\text{NbO}_3$ (KNN), a random alloy with the perovskite ABO_3 structure. KNN has attracted significant attention over the past two decades, during which a substantial body of experimental work has provided a general understanding of its composition–temperature phase diagram. By contrast, DFT studies of this system remain limited in number and scope, due to the presence of several competing phases and to the challenges of modelling chemical disorder in random alloys, which require large supercells to accurately capture the multifaceted local environment.

My contributions originated as theoretical support to the ongoing activity of in-house experimental collaborators. In this context, I first addressed the experimentally observed tendency of KNN to segregate into Na-rich and K-rich domains. I investigated this behaviour via DFT simulations of idealised, tetragonal KNN systems, thereby disentangling chemical substitution from lattice relaxation effects. Analysis of total energies revealed that the preference for regions of unbalanced composition already emerges at the first-principles level, albeit with a very small associated energy gain.

I then turned to a deeper exploration of how KNN properties evolve with composition. After preliminary validation on the sodium niobate end member, I focused on a specific KNN phase, of monoclinic symmetry and intermediate structural complexity, and examined its behaviour on the Na-rich side of the phase diagram. I unveiled how this phase tends to “breathe” with increasing Na content: the lattice vectors in the xz plane alternately open and close, causing the angle β between them to slightly oscillate around 90° . Accordingly, the polarisation follows this structural evolution by progressively oscillating around its reference direction. Analysis of the piezoelectric tensors reveals an overall enhancement of the response at intermediate compositions, corresponding to maximal

chemical disorder; the same regime also favours polarisation rotation towards the non-polar $\hat{y}$ axis. These results are in reasonable agreement with the limited available DFT literature; the calculated d_{33} piezoelectric coefficient also shows moderate resemblance to our in-house experimental data, within a specific compositional window. Finally, repeating the energetic stability analysis within the more realistic monoclinic framework, I found that the energy gain associated with decomposition towards the end members increases by an order of magnitude with respect to the idealised tetragonal case; this strengthens the earlier conclusion regarding the intrinsic preference of KNN for non-equimolar compositions. Beyond complementing experimental observations, my investigation contributes to the more ambitious goal of establishing a foundation for a systematic, large-scale DFT survey of KNN across phases and compositions.

List of publications

This Ph.D. work has resulted in the following publications:

1. Orlando, F., Droghetti, A., Varrassi, L., Cuono, G., Franchini, C., Barone, P., Marrazzo, A., Gibertini, M., Stavrić, S. and Picozzi, S., *AMaRaNTA: Automated First-Principles Exchange Parameters In 2D Magnets*, npj Comput. Mater. 12 (2026) [\[1\]](#).
2. Pavese, G., Orlando, F., Picozzi, S., Albisetti, E., Maspero, F., Asa, M., Melzi, F., Castoldi, L., Bertacco, R. and Badillo, M., *Phase segregation in $K_xNa_{1-x}NbO_3$ films grown by large-scale confocal RF sputtering*, J. Alloys Compd. 1022 (2025) [\[2\]](#).
3. Pavese, G., Piazza, W., Orlando, F., Picozzi, S., Maspero, F., Melzi, F., Gianola, R., Bertacco, R. and Badillo, M., *The KNN rollercoaster: from bulk ceramics to phase engineering in wafer-scale thin films*, in preparation [\[3\]](#).

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Introduction

The early days

Theoretical materials science, as we understand it today, is nearly a century old. Its origins trace back to the formulation of modern quantum mechanics in the mid-to-late 1920s, which for the first time provided an adequate and rigorous formalism for studying matter at the atomic scale.

Already before the turn of the decade, Hartree and Fock (together with Slater) showed how to apply the Schrödinger equation to a system of interacting ions and electrons [4–6]. Their work constituted the first example of an *ab initio* (or *first-principles*) method, i.e., a “bottom-up” framework based entirely on fundamental physical forces and constants, able to predict properties of materials without requiring any empirical parameter. The Hartree-Fock method was successfully applied (by using analog machines, in the beginning,¹ and later with the help of the first generations of modern computers) to a number of basic systems, mainly isolated atoms, ions and simple molecules [7–11]. A series of challenges remained, however, due to the models’s strong level of approximation.

A consistent theoretical breakthrough followed in 1964 when Hohenberg and Kohn introduced Density Functional Theory (DFT) [12], which reshapes the original problem in terms of the previously overlooked electronic density, turning it into a variational minimisation problem. A brilliant implementation of DFT into a set of Schrödinger-like equations was provided in the following year by Kohn and Sham [13], transforming it from just an elegant idea into an applicable, practical tool. The significance of these contributions was ultimately recognized with the awarding of the Nobel Prize in Chemistry to Kohn in 1998 [14].

The golden age of DFT

Nonetheless, for years DFT was rarely applied to complicated systems – let alone employed to predict unknown ones – because this required computational resources not yet available at the time. It was only from the late 1980s, and more extensively throughout the 1990s, that technological progress made large-scale simulations feasible, and widely used modern DFT packages – such as CRYSTAL (1988) [15], VASP (1996) [16, 17], SIESTA (1996) [18], Quantum Espresso (2001) [19] and many others – were developed.

¹The reader will forgive us if we picture this assigned as a tedious job to many a PhD student...

Armed with these tools, researchers became able to use DFT to provide *a posteriori* support to experimental data and, together, to drive research efforts *a priori* by predicting properties of materials whose reality was still unknown or debated. It is not by chance, in this respect, that the existence of two-dimensional (2D) materials – most notably graphene – and later of the subclass of 2D magnets, such as CrI₃, was anticipated theoretically [20,21] prior to experimental evidence [22,23].

In the meantime, as the field evolved, new and more advanced functionalities were incorporated into DFT codes on top of basic electronic structure calculations. To name a few, time-dependent DFT [24] granted access to excited states and optical spectra, linear-response formalisms allowed for calculation of vibrational and mechanical properties [25], and the modern theory of polarisation, developed by Resta, King-Smith and Vanderbilt, enabled rigorous treatment of ferroelectric materials [26–28].

With these advances, DFT could be applied not only to simple atomic or molecular systems, but also to bulk solids, surfaces, and defects, allowing predictions of structural, electronic and magnetic properties with unprecedented accuracy. These successes laid the foundation for a “calculation-first”, materials-oriented framework to emerge, in which individual materials or small families of them were investigated through dedicated, independent studies. This would soon after become the central — and for quite some time essentially the only — computational paradigm in first-principles materials science.

A change of paradigm

Eventually, however, the perspective shifted. As independent DFT studies multiplied on a large scale, researchers started to realise that the huge amount of accumulated results represented a valuable collective resource that could be further mined. If gathered, standardised and organised, these data could allow systematic exploration across materials, revealing patterns and trends hardly detectable on a case-by-case basis.

In the absence of already standardised data – since independent DFT studies may differ in the details of the computational method – these would have to be regenerated. And here lies the essence of the high-throughput approach: performing large-scale DFT simulations within a shared computational setup, in order to generate massive and internally consistent datasets.

Starting in the early 2010s, this vision began to take concrete form through the development of large-scale automated computational frameworks, along with the databases generated from them. A landmark moment was the launch of the Materials Genome Initiative by the U.S.A. government in 2011 [29], a policy that reoriented funding strategies towards automation to accelerate materials discovery. Within this context, the Materials Project [30] was established in 2013, combining automated DFT workflows with a rapidly growing open database. Around the same time, other pioneering infrastructures such as AFLOW [31] and qmpy [32] emerged, resulting in public repositories like AFLOWlib [33] and the Open Quantum Materials Database (OQMD) [32].

As complexity and scale increased, more flexible workflow engines appeared. The Atomic Simulation Environment (ASE) [34] gradually became a widely used interface for

both structure manipulation and interaction with simulation codes. Workflow engines such as FireWorks [35], atomate [36] and pyiron [37] introduced reusable components capable of managing thousands of calculations and handling failures automatically. AiiDA [38] shares a similar focus on workflow automation, but embedded within a broader design, centred on data provenance, in which every step of a calculation is recorded and stored to guarantee reproducibility. The same philosophy underlies repositories such as Materials Cloud [39], built directly on top of AiiDA, as well as that independently developed by the NOMAD Laboratory [40]. Finally, specialised databases have extended the high-throughput approach to new classes of materials: notable examples are the Computational 2D Materials Database (C2DB) [41, 42] and Materials Cloud 2D (MC2D) [43, 44], that catalogue two-dimensional systems.

The rise of high-throughput thinking is by no means limited to materials science, nor to physics itself: it is, indeed, part of a broader transformation across scientific disciplines, naturally extending to any domain where large-scale numerical results can be generated and learned from. Accordingly, as shown in Figure I.1, the majority of high-throughput publications come from areas such as biochemistry, genetics, molecular biology and medicine, with physics and materials science adding up to less than 10% of the share.

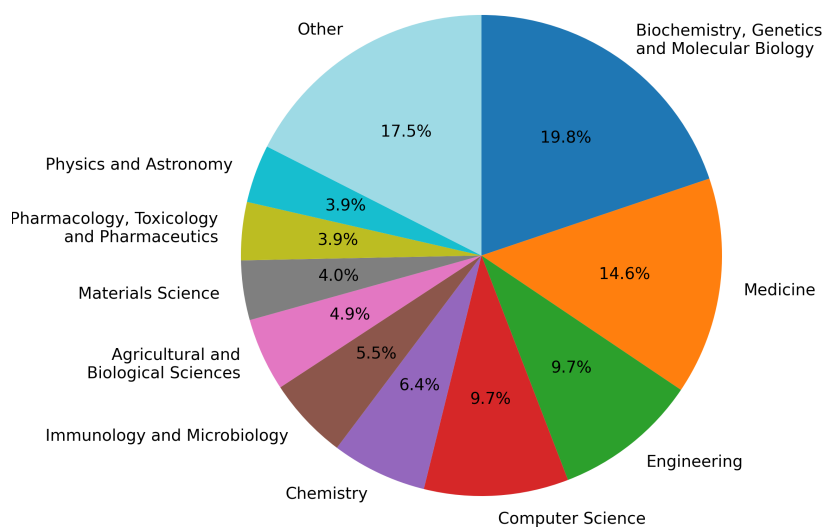


Figure I.1: Repartition by subject area of publications with the tag “high-throughput”. Data collected via the Scopus search engine, referring to the years 1980-2024.

As far as data exploration is concerned, high-throughput-generated datasets provide a natural playground for the application of artificial intelligence (AI) techniques – namely, machine learning – able to disentangle hidden trends and patterns that may, perhaps, point to still unknown physics [45, 46].

Large databases, containing thousands or tens of thousands of entries, enable the use of neural-network approaches, that can capture complex, non-linear relationships

between atomic structures, chemical compositions and material properties [47]. Trained on existing datasets, they can estimate quantities such as formation energies, band gaps or elastic properties far more rapidly than performing new first-principles calculations from scratch [45, 48]. In addition, they can be employed to rapidly scan broad regions of parameter space, identifying promising candidates that can later be examined with more accurate simulations [46].

The use of machine learning, however, is not restricted to extremely large datasets: AI techniques can also be applied when computational or experimental data are scarce. Smaller datasets, of perhaps only a few tens or hundreds of entries, can still be meaningfully explored via Gaussian process regression [45], decision-tree algorithms like random forests [49], or symbolic regression tools such as SISSO [50, 51]. The latter are particularly attractive because, unlike neural networks, they can express complex functional dependencies of a property by means of relatively simple, interpretable analytical formulas, that researchers can scrutinise and understand [52, 53].

The integration of AI thus represents a natural maturation of the high-throughput vision. In this sense, the relationship is symbiotic: massive computation feeds the data hunger of AI, which, in turn, helps navigate the resulting vast information space.

Challenges and perspectives for the future

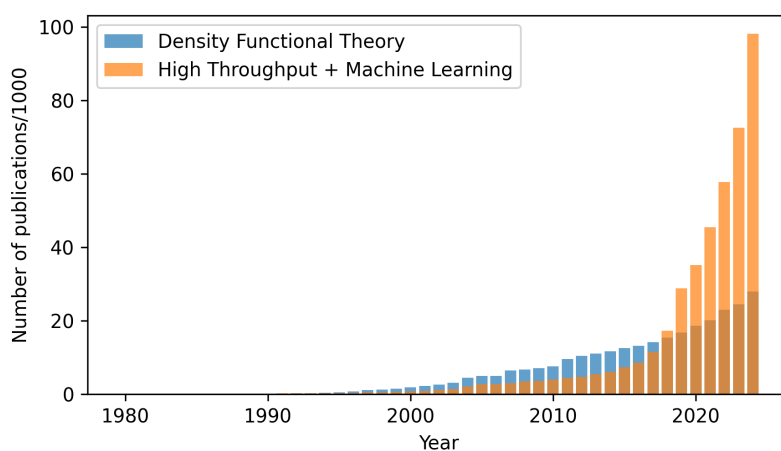


Figure I.2: Number of publications with the tags “Density Functional Theory” and “high-throughput & machine learning” in the years 1980-2024. Data collected via the Scopus search engine, limiting to the following fields: Chemistry, Physics & Astronomy, Materials Science, Chemical Engineering, Engineering.

As of today, the paradigm shift continues to accelerate, as illustrated by Figure I.2, which shows the trends of the number of publications under the tags “Density Functional Theory” and “high-throughput & machine learning”, respectively. An evident surge of the latter can be observed, leading the way since the late 2010s. A transition is thus clearly emerging, from the calculation-first mindset to a data-oriented, high-throughput, machine-assisted

perspective.² This shift reflects what has been dubbed the “fourth paradigm” of science – on the wave of the previous three (empirical, theoretical and computational science) – and will most likely shape theoretical materials science in the years ahead [54].

A word of warning in this regard, however, is in order. Somewhere down the road, caution will be required to ensure that the high-throughput, AI-assisted perspective does not fully take over; a concern felt most strongly when adopting the perspective of someone trained still within the earlier paradigm.³ There is little doubt that high-throughput, AI-assisted approaches will prove increasingly efficient and productive. This said, we invite reflection in any case, at a more fundamental level, on what has traditionally defined the practice of Physics itself. Is its primary value found in the rapid, top-down production of accurate and beneficial results, or in the gradual, bottom-up process of building understanding, critical judgement and confidence through direct engagement with the theory and its limitations? In other words, is it the destination, or the journey?

We believe that the key challenge in this regard for the future will be to strike a balance: to fully exploit the insights made possible by data-driven and machine-assisted tools, while preserving the central role of physical reasoning and intuition. The responsibility for maintaining this balance will ultimately rest with those who carry the discipline forward – within the present generation of physicists, and even more so in those to come.

Purpose of the work

The present thesis aims at advancing materials characterisation within both the traditional calculation-first framework and the more recent data-oriented paradigm, by leveraging *ab initio* DFT investigations, embedded where appropriate into automated and high-throughput workflows.

Two selected branches of materials science are addressed herein, both involving ferroic systems – i.e., materials exhibiting at least one among long-range magnetic, electric, or mechanical order. The first concerns 2D magnets, a class of materials only relatively recently isolated, yet already recognised as fertile ground for unconventional and technologically relevant magnetic phenomena. The second part of the work is devoted to piezoelectric materials, with particular emphasis on the search for lead-free alternatives, capable of competing with or surpassing the Pb-based compounds currently employed in industry.

Although these two research lines are not directly related from a thematic standpoint, their joint inclusion reflects the complementary experimental and theoretical expertise that shape the intellectual environment in which this work was carried out. While the thesis is entirely theoretical in nature, its development unfolded within this dual framework, which fostered both methodological rigour and attention to experimentally relevant questions.

²This certainly does not mean that DFT simulations are no longer carried out: they are simply encompassed within a broader scheme. As has often happened in the history of science, the new paradigm embeds the old one.

³A disclaimer: this paragraph is not intended to be a commentary on the broader societal implications of AI, a timely and relevant topic that, however, lies well beyond the scope of this thesis.

Thesis layout

The thesis is structured as follows.

Chapter 1 provides an overview of the theoretical background (DFT) together with its computational implementation within the VASP software. The foundations of DFT are presented, starting from the cornerstone Hohenberg-Kohn theorems, followed by the introduction of the Kohn-Sham formalism, which recasts the DFT variational problem into an effective single-particle framework, yielding a concrete set of eigenvalue equations. Further DFT-related topics, such as the extension to spin-dependent DFT and general aspects of exchange-correlation functional families, are briefly discussed. The second part of the chapter begins by presenting how the Kohn-Sham equation are written on a plane-wave basis, after which the general features of the VASP software are outlined, with a focus on typical computational settings and parameter choices. Emphasis is placed on the functionalities directly needed for the work presented in this thesis.

Chapter 2 illustrates the design and development of AMaRaNTA, an original, open-source computational package that automates DFT calculations of exchange parameters in 2D magnetic materials. After a concise overview of the basics, the theoretical peculiarities of magnetism in two dimensions are discussed, highlighting the features that make it especially intriguing, and the role that automation tools can play in this context. The four-state method, which relates DFT total energies of suitably constrained magnetic configurations to exchange parameters, is thereafter introduced. The chapter proceeds to describe the internal structure of AMaRaNTA in reasonable detail – though not at the level of a user manual – and includes as an example the output of an actual execution of the code for a selected material. The final part of the chapter illustrates the application of AMaRaNTA to a representative dataset of 2D magnets, in a high-throughput fashion. The consistency of the obtained exchange parameters with previous literature is analysed, with particular attention to cases where the results either deviate from earlier studies or provide predictions not previously reported. The chapter concludes by outlining several possible directions for further development and improvement of the package.

The two distinct theoretical and experimental ecosystems that underpin this thesis intertwine in **Chapter 3**, which presents an *ab initio* investigation of a specific piezoelectric alloy, sodium potassium niobate (KNN). This compound is of particular interest in the context of lead-free piezoelectricity, as it offers a potential replacement for the Pb-based materials most commonly used in industry, which suffer from toxicity concerns. The chapter begins with an introduction to the piezoelectric phenomenon, including a brief historical overview and a discussion of its current technological relevance. The mathematical framework of piezoelectricity is then presented, along with notes on its implementation in VASP. The theoretical section concludes with a discussion of the SQS method for the modelling of random alloys. Original contributions start with an energetic stability analysis, assessing the experimentally observed tendency of KNN to favour regions of unbalanced (Na- or K-rich) composition. This is followed by a systematic investigation of KNN across a broad composition range, focusing on a selected monoclinic phase, first tested on the full-Na endpoint together with other sodium niobate phases. The compositional trends of structural, dielectric, ferroelectric and piezoelectric properties are illustrated

and, where possible, compared with existing literature and in-house experimental data. Finally, the scope of the analysis is delineated, and potential directions for extending and refining it are discussed.

Additional material is provided in the appendices. **Appendix A** contains the complete dataset produced by the AMaRaNTA package, along with sketches of the unit cells used for each material. **Appendix B** presents the conventional forms of piezoelectric tensors for the point groups relevant to this study. Finally, **Appendix C** details the procedure employed within the thesis for rotating piezoelectric tensors, carried out entirely within their symmetry-contracted Voigt form. For completeness, concrete examples of basic operations on piezoelectric tensors are provided as illustrative exercises.

Finally, the **Bibliography** lists all external literature sources referenced throughout this work.

Chapter 1

Theoretical and computational setup

The bulk of the calculations reported in this work rely on Density Functional Theory (DFT) [55, 56] and have been performed with the help of the VASP software [16, 17]. These approaches are addressed here in more detail.

1.1 Density Functional Theory

1.1.1 Introduction to the many-body problem

Assuming the Born-Oppenheimer approximation [57], the time-independent Schrödinger equation for a system of interacting electrons and ions reads

$$H^{(MB)}(\mathbf{r}; \mathbf{R})\psi^{(MB)}(\mathbf{r}; \mathbf{R}) = E\psi^{(MB)}(\mathbf{r}; \mathbf{R}) \quad (1.1)$$

for the Hamiltonian

$$\begin{aligned} H^{(MB)}(\mathbf{r}; \mathbf{R}) &= -\sum_{i=1}^N \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_{i=1}^N \sum_{\alpha=1}^M \frac{Z_{\alpha} e^2}{|\mathbf{r}_i - \mathbf{R}_{\alpha}|} + \frac{1}{2} \sum_{i,j=1}^N \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \\ &:= \sum_{i=1}^N T_i + \sum_{i=1}^N v_{ext}(\mathbf{r}_i) + V_{ee} \\ &:= T + V_{ext} + V_{ee} \quad ^1 \end{aligned} \quad (1.2)$$

where i, j (respectively, α) span the number of electrons (respectively, ions), $\mathbf{R} = \{\mathbf{R}_{\alpha}\}$ is a collective term for the ionic coordinates – treated as mere parameters due to the Born-Oppenheimer separation of ionic and electronic degrees of freedom – and $\mathbf{r} = \{\mathbf{r}_i\}$ is the corresponding shortening for the electronic coordinates.

It is well known that (1.1) is solved exactly only in the trivial case $N = 1$, $M = 1$ (namely, the hydrogen atom), whereas some kind of approximation is required in any other case. Also, perturbative techniques can be of help only for relatively simple systems

¹Unlike T and V_{ext} , V_{ee} cannot be written as a sum of one-body terms.

such as helium, while giving incorrect outcomes as complexity increases. This calls for new classes of approximate methods.

Among the first to be proposed was the Hartree-Fock method, briefly summarised as follows [4–6]. The sum of Coulombic electron-electron repulsion terms in (1.2) is replaced by a local, mean-field *Hartree term*, to which a non-local *Fock term* is added in order to account for the correct antisymmetry of the wavefunction. Applying the Ritz-Rayleigh variational principle leads to a set of Schrödinger-like integro-differential equations called *Hartree-Fock equations*, to be solved iteratively, whose N lowest eigenvalues and eigenfunctions give the approximate electron energies and states.

Despite representing a powerful step forward – as well as the cornerstone of a number of techniques still in use, especially in quantum chemistry – the Hartree-Fock method suffered from two substantial drawbacks:

- it relies upon a strong initial approximation: the many-body wavefunction is written as product of single-particle orbitals, suitably antisymmetrised (in other words, as a single Slater determinant). This leads to neglecting any correlation beyond those purely due to spin.
- most importantly, the computational complexity increasing rapidly with the number of atoms² allows to perform reasonable calculations only for small systems, on the order of $N \simeq 10$ [14]. Indeed, at the bare Hartree level, relatively larger systems can be studied, but computing the non-local Fock term introduces a bottleneck in the calculation.

Over time, physicists were thus led to search for different solutions, possibly not implying strong initial assumptions and able to handle larger systems.

1.1.2 The Hohenberg-Kohn theorems

What DFT is about can be outlined in one single crucial idea: in order to improve computational feasibility, our attention should not be focused on the many-body wavefunction $\psi(\mathbf{r}_1, \mathbf{r}_2 \dots \mathbf{r}_N)$,³ depending on $3N$ scalar coordinates, but rather shifted towards the electron density

$$\begin{aligned}\rho(\mathbf{r}) &= N \int d\mathbf{r}_2 \dots \int d\mathbf{r}_N \psi^*(\mathbf{r}, \mathbf{r}_2 \dots \mathbf{r}_N) \psi(\mathbf{r}, \mathbf{r}_2 \dots \mathbf{r}_N) \\ \rho(\mathbf{r}) &= N \int d\mathbf{r}_2 \dots \int d\mathbf{r}_N |\psi(\mathbf{r}, \mathbf{r}_2 \dots \mathbf{r}_N)|^2\end{aligned}\tag{1.3}$$

satisfying the constraint

$$\int d\mathbf{r} \rho(\mathbf{r}) = N\tag{1.4}$$

²Nominally as $O(N^4)$ due to the calculation of four-centre Coulomb integrals, but actually computational complexity can be reduced to about N^2 [58]. Post Hartree-Fock inclusion of correlation effects (the so called *CI method*) leads to what W. Kohn referred to as an *exponential wall*.

³The explicit parametric dependence on the ionic coordinates has been dropped; the spin degree of freedom is implicitly assumed. From now on, $\mathbf{r}$ is meant as spatial variable and no longer as collective electron coordinate as in 1.1.

which in contrast depends on three spatial coordinates only.

The special role played by the electron density is highlighted in the two *Hohenberg-Kohn theorems* (1964) [12], acting as milestone of the entire theory:

Theorem 1.1.1. *Let us consider the external potential V_{ext} as the only variable of interest of the many-electron problem and suppose everything else in (1.2) is fixed. There is a one-to-one correspondence between the ground-state electronic density ρ_0 and the external potential V_{ext} that gives rise to it.*

V_{ext} uniquely determining ρ_0 through the wavefunction ψ is trivial. The theorem shows that the opposite holds as well: the density uniquely determines the external potential (to within a meaningless global constant). But since all other terms in (1.2) have been supposed as fixed, the knowledge of V_{ext} automatically entails the knowledge of the entire Hamiltonian. As a consequence, all properties of the system are completely determined by the bare ground-state density $\rho_0(\mathbf{r})$. In this sense the density is promoted as the leading physical observable of interest.

Theorem 1.1.2. *The energy of the system can be defined as a functional of the electronic density:*

$$\begin{aligned} E := E[\rho(\mathbf{r})] &= \langle \psi[\rho] | T | \psi[\rho] \rangle + \langle \psi[\rho] | V_{ee} | \psi[\rho] \rangle + \langle \psi[\rho] | V_{ext} | \psi[\rho] \rangle \\ &= T[\rho] + V_{ee}[\rho] + V_{ext}[\rho] \\ &:= F[\rho] + V_{ext}[\rho] \end{aligned} \quad (1.5)$$

This functional is unique (modulo a constant); its minimum is assumed in correspondence of the ground-state electronic density ρ_0 and equals the ground-state energy.

One could then in principle proceed with the minimisation of the energy functional, provided that the explicit form of each term in (1.5) is known.

It is easy to prove that

$$V_{ext}[\rho] = \int d\mathbf{r} \rho(\mathbf{r}) v_{ext}(\mathbf{r}) \quad (1.6)$$

but unfortunately there is no such expression at our disposal for the (universal) functional $F[\rho] = T[\rho] + V_{ee}[\rho]$.

The common strategy is to extract from $F[\rho]$ some realistic estimate. A historically important approach was proposed by Thomas and Fermi in 1927 [59, 60]. Treating the system as a non-interacting Fermi gas with density equal to the local density at any given point, one can assume

$$T[\rho] \propto \int d\mathbf{r} (\rho(\mathbf{r}))^{5/3} \quad (1.7)$$

The electron-electron interaction can then be added as

$$V_{ee}[\rho] \simeq \frac{e^2}{2} \int \int d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} = E_{Hartree} \quad (1.8)$$

The remainder of the approximation may be cast into an unknown functional $E_{xc}[\rho]$, called the *exchange-correlation functional* (despite including also a kinetic contribution). The energy functional built with these prescription should then be minimised in order to obtain the ground-state properties, as explained above.

1.1.3 The Kohn-Sham equations

So far, unlike the Hartree-Fock model, DFT is still an exact theory: the functional $E[\rho]$ has been derived with no approximations and Theorem 1.1.2 ensures that its minimum is precisely the ground-state energy. Still, the Thomas-Fermi expression for the kinetic energy T yields rather inaccurate outcomes for most applications [61]; together with the absence of an explicit form for the exchange-correlation functional, this leaves us with no chance other than forgetting about complete exactness in order to allow for a theory of practical use. Some degree of approximation is therefore unavoidable.

A brilliant solution was found in 1965 by W. Kohn and L.J. Sham [13]. Let us consider working on a fictitious, non-interacting *auxiliary system*, via the replacement

$$V_{ee} \longrightarrow V'_{ee} = \lambda V_{ee} = \begin{cases} V_{ee} & \lambda = 1 \text{ (physical system)} \\ 0 & \lambda = 0 \text{ (auxiliary system)} \end{cases} \quad (1.9)$$

under the constraint that the ground-state density of the auxiliary system be the same as that of the physical, interacting one.

The advantage of this fictitious construction is that, the auxiliary system being non-interacting, the wavefunction can now be expressed as a Slater determinant made up of orthonormal single-particle orbitals ϕ_i , termed the *Kohn-Sham orbitals*. The kinetic-energy term can therefore be rewritten as

$$T[\rho] = T_0[\rho] = \sum_i \int d\mathbf{r} \phi_i^*(\mathbf{r}) \left(-\frac{\hbar^2}{2m_e} \nabla^2 \right) \phi_i(\mathbf{r}) \quad (1.10)$$

where

$$\rho(\mathbf{r}) := \sum_i |\phi_i(\mathbf{r})|^2 \quad (1.11)$$

Restoring the electron-electron interaction term in the Hartree form (1.8), $E[\rho]$ can now be expressed as

$$E[\rho] = T_0[\phi_i] + \int d\mathbf{r} \rho(\mathbf{r}) v_{ext}(\mathbf{r}) + E_{Hartree}[\rho] + E_{xc}[\rho] \quad (1.12)$$

and minimised with respect to the orbitals:⁴

$$0 \equiv \frac{\delta}{\delta \phi_i^*(\mathbf{r})} \left[E[\phi_i, \rho] - \sum_{ij} \varepsilon_{ij} \left(\int \phi_i^* \phi_j - \delta_{ij} \right) \right] \quad (1.14)$$

(where a Lagrangian multiplier ε_{ij} has been added in order to conserve orthonormalisation).

This gives as outcome a system of single-particle equations, known as *Kohn-Sham equations*:

$$\boxed{H^{(KS)} \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r})} \quad (1.15)$$

⁴Since only the kinetic term is explicitly written as a functional of the orbitals, one uses the chain rule

$$\frac{\delta E}{\delta \phi_i^*(\mathbf{r})} = \frac{\delta T_0}{\delta \phi_i^*(\mathbf{r})} + \left[\frac{\delta V_{ext}}{\delta \rho(\mathbf{r})} + \frac{\delta E_{Hartree}}{\delta \rho(\mathbf{r})} + \frac{\delta E_{xc}}{\delta \rho(\mathbf{r})} \right] \frac{\delta \rho(\mathbf{r})}{\delta \phi_i^*(\mathbf{r})} \quad (1.13)$$

for the effective Hamiltonian

$$H^{(KS)} = -\frac{\hbar^2}{2m_e}\nabla^2 + V_{ext}(\mathbf{r}) + V_{Hartree}(\mathbf{r}) + V_{xc}(\mathbf{r}) = -\frac{\hbar^2}{2m_e}\nabla^2 + V_{KS}(\mathbf{r}) \quad (1.16)$$

where

$$\begin{aligned} V_{Hartree} &= \frac{\delta E_{Hartree}}{\delta \rho(\mathbf{r})} = e^2 \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \\ V_{xc} &= \frac{\delta E_{xc}}{\delta \rho(\mathbf{r})} \\ V_{KS} &:= V_{ext} + V_{Hartree} + V_{xc} \end{aligned} \quad (1.17)$$

Kohn-Sham equations are integro-differential equations (just like Hartree-Fock ones) requiring an iterative, self-consistent solution, since their unknown variables (the single-particle orbitals) also appear in the effective Hamiltonian. Hence, starting from an initial guess for the Kohn-Sham orbitals ϕ_i and thus for the ground-state density ρ_0 (which in turn determines V_{KS}), the Kohn-Sham equations are solved and a new set of orbitals ϕ'_i is obtained, yielding a new density ρ'_0 . This new density updates V_{KS} and the Kohn-Sham equations are solved again. This procedure is repeated until the initial and final density of the i -th iteration coincide, up to the desired accuracy.

The total ground-state energy is then obtained by combining 1.12 with

$$\sum_i \varepsilon_i = \langle H^{(KS)} \rangle = \langle T_0 \rangle + \langle V_{ext} \rangle + \langle V_{Hartree} \rangle + \langle V_{xc} \rangle \quad (1.18)$$

and using $\langle V_{xc} \rangle = \int d\mathbf{r} \rho(\mathbf{r}) V_{xc}(\mathbf{r})$, $\langle V_{Hartree} \rangle = 2E_{Hartree}$. A proper rearrangement yields

$$E = \sum_i \varepsilon_i - E_{Hartree} + E_{xc} - \int d\mathbf{r} \rho(\mathbf{r}) V_{xc}(\mathbf{r}) \quad (1.19)$$

1.1.4 DFT vs Hartree-Fock

A first, important difference between the Kohn-Sham Hamiltonian and its Hartree-Fock counterpart lies in the replacement of the non-local Fock term with the local *exchange-correlation potential* V_{xc} , defined in 1.17 as the functional derivative of the exchange-correlation energy.

As far as computational complexity is concerned, Kohn-Sham DFT nominally scales as $O(N^3)$, but once again in practical implementations this overload can be reduced, in some cases even to linear order [18, 62].⁵

Also, the interpretation of Hartree-Fock and Kohn-Sham eigenvalues differs. The *Koopmans theorem* [63] states that the eigenvalue ε_i of the Hartree-Fock problem represents a true ionisation energy, i.e., the energy necessary to subtract from the interacting system an electron initially in the i -th energy level, provided that orbital relaxation and electron correlation effects are neglected. This is no longer true in DFT: the Kohn-Sham eigenvalues ε_i can no longer be thought of as real energy levels of the system. Nonetheless, one should

⁵Orbital-free DFT would scale linearly, as well.

not conclude that Kohn-Sham eigenvalues have no physical meaning at all. It is indeed possible to prove a result known as *Janak theorem* [64], linking them to the average occupation of the corresponding orbital:

Theorem 1.1.3. *Let ε_i be the i -th Kohn-Sham eigenvalue, n_i the occupation of i -th Kohn-Sham orbital, E the total energy. Then*

$$\varepsilon_i = \frac{\partial E}{\partial n_i} \quad (1.20)$$

1.1.5 Spin-dependent DFT

So far, the spin degree of freedom has been treated as idle and therefore “packed” inside electronic spatial coordinates. It must, however, be included explicitly in the presence of an external magnetic field, or in the case of spin-polarised systems. In Hohenberg-Kohn DFT, this is done by generalising the density as a sum of spin-dependent contributions

$$\rho(\mathbf{r}) = \rho_{\uparrow}(\mathbf{r}) + \rho_{\downarrow}(\mathbf{r}) \quad (1.21)$$

and recasting the energy functional as

$$E[\rho_{\uparrow}, \rho_{\downarrow}] = F[\rho_{\uparrow}, \rho_{\downarrow}] + V_{ext}[\rho] \quad (1.22)$$

At the Kohn-Sham level, each orbital ϕ_i is replaced by the pair $\{\phi_{i\uparrow}, \phi_{i\downarrow}\}$ and the spin-dependent density is readily obtained as

$$\rho_{\sigma}(\mathbf{r}) := \sum_i |\phi_{i\sigma}(\mathbf{r})|^2 \quad (\sigma = \uparrow, \downarrow) \quad (1.23)$$

The Kohn-Sham Hamiltonian and equations become, in turn, spin dependent, as follows:

$$\begin{aligned} \left[-\frac{\hbar^2}{2m_e} \nabla^2 + V_{KS}^{\sigma}(\mathbf{r}) \right] \phi_{i\sigma}(\mathbf{r}) &= \varepsilon_{i\sigma} \phi_{i\sigma}(\mathbf{r}) \\ V_{KS}^{\sigma}(\mathbf{r}) &= V_{ext}(\mathbf{r}) + V_{Hartree}(\mathbf{r}) + V_{xc}^{\sigma}(\mathbf{r}) \\ V_{xc}^{\sigma}(\mathbf{r}) &= \frac{\delta E_{xc}[\rho_{\uparrow}, \rho_{\downarrow}]}{\delta \rho_{\sigma}(\mathbf{r})} \end{aligned} \quad (1.24)$$

The self-consistent procedure is carried out as already described above, with the only difference that $\rho_{\uparrow}$ and $\rho_{\downarrow}$ are updated separately (but still simultaneously, of course, since spin channels are coupled in terms such as $V_{Hartree}$ and V_{xc}).

What presented here is, strictly speaking, the *collinear* version of spin-DFT: we implicitly assume that there exists a global quantisation axis (say $\hat{z}$) and spins can only align along it, with either the $\uparrow$ or the $\downarrow$ orientations. In the presence of interactions that break the local spin-rotational symmetry (e.g., spin-orbit coupling), spins are promoted as true 3D vectors and a *non-collinear* framework is needed. The formalism in this case results more complicated and will not be covered here; some basic concepts, however, will be introduced later on when dealing with constrained magnetisation calculations.

1.1.6 Approximations for the exchange-correlation functional

Kohn-Sham equations provide, in principle, an efficient and computationally feasible way to implement DFT, thus enabling us to extend our interest to systems containing up to some hundreds atoms with no overwhelming computational cost. Still, nothing has been said about the exchange-correlation functional, for which approximated forms must be employed, since no exact expression is known to date. In the following, the two main families of functionals are briefly presented.

One starts by introducing an exchange-correlation energy density ε_{xc} via

$$E_{xc}[\rho] = \int d\mathbf{r} \rho(\mathbf{r}) \varepsilon_{xc}([\rho(\mathbf{r})], \mathbf{r}) \quad (1.25)$$

where again ε_{xc} is a functional of the density.

L(S)DA

The *local-density approximation*, building on the original ideas by Thomas and Fermi, consists in 1) assuming ε_{xc} to be depending only upon the local value of the electron density; 2) adopting locally the expression valid for the homogeneous electron gas:

$$\varepsilon_{xc}^{LDA}([\rho(\mathbf{r})], \mathbf{r}) \simeq \varepsilon_{xc}^{HEG}(\rho(\mathbf{r})) \quad (1.26)$$

which in a spin-polarised form (*local-spin-density approximation*) reads

$$\varepsilon_{xc}^{LSDA}([\rho_{\uparrow}(\mathbf{r}), \rho_{\downarrow}(\mathbf{r})], \mathbf{r}) \simeq \varepsilon_{xc}^{HEG}(\rho_{\uparrow}(\mathbf{r}), \rho_{\downarrow}(\mathbf{r})) \quad (1.27)$$

This yields (consider spinless case for simplicity)

$$E_{xc}^{LDA}[\rho] = \int d\mathbf{r} \rho(\mathbf{r}) \varepsilon_{xc}^{HEG}(\rho(\mathbf{r})) \quad (1.28)$$

and thus

$$V_{xc}^{LDA} = \frac{\delta E_{xc}^{LDA}}{\delta \rho(\mathbf{r})} = \varepsilon_{xc}^{HEG}(\rho(\mathbf{r})) + \rho(\mathbf{r}) \frac{\delta \varepsilon_{xc}^{LDA}}{\delta \rho(\mathbf{r})} \quad (1.29)$$

The exchange-correlation energy density may be decomposed as $\varepsilon_{xc}^{HEG} = \varepsilon_X^{HEG} + \varepsilon_C^{HEG}$ where ε_X^{HEG} can be worked out exactly, whereas ε_C^{HEG} is often derived from Quantum Monte Carlo calculations. Widely used forms are due to Ceperley and Alder [65] and to Perdew and Zunger [66].

GGA

It is possible to show that LDA has a tendency to underestimate the exchange energy, as well as to overestimate the correlation term [67]. These sources of error often compensate each other up to some degree, but this is not always the case. In order to account for this, it is customary to introduce a dependence upon the density gradient in the approximation of the functional, namely as

$$\varepsilon_{xc}^{GGA} [\rho_{\uparrow}(\mathbf{r}), \rho_{\downarrow}(\mathbf{r})] \simeq \varepsilon_X^{HEG}(\rho(\mathbf{r})) f_{xc}(\rho_{\uparrow}, \rho_{\downarrow}, \nabla\rho_{\uparrow}, \nabla\rho_{\downarrow} \dots) \quad (1.30)$$

where the functional form of f_{xc} is not unique and may contain empirical parameters. Since gradients can be very large for inhomogeneous systems, they are normally rescaled and made adimensional as

$$s = \frac{|\nabla\rho|}{2k_F\rho} \quad (1.31)$$

This approach is termed *generalised gradient approximation* and is known to generally yield better results than LDA (with due, important exceptions). A frequently used form is that of Perdew, Burke and Ernzerhof (PBE) [68]; a variation of this, specifically optimised for solids and called PBEsol, will be largely used throughout the thesis [69].

1.1.7 DFT+U

Standard exchange-correlation functionals within the LDA or GGA family are normally sufficient to treat the majority of systems with reasonable accuracy. Nonetheless, there are classes of materials that need a specific treatment.

A prominent example is that of the so-called strongly correlated materials. Materials belonging to this class (typically, transition metal or rare-earth-based compounds) normally contain ions with partially filled d or f shells. Due to the strong Coulombic repulsion, these electrons tend to be localised in an atomic-like fashion, much more so than standard DFT functionals can tackle. As a consequence, treating them at the LDA/GGA level often leads to an incorrect prediction of itinerant electrons and metallic behaviour [70, 71].

Among the many techniques proposed to remedy this drawback, the DFT+U method turns out to be the most immediate and easy to implement [71, 72]. Essentially, it consists in “patching” the original DFT energy with an additional term, able to enforce the localisation of the d (f) manifold.

The shape of such term is inherited from the Hubbard Hamiltonian, a lattice model proposed by Hubbard in 1963 to describe the metal-insulator transition in the so-called Mott insulators [73]. In its simplest form, with translational invariance and limited to nearest-neighbour interactions, the Hubbard Hamiltonian reads

$$H = -t \sum_{\langle i,j \rangle} \sum_{\sigma} (a_{i,\sigma}^{\dagger} a_{j,\sigma} + a_{i,\sigma} a_{j,\sigma}^{\dagger}) + U \sum_i n_{i,\uparrow} n_{i,\downarrow} \quad (1.32)$$

The first term in 1.32 is a kinetic term, that promotes (with the choice $t > 0$) the hopping of electrons from one lattice site to another. The second is an on-site Coulomb interaction: provided $U > 0$ is chosen, it penalises multiple occupation of each lattice site i , acting therefore as repulsive. In the limit $U \rightarrow 0$, the model is essentially a tight-binding description of itinerant, band-like electrons; conversely, in the opposite limit $t \rightarrow 0$, electrons are fully localised and atomic-like. In the intermediate regime, by adequately tuning the U and t parameters, the model can picture real cases, including transitions from the conductive to the insulating state as in the case of Mott insulators.

Building on this, the patch introduced in the DFT+U model can be naively sketched as follows:⁶

$$E_{LDA+U} = E_{LDA} + \frac{1}{2}U \sum_{i \neq j} n_i n_j - U \frac{N(N-1)}{2} \quad (1.33)$$

where the first term describes delocalised electrons at the LDA level, the second is the Hubbard-like Coulomb interaction for localised d electrons and the third is the overall d - d interaction as would be given by LDA, to be subtracted in order to avoid double counting ($N = \sum_i n_i$ is the total of d electrons). Orbital energies are then obtained as derivatives with respect to the occupation n_i of the i -th orbital:

$$\epsilon_{i,LDA+U} = \frac{\partial E}{\partial n_i} = \epsilon_{LDA} + U \left(\frac{1}{2} - n_i \right) \quad (1.34)$$

It is easy to verify by simple substitution of $n_i = 0, 1$ that the incorporation of the Hubbard term shifts the LDA energies by $\mp U/2$ for occupied and unoccupied orbitals, respectively. This often reduces – or even suppresses altogether – the metallic character of the LDA bands, accentuating the otherwise insufficient localisation of the d electrons.

In the original implementation by Liechtenstein et al. [72], the problem is expanded on a localised basis set and recast in terms of on-site occupancy matrices $\{n^\sigma\} = n_{mm'}^\sigma$. The energy ultimately reads

$$E_{LDA+U}[\rho^\sigma(\mathbf{r}), \{n^\sigma\}] = E_{LDA}[\rho^\sigma(\mathbf{r})] + E_U[\{n^\sigma\}] - E_{DC}[\{n^\sigma\}] \quad (1.35)$$

where $\rho^\sigma(\mathbf{r})$ is the charge density for spin- σ electrons,

$$E_{DC}[\{n^\sigma\}] = \frac{U}{2} n_{\text{tot}}(n_{\text{tot}} - 1) - \frac{J}{2} \sum_{\sigma} n_{\text{tot}}^\sigma (n_{\text{tot}}^\sigma - 1) \quad (1.36)$$

is the term that avoids double counting, featuring effective on-site Coulomb- and exchange parameters U and J (here, $n_{\text{tot}}^\sigma = \text{Tr}\{n^\sigma\}$ and $n_{\text{tot}} = \sum_{\sigma} n_{\text{tot}}^\sigma$), and

$$E_U[\{n^\sigma\}] = \frac{1}{2} \sum_{\{m\}, \sigma} (U_{mm''m'm'''} - U_{mm''m'''m'}) n_{mm'}^\sigma n_{m''m'''}^\sigma \quad (1.37)$$

where U_{abcd} are matrix elements of the unscreened on-site electron-electron interaction, themselves expressed in terms of U and J .

A popular and simpler implementation was proposed by Dudarev et al. [74]:

$$E_{LDA+U} = E_{LDA} + \frac{U-J}{2} \sum_{\sigma} \left[\left(\sum_m n_{mm'}^\sigma \right) - \left(\sum_{mm'} n_{mm'}^\sigma n_{mm'}^\sigma \right) \right] \quad (1.38)$$

In practice, deviating from the purely *ab initio* philosophy, U and J are often treated as adjustable parameters, though self-consistent procedures to evaluate them exist as well [75, 76].

⁶The formulation – following [71] – is presented in terms of LDA functionals and for d electrons, but equally applies to GGA functionals and f electrons as well.

1.2 Plane-wave DFT

The content of Section 1.1 outlines how DFT works in principle. Turning it into a concrete computational approach requires expanding Kohn-Sham orbitals on a set of basis functions, which converts the secular problem 1.15 into an algebraic one for the expansion coefficients. For periodic systems, the choice of the basis set must in any case respect Bloch theorem [77], which asserts that the orbitals can be written as

$$\psi_{n\mathbf{k}}(\mathbf{r}) = u_{n\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}} \quad (1.39)$$

where the *Bloch wavefunction* $u_{n\mathbf{k}}(\mathbf{r}) = u_{n\mathbf{k}}(\mathbf{r} + \mathbf{R})$ features the same periodicity of the lattice, n is the band index and $\mathbf{k}$ a suitable wavevector, conveniently chosen inside the first Brillouin zone.

The most frequently employed techniques envisage an expansion either on plane waves – namely, a Fourier decomposition – or on localised functions, typically Gaussian or atomic-like orbitals. More advanced approaches, such as the APW method, mix the two types of basis functions.

Each choice has its own benefits and drawbacks [78]. For instance, plane-wave bases are universal, in that they do not depend neither on the atomic positions nor on their chemical nature, and the convergence of the results with respect to the basis size is controlled by a single, quantitative cutoff parameter. However, when treating systems with reduced periodicity (namely, surfaces, interfaces or 2D materials) for which slabs are needed with appropriate vacuum layers (see Section 1.3 below), a plane-wave basis turns out to be rather costly, since the whole simulation space must be filled with plane waves, whereas localised basis functions are appreciably nonzero only in the vicinity of the atom they are centred upon, so that the vacuum comes for free.

The VASP code, used throughout the work, employs plane waves. The problem of how Kohn-Sham equations are explicitly written on such basis set is therefore addressed here.

A normalised plane wave can be defined as

$$\phi_{\mathbf{q}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}}e^{i\mathbf{q}\cdot\mathbf{r}} \quad (1.40)$$

where Ω is the volume of the unit cell and $\mathbf{q}$ is an arbitrary wavevector. In a periodic crystal, translational symmetry restricts the allowed wavevectors to the form $\mathbf{q} = \mathbf{k} + \mathbf{G}$, where $\mathbf{k}$ lies in the Brillouin zone and $\mathbf{G}$ is a reciprocal lattice vector. The Bloch form is then automatically retrieved as⁷

$$\chi_{\mathbf{G}\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}}e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} \quad (1.41)$$

and the expansion of the Kohn-Sham orbital on such basis reads

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{n\mathbf{G}}(\mathbf{k}) \chi_{\mathbf{G}\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} \sum_{\mathbf{G}} c_{n\mathbf{G}}(\mathbf{k}) \frac{1}{\sqrt{\Omega}}e^{i\mathbf{G}\cdot\mathbf{r}} \quad (1.42)$$

⁷ $\chi_{\mathbf{G}\mathbf{k}}(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}}\chi_{\mathbf{G}\mathbf{k}}(\mathbf{r})$ for any lattice vector $\mathbf{R}$ (follows from $e^{i\mathbf{G}\cdot\mathbf{R}} = 1$).

We now consider the secular problem $H\psi_{n\mathbf{k}}(\mathbf{r}) = \varepsilon_n(\mathbf{k})\psi_{n\mathbf{k}}(\mathbf{r})$: multiplying on the left by $\chi_{\mathbf{G}'\mathbf{k}}^*$, integrating over all space and using the expansion 1.42 yields

$$\int d\mathbf{r} \chi_{\mathbf{G}'\mathbf{k}}^*(\mathbf{r}) H \sum_{\mathbf{G}} c_{n\mathbf{G}}(\mathbf{k}) \chi_{\mathbf{G}\mathbf{k}}(\mathbf{r}) = \varepsilon_n(\mathbf{k}) \int d\mathbf{r} \chi_{\mathbf{G}'\mathbf{k}}^*(\mathbf{r}) \sum_{\mathbf{G}} c_{n\mathbf{G}}(\mathbf{k}) \chi_{\mathbf{G}\mathbf{k}}(\mathbf{r}) \quad (1.43)$$

easily rearranged as

$$\sum_{\mathbf{G}} \left[\int d\mathbf{r} \chi_{\mathbf{G}'\mathbf{k}}^*(\mathbf{r}) H \chi_{\mathbf{G}\mathbf{k}}(\mathbf{r}) - \varepsilon_n(\mathbf{k}) \int d\mathbf{r} \chi_{\mathbf{G}'\mathbf{k}}^*(\mathbf{r}) \chi_{\mathbf{G}\mathbf{k}}(\mathbf{r}) \right] c_{n\mathbf{G}}(\mathbf{k}) = 0 \quad (1.44)$$

Introducing the Hamiltonian matrix elements

$$H_{\mathbf{G}'\mathbf{G}}(\mathbf{k}) = \int d\mathbf{r} \chi_{\mathbf{G}'\mathbf{k}}^*(\mathbf{r}) H \chi_{\mathbf{G}\mathbf{k}}(\mathbf{r}) \quad (1.45)$$

and exploiting the orthonormality of plane waves

$$\int d\mathbf{r} \chi_{\mathbf{G}'\mathbf{k}}^*(\mathbf{r}) \chi_{\mathbf{G}\mathbf{k}}(\mathbf{r}) = \delta_{\mathbf{G}'\mathbf{G}} \quad (1.46)$$

the secular equation assumes the compact form⁸

$$\boxed{\sum_{\mathbf{G}} [H_{\mathbf{G}'\mathbf{G}}(\mathbf{k}) - \varepsilon_n(\mathbf{k}) \delta_{\mathbf{G}'\mathbf{G}}] c_{n\mathbf{G}}(\mathbf{k}) = 0} \quad (1.47)$$

We now explicitly evaluate the matrix elements for the Kohn-Sham Hamiltonian 1.16. The kinetic-energy contribution is evaluated as

$$\begin{aligned} \int d\mathbf{r} \chi_{\mathbf{G}'\mathbf{k}}^*(\mathbf{r}) \left(-\frac{\hbar^2}{2m_e} \nabla^2 \right) \chi_{\mathbf{G}\mathbf{k}}(\mathbf{r}) &= \frac{1}{\Omega} \left(-\frac{\hbar^2}{2m_e} \right) \int d\mathbf{r} e^{-i(\mathbf{k}+\mathbf{G}')\cdot\mathbf{r}} \nabla^2 e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} \\ &= \frac{\hbar^2}{2m_e} |\mathbf{k} + \mathbf{G}|^2 \frac{1}{\Omega} \int d\mathbf{r} e^{-i(\mathbf{G}-\mathbf{G}')\cdot\mathbf{r}} = \frac{\hbar^2}{2m_e} |\mathbf{k} + \mathbf{G}|^2 \delta_{\mathbf{G}'\mathbf{G}} \end{aligned} \quad (1.48)$$

The potential-energy term yields

$$\int d\mathbf{r} \chi_{\mathbf{G}'\mathbf{k}}^*(\mathbf{r}) V_{\text{KS}}(\mathbf{r}) \chi_{\mathbf{G}\mathbf{k}}(\mathbf{r}) = \frac{1}{\Omega} \int d\mathbf{r} V_{\text{KS}}(\mathbf{r}) e^{i(\mathbf{G}-\mathbf{G}')\cdot\mathbf{r}} = V_{\text{KS}}(\mathbf{G}' - \mathbf{G}) \quad (1.49)$$

where $V_{\text{KS}}(\mathbf{q})$ denotes the Fourier component of the Kohn-Sham potential.

Combining the two contributions, we eventually obtain

$$\boxed{H_{\mathbf{G}'\mathbf{G}}(\mathbf{k}) = \frac{\hbar^2}{2m_e} |\mathbf{k} + \mathbf{G}|^2 \delta_{\mathbf{G}'\mathbf{G}} + V_{\text{KS}}(\mathbf{G}' - \mathbf{G})} \quad (1.50)$$

In principle, Eqn. 1.47 should be solved for an infinite set of coefficients $c_{n\mathbf{G}}(\mathbf{k})$ at every $\mathbf{k}$ -point in the Brillouin zone (again, *de facto*, an infinite set). In practice, both basis set and $\mathbf{k}$ -mesh are made finite, so that diagonalising the matrix becomes feasible.

⁸A formally analogous equation is obtained when using a localised basis, with the only notable difference that such functions are in general not orthogonal and therefore the Dirac delta of the indexes is replaced by an overlap matrix.

1.3 Computational aspects and VASP code

A series of aspects remain to be dealt with in order to turn DFT into a practical computational scheme. This section is devoted to browsing the most important of them and describing their implementation into the plane-wave software VASP (Vienna Ab-initio Simulation Package) [16, 17], among the oldest and most widely employed DFT codes, adopted throughout the thesis.

Pseudopotentials

As far as electronic structure and chemical bonding are concerned, a detailed knowledge of core states is often unnecessary, since only valence electrons contribute significantly. One can then replace the exact atomic potential (V_{ext} in the Kohn-Sham Hamiltonian 1.16) with an effective *pseudopotential*, which equals the true one only for distances greater than a certain threshold r_c and is smoother below.⁹ The same is done for valence electrons' pseudo-wavefunctions, chosen so as to match the true ones only above r_c . This allows to freeze out localised core shells and thus significantly reduce the computational effort, while still correctly describing energies of valence electrons.

The pseudopotential approach is particularly illuminating for plane-wave bases, since representing pseudo-wavefunctions, lacking one or more nodes below r_c , requires fewer Fourier components and thus a smaller basis set. Anyway, pseudopotentials can be employed with localised bases as well, both to get rid of useless core states and to ease the evaluation of integrals.

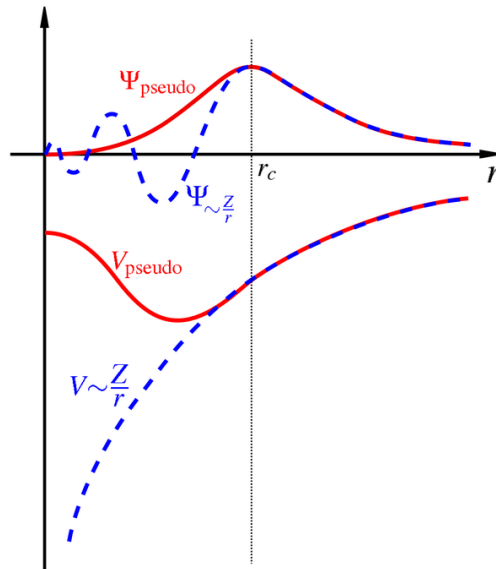


Figure 1.1: A sketch of the behaviour of a typical pseudopotential and pseudo-wavefunction in comparison to the real Coulomb potential and wavefunction. Adapted from <https://vasp.at/wiki/Category:Pseudopotentials>.

⁹In particular, it remains finite for $r = 0$, so as to get rid of the divergence of the Coulombic potential.

A representation on a smaller Fourier basis can be achieved at the expense of the correct normalisation of the pseudo-wavefunctions: in other terms, it would be desirable that integrating the square modulus of the pseudo-wavefunction up to the chosen threshold give the correct core-shell electron charge, but this demands a sufficiently large basis set. *Norm-conserving* pseudopotentials [79] indeed maintain a sizeable number of basis functions in order to yield the correct charge. The norm-conservation constraint is relaxed in the framework of *ultrasoft* pseudopotentials [80], resulting in smoother pseudo-wavefunctions and a smaller basis (the missing charge is recovered through additional augmentation terms). VASP adopts pseudopotentials of the *Projector Augmented Wave* (PAW) type [81, 82], which can be regarded as a generalisation of ultrasoft ones.

Basis size

As introduced earlier (Eqn. 1.42), within the plane-wave approach, the Kohn-Sham wavefunction is expanded as an (infinite) Fourier series

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{G}} c_{n\mathbf{G}}(\mathbf{k}) e^{i(\mathbf{G}+\mathbf{k})\cdot\mathbf{r}} \quad (1.51)$$

and the Kohn-Sham eigenvalue problem turns into an algebraic equation (Eqn. 1.47) for an infinite set of coefficients $c_{n\mathbf{G}}(\mathbf{k})$. In order to allow for computational applications, the plane-wave expansion must be truncated, yielding a finite basis set. This is achieved by introducing a kinetic-energy cutoff E_{cut} , that retains only reciprocal lattice vectors satisfying

$$\frac{\hbar^2}{2m_e} |\mathbf{k} + \mathbf{G}|^2 < E_{cut} \quad (1.52)$$

The quality of the plane-wave basis depends on the choice of the energy cutoff: the higher E_{cut} , the larger and more accurate the basis set. A suitable value for E_{cut} is to be determined by explicitly checking the convergence of relevant observables, typically the total energy, with respect to the cutoff. Typically, values of some hundreds of eV are needed, depending on the system under study (it is worth noting, however, that quantities such as atomic forces, stress tensors and vibrational properties often converge more slowly than the total energy and may require higher cutoff values).

In VASP, each PAW pseudopotential for a given atomic species provides a recommended cutoff, under the tag **ENMAX**. For multi-component systems, the cutoff is usually chosen to be at least as large as the maximum **ENMAX** among the atomic species at stake, and it is good practice to further increase it to ensure accurate convergence.

Brillouin zone sampling

Many physical quantities of interest involve integrals over the Brillouin zone. A paradigmatic example is the electronic density itself $\rho(\mathbf{r}) = \sum_i |\phi_i(\mathbf{r})|^2$ (Eqn. 1.11) which, after resolving the abstract index i as $(n, \mathbf{k})$ in the spirit of Eqn. 1.42, becomes

$$\rho(\mathbf{r}) = \sum_n^{\text{occ}} \int_{\text{BZ}} \frac{d\mathbf{k}}{\Omega_{\text{BZ}}} |\psi_{n\mathbf{k}}(\mathbf{r})|^2 \quad (1.53)$$

In practical calculations, these integrals are replaced by weighted sums over a discrete set of $\mathbf{k}$ -points, sampling reciprocal space. As a consequence, the Kohn-Sham eigenvalue problem (Eq. 1.47), which in principle must be solved for a continuum of $\mathbf{k}$ -vectors, is evaluated only on a finite set of points.

A common choice for the $\mathbf{k}$ -space sampling is provided by regular meshes, defined by a uniform distribution of $\mathbf{k}$ -points in the Brillouin zone. Typical examples are the Γ -centred mesh

$$\mathbf{k}_{n_1, n_2, n_3} = \sum_{i=1}^3 \frac{n_i}{N_i} \mathbf{b}_i \quad (1.54)$$

and the *Monkhorst-Pack* mesh [83]

$$\mathbf{k}_{n_1, n_2, n_3} = \sum_{i=1}^3 \frac{2n_i - N_i - 1}{2N_i} \mathbf{b}_i \quad (1.55)$$

where $\mathbf{b}_i$ are the primitive vectors of the reciprocal lattice, N_i denotes the number of $\mathbf{k}$ -points chosen along $\mathbf{b}_i$ and $n_i = 1, \dots, N_i$.

As for the plane-wave cutoff, convergence tests with respect to the $\mathbf{k}$ -point mesh size must be explicitly performed: increasing the number of sampling points improves the accuracy of the calculated quantities. For reasonably sized unit cells, with lattice constants of the order of a few Å, a sampling of 5-10 $\mathbf{k}$ -points per reciprocal lattice direction is normally sufficient; precise values, however, are necessarily system-dependent, since the convergence is typically slower for metallic systems than for insulators or semiconductors. As a rule of thumb, the relative number of $\mathbf{k}$ -points along the reciprocal lattice directions is chosen according to $N_1 : N_2 : N_3 \simeq |\mathbf{b}_1| : |\mathbf{b}_2| : |\mathbf{b}_3|$. For unit cells with (nearly) orthogonal direct lattice vectors $\mathbf{a}_i$, this prescription corresponds to requiring $N_1 : N_2 : N_3 \simeq \frac{1}{|\mathbf{a}_1|} : \frac{1}{|\mathbf{a}_2|} : \frac{1}{|\mathbf{a}_3|}$.

The computational effort can be significantly reduced by exploiting the symmetries of the crystal. Symmetry operations map equivalent $\mathbf{k}$ -points onto each other, allowing the integration to be restricted to the *irreducible Brillouin zone*, i.e., the smallest portion of reciprocal space containing all independent information. In particular, when time-reversal symmetry is present, electronic states at $\mathbf{k}$ and $-\mathbf{k}$ are equivalent, which reduces the integration domain by at least a factor of two.

SCF calculation; mixing

The self-consistent field (SCF) procedure consists in solving the Kohn-Sham equations in an iterative fashion, starting from an initial guess for the orbitals, and thus for the density. Atomic wavefunctions are used as a default choice, although functions obtained from previous self-consistent calculations can also be provided as input.

At the end of the i -th iteration, whose input density be $\rho_{in}^{(i)}$, a new density $\rho_{out}^{(i)}$ is produced from the computed Kohn-Sham eigenfunctions. Directly feeding $\rho_{out}^{(i)}$ as input for the next iteration may lead to numerical instabilities or slow convergence, especially in metallic or low-dimensional systems, where long-wavelength charge fluctuations (charge sloshing) can occur. Instead, the latest density is mixed with the previous one.

The basic mechanism is linear mixing

$$\rho_{in}^{(i+1)} = \alpha \rho_{out}^{(i)} + (1 - \alpha) \rho_{in}^{(i)} \quad (1.56)$$

where $0 < \alpha < 1$ is the mixing parameter. More efficient and robust schemes, such as Broyden [84] or Pulay mixing [85], are commonly employed in standard electronic-structure codes, including VASP.

Electronic temperature

In principle, DFT describes the electronic ground state at zero temperature, which means that the occupation function (the Fermi-Dirac distribution function at $T = 0$) goes abruptly from 1 to 0 at $\varepsilon = \varepsilon_F$.

Many quantities of interest require sums over occupied states – most notably, the electron density (Eqn. 1.53). These are expressed as an integral in $\mathbf{k}$ -space (turned into a discrete sum over the selected $\mathbf{k}$ -point mesh) times a sum over electronic bands, weighted by the occupation number. One then ends up integrating functions that drop rapidly and discontinuously when crossing the Fermi level, which in turn demands a very accurate $\mathbf{k}$ -point mesh.

In metallic systems, an additional difficulty arises in the form of level-crossing instabilities: during the self-consistent cycle, eigenvalues may cross the Fermi level, causing sudden changes in the occupation pattern and hence in the electronic density. These abrupt variations can severely hinder convergence.

It is therefore customary to use a smeared occupation function, whose descent at ε_F be continuous and less abrupt, in order to be able to employ a standard-size $\mathbf{k}$ -point mesh. In so doing, the total energy ceases to be the variational quantity and a free energy $F = E - \sigma S$ must be introduced, since now everything goes as if the system was simulated at a finite temperature. The $\sigma \rightarrow 0$ energy can then be extrapolated as [86]

$$E(\sigma \rightarrow 0) = \frac{E(\sigma) + F(\sigma)}{2} \quad (1.57)$$

The analytical expression for the smeared function is in principle arbitrary. Standard choices for the smearing procedure – all implemented in VASP – are:

- **Fermi-Dirac** [87]: the smeared function is the actual Fermi-Dirac function at finite temperature

$$\varphi(\varepsilon) = \frac{1}{e^{\beta(\varepsilon - \mu)} + 1} \quad (1.58)$$

($\varepsilon_n(\mathbf{k})$ shortened to ε for brevity; $\beta = \sigma^{-1}$; $\beta\mu = \varepsilon_F$) with an entropy term

$$S(\varepsilon) = -k_B [\varphi \log \varphi + (1 - \varphi) \log(1 - \varphi)] \quad (1.59)$$

Fermi-Dirac smearing is easy to interpret, pointing directly at Mermin's thermal extension of DFT. Yet, if convergence turns out to be troublesome, this smearing can speed it only at the cost of using a rather high temperature, which would take the system far away from the $T = 0$ condition.

- **Gaussian** [88, 89]: the occupation is obtained by integrating a Gaussian broadening of the density of states, resulting in an error-function-like profile. The deviation of the smeared total energy from the $T = 0$ one scales quadratically with σ .
- **Methfessel-Paxton** [90]: the smeared occupation function is the integral of a Gaussian times a Hermite polynomial, normally of first or second order. The deviation can be shown to be quartic in this case, so that the energy functional remains close to the $T = 0$ one even for high values of the (fictitious) electronic temperature (up to thousands of K). A disadvantage arises from unphysical negative occupations that may occur due to oscillations of the Hermite polynomial.¹⁰
- **Tetrahedron method** [92]: the Brillouin zone is partitioned into a set of small tetrahedra, within which the band energies are linearly interpolated. Integrals over $\mathbf{k}$ -space are then evaluated analytically inside each tetrahedron, yielding accurate results for quantities involving sharp features at the Fermi level. The tetrahedron method does not rely on an artificial smearing parameter and is therefore particularly well suited for calculating total energies and densities of states. However, it is less effective in accelerating self-consistent convergence and is typically employed only once self-consistency has been achieved.

Relaxation and forces

After each SCF cycle for the electronic problem, atoms are displaced with the goal of minimising forces among them, thereby yielding a stable structural configuration of the system (compatible with the starting symmetry).¹¹ The electronic SCF loop is thus embedded within an outer relaxation loop for the ionic degrees of freedom.

Forces are evaluated with the help of the *Hellmann-Feynman theorem* [93]:

Theorem 1.3.1. *Let $\hat{H}_\lambda$ be a Hamiltonian operator depending upon some continuous parameter λ , $|\psi_\lambda\rangle$ one of its eigenstates and E_λ the corresponding eigenvalue. Then*

$$\frac{dE_\lambda}{d\lambda} = \left\langle \psi_\lambda \left| \frac{d\hat{H}_\lambda}{d\lambda} \right| \psi_\lambda \right\rangle \quad (1.60)$$

In our case, with $\lambda = \mathbf{R}_I$, the theorem allows us to write the electronic contribution to the force on atom I as

$$\mathbf{F}_I^{\text{el}} = -\frac{\partial}{\partial \mathbf{R}_I} E(\{\mathbf{R}\}) \quad (1.61)$$

that is, involving only those terms in the Kohn-Sham energy that explicitly depend on ionic coordinates.¹² Restoring the ion-ion Coulomb repulsion E_{II} , the total force reads

$$\mathbf{F}_I = -\int d\mathbf{r} \rho(\mathbf{r}) \frac{\partial}{\partial \mathbf{R}_I} V_{\text{ext}}(\mathbf{r}, \{\mathbf{R}\}) - \frac{\partial E_{II}}{\partial \mathbf{R}_I} \quad (1.62)$$

¹⁰This problem can be circumvented in the context of the technique by Marzari and Vanderbilt [91].

¹¹Unless the user requests for a single-step calculation, with no structural minimisation.

¹²In other words, the theorem asserts that terms with derivatives of ψ_λ cancel out.

In addition to ionic forces, structural optimisation may also involve relaxation of the simulation cell itself. In this case, the relevant quantity is the stress tensor, which measures the response of the total energy to lattice strain. During variable-cell relaxations, both atomic positions and lattice vectors are iteratively updated until all forces and stress components fall below prescribed thresholds. Typical convergence criteria are forces smaller than $10^{-2} - 10^{-3}$ eV/Å and stress components below $10^{-2} - 10^{-3}$ GPa, although stricter tolerances may be required depending on the system and on the targeted physical properties.

3D vs 2D modelling: the slab method

Unlike bulk crystals, truly two-dimensional (2D) materials are periodic in two spatial directions only, while the third direction (here taken as $\hat{z}$) is non-periodic. Nevertheless, most electronic-structure codes solve the Kohn–Sham equations within a fully periodic simulation cell subject to Born–von Kármán boundary conditions (VASP being no exception). To accommodate this constraint, a fictitious but practical three-dimensional periodicity is restored by employing the slab method.

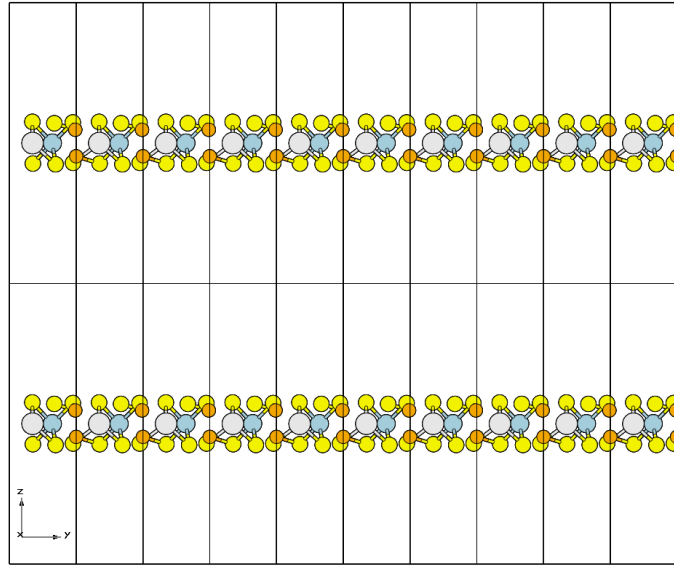


Figure 1.2: A sketch of the application of the slab method to a real case (2D magnet VAgP₂Se₆).

As illustrated in Fig. 1.2, an *ad hoc* supercell is constructed by enclosing the 2D material between two vacuum regions (one is enough, if the atomic layers are placed at the top/bottom of the supercell). Due to the code periodicity, the system is replicated also along $\hat{z}$, giving rise to non-physical periodic images of the slab. Spurious interactions between these periodic images can be made negligible by increasing the vacuum thickness, until convergence of the relevant physical quantities is achieved. Once this condition is satisfied, calculations can be carried out in the same formal way as for bulk systems.¹³

¹³Since the 3D periodicity is unphysical, Brillouin-zone sampling is correspondingly reduced along $\hat{z}$, down to a single $\mathbf{k}$ -point.

Constraining the magnetisation

In spin-polarised DFT, the self-consistent solution corresponds to the magnetic configuration that minimises the Kohn–Sham total energy. In many situations of interest, however, it is useful to gain access to magnetic states different from the unconstrained ground state, such as metastable configurations or states with prescribed orientations of local magnetic moments (the latter case, especially, will be extensively treated in Chapter 2). This can be achieved by means of *constrained magnetisation* techniques, allowing to enforce target values for the direction and/or magnitude of selected local magnetic moments at each step of the SCF cycle. Formally, such constraints are implemented by introducing an additional penalty term in the energy functional, which discourages deviations of magnetic moments from the desired configuration.

In the non-collinear formalism, the relevant quantity is the *magnetisation density*

$$\mathbf{m}(\mathbf{r}) = (m_x(\mathbf{r}), m_y(\mathbf{r}), m_z(\mathbf{r})) \quad (1.63)$$

whose modulus reduces to $m(\mathbf{r}) = \rho_{\uparrow}(\mathbf{r}) - \rho_{\downarrow}(\mathbf{r})$ in the collinear limit (see Eqn. 1.21).

The integrated magnetic moment associated with atom I is then defined as

$$\mathbf{M}_I = \int_{\Omega_I} d\mathbf{r} m(\mathbf{r}) F_I(|\mathbf{r} - \mathbf{R}_I|) \quad (1.64)$$

where Ω_I is a sphere centred on atom I and $F_I(|\mathbf{r}|)$ is a smooth weighting function of unit norm inside Ω_I , which gradually goes to zero at the sphere boundary.

The penalty energy to constrain the direction of magnetic moments is then given by

$$E_{\lambda} = \lambda \sum_I \left[\mathbf{M}_I - \hat{M}_I^0 (\hat{M}_I^0 \cdot \mathbf{M}_I) \right]^2 \quad (1.65)$$

where $\hat{M}_I^0$ is the unit vector defining the target direction for $\mathbf{M}_I$, and λ plays the role of a Lagrange multiplier, governing the strength of the constraint. VASP also provides alternative formulations of the penalty term, allowing for the simultaneous constraint of both direction and magnitude (or direction and sign) of the magnetic moments.

Care must be taken when interpreting energies obtained from constrained magnetisation calculations, as they explicitly depend on the value of the penalty parameter. In particular, meaningful energy comparisons can only be made between calculations performed using the same λ .

Vibrational properties

The vibrational properties of a crystal, within the harmonic approximation, are obtained from a second-order Taylor expansion of the total energy with respect to the ionic displacements around the equilibrium configuration [55]. Denoting by $\mathbf{u}_{\mathbf{n}\nu}$ the displacement of atom ν in the n -th unit cell along Cartesian direction α , the expansion reads

$$E^{(\text{harm})}(\{\mathbf{u}_{\mathbf{n}\nu}\}) = E(\{\mathbf{0}\}) + \frac{1}{2} \sum_{\mathbf{n}\nu\alpha, \mathbf{n}'\nu'\alpha'} D_{\mathbf{n}\nu\alpha, \mathbf{n}'\nu'\alpha'} u_{\mathbf{n}\nu\alpha} u_{\mathbf{n}'\nu'\alpha'} \quad (1.66)$$

where the *dynamical matrix* (matrix of force constants) has been introduced:

$$D_{n\nu\alpha,n'\nu'\alpha'} := \left(\frac{\partial^2 E^{(\text{harm})}}{\partial u_{n\nu\alpha} \partial u_{n'\nu'\alpha'}} \right)_0 \quad (1.67)$$

The classical equations of motion for the ions are

$$M_\nu \ddot{u}_{n\nu\alpha} = - \sum_{n'\nu'\alpha'} D_{n\nu\alpha,n'\nu'\alpha'} u_{n'\nu'\alpha'} \quad (1.68)$$

Looking for normal-mode solutions, and inspired by the presence of translational symmetry, we impose plane-wave displacements of the form $\mathbf{u}_{n\nu}(t) = \mathbf{A}_\nu(\mathbf{q}, \omega) e^{i(\mathbf{q} \cdot \mathbf{R}_n - \omega t)}$. Introducing the Fourier transform of the dynamical matrix

$$\widetilde{D}_{\nu\alpha,\nu'\alpha'}(\mathbf{q}) := \sum_{n'} D_{n\nu\alpha,n'\nu'\alpha'} u_{n'\nu'\alpha'} e^{i\mathbf{q} \cdot (\mathbf{R}_n - \mathbf{R}_{n'})} \quad (1.69)$$

(which has dimension $3N \times 3N$ for a unit cell containing N atoms), the differential equation 1.68 turns into an algebraic problem

$$\sum_{\nu'\alpha'} \left[\widetilde{D}_{\nu\alpha,\nu'\alpha'}(\mathbf{q}) - M_\nu \omega^2 \delta_{\alpha\alpha'} \delta_{\nu\nu'} \right] A_{\nu'\alpha'}(\mathbf{q}) = 0 \quad (1.70)$$

whose $3N$ eigenvalues and eigenvectors correspond to the normal modes and their frequencies. Upon quantisation, these collective excitations are quasiparticles called *phonons*, with dispersion relation $\omega = \omega(\mathbf{q})$.

It can be shown that, for every crystal, there are always three *acoustic modes* – collective in-phase motion of all atoms, with vanishing frequency as $\mathbf{q} \rightarrow 0$. The remaining $3N - 3$ are *optical modes*, characterised by relative antiphase motion of atoms within the cell, conserving the centre of mass, and finite frequency at small $\mathbf{q}$.

Phonon branches (in other words, the phonon band structure) can be obtained by plotting the eigenvalues on a $\mathbf{q}$ -space mesh selected along special paths¹⁴ inside the Brillouin zone, connecting high-symmetry points, as illustrated for a simple cubic lattice in Fig. 1.3.

Beyond thermal aspects, the study of phonons is also essential at the zero-temperature level, as it provides a powerful tool to detect structural instabilities. These manifest themselves through the appearance of so-called *soft modes*, characterised by negative eigenvalues of the dynamical matrix, i.e., $\omega^2 < 0$, corresponding to imaginary phonon frequencies (normally represented as negative frequencies in phonon dispersion plots). The presence of a soft mode indicates that displacing the atoms according to the associated eigenvector lowers the total energy of the system, signalling that the reference structure is not a true minimum of the potential-energy surface. Such instabilities may remain hidden in standard structural optimisations when the initial configuration corresponds to a saddle point of the energy landscape, where all forces — as given by Eqn. 1.61 — vanish

¹⁴Standard choices for such points and paths are tabulated in literature for the various crystalline structures [94].

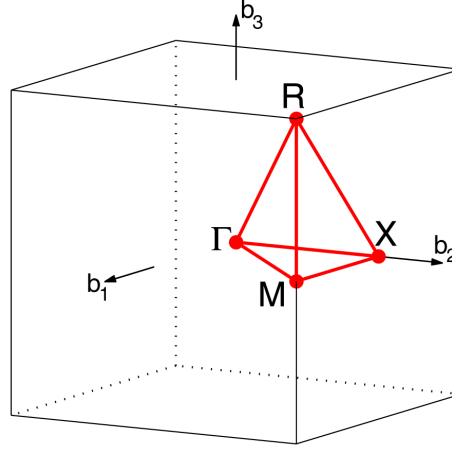


Figure 1.3: Brillouin zone and high-symmetry points for a simple cubic lattice (adapted from [95]).

identically. In these cases, phonon calculations provide crucial information on the unstable directions in configuration space. Once identified, an arbitrarily small displacement along the soft mode eigenvector can drive the system away from the saddle point and trigger a relaxation towards a lower-energy, dynamically stable configuration.

Within DFT codes, the dynamical matrix at a given $\mathbf{q}$ can be evaluated in two ways. In the *frozen phonon* framework, force constants are evaluated in real space through a finite-difference scheme: atoms are displaced back and forth by small amounts along the Cartesian directions, and the resulting forces are computed after self-consistent electronic calculations. These displacements are performed within a suitably chosen supercell in order to accommodate long-wavelength modulations, corresponding to small $\mathbf{q}$ wavevectors (otherwise, a calculation within the primitive cell only yields phonons at the Γ point). The frozen-phonon method has the advantage of relying on calculation of energy and forces as available in essentially any DFT code; on the other hand, the need for a supercell may imply a sizeable computational cost.

An alternative approach is provided by *Density Functional Perturbation Theory* (DFPT) [25], which allows one to compute the dynamical matrix directly in reciprocal space, by treating atomic displacements as perturbations and evaluating the linear response of the electronic density and potential. DFPT enables the calculation of phonons at arbitrary $\mathbf{q}$ using only the primitive unit cell, leading to a substantial reduction in computational effort.

Both methods are routinely implemented in DFT codes. However, the DFPT implementation in VASP is unfortunately somewhat rudimentary and, to date, does not allow for meaningful phonons within the primitive cell. As a consequence, DFPT phonon calculations in VASP must rely on supercells as well, so that the computational advantage over the frozen phonon method is suppressed and the two approaches tend to become essentially equivalent.

Linear-response properties

Finally, we briefly outline another important application of DFPT as implemented in VASP, namely the calculation of linear-response properties. By enabling the Boolean flag `LEPSILON` – either on its own or in combination with additional input tags – it is possible to perform unit-cell calculations that yield the static macroscopic dielectric tensor, the elastic and piezoelectric tensors, and the Born effective charge tensors (as well as, again, the Γ -point phonon frequencies as a byproduct). These quantities are obtained by evaluating the linear response of the electronic system to small external perturbations, such as homogeneous electric fields or infinitesimal atomic displacements. Among the quantities accessible through this approach, the piezoelectric tensor is of particular relevance for the present work and will therefore be discussed in detail in [Chapter 3](#).

Chapter 2

2D magnetism: AMaRaNTA

The present Chapter illustrates the AMaRaNTA package for exchange parameters of two-dimensional magnetic materials. Much of the content has been borrowed from our own original work [1], adjusted and expanded where suitable. A special thanks goes to Dr. Andrea Droghetti and Dr. Giuseppe Cuono (CNR-SPIN), for contributing the DFT calculations behind the dataset in Section 2.7.

The underlying code for this study is publicly available at: <https://github.com/AMaRaNTA-code/AMaRaNTA>.

*Quod super est, agere incipiam quo foedere fiat
naturae, lapis hic ut ferrum ducere possit,
quem Magneta vocant patrio de nomine Grai,
Magnetum quia sit patriis in finibus ortus.*

Lucretius, *De rerum natura* VI, 906-909

2.1 Introduction

Magnetism – as the quotation on the previous page clearly testifies – can be regarded as one of the oldest physical phenomena known to man, with observations dating back as early as the VI century BC. Even its incorporation into a modern physical framework, due to the work of scholars such as Ampère, Ørsted, Biot, Savart, Faraday and ultimately Maxwell, although not as remote in time, is now more than a century and a half old. In the following pages, a very brief, cut-to-the-bone – and necessarily incomplete – overview will be provided, focusing on those essential aspects of magnetism needed for the rest of the chapter [96, 97].

In a classical framework, the Ampère-Maxwell equation in vacuum (time-independent case) states that

$$\nabla \times \mathbf{B} = \mu_0 \mathbf{J} \quad (2.1)$$

Magnetism, accordingly, is understood as being generated by currents. Analogously to the electrostatic case, these can be mapped to an “elemental” field source, the magnetic dipole moment: for instance, a loop enclosing an area A , traversed by a current I , can be shown to be equivalent to a magnetic moment $\mathbf{m} = I\mathbf{A}$. In turn, the magnetic moment of a particle of charge q and mass m is proportional to its orbital angular momentum:

$$\mathbf{m} = \frac{q}{2m} \mathbf{L} \quad (2.2)$$

In matter, treating magnetism classically requires the auxiliary field

$$\mathbf{H} = \frac{\mathbf{B}}{\mu_0} - \mathbf{M} \quad (2.3)$$

where the magnetisation $\mathbf{M}$ is defined as the magnetic dipole moment per unit volume. The microscopical origin of the magnetic dipoles, though, is still undetermined at this level – and is, in fact, entirely quantum (there are no microscopical atomic currents in a classical sense, even though this picture is often employed for pedagogical purposes).

On a quantum level, electrons possess an orbital angular momentum $\mathbf{L}$ (which, despite obeying a quantum algebra, is still defined as $\mathbf{r} \times \mathbf{p}$ and can thus be traced back to the classical counterpart) and an intrinsic angular momentum $\mathbf{S}$, termed *spin*, which instead has no classical analogue.¹ Both orbital and spin angular momenta contribute to the electron’s magnetic moment, as in 2.2, even though with proportionality constants (gyromagnetic ratios) that depend on the nature of the angular momentum.²

A variety of magnetic interactions can arise in matter, most of which due to spin. Without the aim of being exhaustive, we list here some, in increasing order of complexity — which turns out to be an increasing order of relevance, as well [97, 98].

¹The electron is not a spinning top. In fact, it is not even a ball...

²In the solid state, the orbital momentum is often quenched due to crystal field effects and is generally smaller than the spin contribution. This, however, does not mean at all that $\mathbf{L}$ is to be discarded altogether: see the discussion on spin-orbit hereafter.

Having introduced magnetic moments, it seems natural to start from the *dipole-dipole interaction*

$$H_{\text{DD}} = \frac{\mu_0}{4\pi r^3} [\mathbf{m}_1 \cdot \mathbf{m}_2 - 3(\hat{\mathbf{r}} \cdot \mathbf{m}_1)(\hat{\mathbf{r}} \cdot \mathbf{m}_2)] \quad (2.4)$$

which arises from the energy of one magnetic moment in the field produced by another. In practice, this contribution often has a negligible magnitude in solids (10^{-4} eV).

A second mechanism, also arising from direct interactions between magnetic moments, is the *spin-orbit coupling* (SOC)

$$H_{\text{SOC}} = -\frac{e}{2m^2c^2} \frac{1}{r} \frac{d\varphi}{dr} \mathbf{L} \cdot \mathbf{S} \quad (2.5)$$

which – as the name suggests – couples the electron’s spin and orbital angular momentum (or, equivalently, their corresponding magnetic moments). In spite of its relatively small strength (typically $10^{-4} - 10^{-2}$ eV), SOC can have considerable effects, both at the atomic level and in solids, where – among the many aspects – it influences the overall preferential orientation of spins and can give rise to non-trivial magnetic textures.³

Finally, the most important contribution to magnetism, in solids as in isolated atoms, comes from the *exchange interaction*, which turns out to be also the most subtle to introduce. At variance with H_{DD} and H_{SOC} , it is not, in principle, an explicit coupling between magnetic moments. It is, rather, a byproduct of the Coulomb electron-electron interaction, combined with the Pauli exclusion principle, which enforces antisymmetry of the total electron wavefunction. As such, there exists no universal formula for the exchange interaction in terms of fundamental forces: its magnitude and form inevitably depend on both the specific system and the details of the electron wavefunctions involved – including the spatial part, inextricably coupled to spin by virtue of the two-body interaction and the Pauli principle. For instance, in the case of the helium atom, the energy of the state with one electron in the $1s$ orbital and the other in an excited orbital $|nlm\rangle$

$$E_{100,nlm} = -4 \left(1 + \frac{1}{n^2} \right) \quad (2.6)$$

(in Rydberg units) achieves an extra electron-electron term

$$E_{ee} = \begin{cases} I + J & \text{singlet } (\uparrow\downarrow) \\ I - J & \text{triplet } (\uparrow\uparrow) \end{cases} \quad (2.7)$$

$$\begin{aligned} I &= \iint d\mathbf{r}_1 d\mathbf{r}_2 |\psi_{100}(\mathbf{r}_1)|^2 \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} |\psi_{nlm}(\mathbf{r}_2)|^2 \\ J &= \iint d\mathbf{r}_1 d\mathbf{r}_2 \psi_{100}(\mathbf{r}_1) \psi_{nlm}(\mathbf{r}_2) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \psi_{nlm}^*(\mathbf{r}_1) \psi_{100}^*(\mathbf{r}_2) \end{aligned} \quad (2.8)$$

³In the following, SOC will emerge as the driving force behind anisotropic terms in the model Hamiltonian adopted in AMaRaNTA.

I and J are termed *direct* and *exchange integral*, respectively: the former simply represents the electrostatic repulsion between the electron densities, whereas the latter, which arises from the Pauli antisymmetry, is the energy associated with a swap of quantum numbers between the electrons (hence the name “exchange”). The singlet and triplet levels are thus split by a quantity $2J$. A similar result holds for the energy levels of another prototypical two-electron system, the H_2 molecule.

In solids, the exchange interaction can be further classified according to the physical processes by which spin correlations are established [98]. *Direct exchange* arises from the overlap of magnetic ions’ electronic wavefunctions and, as such, is most relevant for spatially close orbitals. *Superexchange* is instead mediated by non-magnetic ions and originates from virtual electron hopping processes; the sign of the coupling is described in detail by the Goodenough–Kanamori–Anderson rules. *Double exchange* occurs in mixed-valence systems, where itinerant electrons can hop between magnetic ions of different oxidation states, favouring parallel spin alignment. Finally, *RKKY exchange* is an indirect interaction mediated by conduction electrons, that oscillates in sign with distance and plays a key role in dilute magnetic systems.

Despite their distinct and intricate microscopic origins, these mechanisms can often be effectively captured by suitable effective spin Hamiltonians, that isolate the spin degrees of freedom in a simpler, tractable form. The most renowned of these is the *Heisenberg Hamiltonian* [99], which for a two-electron system reads

$$H_{\text{Heisenberg}} = 2J\mathbf{s}_1 \cdot \mathbf{s}_2 = J[\mathbf{S}^2 - \mathbf{s}_1^2 - \mathbf{s}_2^2] \quad (2.9)$$

(where $\mathbf{S} = \mathbf{s}_1 + \mathbf{s}_2$). Using $\langle \mathbf{S}^2 \rangle = S(S+1)$ and $\langle \mathbf{s}_i^2 \rangle = s(s+1) = 3/4$, the corresponding energy eigenvalues are $-3J/4$ for the singlet state ($S=0$) and $J/4$ for the triplet state ($S=1$), split by exactly $2J$ as desired.⁴

By extension, the Heisenberg Hamiltonian is generalised to a many-spin system as

$$H_{\text{Heisenberg}} = \sum_{i<j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j = \sum_{i<j} J_{ij} (S_{ix}S_{jx} + S_{iy}S_{jy} + S_{iz}S_{jz}) \quad (2.10)$$

a framework that naturally allows for a variety of extensions, including anisotropic models with different exchange parameters along two (or more) Cartesian directions.

Two important limiting cases, which have developed a history of their own, are the *XY model* [100] and *Ising model* [101]. The XY Hamiltonian (isotropic within the plane, in the form given below) describes exchange restricted to the transverse spin components:

$$H_{\text{XY}} = \sum_{i<j} J_{ij} (S_{ix}S_{jx} + S_{iy}S_{jy}) \quad (2.11)$$

while the Ising model retains only a single (up or down) spin component:

$$H_{\text{Ising}} = \sum_{i<j} J_{ij} S_{iz}S_{jz} \quad (2.12)$$

⁴The factor of 2, convenient to exactly replicate the exchange splitting in He and H_2 , will be absorbed in the exchange parameter hereafter.

In all three models, the sign of J_{ij} determines whether the system favours parallel spin alignment ($J_{ij} < 0$, corresponding to *ferromagnetism*) or antiparallel ($J_{ij} > 0$, corresponding to *antiferromagnetism*).

2.2 2D magnetism and motivations for AMaRaNTA

In light of the long and rich historical record of magnetism, it may seem somewhat ironic that its persistence in two dimensions (2D) remained elusive until relatively recent times. This difficulty, however, is all but accidental.

From a theoretical standpoint, in fact, the existence of magnetism in low dimensions is intriguing and far from trivial. Magnetic order is inherently a collective phenomenon, relying on the establishment of long-range correlations among many interacting spins. In reduced dimensionalities, however, collective order is particularly vulnerable to thermal excitations. This behaviour is formalised by the celebrated *Mermin–Wagner theorem* [102] which states that, in one- and two-dimensional systems with short-range and isotropic interactions, continuous symmetries cannot be spontaneously broken at any finite temperature. This result can also be framed in terms of low-energy collective excitations of the spin system, in the form of gapless spin waves (or, when quantised, *magnons*): long-wavelength modes cost arbitrarily little energy and are entropically favoured in low dimensions, ultimately destroying long-range order. In real materials, however, additional interactions than those included in an isotropic Heisenberg model – such as in (2.10) – may break the continuous spin-rotational symmetry and, with it, the crucial assumption on which the Mermin-Wagner theorem relies to hold strictly. In particular, out-of-plane magnetic anisotropies can open a gap in the spin-wave spectrum: this suppresses the long-wavelength fluctuations responsible for destabilising magnetic order, thereby allowing finite-temperature magnetism even in two dimensions [103, 104].

From an experimental perspective, as a matter of fact, a quasi-2D character of magnetic interactions had been known for decades to occur in layered van der Waals-bonded systems [105, 106]. In such compounds, magnetic atoms form strongly bonded layers with robust in-plane exchange interactions, while adjacent layers are held together by comparatively weak van der Waals forces. Traditionally, however, these systems were investigated in their bulk form, where residual interlayer coupling, finite sample thickness and three-dimensional ordering effects persisted. As a consequence, the strictly 2D limit, in which magnetic order survives in an isolated atomic layer, remained experimentally inaccessible for long.

This situation began to change with the advent of modern exfoliation techniques, most notably following the isolation of graphene in 2004 as the first true 2D material [22]. However, a renewed — and ultimately definitive — surge of interest in layered magnetic materials did not emerge until between 2016 and 2018. During this time, experimental observations demonstrated that well-established theoretical models of magnetism could be realised in monolayers such as CrI_3 [23] and CrGeTe_3 [107] (corresponding to a 2D Ising and a 2D Heisenberg model, respectively). These discoveries were rapidly followed

by reports of magnetic order in other monolayer systems, such as FePS_3 , VSe_2 and MnSe_2 [108], and provided compelling evidence that, under suitable conditions, stable magnetic order can persist upon exfoliation down to the monolayer limit.

Since then, the library of known 2D magnets has continued to expand steadily [109–112] and their incorporation into prototype spintronic devices is already a reality [113–115], with ongoing experimental efforts aiming to raise magnetic ordering temperatures [116,117] and enhance perpendicular magnetic anisotropy for improved device performance [118].

Beyond their technological relevance, 2D magnets provide an exceptional platform for exploring a wide range of emergent magnetic phenomena. Reduced dimensionality, combined with strong SOC, magnetic anisotropies and lattice-specific symmetry constraints, gives rise to a remarkably rich variety of magnetic phases, extending well beyond conventional ferromagnetism (FM) and antiferromagnetism (AFM). For example, a recent theoretical work predicts *alttermagnetism* – a phase characterised by spin-split electronic bands despite the absence of net magnetisation – in RuF_4 monolayers and other 2D compounds [119]. In these (globally) centrosymmetric systems, there is nonetheless an antisymmetric Dzyaloshinskii–Moriya interaction (DMI) [120,121], driven by SOC, between pairs of atoms that locally break space-inversion symmetry, inducing spin canting and weak ferromagnetism [122]. Meanwhile, in systems where space-inversion symmetry is broken not only locally but also globally, DMI acts as a genuinely chiral interaction, stabilising non-collinear and non-coplanar spin textures with a well-defined handedness [123–125]. For instance, *magnetic skyrmions* – topologically protected whirling spin configurations – have been predicted in several so-called Janus 2D materials [126–130], such as MnSeTe and MnSTe [131].

Complex magnetic behaviour can also emerge in centrosymmetric lattices through geometric frustration. In triangular or Kagome lattices, AFM exchange interactions can give rise to highly degenerate ground states and complex spin arrangements, including spin-spiral structures [132–135]. Similar frustration effects may also emerge, even in other lattice geometries, in the presence of competing exchange interactions, for example between the nearest-neighbour coupling and a longer-ranged one [136,137]. Notably, frustrated centrosymmetric systems can still host skyrmion-like spin textures even in the absence of DMI [138]: for example, a spontaneous antibiskyrmion lattice with unique topology, driven by the anisotropic symmetric exchange interaction, has been predicted in the semiconducting NiI_2 monolayer [139]. Interestingly, the onset of helimagnetic phases can spontaneously break the inversion symmetry of the underlying crystal lattice, inducing a polar axis and enabling ferroelectricity [140,141], as demonstrated again in monolayer NiI_2 [142,143].

Computational approaches

Given these premises, accurate computational approaches for predicting the magnetic properties of 2D materials from first-principles are in high demand. Among them, DFT has emerged as the preferred method, offering a relatively good balance between accuracy, computational efficiency and ease of implementation. When integrated into

high-throughput computational frameworks [41, 43, 144], DFT enables the rapid screening of candidate materials with targeted magnetic properties, thereby accelerating materials discovery and providing valuable guidance and support for experiments.

The most established approaches to extract magnetic interactions from DFT include the *energy-mapping method*, the *torque method* and the *spin-spiral method* — each with its own advantages and limitations, depending on the specific system and magnetic phenomena under investigation [145].

Energy mapping The energy-mapping approach [146] is conceptually straightforward and broadly applicable. It involves computing total energies for a set of constrained magnetic configurations, usually constructed to sample different relative orientations of local magnetic moments. These energies are then mapped onto a classical spin Hamiltonian (e.g., Heisenberg or anisotropic models) to extract exchange parameters.

A major point of strength of this method is its flexibility: it can accommodate SOC and non-collinear configurations and can also be extended to complex spin Hamiltonians that include biquadratic terms [147, 148]. The approach is compatible with virtually all DFT codes and is not restricted to DFT alone: it can also be employed with any first-principles method capable of returning total energies for constrained spin configurations, such as Diffusion Monte Carlo, as demonstrated in recent studies [149].

In contrast, its main drawbacks are the following ones. First, it typically requires the use of supercells, which can become quite large when longer-range interactions beyond nearest-neighbours are involved. Second, each magnetic configuration must be treated with a separate self-consistent calculation, meaning that many DFT calculations are required for large configuration sets. Finally, the accuracy and reliability of the extracted parameters depend on the choice and number of configurations used: overfitting or underfitting may occur if the configuration set is not sufficiently representative of the system’s relevant magnetic states, particularly in the presence of competing interactions or frustrated geometries.

Torque method Also known as the Liechtenstein–Katsnelson–Antropov–Gubanov (LKAG) formalism [150, 151], the torque method is based on the magnetic force theorem. In this approach, the Kohn–Sham (KS) Hamiltonian is mapped onto a classical spin Hamiltonian by equating the linear response of the KS electronic system — treated within the Green’s function formalism — to infinitesimal rotations of the magnetic moments in the spin model. This enables the calculation of exchange parameters from a single self-consistent electronic structure calculation, avoiding the need to compute total energies for multiple magnetic configurations. Originally developed for collinear magnetic systems, the method has since been extended to include SOC, enabling the calculation of DMI and magnetic anisotropies [152, 153] (in this case, however, three self-consistent calculations are required, corresponding to magnetisation alignment along each of the Cartesian axes). Moreover, it can be combined with beyond-DFT approaches formulated within the Green’s function framework, such as dynamical mean-field theory [154, 155]. A further advantage is its ability to provide an orbital-resolved decomposition of magnetic exchange

interactions [156, 157], which is especially useful for analysing underlying microscopic mechanisms such as superexchange.

This, however, comes with important limitations. The formalism typically relies on localised basis sets, and the specific choice of orbitals used to define local magnetic moments introduces a degree of arbitrariness, that can significantly affect exchange parameters [158]. Furthermore, while initially employed with the Korringa-Kohn-Rostoker Green’s function [159] and tight-binding linear muffin-tin methods [160], constructing the Green’s function becomes cumbersome in the commonly used plane-wave-based DFT implementations. This difficulty is mitigated using maximally-localised Wannier functions [161, 162] and recently, implementations of the torque method for Wannierised KS Hamiltonians have boosted the popularity of this approach [163, 164]. However, the Wannierisation is a procedure that may depend strongly on the number and nature of the bands [161] and, additionally, Wannier functions are not always centred near the physical atomic sites [161]. An alternative implementation [165, 166] uses pseudo-atomic orbital (PAO) basis sets, as employed in DFT codes like SIESTA [18]. While these localised orbitals provide a natural basis to construct tight-binding representations, they are typically non-orthogonal. Hence, the concept of a localised operator is a non-trivial issue [167, 168], introducing conceptual and numerical complications in the implementation and application of the torque method.

Spin spirals Finally, the spin-spiral approach relies on the generalised Bloch theorem [169, 170]. It imposes a spin-spiral boundary condition within a single unit cell, such that the KS wavefunction undergoes a position-dependent spin rotation by an angle $\mathbf{q} \cdot \mathbf{R}_i$ around the axis normal to the spiral plane, where $\mathbf{q}$ is the spiral wavevector and $\mathbf{R}_i$ is a lattice vector. By computing the total energy for different values of $\mathbf{q}$, one can identify the energetically preferred spiral configuration, thereby gaining direct access to the magnetic ordering tendencies of the system. Exchange parameters may in principle be inferred via a Fourier transform of the magnon dispersion $E(\mathbf{q})$ [145].

A key advantage of this method is its ability to capture long-wavelength, non-collinear magnetic textures without requiring large supercells, making it particularly efficient for studying incommensurate magnetic orders. However, the standard spin-spiral formalism typically neglects SOC, as this breaks the spin-rotational symmetry required for the generalised Bloch theorem. Although SOC effects can be included perturbatively [171], such treatments may become unreliable when SOC plays a central role, such as in systems with strong magnetic anisotropy or DMI. Furthermore, the method is limited to systems that can be well described by a single- $\mathbf{q}$ spiral and may not capture complex multi- $\mathbf{q}$ configurations.

Pros and cons For high-throughput calculations, the torque method is, in principle, the most computationally efficient approach, as it allows all magnetic parameters entering a spin Hamiltonian to be extracted from a single DFT calculations (or three, when SOC is included). In practice, however, its application has so far been limited to individual case studies rather than large-scale materials screening, since Wannierisation and the

optimisation of pseudo-atomic orbitals and other localised basis sets remain difficult to automate reliably.

By contrast, the energy-mapping method has seen the most extensive application to date, owing to its formal simplicity. For example, Torelli *et al.* [144] studied around 150 2D compounds from the C2DB database [41, 42]. In their work, the DFT total energy differences between collinear FM and AFM configurations are mapped onto a spin model that includes nearest-neighbour isotropic Heisenberg exchange, on-site (single-ion) anisotropy and an approximate two-ion anisotropy. This study not only confirmed the magnetic ground states of well-known compounds, but also predicted the properties of several less-studied materials. Despite these successes, the model employed in Ref. [144] shows some limitations, resulting often insufficient to capture the rich variety of possible 2D magnetic phases. Therefore, the same authors later extended their study to a larger set of 192 materials, whose magnetic texture was assessed exploring spin-spiral orders using the generalised Bloch theorem [172]. This strategy allowed for the identification of non-collinear and incommensurate magnetic ground states beyond the scope of simple collinear energy-mapping models. Nevertheless, no systematic extraction of microscopic exchange parameters was performed therein. This is consistent with the intrinsic limitations of the spin-spiral approach: the restriction to single- $\mathbf{q}$ textures, the difficulty of incorporating spin-orbit-induced anisotropic interactions in a fully self-consistent manner, and the non-uniqueness of mapping spiral dispersions onto real-space exchange tensors in complex magnetic systems.

The need for AMaRaNTA

To further extend the systematic application of DFT for predicting the magnetic properties of 2D materials, a valuable approach is represented by the so-called *four-state method* [98, 173, 174]. Within this framework, each magnetic parameter of a spin model is extracted from DFT total energies computed for four distinct relative orientations of the magnetic moments of two selected atoms, while all other magnetic moments are held fixed. This provides a direct estimate of the local interactions between atomic pairs. The method offers a clear advantage over conventional energy-mapping approaches, which typically rely on extensive global sampling of numerous magnetic configurations spanning the entire simulation cell. When implemented for non-collinear DFT calculations including SOC, the four-state method gives access to the fully tensorial – hence anisotropic – nature of the magnetic interactions, enabling their mapping onto general spin models capable of describing complex magnetic states [98, 127, 128, 139, 173–176]. It also naturally captures local interactions leading to canting effects between spin pairs that are difficult to predict with global sampling [122]. However, despite these strengths, applying the four-state method in high-throughput calculations poses several challenges. These include the need to automatically select relevant spin configurations, construct suitable (and potentially large) supercells to capture long-range interactions, and perform a substantial amount of DFT calculations, equal to four times the number of spin model parameters to be determined [98, 173].

To address these challenges, we introduce AMaRaNTA (Automating MAGnetic parameters iN a Tensorial Approach), a computational package designed to streamline the four-state approach for automated, scalable calculations. AMaRaNTA is implemented as a workflow within AiiDA (Automated Interactive Infrastructure and Database for Computational Science) [38], a robust platform for managing complex computational workflows with full data provenance and automation capabilities. The workflow interfaces with the Vienna Ab-initio Simulation Package (VASP) [16, 17] (though it can be in principle adapted to other electronic structure codes) to perform accurate non-collinear DFT total energy calculations including SOC. Designed for user-friendliness, AMaRaNTA requires only a structure file as input; it then automates the setup of simulation cells, the submission of calculations to (and retrieval of results from) high-performance computing facilities through AiiDA and, ultimately, the evaluation of the exchange parameters. Specifically, AMaRaNTA computes the full exchange tensor for nearest-neighbour interactions and scalar isotropic exchange parameters for second- and third-nearest-neighbour ones, as well as single-ion anisotropy terms. These provide a minimal starting set to capture magnetic frustration and anisotropies underpinning the stabilisation of diverse magnetic states in 2D materials. However, the framework lends itself to extensions beyond the present implementation, for instance, to include longer-range interactions – along with their fully tensorial character – allowing mapping onto more complex spin models.

To illustrate its performance, AMaRaNTA is applied to a compact dataset of about thirty 2D magnetic compounds from the Materials Cloud 2D Structure database [43, 44], demonstrating robust and automated screening of magnetic interactions. We successfully recover the expected magnetic features for a number of previously characterised 2D magnets. Furthermore, for previously unreported systems, our calculations predict AFM isotropic exchange in NiF_4Te_2 , sizeable anisotropic symmetric exchange in MnBi_2Te_4 , and antisymmetric exchange in VF_4 and VAgP_2Se_6 .

2.3 The four-state method

The four-state method [98, 173] maps the results of first-principles total energy calculations (here performed within DFT) onto a classical, Heisenberg-like model Hamiltonian, as anticipated in the Introduction. In the following, we outline the specific formulation and conventions adopted in AMaRaNTA, along with the relevant definitions.

Spin model Hamiltonian

The AMaRaNTA effective spin Hamiltonian is based on the bilinear Heisenberg model and is expressed as

$$H = \sum_{\substack{i < j \\ (i,j) \in \text{1NN}}} \mathbf{S}_i \cdot \underline{\mathbf{J}}_{ij}^{(1)} \cdot \mathbf{S}_j + \sum_{\substack{i < j \\ (i,j) \in \text{2NN}}} J_{ij}^{(2)} \mathbf{S}_i \cdot \mathbf{S}_j + \sum_{\substack{i < j \\ (i,j) \in \text{3NN}}} J_{ij}^{(3)} \mathbf{S}_i \cdot \mathbf{S}_j + \sum_i A_i S_{iz}^2 \quad (2.13)$$

where $n\text{NN}$ (with $n = 1, 2, 3$) denotes the set of n -th nearest-neighbour atomic pairs, and

- $\underline{\underline{\mathbf{J}}}_{ij}^{(1)}$ is the full nearest-neighbour second-rank exchange tensor. Each of its elements $J_{ij,\alpha\beta}^{(1)}$ describes the coupling between the spin component S_i^α of atom i and the spin component S_j^β of atom j , where $\alpha, \beta \in \{x, y, z\}$. $\underline{\underline{\mathbf{J}}}_{ij}^{(1)}$ is commonly decomposed as [98]

$$\underline{\underline{\mathbf{J}}}_{ij}^{(1)} = J_{ij}^{(1)} \underline{\underline{\mathbf{I}}} + \underline{\underline{\mathbf{K}}}_{ij} + \underline{\underline{\mathbf{D}}}_{ij} \quad (2.14)$$

that is, into a Heisenberg isotropic exchange parameter $J_{ij}^{(1)} = \frac{1}{3} \text{Tr} \underline{\underline{\mathbf{J}}}_{ij}^{(1)}$, a traceless symmetric matrix $\underline{\underline{\mathbf{K}}}_{ij} = (\underline{\underline{\mathbf{J}}}_{ij}^{(1)} + \underline{\underline{\mathbf{J}}}_{ij}^{(1)\text{T}})/2 - J_{ij}^{(1)} \underline{\underline{\mathbf{I}}}$ (giving rise to anisotropic exchange interactions of the Kitaev type [177, 178]) and an antisymmetric part $\underline{\underline{\mathbf{D}}}_{ij} = (\underline{\underline{\mathbf{J}}}_{ij}^{(1)} - \underline{\underline{\mathbf{J}}}_{ij}^{(1)\text{T}})/2$, whose three independent components form the Dzyaloshinskii–Moriya vector $\mathbf{D}$ [120, 121].

Thus, in our model, the two-ion anisotropy is treated more rigorously than in previous high-throughput studies (e.g., [144], where it was included through a term of the form $H_{ij}^{\text{ani}} = \lambda \sum_{ij} S_i^z S_j^z$ in the spin Hamiltonian).

- $J_{ij}^{(2)}$ and $J_{ij}^{(3)}$ are the second- and third-nearest-neighbour scalar exchange parameters, respectively.
- A_i is the single-ion anisotropy (SIA). In general, the SIA can be represented as a second-rank symmetric tensor, analogous to $\underline{\underline{\mathbf{J}}}_{ij}^{(1)}$. However, this fully tensorial description is often unnecessary for practical purposes. In many 2D systems, the SIA can be effectively characterised by the simplified scalar form adopted here, which captures easy-axis or easy-plane anisotropy (see Appendix C in Ref. [173]).

In total, for a chosen atomic site i , the model contains twelve parameters: the nine components of the nearest-neighbour exchange tensor, the scalar exchange parameters for the second- and third-nearest-neighbours, and the SIA.

According to our sign conventions, a negative (positive) exchange parameter describes FM (AFM) spin alignment. Similarly, positive values of the SIA correspond to easy-plane anisotropy and negative values to easy-axis anisotropy.

Calculation of the spin Hamiltonian parameters

In this work, we restrict to materials containing a single magnetic species, where all magnetic atoms are crystallographically equivalent and thus possess the same spin magnitude S . The DFT calculations underlying the four-state method employ supercells large enough to both capture interactions up to the third-nearest-neighbours – consistently with the spin model – and to suppress spurious interactions between an atom and its periodic replicas.

To extract the parameters of the spin model Hamiltonian, the following different sets of four-state calculations are performed.

Nearest-neighbour exchange tensor The calculations for each element $J_{ij,\alpha\beta}^{(1)}$ of the nearest-neighbour exchange tensor for a pair of magnetic atoms (i, j) are performed within the non-collinear DFT framework with SOC included. We compute the energies $E_{ij,+\alpha,+\beta}$, $E_{ij,+\alpha,-\beta}$, $E_{ij,-\alpha,+\beta}$, and $E_{ij,-\alpha,-\beta}$, corresponding to the four configurations in which the spins of atom i and j are constrained along $\pm\hat{\alpha}$ and $\pm\hat{\beta}$ Cartesian directions, respectively, while the spins of all other magnetic atoms are fixed orthogonal to both α and β , forming a reference magnetic background. The desired parameter is then given by

$$J_{ij,\alpha\beta}^{(1)} = \frac{E_{ij,+\alpha,+\beta} - E_{ij,+\alpha,-\beta} - E_{ij,-\alpha,+\beta} + E_{ij,-\alpha,-\beta}}{4S^2} \quad (2.15)$$

where S denotes the spin magnitude.

By computing all nine combinations of $\alpha, \beta \in \{x, y, z\}$, the full exchange tensor $\mathbf{J}_{ij}^{(1)}$ can be constructed, requiring a total of $4 \times 9 = 36$ calculations. This underscores the necessity of an automated workflow as provided by AMaRaNTA.

In the limit of perfectly isolated spin pairs – achieved using sufficiently large supercells [179] – and assuming that the Heisenberg Hamiltonian (2.13) captures the low-energy physics of the system, the four-state approach ensures that all spurious contributions cancel exactly, guaranteeing that the extracted exchange parameters correspond solely to the intended spin pair.

Second- and third-nearest-neighbour scalar exchange parameters The scalar exchange parameters $J_{ij}^{(2)}$ and $J_{ij}^{(3)}$, corresponding to pairs of second- and third-nearest-neighbour magnetic atoms (i, j) , are obtained using collinear DFT calculations without SOC, where spins are constrained to align along a fixed quantisation axis (in our case, the z -axis). Similarly to above, four distinct spin configurations are considered, in which the spins of atoms i and j are either parallel (i.e., up) or antiparallel (i.e., down) to z , and all other spins are fixed in a collinear reference configuration. This yields four total energies: $E_{ij,\uparrow\uparrow}$, $E_{ij,\uparrow\downarrow}$, $E_{ij,\downarrow\uparrow}$, and $E_{ij,\downarrow\downarrow}$. The scalar exchange parameter is then given by

$$J_{ij}^{(n=2,3)} = \frac{E_{ij,\uparrow\uparrow} - E_{ij,\uparrow\downarrow} - E_{ij,\downarrow\uparrow} + E_{ij,\downarrow\downarrow}}{4S^2} \quad (2.16)$$

Single-ion anisotropy The SIA parameter is calculated using non-collinear DFT with SOC included. We consider four distinct spin configurations, in which the spin of atom i is constrained to point along the $+x$, $-x$, $+z$, and $-z$ directions, while the spins of all other atoms are fixed along the y -axis. This yields the corresponding energies $E_{i,+x}$, $E_{i,-x}$, $E_{i,+z}$, and $E_{i,-z}$. The anisotropy parameter is then given by

$$A_i = \frac{E_{i,+z} - E_{i,+x} - E_{i,-x} + E_{i,-z}}{4S^2} \quad (2.17)$$

In the actual implementation of AMaRaNTA, spin magnitudes S are always normalised to unity. Accordingly, the reported exchange and anisotropy parameters correspond directly to the algebraic sums of energies defined in Eqs. (2.15), (2.16) and (2.17), divided by 4.

2.4 Implementation of AMaRaNTA

Workchain

AMaRaNTA is implemented in Python as an AiiDA workchain [180], specifically employing the AiiDA-VASP plugin.⁵ It consists of three main blocks, as illustrated in Fig. 2.1.

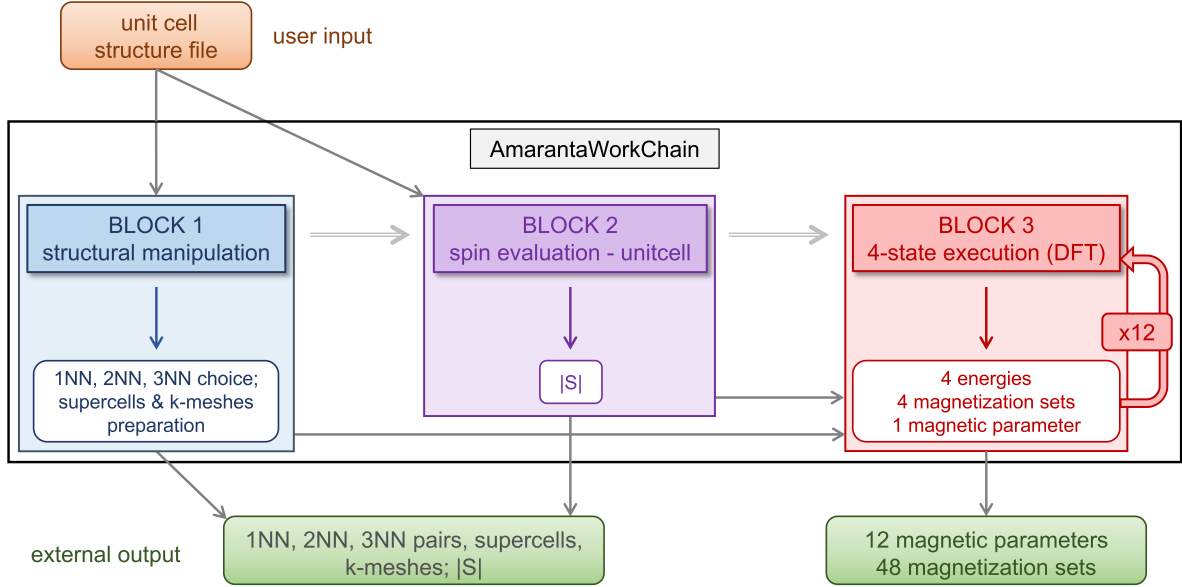


Figure 2.1: Scheme of AMaRaNTA. Coloured boxes represent the three main blocks of the workflow, as discussed in the text. White boxes inside contain the partial output of each block. Thin arrows indicate direct input–output relations, thicker ones represent the procedural progression between blocks.

Pair selection, supercell and reciprocal lattice construction The first block (blue in Fig. 2.1) handles the identification of atomic pairs (i, j) and the generation of appropriate supercells, using tools provided by the Atomic Simulation Environment (ASE) library [34].

Starting from the user-supplied unit cell structure file, AMaRaNTA identifies three pairs (i, j) of magnetic atoms corresponding to the nearest, second-nearest, and third-nearest-neighbour shells. To ensure all neighbours are accounted for, this step is performed in a 5×5 supercell (employed at this stage only, then discarded afterwards). Atom i is chosen once and for all and is thus the same in the three pairs: by default, it is selected as the first magnetic atom appearing in the atomic list (though occasionally, during the dataset production phase, it was chosen as the magnetic atom closest to the centre of the 5×5 supercell, thus avoiding complications arising from periodic boundary conditions

⁵See <https://aiida-vasp.readthedocs.io/en/latest/>

in the presence of neighbours close to the supercell edges). The partner atoms j are chosen as the first three in the atomic list whose distances from i place them within the nearest, second-nearest, or third-nearest-neighbour shell – incidentally, this means that the $\mathbf{J}_{ij}^{(1)}$ tensor will refer to one representative (i, j) pair only; tensors associated with other, symmetry-related neighbour pairs can be obtained from one another by applying suitable rotation operations. Atoms whose distances from i differ by less than 1% are grouped within the same neighbour shell, thereby avoiding artefacts due to negligible atomic distance differences in the input structure.

Appropriate supercells are then constructed to ensure that each spin pair (i, j) and its periodic replicas are separated by a distance of at least 10 Å, a value we found sufficient for the systems studied in this work, that can, however, be easily increased if necessary. The initial guess for the supercell size is a 2×2 of the input unit cell. From this starting point, two nested loops iterate over possible integer values N and M , treated independently, to find the smallest $N \times M$ supercell that satisfies the distance criterion.

For a unit cell with lattice parameters a and b , the $\mathbf{k}$ -point mesh for the DFT calculations is defined as $\left(\text{round}\left(\frac{50}{a}\right), \text{round}\left(\frac{50}{b}\right), 1\right)$ in reciprocal coordinates. When constructing the supercells, the $\mathbf{k}$ -point meshes are rescaled inversely with respect to the corresponding supercell lattice vectors, ensuring a consistent sampling density across different cell sizes.

Spin magnitude evaluation The second block (violet) performs a single DFT calculation for the unit cell, to determine the modulus of the magnetic moment S for the magnetic species. This value is then rounded to the nearest integer and later used to initialise the magnetic configurations, according to the four-state prescriptions.

Execution of four-state calculations The third and main block (red) orchestrates the DFT calculations required by the four-state method. For each of the twelve parameters in the spin model Hamiltonian, a child workchain is launched to perform the four constrained DFT calculations. The resulting total energies are processed using Eqs. (2.15), (2.16) and (2.17), yielding the exchange parameters and the SIA in meV. As anticipated, with spin magnitudes normalised to unity, the parameters are directly obtained as one quarter of the energy combinations defined therein. Finally, information on the converged magnetisation of all atoms - as obtained in the DFT calculations - is collected, to enable users to verify that the assigned spin directions have been respected (AMaRaNTA does not issue automated alerts if deviations occur). This also allows for an *a posteriori* check of the assumption that all magnetic atoms indeed share the same spin magnitude S .

Inputs and outputs

AMaRaNTA is managed and launched via a separate script, where users can specify the structure file and a set of pseudopotentials without modifying the workchain itself. This represents the only required input; all other settings are fixed internally to ensure

consistency across the database. However, selected parameters — such as the 10-Å pair-replica distance or the subset of exchange parameters to compute — can be modified through documented and accessible options. This design aims at ensuring uniformity across the database, while still offering enough flexibility for external users to adapt the high-throughput calculations to their specific needs.

The final output includes the coordinates of the three atomic pairs (i, j) , the constructed supercells, the calculated set of spin model Hamiltonian parameters, and the converged magnetisation data obtained from DFT for all atoms. This information is provided both as AiiDA data nodes and as user-friendly text files, which are also stored within the AiiDA database. Additionally, much of the content is printed to the standard output on-the-fly.

2.5 Execution example

In order for the reader to acquire more familiarity with AMaRaNTA, as well as to begin to showcase its potentiality, we provide here the content of the standard output after an actual execution of the code. VAgP_2Se_6 – one of the materials within the dataset treated hereafter – is taken as a reference material.

AMaRaNTA begins by printing information about the nearest-, second-nearest and third-nearest-neighbour pairs: namely, the coordinates of the atoms involved (shown in Fig. 2.2) and the neighbour-neighbour distance for each pair, as well as the chosen supercells and $\mathbf{k}$ -point meshes:

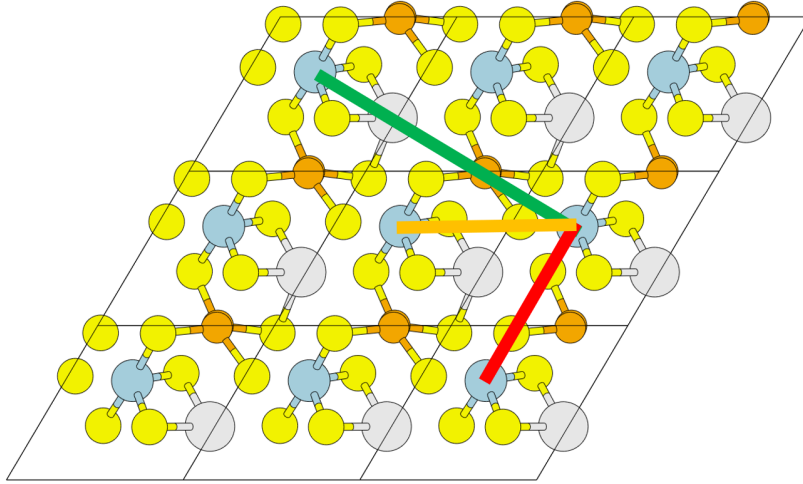


Figure 2.2: Choice of nearest- (yellow), second-nearest- (red) and third-nearest-neighbour (green) pairs for VAgP_2Se_6 . Colour code for the atomic species is as follows: V - dark grey, Ag - light grey, P - orange, Se - yellow. The original unit cell is drawn in black; a smaller portion of the 5×5 supercell employed by AMaRaNTA for the pairs selection is shown here.


```

2025-01-07 11:57:16 [19583 | REPORT]: [62402|AmarantaWorkChain|print_welcome]:

*****
*
*                               AMaRaNTA                               *
*       Automating MAGnetic paRAMeters iN a Tensorial Approach       *
*
*****

2025-01-07 11:57:17 [19584 | REPORT]: [62402|AmarantaWorkChain|run_ASE]:

Material is AgP2Se6V

----- s0 is: [23.891 14.723 11.698]
The 1nn couple is: 12,7 with distance: 6.3771 ---- s1 is: [17.514 14.723 11.698]
The 2nn couple is: 12,11 with distance: 6.4723 ---- s2 is: [20.596 9.152 11.698]
The 3nn couple is: 12,3 with distance: 10.978 ---- s3 is: [14.431 20.294 11.698]

Safety distance chosen: 10 Ang

opt_j_nn1_direct 3      opt_k_nn1_direct 3
opt_j_nn1_reversed 3    opt_k_nn1_reversed 3
Direct = reversed values
Minimal supercell for 1nn: ---- 3 x 3
with distances: [19.1313 12.7542 25.5083 19.1313]

opt_j_nn2_direct 3      opt_k_nn2_direct 3
opt_j_nn2_reversed 3    opt_k_nn2_reversed 3
Direct = reversed values
Minimal supercell for 2nn: ---- 3 x 3
with distances: [19.4169 12.9446 25.8892 19.4169]

opt_j_nn3_direct 4      opt_k_nn3_direct 4
opt_j_nn3_reversed 3    opt_k_nn3_reversed 4
Chosen reversed values
Minimal supercell for 3nn ---- 3 x 4
with distances: [19.1313 11.1615 29.1284 19.1313]

k-point linear density: 50
unit cell parameters: 6.377 6.472
k-mesh for unit cell: 7.841 x 7.725 x 1
k-mesh for 1nn: 3 x 3 x 1
k-mesh for 2nn: 3 x 3 x 1
k-mesh for 3nn: 3 x 2 x 1

```

As a second step, the stand-alone DFT calculation for the unit cell, aimed at extracting the spin modulus, is performed:


```

2025-01-07 11:57:22 [19594 | REPORT]:      [62438|VaspWorkChain|run_process]:
launching VaspCalculation<62440> iteration #1
2025-01-07 11:57:23 [19595 | REPORT]:      [62438|VaspWorkChain|results]: work chain
completed after 1 iterations
2025-01-07 11:57:24 [19596 | REPORT]:      [62438|VaspWorkChain|on_terminated]:
cleaned remote folders of calculations: 62440
2025-01-07 11:57:24 [19597 | REPORT]:      [62434|SubWorkChain|elaborate_results_main]:
ENERGY:   -460.40052471 eV

2025-01-07 11:57:24 [19598 | REPORT]:      [62434|SubWorkChain|init_run_aiida_main]:
MAGMOM 2.0 0.0 0.0 -2.0 0.0 0.0 0.0 0.0 0.0 2.0 0.0 0.0 2.0 0.0 0.0 2.0 0.0 0.0 2.0 0.0
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2025-01-07 11:57:26 [19599 | REPORT]:      [62451|VaspWorkChain|run_process]:
launching VaspCalculation<62453> iteration #1
2025-01-07 11:57:27 [19600 | REPORT]:      [62451|VaspWorkChain|results]: work chain
completed after 1 iterations
2025-01-07 11:57:28 [19601 | REPORT]:      [62451|VaspWorkChain|on_terminated]:
cleaned remote folders of calculations: 62453
2025-01-07 11:57:28 [19602 | REPORT]:      [62434|SubWorkChain|elaborate_results_main]:
ENERGY:   -460.39653404 eV

2025-01-07 11:57:28 [19603 | REPORT]:      [62434|SubWorkChain|init_run_aiida_main]:
MAGMOM -2.0 0.0 0.0 2.0 0.0 0.0 0.0 0.0 0.0 2.0 0.0 0.0 2.0 0.0 0.0 2.0 0.0 0.0 2.0 0.0
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2025-01-07 11:57:30 [19604 | REPORT]:      [62464|VaspWorkChain|run_process]:
launching VaspCalculation<62466> iteration #1
2025-01-07 11:57:31 [19605 | REPORT]:      [62464|VaspWorkChain|results]: work chain
completed after 1 iterations

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2025-01-07 11:57:32 [19606 | REPORT]:      [62464|VaspWorkChain|on_terminated]:
cleaned remote folders of calculations: 62466
2025-01-07 11:57:32 [19607 | REPORT]:      [62434|SubWorkChain|elaborate_results_main]:
ENERGY:      -460.39679492 eV

2025-01-07 11:57:32 [19608 | REPORT]:      [62434|SubWorkChain|init_run_aidia_main]:
MAGMOM -2.0 0.0 0.0 -2.0 0.0 0.0 0.0 0.0 2.0 0.0 0.0 2.0 0.0 0.0 2.0 0.0 0.0 2.0
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2025-01-07 11:57:34 [19609 | REPORT]:      [62477|VaspWorkChain|run_process]:
launching VaspCalculation<62479> iteration #1
2025-01-07 11:57:35 [19610 | REPORT]:      [62477|VaspWorkChain|results]: work chain
completed after 1 iterations
2025-01-07 11:57:36 [19611 | REPORT]:      [62477|VaspWorkChain|on_terminated]:
cleaned remote folders of calculations: 62479
2025-01-07 11:57:36 [19612 | REPORT]:      [62434|SubWorkChain|elaborate_results_main]:
ENERGY:      -460.40052784 eV

2025-01-07 11:57:37 [19613 | REPORT]:      [62434|SubWorkChain|finalize]: J_xx:
-1.930897500003 meV

```

After computing each exchange parameter, AMaRaNTA prints the essential information about the converged magnetic moments of the four configurations, helpful to assess whether the initial magnetic configuration was respected. This information is normally printed for the atoms of the magnetic species only; magnetisation of (nominally) non-magnetic atoms is however included if it exceeds $0.2 \mu_B$.

```

2025-01-07 11:57:38 [19614 | REPORT]:      [62434|SubWorkChain|finalize]:

STATE 1
=====
Atom      M      Mx/M      My/M      Mz/M
1         1.824      1.0      0.0      0.001
2         1.825      1.0      0.0      0.001
3         1.826      0.001      0.0      1.0
4         1.83       0.0      0.0      1.0
5         1.832      0.0      0.0      1.0
6         1.829      0.0      0.0      1.0
7         1.833      0.0      0.0      1.0

```

```

8          1.83    0.0    0.0    1.0
9          1.829   0.0    0.0    1.0

STATE 2
=====
Atom      M      Mx/M   My/M   Mz/M
1          1.819   1.0    0.0    0.001
2          1.818  -1.0    0.0    0.001
3          1.826   0.0    0.0    1.0
4          1.83    0.0    0.0    1.0
5          1.833   0.0    0.0    1.0
6          1.829   0.0    0.0    1.0
7          1.833   0.0    0.0    1.0
8          1.83    0.0    0.0    1.0
9          1.828   0.0    0.0    1.0

STATE 3
=====
Atom      M      Mx/M   My/M   Mz/M
1          1.819  -1.0    0.0    0.001
2          1.818   1.0    0.0    0.001
3          1.826   0.0    0.0    1.0
4          1.83    0.0    0.0    1.0
5          1.832   0.0    0.0    1.0
6          1.829   0.0    0.0    1.0
7          1.833   0.0    0.0    1.0
8          1.831   0.0    0.0    1.0
9          1.829   0.0    0.0    1.0

STATE 4
=====
Atom      M      Mx/M   My/M   Mz/M
1          1.824  -1.0    0.0    0.001
2          1.825  -1.0    0.0    0.001
3          1.826   0.0    0.0    1.0
4          1.83    0.0    0.0    1.0
5          1.833   0.0    0.0    1.0
6          1.829   0.0    0.0    1.0
7          1.833   0.0    0.0    1.0
8          1.831   0.0    0.0    1.0
9          1.829   0.0    0.0    1.0

```

Finally, after computing all the 12 exchange parameters in the model, the execution ends with a goodbye message:

```

2025-01-07 12:17:02 [19868 | REPORT]: [62402|AmarantaWorkChain|print_goodbye]:

=====
                        Job done
=====

```

2.6 Benchmarking of DFT parameters

Before entering the dataset production phase, we first verified that our workflow was able to reproduce representative test cases from the existing literature. We then performed an appropriate exploration of the most impactful DFT variables and parameters, with the aim of converging on a reliable and internally consistent computational setup, to be applied uniformly across the full batch of materials in the dataset.

Test cases: NiI₂ and CrGeTe₃ As benchmark systems, we consider NiI₂ and CrGeTe₃, two well-studied 2D magnets for which detailed exchange parameters are available in the literature. Tables 2.1 and 2.2 report the components of the nearest-neighbour exchange tensor $\mathbf{J}^{(1)}$ obtained with AMaRaNTA, alongside the corresponding reference values.⁶ In both cases, the level of agreement is very good and the discrepancies may be ascribed to small differences in the computational setup.

Table 2.1: Exchange tensor $\mathbf{J}^{(1)}$ for NiI₂ obtained with AMaRaNTA compared to Ref. [139] by Amoroso *et al.*. Values from Ref. [139] have been adjusted to account for a different Ni–Ni pair definition. Units are meV.

AMaRaNTA				Amoroso et al.			
	x	y	z		x	y	z
x	−6.14	1.01	1.27	x	−6.20	1.04	1.21
y	1.00	−7.38	0.71	y	1.04	−7.40	0.70
z	1.27	0.71	−7.26	z	1.21	0.70	−7.30

Table 2.2: Exchange tensor $\mathbf{J}^{(1)}$ for CrGeTe₃ obtained with AMaRaNTA compared to Ref. [175] by Xu *et al.* (specifically, with the $U = 0$ case reported in Supplementary Table 1). Values from Ref. [175] have been multiplied by a factor of $S^2 = 9/4$, as the authors do not adopt the convention of unit-normalised spins as we do. Units are meV.

AMaRaNTA				Xu et al.			
	x	y	z		x	y	z
x	−13.68	0.19	0.05	x	−14.13	0.27	−0.07
y	0.19	−13.31	0.09	y	/	−13.86	−0.11
z	0.05	0.09	−13.86	z	/	/	−14.24

DFT computational details Having established that AMaRaNTA reliably reproduces literature results, we now summarise the final computational setup adopted for the dataset

⁶Starting unit cells and DFT parameters were chosen so as to mimic the setup of each reference as closely as possible (inevitably, published descriptions almost never fully specify all technical details of the calculations). As a consequence, the values reported here do not coincide with those listed in the final dataset for the same materials.

production phase. All calculations are carried out using VASP version 6.4.0 [16, 17]. The Local Spin-Density Approximation (LSDA) is employed for the exchange-correlation functional, which avoids the issues of symmetry breaking and numerical instabilities, known to occur in non-collinear calculations with the Generalised Gradient Approximation (GGA) [181]. For magnetic species, the so-called “_pv”-type pseudopotentials are used, treating semicore p states as valence electrons [81, 82]. Electron correlation is treated at the LDA+ U level, following the Liechtenstein scheme [72], with $U = 2.8$ eV and $J = 0.8$ eV. This set of parameters was applied uniformly to all magnetic species in the studied compounds, to ensure consistency across our dataset. The plane-wave kinetic energy cutoff is set to 1.3 times the largest ENMAX value among all elements in each particular system. Total energies are converged to within 10^{-6} eV. All symmetry operations are explicitly disabled to ensure that every element of the nearest-neighbour exchange tensor is computed independently.

Precision of exchange parameters We estimate the precision of our results to be on the order of 0.1 meV, even though we report an additional significant digit. Our tests indicate that this uncertainty is primarily determined by the choice of supercell size. Secondary factors, contributing 0.01–0.04 meV, include the energy cutoff, $\mathbf{k}$ -point mesh density, and small deviations arising from unfulfilled symmetry constraints.

In this analysis, only parameters requiring convergence are treated as sources of error. Categorical choices, such as the pseudopotential family or type, are not included, as they do not affect the internal consistency of the database. Consequently, users attempting to reproduce our results with different choices may observe larger deviations. Additional discrepancies, estimated at roughly 0.1–0.15 meV, can also arise from differences in VASP versions or variations in hardware and high-performance computing environments.

2.7 Application to a material dataset

To illustrate the potential and performance of AMaRaNTA, we apply it to a dataset of 29 2D magnets, extracted from the Materials Cloud 2D Structure (MC2D) database [43, 44]. This dataset is limited to insulating compounds (primarily binary and ternary) with a calculated band gap larger than 0.1 eV at the Perdew-Burke-Ernzerhof (PBE) level, as reported in MC2D, and containing a single magnetic species — specifically, transition metals ranging from V to Ni — as mentioned above.

The results are analysed in terms of the magnitudes of the different magnetic parameters introduced in Eq. (2.13), highlighting distinct trends across the various compounds and predicting whether their ground states are more likely to be collinear or non-collinear, based on the degree of magnetic frustration. The complete raw data of all calculations, performed by Dr. Andrea Droghetti and Dr. Giuseppe Cuono (CNR-SPIN, Chieti), are provided in Appendix A.

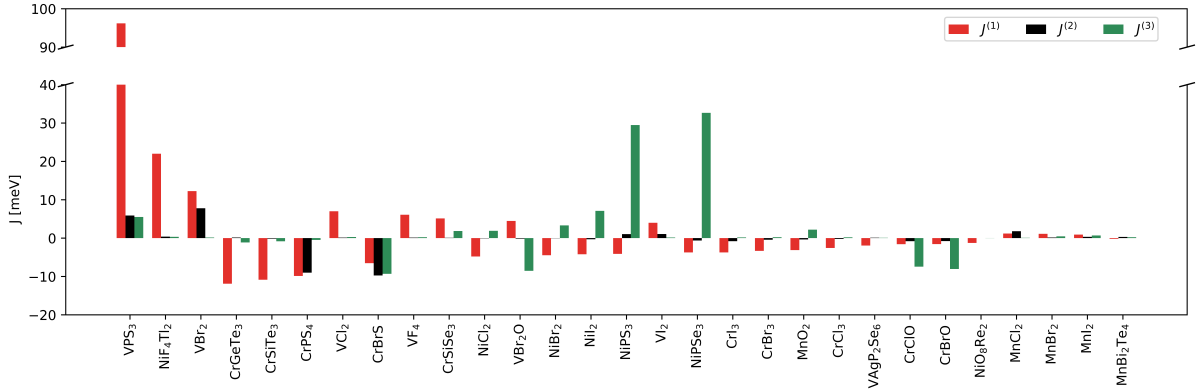


Figure 2.3: Isotropic exchange parameters $J^{(1)}$, $J^{(2)}$ and $J^{(3)}$ for our dataset, shown in decreasing order of $|J^{(1)}|$.

Isotropic exchange

The magnitude and sign of the isotropic exchange interactions — reported in Fig. 2.3 for our dataset up to the third-nearest-neighbour level — are among the most fundamental descriptors of a magnetic material. As discussed above, the inclusion of these longer-range interactions marks a major advancement introduced by AMaRaNTA, distinguishing it from prior approaches.

The materials in our dataset can be broadly categorised into three distinct subsets, based on the relative magnitude of isotropic exchange: (i) those with a dominant nearest-neighbour interaction, (ii) those in which second- or third-nearest-neighbour interactions prevail, and (iii) those where interactions at different distances have comparable magnitudes, giving rise to competing effects.

Materials with dominant nearest-neighbour interaction A significant subset of materials in our dataset exhibits a large isotropic exchange parameter between nearest-neighbour atoms and negligible interactions beyond. If this parameter is negative, such systems are expected to display a FM ground state, stable against thermal fluctuations in the presence of easy-axis anisotropy. Notable examples include the well-known compounds CrGeTe_3 and CrSiTe_3 : our calculations reproduce the dominant negative $J^{(1)}$,⁷ consistent with collinear ferromagnetism, as reported in the literature [107, 179, 182].

The most striking result in our dataset, however, is for VPS_3 . We find a positive and exceptionally large $J^{(1)} = 96$ meV — roughly 16–17 times larger than both $J^{(2)}$ and $J^{(3)}$ — pointing to a robust AFM order. Comparing to previous theoretical studies, Torelli *et al.* [144] reported a $J^{(1)}$ value of 108 meV; Chittari *et al.* [183] found $J^{(1)} = 94.7$ meV, which was 6–8 times larger than $J^{(2)}$ and $J^{(3)}$; finally, Yang *et al.* [184] predicted $J^{(1)} = 53.5$ meV, approximately 50 times larger than the higher-order terms.⁸ Despite some quantitative discrepancies — possibly due to the different values of the Hubbard

⁷For convenience, we omit the atomic indices i, j from the exchange parameters hereafter, wherever they are redundant.

⁸The values in Refs. [183] and [184] have been corrected to adhere to our $S = 1$ convention.

U – all the above predictions qualitatively agree in identifying the strongly AFM $J^{(1)}$ as the leading magnetic parameter. This conclusion is further supported by experimental evidence for a Néel-type AFM structure, consistent with the compound’s honeycomb lattice [185].

NiF_4Ti_2 is another example of a material with a dominant AFM $J^{(1)}$, for which no prior literature exists. This lack of data is likely due to thallium’s toxicity, which limits experimental research.

Finally, our results also predict a leading AFM $J^{(1)}$ in the two families of dihalides MnX_2 and VX_2 ($X = \text{Cl}, \text{Br}, \text{I}$). However, unlike the previously discussed materials, these compounds crystallise in a structure where the magnetic ions form a triangular lattice. In such conditions, strong AFM interactions can give rise to geometric frustration, which may suppress simple collinear ordering and promote more complex magnetic states instead, as discussed, for example, in Ref. [186].

Materials with dominant beyond-nearest-neighbour interactions Some materials in our dataset, notably NiPS_3 and NiPSe_3 , are characterised by a very strong and AFM $J^{(3)}$ of about 30 meV, which dominates over a weak FM $J^{(1)}$ and a negligible $J^{(2)}$. This interaction pattern, when combined with the honeycomb lattice formed by the Ni atoms, leads to AFM spin textures – either Néel or zigzag, depending on the specific values of the parameters – as reported in many studies [183, 187–191]. Tables 2.3 and 2.4 summarise our results, compared to previous theoretical predictions and experimental measurements.

Table 2.3: Exchange parameters for NiPS_3 from various studies.

Reference	$J^{(1)}$ [meV]	$J^{(2)}$ [meV]	$J^{(3)}$ [meV]
This work	−4.1	1.1	29.5
Chittari <i>et al.</i> [183] (DFT)	−11.3	−0.1	36.0
Gu <i>et al.</i> [187] (DFT)	−5.5	−0.4	45.5
Bazazzadeh <i>et al.</i> [188] (DFT)	−1.0	−0.2	3.9
Autieri <i>et al.</i> [192] (DFT)	−3.3	−0.2	13.7
Olsen ^a [193] (DFT)	−2.6	−0.3	14.0
Basnet <i>et al.</i> [189] (DFT)	−3.5	−0.3	14.1
Peng <i>et al.</i> [190] (DFT)	−2.5	/	9.5
Yang <i>et al.</i> ^a [191] (DFT)	−5.6	0.7	32.0
Lançon <i>et al.</i> ^b [194] (exp)	−3.8	0.2	13.8

^a A detailed analysis of the exchange parameters as a function of U is also provided in these works.

^b Values in the table are twice those in the paper due to different definitions of exchange parameters.

Table 2.4: Exchange parameters for NiPSe₃ from various studies.

Reference	$J^{(1)}$ [meV]	$J^{(2)}$ [meV]	$J^{(3)}$ [meV]
This work	−3.7	−0.6	32.7
Chittari <i>et al.</i> [183] (DFT)	−3.1	1.0	18.2
Gu <i>et al.</i> [187] (DFT)	−9.3	−0.1	43.0
Bazazzadeh <i>et al.</i> [188] (DFT)	−1.1	−0.1	4.0
Musari <i>et al.</i> [195] (DFT)	−11.3	−0.3	4.7
Basnet <i>et al.</i> [189] (DFT)	−4.5	0.1	16.1
Sun <i>et al.</i> ^a [196] (DFT)	−7.9	2.9	1.5
Peng <i>et al.</i> [190] (DFT)	−1.3	/	12.8
Yang <i>et al.</i> [191] (DFT)	−7.6	0.5	40.4

^a The authors also provide $J^{(4)} = 1.0$ meV.

Most earlier results qualitatively agree with ours in identifying $J^{(3)}$ as the dominant magnetic interaction in these nickel compounds. Several works provide physical insight into this behaviour [187, 189, 191, 192], suggesting that $J^{(3)}$ arises from a Ni–X₁–X₂–Ni superexchange pathway entirely contained within a single sublattice. In contrast, the pathway responsible for $J^{(2)}$ involves two chalcogen atoms belonging to different sublattices, which weakens its effectiveness. Furthermore, the fact that $J^{(3)}$ is even larger than $J^{(1)}$ has been explained using a simple model considering direct exchanges only [192]. Due to the trigonal crystal field, the Ni d -manifold splits into lower-energy even orbitals and higher-energy odd orbitals (with respect to the basal plane). Even orbitals are fully occupied because Ni²⁺ corresponds to a d^8 configuration: the only contribution to exchange comes therefore from the odd orbitals. For these, it has been shown [192] that the third-nearest-neighbour couplings are indeed larger than the nearest-neighbour ones.

Interestingly, both NiPS₃ and NiPSe₃ are also reported in Ref. [144], where only nearest-neighbour interactions are considered. That work assigns a large $J^{(1)}$ (around 30 meV) to both compounds. We speculate that this value may effectively incorporate longer-range contributions, particularly from $J^{(3)}$. This interpretation is further supported by results from a later study by the same group on NiPS₃ [193].

Materials with comparable exchange interactions A considerable amount of materials features comparable exchange interactions involving multiple neighbours. Specifically, we identify 10 materials for which the ratio $J^{(2)}/J^{(1)}$ is as large as 25%, and 14 for which $J^{(3)}/J^{(1)}$ reaches the same value. Particularly interesting are those cases where $J^{(3)}$ (or $J^{(2)}$) and $J^{(1)}$ have opposite sign, as this is another typical situation that can give rise to magnetic frustration and non-collinear ground states. Examples include NiX₂ (X = Cl, Br, I), NiPX₃ (X = S, Se), MnO₂, MnBi₂Te₄ and VBr₂O. We however emphasise that such constraints on the ratios are merely necessary conditions for non-collinear order to emerge: the geometry of the magnetic lattice plays an equally important role. For instance, VBr₂O, despite meeting the ratio-based criteria, should be excluded from the list of potentially frustrated systems, as the pattern given by an AFM $J^{(1)}$, a negligible $J^{(2)}$ and a FM $J^{(3)}$ on a square lattice actually precludes any kind of frustration.

Magnetic anisotropies

Magnetic anisotropy breaks the otherwise rotational symmetry of the Heisenberg Hamiltonian. It consists of two contributions: the SIA, denoted as A in Eq. (2.13), and the two-ion anisotropic exchange, captured by the symmetric Kitaev-like matrix $\underline{\mathbf{K}}$ and the antisymmetric DMI matrix $\underline{\mathbf{D}}$ in Eq. (2.14). The ultimate preferential spin direction is decided by the interplay of the two contributions, which should therefore be treated on equal footing (see, e.g., Ref. [175] for a practical prescription). Moreover, two-ion anisotropic exchange can itself be a driving force behind exotic, non-collinear spin textures [139], along with the effects of lattice geometry and competing isotropic exchange interactions discussed above.

The accurate evaluation of anisotropies – in particular, the two-ion contribution – beyond the approximations used in previous works constitutes the second crucial improvement provided by our approach.

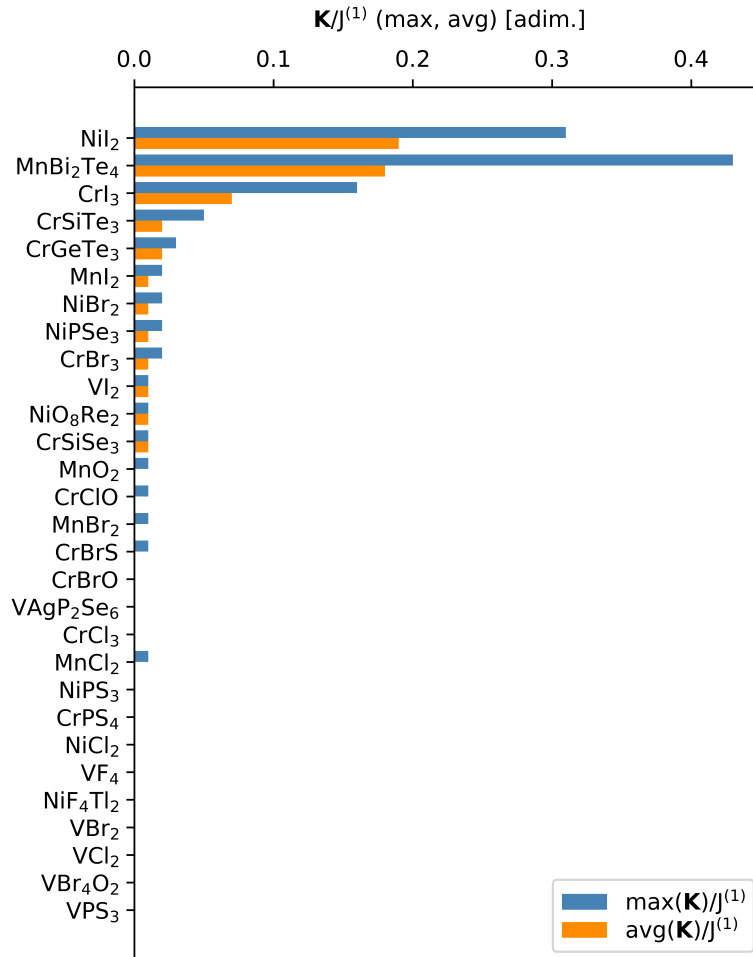


Figure 2.4: Ratio between maximum (respectively, average) element of $\underline{\mathbf{K}}$ and $J^{(1)}$.

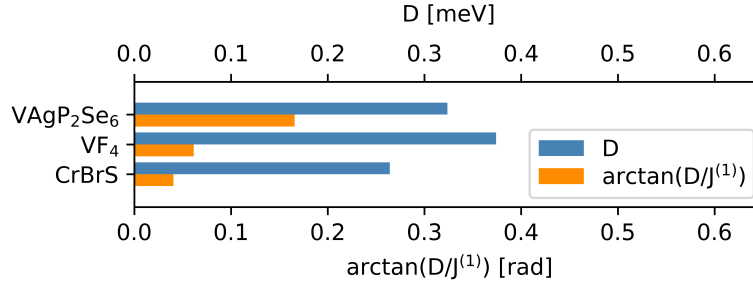
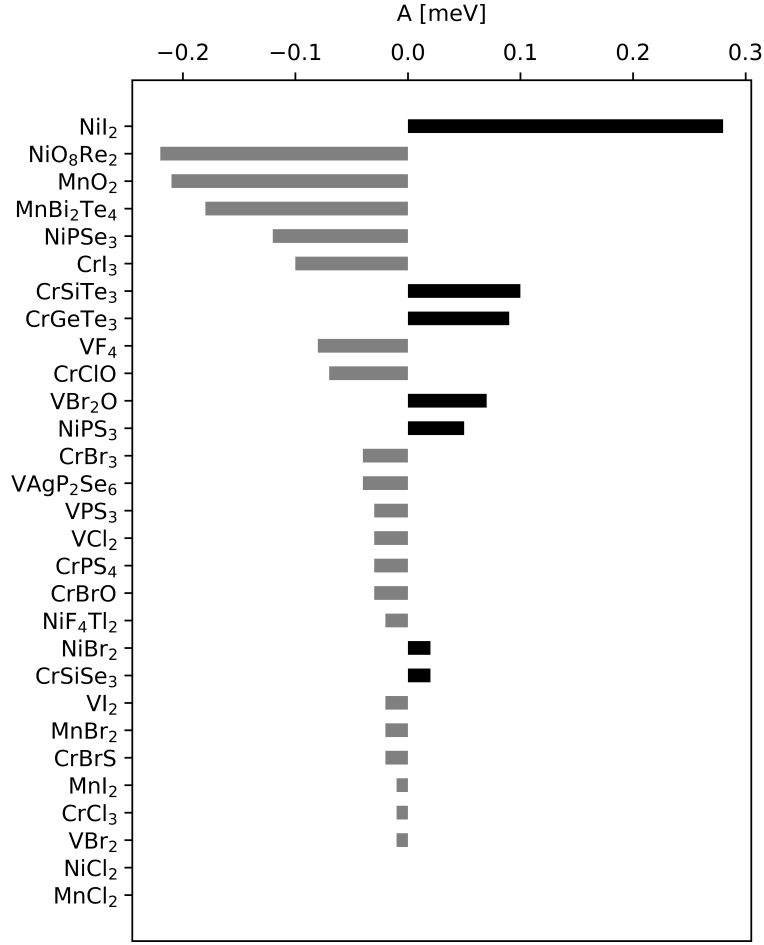


Figure 2.5: Modulus of the Dzyaloshinskii–Moriya vector $D = |\mathbf{D}|$ and $\arctan(D/J^{(1)})$, shown for the only three materials with a non-vanishing antisymmetric exchange.

Two-ion anisotropic exchange Fig. 2.4 presents both the maximum and the average element of $\underline{\mathbf{K}}$ (in absolute value) normalised by the isotropic term $J^{(1)}$. As expected, the strongest anisotropies are found in materials containing heavy elements such as tellurium and iodine, where SOC is more pronounced. We identify three materials where the average Kitaev-like interaction reaches at least 10% of $J^{(1)}$. For two of them, the Kitaev-like magnetism is already well known in the literature: in CrI₃, it enhances the easy-axis anisotropy in cooperation with the SIA [175], whereas in NiI₂ its interplay with the strong $J^{(3)}$ induces the antiskyrmionic texture predicted in [139]. The remaining one, MnBi₂Te₄, gained a certain attention some years ago due to its topological properties [197]. The monolayer ground state is widely reported to be FM with out-of-plane anisotropy, in agreement with our prediction [198–200]. In contrast, it is listed in the database of Ref. [144] as weakly AFM, but switching to a FM state in DFT+U calculations for a Hubbard interaction $U > 2$ eV. Notably, no previous work has investigated the two-ion anisotropic terms in this system, except for [198]. However, that study found no significant Kitaev-like contribution, at variance with our results. A deeper investigation of this material is therefore warranted in future studies.

Fig. 2.5 shows both the magnitude D of the Dzyaloshinskii–Moriya vector and the angle $\arctan(D/J^{(1)})$, which governs the degree of non-collinearity between spins. DMI can arise only when the bond centre lacks inversion symmetry, imposing a strong structural constraint. Accordingly, non-vanishing DMI is found in only three materials. For CrBrS, a comprehensive study of the DMI – also extended to beyond nearest-neighbours – found it to be crucial for the formation of a topological bimeron texture [201]. On the other hand, VF₄ has recently been highlighted for its altermagnetic behaviour [119] and VAgP₂Se₆ was treated in detail in [202] as a paradigmatic case of a polar 2D magnet. To the best of our knowledge, though, no DMI analysis has been reported to date for any of the two.

Single-ion anisotropy Finally, in Fig. 2.6 we report the values of the SIA. We identify eight materials exhibiting a significant such value ($A \gtrsim 0.1$ meV). Three of them – NiI₂, CrSiTe₃ and CrGeTe₃ – show $A > 0$, pointing to an easy-plane tendency. The remaining five – NiO₈Re₂, MnO₂, MnBi₂Te₄, NiPSe₃ and CrI₃ – exhibit $A < 0$, suggesting an easy-axis tendency instead. All predictions are in agreement with existing literature [41, 42, 139, 175, 189, 198].

Figure 2.6: SIA parameter A .

We stress again, however, that the sign of the SIA alone does not fully determine the overall magnetic anisotropy. For instance, CrGeTe_3 and CrSiTe_3 , which would be expected to favour easy-plane configurations based on their positive A , actually do not, owing to the counteracting effect of the Kitaev-like term. In CrGeTe_3 , the single-ion and Kitaev-like contributions essentially cancel out, resulting in an almost isotropic magnetic ground state. In CrSiTe_3 , the Kitaev-like term outweighs the SIA, ultimately producing an easy-axis texture [175].

2.8 Conclusions and future perspectives

We outlined the features of AMaRaNTA, an open-source computational workflow designed to automate DFT calculations of exchange parameters in 2D magnets. The full nearest-neighbour exchange tensor, scalar exchange parameters for second- and third-nearest-neighbours, and the single-ion anisotropy were included in the underlying spin model,

providing a comprehensive and robust description of the minimal interactions required to stabilise the complex magnetic states observed in 2D materials.

To validate its functionality, we tested AMaRaNTA on a compact dataset of 2D magnets, consistently recovering the expected results for well-known materials, while also providing the added value of a uniform description across the dataset – namely, with the same set of parameters. In selected cases, our calculations even suggested previously unreported exchange phenomena, demonstrating the potential of our package for applications in material discovery.

In this context, AMaRaNTA contributes to the growing ecosystem of computational tools to automate the calculation of the magnetic parameters. It complements other methods based on a similar philosophy, such as energy-mapping schemes relying on global magnetic configurations, as implemented in the recently released OstravaJ [203], as well as in dedicated four-state codes like sym4state [204] and the corresponding module in the Property Analysis and Simulation Package for materials (PASP) [205]. Furthermore, it enables systematic comparison with non-four-state approaches, including the LKAG method implemented in TB2J [164] and in other recent packages [165, 166].

In this respect, although AMaRaNTA may appear similar to the existing four-state implementations, it distinguishes itself by being designed expressly for 2D magnets, internally generating all required configurations and ensuring a dataset-wide, consistent treatment of spin interactions. More importantly, it provides the distinct advantage of a fully automated, AiiDA-integrated workflow, enabling seamless interoperability with other AiiDA-based materials-informatics infrastructures developed for the discovery and analysis of 2D materials [43, 44].

Beyond the results presented in this work, AMaRaNTA can already be employed in its current version for larger-scale studies, such as investigations of rare-earth-based compounds [206] or of the effect of strain on exchange interactions, which can be substantial, as shown for NiI_2 [207]. In this case, the workflow’s automation infrastructure enables systematic exploration of the strain parameter space with minimal manual effort.

In terms of future developments, AMaRaNTA can be extended in several directions with relatively modest additional endeavour. First, from a methodological viewpoint, the spin model could be generalised to capture more complex behaviours. Examples include beyond-nearest-neighbour anisotropic exchange [208], isotropic exchange beyond the third-nearest-neighbour level [209], biquadratic exchange [210, 211] and refinement of the single-ion anisotropy by lifting the current assumption of in-plane isotropy – an improvement particularly relevant for systems with spatially anisotropic lattices. At the same time, the automatic generation of tensors for symmetry-equivalent nearest-neighbour pairs could be achieved via a post-processing routine that applies the relevant symmetry operations, without requiring additional DFT calculations. The framework could also benefit from a further expansion, in order to handle symmetry-inequivalent magnetic sites, which instead requires determining more than a single set of parameters, but would significantly broaden the class of materials that can be addressed. Even more ambitiously, the four-state protocol underpinning AMaRaNTA could be extended beyond the evaluation of exchange and anisotropy parameters, for instance to compute the coupling matrix between spin directions in a pair of magnetic sites and electric polarisation in the context of

spin-induced ferroelectricity, which relies on a similar computational machinery [212, 213].

Second, from the DFT perspective, AMaRaNTA could be extended to adopt material-specific, first-principles values for the Hubbard U parameter [75, 76], which is kept fixed in the current implementation. Although qualitative trends are generally robust against moderate variations in U , the choice of this parameter can affect the results for materials where the computed exchange interactions are small, as exemplified by MnBi_2Te_4 . In such cases, computing U from first principles would remove much of the ambiguity associated with an empirical or arbitrary choice. Moreover, AMaRaNTA is not intrinsically tied to the DFT+ U framework and could equally be combined with more advanced exchange–correlation schemes, including hybrid and self-interaction–corrected functionals, which are known to impact exchange interactions [214].

Finally, on the software side, two natural extensions would involve making AMaRaNTA compatible with DFT codes beyond VASP, provided they support constrained-magnetisation calculations, and developing a streamlined interface to Monte Carlo or atomistic spin-dynamics simulation packages. This would pave the way toward a fully automated pipeline for the systematic, high-throughput exploration of complex magnetic phenomena in 2D materials.

Chapter 3

Lead-free piezoelectricity: KNN

KNN (sodium potassium niobate) is among the most extensively investigated systems in the search for novel lead-free piezoelectrics. In this chapter, we present original research on this material, developed in collaboration with the experimental group led by Prof. Riccardo Bertacco at Politecnico di Milano – notably, Dr. Giulia Pavese and Dr. Miguel Badillo, to whom we are particularly grateful. Part of the content has been adapted from our own published work [\[2\]](#), as well as from another manuscript currently in preparation [\[3\]](#).

Le grandi distorsioni, le sperimentazioni...

Lucio Corsi, *L'upupa*

3.1 Introduction

Piezoelectricity (from the Ancient Greek term $\pi\acute{\epsilon}\zeta\epsilon\iota\nu$, “to squeeze”) is the phenomenon whereby electronic and mechanical degrees of freedom are coupled in a broad class of materials. Specifically, one refers to *direct piezoelectric effect* when an applied mechanical stress induces an electric polarisation (or enhances an existing one), in turn giving rise to a voltage. Assuming linear response, in the simplest configuration, the direct piezoelectric effect can be outlined as straightforwardly as

$$P_z = d_{33}\sigma_z \quad (3.1)$$

where σ_z denotes the uniaxial (compressive or tensile) stress along $\hat{z}$, P_z the (change in) polarisation induced along the same axis, and d_{33} is a coefficient that measures the strength of the response.¹ In the specular situation, where the application of a voltage produces a mechanical deformation of the crystal, one has the *converse piezoelectric effect*. The two mechanisms are schematically depicted in Fig. 3.1 below.

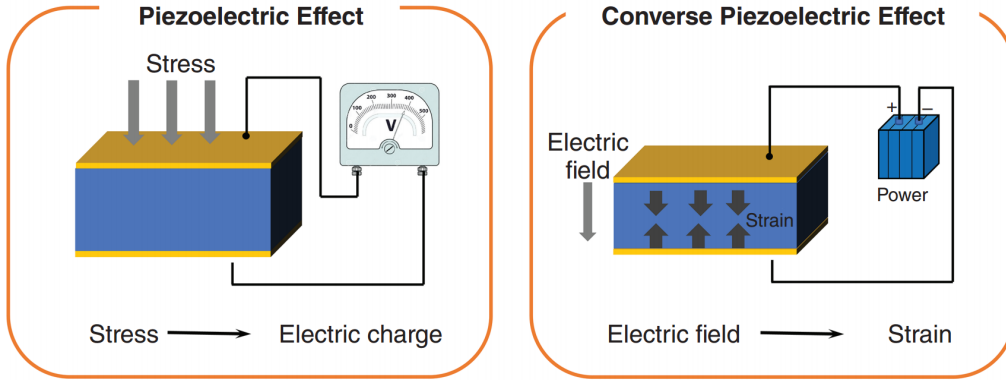


Figure 3.1: Graphical illustration of direct and converse piezoelectric effects (adapted from [215]).

In principle, piezoelectricity can be exhibited by any material satisfying the following constraints: (i) it must be an insulator; (ii) it must lack inversion symmetry. Both conditions are to be matched in order for the material to sustain a polarisation. The reason behind the first is trivial: in metals, nearly free electrons would immediately screen any externally induced electric field. The requirement of broken inversion symmetry might be less intuitive; to keep this section light, we provide here just a heuristic explanation with the aid of Fig. 3.2 (a more rigorous mathematical treatment will be provided soon after, in Section 3.3). In both cases depicted therein, at zero applied stress, the centres of positive and negative charge coincide, resulting in a vanishing polarisation. In a centrosymmetric crystal, as in panel a), the centres of charge are left unchanged under stress, even though individual ions are displaced. Conversely, in a non-centrosymmetric crystal, as in panel b), they shift relative to one another under stress, and a polarisation is established.

¹The reason for the subscripts will be clarified in Section 3.3.

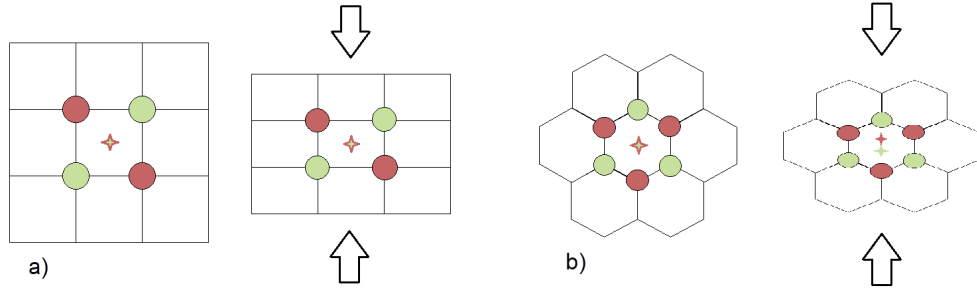


Figure 3.2: Response of crystals of different symmetries under uniaxial mechanical stress, in a simplified ionic picture (adapted from <https://lampz.tugraz.at/~hadley/ss2/crystalphysics/piezo.php>).

This argument can be placed on a more solid ground from a symmetry perspective, as illustrated by the hierarchy in Fig 3.3. Out of the 32 crystallographic point groups, 21 do not exhibit inversion symmetry and all but one (point group 432) are compatible with piezoelectricity. Half of these 20 allow for *pyroelectricity*, i.e., the onset of a spontaneous, temperature-driven polarisation. Finally, within a subset of pyroelectric materials, such polarisation is also switchable by an external electric field, and materials displaying this behaviour are termed *ferroelectric*. Although ferroelectricity is not a prerequisite for piezoelectricity (it is, indeed, the other way around), many well-known piezoelectric materials also exhibit sizeable ferroelectric behaviour.

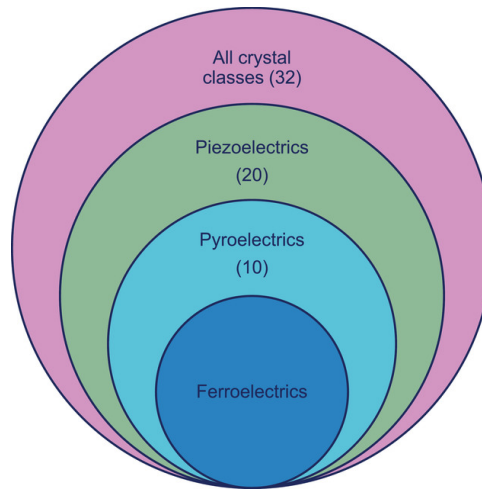


Figure 3.3: Hierarchy of ferroic materials (adapted from [216]).

The history of piezoelectricity spans nearly a century and a half, dating back to 1880, when the direct effect was discovered by Jacques and Pierre Curie in a variety of crystals, finding the strongest response in quartz and Rochelle salt [217].² The converse effect was uncovered shortly thereafter, again by the Curie brothers [219], following a theoretical

²Rochelle salt reappears in our chronology in 1920, when Joseph Valasek identified it as the first

prediction by Lippmann [220]. Some decades later, in 1910, Voigt provided a rigorous and systematic formulation of the piezoelectric phenomenon by means of tensor analysis [221]. Around this time, the first technological applications of piezoelectricity began to emerge: notable examples include sonar, developed during World War I independently by A.M. Nicholson and P. Langevin, and Thomas Edison's ceramic phonograph cartridges, which enabled the electrical reproduction of sound [222].

Scientific interest in piezoelectrics was renewed in the 1940s, with the discovery of ferro- and piezoelectricity in barium titanate (BaTiO_3) by a number of independent groups [223, 224]. A decisive breakthrough followed in 1954, when Jaffe *et al.* reported exceptional piezoelectric properties in lead zirconate titanate (PZT) [225]. In the decades that followed – and as our historical overview approaches the present day – PZT-based ceramics established themselves as the absolute standard on the piezoelectric market.

Besides PZT and BaTiO_3 , several other piezoelectric materials have been identified over time [226, 227]. Like these two archetypes, many belong to the perovskite-oxide family, with general formula ABO_3 : prominent examples are lead titanate PbTiO_3 , a prototypical ferroelectric with large spontaneous polarisation, and lead zirconate PbZrO_3 (i.e., the two parent compounds of PZT, by themselves), as well as bismuth ferrite BiFeO_3 , notable for its room-temperature multiferroicity, alkali niobates such as NaNbO_3 and KNbO_3 , together with lithium niobate LiNbO_3 and lithium tantalate LiTaO_3 . Furthermore, along the lines of PZT, there exists a vast array of solid solutions, of the aforementioned compounds and not only, offering tunable piezoelectric properties across a wide range of materials. Beyond perovskite oxides, we find wurtzite-structure compounds such as ZnO and AlN , classic single crystals like quartz (SiO_2) and, more recently, non-perovskite ferroelectrics based on hafnium oxide (HfO_2 , commonly referred to as hafnia) [228]. Finally, polymers such as polyvinylidene fluoride (PVDF) constitute an important class of piezoelectric materials outside the realm of inorganic crystals [229].

Today, applications of piezoelectricity are countless and ubiquitous, spanning fundamental science as well as everyday technology. They may be broadly classified according to whether they exploit the direct or the converse piezoelectric effect. Devices leveraging the direct effect primarily function as sensors or energy generators. As sensors, they convert mechanical stimuli – most commonly pressure variations from sound waves – into electrical signals, finding widespread use in applications from acoustic instrument amplification and medical ultrasound imaging to hydrophones, vibration sensors, and automotive knock detection. As energy generators, they directly convert mechanical work into usable voltage, as in the familiar cigarette lighter where a button press generates a spark, and in broader energy-harvesting systems. Devices based on the converse effect, by contrast, operate as actuators, in which an applied electric signal induces a controlled mechanical deformation. This mechanism enables precise motion and positioning at micro- and nanoscale dimensions and underlies technologies such as Micro-Electro-Mechanical Systems (MEMS), inkjet printers, adaptive optics, scanning probe microscopy, and specialised loudspeakers [230].

ferroelectric material [218]. In light of the discussion above, it is not surprising that the histories of piezoelectricity and ferroelectricity are so closely intertwined.

3.2 Lead-free hunt and KNN

As already mentioned, the most popular family of piezoelectric materials on the market today is that of PZT, namely, a solid solution of lead zirconate and lead titanate of the form $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$. Reasons behind the dominant role of PZT lie in a combination of outstanding properties, not only limited to piezoelectric coefficients (d_{33} up to 500 pm/V) but also including high Curie temperature³ (300 – 400 °C), ease of poling, and affordable production costs [231]. However, the toxicity of lead raises a serious concern to human health: a variety of adverse effects of lead exposure have been reported, including neurological damage, kidney dysfunction, hypertension, and developmental delays in children [232], and the associated death toll is presently estimated at the frightening figure of 5.5 million people yearly [233]. Therefore, over time, numerous legislative measures have been adopted worldwide in order to limit the presence of lead, as well as other hazardous substances. In the European Union, for example, the Restriction of Hazardous Substances Directive (RoHS 1, 2002/95/EC) and its subsequent amendments, most recently Directive 2011/65/EU, have enforced strict limits on lead content in electronic components, as well as in everyday consumer products [234, 235].

The pressure of such regulations has in turn pushed forward the research into lead-free piezoelectrics. Although no single material has proven able to match – let alone to surpass – all the performance metrics of PZT as of yet, some promising classes of lead-free alternatives have been nonetheless identified, including bismuth-based compounds (e.g., BiFeO_3), alkali niobates and BaTiO_3 derivatives [215]. With appropriate compositional and microstructural engineering, these materials have shown satisfactory piezoelectric and ferroelectric properties, positioning them as true potential future replacements for PZT in environmentally compliant applications.

Sodium potassium niobate $\text{K}_{1-x}\text{Na}_x\text{NbO}_3$ (KNN) has emerged in the last two decades as one of the most promising such candidate materials. Extensive research on bulk KNN ceramics, especially following the 2004 seminal work by Saito [231], has led to achieving remarkable performances in terms of Curie temperature (400 °C) [236] and d_{33} coefficient (416 pm/V upon texturing, increased to as high as 570 pm/V via suitable doping) [231, 237]. Nevertheless, despite such appealing properties, KNN still presents significant challenges – both intrinsic, related to its compositional and structural complexity, and extrinsic, associated with processing and technological integration – which have so far hindered its widespread use in practical applications.

KNN is a solid solution of two end members, KNbO_3 and NaNbO_3 , both of which are themselves well-known ferroelectric and piezoelectric perovskites, investigated since as early as the 1950s [238]. KNbO_3 displays a relatively simple sequence of temperature-driven structural phase transitions, shared with the archetypal perovskite BaTiO_3 : rhombohedral (space group $R3m$) $\rightarrow$ orthorhombic ($Amm2$) $\rightarrow$ tetragonal ($P4mm$) $\rightarrow$ cubic ($Pm\bar{3}m$, the high-symmetry paraelectric phase, with vanishing ferro- and piezoelectric response), in order of increasing temperature.⁴ As in BaTiO_3 , ferroelectricity arises primarily from

³In analogy to ferromagnets, the *Curie temperature* is defined as the temperature above which the materials transitions to a centrosymmetric phase, losing its piezoelectric and ferroelectric properties.

⁴ KNbO_3 and BaTiO_3 are, in fact, the only two perovskites sharing this precise phase sequence [239].

the off-centring of Nb cations within the O_6 octahedral cage, driven by Nb–O interactions; the oxygen atoms move in the opposite direction to the Nb displacement, so that the octahedron as a whole remains essentially rigid. K atoms, conversely, are only slightly perturbed away from their equilibrium position [239, 240].⁵ The spontaneous polarisation aligns along the [111], [011] and [001] pseudocubic directions for the $R3m$, $Amm2$ and $P4mm$ phases, respectively, with magnitude between 31 and 41 $\mu\text{C}/\text{cm}^2$ depending on the phase [239, 241–243].

In contrast, the other endpoint, NaNbO_3 , is often dubbed as “the most complex ferroelectric perovskite” [244]. As a result of earlier investigations, already in 1974 as many as seven distinct phases were summarised in a work by Megaw⁶ [245, 246], and more have been reported since the late 1990s [247–251]. A concise experimental overview is provided below.

- The ground state, termed phase N , is rhombohedral ($R3c$) and ferroelectric [248].
- At room temperature, the antiferroelectric phase P is the most common. This has mostly been classified as orthorhombic $Pbma/Pbcm$ (No. 57) since the earliest investigations [252], even though it was later occasionally claimed as monoclinic [253]; additional studies suggested that it may actually be composed of three sub-phases, with the room-temperature one having indeed monoclinic symmetry [248, 249].
- Roughly in the same temperature range, a ferroelectric phase Q , with orthorhombic symmetry $Pmc2_1/P2_1ma$ (No. 26), is frequently reported. In bulk NaNbO_3 , this phase is typically stabilised, as a descendant of the antiferroelectric P phase, by (even weak) chemical substitution [252, 254, 255], by an applied electric field [254, 256] or by external stress [257]. There exists, though, evidence of this phase occurring even without external manipulation, such as in Refs. [248, 250] and [258] – where, interestingly, it is classified as $Pmc2_1$ but “very subtly monoclinic” (here the authors suggest that the monoclinic phase reported in [253] could actually be a $Pbcm$ – $Pmc2_1$ coexistence). Phase Q has also been observed in non-bulk NaNbO_3 systems such as sub-micrometre particles [259, 260] and thin films [261].
- The room-temperature, ferroelectric phase has been anyway unambiguously classified as monoclinic (symmetries Pm , Pc , Cm and Cc and various mixtures of these) in many studies, both in the bulk [262–264] and in thin films, the latter being often stabilised by epitaxial strain [251, 265].
- The remaining phases in the list by Megaw (R , S , T_1 , T_2 and U) are paraelectric, with the only exception of the antiferroelectric R , and occur at temperatures higher than $\simeq 360^\circ\text{C}$ [248]. As such, they are of limited relevance for room-temperature

⁵The exact nature of the phase transitions – displacive, with the condensation of zone-centre optical soft phonon modes, or of the order-disorder type, with progressive alignment of ubiquitous local distortions upon cooling – has long been debated. The current consensus is that both mechanisms are present, with a gradual crossover of displacive to order-disorder behaviour with increasing temperature [239].

⁶Helen D. Megaw (1907–2002), pioneer in X-ray crystallography, to whom we owe the first quantitative determination of the perovskite crystal structure (in tetragonal BaTiO_3) [224].

ferroelectric or piezoelectric applications, although they provide important reference structures for understanding the lattice instabilities at lower temperature.

First-principles and model-Hamiltonian studies largely confirm this complex landscape, showing a plurality of low-energy structures often very close to one another [265–273]. In addition to the phases discussed above, some studies report another competitive orthorhombic, ferroelectric state, with $Pca2_1$ symmetry (No. 29) [244, 274].

In the case of NaNbO_3 , besides Nb off-centring, a pivotal role in driving the phase transitions is played by another degree of freedom, this time also involving the A-site: namely, the tilting of the O_6 octahedra, favoured by the smaller ionic radius of Na atoms compared to K. Octahedral tilts dominate the high-temperature, non-polar phases, where Nb displacements disappear; the two mechanism are strongly coupled at lower temperature, influencing ferroelectricity together [245, 246]. A thorough study and classification of octahedral tilts is due to Glazer, who also provided a practical notation system that was later named after him [275].

To conclude this summary, we report literature values for the spontaneous polarisation. This was quantified for the N ($R3c$) phase as $59 \mu\text{C}/\text{cm}^2$, consistent with DFT predictions in the range $35\text{--}58 \mu\text{C}/\text{cm}^2$; for the Q ($Pmc2_1$) phase, experimental data are widely scattered ($9\text{--}40 \mu\text{C}/\text{cm}^2$), likely reflecting coexistence with the antiferroelectric phase P and field-induced effects, while DFT predicts values of $32\text{--}47 \mu\text{C}/\text{cm}^2$; finally, experimental reports for the monoclinic phases lie between 30 and $40 \mu\text{C}/\text{cm}^2$ [244, 251, 257, 268, 270–272, 274, 276–280].

The solid solution KNN inherits such features and complexity from its parent compounds. The coupling of octahedral tilting and Nb off-centring mechanisms persists over a large composition range on the Na-rich side, as does the presence of several competing, low-energy phases. This yields a multifaceted structural landscape, captured by the elaborate temperature-composition phase diagrams available in the literature [281–286].⁷ A representative example of a relatively recent one is shown in Fig. 3.4 below; it should be noted, however, that different experimental studies are not always mutually consistent with respect to the number, ordering, symmetry, and tilt systems of the various phases.

Piezoelectric alloys often exhibit *morphotropic phase boundaries* (MPB) in the vicinity of certain critical compositions, where two or more ferroelectric phases with different symmetries become nearly degenerate in energy and can readily transform into one another.⁸ The presence of a MPB is typically associated with enhanced piezoelectricity, by virtue of the softening of the crystal lattice, the flattening of the free energy profile and the increased ease of polarisation rotation and extension [286–290]. The most well-known and extensively studied MPB among perovskite piezoelectrics is found in PZT at $x \simeq 0.48$, where the system transitions between tetragonal and rhombohedral symmetries via an intermediate monoclinic phase [291–293].

⁷We deliberately avoid considering the effects of further doping of KNN with different atomic species, which for our purposes here would just increase the complexity unnecessarily.

⁸More generally, phase boundaries are referred to as *polymorphic* when driven by temperature, and *morphotropic* when induced by changes in composition or pressure. In a temperature-composition phase diagram, MPBs therefore appear as quasi-vertical lines [286, 287].

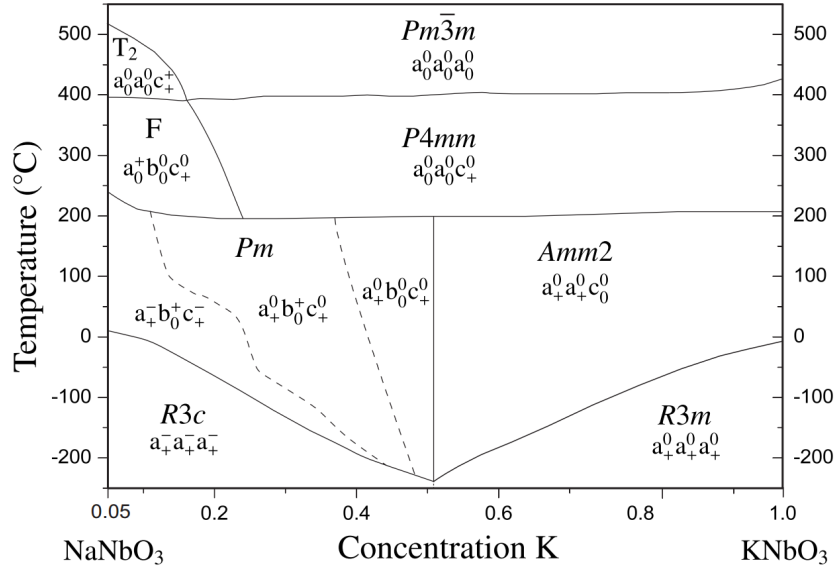


Figure 3.4: KNN phase diagram (as in Ref. [285]). The simple phase sequence of KNbO_3 can be recognised on the right side, whereas the complicated landscape of NaNbO_3 appears to be smoothened already at a small doping level (the plot starts at $x_{\text{Na}} = 0.95$, pure NaNbO_3 is not encompassed). Notably, a considerable portion of the diagram, extending until around $x_{\text{Na}} = 0.5$, displays monoclinic symmetry Pm , with three sub-phases differing by the octahedral tilt system.

In KNN, several studies have suggested the presence of a similar MPB around $x_{\text{Na}} \simeq 0.45 - 0.5$, separating a K-rich $Amm2$ orthorhombic phase from a Na-rich Pm monoclinic one (solid vertical line in Fig. 3.4) [231, 285, 294–296]. Here, pre-translational short-range octahedral rotations are thought to occur, softening local bonds and lowering the barrier for polarisation rotation through coupled Na–Nb off-centring [296]. Bulk ceramics with the above composition have indeed demonstrated enhanced piezoelectric coefficients and dielectric constants, making this phase boundary the most intensively investigated in KNN to date [294, 295, 297]. However, on the Na-rich side, the KNN phase diagram shows two additional (mainly) composition-driven transitions, at $x_{\text{Na}} \simeq 0.65$ and $x_{\text{Na}} \simeq 0.8$ (dashed lines in Fig. 3.4),⁹ associated with a change not in symmetry, that remains monoclinic, but rather in the tilt system of the NbO_6 octahedra [285]. In the range $0.5 < x_{\text{Na}} < 0.65$, KNN is stable in a non-tilted phase ($a^0b^0c^0$ in Glazer notation).¹⁰ At $x_{\text{Na}} \simeq 0.65$, this transitions to an $a^0b^+c^0$ configuration, characterised by in-phase tilts around the y pseudocubic axis. Finally, a third transition occurs at $x_{\text{Na}} \simeq 0.8$ to a more complex $a^-b^+c^-$ structure, where, in addition to the in-phase $\hat{y}$ tilt, neighbouring octahedra are antiphase tilted around the $\hat{x}$ and $\hat{z}$ axes. For these two phase boundaries, as well, sizeable piezoelectric coefficients and remnant polarisation have been revealed experimentally [298–300].

KNN, overall, manifests itself as a non-trivial playground already when treated within

⁹The exact compositions vary from study to study, likely due to the phase boundaries also having a non-negligible temperature dependence (accordingly, authors in [285] are cautious in calling these MPBs).

¹⁰In Glazer notation, superscripts denote tilt phase relation (0 = none, + = in-phase, − = antiphase) about pseudocubic axes, while a , b , c label the corresponding crystallographic directions.

an idealised, monodomain framework. In realistic experimental conditions, additional extrinsic factors come into play, further complicating the picture. These include the high processing temperatures, typically in the range of 500–700 °C, required to stabilise the most desirable polar phases (tetragonal or orthorhombic) [301, 302], as well as the high electrical leakage currents caused by A-site and oxygen vacancies [303–306]. Such factors can substantially limit the operational voltage of devices and, in extreme cases, lead to catastrophic failure [307]. In the case of KNN thin films, an additional major challenge is the scalability from small laboratory samples to wafer-scale production. For industrial purposes, the material should ideally be grown at relatively low temperatures, with good thickness and compositional uniformity over large areas, and at reasonably high growth rates [308]. Complying with those requirements, however, can have significant side effects on the film quality. For instance, several studies report the formation – in KNN as well as in PZT – of non-polar pyrochlore secondary phases at low processing temperatures: by symmetry, these cannot contribute to the piezoelectric response and are therefore undesirable [305, 309–314].

In the recent years of markedly increased interest in KNN, many of these challenges have been addressed and a substantial body of experimental data has been accumulated. Curiously, the amount of published first-principles studies on (undoped) KNN in the same period seems to be considerably smaller – to the best of our knowledge, on the order of a couple dozens only.¹¹ Within the existing literature, the earliest work we could trace is Ref. [315], which investigated the $x_{\text{Na}} = 0.5$ case with a combined model Hamiltonian – Monte Carlo approach. Subsequently, Ref. [316] was the first to address the compositional dependence of selected properties over a broader range. Finally, the exploration of piezoelectric properties as a function of the composition was first performed in Ref. [317] and further examined in Refs. [318–320] (other works devoted to piezoelectricity treated the selected composition $x_{\text{Na}} = 0.5$ only). All these studies leverage different alloy-modelling techniques, exchange–correlation functionals and choices of crystal symmetry: as a result, their predictions are not always directly comparable to one another and, when they are, may differ significantly. Furthermore, some of these methodological choices carry intrinsic limitations, either because certain approaches to model the alloy randomness may not fully capture local structural effects, or because assuming idealised symmetries can overlook relevant structural features of the material. Adding this to the overall scarcity of first-principles works on the subject, considerable scope appears to be left for further, systematic DFT investigations of KNN.

In this chapter, we report on *ab initio* investigations of this material. Our interest in it initially arose from providing theoretical support to the experimental work conducted by the group of Prof. Riccardo Bertacco, aimed at the fabrication of high-quality, industry-ready KNN thin films with controlled composition and functional properties. Within this perspective, we first addressed a key phenomenon emerging from experiments: a pronounced segregation of KNN – initially prepared at the nominal composition $x_{\text{Na}} = 0.5$ – into Na-rich clusters with composition in the range $0.7 < x_{\text{Na}} < 0.8$ (accompanied by K-rich pyrochlore regions) [2]. We investigate this behaviour by means of DFT simulations, in

¹¹The topic appears to also constitute a geographical niche, having been carried on almost exclusively by research groups based in China.

order to assess to what extent it can be captured within a first-principles, zero-temperature framework.

Subsequently, as the experimental activity evolved toward systematic mapping of ferroelectric and dielectric properties across a broad compositional range [3], we realised that a conceptually analogous theoretical analysis could not only complement experimental observations, but also contribute to the more ambitious goal of a likewise systematic first-principles exploration of KNN. To this end, we focus on a selected monoclinic phase, suggested by literature phase diagrams. We examine whether and how well DFT predictions for this configuration align – at least qualitatively – with the existing literature and the experimental scenario, and discuss intrinsic limitations and idealisations of our description that may account for discrepancies or incomplete agreement.

3.3 Theory and implementation of piezoelectricity

3.3.1 Tensorial constitutive relations

We have already anticipated (Eqn. 3.1) how the stress-polarisation relation, defining direct piezoelectricity, looks like in the simplest of cases: $P_z = d_{33}\sigma_z$. However, this is but the most immediate, scalar version of a more general, tensorial relation, which we now proceed to formulate.

Let us start from clarifying the dimensionality of the problem. The stress is naturally described by a second-rank, 3×3 tensor σ_{ij} , whose diagonal terms represent uniaxial stresses and off-diagonal ones represent shear stresses. Polarisation, conversely, is an ordinary, three-dimensional polar vector of components P_i . As a consequence, the quantity relating them must be a third-rank tensor, with $3^3 = 27$ independent components, and the above relation (assuming Einstein convention for summations) is generalised to

$$\boxed{P_i = d_{ijk}\sigma_{jk}} \quad (3.2)$$

A first, important step to simplify the problem consists in exploiting the symmetry of the stress tensor ($\sigma_{jk} = \sigma_{kj}$), which reduces its independent components from 9 to 6. Accordingly, the symmetry carries over to the piezoelectric tensor ($d_{ijk} = d_{ikj}$), whose independent components scale down to 18.

To explicitly get rid of the redundant terms, it is convenient to operate a formal reduction of the rank of the tensors d_{ijk} and σ_{jk} , according to the so-called *Voigt notation* [221]. The stress tensor is compacted into a six-component vector as

$$\sigma_\alpha = \begin{bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \sigma_5 \\ \sigma_6 \end{bmatrix} = \begin{bmatrix} \sigma_{11} \\ \sigma_{22} \\ \sigma_{33} \\ \sigma_{23} \\ \sigma_{13} \\ \sigma_{12} \end{bmatrix} \quad (3.3)$$

and the piezoelectric tensor into a 6×3 matrix as

$$d_{\alpha\beta} = \begin{bmatrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\ d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36} \end{bmatrix} \quad (3.4)$$

With the new indexing, Eqn. 3.2 is recast as

$$\boxed{P_\alpha = d_{\alpha\beta} \sigma_\beta} \quad (3.5)$$

where α (spanning 1 to 3) labels the polarisation direction and β (1 to 6) runs over the Voigt stress components.

Note that the rule for wrapping up the uniaxial stress components $\sigma_1 - \sigma_3$ is universal ($11 \rightarrow 1, 22 \rightarrow 2, 33 \rightarrow 3$), but different conventions exist for the shear components $\sigma_4 - \sigma_6$, and consequently for the shear piezoelectric elements $d_{\alpha 4} - d_{\alpha 6}$. We have adopted in Eqns. 3.3 and 3.4 the most common mapping ($23 \rightarrow 4, 13 \rightarrow 5, 12 \rightarrow 6$), but we report that, for instance, VASP employs a different internal ordering ($12 \rightarrow 4, 23 \rightarrow 5, 13 \rightarrow 6$) which leads to a reshuffling of the three rightmost columns of $d_{\alpha\beta}$. Therefore, caution is needed when making comparisons.

Eqn. 3.5 is the most general form of the direct piezoelectricity constitutive relation. In specific cases, the number of independent components of the $d_{\alpha\beta}$ tensor is further reduced by crystal symmetry arguments, depending on the point group (a more detailed list of tensor shapes for a number of relevant groups can be found in Appendix B). For instance, in the tetragonal $4mm$ case one has

$$d_{\alpha\beta} = \begin{bmatrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & 0 & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{bmatrix} \quad (3.6)$$

It is instructive at this point to explain in detail what each $d_{\alpha\beta}$ element means. The first index α always refers to the induced polarisation direction, whereas β denotes the type of stress. Fig. 3.5 below illustrates the case of tetragonal symmetry, with the three independent components introduced above: d_{33} (respectively, d_{31}) represents polarisation along $\hat{z}$ due to normal stress along $\hat{z}$ (respectively, $\hat{x}$), d_{15} describes polarisation along $\hat{x}$ due to shear stress along $\hat{x}$ on crystal planes orthogonal to $\hat{z}$.

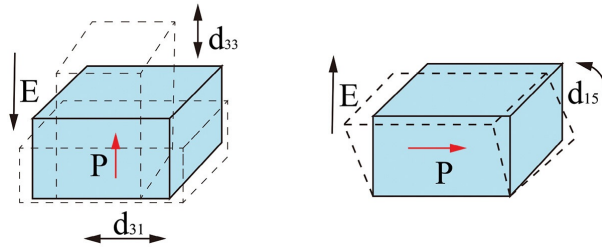


Figure 3.5: Interpretation of the components d_{33} , d_{31} and d_{15} for a tetragonal crystal (adapted from [321]).

3.3.2 The strain-charge equations

The piezoelectric effect can be embedded within a more general framework, that also describes

- Linear dielectric response $D_i = \varepsilon_{ij}\mathcal{E}_j$, where D_i is the electric displacement, ε_{ij} is the familiar second-rank dielectric tensor and $\mathcal{E}_j$ is the applied electric field (alternatively, $D_i = \varepsilon_0\mathcal{E}_i + P_i$).
- Linear elasticity $\eta_{ij} = S_{ijkl}\sigma_{kl}$, where η_{ij} is the second-rank, symmetric strain tensor and S_{ijkl} is a fourth-rank tensor, termed *elastic compliance*.

Including the piezoelectric contribution leads to a pair of coupled equation, that in the so-called *strain-charge form* read

$$\begin{cases} \eta_{ij} = S_{ijkl}\sigma_{kl} + d_{ijk}^T\mathcal{E}_k \\ D_i = d_{ijk}\sigma_{jk} + \varepsilon_{ij}\mathcal{E}_j \end{cases} \quad (3.7)$$

where the second equation reduces to Eqn. 3.2 for vanishing electric field (in which case $D_i = P_i$) and, most importantly, the first equation now incorporates the converse piezoelectric effect, which is – unsurprisingly – mediated by the transpose of the same tensor d_{ijk} that governs the direct effect.¹²

The Voigt notation can be equally applied to the compliance tensor S_{ijkl} , which inherits both the symmetry in the last two indices from the stress tensor, and that in the first two indices from the strain tensor. Therefore, its independent components are decreased from $3^4 = 81$ to a maximum of 36 in the most general case (and are further reduced in real crystals, depending on the symmetry), which allows for packing it up into a 6×6 matrix

$$S_{\alpha\beta} = \begin{bmatrix} S_{11} & S_{12} & S_{13} & S_{14} & S_{15} & S_{16} \\ S_{21} & S_{22} & S_{23} & S_{24} & S_{25} & S_{26} \\ S_{31} & S_{32} & S_{33} & S_{34} & S_{35} & S_{36} \\ S_{41} & S_{42} & S_{43} & S_{44} & S_{45} & S_{46} \\ S_{51} & S_{52} & S_{53} & S_{54} & S_{55} & S_{56} \\ S_{61} & S_{62} & S_{63} & S_{64} & S_{65} & S_{66} \end{bmatrix} \quad (3.8)$$

Accordingly, Eqns. 3.7 are rewritten in Voigt notation as

$$\begin{cases} \eta_\alpha = S_{\alpha\beta}\sigma_\beta + d_{\alpha\beta}^T\mathcal{E}_\beta \\ D_\alpha = d_{\alpha\beta}\sigma_\beta + \varepsilon_{\alpha\beta}\mathcal{E}_\beta \end{cases} \quad (3.9)$$

(with the caveat that indices α and β span different ranges depending on the tensor).

¹²The transpose here is meant as $d_{ijk}^T = d_{kji} = d_{kij}$ (the last passage follows from the stress-induced symmetry in the last two indices, as discussed above).

3.3.3 Relating tensors $d_{\alpha\beta}$ and $e_{\alpha\beta}$

From Eqns. 3.5, 3.7 and 3.9, it is clear that

$$d_{ijk} = \left. \frac{\partial D_i}{\partial \sigma_{jk}} \right|_{\mathbf{E}=0} = \frac{\partial P_i}{\partial \sigma_{jk}} \quad (3.10)$$

or equivalently, in Voigt notation

$$d_{\alpha\beta} = \left. \frac{\partial D_\alpha}{\partial \sigma_\beta} \right|_{\mathbf{E}=0} = \frac{\partial P_\alpha}{\partial \sigma_\beta} \quad (3.11)$$

It is convenient to also be able to express $d_{\alpha\beta}$ in terms of strain, rather than stress. To this end, we introduce another piezoelectric tensor $e_{\alpha\beta}$, such that

$$e_{\alpha\beta} := \left. \frac{\partial D_\alpha}{\partial \eta_\beta} \right|_{\mathbf{E}=0} = \frac{\partial P_\alpha}{\partial \eta_\beta} \quad (3.12)$$

The two tensors $d_{\alpha\beta}$ and $e_{\alpha\beta}$ are related as follows: defining the *elastic stiffness* as the inverse of the compliance

$$C_{\alpha\beta} := (S^{-1})_{\alpha\beta} \quad (3.13)$$

one has, setting the electric field to zero for simplicity,

$$P_\alpha = d_{\alpha\beta} \sigma_\beta = d_{\alpha\beta} (S^{-1})_{\beta\gamma} \eta_\gamma = d_{\alpha\beta} C_{\beta\gamma} \eta_\gamma = e_{\alpha\gamma} \eta_\gamma \quad (3.14)$$

whence

$$\boxed{e_{\alpha\gamma} = d_{\alpha\beta} C_{\beta\gamma} = d_{\alpha\beta} (S^{-1})_{\beta\gamma}} \quad (3.15)$$

and of course also

$$\boxed{d_{\alpha\beta} = e_{\alpha\gamma} S_{\gamma\beta} = e_{\alpha\gamma} (C^{-1})_{\gamma\beta}} \quad (3.16)$$

3.3.4 Symmetry and sign clarifications

At this point, it is useful to leap into a concrete physical scenario. To begin with, although we have described from the outset that direct piezoelectricity relates a change in polarisation to a mechanical stress, we have not yet specified the sign convention that links compressive and tensile stresses to increases or decreases in polarisation. We follow here the standard (though not unique) convention that tensile stresses are positive and compressive stresses are negative [322]. In the vast majority of cases, a tensile stress increases the separation between charge centres and therefore enhances the polarisation, whereas a compressive stress reduces it. Considering a simple example along $\hat{z}$, both phenomena are consistent with Eqn. 3.1 provided that $d_{33} > 0$.

Clarified this, we now develop some considerations on the behaviour of the piezoelectric tensor under spatial inversion $\mathbf{r} \rightarrow -\mathbf{r}$. This operation reverses the sign of the polarisation

vector P_α but leaves the stress tensor σ_β unchanged, since it does not alter the physical act of stretching or compressing the crystal. Eqn. 3.5 therefore implies that the piezoelectric tensor elements $d_{\alpha\beta}$ must change sign as well, independently of the crystal symmetry.

This observation immediately explains in a rigorous way why there can be no centrosymmetric material displaying piezoelectricity. A centrosymmetric crystal is invariant under inversion: therefore, all material tensors must be left unchanged under such operation.¹³ But since inversion implies $d_{\alpha\beta} = -d_{\alpha\beta}$, the only possibility of reconciling both requirements is that $d_{\alpha\beta}$ vanish identically.

Turning now to non-centrosymmetric crystals, we seize the chance to raise a subtle yet important point, concerning the sign of individual tensor elements. For simplicity, let us take the $\hat{z}$ -axis version of Eqn. 3.5, namely

$$\Delta P_3 = d_{33}\sigma_3 \quad (3.17)$$

(the crystal might already possess a spontaneous polarisation; this way, only the piezoelectric contribution is isolated) and assume $d_{33} > 0$. This is interpreted as follows: a positive (tensile) stress along $\hat{z}$ induces a $\Delta P_3 > 0$ along $+\hat{z}$, a negative (compressive) stress decreases the magnitude of the polarisation ($\Delta P_3 < 0$) which, however, still points towards $+\hat{z}$. Now consider the effect of spatial inversion: σ_3 is left unchanged, but ΔP_3 is reversed and so is d_{33} . Physically, this corresponds to turning the crystal upside down, reversing its polar axis. But, importantly, this operation must not alter the underlying physics: the induced polarisation must now be interpreted as pointing along $-\hat{z}$, consistently with the new polar direction. The point then is: does the sign of d_{33} – and, by extension, of any individual tensor component $d_{\alpha\beta}$ – have an intrinsic physical meaning at all, within our theoretical perspective?¹⁴

The answer is subtle and is: *no, as long as only one tensor element at a time is considered; what does carry physical meaning is the full tensor or, in other words, the whole set of independent components, along with their relative signs.* For instance, suppose that in a tetragonal crystal one has $d_{33} > 0$ and $d_{31} < 0$ – as is, in fact, not uncommon. Physically, this means that a positive (tensile) stress σ_β induces an increase in P_3 if applied along $\hat{z}$, and a decrease in P_3 if applied along the transversal direction $\hat{x}$. Both coefficients reverse sign simultaneously under inversion; however, since their relative signs remain opposite, the observable physical response is left unchanged.¹⁵

¹³By *material tensors* one generally refers to tensors that describe a response of the crystal to some external stimuli. Since they reflect intrinsic crystalline properties, material tensors must be invariant under the symmetry operations of the crystal's point group. In contrast, “external” tensors such as stress or strain, that transform as ordinary tensors under symmetry operations and need not remain invariant, are termed *field tensors*.

¹⁴We strictly refer herein to a computational scenario; experimentally, the sign of piezoelectric coefficients is determined by the direction of the induced electrical current or voltage relative to the electrodes, which is fixed by the measurement setup.

¹⁵In this regard, some materials – including PVDF [323] and hafnia [228] – are known to display *negative piezoelectricity*: they undergo a decrease in polarisation when stretched, and contract under an external electric field. The physics here is intrinsically different, and not at all dictated by mathematical artifacts. To the best of our knowledge, however, this phenomenon has so far never been reported in simple ABO_3 perovskites under standard conditions, and we will safely neglect it in the following.

3.3.5 Implementation in VASP

To evaluate the (zero-temperature) piezoelectric tensor $d_{\alpha\beta}$ within VASP, a simple and efficient procedure can be adopted, based on linear-response theory. We highlight this is a post-processing strategy, to be performed once the material has been structurally optimised. In this framework, one

1. instructs VASP to directly compute the piezoelectric tensor $e_{\alpha\beta}$ and the elastic stiffness tensor $C_{\alpha\beta}$;
2. inverts (separately) $C_{\alpha\beta}$, which yields the compliance $S_{\alpha\beta}$;
3. retrieves the desired piezoelectric tensor via $d_{\alpha\beta} = e_{\alpha\gamma} S_{\gamma\beta}$ (as per Eqn. 3.16).

The calculation of linear-response material tensors in VASP is switched on by two different Boolean flags; the one employed here is `LEPSILON`, already briefly introduced in Section 1.3. `LEPSILON` leverages Density Functional Perturbation Theory (DFPT) [25] to compute response tensors as second derivatives of the total energy, obtained from its second-order Taylor expansion

$$E = E_0 + \frac{1}{2} \sum_{ab} \frac{\partial^2 E}{\partial \lambda_a \partial \lambda_b} \lambda_a \lambda_b \quad (3.18)$$

with respect to generic perturbations λ_a (representing a component of electric field $\mathcal{E}_\alpha$, strain η_α , or atomic displacement $u_{\kappa\alpha}$, as needed).¹⁶

By default, `LEPSILON` evaluates ion-clamped responses, i.e., neglecting contributions arising from internal ionic relaxations. In this regime, the following tensors are computed:

- *Clamped-ion static dielectric tensor*

$$\bar{\epsilon}_{\alpha\beta} = \delta_{\alpha\beta} - \frac{4\pi}{\Omega} \frac{\partial^2 E}{\partial \mathcal{E}_\alpha \partial \mathcal{E}_\beta} \bigg|_{u,\eta} \quad (3.19)$$

- *Clamped-ion piezoelectric tensor*

$$\bar{e}_{\alpha\beta} = -\frac{1}{\Omega} \frac{\partial^2 E}{\partial \mathcal{E}_\alpha \partial \eta_\beta} \bigg|_u \quad (3.20)$$

- *Clamped-ion elastic stiffness tensor*

$$\bar{C}_{\alpha\beta} = \frac{1}{\Omega} \frac{\partial^2 E}{\partial \eta_\alpha \partial \eta_\beta} \bigg|_u \quad (3.21)$$

¹⁶The `LEPSILON` approach is applicable to a wide range of materials. However, it does not offer compatibility with all exchange–correlation functionals: in particular, it is presently unavailable for functionals that depend explicitly on the orbitals, such as hybrid functionals. For the record, the other related VASP flag, `LCALCEPS`, evaluates the same tensors via finite-difference response to an electric field. By contrast, this is compatible with all VASP functionals, but is restricted to systems with a finite band gap. In practice, the choice between the two approaches is largely a matter of preference, although the VASP manual mildly recommends `LEPSILON` whenever applicable.

- *Born effective charge tensor*

$$Z_{\kappa,\alpha\beta}^* = \frac{\Omega}{e} \frac{\partial P_\alpha}{\partial u_{\kappa\beta}} = - \frac{\partial^2 E}{\partial u_{\kappa\beta} \partial \mathcal{E}_\alpha} \quad (3.22)$$

- *Dynamical matrix*

$$\Phi_{\kappa\alpha,\kappa'\beta} = \frac{\partial^2 E}{\partial u_{\kappa\alpha} \partial u_{\kappa'\beta}} \quad (3.23)$$

- *Internal-strain tensor*

$$\Lambda_{\kappa,\alpha\beta} = \frac{\partial^2 E}{\partial u_{\kappa\alpha} \partial \eta_\beta} \quad (3.24)$$

Relaxed-ion tensors are obtained by combining `LEPSILON = .TRUE.` with a phonon-type algorithm for the `IBRION` flag, governing ion motion (e.g. `IBRION = 5-8`). In this case, VASP inverts the dynamical matrix $\Phi_{\kappa\alpha,\kappa'\beta}$ and reuses it internally to assemble the full response tensors. All of these share a common overall structure, involving contractions with Φ^{-1} . The resulting expressions are:

- *Static dielectric tensor*

$$\varepsilon_{\alpha\beta} = \bar{\varepsilon}_{\alpha\beta} + \frac{4\pi}{\Omega} \sum_{\kappa\alpha',\kappa'\beta'} Z_{\kappa,\alpha\alpha'}^* (\Phi^{-1})_{\kappa\alpha',\kappa'\beta'} Z_{\kappa',\beta\beta'}^* \quad (3.25)$$

- *Elastic stiffness tensor*¹⁷

$$C_{\alpha\beta} = \bar{C}_{\alpha\beta} - \frac{1}{\Omega} \sum_{\kappa\alpha',\kappa'\beta'} \Lambda_{\kappa,\alpha'\alpha} (\Phi^{-1})_{\kappa\alpha',\kappa'\beta'} \Lambda_{\kappa',\beta'\beta} \quad (3.26)$$

- *Piezoelectric tensor*

$$e_{\alpha\beta} = \bar{e}_{\alpha\beta} + \frac{1}{\Omega} \sum_{\kappa\alpha',\kappa'\beta'} Z_{\kappa,\alpha\alpha'}^* (\Phi^{-1})_{\kappa\alpha',\kappa'\beta'} \Lambda_{\kappa',\beta'\beta} \quad (3.27)$$

DFPT calculations are performed with a set of computational parameters similar to those used in standard self-consistent and structural relaxation runs. It is common practice, however, to tighten the self-consistency convergence threshold, for instance, from the typical 10^{-6} eV to 10^{-8} eV. In our experience, this stricter criterion affects tensor components only marginally, and since our focus is not on ultimate numerical precision, we adopt the 10^{-6} eV threshold throughout. It should be noted, however, that occasionally - particularly for high-energy or unstable phases - shear components prove highly sensitive to this parameter, and do not exhibit clear convergence trends upon further tightening. Consequently, large shear values reported below should be regarded as reliable only in a qualitative fashion.

¹⁷VASP returns the total stiffness tensor, together with its decomposition into ion-clamped and relaxed-ion contributions; however, for the piezoelectric tensor, it reports only the two contributions separately, which must then be summed *a posteriori*.

3.4 The SQS method

To model a random alloy such as KNN within DFT, one needs an appropriate strategy to account for its intrinsic chemical disorder.

Among the approaches devised over time to address this problem, some are able to operate within the primitive unit cell and are thus more computationally efficient. One such method is the Virtual Crystal Approximation (VCA) [324], in which the atoms of the alloy – or, more precisely, those belonging to the sublattice affected by chemical disorder – are replaced by fictitious, virtual atoms. The corresponding pseudopotentials are constructed as linear combinations of those of the actual atomic species, weighted according to the alloy stoichiometry. For the purposes of the present study, however, VCA presents significant limitations. By construction, its averaging framework neglects local atomic relaxations, to which piezoelectric properties are particularly sensitive. Furthermore, the automatic mixing of pseudopotentials is claimed to potentially give rise to unphysical extra bound states, termed ghost states, that affect the correctness of orbital occupancies and thus the reliability of predictions [325].¹⁸

A conceptually different approach consists in adopting a supercell, large enough to accommodate a suitable number of atoms of each species involved in the disorder, so as to reproduce the desired stoichiometry. Still, the challenge remains of how to actually distribute the different atomic species over the available disordered lattice sites. Intuitively, this choice could be made in a completely random manner. But there exists a more physically grounded tool: the theory of Special Quasirandom Structures (SQS) [326]. The central idea behind the SQS method is to reproduce the properties of a truly $A_{1-x}B_x$ random alloy by arranging A and B atoms in such a way that the most relevant radial correlation functions match those of an ideal random alloy, as much as possible. The method has already seen applications to perovskite oxides (including KNN) over the years and has been found to reproduce many of their properties of interest with reasonable accuracy [319, 327–334]. In the following, the essentials of the SQS approach are outlined.¹⁹

Let's start from recalling the nearest-neighbour Ising model, in the form

$$H = C_0 - \mu h \sum_i s_i + \sum_{\langle ij \rangle} J_{ij} s_i s_j \quad (3.28)$$

(where h is the external magnetic field, μ a suitable coupling constant to adjust physical dimensions and C_0 an arbitrary reference energy).

Although formulated for a spin system, the Ising Hamiltonian can actually describe a variety of physical problems,²⁰ whose fundamental degree of freedom consists in different occupations of a fixed lattice. Binary alloys $A_{1-x}B_x$ make no exception, provided H is recast in a form such as

¹⁸The VASP implementation of VCA has indeed been reported to occasionally yield unreliable results and is therefore discouraged in the official code documentation (see <https://vasp.at/wiki/VCA>).

¹⁹We follow here the pedagogical approach given in <https://indico.ictp.it/event/a12198/session/59/contribution/38/material/0>.

²⁰And, as it happens, not limited to physics: see, e.g., [335, 336].

$$H = J_0 + J_1 \sum_i \sigma_i + J_{21} \sum_{\langle ij \rangle} \sigma_i \sigma_j \quad (3.29)$$

where $\sigma_k = \pm 1$ if site k is occupied by an atom of the A or B species, respectively, and the subscripts in the J_{21} constant are meant to indicate a pair (2) of lattice sites of the shortest (1) type – namely, nearest-neighbours.

In Eqn. 3.29, the constant offset J_0 represents the average lattice energy. The second, one-body term counts the overall number of atoms A and B on the lattice (accounting for the generally different total energies of the two species) and is fixed by the alloy composition. Finally, the two-body term governs the preferred local arrangement of the lattice, compatibly with the composition: $J_{21} < 0$ promotes a “ferromagnetic”, cluster-like ordering where atoms A (B, respectively) are preferentially surrounded by A-type (B-type, respectively) nearest-neighbours, whereas $J_{21} > 0$ favours an “antiferromagnetic” pattern of unlike nearest-neighbour pairs.

In principle, considering that H has three free parameters to be determined, one could extract the first-principles energy for as many distinct spin-like configurations – for instance, $\sigma_i = 1 \forall i$ (A endpoint), $\sigma_i = -1 \forall i$ (B endpoint) and some intermediate mixture – and solve the system for the set $\{J_0, J_1, J_{21}\}$. It is easy to realise, though, that there is no reason that justifies adopting such an overly simplistic form for H .

The step forward consists then in generalising the Ising model beyond pair interactions – namely, taking into account atomic clusters, or *figures*, $f_{k,m}$ of order k (triplets, quadruplets and so forth) within a m -th neighbour distance.²¹ An example of possible figures in a BCC lattice is given in Fig. 3.6 below.

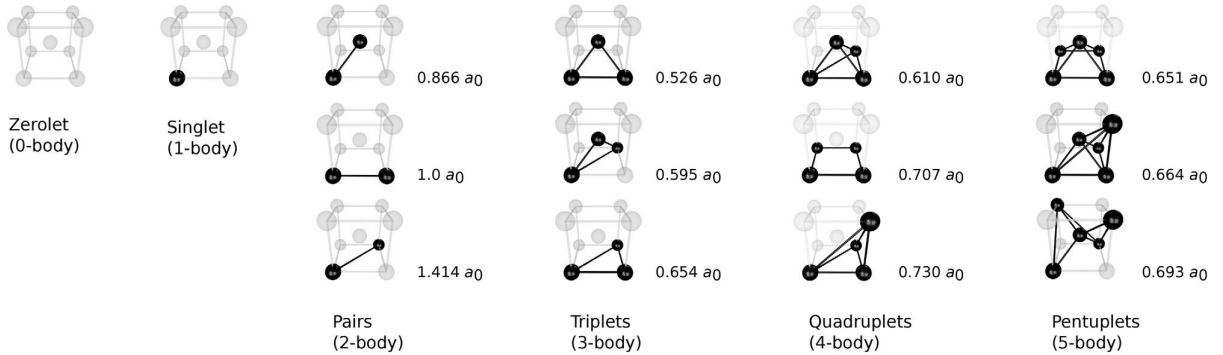


Figure 3.6: Illustration of clusters on a BCC lattice. The clusters are ordered by radius from top to bottom, with the size given in units of the lattice constant a_0 . The cluster radius is defined as the average distance of the sites to the centre of the cluster. Adapted from Fig. 2 in Ref. [337].

Each $f_{k,m}$, centred at lattice site i , will contribute to H with a term involving a product $\Pi_{k,m}(i, \sigma)$ of k spin-like variables, where $\sigma = \{\sigma_\mu\}_{\mu=1\dots k}$ is the *configuration* generated by the arrangement of A and B atoms within the figure, and thus by the corresponding collection of spin-like variables.

²¹For instance, a pair of nearest-neighbours form a figure $f_{2,1}$ – which incidentally explains the choice of subscripts for the parameter J_{21} above.

We introduce now the lattice average of the spin product

$$\bar{\Pi}_{k,m}(\sigma) = \frac{1}{MD_{k,m}} \sum_i \Pi_{k,m}(i, \sigma) \quad (3.30)$$

where the normalisation prefactors $D_{k,m}$ (the multiplicity of $f_{k,m}$) and M (the number of lattice cells) account for rotational and translational symmetry, respectively. These $\bar{\Pi}_{k,m}(\sigma)$ play the role of k -body correlation functions.

With the shortening $\alpha = (k, m)$, we can now write the energy (per unit cell) as

$$E = E(\sigma) = \sum_{\alpha} J_{\alpha} \bar{\Pi}_{\alpha}(\sigma) \quad (3.31)$$

This mapping, called a *cluster expansion* [338, 339], is exact as long as any figure f_{α} is included (in practice, of course, this expression must be truncated, considering that M does not need to be finite and, consequently, neither does α). The power of the cluster expansion approach consists in the fact that, equipped with a model having N free parameters J_{α} – termed *effective cluster interactions (ECI)* – one can evaluate the DFT energy for as many distinct configurations, map them to the model 3.31 and solve the resulting system of N equations for the J_{α} .²² These can then be employed to predict the energy of any other configuration (not among the previous N) at a glance, without further DFT calculations. The challenge then reduces to determining where to truncate the expansion, in order to retain as few figures as possible while still maintaining the approximation accurate.

Our goal here, however, is different. We aim at obtaining SQS as a byproduct of the cluster expansion formalism, without pushing the procedure to the point of extracting a set of J_{α} : we just need to build special structures whose correlation functions – as defined above – resemble those of a perfect binary alloy. We present here the details of the procedure as in the software ICET (Integrated Cluster Expansion Toolkit), which we have adopted for SQS generation [337].

To start with, a methodological clarification is in order. In the original implementation (Eqn. 3.31), lattice averages $\bar{\Pi}_{\alpha}(\sigma)$ are directly employed as basis functions. ICET introduces an additional layer of M orthogonal point functions

$$\Theta_n(\sigma_i) = \begin{cases} 1 & n = 0 \\ -\cos(\pi(n+1)\sigma_i/M) & n \text{ odd} \\ -\sin(\pi n\sigma_i/M) & n \text{ even} \end{cases} \quad (3.32)$$

for each lattice site i , where M is the allowed number of species and n runs from 0 to $M - 1$. These point functions can be proven to form an orthogonal set over all possible

²²In practice, one rarely employs as many configurations as the number of ECIs, if the latter is large, and the system often turns out underdetermined, preventing exact inversion. A variety of regression techniques are however available for the task (see Ref. [337]).

occupation numbers [340]. The products Π_α no longer involve spin-like variables directly, but rather the above point functions:

$$\Pi_\alpha(\sigma) = \Theta_{n_1}(\sigma_1)\Theta_{n_2}(\sigma_2)\dots\Theta_{n_l}(\sigma_l) \quad (3.33)$$

With this amendment, basis functions are obtained via a lattice average as in Eqn. 3.30 and the expansion as in Eqn. 3.31 is retrieved.

The first step of the cluster expansion procedure involves creating a *cluster space*. This consists in a prototype structure, the details of the species allowed on each site (with of course the possibility to treat ordered and disordered sublattices separately), the set of figures to be included and a numerical cutoff radius for each figure, as a threshold for its space extension.²³ Cutoffs can be chosen on the basis of physical intuition and/or to match a desired quantity of ECIs, with O(10) being normally sufficient.²⁴

Once the user has specified the size of the desired supercell, ICET is then able to generate the SQS via the simulated annealing technique with Monte Carlo trial swaps [341], gradually minimising the difference between the *cluster vector* $\mathbf{\Pi} = \{\bar{\Pi}_\alpha\}$ of the SQS and that of the ideal random alloy.

The question remains of how to evaluate the quality of the obtained SQS, for which there is no unique measure. ICET adopts internally the objective function proposed in [342]:

$$Q = -\omega L + \sum_{\alpha} \left[\bar{\Pi}_\alpha(\sigma) - \bar{\Pi}_\alpha^{target}(\sigma) \right] \quad (3.34)$$

where ω is the radius (in Ångström) of the largest pair cluster such that all clusters with the same or smaller radii satisfy $\bar{\Pi}_\alpha(\sigma) = \bar{\Pi}_\alpha^{target}(\sigma)$; the parameter L , set to 1 by default, can be modified by the user.

An alternative metric may be a root-mean-square (RMS, i.e., a normalised ℓ^2 -norm) of the cluster vector

$$|\Delta\mathbf{\Pi}|_{\ell^2} = \sqrt{\sum_{\alpha} \frac{1}{N} \left[\bar{\Pi}_\alpha(\sigma) - \bar{\Pi}_\alpha^{target}(\sigma) \right]^2} \quad (3.35)$$

which has the benefit of not scaling with the number N of ECIs, thus allowing for comparisons between structures with cluster vectors of different size. To stress pair correlations, this can be reduced to a pair-RMS

$$|\Delta\mathbf{\Pi}|_{\ell^2}^{pairs} = \sqrt{\sum_{\alpha \in pairs} \frac{1}{N_{pairs}} \left[\bar{\Pi}_\alpha(\sigma) - \bar{\Pi}_\alpha^{target}(\sigma) \right]^2} \quad (3.36)$$

²³Zerolet and singlet are included by construction in any cluster expansion.

²⁴See https://icet.materialsmodeling.org/advanced_topics/sqs_generation.html.

3.5 Segregation into Na-rich and K-rich clusters

We start by dealing with the observed KNN segregation into Na-rich clusters. Despite having attracted some moderate interest from experimental groups [2], this phenomenon has so far never been addressed within a first-principles approach, to the best of our knowledge.

In the chosen experimental framework, KNN films are grown on 8" wafers with an industrial RF sputtering in Ar atmosphere, from a stoichiometric $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ target. Annealing in a $\text{N}_2 + \text{O}_2$ atmosphere at high temperature promotes a partial crystallisation of the initially amorphous films, resulting in (100/001) preferential orientation and in ferroelectric behaviour, superimposed to a leaky dielectric characteristic.

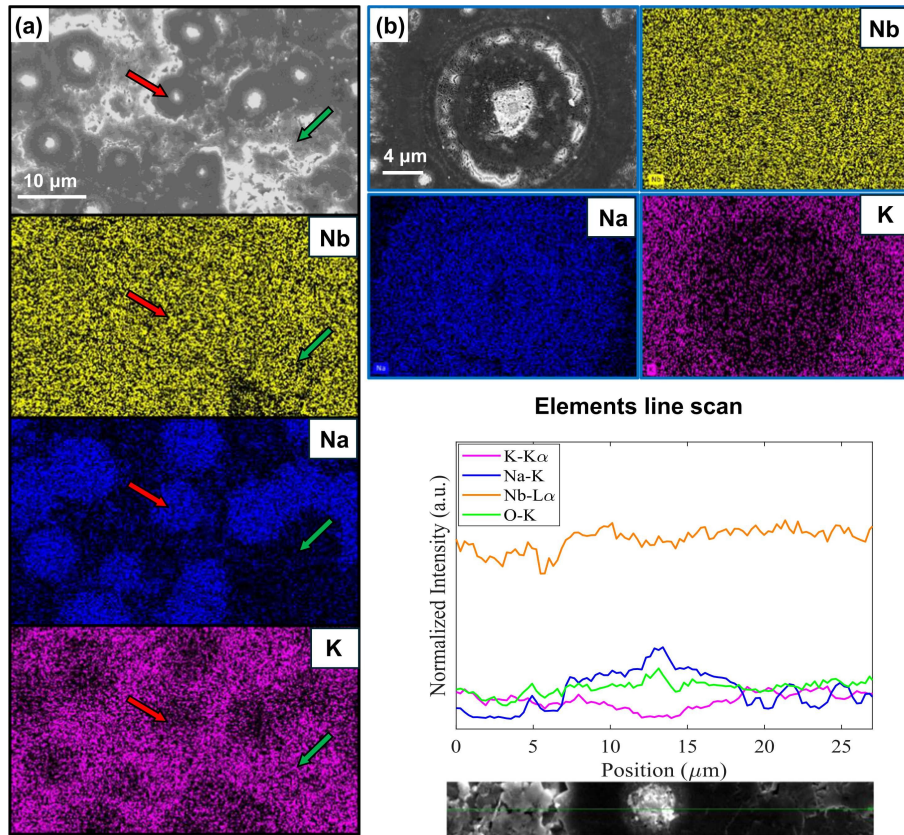


Figure 3.7: (a) Elemental EDX (Energy-Dispersive X-ray Spectroscopy) maps of Na, K and Nb of a large area of a sample grown at low Ar pressure and annealed at 700 °C. The red arrow is pointing to the same Na-rich region in every image, the green one at an alkali deficient region. (b) Top: EDX line scan of K, Na, Nb of a Na-rich region and surrounding regions; bottom: elemental maps of Na, K and Nb for a single Na-rich feature. Adapted from Fig. 9 in Ref. [2].

On average, all films are characterised by a deficiency of alkali ions, with a $(\text{K}+\text{Na})/\text{Nb}$ ratio around 0.8. Potassium tends to evaporate at high annealing temperatures, while sodium follows an opposite trend. In particular, as sketched in Fig. 3.7, the nucleation of a segregated Na-rich $\text{K}_{1-x}\text{Na}_x\text{NbO}_3$ perovskite phase ($0.7 < x_{\text{Na}} < 0.8$) is observed,

together with an unwanted pyrochlore phase with a composition close to $A_4\text{Nb}_6\text{O}_{17}$ (where $A = \text{K}+\text{Na}$). The composition of the Na-rich perovskite phase is close to the two MPBs with $x_{\text{Na}} \simeq 0.65$ and $x_{\text{Na}} \simeq 0.8$, that are relatively less reported in literature [298, 343, 344]. The ferroelectric response of the films is given, as expected, by the Na-rich perovskite domains, while the pyrochlore regions display a leaky dielectric behaviour.²⁵

We performed DFT simulations with the aim of providing theoretical support to the observed segregation, by means of total energy comparisons.

As a common simulation framework, we adopted a $3 \times 3 \times 2$ multiple of a 5-atom tetragonal perovskite unit cell – in other words, a 90-atom supercell, 18 of which form the A-site sublattice by construction. We realised *disordered* KNN systems at different Na concentrations $x_{\text{Na}} = N_{\text{Na}}/18$ by tuning the number of Na and K atoms on the A sublattice, under the constraint $N_{\text{Na}} + N_{\text{K}} = 18$, spanning compositions from the equimolar case ($N_{\text{K}} = N_{\text{Na}} = 9$) to the fully segregated limits ($N_{\text{K}} = 18$ or $N_{\text{Na}} = 18$).

As in the previous chapter, DFT simulations were performed using the PBEsol exchange-correlation functional [69]. Projector-augmented wave (PAW) [81] pseudopotentials were used, with the following valence states: K $3s, 3p, 4s$; Na $2s, 2p, 3s$; Nb $4p, 5s, 4d$; O $2s, 2p$. In all cases, the kinetic energy cutoff was set to 800 eV and the Brillouin zone was sampled with a $3 \times 3 \times 4$ $\mathbf{k}$ -point mesh (which would correspond to a $9 \times 9 \times 8$ mesh for the 5-atom tetragonal unit cell).²⁶ The initial lattice parameters were initialised according to the Vegard law as a linear interpolation between the (suitably multiplied) equilibrium values of KNbO_3 and those of NaNbO_3 , as obtained in separate simulations for their tetragonal unit cells (KNbO_3 : $a = 3.973$ Å, $c = 4.053$ Å; NaNbO_3 : $a = 3.918$ Å, $c = 4.021$ Å). All systems were then fully optimised to their own equilibrium structure. Energy convergence thresholds were set to 10^{-6} and 10^{-4} eV concerning electronic and structural optimisation, respectively, yielding residual forces below 0.03 eV/Å. The cluster expansion, common to all KNN systems, was constructed with cutoffs of 13 Å for doublets and 8.5 Å for triplets, yielding a total of 39 (non-trivial) ECIs and a pair-RMS around 0.3 across all structures.

To probe the energetic stability of the equimolar alloy with respect to composition fluctuations, we first introduce the quantity

$$\Delta E(x_{\text{Na}}) = \frac{E(x_{\text{Na}}) + E(1 - x_{\text{Na}})}{2} - E(0.5) \quad (3.37)$$

Here, for each structure at concentration $x_{\text{Na}} > 0.5$ we explored the $x_{\text{Na}} < 0.5$ range by constructing its mirror image, in which the Na and K atoms are interchanged within the same SQS pattern.²⁷ For a given x_{Na} , $\Delta E(x_{\text{Na}})$ is thus the average of the total energies of two “compositionally imbalanced” structures, referenced to $E(0.5) = E_{\text{Na}=9, \text{K}=9}$, i.e., the energy of the equimolar configuration (which by construction needs no mirror image).

²⁵The reader is referred to our publication [2] for further details.

²⁶Such a high energy cutoff was deemed necessary in separate simulations for a set of representative NaNbO_3 phases, in order to converge energy differences to within $\simeq 1$ meV.

²⁷Different SQS structures were necessarily generated for systems with different compositions $x_{\text{Na}} > 0.5$. However, the fact that each of these and its mirror image share the same SQS arrangement evens out biases associated with configurational randomness when comparing the energies.

Physically, what $\Delta E(x_{\text{Na}})$ measures is whether the equimolar system prefers to remain compositionally uniform or to decompose into regions of unequal composition – while conserving the overall Na and K contents – and quantifies the energetic preference for a given imbalance $x_{\text{Na}} > 0.5$. We stress that this approach does probe segregation to a fair extent, even though explicit clusters are never constructed: in fact, strongly imbalanced disordered (SQS) configurations effectively act as proxies for clustered regions.

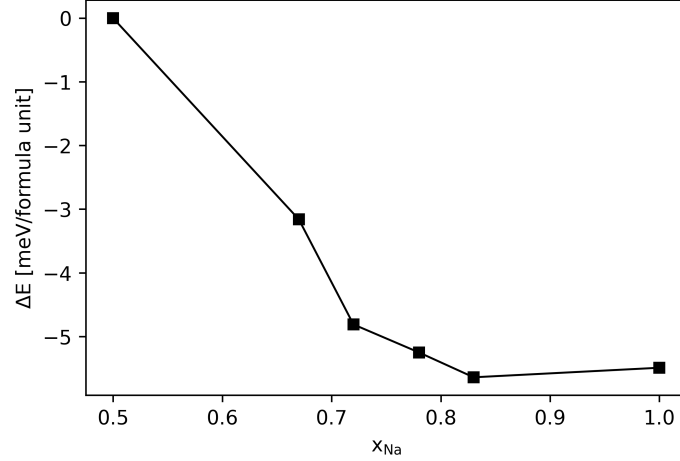


Figure 3.8: $\Delta E(x_{\text{Na}})$ [meV], normalised per 5-atom formula unit.

We examined the behaviour of $\Delta E(x_{\text{Na}})$ between $x_{\text{Na}} = 0.5$ (equimolar case) and $x_{\text{Na}} = 1$ (fully segregated limit) together with four in-between compositions $x_{\text{Na}} = 0.67, 0.72, 0.78, 0.83$.²⁸ As shown in Fig. 3.8, ΔE is negative throughout the entire range, indicating that the equimolar KNN system is unstable with respect to composition fluctuations of any extent. Furthermore, the presence of a minimum – although broad and shallow – in the intermediate regime, namely at $x_{\text{Na}} = 0.83$, suggests that the energetically preferred segregation is not complete, i.e., not into pure KNbO_3 and NaNbO_3 , but rather partial, albeit strongly asymmetric. This picture is consistent with the experimental data, showing segregation into Na-rich regions with composition $0.7 < x_{\text{Na}} < 0.8$ (and, accordingly, into K-rich regions as well, with $0.2 < x_{\text{Na}} < 0.3$).

A complementary perspective on stability and segregation tendencies is provided by the mixing enthalpy

$$E_{\text{mix}}(x_{\text{Na}}) = E(x_{\text{Na}}) - [(1 - x_{\text{Na}})E(0) + x_{\text{Na}}E(1)] \quad (3.38)$$

which instead does not focus on the equimolar case, but rather compares a homogeneous alloy at any given composition x_{Na} to a macroscopic mixture of pure KNbO_3 and pure NaNbO_3 , by quantifying the deviation of the alloy energy from a linear interpolation

²⁸Compositions $x_{\text{Na}} < 0.5$ are implicitly included due to the mirror image construction strategy. Accordingly, by inspecting Eqn. 3.37, ΔE is clearly symmetric under the operation $x_{\text{Na}} \rightarrow 1 - x_{\text{Na}}$ (the full plot in Fig. 3.8 would be equally symmetric around $x_{\text{Na}} = 0.5$).

between the energies of the end members. In this case, we can – in principle – scan the whole composition range, since the energies of any composition $E(x_{\text{Na}})$ now appears independently in the expression of E_{mix} (whereas, in ΔE , $E(x_{\text{Na}})$ and $E(1 - x_{\text{Na}})$ were always coupled and never appearing stand-alone).

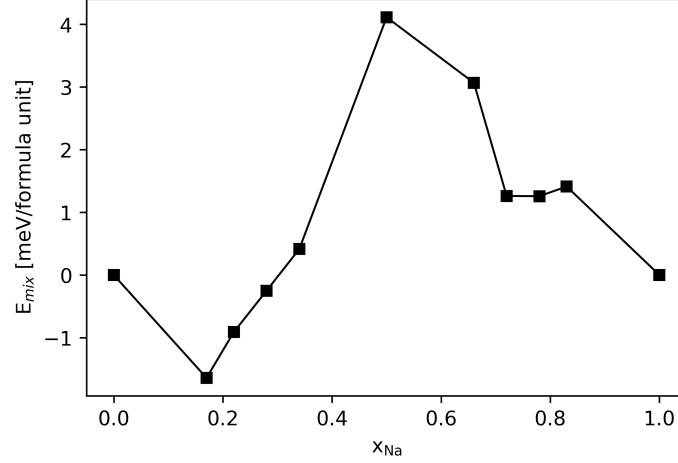


Figure 3.9: Mixing enthalpy E_{mix} [meV], normalised per 5-atom formula unit.

As shown in Fig. 3.9, E_{mix} is positive in the range $0.33 < x_{\text{Na}} < 1$, showing a wide composition interval in which the alloy is unstable with respect to phase separation into the pure end members. A narrower window with slightly negative E_{mix} is observed on the K-rich side ($0 < x_{\text{Na}} < 0.33$); however, the associated energy gain is very small, and the corresponding structures are not fully independent, since their SQS configurations are constrained to mirror their Na-rich counterparts. As a consequence, the quantitative reliability of E_{mix} in the $x_{\text{Na}} < 0.5$ regime should be interpreted with caution.

Taken together, therefore, the two metrics convey a consistent message: E_{mix} indicates an overall instability of KNN with respect to phase separation, whereas ΔE reveals that the energetically preferred decomposition is asymmetric, favouring mixing of Na-rich and K-rich regions rather than complete separation into pure end members. The quantitative agreement of this picture with the experimental scenario warrants further assessment, as the present structural modelling is deliberately idealised. We however emphasise that the aim of this section was not to necessarily reproduce experimental observations in full detail, but rather to isolate the energetic effects associated with A-site compositional disorder. As such, no detailed analysis of crystal symmetry – here restricted to a tetragonal phase for simplicity, which may constitute a significant structural constraint – is undertaken, nor are additional non-idealities accounted, such as the emergence of pyrochlore phases in K-rich systems, or the overall alkali deficiency with respect to Nb. Furthermore, given the small energy differences at stake, of the order of meV per formula unit (at least within the assumed tetragonal symmetry), even more realistic zero-temperature DFT models may not yield definitive conclusions. A proper description would require the inclusion of thermodynamic effects, which however exceed the scope of the present work (besides, as shown in [329], SQS are generally no longer reliable beyond some material-dependent

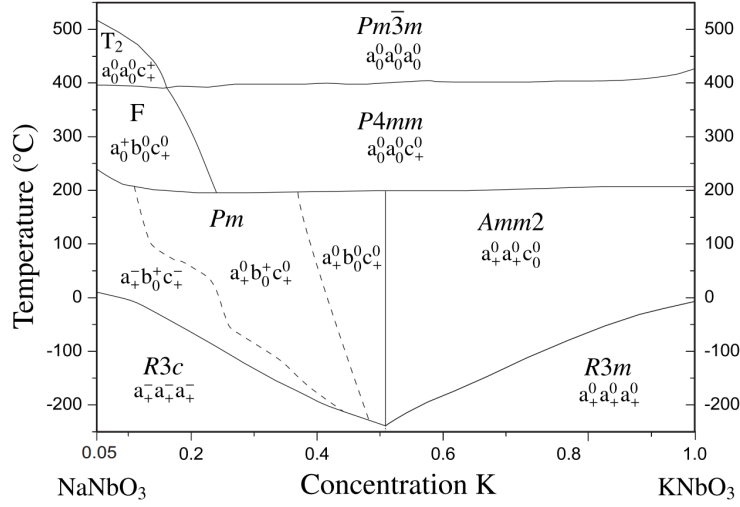


Figure 3.10: KNN phase diagram (replicated from Fig. 3.4).

temperature). In any case, our results suggest that, already at the first-principles, zero-temperature level, KNN exhibits a tendency towards partial segregation into Na-rich and K-rich regions, with energetically favoured compositions that are compatible with experimental observations.

3.6 Phase comparison for pure NaNbO_3

Having shed light on the aspect of segregation, we now set ourselves the goal of exploring, in a systematic fashion, how structural, ferroelectric and piezoelectric properties of KNN depend on the A-site concentrations, specifically considering the Na-rich half of the compositional window (also addressed by our experimental partners).

According to the literature phase diagram, reproduced again in Fig. 3.10 for convenience, KNN is expected to exhibit monoclinic symmetry (space group Pm) in this compositional range, spanning three distinct, concentration-dependent phases that differ from one another by their octahedral tilt systems. In the rest of this chapter (mostly, in the following Section 3.7), we investigate, by means of DFT simulations, one of these phases – namely, that with tilt system $a^0b^+c^0$ – assessing its compatibility with the experimental observations. We select this particular phase (hereafter, $Pm - a^0b^+c^0$) as a target because it displays a non-trivial, yet not excessively intricate, structural complexity – being sandwiched between the non-tilted $Pm - a^0b^0c^0$ and the fully-tilted $Pm - a^-b^+c^-$ – while at the same time allowing for a relatively small (10-atom) unit cell.²⁹

We begin in this section by considering $Pm - a^0b^+c^0$, together with a set of competing structures, in the simpler case of pure Na composition ($x_{\text{Na}} = 1$). This choice serves a twofold purpose. First, it allows us to validate our DFT computational setup against a

²⁹By contrast, the $a^-b^+c^-$ phase for example requires a 40-atom unit cell, which becomes computationally demanding within the supercell-based SQS framework.

well-defined reference system, that also allows for more complicated phases with larger unit cells (the additional computational complexity of the SQS formalism is obviously not needed at this stage). Second, it provides an opportunity to introduce some characteristic physical features, more easily identified in the absence of compositional disorder, with which it is useful to familiarise beforehand.

To assemble a representative set, in addition to $Pm - a^0b^+c^0$, we include the tetragonal $P4mm$, orthorhombic $Amm2$ and rhombohedral $R3c$ phases – three paradigmatic symmetries for perovskites, although the first two are not known to occur in NaNbO_3 – as well as orthorhombic $Pmc2_1$ (NaNbO_3 's phase Q) and the fully-tilted monoclinic $Pm - a^-b^+c^-$, which also has been proposed as a candidate for phase Q .³⁰ Table 3.1 summarises the essential structural information for these phases. The DFT setup is inherited for consistency from the segregation study in Section 3.5; $\mathbf{k}$ -point meshes are generated so as to be consistent with a $9 \times 9 \times 9$ for the pseudocubic 5-atom cell.

Table 3.1: Structural data for the selected NaNbO_3 phases. The $P4mm$ cell is derived from that used in Section 3.5. For the other phases, the initial structure was collected from literature sources, as detailed in the table. Lattice parameters and angles are those of the relaxed structures.

Phase	Space group	Source	N° atoms	Tilt system	a [Å]	b [Å]	c [Å]	Angle(s) $\neq 90^\circ$
Tetragonal	$P4mm$	This work	10	$a^0a^0c^0$	5.614	3.919	5.614	$\beta = 88.56^\circ$
Orthorhombic	$Amm2$	[345]	10	$a^0b^0c^0$	3.912	5.594	5.638	/
Monoclinic	Pm	[284]	10	$a^0b^+c^0$	5.535	3.920	5.522	$\beta = 89.95^\circ$
Orthorhombic	$Pmc2_1$	[346]	20	$a^+b^-c^-$	7.747	5.503	5.559	/
Monoclinic	Pm	[347]	40	$a^-b^+c^-$	7.823	7.747	7.824	$\beta = 90.58^\circ$
Rhombohedral	$R3c$	[284]	30	$a^-a^-a^-$	5.488	5.488	13.700	$\gamma = 120.00^\circ$

Fig. 3.11 illustrates the relaxed unit cells in relevant planes in terms of polar distortions and octahedral tilting. With the only exception of $R3c$, the a and c axes are oriented so that all cells share the same in-plane square-grid arrangement of Na atoms, forming the A-site sublattice. For the tetragonal structure, although the $P4mm$ symmetry is of course naturally described by a 5-atom unit cell, we have adopted a $\sqrt{2} \times 1 \times \sqrt{2}$ (10-atom) cell, which shares size and orientation with the $Amm2$ and $Pm - a^0b^+c^0$ cells, thereby facilitating direct comparison (incidentally, this choice of cell, coupled to the polar elongation, is the reason why $\beta < 90^\circ$ for $P4mm$).

$P4mm$ and $Amm2$ relax to very similar equilibrium structures, characterised by displaced Nb cations and distorted octahedra that nonetheless show no tilting, in accord with the $a^0a^0c^0$ system. Notably, the polar direction is different: along $\hat{z}$ for $P4mm$, and along the bisector of the second and fourth quadrants of the yz plane for $Amm2$.

Conversely, the two monoclinic phases and $Pmc2_1$ exhibit more complex tilting patterns. In $Pm - a^0b^+c^0$, octahedra are tilted in-phase around $\hat{y}$ only – as visible from the xz -plane view – whereas no tilting is present around the remaining axes, consistent with its tilt system. The same in-phase tilts appear in $Pm - a^-b^+c^-$, around $\hat{y}$ as well (xz -plane view), and in $Pmc2_1$, this time around $\hat{x}$ (yz -plane view). These two phases, additionally, exhibit antiphase tilts around the remaining axes.

³⁰For an overview of proposed NaNbO_3 phases, see Section 3.2.

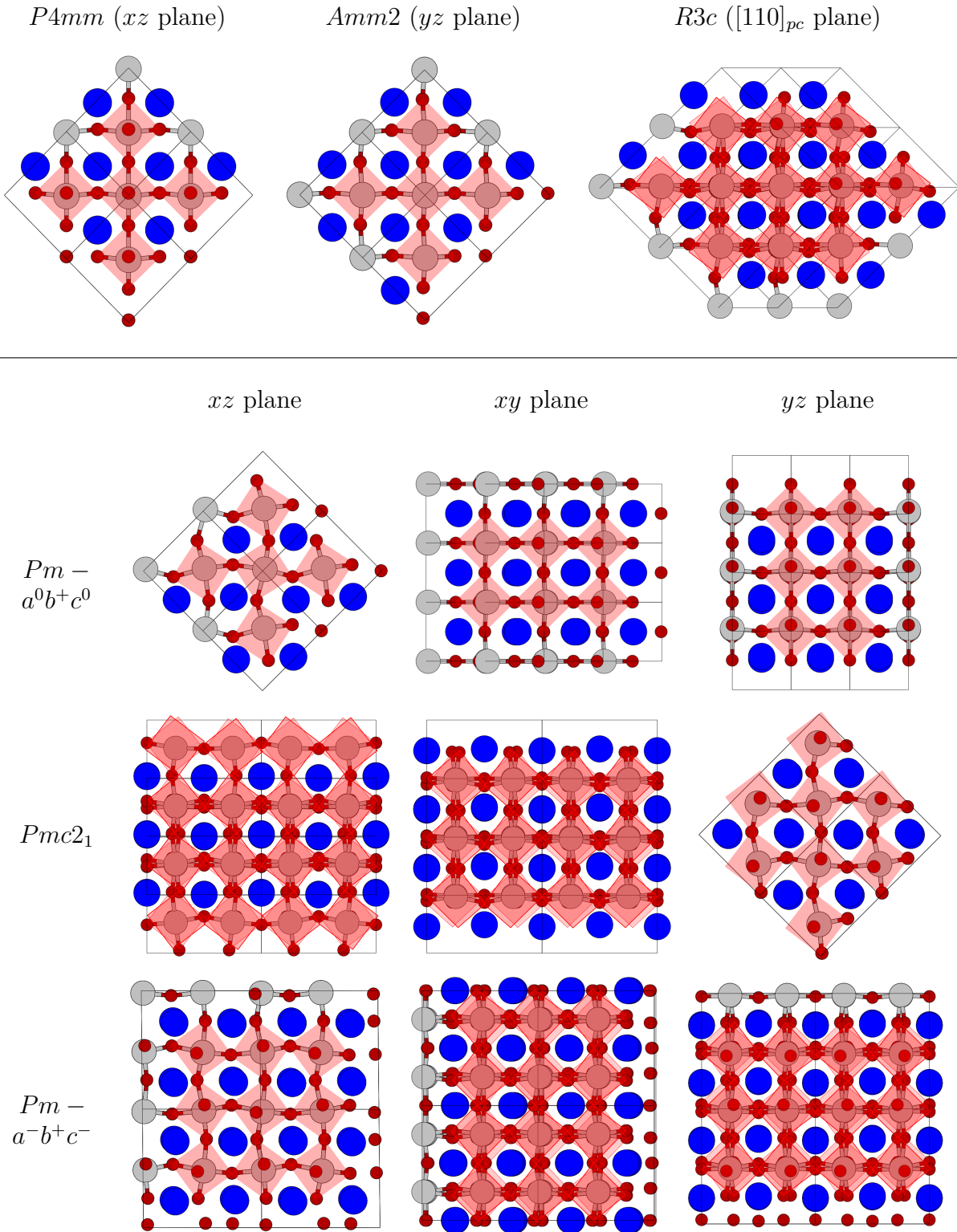


Figure 3.11: Views of the relaxed cells adopted for the structures in Table 3.1. Top block: from left to right, phases $P4mm$, $Amm2$ and $R3c$, in selected planes. Bottom block: phases $Pm - a^0b^+c^0$, $Pmc2_1$ and $Pm - a^-b^+c^-$, in all three planes xz , xy and yz . Colour code for the atomic species is as follows: Na - blue, Nb - grey, O - red. All cells have been suitably replicated in order to properly show tilting patterns of the octahedra (drawn in light red).

Table 3.2: Energy ordering and polarisation (both vector components and modulus) of the selected NaNbO_3 phases. Energies are normalised per 5-atom perovskite formula unit, and referenced to the ground state $R3c$.

Phase	Space group (tilt system)	E [meV/f.u.]	$\mathbf{P}$ [$\mu\text{C}/\text{cm}^2$]	P [$\mu\text{C}/\text{cm}^2$]
Tetragonal	$P4mm$ ($a^0a^0c^0$)	80.1	[0.00, 0.00, -40.77]	40.77
Orthorhombic	$Amm2$ ($a^0b^0c^0$)	78.1	[0.00, 29.29, -29.29]	41.42
Monoclinic	Pm ($a^0b^+c^0$)	20.6	[27.29, 0.00, 28.13]	39.19
Orthorhombic	$Pmc2_1$ ($a^+b^-c^-$)	2.5	[0.00, 25.72, -25.72]	36.37
Monoclinic	Pm ($a^-b^+c^-$)	2.4	[25.82, 0.00, -25.60]	36.36
Rhombohedral	$R3c$ ($a^-b^-c^-$)	0.0	[0.00, 0.00, 43.78]	43.78

Table 3.2 reports energy ordering and polarisation of the selected phases. Polarisation components (referred to the global Cartesian frame) are evaluated as

$$P_\alpha = \frac{e}{\Omega} \sum_{\kappa\beta} Z_{\kappa,\alpha\beta}^* u_{\kappa\beta} \quad (3.39)$$

i.e., by inverting Eqn. 3.22; atomic displacements $u_{\kappa\beta}$ are computed with respect to a centrosymmetric reference structure, obtained by symmetrising the atomic positions of the polar phase while keeping the lattice parameters fixed.

As expected, the ground state is $R3c$, but immediately above we find the two competing – and essentially isoenergetic – phases $Pm - a^-b^+c^-$ and $Pmc2_1$, which confirms the elaborate scenario of multiple low-energy structures in NaNbO_3 , discussed earlier in Section 3.2, and suggests that the distinction between orthorhombic and monoclinic is subtle – likely a matter of nomenclature, rather than a physically significant difference. The target phase $Pm - a^0b^+c^0$ lies higher in energy, although still reasonably competitive, whereas $P4mm$ and $Amm2$ are the least stable (and accordingly not observed). This picture clearly confirms octahedral tilting, increasing in complexity down the series, to be a stabilising mechanism in NaNbO_3 . Polarisation, on the other hand, varies little (around $40 \mu\text{C}/\text{cm}^2$) across the series, reaching the highest value in the $R3c$ phase, whereas the lowest is shared by $Pm - a^-b^+c^-$ and $Pmc2_1$ – a further clue of the similarity of these two phases. The order of magnitude of the computed polarisations are in line with the values reported in literature (see, again, Section 3.2 for overview and references).

Additional insights into stability can be gained from phonon calculations. Here, for computational convenience, we restrict the analysis to Γ -point modes; we are well aware, nonetheless, that an exhaustive picture would require inspecting the whole Brillouin zone. A Γ -point analysis, indeed, is sufficient to identify soft polar instabilities in systems like BaTiO_3 or KNbO_3 , dominated by cation displacements; it is, however, not certainly so when the picture involves octahedral tilting modes, that do not necessarily soften at the Γ point, and may well do so away from it [267].

In any case, the phonon analysis tells us that the four lowest-energy phases ($R3c$ to $Pm - a^0b^+c^0$) are also dynamically stable at Γ . $Amm2$ displays a single unstable mode, at $\omega^2 = -13.8 \text{ meV}$, whose eigenvector describes an in-phase tilting pattern around $\hat{y}$, as illustrated in Fig. 3.12 (left panel), which is precisely that observed in the two Pm phases

and $Pmc2_1$.³¹ $P4mm$ shows a similar soft mode ($\omega^2 = -13.5$ meV), whose pattern is reported also in Fig. 3.12 (right panel), accompanied by two modes at $\omega^2 = -7.7$ meV (not shown), that are instead polar modes along $\hat{x}$ and $\hat{y}$, i.e., the directions where spontaneous polarisation does not arise. Collectively, these results provide further confirmation of the stabilising role played by octahedral tilts, particularly those around the $\hat{y}$ axis.

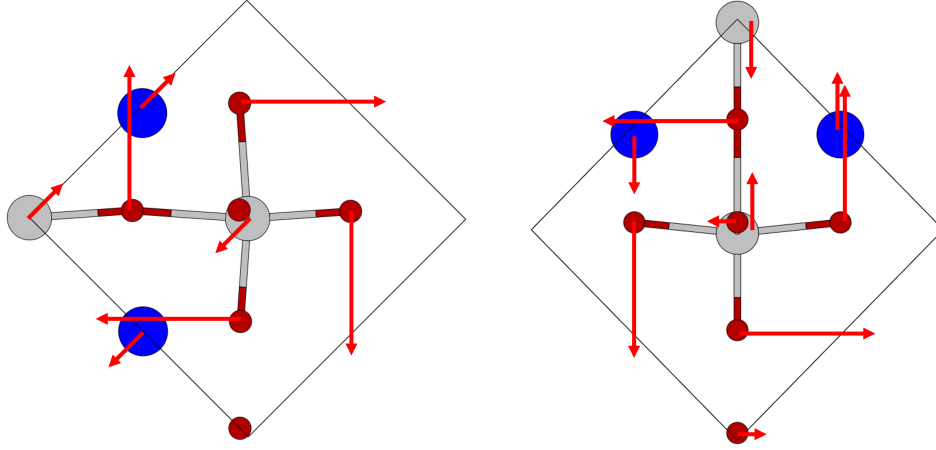


Figure 3.12: Tilting modes softening at Γ for $Amm2$ (left, yz plane) and $P4mm$ (right, xz plane). Red arrows indicate extent and direction of atomic displacements.

To conclude, we report in Fig. 3.13 the piezoelectric tensors $d_{\alpha\beta}$ and dielectric tensors ε_{ij} for all structures. We point out that, in the case of $Amm2$, $Pmc2_1$ and $Pm - a^0b^+c^0$, the tensors are not computed according to conventional settings (reported in Appendix B), because VASP defines them relative to the user’s choice of axes, and in these three cases we rotated the structures away from their standard orientations, as noted earlier. As a result, d_{33} represents here the response along the global $\hat{z}$ axis, which needs not coincide with the polar direction. For completeness, however, we also report the back-rotated tensors in the conventional setting, denoted as $d_{\alpha\beta}^{(\text{conv})}$ and $\varepsilon_{ij}^{(\text{conv})}$, respectively (details of the rotation procedure are provided in Appendix C).³²

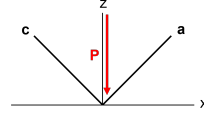
For the $P4mm$ phase, d_{33} is the leading direct piezoelectric component, consistent with expectations; its negative sign reflects the spontaneous polarisation pointing along $-\hat{z}$, as reported in Table 3.2 (see also Section 3.3 for a discussion of sign conventions). The dielectric tensor shows the largest response in the xy plane, indicating that the material is more easily polarisable away from the spontaneous polarisation direction. Unexpected asymmetries in the piezoelectric shear elements ($d_{24} \neq d_{15}$) as well as in the in-plane dielectric tensor elements ($\varepsilon_{11} \neq \varepsilon_{22}$) arise from a very tiny structural in-plane anisotropy, on the order of 10^{-4} Å.

³¹Antiphase tilting modes, requiring cells larger than the 10-atom one employed here for the phonon calculations, cannot be expected to appear.

³²Herein, “conventional setting” – in accordance with the IEEE crystallographic convention [322] – is meant in terms of polarisation direction only.

P4mm

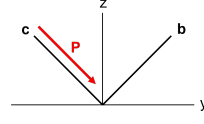
$$d_{\alpha\beta} = \begin{bmatrix} 0 & 0 & 0 & 0 & -67.6 & 0 \\ 0 & 0 & 0 & -194.7 & 0 & 0 \\ 9.9 & 10.0 & -38.7 & 0 & 0 & 0 \end{bmatrix}$$



$$\varepsilon_{ij} = \begin{bmatrix} 662.8 & 0 & 0 \\ 0 & 643.4 & 0 \\ 0 & 0 & 25.4 \end{bmatrix}$$

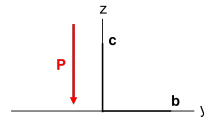
Amm2

$$d_{\alpha\beta} = \begin{bmatrix} 0 & 0 & 0 & 0 & -149.9 & 149.9 \\ -8.5 & -289.3 & 310.2 & -14.0 & 0 & 0 \\ 8.5 & -310.2 & 289.3 & 14.0 & 0 & 0 \end{bmatrix}$$



$$\varepsilon_{ij} = \begin{bmatrix} 610.8 & 0 & 0 \\ 0 & 54.0 & 22.2 \\ 0 & 22.2 & 54.0 \end{bmatrix}$$

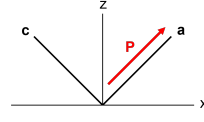
$$d_{\alpha\beta}^{(\text{conv})} = \begin{bmatrix} 0 & 0 & 0 & 0 & -211.9 & 0 \\ 0 & 0 & 0 & 847.9 & 0 & 0 \\ 12.0 & -4.8 & -24.7 & 0 & 0 & 0 \end{bmatrix}$$



$$\varepsilon_{ij}^{(\text{conv})} = \begin{bmatrix} 610.8 & 0 & 0 \\ 0 & 76.2 & 0 \\ 0 & 0 & 31.9 \end{bmatrix}$$

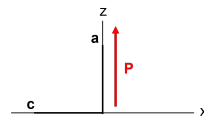
Pm - a⁰b⁺c⁰

$$d_{\alpha\beta} = \begin{bmatrix} 73.2 & -12.0 & -44.3 & 0 & 8.0 & 0 \\ 0 & 0 & 0 & 18.8 & 0 & 17.8 \\ -43.6 & -11.0 & 69.9 & 0 & 5.9 & 0 \end{bmatrix}$$



$$\varepsilon_{ij} = \begin{bmatrix} 43.6 & 0 & -8.0 \\ 0 & 217.9 & 0 \\ -8.0 & 0 & 41.3 \end{bmatrix}$$

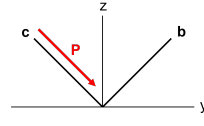
$$d_{\alpha\beta}^{(\text{conv})} = \begin{bmatrix} 0.2 & -0.7 & 1.7 & 0 & 163.4 & 0 \\ 0 & 0 & 0 & 25.9 & 0 & -0.7 \\ 14.6 & -16.3 & 24.4 & 0 & 2.8 & 0 \end{bmatrix}$$



$$\varepsilon_{ij}^{(\text{conv})} = \begin{bmatrix} 34.5 & 0 & -1.6 \\ 0 & 217.9 & 0 \\ -1.6 & 0 & 50.4 \end{bmatrix}$$

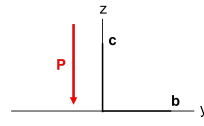
Pmc2₁

$$d_{\alpha\beta} = \begin{bmatrix} 0 & 0 & 0 & 0 & -62.3 & 62.3 \\ -6.7 & 68.1 & -42.0 & -0.9 & 0 & 0 \\ 6.7 & 42.0 & -68.1 & 0.9 & 0 & 0 \end{bmatrix}$$



$$\varepsilon_{ij} = \begin{bmatrix} 541.5 & 0 & 0 \\ 0 & 55.6 & 8.7 \\ 0 & 8.7 & 55.6 \end{bmatrix}$$

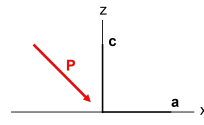
$$d_{\alpha\beta}^{(\text{conv})} = \begin{bmatrix} 0 & 0 & 0 & 0 & -88.1 & 0 \\ 0 & 0 & 0 & -155.7 & 0 & 0 \\ 9.5 & -17.8 & -19.1 & 0 & 0 & 0 \end{bmatrix}$$



$$\varepsilon_{ij}^{(\text{conv})} = \begin{bmatrix} 541.5 & 0 & 0 \\ 0 & 64.3 & 0 \\ 0 & 0 & 47.0 \end{bmatrix}$$

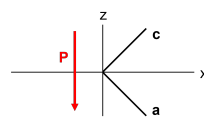
Pm - a⁻b⁺c⁻

$$d_{\alpha\beta} = \begin{bmatrix} 68.5 & -6.6 & -40.4 & 0 & 0.4 & 0 \\ 0 & 0 & 0 & -61.0 & 0 & 61.8 \\ 42.1 & 5.4 & -67.7 & 0 & 0.3 & 0 \end{bmatrix}$$



$$\varepsilon_{ij} = \begin{bmatrix} 54.2 & 0 & 8.1 \\ 0 & 530.4 & 0 \\ 8.1 & 0 & 56.6 \end{bmatrix}$$

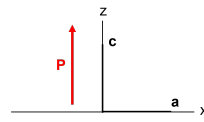
$$d_{\alpha\beta}^{(\text{conv})} = \begin{bmatrix} 1.1 & -0.9 & 0.6 & 0 & -154.7 & 0 \\ 0 & 0 & 0 & -86.8 & 0 & 0.5 \\ -19.1 & 8.5 & -19.0 & 0 & -0.6 & 0 \end{bmatrix}$$



$$\varepsilon_{ij}^{(\text{conv})} = \begin{bmatrix} 63.6 & 0 & 1.2 \\ 0 & 530.4 & 0 \\ 1.2 & 0 & 47.3 \end{bmatrix}$$

R3c

$$d_{\alpha\beta} = \begin{bmatrix} 0 & 0 & 0 & 0 & 148.0 & -86.5 \\ -43.2 & 43.2 & 0 & 148.0 & 0 & 0 \\ -0.3 & -0.3 & 15.7 & 0 & 0 & 0 \end{bmatrix}$$



$$\varepsilon_{ij} = \begin{bmatrix} 60.5 & 0 & 0 \\ 0 & 60.5 & 0 \\ 0 & 0 & 38.0 \end{bmatrix}$$

Figure 3.13: Piezoelectric [pm/V] and dielectric tensors [adim.]. Schemes of the polar planes and (approximate) polarisation direction have been added for convenience.

For the $Amm2$ phase, in the chosen rotated setting, d_{33} reaches nearly 300 pm/V. Back-rotating the tensor into the conventional setting (via a 45° rotation in the yz plane) shows that such a large d_{33} is driven by anomalously large shear components, particularly $d_{24}^{(\text{conv})}$. In the conventional setting, the direct response is to some extent reminiscent of that of $P4mm$, with which now $Amm2$ shares the polarisation direction along $-\hat{z}$. As in $P4mm$, the strongest dielectric response (in the rotated setting) is ε_{11} , away from the spontaneous polarisation plane yz ; this remains the case in the conventional setting, as the rotation is confined to the yz plane. ³³

The two monoclinic phases $Pm - a^0b^+c^0$ and $Pm - a^-b^+c^-$ share the same overall structure for the $d_{\alpha\beta}$ tensor, with close resemblance especially for elements d_{11} , d_{13} , d_{31} and d_{33} (with sign discordances again directly descending from oppositely oriented polarisation components, as per Table 3.2); by contrast, d_{24} and d_{26} are roughly three times larger in $Pm - a^-b^+c^-$. The dielectric tensors also share the same qualitative pattern, with the strongest response along $\hat{y}$, thus in ε_{22} , which is, however, significantly enhanced in $Pm - a^-b^+c^-$.

The orthorhombic $Pmc2_1$ phase is strikingly similar to $Pm - a^-b^+c^-$ – as we have repeatedly observed earlier – in both tensors, provided the polar planes of the two structures are aligned accordingly; a glance at their octahedral tilts in Fig. 3.11, together with direct inspection of their tensors, reveals that, to do so, coordinates x and y should be interchanged (a mirror operation of the type described in Appendix C, specifically with respect to the xy bisector). $Pmc2_1$ also bears some resemblance to the other orthorhombic prototype $Amm2$, although with a much reduced shear element d_{24} .

Browsing the existing literature, given the interest devoted over time to NaNbO_3 , one would expect to find several DFT studies addressing its piezoelectricity. As a matter of fact, to the best of our knowledge, there are only three such works, all very recent. Jia *et al.* [348], as part of a larger high-throughput perovskite dataset, find $d_{33} = 36.5$ pm/V and $d_{31} = -10.4$ pm/V for the tetragonal phase, in good agreement with our results in both magnitude and relative sign. Tan *et al.* [349], quoting from Liu *et al.* [350], report $d_{33} = 18.3$ pm/V, $d_{31} = -6.6$ pm/V and $d_{15} = 0.9$ pm/V for a likewise tetragonal symmetry, values smaller than ours in magnitude although with a similar d_{33}/d_{31} ratio. Alvarenga *et al.* [273] provide the only systematic analysis of NaNbO_3 piezoelectricity available to date, across phases of symmetry Pm , $Pmc2_1$ and $R3c$. Their results, reproduced in Table 3.3, agree well with ours once appropriate adjustments for different crystal settings are applied.

Table 3.3: Piezoelectric tensor components from Ref. [273] by Alvarenga *et al.* [pm/V].

Space group	d_{11}	d_{12}	d_{13}	d_{15}	d_{24}	d_{26}	d_{31}	d_{32}	d_{33}	d_{35}
Pm	0.65	0.01	1.02	136.91	73.66	0.51	15.28	-8.74	23.47	0.08
$Pmc2_1$	0.00	0.00	0.00	-76.77	-136.34	0.00	8.87	-15.36	-23.45	0.00
$R3c$	-60.96	60.96	0.00	-223.29	-223.29	121.93	1.20	1.20	-15.57	0.00

³³Incidentally, observe here how $\varepsilon_r := \text{Tr}(\varepsilon_{ij}) = \varepsilon_r^{(\text{conv})}$: the trace of the dielectric tensor, i.e., the isotropic response, is correctly invariant under rotation. By contrast, the piezoelectric tensor $d_{\alpha\beta}$ (or d_{ijk} , in its full third-rank form) has no uniquely-defined trace, and no isotropic part can be extracted from it for symmetry reasons (an isotropic third-rank tensor would be proportional to the totally antisymmetric tensor ϵ_{ijk} ; however, d_{ijk} is symmetric in its last two indices).

For the dielectric tensor, the only literature source available is the aforementioned work by Tan *et al.* – again, quoting Liu *et al.* – for the tetragonal phase, where $\varepsilon_{11} = \varepsilon_{22} = 25.5$ and $\varepsilon_{33} = 35.4$, in evident disagreement with our findings [349, 350]. In absence of other previous systematic DFT studies for pure sodium niobate, we mention that a paper by Lebedev on $\text{NaNbO}_3/\text{KNbO}_3$ superlattices identifies – as we do – a strong anisotropy in the dielectric tensor, with values $\varepsilon_{33} = 534.4$ and 334.7 for symmetries $Amm2$ and $Pmc2_1$, respectively (with $\hat{z}$ being the non-polar direction) [351]. Furthermore, a number of experimental works report dielectric constants between 200 and 600 at temperatures below $\simeq 350^\circ\text{C}$ (the onset of the higher-temperature phase R) [247, 249, 270]. This order of magnitude agrees with our predictions for phases $Pm - a^-b^+c^-$ and $Pmc2_1$ – i.e., the two most reliable candidate structures for NaNbO_3 in the considered low-temperature regime – and suggests that the results reported in Refs. [349, 350] may warrant further examination.

3.7 Ferro- and piezoelectricity in KNN at varying composition

We now turn back to the original problem, and perform a systematic study of the monoclinic $Pm - a^0b^+c^0$ phase of KNN across different compositions.

Since the reference unit cell contains 10 atoms, to keep the computational overload at bay, we now adopt a $2 \times 3 \times 2$ supercell, corresponding to a total of 120 atoms (comparable in size to the supercell used for the segregation study), of which 24 belong to the A-site sublattice. The Na concentration is then naturally defined as $x_{\text{Na}} = N_{\text{Na}}/24$. Within this framework, we sample a wide compositional range, chosen so as to overlap with experimental data points as closely as possible, by addressing the concentrations $x_{\text{Na}} = 0.50, 0.67, 0.71, 0.75, 0.79, 0.83, 1$. To these, we also add $x_{\text{Na}} = 0$ (i.e., pure KNbO_3) as a reference endpoint, for completeness, even though this is not part of the present experimental scenario.

For consistency, we once more retain the computational setup from the two previous sections, except for adjustments required by the larger supercell: in particular, the $\mathbf{k}$ -point mesh is rescaled from $6 \times 9 \times 6$ (used for the NaNbO_3 monoclinic $Pm - a^0b^+c^0$ unit cell) to $3 \times 3 \times 3$. As in the segregation study, the initial lattice parameters are generated via linear interpolation – and suitable rescaling – between the equilibrium values of $Pm - a^0b^+c^0$ KNbO_3 ($a_1 = 5.698 \text{ \AA}, a_2 = 3.962 \text{ \AA}, a_3 = 5.682 \text{ \AA}$) and $Pm - a^0b^+c^0$ NaNbO_3 ($a_1 = 5.535 \text{ \AA}, a_2 = 3.920 \text{ \AA}, a_3 = 5.522 \text{ \AA}$ – the same values reported in Table 3.1). As for the SQS cluster expansion, only doublets are retained this time, with a cutoff of $9 \text{ \AA}$, resulting in 39 (non-trivial) ECIs and a pair-RMS between 0.12 and 0.20, depending on composition.

Table 3.4: Structural data for the selected KNN compositions, after relaxation. Upper-case lattice vectors are those of the $2 \times 3 \times 2$ supercell, lower-case ones are resized in terms of the original 10-atom cell.

Composition	A_1 [Å]	A_2 [Å]	A_3 [Å]	a_1 [Å]	a_2 [Å]	a_3 [Å]	α [°]	β [°]	γ [°]
$x_{\text{Na}} = 0.00$	11.396	11.889	11.364	5.698	3.963	5.682	90.000	89.957	90.000
$x_{\text{Na}} = 0.50$	11.329	11.815	11.271	5.664	3.938	5.636	89.978	90.226	89.997
$x_{\text{Na}} = 0.67$	11.259	11.795	11.211	5.630	3.932	5.605	90.008	90.320	89.974
$x_{\text{Na}} = 0.71$	11.253	11.791	11.190	5.617	3.930	5.595	90.003	89.865	89.987
$x_{\text{Na}} = 0.75$	11.216	11.784	11.172	5.608	3.928	5.586	89.997	89.627	89.980
$x_{\text{Na}} = 0.79$	11.189	11.778	11.147	5.594	3.926	5.574	89.995	90.210	90.022
$x_{\text{Na}} = 0.83$	11.159	11.775	11.123	5.580	3.925	5.562	90.000	90.016	89.994
$x_{\text{Na}} = 1.00$	11.070	11.757	11.043	5.535	3.919	5.521	90.000	89.949	90.000

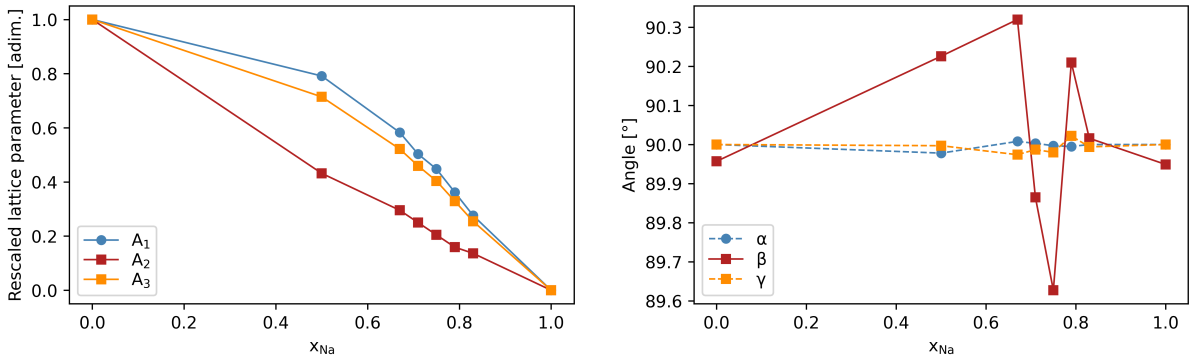


Figure 3.14: Overview of the DFT structural trends in the supercell lattice parameters (left) and angles (right) as a function of the Na concentration x_{Na} . Lattice parameters are rescaled via an affine transformation so that they equal 1 and 0 at $x_{\text{Na}} = 0$ and $x_{\text{Na}} = 1$, respectively (e.g. $A_1(x_{\text{Na}}) \rightarrow [A_1(x_{\text{Na}}) - A_1(1)]/[A_1(0) - A_1(1)]$).

Table 3.4 and, contextually, Fig. 3.14 report structural information for each KNN composition. The supercell lattice parameters (rescaled in Fig. 3.14) decrease across the series as expected from Vegard law, with an almost linear trend for A_2 , whereas A_1 and A_3 exhibit a slight downward concavity. The monoclinic angle β has an irregular behaviour around the 90° baseline: in particular, it is enhanced for the cases $x_{\text{Na}} = 0.50$ and $x_{\text{Na}} = 0.67$ (meaning that the structure is “flatter” in the xz plane), abruptly reduced at $x_{\text{Na}} = 0.71$ and $x_{\text{Na}} = 0.75$, again increased at $x_{\text{Na}} = 0.79$ and ultimately essentially back to 90° from $x_{\text{Na}} = 0.83$ onwards.³⁴ Finally, α and γ , that should be right angles in an ideal monoclinic lattice, also oscillate around 90° – although on a much smaller scale, with a maximum deviation of only 0.03% at $x_{\text{Na}} = 0.67$ – thus formally lowering the symmetry to triclinic, yet without any significant structural distortion.

³⁴For the $x_{\text{Na}} = 0.75$ case, the most pronounced outlier, we have separately verified that the structure relaxes to an angle $\beta < 90^\circ$ even when initialised with $\beta > 90^\circ$. The robustness of the trend in Fig. 3.14 is thus enforced.

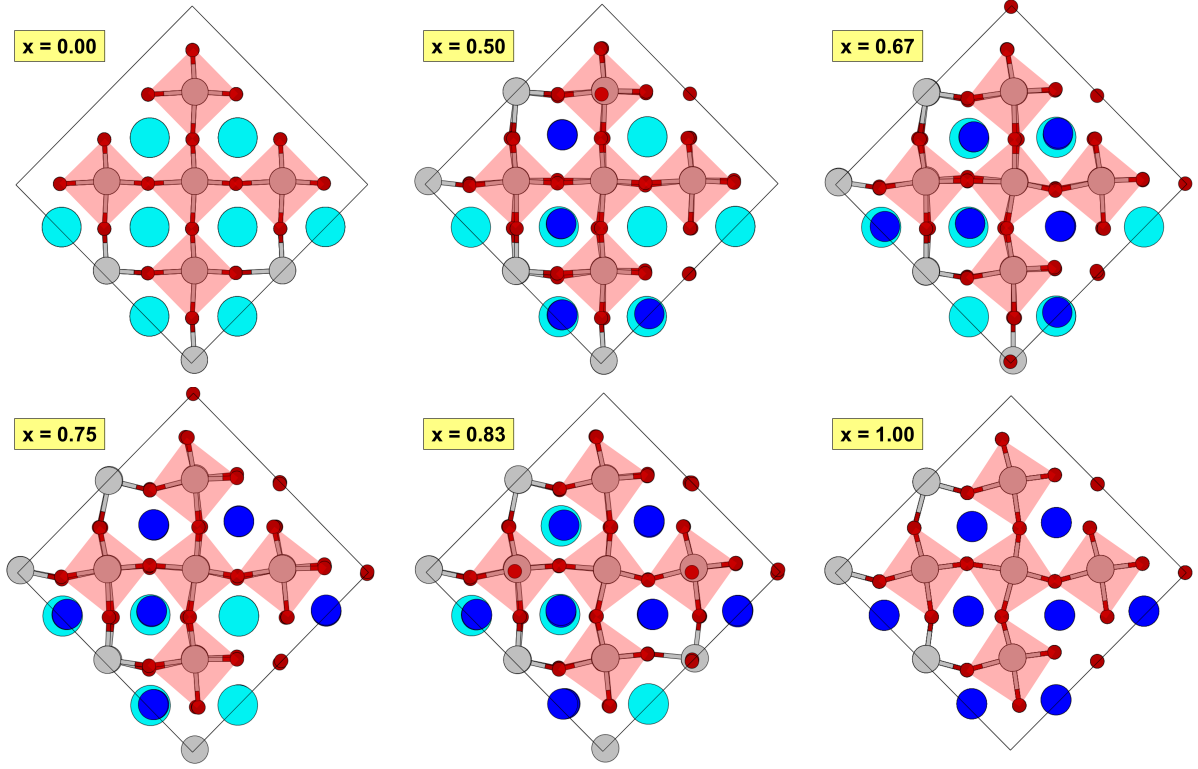


Figure 3.15: Views of the relaxed cells (xz plane) adopted for a representative subset of the KNN systems in Table 3.4. Colour code for the atomic species is as follows: Na - blue, K - turquoise, Nb - grey, O - red. Oxygen octahedra are drawn in light red.

Fig. 3.15 illustrates the relaxed unit cells in the xz polar plane. Octahedral tilting increases across the series, although not strictly linearly and in a locally dependent manner, since tilt amplitudes are governed by the quasirandom distribution of Na and K atoms on the A sites surrounding each individual octahedron.

Table 3.5: Octahedral tilt angles around axes $\hat{x}$, $\hat{y}$ and $\hat{z}$ for the selected KNN compositions, after relaxation.

Composition	ω_x [°]	ω_y [°]	ω_z [°]
$x_{\text{Na}} = 0.00$	/	0.14 ± 0.04	/
$x_{\text{Na}} = 0.50$	0.36 ± 0.21	1.36 ± 1.41	0.39 ± 0.21
$x_{\text{Na}} = 0.67$	1.09 ± 0.58	5.56 ± 1.19	0.78 ± 0.49
$x_{\text{Na}} = 0.71$	0.82 ± 0.50	6.57 ± 1.32	0.89 ± 0.51
$x_{\text{Na}} = 0.75$	0.90 ± 0.55	7.26 ± 1.54	0.83 ± 0.57
$x_{\text{Na}} = 0.79$	1.25 ± 0.76	8.15 ± 1.23	1.12 ± 0.63
$x_{\text{Na}} = 0.83$	1.17 ± 0.72	8.97 ± 0.87	1.46 ± 0.83
$x_{\text{Na}} = 1.00$	/	11.35 ± 0.04	/

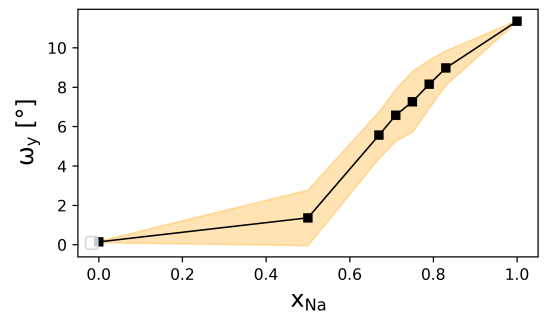


Figure 3.16: Octahedral tilt angle ω_y as a function of x_{Na} .

Table 3.5 reports, for each composition, the tilt angles about the three Cartesian axes, averaged over all octahedra in the supercell. As anticipated, the dominant tilting

occurs about $\hat{y}$, consistent with the $a^0b^+c^0$ tilt system of the parent structure. The corresponding angle ω_y , illustrated in Fig. 3.16, remains essentially quenched on the K-rich side and becomes appreciably non-zero only from $x_{\text{Na}} = 0.5$ onwards, following then an approximately linear trend across the rest of the composition range. The associated spread $\Delta\omega_y$ is gradually reduced for $x_{\text{Na}} > 0.5$, reflecting the decreasing disorder, except within the $x_{\text{Na}} = 0.71 - 0.75$ pocket, where a modest enhancement in disorder is observed. The A-site randomness also induces small tilts about $\hat{x}$ and $\hat{z}$, giving rise to irregular local patterns, that cannot be classified within the usual in-phase or antiphase categories.³⁵

To better quantify the evolution of structural degrees of freedom, we examine the effective lattice parameters a , b and c , reported in Fig. 3.17, estimated as average nearest-neighbour A–A (equivalently, B–B) distances along $\hat{x}$, $\hat{y}$ and $\hat{z}$, respectively. This representation complements the supercell lattice parameters, by providing a metric directly comparable with experimental interplanar spacings, extracted from X-ray diffraction spectra. Wherever appropriate, each data point is accompanied by an error bar, given by the standard deviation σ of the bond length distribution along the considered direction – further decomposed into contributions of the A–A and B–B type – which reflects structural disorder arising from both compositional randomness and local distortions.

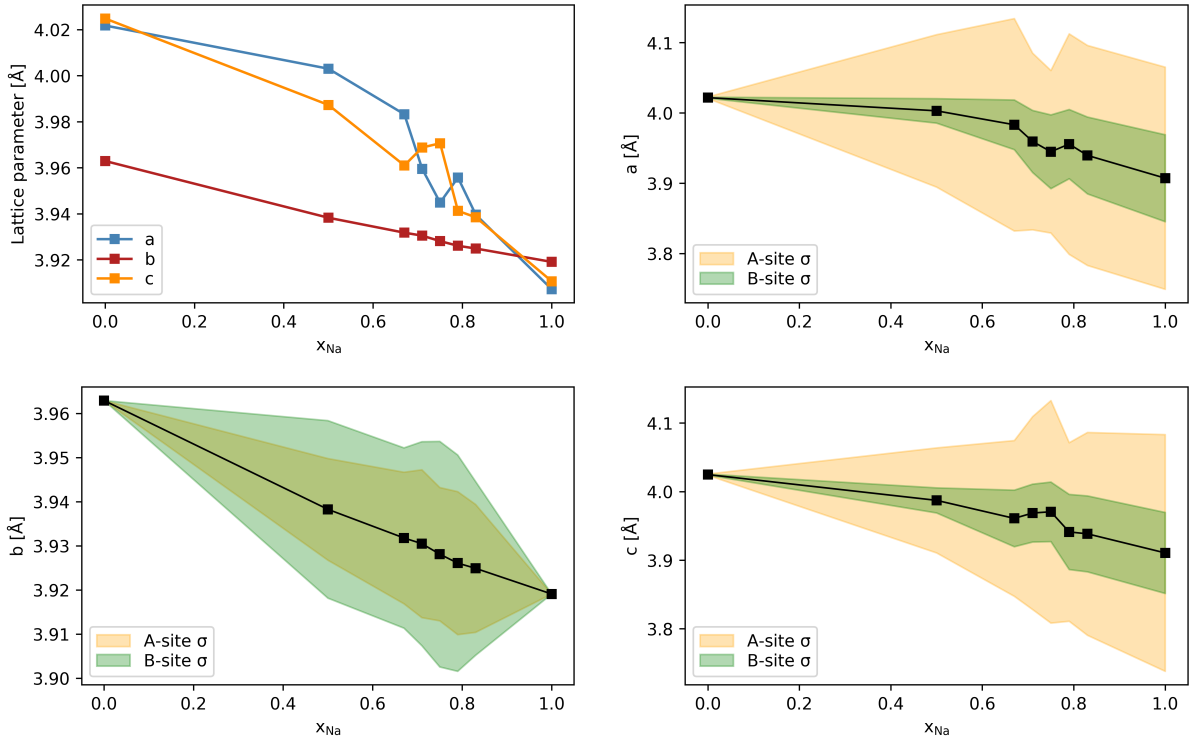


Figure 3.17: Top-left panel: average A–A (equivalent to B–B) interatomic distances a , b , c as a function of the Na concentration x_{Na} . Remaining panels: detail of the distribution of values for each interatomic distance; spreads due to A–A and B–B contributions are plotted separately.

³⁵The pattern is irregular even around $\hat{y}$ for the $x_{\text{Na}} = 0.5$ composition, at which KNN is indeed expected to adopt an $a^0b^0c^0$ tilt system (see Fig. 3.10).

At a glance, a and c do not follow the same smooth trend as the xz -plane supercell parameters A_1 and A_3 do (Fig. 3.14, left panel). Instead, a becomes increasingly larger than c until $x_{\text{Na}} = 0.67$; between $x_{\text{Na}} = 0.71$ and $x_{\text{Na}} = 0.83$, the two reverse roles twice; onwards, they converge toward equality.³⁶ The overall picture mirrors the evolution of the monoclinic angle β (Fig. 3.14, right panel), indicating a flatter structure at first, that suddenly elongates for $x_{\text{Na}} = 0.71 - 0.75$, flattens out a second time at $x_{\text{Na}} = 0.79$ and ultimately equilibrates at $\beta \simeq 90^\circ$ at high Na content. The spreads for both a and c are sizeable ($\sigma \lesssim 0.15$ Å) and dominated by A-A terms, whereas the B-site sublattice remains comparatively regular.

On the other hand, b follows a linear trend, clearly decoupled from the behaviour of a and c , reflecting the different symmetry constraints acting along $\hat{y}$ and on the xz plane. The decoupling persists in the spread of values, now narrower ($\sigma \lesssim 0.02$ Å) and mostly contributed to by B-B terms. This is fully consistent with an ideal, free-standing $Pm - a^0b^+c^0$ lattice; in an experimental realisation, however, the presence of a substrate may well impose more similar – if not identical – in-plane distances a and b .

Table 3.6: Mixing enthalpy of the KNN systems [meV], normalised per 5-atom perovskite formula unit.

Composition	E_{mix} [meV/f.u.]
$x_{\text{Na}} = 0.00$	0.0
$x_{\text{Na}} = 0.50$	34.0
$x_{\text{Na}} = 0.67$	40.5
$x_{\text{Na}} = 0.71$	38.3
$x_{\text{Na}} = 0.75$	34.0
$x_{\text{Na}} = 0.79$	30.6
$x_{\text{Na}} = 0.83$	27.1
$x_{\text{Na}} = 1.00$	0.0

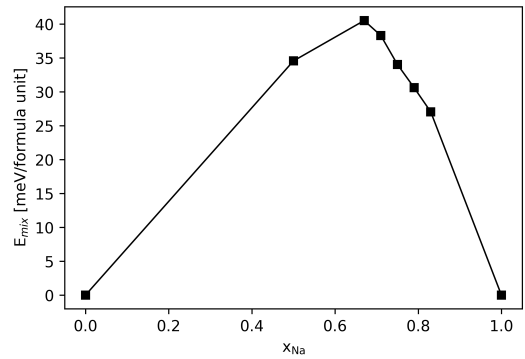


Figure 3.18: Mixing enthalpies from Table 3.6.

As in the segregation analysis, we evaluate the mixing enthalpy E_{mix} of the KNN systems, reported in Table 3.6 and Fig. 3.18 – namely, the analogue of Fig. 3.9, but now with a much more realistic assumption on the symmetry of the structure, which is no longer just an idealised prototype. As a matter of fact, the conclusion we had formulated – that KNN is overall unstable with respect to phase separation into the pure end members – is strengthened: E_{mix} is now not only positive throughout the whole compositional range, but also reaches values ($\simeq 40$ meV) an order of magnitude larger than those obtained under the tetragonal approximation ($\simeq 5$ meV). These higher values also allow for a more realistic comparison with experimental observations at finite temperature.

Concerning energetic considerations, inspection of Γ -point phonons reveals no soft modes in any of the alloyed composition, supporting the dynamical stability of the

³⁶The same behaviour was retrieved when testing a second, independent set of SQS configurations, generated with a different random seed.

considered KNN systems.³⁷ The only exception is $x_{\text{Na}} = 0$ (pure KNbO_3), which exhibits an antipolar instability along $\hat{y}$ ($\omega^2 = -5.3$ meV), in agreement with previous literature sources suggesting a chain-like structure, orthogonal to the polarisation direction, in this material [352, 353]. In any case, this does not affect the present discussion, as our experimental focus lies on the Na-rich region of the phase diagram.

Table 3.7: Polarisation (both vector components and modulus) of the KNN systems, referred to the global xyz Cartesian frame.

Composition	$\mathbf{P}$ [$\mu\text{C}/\text{cm}^2$]	P [$\mu\text{C}/\text{cm}^2$]
$x_{\text{Na}} = 0.00$	[24.88, 0.00, 25.39]	35.55
$x_{\text{Na}} = 0.50$	[28.76, 0.54, 25.03]	38.13
$x_{\text{Na}} = 0.67$	[29.65, 2.40, 24.85]	38.76
$x_{\text{Na}} = 0.71$	[26.40, 1.07, 28.24]	38.68
$x_{\text{Na}} = 0.75$	[24.52, 1.45, 30.13]	38.87
$x_{\text{Na}} = 0.79$	[29.01, -1.88, 25.89]	38.92
$x_{\text{Na}} = 0.83$	[27.66, 1.58, 27.15]	38.79
$x_{\text{Na}} = 1.00$	[27.29, 0.00, 28.17]	39.22

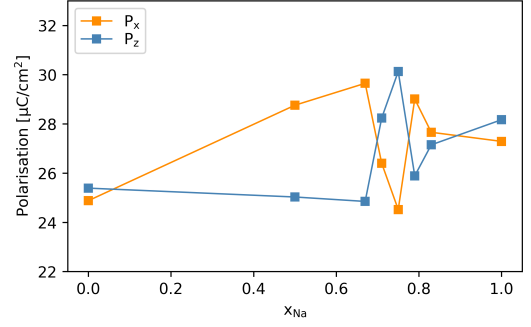


Figure 3.19: Polarisation components P_x and P_z from Table 3.7.

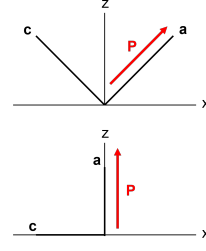
Polarisation (Table 3.7 and Fig. 3.19 – again, computed according to Eqn. 3.39) is predominantly confined to the xz plane, as in the NaNbO_3 parent phase, with only a small P_y component at intermediate compositions, driven by the A-site disorder. The magnitude P increases approximately linearly with the Na content. More revealing, however, is the behaviour of P_x and P_z , that mirror the trends already observed for the monoclinic angle β and for the interatomic distances a and c , by exchanging one another twice in the range $x_{\text{Na}} = 0.67 - 0.83$.

³⁷As commented earlier, a rigorous assessment would require phonon dispersions over the entire Brillouin zone. However, additional instabilities away from Γ appear not so likely. The considered monoclinic structures, on the one hand, already incorporate polar distortions. As for octahedral tilts, they could in principle develop about any axis – differently than in the 10-atom prototype – because of the increased cell size combined with the symmetry breaking generated by the A-site disorder; however, only tilts around $\hat{y}$ maintain a significant amplitude upon relaxation. What may, technically, yield soft modes are antiphase tilts around $\hat{y}$, not allowed by the present supercell, which is formed by an odd number of replicas of the 10-atom unit cell along that direction. In any case, these specific tilts are not reported in literature phase diagrams.

$x_{\text{Na}} = 0.00$

$$d_{\alpha\beta} = \begin{bmatrix} 80.5 & -7.6 & -55.9 & 0 & 4.9 & 0 \\ 0 & 0 & 0 & 121.3 & 0 & 123.2 \\ -54.4 & -7.4 & 78.3 & 0 & 4.3 & 0 \end{bmatrix}$$

$$d_{\alpha\beta}^{(\text{conv})} = \begin{bmatrix} 0.1 & -0.2 & 0.5 & 0 & 190.3 & 0 \\ 0 & 0 & 0 & 172.3 & 0 & 1.3 \\ 13.9 & -10.6 & 20.4 & 0 & 2.5 & 0 \end{bmatrix}$$



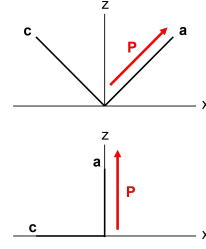
$$\varepsilon_{ij} = \begin{bmatrix} 31.8 & 0 & -5.7 \\ 0 & 1539.6 & 0 \\ -5.7 & 0 & 30.3 \end{bmatrix}$$

$$\varepsilon_{ij}^{(\text{conv})} = \begin{bmatrix} 25.3 & 0 & -0.8 \\ 0 & 1539.6 & 0 \\ -0.8 & 0 & 36.7 \end{bmatrix}$$

 $x_{\text{Na}} = 0.50$

$$d_{\alpha\beta} = \begin{bmatrix} 144.7 & -5.8 & -131.2 & -1.2 & -3.2 & -0.8 \\ 10.4 & 67.5 & -89.8 & 391.1 & -9.2 & 517.7 \\ -139.8 & -12.5 & 175.7 & -9.4 & 21.1 & -13.3 \end{bmatrix}$$

$$d_{\alpha\beta}^{(\text{conv})} = \begin{bmatrix} 0.6 & 4.7 & -16.5 & 10.4 & 418.1 & 2.1 \\ -35.1 & 67.5 & -44.3 & 642.6 & 100.2 & 89.5 \\ 11.1 & -12.9 & 23.8 & -12.4 & -28.0 & -1.8 \end{bmatrix}$$



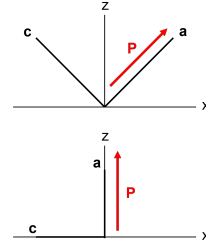
$$\varepsilon_{ij} = \begin{bmatrix} 36.5 & -14.1 & -11.1 \\ -14.1 & 1946.4 & -9.1 \\ -11.1 & -9.1 & 45.4 \end{bmatrix}$$

$$\varepsilon_{ij}^{(\text{conv})} = \begin{bmatrix} 29.8 & -16.5 & 4.5 \\ -16.5 & 1946.4 & 3.5 \\ 4.5 & 3.5 & 52.1 \end{bmatrix}$$

 $x_{\text{Na}} = 0.67$

$$d_{\alpha\beta} = \begin{bmatrix} 90.6 & -10.9 & -65.0 & -6.1 & 3.8 & -4.9 \\ -42.0 & 68.2 & -41.0 & 80.0 & -17.4 & 110.3 \\ -73.1 & -14.3 & 104.2 & -1.8 & 15.4 & -6.8 \end{bmatrix}$$

$$d_{\alpha\beta}^{(\text{conv})} = \begin{bmatrix} 2.2 & 2.4 & -6.0 & -1.2 & 235.4 & 3.1 \\ -32.8 & 68.2 & -50.2 & 134.6 & -1.0 & 21.5 \\ 13.3 & -17.8 & 26.8 & -9.8 & -15.3 & -1.9 \end{bmatrix}$$



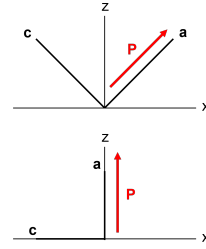
$$\varepsilon_{ij} = \begin{bmatrix} 35.7 & -15.2 & -8.5 \\ -15.2 & 621.6 & -12.9 \\ -8.5 & -12.9 & 47.7 \end{bmatrix}$$

$$\varepsilon_{ij}^{(\text{conv})} = \begin{bmatrix} 33.2 & -19.8 & 6.0 \\ -19.8 & 621.6 & 1.7 \\ 6.0 & 1.7 & 50.2 \end{bmatrix}$$

 $x_{\text{Na}} = 0.71$

$$d_{\alpha\beta} = \begin{bmatrix} 95.2 & -10.7 & -68.8 & -3.5 & 10.0 & -1.6 \\ -17.3 & 23.0 & -12.3 & 74.5 & -5.7 & 63.4 \\ -66.2 & -8.7 & 89.5 & -0.1 & 6.2 & -1.0 \end{bmatrix}$$

$$d_{\alpha\beta}^{(\text{conv})} = \begin{bmatrix} -0.3 & -1.4 & 2.5 & -2.0 & 226.1 & 1.4 \\ -12.0 & 23.0 & -17.6 & 97.5 & -5.0 & -7.8 \\ 11.9 & -13.8 & 23.3 & -3.1 & 5.9 & 0.5 \end{bmatrix}$$



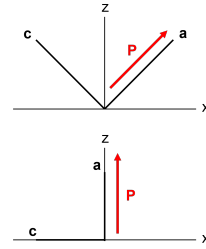
$$\varepsilon_{ij} = \begin{bmatrix} 43.4 & -6.3 & -8.6 \\ -6.3 & 545.1 & -4.9 \\ -8.6 & -4.9 & 38.7 \end{bmatrix}$$

$$\varepsilon_{ij}^{(\text{conv})} = \begin{bmatrix} 32.5 & -8.0 & -2.3 \\ -8.0 & 545.1 & 1.0 \\ -2.3 & 1.0 & 49.6 \end{bmatrix}$$

 $x_{\text{Na}} = 0.75$

$$d_{\alpha\beta} = \begin{bmatrix} 93.4 & -12.7 & -65.4 & -4.9 & 13.1 & -1.8 \\ -23.4 & 23.0 & -7.7 & 65.9 & -5.4 & 44.4 \\ -56.6 & -7.7 & 79.4 & 0.6 & 3.4 & -0.8 \end{bmatrix}$$

$$d_{\alpha\beta}^{(\text{conv})} = \begin{bmatrix} -1.6 & -3.5 & 5.3 & -3.2 & 208.5 & 2.3 \\ -12.8 & 23.0 & -18.2 & 78.0 & -15.7 & -15.2 \\ 12.1 & -14.5 & 23.8 & -3.4 & 16.2 & 0.9 \end{bmatrix}$$



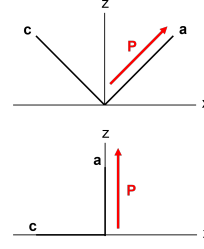
$$\varepsilon_{ij} = \begin{bmatrix} 49.2 & -8.7 & -8.2 \\ -8.7 & 447.7 & -4.0 \\ -8.2 & -4.0 & 34.8 \end{bmatrix}$$

$$\varepsilon_{ij}^{(\text{conv})} = \begin{bmatrix} 33.8 & -9.0 & -7.2 \\ -9.0 & 447.7 & 3.3 \\ -7.2 & 3.3 & 50.2 \end{bmatrix}$$

$x_{\text{Na}} = 0.79$

$$d_{\alpha\beta} = \begin{bmatrix} 78.1 & -8.8 & -53.7 & 2.1 & 5.5 & 0.1 \\ 11.0 & -26.3 & 13.9 & 35.6 & 4.7 & 43.9 \\ -58.6 & -12.3 & 85.5 & 0.4 & 10.2 & 3.2 \end{bmatrix}$$

$$d_{\alpha\beta}^{(\text{conv})} = \begin{bmatrix} 0.8 & 2.5 & -2.5 & -0.7 & 195.1 & -2.4 \\ 10.1 & -26.2 & 14.9 & 56.2 & -2.8 & 5.8 \\ 12.6 & -14.9 & 23.7 & 2.8 & -8.7 & 0.4 \end{bmatrix}$$



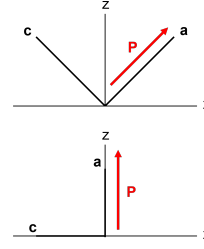
$$\varepsilon_{ij} = \begin{bmatrix} 37.6 & 6.3 & -7.9 \\ 6.3 & 367.3 & 6.4 \\ -7.9 & 6.4 & 45.1 \end{bmatrix}$$

$$\varepsilon_{ij}^{(\text{conv})} = \begin{bmatrix} 33.4 & 9.0 & 3.8 \\ 9.0 & 367.3 & 0.0 \\ 3.8 & 0.0 & 49.3 \end{bmatrix}$$

 $x_{\text{Na}} = 0.83$

$$d_{\alpha\beta} = \begin{bmatrix} 77.2 & -10.2 & -52.3 & -2.7 & 6.9 & -1.1 \\ -15.8 & 18.6 & -10.5 & 33.9 & -4.3 & 35.2 \\ -53.1 & -10.3 & 79.1 & 0.6 & 7.7 & -1.3 \end{bmatrix}$$

$$d_{\alpha\beta}^{(\text{conv})} = \begin{bmatrix} -0.1 & 0.1 & -0.7 & -1.6 & 185.1 & 1.2 \\ -11.0 & 18.6 & -15.4 & 48.9 & -5.3 & 0.9 \\ 12.8 & -14.5 & 23.1 & -2.2 & -1.9 & -0.1 \end{bmatrix}$$



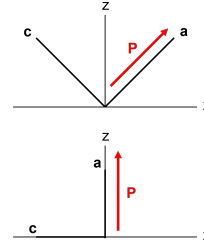
$$\varepsilon_{ij} = \begin{bmatrix} 40.7 & -6.7 & -8.1 \\ -6.7 & 349.4 & -4.5 \\ -8.1 & -4.5 & 42.0 \end{bmatrix}$$

$$\varepsilon_{ij}^{(\text{conv})} = \begin{bmatrix} 33.2 & -8.0 & 0.7 \\ -8.0 & 349.4 & 1.5 \\ 0.7 & 1.5 & 49.5 \end{bmatrix}$$

 $x_{\text{Na}} = 1.00$

$$d_{\alpha\beta} = \begin{bmatrix} 65.7 & -11.4 & -40.8 & 0 & 9.8 & 0 \\ 0 & 0 & 0 & 17.6 & 0 & 17.0 \\ -39.4 & -10.4 & 63.2 & 0 & 4.1 & 0 \end{bmatrix}$$

$$d_{\alpha\beta}^{(\text{conv})} = \begin{bmatrix} -1.6 & -0.7 & 2.4 & 0 & 148.0 & 0 \\ 0 & 0 & 0 & 24.5 & 0 & -0.4 \\ 12.3 & -15.4 & 22.1 & 0 & 2.8 & 0 \end{bmatrix}$$



$$\varepsilon_{ij} = \begin{bmatrix} 42.4 & 0 & -7.9 \\ 0 & 206.2 & 0 \\ -7.9 & 0 & 39.9 \end{bmatrix}$$

$$\varepsilon_{ij}^{(\text{conv})} = \begin{bmatrix} 33.2 & 0 & -1.2 \\ 0 & 206.2 & 0 \\ -1.2 & 0 & 49.0 \end{bmatrix}$$

Figure 3.20: Piezoelectric [pm/V] and dielectric tensors [adim.] for the KNN systems. Schemes of the polar planes and (approximate) polarisation direction have been added for convenience.

Lastly, we analyse piezoelectric and dielectric tensors, reported in Fig. 3.20. To better visualise compositional trends, the piezoelectric coefficients (in the rotated reference frame) are also regrouped and plotted as a function of the Na concentration in Fig. 3.21. Because of the formally triclinic symmetry of most relaxed structures, all 18 tensor components are, in principle, independent and must be considered.

The dominant longitudinal coefficients (Fig. 3.21, top panels) are d_{11} , d_{13} , d_{31} and d_{33} – i.e., those involving only x and z indices. These components display a clear pairing behaviour ($d_{11} \simeq d_{33}$, $d_{13} \simeq d_{31}$) which originates from the chosen lattice orientation: directions $\hat{x}$ and $\hat{z}$ are treated essentially likewise, since the polarisation vector lies approximately along the xz bisector. As a whole, these four coefficients reach their maximum magnitude at $x_{\text{Na}} = 0.5$, with d_{33} attaining values as high as 176 pm/V, and then decrease progressively with increasing Na content: the A-site randomness, therefore, softens the lattice with respect to in-plane longitudinal stresses. Notably, d_{11} and d_{33} cross twice between $x_{\text{Na}} = 0.71$ and $x_{\text{Na}} = 0.83$, mirroring the previously discussed behaviour

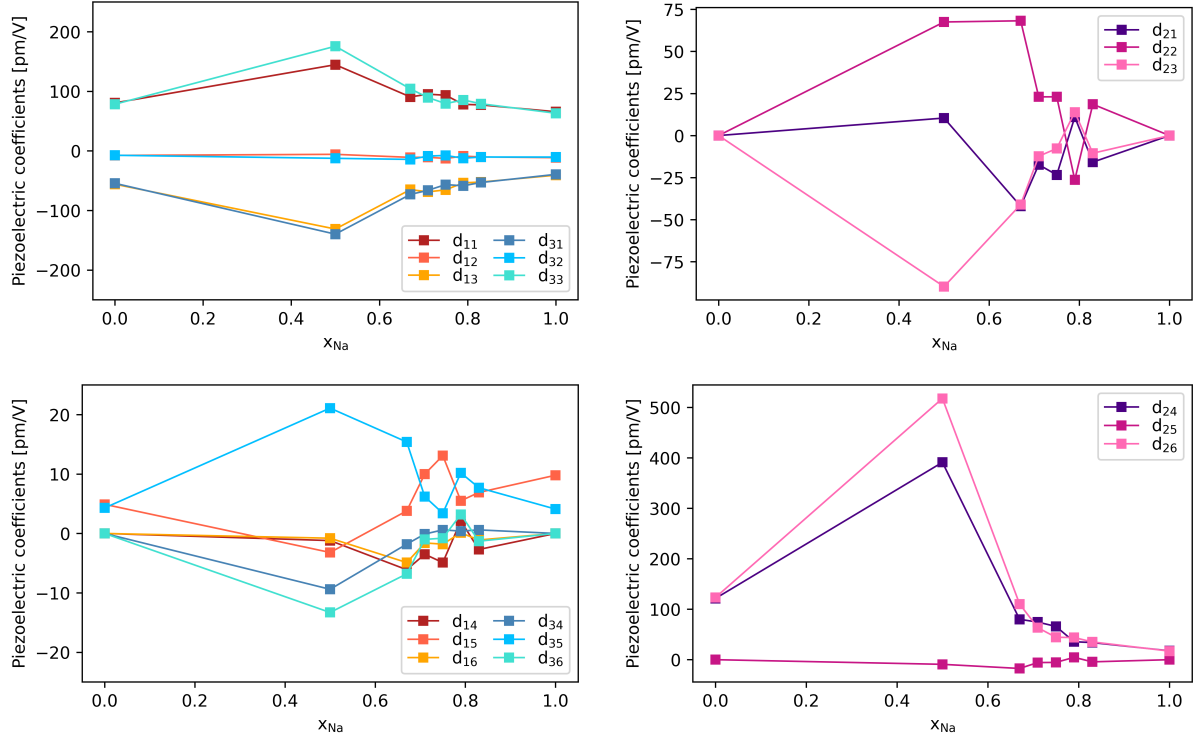


Figure 3.21: Piezoelectric coefficients from Fig. 3.20 [pm/V].

of structural parameters (a , c , and β) and polarisation components.³⁸

The remaining longitudinal components d_{21} , d_{22} , d_{23} , d_{12} and d_{32} are comparatively smaller, particularly the last two. Since all these terms involve $\hat{y}$ within the indices – either labelling polarisation, or stress, or both – we draw a twofold conclusion. First, longitudinal stress along $\hat{y}$ has but a weak influence on the polarisation in the xz plane. Second, under any (*longitudinal*) stress, the lattice is globally stiffer along $\hat{y}$ than along the remaining directions, so that generating a sizeable P_y component (i.e., rotating the polarisation out of the xz plane) is energetically disfavoured. This claim should, however, be interpreted in relative terms: for instance, d_{22} still reaches values close to 70 pm/V at $x_{\text{Na}} = 0.5$, which are far from negligible.

Shear responses (Fig. 3.21, bottom panels) exhibit a distinct hierarchy. In particular, d_{24} and d_{26} stand out as strikingly larger across all compositions, and anomalously so at $x_{\text{Na}} = 0.5$, exceeding 500 pm/V. In contrast to the longitudinal case, shear stresses in the yz or xy planes (indices $\beta = 4, 6$ respectively) can easily induce a P_y component; this suggests a coupling between such shear stress fields and the local, minor octahedral tilts, that occur in planes containing $\hat{y}$. The remaining shear coefficients are smaller than their longitudinal counterparts. Again, we find paired components ($d_{14} \simeq d_{16}$, $d_{34} \simeq d_{36}$) reflecting the near-equivalence of $\hat{x}$ and $\hat{z}$; the remaining terms d_{15} and d_{35} – the largest shear terms at high Na content ($x_{\text{Na}} > 0.67$) – form instead a mirrored pair.

³⁸This interchange is in fact systematic: similar crossings occur for several other pairs of coefficients throughout Fig. 3.21, whose indices differ by a swap between x and z .

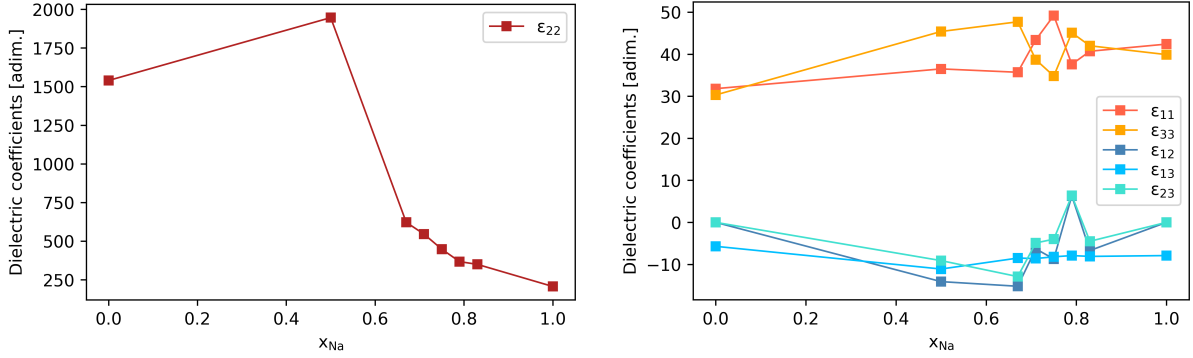


Figure 3.22: Dielectric coefficients from Fig. 3.20 [adim.].

The dielectric response (Fig. 3.22) is markedly anisotropic – as observed for the NaNbO_3 parent phase – and strongest, by one to two orders of magnitude, in the $\hat{y}$ -component ε_{22} ; this once again means that the KNN systems are more polarisable under external electric fields along directions where no spontaneous polarisation exists. Analogously to the shear-dominated piezoelectric response, ε_{22} reaches its maximum at $x_{\text{Na}} = 0.5$ and then decreases monotonically with increasing Na content. The remaining diagonal components ε_{11} and ε_{33} vary only slightly (between 30 and 50) across the composition range, displaying the characteristic double-crossing between $x_{\text{Na}} = 0.71$ and $x_{\text{Na}} = 0.83$. Off-diagonal elements remain closer to zero throughout, confirming that the dielectric response is mostly longitudinal, with minimal cross-axis coupling.

We now turn to comparing our results with those from earlier studies. To start with, we consider the KNbO_3 end member, for which the literature is richer than for NaNbO_3 (already treated in the previous section). A survey of experimental and theoretical works reveals overall good agreement with our findings. Notably, a strictly one-to-one mapping is not possible, since KNbO_3 adopts an orthorhombic ($Amm2$) structure at room temperature, whereas ours is nominally monoclinic. However, the nearly complete absence of octahedral tilting and the minimal deviation of the monoclinic angle β from 90° in our case ultimately justify a direct comparison with data reported for the $Amm2$ phase.

Table 3.8: Piezoelectric tensors elements for orthorhombic KNbO_3 from various studies [pm/V].

Reference	$d_{31}^{(\text{conv})}$	$d_{32}^{(\text{conv})}$	$d_{33}^{(\text{conv})}$	$d_{24}^{(\text{conv})}$	$d_{25}^{(\text{conv})}$
This work	13.9	-10.6	20.4	172.3	190.3
Liang <i>et al.</i> [354] (theo)	9.5	-24.6	21.6	205.1	241.5
Wan <i>et al.</i> [355] (theo)	12.7	-10.0	20.1	-91.1	175.0
Li <i>et al.</i> [317] (theo)	/	/	24.3	/	/
Peng <i>et al.</i> [319] (theo)	16.1	-10.6	23.2	84.7	281.2
Tan <i>et al.</i> [356] (theo)	16.0	-10.5	23.5	168.0	278.6
Gunter <i>et al.</i> [357] (exp)	9.8	-19.5	24.5	159.0	215.0
Nakamura <i>et al.</i> [358] (exp)	/	/	30.3	/	/
Zgonik <i>et al.</i> [359] (exp)	/	/	29.3	/	/
Wada <i>et al.</i> [360] (exp)	18.4	/	/	/	/

Table 3.8 summarises previously reported piezoelectric coefficients for orthorhombic KNbO_3 , compared with our results from Fig. 3.20 ($x_{\text{Na}} = 0$, conventional setting). Although quantitative discrepancies occur among different sources, the agreement is qualitatively good; the negative sign in front of $d_{24}^{(\text{conv})}$ in the work by Wan *et al.* is the only true anomaly.³⁹ Furthermore, in the experimental studies by Nakamura *et al.* and Wada *et al.*, additional configurations are considered, where the polarisation lies at approximately 45° with respect to the $\hat{z}$ axis, consistently with our rotated reference frame. These authors report values of $d_{33} = 87.2$ pm/V and $d_{31} = 51.7$ pm/V, in very good agreement with our corresponding results in the rotated setting ($d_{33} = 78.3$ pm/V, $|d_{31}| = 54.4$ pm/V).

Table 3.9: Dielectric tensors elements for orthorhombic KNbO_3 from various studies [adim.].

Reference	$\varepsilon_{11}^{(\text{conv})}$	$\varepsilon_{22}^{(\text{conv})}$	$\varepsilon_{33}^{(\text{conv})}$
This work	25.3	1539.6	36.7
Liang <i>et al.</i> [361] (theo)	171	996	57
Wiesendanger <i>et al.</i> (quoted in Ref. [359]) (exp)	160	1000	55
Fukuda <i>et al.</i> [362] (exp)	140	1200	40
Zgonik <i>et al.</i> [359] (exp)	150	985	44

For the dielectric tensor (Table 3.9), the quantitative agreement is less precise yet still qualitatively satisfactory. All referenced studies report a strongly anisotropic response, characterised by a dominant component $\varepsilon_{22}^{(\text{conv})}$ (along a non-polar direction) of the order of 10^3 . The quantitative spread of this coefficient across different sources can likely be attributed to its pronounced temperature dependence: as shown in the works by Liang *et al.* [354, 361], its value does approach 1500 at the lower end of the temperature range where the *Amm2* phase is stable (-30 to 0°C), in accord with our result. Additional works further support the overall picture: Matsumoto *et al.* [363] report dielectric constants on the order of 800, Wada *et al.* [360] measure $\varepsilon_{33} = 83$ and 447 for crystals poled along $[110]_c$ and $[001]_c$, respectively, and Wan *et al.* [355], although reporting only the electronic contribution $\bar{\varepsilon}_{ij}$, likewise find a reduced component along the polar direction.

Finally, we consider the available literature on KNN. As noted in Section 3.2, in contrast with the abundance of experimental works, DFT studies of this system are limited in number and cumbersome to compare in a systematic way. Most are not comprehensive, but rather focused on specific properties only and/or selected compositions or composition ranges. Notably, they differ significantly in alloy-modelling strategies: only three studies adopt the SQS approach as we do [319, 328, 334], while the others leverage either ordered supercells or, worse, the VCA. As observed in Section 3.4, the latter method is generally inadequate for properties such as piezoelectricity, highly sensitive to the local atomic

³⁹Therein, $d_{24}^{(\text{conv})}$ is compared to data from experimental sources only, all displaying a positive sign. This discrepancy is tentatively ascribed to crystal defects affecting the experimental measurements; however, considering the abundance of other theoretical sources (listed in Table 3.8), all of which report $d_{24}^{(\text{conv})} > 0$, this explanation appears unlikely.

environment. In addition, the use of VCA in very small cells – in some works containing as few as five atoms – cannot encompass octahedral tilts, a structural degree of freedom that we have shown to be relevant in KNN on the Na-rich side of the phase diagram. As a result, altogether, we found no previous study that simultaneously (i) addresses the monoclinic phase, either exclusively or alongside other phases; (ii) employs the SQS approach; and (iii) provides an analysis of polarisation, dielectric and piezoelectric coefficients. Nevertheless, we attempt below to organise and critically compare a selection of representative studies from the available literature, focusing on those aspects that can be directly related to the results presented in this work.

In one of the earliest DFT studies on KNN [364], Liu *et al.* report calculated structural parameters for phases of different symmetry at the composition $x_{\text{Na}} = 0.5$, comparing different exchange–correlation functionals and employing both ordered supercell and the VCA. For the monoclinic phase, they obtain values for β ranging from 90.01° to 90.51° , strongly dependent on the computational setup. Lattice parameters show an even greater sensitivity, varying both in magnitude and in overall trend with the chosen approach. Interestingly, the experimental data referenced therein – $a \simeq c = 4.00 \text{ \AA}$, $b = 3.94 \text{ \AA}$ and $\beta = 90.33^\circ$ – are in reasonable agreement with our findings (Table 3.4 and Fig. 3.17).

The same authors, in a follow-up publication [316], were the first to investigate compositional dependences (albeit within the VCA). They report c values between 4.0 and $4.1 \text{ \AA}$, always larger than a and b , which remain closer to one another for most compositions. The trend of β exhibits an irregular profile, with a maximum at $x_{\text{Na}} = 0.7$ followed by a descent, broadly resembling our results in Fig. 3.14 (with the difference that in their case $\beta > 90^\circ$ everywhere).

The study by Li *et al.* [317] is the first to include piezoelectric coefficients in an analysis of compositional trends (again, within the VCA). Their investigation focuses on the orthorhombic phase (presumably, $Amm2$, 10-atom cell), and is limited to $x_{\text{Na}} \leq 0.7$, as they report mechanical instability at higher Na content.⁴⁰ Since our monoclinic phase closely resembles $Amm2$ at $x_{\text{Na}} = 0$, but progressively departs from it as the Na fraction increases, it is not surprising that their $d_{33}^{(\text{conv})}$ and $d_{15}^{(\text{conv})}$ coefficients resemble ours only vaguely. Nonetheless, they identify an enhanced – and indeed maximal – longitudinal response d_{33} away from the polar direction (specifically at 50°), together with a large $d_{15}^{(\text{conv})}/d_{33}^{(\text{conv})}$ ratio of 7.3. Both features point to favouring polarisation rotation mechanisms, traces of which also emerge from our analysis, and are therefore consistent with our predictions, albeit with quantitative discrepancies.

Yang *et al.* [318], in a combined theoretical–experimental study, report experimental values for d_{33} within a narrow composition window, $x_{\text{Na}} = 0.54 - 0.57$. They observe a peak in d_{33} of 200 pm/V at the midpoint of this interval, not far from our predicted maximum of 176 pm/V at $x_{\text{Na}} = 0.5$.

The study by Peng *et al.* [319] represents the closest precedent to the present thesis, both in terms of methodology (use of SQS) and objectives (compositional analysis of ferro-

⁴⁰*Mechanical instability* denotes the violation of the Born stability criteria, which occurs when the elastic energy of the crystal ceases to be positive definite. This situation is reflected in negative elastic constants or, more generally, in negative eigenvalues of the elastic tensor. Necessary and sufficient conditions for mechanical stability, specified for each crystal symmetry group, are reported in Ref. [365].

and piezoelectric properties). The main differences concern the target phase – *Amm2* in their case – and the explored composition range, limited to $x_{\text{Na}} \leq 0.625$. Although these aspects, particularly the latter, prevent a strict one-to-one comparison, several points of agreement nonetheless emerge. First, they also find a gradual, moderate increase in polarisation, from 39 to 44 $\mu\text{C}/\text{cm}^2$ with increasing Na content (in their convention, $\hat{z}$ is the polar axis). Likewise, they report small yet finite octahedral tilting angles $\omega_i \leq 0.9^\circ$, consistent with our ω_x and ω_z values (Table 3.5; since *Amm2* is nominally untilted, they do not recover the larger ω_y angle appearing in our analysis). The comparison is, however, particularly instructive for the piezoelectric response. A broad agreement is observed in the evolution of the tensor elements $d_{\alpha\beta}^{(\text{conv})}$: in particular, they report a moderate increase of $d_{33}^{(\text{conv})}$ with Na content, from 16.1 to 28.3 pm/V over $0 \leq x_{\text{Na}} \leq 0.625$, comparable to our range of 20.4–26.8 pm/V for $0 \leq x_{\text{Na}} \leq 0.67$. Likewise, they obtain a very large shear response, with $d_{15}^{(\text{conv})}$ peaking at 716.3 pm/V for $x_{\text{Na}} = 0.5625$, whereas we find a maximum $d_{24}^{(\text{conv})} = 742.6$ pm/V at $x_{\text{Na}} = 0.5$ (most likely, frame adjustments reconcile the different roles of tensor elements). Furthermore, via an orientation analysis, Peng *et al.* report a maximal d_{33} (exceeding 200 pm/V) at approximately 45° from the polar axis, in line with our rotated-frame results. Averaging tensor elements over all possible orientations, they identify maxima in d_{33} , d_{31} , and d_{15} at $x_{\text{Na}} = 0.5625$, consistent with our observation of enhanced piezoresponse at maximal chemical disorder. Finally, although no numerical values are provided, they note enhanced responses at higher Na contents ($x_{\text{Na}} = 0.6875 - 0.75$), which they could not reconcile with available experimental data, yet may correspond to local maxima of our longitudinal coefficients shown in Fig. 3.21.

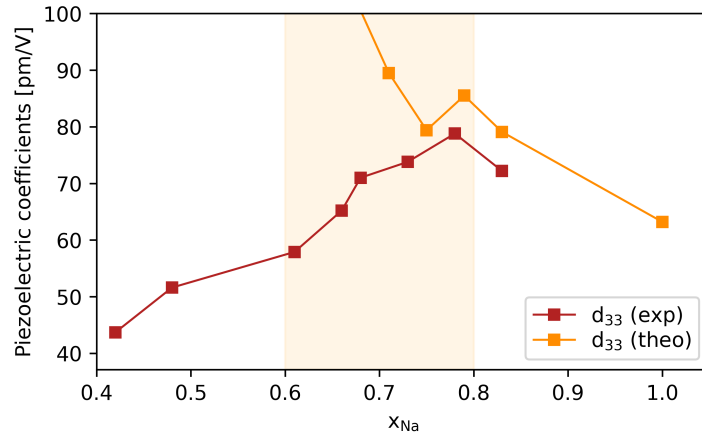


Figure 3.23: Comparison between DFT and experimental values for d_{33} [pm/V] (the latter are adapted, with permission, from Ref. [3]). The shaded orange band indicates the approximate range of compositions where the $Pm - a^0b^+c^0$ phase is expected, according to phase diagrams from Refs. [285] and [284].

To conclude, we report in Fig. 3.23 a comparison between our calculated d_{33} values, from Fig. 3.20, and the in-house experimental data provided by our partner group. A notable agreement emerges in the compositional window $x_{\text{Na}} \simeq 0.75 - 0.83$, where the local maximum predicted by DFT coincides with the global maximum observed

experimentally, with more than satisfactory quantitative correspondence. This result suggests that the monoclinic phase investigated here may indeed be present in the experimental samples; although the agreement is confined to a limited compositional range, it is worth emphasising that this interval falls roughly within the proposed stability region of the monoclinic symmetry (that may well be affected by substrate effects in the present experimental scenario). Furthermore, the (*a priori* arbitrary) structural setting adopted in our calculations – featuring a polar axis rotated by approximately 45° away from the $\hat{z}$ direction – may in fact reflect, to a fair extent, the effective configuration realised in the experimental samples. In any event, further considerations on the matching between our prediction and in-house experimental data will be developed in the forthcoming publication [3].

3.8 Conclusions and future perspectives

In this chapter, we presented a DFT-based investigation of selected properties of KNN. To begin with, inspired by the experimental observation of a tendency of this material to segregate, under specific conditions, into Na-rich and K-rich regions rather than maintaining the equimolar stoichiometry, we performed an energetic stability analysis on KNN systems constrained in an idealised tetragonal symmetry. As a result, we found that partial segregation into regions of imbalanced composition – similar to those retrieved in experiments – is indeed favoured, although the energy differences involved are very tiny. Thereafter, once again prompted by the activity of our experimental partners, we set out to investigate different compositions of monoclinic ($Pm - a^0b^+c^0$) KNN, on the Na-rich side of the phase diagram, providing a detailed and systematic account of their structural, ferroelectric and piezoelectric properties. These resulted in fair agreement with the available literature; the d_{33} coefficient also showed moderate resemblance to the present experimental data, within a limited compositional range that is, however, consistent with the expected stability window of the monoclinic phase at stake. Furthermore, by repeating the energetic analysis within the more realistic monoclinic framework, we found that the associated energy scale is increased by an order of magnitude with respect to the previously adopted tetragonal symmetry, strengthening our earlier conclusion regarding the preference of KNN for non-equimolar compositions.

While providing a consistent and satisfactory picture, these results are not intended to be fully exhaustive and naturally call for broader, systematic investigations. First-principles studies of KNN are intrinsically demanding, already at the level of the end members: as discussed in Section 3.2, NaNbO_3 – particularly near room temperature – exhibits a rich landscape of competing phases, highly sensitive to even minor amounts of doping, whose complex crystal structures often require a description well beyond the five-atom primitive cell. This structural complexity extends to KNN over a sizeable compositional range and combines with the additional computational challenges arising from the random-alloy nature of the material. Addressing these aspects properly demands careful selection and validation of the DFT setup, as well as substantial computational

resources – and, inevitably, time.

In this respect, we would like to close this chapter – and the thesis as a whole – with an open invitation to the DFT community: there remains both need and opportunity for a systematic, consistent, rigorous first-principles investigation of KNN, encompassing all possible phases proposed in the literature, over the entire compositional range. To the best of our knowledge, such a study has not yet been undertaken in these exact terms: as discussed earlier in the chapter, the few existing DFT investigations of KNN have generally focused on narrower composition windows (if not altogether a single, selected composition, typically $x_{\text{Na}} = 0.5$) and have explored only a subset of the possible crystal symmetries. As of today, however, advanced exchange–correlation functionals and alloy-modelling approaches are available, and their combination appears to form a suitable setup for handling the complexity of materials such as KNN in a holistic fashion, as partially showcased in this work. While the computational cost remains a significant factor, it is likely within the capabilities of state-of-the-art HPC facilities and, therefore, neither prohibitive nor discouraging (in case of insufficient computational resources, lighter approaches such as the VCA might still turn out useful for the most demanding calculations – phonon dispersions over the full Brillouin zone being a primary example – provided that careful benchmarking against SQS results is carried out beforehand).

We sincerely hope that our call to action will be answered in the coming years, and propose the computational strategies adopted in this work as a sort of “starter pack” for anyone willing to embark on a large-scale first-principles investigation of KNN. Such an effort would be of clear benefit to the experimental community, in the spirit of further promoting this material as a valuable platform for future generations of lead-free piezoelectric devices.

Appendix A

AMaRaNTA dataset

We report here the (extended) dataset of exchange parameters for the 2D magnetic materials discussed in Chapter 2, together with a sketch of the unit cells employed for the DFT calculations.

In Table A.1, we provide the 12 parameters (exchange plus SIA) that are directly output of AMaRaNTA, without any further processing.

Material	$J_{xx}^{(1)}$	$J_{yy}^{(1)}$	$J_{zz}^{(1)}$	$J_{xy}^{(1)}$	$J_{yx}^{(1)}$	$J_{xz}^{(1)}$	$J_{zx}^{(1)}$	$J_{yz}^{(1)}$	$J_{zy}^{(1)}$	$J^{(2)}$	$J^{(3)}$	A
CrBrO	-1.56	-1.56	-1.57	0.00	0.00	-0.01	-0.01	0.00	0.00	-0.78	-8.05	-0.03
CrBrS	-6.53	-6.48	-6.56	0.00	-0.00	0.26	-0.27	0.02	0.02	-9.74	-9.31	-0.02
CrBr ₃	-3.34	-3.28	-3.36	0.05	0.05	-0.03	-0.03	-0.05	-0.05	-0.43	0.23	-0.04
CrClO	-1.58	-1.56	-1.58	-0.00	-0.00	-0.01	-0.01	0.01	0.00	-0.80	-7.44	-0.07
CrCl ₃	-2.58	-2.57	-2.58	-0.00	0.00	0.01	0.01	-0.00	-0.00	-0.23	0.21	-0.01
CrGeTe ₃	-11.96	-11.52	-12.21	-0.30	-0.30	-0.04	-0.04	0.04	0.04	0.16	-1.13	0.09
CrI ₃	-3.15	-4.22	-3.83	0.00	-0.00	0.48	0.48	0.00	0.00	-0.81	0.18	-0.10
CrPS ₄	-9.86	-9.86	-9.86	-0.01	-0.01	-0.02	-0.02	-0.01	-0.01	-9.01	-0.48	-0.03
CrSiSe ₃	5.13	5.18	5.11	-0.04	-0.04	0.01	0.01	-0.02	-0.02	0.08	1.85	0.02
CrSiTe ₃	-10.30	-11.16	-11.10	0.01	0.01	0.12	0.12	-0.00	0.00	-0.13	-0.83	0.10
MnO ₂	-3.13	-3.12	-3.12	-0.02	-0.02	0.03	0.03	0.02	0.02	-0.35	2.19	-0.21
MnBi ₂ Te ₄	-0.21	-0.29	-0.12	0.02	0.02	-0.00	-0.00	0.02	0.02	0.32	0.22	-0.18
MnBr ₂	1.12	1.12	1.11	0.01	0.01	0.00	0.00	0.00	0.00	0.16	0.45	-0.02
MnCl ₂	1.20	1.19	1.19	0.01	0.01	-0.00	-0.00	0.00	0.00	1.80	0.07	-0.00
MnI ₂	0.91	0.93	0.90	0.02	0.02	-0.01	-0.01	-0.01	-0.01	0.34	0.68	-0.01
NiBr ₂	-4.41	-4.51	-4.48	0.08	0.08	0.11	0.11	0.06	0.06	-0.05	3.33	0.02
NiCl ₂	-4.80	-4.79	-4.79	-0.00	-0.00	-0.01	-0.01	-0.00	-0.00	-0.06	1.89	0.00
NiI ₂	-3.39	-4.62	-4.60	1.13	1.13	1.31	1.31	0.69	0.69	-0.30	7.10	0.28
NiO ₈ Re ₂	-1.26	-1.26	-1.28	-0.00	-0.00	-0.01	-0.01	-0.00	-0.01	0.01	0.03	-0.22
NiF ₄ Tl ₂	22.02	22.02	22.00	0.04	0.04	0.00	-0.00	-0.00	-0.00	0.39	0.34	-0.02
NiPS ₃	-4.10	-4.10	-4.12	-0.00	-0.00	-0.00	-0.00	-0.00	-0.00	1.05	29.49	0.05
NiPSe ₃	-3.69	-3.73	-3.80	0.03	0.03	-0.04	-0.04	0.07	0.07	-0.63	32.67	-0.12
VAgP ₂ Se ₆	-1.93	-1.93	-1.94	-0.27	0.26	-0.07	0.06	-0.17	0.17	0.10	0.07	-0.04
V1Cl ₂	7.01	7.01	7.01	-0.00	-0.00	0.00	0.00	0.00	0.00	0.13	0.27	-0.03
VBr ₂ O	4.48	4.48	4.48	0.00	-0.00	-0.00	-0.00	0.00	0.00	-0.14	-8.52	0.07
VBr ₂	12.26	12.26	12.27	-0.01	-0.01	0.01	0.01	-0.01	-0.01	7.78	0.17	-0.01
VF ₄	6.09	6.08	6.07	0.02	-0.02	0.30	-0.30	-0.22	0.22	0.13	0.25	-0.08
VI ₂	3.98	4.02	4.01	-0.04	-0.04	0.04	0.04	-0.07	-0.07	1.06	0.15	-0.02
VPS ₃	96.20	96.19	96.20	0.01	0.01	0.01	0.01	0.01	0.01	5.90	5.51	-0.03

Table A.1: Exchange parameters and SIA [meV], as directly produced by AMaRaNTA.

In the following, we provide quantities not directly produced by AMaRaNTA, yet easily obtained by simple post-processing of the code's direct output. Table A.2 shows the decomposition of the nearest-neighbour exchange tensor into the matrices $\underline{\underline{\mathbf{K}}}_{ij}$ and $\underline{\underline{\mathbf{D}}}_{ij}$, as introduced in Section 2.3 (only the independent matrix elements are reported).

Material	K_{xx}	K_{yy}	K_{zz}	K_{xy}	K_{xz}	K_{yz}	D_{xy}	D_{xz}	D_{yz}
CrBrO	0.00	0.00	-0.01	0.00	-0.01	0.00	0.00	0.00	0.00
CrBrS	-0.01	0.05	-0.04	-0.04	0.00	-0.00	0.02	0.26	-0.00
CrBr ₃	-0.01	0.05	-0.03	-0.03	0.05	-0.03	-0.05	-0.00	0.00
CrClO	-0.00	0.01	-0.01	-0.01	0.01	0.01	0.00	0.00	0.00
CrCl ₃	-0.00	0.01	-0.00	-0.00	0.00	0.01	-0.00	-0.00	-0.00
CrGeTe ₃	-0.07	0.38	-0.31	-0.30	0.04	0.04	-0.00	0.00	0.00
CrI ₃	-0.10	0.59	-0.49	-0.10	0.48	0.00	0.00	0.00	0.00
CrPS ₄	-0.00	0.00	-0.00	-0.00	-0.02	-0.01	-0.01	-0.01	0.00
CrSiSe ₃	-0.01	0.04	-0.03	-0.04	0.01	-0.02	0.00	0.00	0.00
CrSiTe ₃	0.56	-0.31	-0.25	0.01	0.12	0.00	0.00	0.00	0.00
MnO ₂	-0.01	0.01	-0.00	-0.02	0.03	0.02	0.00	-0.00	-0.00
MnBi ₂ Te ₄	-0.00	-0.09	0.09	0.02	-0.00	0.02	-0.00	-0.00	-0.00
MnBr ₂	0.00	0.00	-0.00	0.00	0.00	0.00	0.00	0.00	0.00
MnCl ₂	0.00	0.00	-0.00	0.00	0.00	0.00	0.00	0.00	0.00
MnI ₂	-0.00	0.02	-0.02	0.02	-0.01	-0.01	-0.00	-0.01	0.00
NiBr ₂	0.05	-0.04	-0.01	0.08	0.11	0.06	0.00	-0.00	0.00
NiCl ₂	-0.00	0.00	-0.00	-0.00	-0.00	-0.00	0.00	0.00	0.00
NiI ₂	0.28	0.82	-0.42	-0.40	1.13	1.31	0.69	0.00	0.01
NiO ₈ Re ₂	0.01	0.01	-0.02	0.01	-0.00	-0.01	0.00	0.00	0.00
NiF ₄ Tl ₂	0.00	-0.01	-0.01	0.00	0.04	-0.00	-0.00	0.00	0.01
NiPS ₃	0.01	0.00	-0.01	0.00	-0.00	-0.00	-0.00	0.00	0.00
NiPSe ₃	0.05	0.01	-0.06	0.03	-0.00	0.03	0.07	-0.00	-0.00
VAgP ₂ Se ₆	-0.00	-0.01	-0.01	-0.01	-0.27	-0.06	0.06	-0.17	0.17
VlCl ₂	-0.00	0.00	-0.00	-0.00	0.00	0.00	0.00	0.00	0.00
VBr ₂ O	0.00	-0.00	-0.00	-0.00	-0.00	0.00	0.00	0.00	0.00
VBr ₂	-0.01	-0.00	0.00	0.00	-0.01	-0.01	0.00	0.00	0.00
VF ₄	0.02	-0.00	-0.01	-0.00	0.30	-0.22	0.02	0.30	-0.22
VI ₂	-0.04	0.02	0.01	0.01	0.04	-0.07	-0.04	0.04	-0.07
VPS ₃	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.01	0.01

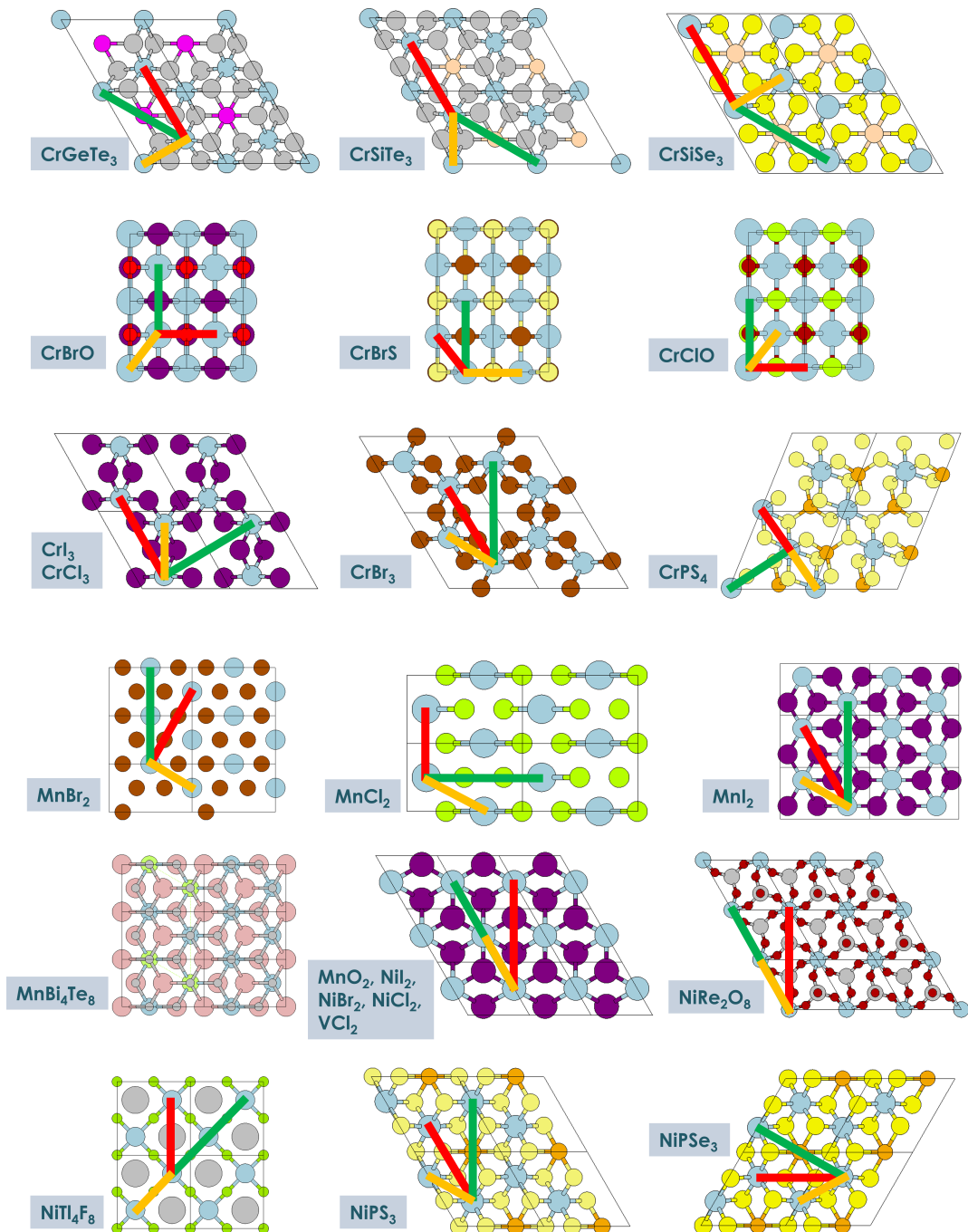
Table A.2: Decomposition of the nearest-neighbour exchange tensor into the matrices $\underline{\underline{\mathbf{K}}}_{ij}$ and $\underline{\underline{\mathbf{D}}}_{ij}$ [meV].

In Table A.3, we list some other useful quantities obtained after post-processing and discussed in Chapter 2.

Material	$J^{(1)}$	$\max(\underline{\mathbf{K}})/J^{(1)}$	$\text{avg}(\underline{\mathbf{K}})/J^{(1)}$	D	$\arctan(D/J^{(1)})$	$J^{(2)}/J^{(1)}$	$J^{(3)}/J^{(1)}$
CrBrO	-1.57	0.00	0.00	0.00	0.00	0.50	5.14
CrBrS	-6.52	0.01	0.00	0.26	0.04	1.49	1.43
CrBr ₃	-3.33	0.02	0.01	0.00	0.00	0.13	-0.07
CrClO	-1.57	0.01	0.00	0.00	0.00	0.50	4.72
CrCl ₃	-2.57	0.00	0.00	0.00	0.00	0.09	-0.08
CrGeTe ₃	-11.90	0.03	0.02	0.00	0.00	-0.01	0.09
CrI ₃	-3.73	0.16	0.07	0.00	0.00	0.22	0.10
CrPS ₄	-9.86	0.00	0.00	0.00	0.00	0.91	0.05
CrSiSe ₃	5.14	0.01	0.01	0.00	0.00	0.02	0.36
CrSiTe ₃	-10.85	0.05	0.02	0.00	0.00	0.01	0.08
MnO ₂	-3.12	0.01	0.00	0.00	0.00	0.11	0.70
MnBi ₂ Te ₄	-0.21	0.43	0.18	0.00	0.00	-1.53	-1.08
MnBr ₂	1.12	0.01	0.00	0.00	0.00	0.15	0.40
MnCl ₂	1.19	0.01	0.00	0.00	0.00	1.50	0.06
MnI ₂	0.91	0.02	0.01	0.00	0.00	0.37	0.74
NiBr ₂	-4.47	0.02	0.01	0.00	0.00	0.01	-0.74
NiCl ₂	-4.79	0.00	0.00	0.00	0.00	0.01	-0.39
NiI ₂	-4.20	0.31	0.19	0.00	0.00	0.07	-1.69
NiO ₈ Re ₂	-1.27	0.01	0.01	0.00	0.00	-0.01	-0.02
NiF ₄ Tl ₂	22.01	0.00	0.00	0.00	0.00	0.02	0.02
NiPS ₃	-4.10	0.00	0.00	0.00	0.00	-0.26	-7.19
NiPSe ₃	-3.74	0.02	0.01	0.00	0.00	-0.17	-8.73
VAgP ₂ Se ₆	-1.94	0.00	0.00	0.32	0.17	-0.05	-0.04
VICl ₂	7.01	0.00	0.00	0.00	0.00	0.02	0.04
VBr ₂ O	4.48	0.00	0.00	0.00	0.00	-0.03	-1.90
VBr ₂	12.27	0.00	0.00	0.00	0.00	0.63	0.01
VF ₄	6.08	0.00	0.00	0.37	0.06	0.02	0.04
VI ₂	4.00	0.02	0.01	0.00	0.00	0.26	0.04
VPS ₃	96.20	0.00	0.00	0.00	0.00	0.06	0.06

Table A.3: Remaining post-processing quantities: isotropic nearest-neighbour scalar parameter $J^{(1)}$ [meV], ratios $\max(\underline{\mathbf{K}})/J^{(1)}$ and $\text{avg}(\underline{\mathbf{K}})/J^{(1)}$ (discussed in Fig. 2.4 of the main text), length of the Dzyaloshinskii–Moriya vector D [meV] and angle $\arctan(D/J^{(1)})$ (discussed in Fig. 2.5 of the main text), ratios $J^{(2)}/J^{(1)}$ and $J^{(3)}/J^{(1)}$.

Finally, in Figure A.1, we depict our choices for the nearest-, second-nearest, and third-nearest-neighbour pairs.



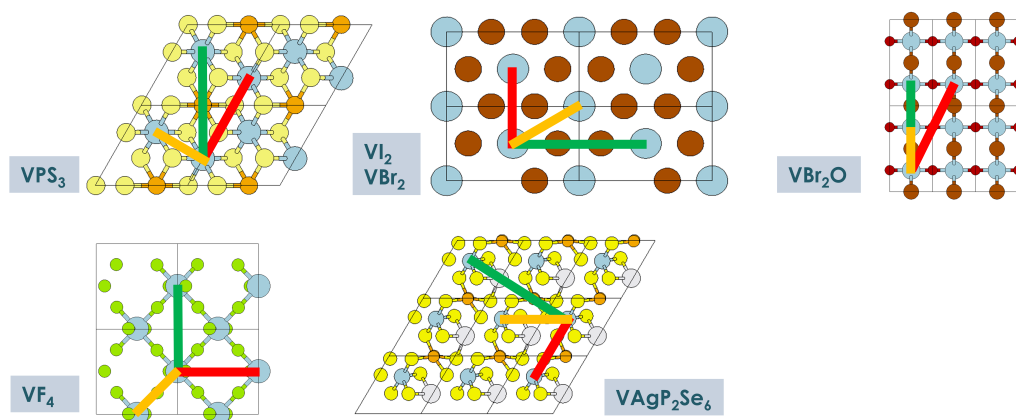


Figure A.1: Nearest- (yellow), second-nearest (red), and third-nearest (green) neighbour pairs adopted for the dataset. Materials with same lattice and same pair orientation have been grouped in a single panel.

Appendix B

Conventions for piezoelectric tensors

We report in the following, for the reader's convenience, the conventional shapes for the piezoelectric tensor $d_{\alpha\beta}$ (in Voigt notation) for some relevant point groups [322]. The mapping used for the stress tensor (see Section 3.3) is: $11 \rightarrow 1$, $22 \rightarrow 2$, $33 \rightarrow 3$, $23 \rightarrow 4$, $13 \rightarrow 5$, $12 \rightarrow 6$.

Tetragonal (point group $4mm$)

$$d_{\alpha\beta} = \begin{bmatrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & 0 & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{bmatrix} \quad (\text{B.1})$$

Orthorhombic (point group $mm2$)

$$d_{\alpha\beta} = \begin{bmatrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{24} & 0 & 0 \\ d_{31} & d_{32} & d_{33} & 0 & 0 & 0 \end{bmatrix} \quad (\text{B.2})$$

Monoclinic (point group m)

$$d_{\alpha\beta} = \begin{bmatrix} d_{11} & d_{12} & d_{13} & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{24} & 0 & d_{26} \\ d_{31} & d_{32} & d_{33} & 0 & d_{35} & 0 \end{bmatrix} \quad (\text{B.3})$$

Trigonal (point group $3m$)

$$d_{\alpha\beta} = \begin{bmatrix} 0 & 0 & 0 & 0 & d_{15} & d_{16} \\ d_{16} & -d_{16} & 0 & d_{15} & 0 & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{bmatrix} \quad (\text{B.4})$$

Triclinic (point group 1)

$$d_{\alpha\beta} = \begin{bmatrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\ d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36} \end{bmatrix} \quad (\text{B.5})$$

Appendix C

Manipulation of piezoelectric tensors

C.1 Rotations: general formalism

When studying properties expressed by tensors, it is now and then necessary to manipulate them under changes of reference frame. Among the most common operations are rotations, whether to express a piezoelectric tensor in a different crystal orientation, or to refer a magnetic exchange tensor to another atomic pair. However, while rotating low-rank tensors (vectors and matrices) is not something particularly obscure, the treatment of higher-rank tensors may be somewhat less intuitive. In the following, we therefore provide practical instructions for handling rotations of third- and fourth-rank tensors, with particular emphasis on piezoelectric and elastic tensors.

A generic rank- n tensor T transforms under an (active) rotation A as

$$T'_{i_1 i_2 \dots i_n} = A_{i_1 j_1} A_{i_2 j_2} \dots A_{i_n j_n} T_{j_1 j_2 \dots j_n} \quad (\text{C.1})$$

This transformation law can be specialised to

- rank-1 tensors (vectors), as $V'_i = A_{ij} V_j$
- rank-2 tensors (matrices), as $M'_{ij} = A_{ik} A_{jl} M_{kl}$
- rank-3 tensors, as $T'_{ijk} = A_{ip} A_{jq} A_{kr} T_{pqr}$

and so forth (the Einstein summation convention is implicitly assumed throughout).

The procedure required to rotate, for instance, a third-rank piezoelectric tensor $d_{\alpha\beta}$, expressed in Voigt notation, would then consist in

1. “unwrapping” $d_{\alpha\beta}$ into the extended form d_{ijk}
2. applying the third-rank tensor rotation formula $d'_{ijk} = A_{ip} A_{jq} A_{kr} d_{pqr}$
3. “refolding” the rotated tensor into the Voigt form $d'_{\alpha\beta}$.

This direct approach is already sufficient for the task, but we also provide an alternative formulation, known as the *Bond formalism* [366], whose central idea is to introduce effective

rotation matrices that act directly on Voigt-contracted tensors. Since the Bond approach is most transparently illustrated for fourth-rank tensors, we first apply it to elastic tensors, specialising it to third-rank piezoelectric tensors immediately afterwards.

First off, as an instructive exercise, we explicitly derive the rotation law for fourth-rank elastic tensors in their extended (non-Voigt) form. From Section 3.3, we recall

$$\begin{aligned}\sigma_{ij} &= C_{ijkl}\eta_{kl} \\ \eta_{ij} &= S_{ijkl}\sigma_{kl}\end{aligned}\tag{C.2}$$

where σ_{ij} is the stress, η_{ij} the strain, C_{ijkl} the elastic stiffness and S_{ijkl} the elastic compliance, the last two being the inverse of one another: $C_{ijkl} = (S^{-1})_{ijkl}$.

Under a rotation A_{ij} , stress and strain – both second-rank tensors – transform as

$$\begin{aligned}\sigma'_{mn} &= A_{mi}A_{nj}\sigma_{ij} \\ \eta'_{op} &= A_{ok}A_{pl}\eta_{kl}\end{aligned}\tag{C.3}$$

We seek rotated tensors C' and S' such that the constitutive relations C.2 maintain their formal structure in the rotated frame; in other words, such that

$$\begin{aligned}\sigma'_{mn} &= C'_{mnop}\eta'_{op} \\ \eta'_{mn} &= S'_{mnop}\sigma'_{op}\end{aligned}\tag{C.4}$$

From C.2 and C.3,

$$\sigma'_{mn} = A_{mi}A_{nj}\sigma_{ij} = A_{mi}A_{nj}C_{ijkl}\eta_{kl}\tag{C.5}$$

But since $\eta_{kl} = (A^{-1})_{ko}(A^{-1})_{lp}\eta'_{op} = A_{ok}A_{pl}\eta'_{op}$, then

$$\sigma'_{mn} = A_{mi}A_{nj}C_{ijkl}\eta_{kl} = A_{mi}A_{nj}C_{ijkl}A_{ok}A_{pl}\eta'_{op}\tag{C.6}$$

which is precisely the desired mapping C.4 for the stress tensor. Applying an analogous procedure to the strain, we end up with

$$\boxed{\begin{aligned}C'_{mnop} &= A_{mi}A_{nj}A_{ok}A_{pl}C_{ijkl} \\ S'_{mnop} &= A_{mi}A_{nj}A_{ok}A_{pl}S_{ijkl}\end{aligned}}\tag{C.7}$$

i.e., none other than realisations of the general formula C.1, as expected.

We now turn to the Voigt-contracted representation. In this framework, stress and strain are six-component vectors and therefore their transformation under rotations no longer follows the second-rank tensor rule, as in C.3, but rather

$$\begin{aligned}\sigma'_\alpha &= M_{\alpha\beta}\sigma_\beta \\ \eta'_\alpha &= N_{\alpha\beta}\eta_\beta\end{aligned}\tag{C.8}$$

where M, N are suitable 6×6 generalised rotation matrices.¹

¹ M and N do not necessarily have unit determinant.

Explicit expressions for the Bond matrices in terms of the rotation matrix A are

$$M = \begin{bmatrix} A_{xx}^2 & A_{xy}^2 & A_{xz}^2 & 2A_{xy}A_{xz} & 2A_{xz}A_{xx} & 2A_{xx}A_{xy} \\ A_{yx}^2 & A_{yy}^2 & A_{yz}^2 & 2A_{yy}A_{yz} & 2A_{yz}A_{yx} & 2A_{yx}A_{yy} \\ A_{zx}^2 & A_{zy}^2 & A_{zz}^2 & 2A_{zy}A_{zz} & 2A_{zz}A_{zx} & 2A_{zx}A_{zy} \\ A_{yx}A_{zx} & A_{yy}A_{zy} & A_{yz}A_{zz} & A_{yy}A_{zz} + A_{yz}A_{zy} & A_{yx}A_{zz} + A_{yz}A_{zx} & A_{yy}A_{zx} + A_{yx}A_{zy} \\ A_{zx}A_{xx} & A_{zy}A_{xy} & A_{zz}A_{xz} & A_{xy}A_{zz} + A_{xz}A_{zy} & A_{xz}A_{xx} + A_{xx}A_{zz} & A_{xx}A_{zy} + A_{xy}A_{zx} \\ A_{xx}A_{yx} & A_{xy}A_{yy} & A_{xz}A_{yz} & A_{xy}A_{yz} + A_{xz}A_{yy} & A_{xz}A_{yx} + A_{xx}A_{yz} & A_{xx}A_{yy} + A_{xy}A_{yx} \end{bmatrix} \quad (C.9)$$

$$N = \begin{bmatrix} A_{xx}^2 & A_{xy}^2 & A_{xz}^2 & A_{xy}A_{xz} & A_{xz}A_{xx} & A_{xx}A_{xy} \\ A_{yx}^2 & A_{yy}^2 & A_{yz}^2 & A_{yy}A_{yz} & A_{yz}A_{yx} & A_{yx}A_{yy} \\ A_{zx}^2 & A_{zy}^2 & A_{zz}^2 & A_{zy}A_{zz} & A_{zz}A_{zx} & A_{zx}A_{zy} \\ 2A_{yx}A_{zx} & 2A_{yy}A_{zy} & 2A_{yz}A_{zz} & A_{yy}A_{zz} + A_{yz}A_{zy} & A_{yx}A_{zz} + A_{yz}A_{zx} & A_{yy}A_{zx} + A_{yx}A_{zy} \\ 2A_{zx}A_{xx} & 2A_{zy}A_{xy} & 2A_{zz}A_{xz} & A_{xy}A_{zz} + A_{xz}A_{zy} & A_{xz}A_{xx} + A_{xx}A_{zz} & A_{xx}A_{zy} + A_{xy}A_{zx} \\ 2A_{xx}A_{yx} & 2A_{xy}A_{yy} & 2A_{xz}A_{yz} & A_{xy}A_{yz} + A_{xz}A_{yy} & A_{xz}A_{yx} + A_{xx}A_{yz} & A_{xx}A_{yy} + A_{xy}A_{yx} \end{bmatrix}$$

with the two related as $N^{-1} = M^T$.

By means of these matrices, we can now state the Voigt-contracted analogue of Eqns. C.7 as

$$\begin{cases} C'_{\gamma\delta} = M_{\gamma\alpha}M_{\delta\beta}C_{\alpha\beta} \\ S'_{\gamma\delta} = N_{\gamma\alpha}N_{\delta\beta}S_{\alpha\beta} \end{cases} \quad (C.10)$$

or, in compact form: $C' = MCM^T$, $S' = NSN^T$. In practical terms, two applications of the physical rotation matrix in the extended formulation C.7 correspond to a single application of the Bond matrix M or N in the Voigt-contracted framework C.10.

Finally, we adapt this formalism to the third-rank piezoelectric tensor $d_{\alpha\beta}$, whose transformation under rotation reads, in extended form,

$$d'_{mno} = A_{mi}A_{nj}A_{ok}d_{ijk} \quad (C.11)$$

Since an odd number of rotation matrices is involved herein, the Voigt-contracted expression necessarily contains both one of these and a Bond matrix. Accordingly, we find

$$d'_{\gamma\delta} = A_{\gamma\alpha}(M^{-1})_{\delta\beta}d_{\alpha\beta} = A_{\gamma\alpha}N_{\delta\beta}^Td_{\alpha\beta} \quad (C.12)$$

or, in compact form: $d' = AdM^{-1} = AdN^T$.²

The rotation procedure then simply consists in encoding the Bond matrices and applying Eqn. C.12. We conclude with a final, important remark, though: *all expressions derived above assume the conventional Voigt ordering* (see Section 3.3). If one operates on tensors with a different column arrangement, such as those produced by VASP, it is essential to first restore the conventional Voigt ordering before implementing the rotation procedure. Rotated tensors can be reordered again afterwards, if a direct comparison with the original output format is needed.

²Here, α and β span different ranges depending on the term: A is 3×3 , M is 6×6 and d is 3×6 .

C.2 Explicit transformation in selected cases

Sometimes, when the considered operation is particularly simple – such as a 90° rotations around a Cartesian axis, or a reflection with respect to a Cartesian axis or plane – the effect on a tensor can be understood directly pen-on-paper, without necessarily having to implement the general formalism above, by changing the signs of selected components and/or by swapping rows and columns, in accordance with the transformation. For the reader's convenience, we report below a few paradigmatic examples worked out explicitly.

As a starting point, we consider the most general piezoelectric tensor, in Voigt-contracted form

$$d_{\alpha\beta} = \begin{array}{c|cccccc} & xx & yy & zz & xy & yz & zx \\ \hline x & d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ y & d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\ z & d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36} \end{array}$$

where we have explicitly indicated the labels for the polarisation components (rows, lower case) and the stress components (columns, upper case). Note that, herein, we switch to the VASP convention for the ordering of shear components, since the transformations discussed here were originally carried out explicitly as exercises within our practice with VASP tensors. The general rules outlined below, however, can be straightforwardly applied within any Voigt convention.

Reflection across an axis

To start with, we consider a reflection with respect to the $\hat{z}$ axis, i.e., the transformation

$$M_z : \begin{cases} x \rightarrow x \\ y \rightarrow y \\ z \rightarrow -z \end{cases} \quad (\text{C.13})$$

We outline, in this case, the step-by-step procedure, following the approach we have found most instructive from a pedagogical standpoint. This particular transformation does not interchange coordinates, but simply introduces sign changes. We begin by identifying rows in which the index z appears an odd number of times, which in this case occurs only for the third row, and change the sign of the label accordingly:

$$\begin{array}{c|cccccc} & xx & yy & zz & xy & yz & zx \\ \hline x & d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ y & d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\ -z & d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36} \end{array}$$

Since we wish to ultimately restore the original row labelling, we absorb the minus sign from the z label into the tensor components and change sign to the whole third row:

	xx	yy	zz	xy	yz	zx
x	d_{11}	d_{12}	d_{13}	d_{14}	d_{15}	d_{16}
y	d_{21}	d_{22}	d_{23}	d_{24}	d_{25}	d_{26}
z	$-d_{31}$	$-d_{32}$	$-d_{33}$	$-d_{34}$	$-d_{35}$	$-d_{36}$

We now turn to the columns. As for the rows, we change the sign of any column whose label contains the index z an odd number of times (the zz column, for example, is invariant under this operation, since z appears twice):

	xx	yy	zz	xy	$-yz$	$-zx$
x	d_{11}	d_{12}	d_{13}	d_{14}	d_{15}	d_{16}
y	d_{21}	d_{22}	d_{23}	d_{24}	d_{25}	d_{26}
z	$-d_{31}$	$-d_{32}$	$-d_{33}$	$-d_{34}$	$-d_{35}$	$-d_{36}$

Finally, by absorbing the minus signs in columns $-yz$ and $-zx$ into the corresponding tensor components, we obtain

$d_{\alpha\beta}^{M_z} =$		xx	yy	zz	xy	yz	zx
	x	d_{11}	d_{12}	d_{13}	d_{14}	$-d_{15}$	$-d_{16}$
	y	d_{21}	d_{22}	d_{23}	d_{24}	$-d_{25}$	$-d_{26}$
	z	$-d_{31}$	$-d_{32}$	$-d_{33}$	$-d_{34}$	d_{35}	d_{36}

We may thus state the general rule: *a reflection with respect to a Cartesian axis $\hat{k}$ changes the sign of all tensor components whose indices contain $\hat{k}$ an odd number of times (i.e., either 1, or 3).*

Reflection across a plane

Let us now consider a reflection with respect to the $\hat{x}y$ plane, i.e., the transformation

$$M_{xy} : \begin{cases} x \rightarrow -x \\ y \rightarrow -y \\ z \rightarrow z \end{cases} \quad (\text{C.14})$$

Following the same logic, we obtain the transformed tensor

$d_{\alpha\beta}^{M_{xy}} =$		xx	yy	zz	xy	yz	zx
	x	$-d_{11}$	$-d_{12}$	$-d_{13}$	$-d_{14}$	d_{15}	d_{16}
	y	$-d_{21}$	$-d_{22}$	$-d_{23}$	$-d_{24}$	d_{25}	d_{26}
	z	d_{31}	d_{32}	d_{33}	d_{34}	$-d_{35}$	$-d_{36}$

according to the following rule: *a reflection with respect to the $\hat{i}\hat{j}$ plane changes the sign of all tensor components whose indices contain the remaining coordinate $\hat{k}$ an even number of times (i.e., either 0, or 2).*

Inversion

The inversion operation (point reflection about the origin)

$$M_{xyz} : \begin{cases} x \rightarrow -x \\ y \rightarrow -y \\ z \rightarrow -z \end{cases} \quad (\text{C.15})$$

yields, as expected, a global change of sign:

$d_{\alpha\beta}^{M_{xyz}}$	=		xx	yy	zz	xy	yz	zx
		x	$-d_{11}$	$-d_{12}$	$-d_{13}$	$-d_{14}$	$-d_{15}$	$-d_{16}$
		y	$-d_{21}$	$-d_{22}$	$-d_{23}$	$-d_{24}$	$-d_{25}$	$-d_{26}$
		z	$-d_{31}$	$-d_{32}$	$-d_{33}$	$-d_{34}$	$-d_{35}$	$-d_{36}$

90° rotations around $\hat{y}$

Rotations are slightly more elaborate, as they generally involve permutations of rows and columns and sign changes together. We consider for instance $\pm 90^\circ$ rotations around $\hat{y}$:

$$R_y(90^\circ) : \begin{cases} x \rightarrow -z \\ y \rightarrow y \\ z \rightarrow x \end{cases} \quad R_y(-90^\circ) : \begin{cases} x \rightarrow z \\ y \rightarrow y \\ z \rightarrow -x \end{cases} \quad (\text{C.16})$$

Let us work out the procedure step by step for the clockwise rotation ($+90^\circ$, with $\hat{y}$ pointing into the page). We first operate on rows by applying the transformation rules to the x and z labels:

	xx	yy	zz	xy	yz	zx
$-z$	d_{11}	d_{12}	d_{13}	d_{14}	d_{15}	d_{16}
y	d_{21}	d_{22}	d_{23}	d_{24}	d_{25}	d_{26}
x	d_{31}	d_{32}	d_{33}	d_{34}	d_{35}	d_{36}

Then, we reorder the rows, absorbing the minus sign inside the tensor:

	xx	yy	zz	xy	yz	zx
x	d_{31}	d_{32}	d_{33}	d_{34}	d_{35}	d_{36}
y	d_{21}	d_{22}	d_{23}	d_{24}	d_{25}	d_{26}
z	$-d_{11}$	$-d_{12}$	$-d_{13}$	$-d_{14}$	$-d_{15}$	$-d_{16}$

We now perform swaps and sign changes to the column labels (observe that, due to the stress tensor symmetry, $-zy = -yz$ and $yx = xy$):

	zz	yy	xx	$-yz$	xy	$-zx$
x	d_{31}	d_{32}	d_{33}	d_{34}	d_{35}	d_{36}
y	d_{21}	d_{22}	d_{23}	d_{24}	d_{25}	d_{26}
z	$-d_{11}$	$-d_{12}$	$-d_{13}$	$-d_{14}$	$-d_{15}$	$-d_{16}$

Finally, we reorder the columns according to our convention and absorb minus signs inside the tensor:

		xx	yy	zz	xy	yz	zx
$d_{\alpha\beta}^{R_y(90^\circ)}$	x	d_{33}	d_{32}	d_{31}	d_{35}	$-d_{34}$	$-d_{36}$
	y	d_{23}	d_{22}	d_{21}	d_{25}	$-d_{24}$	$-d_{26}$
	z	$-d_{13}$	$-d_{12}$	$-d_{11}$	$-d_{15}$	d_{14}	d_{16}

For completeness, we report, without explicit derivation, the result for the corresponding counter-clockwise rotation:

		xx	yy	zz	xy	yz	zx
$d_{\alpha\beta}^{R_y(-90^\circ)}$	x	$-d_{33}$	$-d_{32}$	$-d_{31}$	d_{35}	$-d_{34}$	d_{36}
	y	d_{23}	d_{22}	d_{21}	$-d_{25}$	d_{24}	$-d_{26}$
	z	d_{13}	d_{12}	d_{11}	$-d_{15}$	d_{14}	$-d_{16}$

90° rotation around $\hat{x}$

For $\pm 90^\circ$ rotations around $\hat{x}$

$$R_x(90^\circ) : \begin{cases} x \rightarrow x \\ y \rightarrow z \\ z \rightarrow -y \end{cases} \quad R_x(-90^\circ) : \begin{cases} x \rightarrow x \\ y \rightarrow -z \\ z \rightarrow y \end{cases} \quad (\text{C.17})$$

one finds

		xx	yy	zz	xy	yz	zx
$d_{\alpha\beta}^{R_x(90^\circ)}$	x	d_{11}	d_{13}	d_{12}	$-d_{16}$	$-d_{15}$	d_{14}
	y	$-d_{31}$	$-d_{33}$	$-d_{32}$	d_{36}	d_{35}	$-d_{34}$
	z	d_{21}	d_{23}	d_{22}	$-d_{26}$	$-d_{25}$	d_{24}
		xx	yy	zz	xy	yz	zx
$d_{\alpha\beta}^{R_x(-90^\circ)}$	x	d_{11}	d_{13}	d_{12}	d_{16}	$-d_{15}$	$-d_{14}$
	y	d_{31}	d_{33}	d_{32}	d_{36}	$-d_{35}$	$-d_{34}$
	z	$-d_{21}$	$-d_{23}$	$-d_{22}$	$-d_{26}$	d_{25}	d_{24}

90° rotation around $\hat{z}$

Finally, for $\pm 90^\circ$ rotations around $\hat{z}$

$$R_z(90^\circ) : \begin{cases} x \rightarrow y \\ y \rightarrow -x \\ z \rightarrow z \end{cases} \quad R_z(-90^\circ) : \begin{cases} x \rightarrow -y \\ y \rightarrow x \\ z \rightarrow z \end{cases} \quad (\text{C.18})$$

one has

$d_{\alpha\beta}^{R_z(90^\circ)} =$			xx	yy	zz	xy	yz	zx
		x	$-d_{22}$	$-d_{21}$	$-d_{23}$	d_{24}	$-d_{26}$	d_{25}
		y	d_{12}	d_{11}	d_{13}	$-d_{14}$	d_{16}	$-d_{15}$
		z	d_{32}	d_{31}	d_{33}	$-d_{34}$	d_{36}	$-d_{35}$
$d_{\alpha\beta}^{R_z(-90^\circ)} =$			xx	yy	zz	xy	yz	zx
		x	d_{22}	d_{21}	d_{23}	$-d_{24}$	$-d_{26}$	d_{25}
		y	$-d_{12}$	$-d_{11}$	$-d_{13}$	d_{14}	d_{16}	$-d_{15}$
		z	d_{32}	d_{31}	d_{33}	$-d_{34}$	$-d_{36}$	d_{35}

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