

#### Computational study of multiferroic materials

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Publication date: 2023

Document Version Publisher's PDF, also known as Version of record

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*Citation (APA):* Kruse, M. (2023). *Computational study of multiferroic materials*. Department of Physics, Technical University of Denmark.

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**DTU Physics** Department of Physics

Ph.D. Thesis

## Computational study of multiferroic materials

Mads Kruse, March 2023



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**DTU Physics** Department of Physics

Ph.D. Thesis

# Computational study of multiferroic materials

Mads Kruse

Kongens Lyngby, 2023

#### Computational study of multiferroic materials

Ph.D. Thesis Mads Kruse March 31st, 2023

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- Cover: The three degenerate groundstates of the magnetoelectric multiferroic VAgP<sub>2</sub>Se<sub>6</sub>, found in [I]. The red arrows indicates directions of the spontaneous polarization.

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## Preface

This thesis is submitted in candidacy for a Ph.D. degree in Physics from the Technical University of Denmark (DTU). The Ph.D project was carried out at the Center for Atomic-scale Materials Design (CAMD) at the DTU Department of Physics between January 2020 and March 2023. The project was supervised by Main Supervisor Associate Professor Thomas Olsen and Supervisor Associate Professor Hugh Simons. The research conducted in this thesis was funded by the Danish Independent Research Foundation, Grant number 9040-00269B.

Ann Mur

Mads Kruse Kongens Lyngby, March 31st, 2023

## Abstract

This thesis examines computational approaches to finding novel multiferroic materials in two dimensions. Ferroic materials are characterized by the presence of at least one type of primary ferroic order such as ferromagnetism, ferroelectricity or ferroelasticity. Multiferroics on the other hand contain at least two of these orders simultaneously. This feature has lead to a surge of interest in recent years, from researchers trying to understand the fundamental mechanisms that drive multiferroism. In addition there has been speculation that these materials could potential have various technological applications.

The relevant theoretical framework for understanding the properties of materials is quantum mechanics. This thesis applies density functional theory (DFT), a quantum mechanical computational method that has proven very useful for investigating the electronic structure of solids as well as a variety of condensed phases. Density functional theory is applied in conjunction with the modern theory of polarization to compute the spontaneous polarization in ferroelectric materials from first-principles. This method is applied in order to systematically screen databases for potential ferroelectric candidates. This is achieved by applying high-throughput frameworks that allows researchers to automate a large part of the computational process. The main result presented is a screening for novel two dimensional ferroelectric materials. Spontaneous polarizations are computed for identified ferroelectric candidates. Further analysis includes a thermodynamic classification using phonons as well as computations of upper bounds on coercive electric fields. The identified ferroelectric materials include previously known materials as well as novel ones that will likely be the subject of future investigation.

In addition recent results obtained for the Computational 2D materials database (C2DB) are presented, with an emphasis on the addition of electric polarizations. The thesis also briefly covers a computational study of the formation of charged domain walls due to oxygen vacancies in  $BaTiO_3$ . Our results indicate that the vacancies are not only stabilizing agents for the negatively charged walls, but are also critical in order to explain how these are formed in the first place.

A chapter of this thesis deals with the anomalous Hall effect in metallic magnets. The chapter covers the necessary theoretical background specifically linear response theory. Benchmark calculations are performed using an implementation of the anomalous Hall conductivity into the DFT code GPAW. The results indicate good agreement with literature in some cases, but is inconclusive in some scenarios. It is concluded that adaptive refinement of k-point grids are necessary in order to conclusively demonstrate the accuracy of the implemented code.

## Resumé

Denne afhandling undersøger beregningsmæssige tilgange til at opdage nye multiferroiske materialer i to dimensioner. Ferroiske materialer er karakteriseret ved tilstedeværelsen af mindst én type af primær ferroisk orden, såsom ferromagnetisme, ferroelektricitet eller ferroelasticitet. Multiferroiske materialer indeholder mindst two af disse typer af orderden samtidigt. Denne egenskab har ført til en bølge af interesse i de senere år, fra forskere, der forsøger at forstå de grundlæggende mekanismer, der driver multiferroisme. Derudover har der været spekulationer om, at disse materialer potentielt kunne have forskellige teknologiske anvendelser. Fokus i denne afhandling er specifikt todimensionelle multiferroiske materialer.

Det relevante teoretiske værktøj til at forstå materialers egenskaber er kvantemekanik. Denne afhandling anvender tæthedsfunktional teori, en kvantemekanisk beregningsmetode der har vist sig at være meget brugbar i forbindelse med at bestemme den elektroniske struktur i materialer og ligeledes i adskellige kondenserede faser. Tæthedsfunktional teori er anvendt sammen med den moderne teori for polarisation til at beregne den spontane polarization i ferroelektriske materialer fra første principper. Denne metode bliver anvendt til systematisk at screene databaser for nye potentielle ferroelektriske kandidater. Dette opnås ved anvendelse af såkaldte high-throughput metoder der tillader forskere at automatisere en stor del af den beregningsmæssige proces. Det primære resultat som præsenteres er et screening-studie af nye todimensionelle ferroelektriske materialer. Spontane polarisationer beregnes for identificerede kandidater. Yderligere analyse inkludere en termodynamisk classification ved brug af fonon beregninger såvel som beregninger af øvre bånd på elektriske koersivfelter. De identificerede materialer inkluderer tidligere kendte materialer såvel som nye materialer der formentlig vil blive undersøgt nærmere i fremtiden.

Derudover præsenteres nyligt fundne resultater fra databasen Computational 2D materials database (C2DB), hvor der særligt er lagt vægt på de fundne polarizationer. Afhandlingen dækker også kort et beregningsmæssigt studie af formationen af ladede domænevægge med manglende ilt atomer i BaTiO<sub>3</sub>. Vores resultater indikerer at manglende ilt atomer ikke bare har en stabiliserende effekt på negativt ladede vægge, men også forklare hvorfor disse opstår til at starte med.

Et kapitel i denne afhandling omhandler den anomale Hall effect i metalliske magneter. Kapitlet dækker den nødvendige teoretiske viden specifikt lineær respons teori. Benchmark beregninger er blevet udført ved brug af en implementering af den anomale Hall ledningsevne i computer koden GPAW. Resultaterne indikerer en god overenstemmelse med tidligere fundne resultater i nogle områder. Resultaterne er dog inkonklusive i nogle tilfælde. Det konkluderes at en adaptiv refinering af k-punkts gittre er nødvendig for endegyldigt at demonstrere nøjagtigheden af den implementerede kode.

## Acknowledgements

It is my name that is displayed on the cover of this thesis. But the truth is that I probably would have never made it this far without help from a range of extraordinary people. First I would like to thank my supervisor Thomas Olsen for his guidance and during the last three years. Your enthusiasm for physics is infectious and your support has been never wavering, even when things were not progressing as planned.

I would like to thank Prof. Ivo Souza for hosting me at CFM during the spring of 2022. I have benefited greatly from our many discussions and I was meet with hospitality from everyone at the center from day one so thank you. I would also like to thank Cheol-Hwan, Ronen, Julen, and Stepan for greet company during lunch.

Thanks to Ole for the great work you have done maintaining Niflheim hardware and for the entertaining anecdotes ranging from your time as a postdoc at Stanford to smuggling software through books during the cold war. Thanks to JJ and Ask for assistance with ASR, GPAW and all the countless questions I have bothered you with over the years. I owe you guys a beer. Thanks to Bettina and Lone for assistance with the countless number of administrative tasks. Such tasks might seem trivial to some people, but being an absentminded person I would have no doubt forgotten to fill out a document or violated some university guideline without knowing it, so thank you.

Doing research is hard, but I have been lucky enough to have fantastic colleagues in my time at CAMD. I would therefore like to thank all the current and previous Ph.d. students and Postdocs from the group, they are: Alireza, Anders, Asbjørn, Ask, Casper, Cuauhtémoc, Estefanía, Fabian, Frederik, Fredrik, Hadeel, Jens Jørgen, Jiban, Joachim, Julian, Luca, Mark, Martin, Matthew, Mikael, Morten, Nikolaj, Peder, Peter, Sajid, Sami, Simone, Stefano, Tara, Thorbjørn, Urko. I am going to miss all of our interesting discussions on anything from using Brazilian forest frogs as pregnancy detectors to debates on whether we should white tigers to guard our doors. I say interesting discussion because I doubt that my future colleagues will be as entertaining.

To the guys in office 209, thank you for providing me with such great company in the last three years. I am going to miss the office atmosphere, the various shenanigans not to mentioned being "fired" on a daily basis (talk about a hostile work environment).

A special thanks to my friends and family for support in the last three years. I say last three years but the truth is your have been supportive always.

Thanks to Kasper for being a great friend and roommate. Looking back on the COVID-19 lockdowns I am not sure how I made it through without going insane. But I would like to think you had an enormous influence. Now that the bars are open and I have more time on my hands maybe we can continue our quest for the best beer in

Copenhagen.

Kathrine, Maria, Hans and Britta you have been like a second family to me. Life is not always easy, but your door has always been open for me and for that I am very grateful.

Thank you Jakob for being a great brother. You often believe in me more than I do myself. We have had our fair share of sibling rivalry over the years but I have always you to be very supportive. Now that I have officially signed up for half marathon in September it is time bring back that competitive spirit!

Finally I would like to thank my mother. You have always supported and encouraged me to follow my dreams. I am immensely grateful for everything that you have done for me and I am very proud to be your son.

## List of Publications

M. Kruse, U. Petralanda, M. N. Gjerding, K. W. Jacobsen, K. S. Thygesen, T. Olsen
 "Two-dimensional ferroelectrics from high throughput computational screening" npj Computational Materials volume 9, Article number: 45 (2023).

Printed in copy from page 68.

[II] M. Gjerding, A. Taghizadeh, A. Rasmussen, S. Ali, F. Bertoldo, T. Deilmann, N. R. Knøsgaard, <u>M. Kruse</u>, A. H. Larsen, S. Manti, T. G. Pedersen, U. Petralanda, T. Skovhus, M. K. Svendsen, J. J. Mortensen, T. Olsen and K. S. Thygesen, "Recent Progress of the Computational 2D Materials Database (C2DB)"

2D Mater. 2021, **8**, 044002.

Printed in copy from page 86.

 [III] U. Petralanda, <u>M. Kruse</u>, H. Simons, and T. Olsen, "Oxygen Vacancies Nucleate Charged Domain Walls in Ferroelectrics" Phys. Rev. Lett. (2021), **127**, 117601.

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## CHAPTER

# Introduction

The word technology has in the 21st century largely become synonymous with information technology. If one looks at the development in society over the last 50 years it quickly becomes apparent why this is the case. Most people in the developed world owns an smartphone, a personal computer and likely some other electronic device. These new technologies have been made possible by the development in quantum mechanics by physicists in the first half of the 20th century. Perhaps the most famous example being the invention of the transistor[1]. The impact of this invention alone is well summarized by Moore's law which back in 1965 predicted that the number of transistors in an integrated circuit would double every two years [2]. So far, it has held up quite well and today computers form the basis for information technology [3]. Transistors are like all electronic components build from materials, specifically semiconductors.

Electronic components however, are just one example of the role that materials have played in shaping modern human societies. In fact a lot of progress through human history have been driven by advances in the applications of materials. So much so, that historians have named entire epochs after the materials that played the most significant role in the relevant time period [4]. When the history books of the future are written our era may well be characterized as the silicon age due to the significance it has played as a building block for the electronic components used in computers.

In spite of all the discoveries made so far, material science is hardly a dead discipline. According to the American Physical Society (APS) the majority of its members identify as solid state or condensed matter physicists [5]. Scientists are still discovering new phenomena as well as new materials. One example of which is the discovery of multiferroics, materials that exhibit several blends of ferroic order at the same time. The most famous examples are ferromagnetism, ferroelectricity, ferroelasticity. While many examples of these types of ferroics are known, it is far less common to find materials that posses several types simultaneously. For a long time the number of known multiferroic materials was small, and only few papers had been published within this area [6]. From 1960 to 1980 less than 20 papers were published a year, by 2000 the number was close to 50 and in 2005 about 100 papers were published a year[7]. Over the last 20 years the interest in the field as well as the number of materials found has increased significantly.

Besides a fundamental interest in this new family of materials, multiferroics may turn out to offer unique applications in a variety of different technologies. Because one can utilize the properties of several types of ferroic order using the same material, it may be possible to design new technologies that utilize the advantages of each material property while circumventing any potential disadvantage. Perhaps the most prominent example is within the world of computing where a non-volatile, low energy memory has long been sought after. For example ferroelectrics can be used to write information using small voltages which are convenient and have a low energy consumption. Ferromagnets store information in magnetic degrees of freedom, which can be read without destroying any written information. A material that posses both properties, can store and read information using electric- and magnetic fields respectively.

Other potential applications of multiferroics include: as platforms for neuromorphic computing [8], new forms of field effect transistors and logical gates within computing[9–12], as potential catalysts[13, 14], as antennas[15] and new forms of photovoltaic devices[16]. Recently is has even been proposed that there may be similarities between phenomena in multiferroics and those found in the cosmology of the early universe [17, 18].

The aim of this thesis is to search for new multiferroics, specificially those found in two dimensions. These are materials that exist down to thickness of one atomic layer. This a research field that, like multiferroics has grown rapidly in the last two decades. It all started around 2004 when it was discovered that graphene could be exfoliated from graphite using scotch tape[19]. Since then many other examples have been found. In 2017, magnetism was observed in the two dimensional material  $CrI_3$ [20]. Two dimensional ferroelectrics have also both been predicted theoretically [21–29] and observed experimentally [30-36]. In this work the focus has been to predict new potential material candidates using first-principle methods. That means using basic tenets of quantum mechanics that govern the laws of electrons and atoms without relying on specific empirical data or constructing specific models based on approximations or assumptions. The framework being used is density functional theory (DFT). This computational method is used in conjunction with various theoretical methods and frameworks that are applied to investigate the different topics covered in the thesis. All figures presented are either made by the author or reprinted from one of the publications with permission from the author(s).

## 1.1 Outline

The thesis is structured as follows:

- Chapter 2 gives an overview of the various forms of primary ferroic orders, as well as multiferroics. The emphasis of the chapter is on the ferroelectricity and ferromagnetism since these are the type of ferroic order most central to this thesis. Towards the end of the chapter domains, and domain walls are briefly discussed, with an emphasis on ferroelectrics as it applies to the work done in [III].
- Chapter 3 introduces density functional theory (DFT) as a central tool in materials science. The chapter goes on to cover the most basic elements of density functional theory like the Hohenberg-Kohn theorems, the Kohn-Sham equations and exchange correlation functionals. Finally additional extensions spin-orbit coupling and DFT + U are also discussed.

- Chapter 4 shortly introduces the concept of high-throughput methods in materials science, as it applies to paper [I]. The utility of high throughput frameworks and databases are discussed and relevant examples are given.
- Chapter 5 explains the modern theory of polarization, and how it is used for ab initio calculations. The chapter covers the fallacies of Claussius-Mosetti picture of polarization, the berry phase and the adiabatic theorem. It is also discussed how to compute polarizations in practice. Furthermore related topics like the Born effective charge tensor, and ferroelectric metals are also discussed. These topics form the basis for understanding the work done in papers [I] and [III].
- Chapter 6 summarizes the work done in the publications [I]-[III]. The emphasis of each section is not to describe each paper in detail, but rather to give an overview of the motivation, method and results of each work. The necessary background information is covered in chapters 2-5, and the papers themselves are found in chapter 8.
- Chapter 7 concerns the anomalous Hall effect and how to predict this effect by calculating the anti-symmetric conductivity tensor using linear response theory. First the various types of Hall effect are summarized, then the anomalous Hall conductivity is introduced, with an emphasis on the intrinsic component. Linear response theory is used to derive a formula for the anomalous Hall conductivity. We discuss the necessity of using adaptive refinement for practical computations. The chapter concludes with a presentations of the benchmark results, using a software implementation of the anomalous Hall conductivity in GPAW[37]. Since no publication has come out of this work yet, the chapter is written as a standalone chapter.
- Chapter 8 briefly summarize and conclude on the content of the thesis and give an outline for future directions of research within the various areas covered in the thesis.
- Chapter 9 contains copies of published works that are summarized in chapter 6.
- The final chapter is followed up by appendices that contain calculations necessary for a thorough understanding of certain topics in the thesis. These are largely technical sections, that are deemed to detailed to cover in the main text.

## CHAPTER 2

## Ferroic order

The term ferroic is a prefix that indicates the presence of ferrous iron [38]<sup>1</sup>. The name refers to the prototypical example of a ferromagnet, one of the most commonly known types of ferroic order. It means the presence of long-range order where microscopic dipoles align to form some form of spontaneous macroscopic order such as magnetization in the case of ferromagnetic materials. A characteristic feature of such materials is that macroscopic magnetization, polarization or strain can be manipulated using magnetic, electric or mechanical fields. At a first glance it seems as if ferromagnetism and ferroelectricity occur for different reasons. However there are several underlying theoretical as well as physical similarities between these phenomena. This chapter introduces fundamental concepts of types of ferroic orders. The primary focus are ferromagnetic and ferroelectric order as these has the largest relevance for the thesis. Different types of ordering are discussed for magnetic and ferroelectrics, and examples of the physical origins of their ordering are given. Other examples of ferroic order are given, such as ferroelasticity, ferrotoroidicity and multiferroism. Lastly we discuss the role of domains and domain walls for ferroic materials.

## 2.1 Ferromagnetism

The characteristic feature of ferromagnets, which distinguishes them from other phases of matter is that they contain ordered magnet moments. That is the magnetic moments, whether they arise from localized electrons at residing on atoms or itinerant electrons that are freely moving about, are all aligned in a given direction such that they give rise to a finite total magnetic moment M. Such materials are referred to as ferromagnets and their characteristics distinguishes them from most other material phases, because most materials either don't contain finite magnetic moments or those magnetic moments are oriented randomly resulting in a material with a net magnetic moment of zero. The latter type of material is known as a paramagnetic material, in such material a finite magnetization can be induced by the application of an external magnetic field H. In fig. 2.1 different types of ordered moments are depicted, including also the case where moments are anti-aligned, which in the case of magnets is known as antiferromagnetism. Another option is for some moments to be larger in size than others, for magnets this is known as ferrimagnetism. The specific mechanisms that lead to magnetism varies across materials, but it is generally accepted that the quantum mechanical exchange interaction is central to explain long-range magnetic ordering in magnetic compounds. At first sight it seems strange that quantum mechanics should

 $<sup>^1\</sup>mathrm{It}$  comes from  $\mathit{ferrum},$  the latin word for iron.



Figure 2.1: The figure shows an illustration of localized magnetic moments in a variety of different configurations. On the upper left side the magnetic moments are all aligned, like in a ferromagnet. On the upper right the magnetic moments have a random orientation, like in a paramagnet material. The bottom left depicts the alignment in a antiferromagnet system. The final sketch is of a ferrimagnetic configuration where the orientation of magnetic moments are similar to the antiferromagnetic case but the magnitude of the moments pointing downward is smaller than their opposites. As a result the the sum of magnetic moments still leads to a finite magnetization.

play a role. It was first shown by Bohr and von Leeuwen, that a purely classical treatment of magnetism leads one to the conclusion that magnetism isn't possible, at least starting from the principles of statistical mechanics [39]. The reason for this perplexing result is that the origin of magnetism in inherently quantum mechanical and not classical. This can be understood intuitively by considering a simple quantum system with two electrons which reside on the same atom. The Pauli exclusion principle states two electrons cannot share the same quantum state. Furthermore because electrons are fermions their wavefunction have a spatial and a spin component. If the two electrons occupy the same orbital they must have different spin orientations. On the other hand if they have the same spin orientation they cannot reside on the same orbital. In other words the spin state actually determines what spatial state is possible. Because spatial and spin degrees of freedom are mixed this way, electrostatic Coulomb repulsions between two electrons is minimized if the two electrons are aligned. The exchange interactions is purely quantum mechanical in nature and exists as a consequence of the Pauli exclusion principle. The argument can be generalized to systems of many electrons, even if those electrons are not localized spatially at some atom.

Like all phases of matter a magnets properties depends on the temperature at which one measures them. The typical way to treat the thermodynamics is to apply Landau theory. These are theories that model the total free energy of system with some form of ferroic order that is characterized by a so called order parameter. In the case of magnets the order parameter is the total magnetization and typical expression for the free energy would read something like the following [39]:

$$F(M) = aM^2 + bM^4 (2.1)$$

where F is the free energy, M is the magnetization, b is a parameter satisfying b > 0and  $a = a_0(T - T_c)$  with  $a_0$  being a positive constant. Here the temperature T is introduced through the parameter a, which changes sign ones the temperature exceeds the critical temperature  $T_c$ . In this way one can capture much of the phenomenology of phase transitions from a relatively simple model. The solutions to the model is the paramagnetic phase M = 0 at high temperatures and finite magnetization  $M = \pm M_0$ that is either up or down in the ferromagnetic low temperature phase. The model presented here have made many implicit assumptions such as the magnetization being perfectly uniform. However the models can be extended in many cases. One can use similar tools to analyze phase transitions in other types of ferroics, for instance ferroelectrics which are discussed in the next section. In real experiments magnets order is often probed by applying an external magnetic field H. A typical type of measurement is applying a field to form hysteresis loops, a sketch of which is depicted in 2.2. In such experiments one can extrapolate the critical field required to switch the material from one state to another. Whether a magnet is easily switchable or not is of huge importance for some applications. Many of the concepts introduced here have analogies for other ferroic orders, but there are also some significant differences that will be covered in the remainder of this chapter. The concepts introduced here therefore also serves as a conceptual reference for understanding the other types of ferroic order.



Figure 2.2: a). In the figure on the left is a sketch of a hysteresis loop for a ferromagnet. The figure depicts how the magnetization changes sign as a function of applied auxiliary field. The value  $H_c$  denotes the magnitude of auxiliary field for which the magnetization switches sign, and  $M_0$  the saturated value once the magnetization is flipped entirely. The figure to the right is a similar copy but for a ferroelectric. Here the quantity being flipped is the electric polarization and the external field is an electric field.

#### 2.2 Ferroelectricity

Ferroelectricity is an analog of ferromagnetism but for electric dipoles as supposed to magnetic ones. The first experimentally known ferroelecric was the Rochelle salt, discovered by J. Valasek in 1920 [40], who demonstrated the existence of a hysteresis loop. The main driver of ferroelectricity is long range dipole-dipole interactions, unlike ferromagnets where the dipole-dipole interaction is weak. The main competing interaction is the short ranged repulsive interactions between neighboring electron clouds. Such interactions tend to prevent the atomic displacements that cause ferroelectricity and instead prefer high-symmetry structures where atomics are more or less situated in an equidistant manner[41]. A key feature of ferroelectrics is that they are characterized by a polar axis and that ferroelectricity occur in materials due to some symmetry lowering distortion from a non-polar structure. In other words the long-range interactions have to win out over the shorter range interactions in order for it to be energetically favourable for a material to form electric dipoles. Ferroelectricity occur in materials with the formation of new chemical bonds that stabilize an off-centering distortion of an initial high-symmetry structure [42].

Perhaps the most well known type of ferroelectrics are those found in perovskite oxides. The canonical textbook example in this family is  $BaTiO_3$ . Here the primary driver of ferroelectricity is second order Jahn-Teller distortions <sup>2</sup>. These are displacements of the active cations, which often happen in closed shell systems where the Coulomb repulsions between atoms is weaker. This happens because there are no extended valence electrons and an atomic distortion that leads to the formation of new chemical bonds is therefore energetically favourable [43]. For this reason these are sometimes called *Jahn-Teller ferroelectrics*.

Some ferroelectrics are known as geometric ferroelectrics. Here ferroelectricity is in purely geometric and is often caused by so called Glazer tiltings [38]. In many cases these are combined with the aforementioned Jahn-Teller distortions to create electric dipole moments. These effects often lead to material with locally ordered dipole moments that are either antialigned or of different magnetitude. They can be therefore be thought of as anti-ferroelectric or ferrielectric in analogy their magnetic counterpart <sup>3</sup>.

Finally some ferroelectrics do not involve ionic displacement at all. Such ferroelectrics are known as *Charge-order ferroelectrics* are less common type of ferroelectric. Here ferroelectricity is caused by the fact the otherwise identical ions have a different number of electrons. This asymmetry in valence number in conjunction with geometric frustration can in certain cases lead to a finite electric dipole. Currently there are not many known ferroelectrics in this category. The most studied being  $\text{LiFe}_2\text{F}_6[45]$ ,  $\text{LuFe}_2\text{O}_4[46, 47]$  and  $\text{Fe}_3\text{O}_4[48]$ . The few materials where this is the only driver of ferroelectricity tend to be magnetic materials [49]. Such double ferroic materials will be discussed later in this chapter.

 $<sup>^2 \</sup>rm Second$  is emphasized here because formally speaking the energetically dominant term stems from second order perturbation theory.

<sup>&</sup>lt;sup>3</sup>This has caused some debate among researchers because the analogy between antiferromagnetism and antiferroelectricity does not hold op in all cases [44].

Unlike magnets, which can be either metallic or insulating, ferroelectrics are all insulators. It is not that one can't find metallic materials with a polar symmetry group. Out of the total 32 crystallographic point groups only 10 of them are polar point groups. Each polar point group puts a certain restriction on what orientations the polarization can have. In order for a material to be ferroelectric, it needs not only a polar axis, but a switchable polarization. Switchability is best demonstrated experimentally by measuring hysteresis loop, analogous to what is done for magnets. A picture of the same process for ferroelectrics is shown in figure 2.2. Electric fields cannot switch polarizations because local charges screen the electric field. There is no magnetic analog of this because there are no magnetic monopoles [38].

The phase transitions that occur in ferroelectrics can be described using Landau theory, in a similar way as was done for ferromagnets in section 2.1<sup>4</sup>. For ferroelectrics the appropriate order parameter is the electric polarization  $\boldsymbol{P}$ . For ferroelectrics phase transitions can be either first or second order [50]. Like for ferromagnetics the specific Landau theory depends on the material considered. For ferroelectrics a symmetry analysis of the crystal structure can often be used to exclude certain terms, but generally speaking expressions are often more complicated than the simplistic version shown in eq. 2.1.

In the literature on the phase transitions of ferroelectrics one tends to distinguish between proper and improper ferroelectrics. The first category describe ferroelectrics which can be described by a Landau theory where the free energy is a function of only a single order parameter. This may be the polarization itself or some other parameter which is a function of the polarization itself. The second category describes ferroelectrics where the Landau free energy cannot be written as a function of a single order parameter, but at least to order parameters are needed. In this case ferroelectricity is often caused by the fact that the different order parameters are coupled together such that they collectively give rise to a polar distortion. In practice one can distinguish the two by investigating the symmetries of the modes that produce the distortions that lead to ferroelectricity.

#### 2.3 Other types of ferroic order

There are other interesting types of ferroic order besides ferromagnetic and ferroelectric order. One other such example is ferroelastic order [51]. These are materials where the key characteristic is the formation of spontaneous strain  $\eta$ . A finite strain corresponds to a material being stretched or compressed relative to a state of zero strain. It is a kind of mechanical analog of ferroelectricity and ferromagnetism, in that a spontaneous strain occur without the application of any external electric, magnetic or mechanical fields. In ferroelastic materials the application of external mechanical stress can structurally "switch" the strain in the ferroelastic in such a way that the material undergoes a structural phase transformation to a twin-phase. This is depicted in figure 2.3 where three crystal structures are sketched. They are identical except for

 $<sup>^4{\</sup>rm For}$  historical reasons, the literature often refers to this as Landau-Devonshire theory when ferroelectrics are described.

differences in strain.

A less common and perhaps more complicated type of ferroic order is ferrotoroidal



Figure 2.3: The the left is an illustration of a ferroelastic material that has been elongated in the longitudinal direction on the left and the horizontal direction on the right. The material in the middle has no finite strain. The figure on the right is a sketch of two toroidal moments, one oriented upwards and the other one downwards.

order [52]. These are material systems where non-collinear magnetic moments form toroidal moments. These are defined as  $\tau = \mathbf{r} \times \mathbf{S}$ , where  $\mathbf{S}$  is the electronic spin and  $\mathbf{r}$  their positions. Toroidal moments can be thought of as analogous to the mechanical torque defined in classical mechanics. This type of order is however the least studied, and a lot of research question in this area are still open.

## 2.4 Multiferroic order

Some materials contain more than one type of ferroic order simultaneously, without any external field present. Such materials are known as multiferroics. The term was first applied by Schmid in a paper in 1994 [53], in which he was referring specifically to magnetoelectric multiferroics, that is materials that posses magnetic and electric order simultaneously. By combining the different types of primary ferroic order one obtains the different types of multiferroics. By combining one ferroelectrity and ferroelasticity one gets ferroelectric-ferroelastic materials [54], where a material exhibit spontaneous strain and simultaneously supports a finite electric dipole moment. If instead magnetic and elastic order are simultaneously present one is dealing with a magnetoelastic multiferroic [55]. The different types of ferroic alignment possible for single ferroic phases are also possible in multiferroics. A material can be ferroelectric and antiferromagnetic, or antiferromagnetic and ferroelastic just to give to examples. The number of ferroic orders present need not be limited to just two for something to be multiferroic. In principle three or more orders can be present simultaneously [56]. If a material is simply refered to as multiferroic it tends to mean magnetoelectric multiferroics.

Magnetoelectric multiferroics should not be conflated with materials that are simply magnetoelectric. Magnetoelectric materials are simply materials in which an external electric field can change the value or orientation of the magnetization or vice versa that an external magnetic field can lead to a change in electric polarization within the material. However it is not a requirement and rarely the case that such materials have finite magnetic or electric orders when no external fields are present. In summary all magnetoelectric multiferroics are also magnetoelectric but not the other way around as illustrated in figure 2.4. The best known example of a magnetoelectric material that is not multiferroic is the antiferromagnet  $Cr_2O_6$  which doesn't have any polarization in



Figure 2.4: A Venn diagram that illustrates the similarities and differences between different types of materials that are either instrinsically ferroic or polarizable using external fields. The largest sets in blue and red denote magnetically- and electrically polarizable materials respectively. The orange and turquoise subsets represent the subset of materials that have electric ferroic order (ferroelectric, anti-ferroelectric etc.) and magnetic order (ferromagnetic, anti-ferromagnetic etc.) respectively. The joint set of the magenta and orange sets represent magnetoelectric multiferroics. The larger set in green represent materials that are merely magnetoelectric. These include all the magnetoelectric multiferroics and a subset of materials belonging to the remaining four categories.

its antiferromagnetic phase[57]. It does however have a finite magnetoelectric constant  $\alpha_{ij} = \frac{\partial M}{\partial \mathcal{E}} = \frac{\partial P}{\partial H}$ . This argument also applies to other types of multiferroics. For example a multiferroic that is ferroelastic and ferroelectric must be a piezoelectric material, but not the other way around. A material that has magnetic and elastic order is automatically piezomagnetic but not vice versa. This thesis is primarily been concerned with magnetoelectric multiferroics. They are generally categorized in two classes: Type-I and type-II Multiferroics [58].

Type-I Multiferroics are materials where the two types of ferroic orders arise independently of each other. In such materials the underlying mechanism responsible for each type of ferroic order is different. For this reason the temperature ranges in which the orders are present may be different, but overlapping. The characteristic feature of these materials however is that the different underlying mechanisms are not inhibiting each other, or at least are only doing so partially. As a result the magnetoelectric coupling in type-I multiferroics tend to be smaller than in type two multiferroics. The perhaps most famous examples of type-I multiferroics would be  $BiFeO_3[59]$  and  $YMnO_3[60]$ .

Type-II Multiferroics are materials where the different types of ferroic order simultaneously present are somehow interlinked. Typically this is caused by some type of non-collinear magnetic ordering which causes the overall symmetry group of the material to become polar. Even if the material does not undergo a structural change, a breaking away from collinear order like that of ferromagnetism changes the magnetic point group of a material. If the new magnetic point group is a polar point group then the material can support a finite electric dipole, thus inducing ferroelecric order via magnetism. A good example of a type-II multiferroic would be TbMnO<sub>3</sub> where ferroelectricity is caused by a magnetic spiral configuration[61].

## 2.5 Domains, and domain walls

Real materials, unlike idealized models of materials, cannot be described by only using the simple concepts described so far. For example materials that are known as ferromagnets do not consist of one large region where all magnet moments are similarly ordered. Instead ferroic orders in such materials tend to persist within finite regions in what are kmown as *domains*. These are regions were all moments, for example magnetic ones, are oriented along the same direction. However neighboring regions inside materials can similarly form domains that exhibit ferromagnetic order but with magnetic moments pointing in a direction which is for example opposite that of their neighboring domains. In real materials these different domains are then stitched together via intersecting regions that are known as *domain walls*. The reason why materials come with



Figure 2.5: Left: Sketch of material where all domains are aligned. Right: Illustration of a material where domains are anti-aligned in orientated and as a result.

multiple domains as supposed to a single one, has to do with variety of factors such as

sample size, shape and competing interactions. Because real materials are finite, that have a boundary. The existence of a finite ferroics orders in the case of ferromagnetic or ferroelectrics produces external magnetic, or electric fields. These fields then lead to the emergence of a demagnetization field, in the case of a ferromagnetic and a depolarization field in the case of a ferroelectric. Such fields result in an energy penalty [39]. If we consider the example of magnets, it is not an advantage to have a single domain that permeate an entire material, because this would lead to a large demagnetization field and thus a large energy penalty. Instead such materials can form domains that are opposite in orientation in the case of a 180 degree domain wall, or ones were the difference in orientation is 90 degrees depending on the shape and on the material in question. These examples are depicted in figures 2.5 and 2.6.

There is also competition between interactions that are solely internal. Different types of ferroics tend to have domains and domain walls of different sizes and shapes. Because magnetic moments are caused by the spin of electrons they cannot simply decrease in size, but in order to get from one domain to another, there has to be a difference in orientation. Therefore magnetic moments perform rotations at the domain walls. In ferromagnets perfect alignment of neighboring moments are favoured by the exchange interaction. Therefore this type of interaction tends to favour thick walls such that angle between neighboring moments is small. On the other hand the so called magnetocrystalline anisotropy tends to favour one easy-axis over the others. This interaction is minimized if fewer magnetic moments are pointing away from the easy-axis, in other words it prefers narrow domain walls since these would have fewer magnetic moments deviating from the easy axis. The first effect is produced by Coulomb interactions and the second by the spin-orbit coupling. Because the first interaction is much larger than the second one, ferromagnets tend to favour large domains walls, typically on the order of magnetitude of several hundred atomic planes [38].

In ferroelectrics the case is different. The concept of exchange interaction doesn't strictly speaking apply here, but if one thinks of the exchange interaction in magnets as the difference between a ferromagnetic and anti-ferromagnetic state, then by analogy one can think of a ferroelectric analogue of the exchange energy as the difference in energy between a ferroelectric and anti-ferroelectric state [62]. Likewise a parameter that would be analogous to the anisotropy for ferroelectrics would be the difference in energy between ferroelectric states pointing in different directions [63]. These are of cause not strictly speaking as well defined as the exchange interaction and the magnetocrystalline anistropy but they can offer some rough estimates of the size of different interactions in ferroelectrics [38]. Calculations have shown that these two types of interactions tend to have a similar order of magnitude and ferroelectric domain walls have also been shown to be very narrow, typically only a few lattice constants [64]. Due to the relevant length scale being this short one can in fact perform simulations of ferroelectric domain walls using supercell sizes that are within computational reach. In ferroelectric materials, domain walls can in some cases become charged. This introduces an extra important degree of freedom which can determine which type of domain wall will be stable. A point to which we will return in section 6.3. The size of both domains and domain walls can vary depending on both the material in question,



**Figure 2.6:** a) Sketch of a material where the domains are oriented to cancel out any external field. The domain walls are a mixture of 180 degree and 90 degree domain walls. b) A sketch of a material with domains shaped more according to what is observed in experiments.

the type of ferroic order and other extrinsic factors such as the occurrence of defects and grain boundaries. The illustrations in 2.5 are idealised pictures of domains. A more realistic picture of how domains are shaped is depicted in fig. 2.6 b). where the domains take on more arbitrary shapes resembling those found in experiments [18].

# CHAPTER **3**Density Functional Theory

In order to understand materials one first needs a solid theoretical foundational framework to describe them. The relevant framework in this case is quantum mechanics. It seems unintuitive to worry about the quantum description of electrons when one is merely concerned with macroscopic objects however small, such as a thin slab of material or a molecule. But ever since it's discovery, quantum mechanics has only proven itself more critical in understanding and describing physical phenomena. As already mentioned, the concern in this thesis is to describe materials from first-principles. But up till now it has not been specified what this actually entails. In this chapter we will discuss the Schrödinger equation and the so called many-body problem of quantum mechanics, as well as discuss how to solve it for materials using a minimal set of approximations. Subsequently it is shown how density functional theory (DFT) allows a reformulation of the problem using the Hohenberg-Kohn theorem. The most basic exchange correlation functionals are described, and their utility and limitation are discussed. Finally we discuss extensions to DFT like spin-density functional theory, spin-orbit coupling and Hubbard corrections.

## 3.1 The many body problem

The quantum many body problem is one of the most studied problems in all of physics. In the context of condensed matter and solid state physics the problem manifests itself attempting to to solve the Schrödinger equation [65, 66]:

$$H\Psi(\mathbf{r}_{1}, \mathbf{r}_{2}, ..., \mathbf{r}_{N}) = E\Psi(\mathbf{r}_{1}, \mathbf{r}_{2}, ..., \mathbf{r}_{N})$$
(3.1)

where  $\Psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)$  is a many-body wavefunction with the energy E and the many body Hamiltonian H. The most general quantum description of solids describe electrons, ions and their mutual interaction through the Hamiltonian:

$$H = -\sum_{i=1}^{N_e} \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_{i=1}^{N_{ion}} \frac{\hbar^2}{2m_N} \nabla_i^2 + \sum_{i=1}^{N_e} \sum_{j \neq i}^{N_e} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$
(3.2)

$$+\sum_{i=1}^{N_{\rm ion}}\sum_{j=1}^{N_e} \frac{Z_i e}{|\mathbf{R}_i - \mathbf{r}_j|} + \sum_{i=1}^{N_{\rm ion}}\sum_{j=1}^{N_{\rm ion}} \frac{Z_i Z_j}{|\mathbf{R}_i - \mathbf{R}_j|} + \sum_{i=1}^{N} V_{ext}(\mathbf{r}_i),$$
(3.3)

where the first two terms represents the kinetic energy of the system, the second, third and fourth terms the Coulomb interaction between electrons, between electrons and ions, and between ions respectively. The final term represents a potential in the case where external field are present. A lot of interesting physics has to do specifically with the role of the electrons, and because these are much lighter than ions, the motion of ions can be assumed to be fixed relative to that of the electrons. The equations that describe the two sets of particles can therefore be decoupled, and the electron many-body problem can be studied in isolation. This was first formalized by Born and Oppenheimer in 1927[67]. The electron many-body problem is given by:

$$H = -\sum_{i=1}^{N} \frac{\hbar^2}{2m} \nabla_i^2 + \sum_{i=1}^{N} \sum_{j \neq i}^{N} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i=1}^{N} V_{ext}(\mathbf{r}_i).$$
(3.4)

With the ion-electron interaction now modelled as an external potential. Despite of this simplification the many-body problem is still in general insoluble. Physicists are often concerned with finding the groundstate, the lowest eigenstate solution. But even this problem turns out to be notoriously difficult. Further approximations are therefore necessary in order to proceed. One of the most used theoretical frameworks that addresses this issue is density functional theory (DFT). Here one is concerned with the ground state electron density, which can be obtained from the many-body groundstate as:

$$\rho(\mathbf{r}) = N \int d^3 \mathbf{r}_2 \dots \int d^3 \mathbf{r}_N \Psi^*(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N) \Psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N), \qquad (3.5)$$

In the reminder of this chapter we will cover the basics of DFT, such as the Hohenberg-Kohn theorems, the Kohn-Sham equations as well as how to incorporate spin-orbit interactions and Hubbard corrections.

## 3.2 The Hohenberg-Kohn theorems

The idea of studying the ground state density as supposed to the more complicated many-body function, dates back to a theory known as Thomas-Fermi theory. Some time later the idea was picked up by Hohenberg and Kohn who formalized two theorems about the relationship between groundstate density, that now forms the basis for modern density functional theory [68, 69].

According to the first Hohenberg-Kohn theorem, the many-body ground state and the external potential are both uniquely determine by the density  $\rho(r)$  (up to a constant). A corollary to this is that any groundstate property is therefore a functional of the ground state density alone. The theorem seems very strange at a first glance. After all the density itself is scalar function of the three spatial variables, whereas the many body groundstate is a function of 3N variables, and therefore contains much more information. The implication being that a certain subset of the larger information space contains all the information necessary to derive groundstate properties.

The second Hohenberg-Kohn theorem states that density that corresponds to the groundstate wavefunction is the density that minimizes the energy functional:

$$E_{GS} = \min_{\rho \to \Phi} \left\langle \Phi[\rho] \right| \left( \hat{T} + \hat{U}_{ee} + \hat{V}_{ext} \right) \left| \Phi[\rho] \right\rangle, \tag{3.6}$$

Where the arrow indicates that one finds the density, corresponding to the  $\Phi[\rho]$  which minimizes the energy functional. In other words that this ensures that the ground state energy which is found is in fact the ground state density. Together the two theorems ensures that a unique relationship exist between the density, and the wavefunction. Furthermore they demonstrate that the density which qualifies as the groundstate density can be found, at least in theory, by minimizing the energy functional in eq. 3.6.

# 3.3 Density functional theory and the Kohn-Sham equations

Even though the density is a significantly simpler object than the many-body groundstate wavefunction, one still needs a way to determine the density. To solve this problem Kohn and Sham came up with the idea to define an auxiliary single-particle problem with an electron density identical to that of the many-body electron problem[70]. Suppose such basis of single particles states exists. In that case we need to solve the single particle problem:

$$H_{KS} \left| \phi_i \right\rangle = \epsilon_i \left| \phi_i \right\rangle \tag{3.7}$$

where  $\epsilon_i$  are called the Kohn-Sham energies,  $|\phi_i\rangle$  are called Kohn-Sham states and H:

$$H_{KS} = \sum_{i=1}^{N} \left( -\frac{h^2}{2m} \nabla_i^2 + V_R(\boldsymbol{r}_i) \right)$$
(3.8)

is the Kohn-Sham Hamiltonian, with the reference potential  $V_R(\mathbf{r}_i)$ . The potential is defined such that the density of the fictitious system equals the density of the many body problem in question. Since this is a single particle problem one can define a Slater determinant of single particle Kohn-Sham states. The density can then be constructed from the Kohn-Sham states as:

$$\rho(\mathbf{r}) = 2\sum_{i=1}^{N} f_i |\phi_i(\mathbf{r})|^2$$
(3.9)

where  $f_i$  denote occupation factors,  $\phi_i$  Kohn-Sham eigenstates and the factor of 2 is due to spin degeneracy. The reference potential in Eq. (3.8) explicitly depends on the electron density:

$$V_R(\boldsymbol{r}_i) = v_{ext}(\boldsymbol{r}_i) + v_H(\boldsymbol{r}_i) + v_{xc}(\boldsymbol{r}_i)$$
(3.10)

$$= v_{ext}(\boldsymbol{r}_i) + \int \frac{\rho(\boldsymbol{r})}{\boldsymbol{r} - \boldsymbol{r}_i} + \frac{\delta E_{XC}[\rho]}{\delta \rho(\boldsymbol{r})}$$
(3.11)

The first term is the external potential, the second is the functional derivative of the Hartree potential and the final term is the functional derivative of the exchangecorrelation potential with respect to the density. The final term is a formal one that
makes the expression exact. This functional is not known though, which posses a practical problem that we will discuss shortly. Since the Kohn-Sham states are both needed to construct the density and also depends on it the two sets of equations needs to be solved self-consistently with respect to the electron density. The total energy of the ground state system is obtained be summing up the eigenenergies of all occupied Kohn-Sham states obtained via eq 3.8. Now that we have established the main idea behind DFT we now discuss how to deal with the exchange-correlation functional.

#### 3.4 Spin-density functional theory

So far we have treated electrons with different spin quantum numbers on equal footing. However there are many physical phenomena that can only be accounted for by including spin as a variable in the problem description. This is particularly important when discussing certain properties like magnetism which can only be accounted for by including the spin degrees of freedom. In the most simple case where spins are treated as collinear, one can simple define two new densities, one for spin up and one for spin down electrons. From these one can define the magnetization density as the difference between the two and the charge density as the sum of the two. Here we will instead present the formalism in a more general way where the electron spin is non-collinear and can have arbitrary orientation [71]. This is done by decomposing the total density into a scalar density and a spin density:

$$\tilde{\rho}(\boldsymbol{r}) = \frac{1}{2} \left( \rho(\boldsymbol{r}) \boldsymbol{I} + \boldsymbol{\sigma} \cdot \boldsymbol{m}(\boldsymbol{r}) \right), \qquad (3.12)$$

here I is the 2×2 identity matrix,  $\sigma = (\sigma_x, \sigma_y, \sigma_z)$  denote the Pauli matrices,  $m(r) = (m_x(r), m_y(r), m_z(r))$  the magnetization density and  $\rho(r)$  the scalar density. The charge density, can then be obtained as  $\text{Tr}(\tilde{\rho}(r))$ . The Kohn-Sham potential is now spin-dependent due to the additional term:

$$\boldsymbol{V}_{R}(\boldsymbol{r}_{i}) = \left(v_{ext}(\boldsymbol{r}_{i}) + v_{H}(\boldsymbol{r}_{i}) + v_{xc}(\boldsymbol{r}_{i})\right)\boldsymbol{I} + \mu_{B}\boldsymbol{\sigma} \cdot \left(\boldsymbol{B}_{xc}(\boldsymbol{r}) + \boldsymbol{B}_{ext}(\boldsymbol{r})\right)$$
(3.13)

where:

$$\boldsymbol{B}_{xc}[n,\boldsymbol{m}] = \frac{\delta E_{XC}[\rho,\boldsymbol{m}]}{\delta \boldsymbol{m}(\boldsymbol{r})}.$$
(3.14)

The additional spin dependent xc-potential couple to the spins similar to the way a magnetic field does, and the term takes a form similar to that of the Zeeman-effect. In addition an actual Zeeman-term has been added to take into account a potential external magnetic field. The Kohn-Sham equations for a spinful system take the form:

$$\sum_{i=1}^{N} \left( -\frac{h^2}{2m} \nabla_i^2 \boldsymbol{I} + \boldsymbol{V}_R(\boldsymbol{r}_i) \right) \boldsymbol{\phi}_i(\boldsymbol{r}) = \epsilon_i \boldsymbol{\phi}_i(\boldsymbol{r}), \qquad (3.15)$$

where we introduced the spinors:

$$\boldsymbol{\phi}_{i}(\boldsymbol{r}) = \begin{pmatrix} \phi_{i,\uparrow}(\boldsymbol{r}) \\ \phi_{i,\downarrow}(\boldsymbol{r}) \end{pmatrix}.$$
(3.16)

If one works in a basis where the potential term is diagonalized the problem leads to two decoupled equations:

$$\sum_{i=1}^{N} \left( -\frac{h^2}{2m} \nabla_i^2 + \boldsymbol{V}_R(\boldsymbol{r}_i) \right) \phi_{i,\uparrow}(\boldsymbol{r}) = \epsilon_{i,\uparrow} \phi_{i,\uparrow}(\boldsymbol{r}).$$
(3.17)

$$\sum_{i=1}^{N} \left( -\frac{h^2}{2m} \nabla_i^2 + \boldsymbol{V}_R(\boldsymbol{r}_i) \right) \phi_{i,\downarrow}(\boldsymbol{r}) = \epsilon_{i,\downarrow} \phi_{i,\downarrow}(\boldsymbol{r}).$$
(3.18)

In this case one can distinguish the eigenenergies of spin-up and spin-down eigenstates. This is useful if for example one wishes to perform bandstructure calculations.

#### 3.5 Exchange-correlation functionals

Even though the Kohn-Sham equations in principle gives an exact solution to the ground state energy in terms of the density, the true exchange correlation functional is not actually known. As a consequence an approximation has to be made for the exchange-correlation functional and DFT is therefore not in practice an exact theory. However DFT has proven to be a quite accurate tool for predicting certain material properties. One of the most common functionals is the local density approximation (LDA)[70]. The local density approximation is modelled after the homogeneous electron gas (HEG), such that one obtains exact results for this model. The XC-functional for the LDA reads:

$$E_{XC}^{LDA} = \int \rho(\mathbf{r}) \epsilon_{XC}^{LDA}[\rho(\mathbf{r})] d\mathbf{r}.$$
(3.19)

The exchange correlation energy density is given by the two terms:  $\epsilon_{XC}^{LDA}[\rho(\mathbf{r})] = \epsilon_X^{LDA}[\rho(\mathbf{r})] + \epsilon_C^{LDA}[\rho(\mathbf{r})]$ . In the LDA the first term is given by

$$\epsilon_X^{LDA}[\rho(\mathbf{r})] = -\frac{3}{4} \left(\frac{3}{\pi}\right)^{1/3} \rho^{1/3}$$
(3.20)

The  $\epsilon_C^{LDA}[\rho(\mathbf{r})]$  is obtained using Monte Carlo simulations and does not have a simple analytic form [72]. In spin density functional theory LDA is generalized to the local spin density approximation (LSDA), although it is still often just referred to as the LDA. In this case the exchange-correlation energy is given by:

$$E_{XC}^{LSDA} = \int \rho(\boldsymbol{r}) \epsilon_{XC}^{LSDA}[\rho(\boldsymbol{r}), |\boldsymbol{m}(\boldsymbol{r})|] d\boldsymbol{r}.$$
(3.21)

Another commonly used type functional are the ones that rely on the generalized gradient approximation (GGA) [68]. GGA functionals attempt to improve upon the upon the LDA by adding gradient terms in the exchange correlation functional. Physically this corresponds to modeling the density in local way like in the LDA however now changes in the density are taken into account. GGA functionals generally take the form:

$$E_{XC}^{GGA} = \int \rho(\boldsymbol{r}) \epsilon_{XC}[\rho(\boldsymbol{r})] F_{XC}[\rho(\boldsymbol{r}), \nabla \rho(\boldsymbol{r}), \nabla^2 \rho(\boldsymbol{r}), ...] d\boldsymbol{r}.$$
(3.22)

where  $F_{XC}$  is known as the enhancement factor. The enhancement factor modifies the LDA expression by introducing gradient terms. The most common one being the Perdew-Burke-Ernzerhoff (PBE) functional[73]. In the case of PBE one chooses  $\epsilon_{XC} = \epsilon_{XC}^{LDA}$  and the exchange enhancement factor reads:

$$F_X^{PBE}(s) = 1 + \kappa - \frac{\kappa}{1 + \mu s^2/\kappa},\tag{3.23}$$

where  $\mu = \beta(\pi^2/3)$ ,  $\beta = 0.0667$ ,  $\kappa = 0.804$  and  $s = \frac{|\nabla \rho(\mathbf{r})|}{2k_F \rho}$  is the scaled density gradient. The enhancement factor satisfies  $F_X(0) = 1$ , such that uniform electron gas is recovered in this limit [69]. Furthermore the PBE satisfy several other formal properties and limits, while violating others. This choice was made because the properties that are deemed energetically are fulfilled for the PBE functional [73].

While these functionals have been widely used they do have certain limitations. Both the LDA and GGA approximations tend to underestimate band gaps. This is due to the so called derivative discontinuity problem [74]. The problem arises due to the fact that densities obtained are under the constraint that the number of electrons is held constant and certain quantities are continuous functions of the number of electrons.

Other popular DFT functionals include hybrid and meta-GGA functionals. The first type of functionals are ones that aim to correct for the problems with the semi-local functionals by mixing the exchange part of the exchange correlation functional with the exact exchange from Hartree-Fock. The idea behind this is that since Hartree-Fock tends to overestimate bandgaps, one might get more accurate results by constructing a functional that mixes the exchange energy of Hartree-Fock with that of some functional that underestimates band gaps. A popular example of a hybrid functional would be HSE06 which has been widely used [75]. Practical computations with HSE06 are however computationally quite expensive in comparison to using cheaper functionals like PBE or LDA. The meta-GGAs on the other hand attempts to improve upon the GGA-functionals by derivatives of the order two or higher to improve upon functionals like PBE which contains only the first derivative [76].

#### 3.6 Spin-orbit coupling within density functional theory

So far relativistic effects have not been mentioned. The many-body problem introduced in section 3.1 is only a good description in the non-relativistic case. However there are many real quantum systems like materials where the relativistic effect of spinorbit coupling (SOC) plays a crucial role. It principle one can formulate a relativistic version of DFT and prove a relativistic version of the Hohenberg-Kohn theorems by starting from the Dirac equation instead of the Schrödinger equation. However for many purposes it is sufficient to keep the formulation non-relativistic and then add the leading corrections one gets from the Dirac equation. The relativistic corrections to the Hamiltonian given in eq. 3.15 are given by:

$$H^{SOC} = -\frac{p^4}{8m^3c^2} - \frac{i\hbar\mathbf{p}\cdot\nabla V}{4m^2c^2} + \frac{\boldsymbol{\sigma}\cdot\mathbf{p}\times\nabla V}{4m^2c^2},\tag{3.24}$$

where the first to terms are scalar corrections known as the kinetic and the Darwin correction and the last correction is the spin-orbit interaction. The first two corrections can simply be included in the potential in eq. 3.15. The spin-orbit interaction has to be treated separately. The SOC Hamiltonian can be added in a spin-polarized calculation to the Kohn-Sham Hamiltonian in eq. 3.15 and thus enter at the level of the self-consistent calculations done in spin density functional theory.

Another option is to first perform a DFT calculation and then compute matrix elements of the SOC Hamiltonian in eq. 3.15 in the basis of the KS states obtained from the self-consistent calculations. In that case the spin-orbit corrected eigenvalues can be obtained as [77]:

$$E_{nm\boldsymbol{k}\sigma\sigma'}^{SOC} = E_{n\boldsymbol{k}\sigma}^{0}\delta_{nn'\sigma\sigma'} + \langle \phi_{n\boldsymbol{k}\sigma}^{KS} | H^{SOC} | \phi_{m\boldsymbol{k}\sigma'}^{KS} \rangle.$$
(3.25)

Furthermore the new eigenstates will be a linear combination of the ones obtained from the original DFT calculation without spin-orbit coupling and will be given by:

$$|u_{n\boldsymbol{k}}\rangle = \sum_{m} \sum_{s=\uparrow,\downarrow} C_{nms} |u_{sm\boldsymbol{k}}^{0}\rangle, \qquad (3.26)$$

where  $|\phi_{mk}^0\rangle$  denotes the eigenstates obtained without spin-orbit coupling and denotes  $|\phi_{mk}^0\rangle$  the eigenstates obtained with spin-orbit coupling. One important application of spin-orbit coupling in DFT calculations is the lifting of degeneracies in bandstructure calculations. Another of importance to this thesis is the calculation of magnetic anisotropies. This is important if the wish is to find the easy/hard axis of a magnet, since some quantization axis is prefered due to magnetocrystalline anisotropies that can only be captured by including spin-orbit interactions. To get the anisotropy  $\Delta_{\alpha\beta}$  one simply computes the energy differences:

$$\Delta_{\alpha\beta} = E(\theta_{\alpha}, \phi_{\alpha}) - E(\theta_{\beta}, \phi_{\beta}). \tag{3.27}$$

where  $E(\theta_{\alpha}, \phi_{\alpha})$  are total energies evaluated at set of angles  $(\theta_{\alpha}, \phi_{\alpha}), (\theta_{\beta}, \phi_{\beta})$ . There are however physical quantities affected by spin-orbit coupling that can only be accurately predicted by including the spin-orbit coupling in self-consistent calculations. One example of this would be to predict the correct orientations of non-collinear magnetic moments.

#### 3.7 Density functional theory with Hubbard corrections

There are several discrepancies between results obtained functionals like LDA and PBE and real quantum systems. Besides the ones already mentioned, both of those functionals often give erroneous results when dealing with magnetic systems. This is

largely due to the so called self-interaction error (SIE). The SIE is a feature of semilocal functionals like LDA and PBE where electrons experience a repulsive interaction from themselves, which leads to a delocalization of the electron density. This in turn leads to wrong results for systems where electrons are highly localized.

One field of study where this leads to problems is magnetic materials where the localized character of d and f shells are crucial to capture the correct qualitative features. Famously physicists wrongly characterized the anti-ferromagnetic Mott insulators as ferromagnetic metals [78]. This problem was resolved by describing these systems using the Hubbard model, a tight binding model with an on-site Coulomb interactions:

$$H_{Hubbard} = \sum_{s=\uparrow,\downarrow} \sum_{ij} t_{ij} c_{i,s}^{\dagger} c_{j,s} + U \sum_{i} n_{i,\downarrow} n_{i,\uparrow}$$
(3.28)

where *i* is a local site index, *U* is the interaction strength of the Coulomb interaction,  $n_{i,\uparrow/\downarrow} = c^{\dagger}_{i,\uparrow/\downarrow}c_{i,\uparrow/\downarrow}$  is the number operator for the *i*'th site,  $c^{\dagger}_{i,\uparrow/\downarrow}$  is the creation operator for an electron with spin-up or spin-down and  $c_{i,\uparrow/\downarrow}$  is the annihilation operator for an electron with spin-up or spin-down. Here it has been assumed that there is only one orbital per site. But the model can easily be generalized to multi-orbital systems.

This model has subsequently inspired researchers within the field of DFT to create a similar approach known as DFT + U, where Hubbard interactions are included in the exchange-correlation energy [79, 80]. Here we will follow the approach first conceived of by Dudarev [80]. The goal is to derive a correction from local Coulomb interactions to the LSDA. We start by considering a general expression for the Coulomb interaction on a given atom j [81]:

$$U_{j} = \frac{\overline{U}}{2} \sum_{m,m'} \sum_{s} \hat{n}_{m,s} \hat{n}_{m',-s} + \frac{\overline{U} - \overline{J}}{2} \sum_{m \neq m'} \sum_{s} \hat{n}_{m,s} \hat{n}_{m',s}.$$
(3.29)

Here we have included spin and orbital degrees of freedom s and m respectively. The index -s denotes a spin that is the opposite of s. Furthermore it has been assumed that the Coulomb and exchange energy integrals U and J are more are less independent orbital and spin degrees of freedom such that we need only concern ourselves with their average values  $\overline{J}$  and  $\overline{U}$  respectively. The full expression for the local Coulomb interaction includes a term corresponding to a spin-flip, but it is neglected in the Dudarev approach since its magnitude is set by the exchange energy integral which is usually smaller than the Coulomb energy integral in strongly correlated materials. We will now proceed to treat the Coulomb interactions at a mean-field level:

$$\hat{n}_{m,s} = \langle \hat{n}_{m,s} \rangle + \delta \hat{n}_{m,s}. \tag{3.30}$$

where  $\delta \hat{n}_{m,s} = \hat{n}_{m,s} - \langle \hat{n}_{m,s} \rangle$ . In the mean-field approximation fluctuations are only included up to a first order such that second and higher order terms of the form  $\delta \hat{n}_{m,s} \delta \hat{n}_{m',s'}$  are neglected. In this approximation the expression for the local Coulomb energies become:

$$U_{j}^{MF} = \frac{\overline{U}}{2} \sum_{m,m'} \sum_{s} \left\langle \hat{n}_{m,s} \right\rangle \left\langle \hat{n}_{m',s'} \right\rangle + \frac{\overline{U} - \overline{J}}{2} \sum_{m \neq m'} \sum_{m'} \sum_{s} \left\langle \hat{n}_{m,s} \right\rangle \left\langle \hat{n}_{m',s} \right\rangle.$$
(3.31)

We now add Hubbard corrections by formulating a conjecture for how the LDA treats Coulomb interactions in a mean field context. The Dudarev approach postulates that the LSDA only accounts for fluctuations in the total number of electrons at a given site  $\hat{n}_s = \sum_m \hat{n}_{m,s}$  [80, 82]. This make sense since the LSDA is formulated for the density with no reference to any particular orbitals. With this conjecture the Coulomb interactions for the LSDA become

$$U_j^{LDA} = \frac{\overline{U}}{2} \sum_s \left( \sum_m \hat{n}_{m,s} \right) \left( \sum_{m'} \hat{n}_{m',-s} \right) + \frac{\overline{U} - \overline{J}}{2} \sum_s \left( \sum_m \hat{n}_{m,s} \right) \left( \sum_{m'} \hat{n}_{m',s} \right)$$
(3.32)

$$-\frac{U-J}{2}\sum_{s}\sum_{m}\hat{n}_{m,s}\hat{n}_{m,s}$$

$$(3.33)$$

$$=\frac{\overline{U}}{2}\sum_{s}\hat{n}_{s}\hat{n}_{-s} + \frac{\overline{U}-\overline{J}}{2}\sum_{s}\hat{n}_{s}\hat{n}_{s} - \frac{\overline{U}-\overline{J}}{2}\sum_{s}\hat{n}_{s}.$$
(3.34)

Within the mean field approximation the expression for LSDA becomes:

$$\left\langle U_{j}^{LSDA}\right\rangle^{MF} = \frac{\overline{U}}{2} \sum_{s} \left\langle n_{s} \right\rangle \left\langle n_{-s} \right\rangle + \frac{\overline{U} - \overline{J}}{2} \sum_{s} \left\langle n_{s} \right\rangle \left\langle n_{s} \right\rangle - \frac{\overline{U} - \overline{J}}{2} \sum_{s} \left\langle n_{s} \right\rangle.$$
(3.35)

By comparing this expression with the proper treatment of the Coulomb interaction at the mean-field level stated in eq. (3.31), we get the local energy correction missed by the LSDA. The The Hubbard corrected expression for the exchange-correlation energy using the Dudarev apporach can now be written as:

$$E_{LSDA}^{DFT+U} = E_{LSDA}^{DFT} + \frac{1}{2} \sum_{j} U_{j}^{eff} \sum_{ns} \left( n_{jms} - n_{jms}^{2} \right), \qquad (3.36)$$

where  $U_j^{eff} = \hat{U} - \hat{J}$ . The DFT + U method is not be limited to the LDA and it is often applied in conjunction with other DFT functionals like PBE. The issue with DFT + U is that it doesn't offer any insight as to which value of U will give the correct results for a given system. It is often necessary to try different values and pick the one that yields results that are consistent with experiments. From a theoretical point of view this is still unsatisfying since one should be able to make predictions even when no experimental data is available. It has been shown that the value of U can in fact be determined self-consistently in a number of different ways[83–85]. Despite this shortcoming DFT + U is still widely applied, and it has the advantage that it is computational cheaper than advanced DFT functionals while often being in good agreement with experiments.

#### 3.8 DFT and numerical computations

In order to apply DFT one needs a computer code that implements a self-consistent solution to the Kohn-Sham equations given a start guess. There are several existing

computer codes in existence that can be used to do so. All work done in this thesis has been done using the CPAN code [37] which solves on 3.7 using the projector sugmented

been done using the GPAW code [37] which solves eq. 3.7 using the projector-augmented wave (PAW) method. Specific details like energy cutoff for plane waves, choice of exchange correlation functional and k-point sampling are specified in each published paper in section 9 or in the result sections in the following chapters.

# CHAPTER **4** High-throughput methods in materials science

Much of science, has to do with discovering hitherto unknown phenomena. However an area of research just as important is to investigate known phenomena in all the different varieties that they may manifest themselves. Within the field of multiferroics researchers are particularly eager to find new examples of materials, both to find examples that might be more technologically applicable, but also to understand new mechanisms that can lead to a material exhibiting multiferroic properties. The issue however is that researchers often have to rely on intuitions that are based on what is already known. This limits the scope of what one can do as a theoretician, since the number of materials in the category of investigation may be small or may not constitute a good basis on which to search for new materials that have similar properties.

High-throughput screening methods are increasingly becoming an ever larger tool, in search for new materials with specific desirable properties [86]. The idea is similar to what has been done in other fields, like medical science where one systematically tests the properties of many candidate drugs [87]. Due to the increase in computational resources made available, by high performance supercomputers it is now possible to perform many computations in parallel, for many materials upon demand. This chapter summarize the basic components of high-throughput studies, such as how to automate the search process with workflows and the role of open source databases.

#### 4.1 Databases and workflows

In the context of computational material science, the role of high-throughput studies is that of automating computations with the goal of investigating the properties of potential candidates, in an attempt to discover and characterize novel materials. This runs contrary to the more conventional approach which is to manually investigate specific materials that the researcher might see as interesting. The problem is that the number of potential candidates is often too large and the number of actual materials that satisfy various search criteria is often small. Therefore it is necessary to create a kind of funnel that allows researchers to select specific candidates that can then be the subject of further investigation. This is done using a variety of different tools.

The first tool is workflows, that allows scientists to systematically compute desired properties of a large set of materials by automating the different parts of the computation process. There exists quite a lot of different software tools for high throughput applications specifically within materials science. Examples include the AiiDA [88–90], fireworks [91], AFLOW [92] and ASR [93] packages. For this thesis we will be using the atomic simulation environment (ASR) which is a Python based software package that has been developed at the CAMD group at DTU, for the purpose of automating the most common computations used in materials science. Before discussing details specific to ASR, it is however worth giving a concrete example of how workflows are used. If a group of researchers were interested in looking for new ferroelectric materials, the first thing to do would be to list search criteria and what computations had to be carried out to get the relevant data. The utility of workflows is to integrate all the different tasks into a unified framework that can be automatically applied to all the materials under investigation. In ASR this is concretely being done using ASR recipes. These carry out standardized calculations for materials or molecules like finding the groundstate, bandstructure, phonon spectra, magnetic moments to mention a few. In addition a high-throughput framework, one needs a high performance computing task manager to adequately manage and track computations. All projects in this thesis relied on the MyQueue software package which is high performance computating task scheduler with a python interface [94].

Having performed calculations the next step is to store the data obtained from computations in a way that makes it easy accessible for further analysis, or for a third party. This need is typically meet by storing gathered data in openly available materials databases. These can serve as repositories of data obtained from calculations and in some cases also as the sources of data used as input for high-throughput workflows. The data on material structures found in these databases are often either based on experimentally known materials or molecules or they can be databases hypothetical structures that may potentially be synthesized experimentally. They can for example be constructed using methods like lattice decoration, which is the basis for many materials in the C2DB[95], which we will discuss later in the thesis. Here one simply starts from a lattice type and then run through the periodic table of elements substituting in all possible combination of elements in order to try to find new compounds. Most databases uses a variety of combination of methods to increase the number of materials. Popular material databases include for example the ICSD [96], COD [97] databases and the Materials project [98]. More recently entire databases have been created for two dimensional compounds alone such as the C2DB database [95], the MC2D database [99, 100] and 2DMatPedia [101].

As an end note it should be emphasized that high-throughput methods do not form a viable basis for materials discovery on their own. Not all materials can be found using a given workflow because certain choices and trade offs have to be made when selecting candidates as well when performing computations. Therefore traditional in detail studies of materials are still very much relevant and necessary and high throughput studies cannot replace these. They may however help narrow ones search scope, as well as save researchers hours of work on materials that are actually unlikely to yield fruitful results. Secondly, potential material candidates should ideally be tested experimentally. High-throughput may help experimentalists in finding a viable way to pick new materials for synthesis or characterization. Since such work is often either difficult, cumbersome, time consuming or expensive in terms of the necessary resources. It can be of great help to start with materials that at least in theory hold a greater chance of being experimentally interesting.

## CHAPTER 5

## Ferroelectricity

Since their experimental discovery in 1920 [40], the interest in ferroelectrics have increased dramatically. Yet a proper theoretical understanding of this class of materials alluded physicists for decades. Despite the fact that a theory of phase-transitions as well as prototypical experimental studies were in place already in the middle of the 20'th century, it was not until the 1990's that a proper unified theory of ferroelectrics existed.

In the following chapter the relevant theoretical foundations of polarization densities and their computation is given. First the classical Clausius-Mossotti theory is introduced and its fallacies for periodic systems are pointed out. Subsequently the modern theory by Resta, King-Smith and Vanderbilt is introduced, followed by some practical examples. Born effective charges are defined and it is shown how these can be useful to compute the polarization in various cases. Finally some exceptional cases are discussed such as the polarization from many-body states and the special case of polar metals.

#### 5.1 Formal polarization: a classical approach

Originally the polarization density of a physical system, whether one was dealing with a material or a molecule, was simply defined as the integral of the charge density times the position within a given volume V:

$$\boldsymbol{P} = \frac{e}{V} \int d\boldsymbol{r} n(\boldsymbol{r}) \boldsymbol{r}. \tag{5.1}$$

This definition certainly seems physically intuitive and it is in principle straightforward to compute the polarization density from first-principles using DFT. The electric charge density has two components, an ionic one and an electronic one. The ionic density has the form  $n_{\text{ion}} = \sum_i Z_i \delta(\mathbf{R}_i - \mathbf{r})$ , where  $\mathbf{R}_i$  is the atomic positions and  $Z_i$  the ionic charge of the *i*'th atom. The ionic contribution to the polarization is then simply given by:

$$\boldsymbol{P}_{\text{ionic}} = \frac{e}{V} \sum_{i} Z_{i} \boldsymbol{R}_{i}.$$
(5.2)

The electronic contribution can be obtained from DFT by using the Kohn-Sham density in eq. 3.9. This simple classical picture of the polarization density is also known as the Clausius-Mossotti picture [102].

The approach works for finite systems like molecules. However the picture breaks down when one considers the polarization density of a system with periodic boundary conditions, like a bulk solid. To see why this picture breaks down, we consider a simple scenario where the periodic system is a one-dimensional chain with a unit cell of just two atoms, as depicted in figure 5.1. For simplicity we will assume that the red atom has a net charge of +e and the blue atom a net charge of -e. Due to the periodicity of the chain we can choose to place the unit cell boundary as we like. This ambiguity leads to a problem when one tries to determine the polarization density using any given unit cell as reference, because one will get conflicting answers depending on how the unit cell is placed.

It is straightforward to illustrate the practical implications of this problem with the application of eq. 5.2 to the one dimensional chain in the two different scenarios. In the first scenario the polarization is  $P = \frac{e(-\frac{a_0}{4})}{a_0} + \frac{-e(\frac{a_0}{4})}{a_0} = -\frac{e}{2}$  and in the second case it is  $P = \frac{e(-\frac{a_0}{2})}{a_0} + \frac{-e*0}{a_0} + \frac{e(\frac{a_0}{2})}{a_0} = 0$ . In the first picture there is a finite polarization density and in the second the polarization density is 0 according to 5.2. This inconsistency reveals a fallacy inherent in the definition of polarization density given eq. 5.1, namely that one can get different answers depending on which unit cell one uses to measure the polarization density.

#### 5.2 The modern theory of polarization

The issue of how to compute the polarization density for a periodic systems went unsolved for many years until 1992 when R. Resta resolved the problem by phrasing a different question: which polarization is physically measurable? The answer, already known by experimentalists, is to measure the change in polarization under an applied



Figure 5.1: Depicted is an illustration of an imagined example presented in the main text, of a one-dimensional chain of atoms. There are two atoms within one unit cell, which contain a charge of -e and +e respectively. In the first picture the polarization density is  $-\frac{e}{2}$  and in the second picture it is 0. The illustration shows how the so called Clausius-Mossotti picture of the polarization density is ambiguous and ill defined in periodic systems.

electric field, such as when constructing hysteresis loops like the ones shown in fig. 2.2. What is done in practice is to measure the current which arises due to a change in polarization [103]. From this it is possible to infer that the relevant quantity is not the polarization in a given state but the change in polarization from one reference to another, since this is the experimentally observable quantity. The key to this insight came from the observation that the change in polarization is induced *adiabatically* by the flow of a current:

$$\Delta \boldsymbol{P} = \boldsymbol{P}(T) - \boldsymbol{P}(0) = \int_0^T \boldsymbol{J}(t').$$
(5.3)

It wasn't long after Resta published his paper that King-Smith and Vanderbilt came up with the modern theory of polarization [104]. The idea of Smith and Vanderbilt was to compute the change in polarization with respect to an explicit parameter that was slowly changing. Specifically they considered what would happen to the polarization if the systems potential was subject to an *adiabatic* change. A theory for how quantum systems change under adiabatic conditions was already developed nu by the time the modern theory of polarization was put forward [66, 105]. Such systems can be studied by invoking the adiabatic approximation which states that if a Hamiltonian depends on a time dependent parameter that varies at a sufficiently slow rate, then the system will still have the same energy solutions and that the value of these also change slowly with the changing parameter. To quantify what is meant by slowly varying, we introduce the a time scale  $\tau \sim \frac{\hbar}{E_n - E_m}$ , which is determined by the difference between energy levels. If the Hamiltonian changes on a scale slower than  $\tau$  the adiabatic approximation holds. The eigenvalues are then obtained by solving the stationary Schrödinger equation at each time step. Furthermore it is assumed that the values remain ordered and that the solutions are non-degenerate. In such scenarios the solutions can be shown to take the form [106]:

$$|\Psi_n(t)\rangle = |\phi_n\rangle \, e^{-\frac{i}{\hbar} \int^t E_n(t')dt'} e^{i\gamma_n(t)}.$$
(5.4)

This is the familiar form that solutions to the Schrödinger equation take, except for the additional complex phase  $i\gamma_n(t)$ . This phase takes the form:

$$\gamma(t) = \int^{t} dt' \left\langle \phi_n(t') \right| \frac{\partial}{\partial t'} \left| \phi_n(t') \right\rangle.$$
(5.5)

It is in many cases useful to think of the adiabatic change in terms of one or several changing parameters  $\mathbf{R}(t)$  which then in turn is time dependent, like a set of knobs that are being slowly turned over a time period T. In that case the phase can be written as:

$$\gamma(T) = \int_0^T dt' \langle \phi_n(\boldsymbol{R}(t')) | \nabla_{\boldsymbol{R}} | \phi_n(\boldsymbol{R}(t')) \rangle \cdot \frac{d\boldsymbol{R}}{dt} = \int_{R(0)}^{R(T)} \langle \phi_m(\boldsymbol{R}) | \nabla_{\boldsymbol{R}} | \phi_n(\boldsymbol{R}) \rangle \cdot d\boldsymbol{R},$$
(5.6)

where  $\nabla_{\mathbf{R}} = \frac{\partial}{\partial \mathbf{R}}$ . For a closed look the phase is given by:

$$\gamma(\mathcal{C}) = \oint_{\mathcal{C}} \langle \phi_m(\mathbf{R}) | \nabla_{\mathbf{R}} | \phi_n(\mathbf{R}) \rangle \cdot d\mathbf{R}.$$
(5.7)

From these definitions we see that the phase is purely a function of the path traced out in the parameter space  $\mathbf{R}$ , independently of the time it took. This is of course only true provided that the adiabatic approximation is valid. The phase is known as the Berry phase [107] and it has a physical significance that in many cases can be measured. To see what implications this have for the modern theory of polarization we will follow the approach of King-Smith and Vanderbilt and derive an expression for the electronic part of the polarization for a quantum system. We start by considering the electronic part of the polarization density definition given in equation 5.1, but where the electron density is written in terms of wavefunctions:

$$\boldsymbol{P}_{el} = \frac{-e}{V} \sum_{n}^{occ} \int d\boldsymbol{r} f_{n\boldsymbol{k}} |\psi_{n\boldsymbol{k}}(\boldsymbol{r})|^2 = \frac{e}{V} \sum_{n}^{occ} \sum_{\boldsymbol{k}} \langle u_{n\boldsymbol{k}} | \boldsymbol{r} | u_{n\boldsymbol{k}} \rangle, \qquad (5.8)$$

where  $f_{nk}$  denote occupation factors, the sum is over the Bloch functions  $u_{nk}(\mathbf{r}) = \psi_{nk}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}$  of occupied bands. The inner product in eq. 5.8 is ill-defined because the diagonal elements of  $\mathbf{r}$  is not defined in periodic systems, due to the same issues of ambiguity that we discussed for the Clausius-Mossotti picture.

Following Resta, we will now focus on the change in the polarization in eq. 5.8 rather than the polarization itself. The idea is to write the change in polarization in terms of a reaction coordinate  $\lambda$ :

$$\Delta \boldsymbol{P}_{el} = \int_0^1 \frac{\partial \boldsymbol{P}_{el}(\lambda)}{\partial \lambda}.$$
(5.9)

Inserting eq. 5.8 into eq. 5.9 one obtains the expression:

$$\Delta \boldsymbol{P}_{el} = \frac{e}{V} \int_0^1 \sum_{n=1}^{\infty} \sum_{\boldsymbol{k}} 2 \operatorname{Re}\left( \langle u_{n\boldsymbol{k}}^{(\lambda)} | \, \boldsymbol{r} \, | \frac{du_{n\boldsymbol{k}}^{(\lambda)}}{d\lambda} \rangle \right).$$
(5.10)

By inserting a projection operator, eq. 5.10 becomes:

$$\Delta \boldsymbol{P}_{el} = \frac{e}{V} \int_{0}^{1} \sum_{\alpha} \sum_{n}^{occ} \sum_{\boldsymbol{k}} 2 \operatorname{Re} \left( \langle u_{n\boldsymbol{k}}^{(\lambda)} | \boldsymbol{r} | u_{\alpha\boldsymbol{k}}^{(\lambda)} \rangle \langle u_{\alpha\boldsymbol{k}}^{(\lambda)} | \frac{du_{n\boldsymbol{k}}^{(\lambda)}}{d\lambda} \rangle \right)$$
(5.11)

$$= \frac{e}{V} \int_{0}^{1} \sum_{\alpha \neq n} \sum_{n}^{occ} \sum_{\boldsymbol{k}} 2 \operatorname{Re} \left( \left\langle u_{n\boldsymbol{k}}^{\lambda} | \, \boldsymbol{r} \, | u_{\alpha \boldsymbol{k}}^{(\lambda)} \right\rangle \left\langle u_{\alpha \boldsymbol{k}}^{(\lambda)} | \frac{d u_{n\boldsymbol{k}}^{(\lambda)}}{d \lambda} \right\rangle \right), \tag{5.12}$$

where the change of summation to off diagonal components  $\alpha \neq n$  stems from the fact that the diagonal component is purely imaginary. The off diagonal matrix elements of  $\boldsymbol{r}$  obey the relation:

$$\langle u_{n\boldsymbol{k}}^{(\lambda)} | \boldsymbol{r} | u_{\alpha\boldsymbol{k}}^{(\lambda)} \rangle = -i \langle \frac{du_{n\boldsymbol{k}}^{(\lambda)}}{d\boldsymbol{k}} | u_{\alpha\boldsymbol{k}}^{(\lambda)} \rangle$$
(5.13)

Inserting this into equation 5.11 yields an expression solely in terms of derivatives:

$$\Delta \boldsymbol{P}_{el} = \frac{e}{V} \int_0^1 \sum_n^{occ} \sum_{\boldsymbol{k}} 2 \operatorname{Im} \left( \langle \frac{du_{n\boldsymbol{k}}^{(\lambda)}}{d\boldsymbol{k}} | \frac{du_{n\boldsymbol{k}}^{(\lambda)}}{d\lambda} \rangle \right), \tag{5.14}$$

after removing the projection operator due to the closure property:  $I = \sum_{\alpha} |u_{\alpha k}\rangle \langle u_{\alpha k}|$ . Finally we rewrite the expression in eq. 5.14 such that the sum over k becomes an integral:

$$\Delta \boldsymbol{P}_{el} = -\frac{e}{(2\pi)^d} \int_0^1 \sum_n^{occ} \int_{\mathrm{BZ}} d\boldsymbol{k} 2 \mathrm{Im} \left( \langle \frac{du_{n\boldsymbol{k}}^{(\lambda)}}{d\boldsymbol{k}} | \frac{du_{n\boldsymbol{k}}^{(\lambda)}}{d\lambda} \rangle \right).$$
(5.15)

This  $\lambda$  dependence in this expression can be eliminated using Stokes theorem. First the integrand is rewritten in the following way:

$$2\mathrm{Im}\left(\langle \frac{du_{n\boldsymbol{k}}^{(\lambda)}}{d\boldsymbol{k}} | \frac{du_{n\boldsymbol{k}}^{(\lambda)}}{d\lambda} \rangle\right) \tag{5.16}$$

$$= \operatorname{Im}\left(\langle \frac{du_{n\boldsymbol{k}}^{(\lambda)}}{d\boldsymbol{k}} | \frac{du_{n\boldsymbol{k}}^{(\lambda)}}{d\lambda} \rangle - \langle \frac{du_{n\boldsymbol{k}}^{(\lambda)}}{d\lambda} | \frac{du_{n\boldsymbol{k}}^{(\lambda)}}{d\boldsymbol{k}} \rangle\right)$$
(5.17)

$$= \operatorname{Im}\left(\frac{d}{d\boldsymbol{k}}\left(\langle u_{n\boldsymbol{k}}^{(\lambda)} | \frac{d}{d\lambda} | u_{n\boldsymbol{k}}^{(\lambda)} \rangle\right) - \frac{d}{d\lambda}\left(\langle u_{n\boldsymbol{k}}^{(\lambda)} | \frac{d}{d\boldsymbol{k}} | u_{n\boldsymbol{k}}^{(\lambda)} \rangle\right)\right)$$
(5.18)

$$= \operatorname{Im}\left(\nabla_{(\lambda,\boldsymbol{k})} \times \langle u_{n\boldsymbol{k}}^{(\lambda)} | \nabla_{(\lambda,\boldsymbol{k})} | u_{n\boldsymbol{k}}^{(\lambda)} \rangle\right), \tag{5.19}$$

where  $\nabla_{(\lambda, \mathbf{k})}$  and  $\nabla_{(\lambda, \mathbf{k})} \times$  denotes the partial derivative in the  $(\lambda, \mathbf{k})$  space and the curl  $\nabla \times \mathbf{A} = \frac{d\mathbf{A}}{d\mathbf{k}} - \frac{d\mathbf{A}}{d\lambda}$  respectively. Inserting equation. 5.16 back into eq. 5.15 we get:

$$\Delta \boldsymbol{P}_{el} = -\frac{e}{(2\pi)^d} \int_0^1 \sum_n^{occ} \int_{\mathrm{BZ}} d\boldsymbol{k} \mathrm{Im} \left( \nabla_{(\lambda,\boldsymbol{k})} \times \langle u_{n\boldsymbol{k}}^{(\lambda)} | \nabla_{(\lambda,\boldsymbol{k})} | u_{n\boldsymbol{k}}^{(\lambda)} \rangle \right).$$
(5.20)

The integral in eq. 5.20 can now be recast as a surface integral using Stokes theorem:

$$\Delta \boldsymbol{P}_{el} = -\frac{e}{(2\pi)^d} \operatorname{Im}\left(\sum_{n}^{occ} \oint_{\mathrm{BZ}} d(\lambda, \boldsymbol{k}) \left\langle u_{n\boldsymbol{k}}^{(\lambda)} | \nabla_{(\lambda, \boldsymbol{k})} | u_{n\boldsymbol{k}}^{(\lambda)} \right\rangle\right).$$
(5.21)

Due to the periodicity of the Brillouin zone, the values at its surface are identical and thus the only contribution to the integral comes with the difference at the boundary of the  $\lambda$  space, in other words the difference between  $\lambda = 0$  and  $\lambda = 1$ . Finally the change in polarization density (including the ionic contribution) can be written as:

$$\Delta \boldsymbol{P} = \Delta \boldsymbol{P}_{\text{ionic}} + \boldsymbol{P}_{el}(\lambda = 1) - \boldsymbol{P}_{el}(\lambda = 0)$$
(5.22)

where:

$$\Delta \boldsymbol{P}_{\text{ionic}} = \frac{e}{V} \sum_{i} \left( Z_{i}^{\lambda=1} \boldsymbol{R}_{i}^{\lambda=1} - Z_{i}^{\lambda=0} \boldsymbol{R}_{i}^{\lambda=0} \right)$$
(5.23)

and

$$\boldsymbol{P}_{el}(\lambda) = -\frac{e}{(2\pi)^d} \operatorname{Im}\left(\sum_{n}^{occ} \int_{\mathrm{BZ}} d\boldsymbol{k} \left\langle u_{n\boldsymbol{k}}^{(\lambda)} | \nabla_{(\boldsymbol{k})} | u_{n\boldsymbol{k}}^{(\lambda)} \right\rangle\right)$$
(5.24)

$$= -\frac{e}{V} \operatorname{Im}\left(\sum_{n}^{occ} \sum_{\boldsymbol{k} \in \mathrm{BZ}} \langle u_{n\boldsymbol{k}}^{(\lambda)} | \nabla_{(\boldsymbol{k})} | u_{n\boldsymbol{k}}^{(\lambda)} \rangle\right)$$
(5.25)

For practical numerical computations of polarization of materials, one has to first computes Berry phases. The expression obtained in eq. 5.24 is not the most straightforward way compute Berry phases numerically [108]. Instead we use the formula:

$$\boldsymbol{P} = \frac{1}{2\pi} \frac{e}{V} \sum_{l} \phi_l \mathbf{a}_l.$$
(5.26)

where  $\mathbf{a}_l$  denote lattice vectors and the phase  $\phi_l$  is:

$$\phi_l = \sum_i Z_i \mathbf{b}_l \cdot \mathbf{R}_i - \phi_l^{\text{elec}},\tag{5.27}$$

where the first part represent the contribution to the polarization from the ions and the second the electronic contribution which is given by:

$$\phi_l^{\text{elec}} = \frac{1}{N_{k\perp\mathbf{b}_l}} \text{Im}\left(\sum_{\boldsymbol{k}\in\text{BZ}_{\perp\mathbf{b}_l}} \ln\prod_{j=0}^{N_{k\parallel\mathbf{b}_l}-1} \det_{occ}\left(\langle u_{n\mathbf{k}+j\delta k} | u_{m\mathbf{k}+(j+1)\delta k}\rangle\right)\right),\tag{5.28}$$

where  $\mathrm{BZ}_{\perp\mathbf{b}_l}$  represent a plane of **k**-points that are orthogonal to the reciprocal lattice vectors  $\mathbf{b}_l$ ,  $\delta k$  is the distance between neighbouring **k**-points in the  $\mathbf{b}_l$  direction,  $N_{k\parallel\mathbf{b}_l}$ and  $N_{k\perp\mathbf{b}_l}$  are the number of **k**-points along and perpendicular to the  $\mathbf{b}_l$  direction respectively. The derivation of this formula starting from eq. (5.24) is derived in detail Appendix A. The logarithm of a determinant in eq. 5.28 is equivalent to a sum over phases that ammounts to the total accumulated Berry phase along the string of k-points from j = 0 to N - 1. The Berry phase is gauge dependent, which means it is only defined modulo  $2\pi n$  where n is an integer. This means that the polarization also is not uniquely defined but can be written as:

$$\tilde{\boldsymbol{P}} = \boldsymbol{P} + n \frac{e}{V} \boldsymbol{R},\tag{5.29}$$

where *n* can be any integer and the quantity  $\frac{e}{V}\mathbf{R}$  is known as the polarization quantum. The fact that the polarization in eq. 5.29 is not unique reflects the point made by Resta, namely that only differences in polarization are physically meaningful. Here it is useful to define a the polarization lattice as the set of polarizations produced by inserting all integers into the expression in eq. 5.29.

In chapter 2 it was stated that a material must have a polar point group in order to be a ferroelectric. In other words that materials with a non-polar pointgroup do not have a finite polarization. This does seem at odds with eq. 5.29, because if  $\boldsymbol{P} = 0$  one can always add a polarization quantum and obtain a finite  $\tilde{\boldsymbol{P}}$ . The answer to what seems to be a paradox is that for non-polar structures the polarization lattice obeys  $\tilde{\boldsymbol{P}} = -\tilde{\boldsymbol{P}}$ . This is the correct definition of a material being non-polar as there are actually counterexamples where the value  $\boldsymbol{P} = 0$  does not appear in the polarization lattice. One such example is KNbO<sub>3</sub> [102].

In order to compute polarization differences one has to use eqs. (5.26-5.28) together with eq. (5.29) in order to calculate a polarization that is physically meaningful. What one has to do compute the difference in polarization for a system in a non-polar system where the polarization lattice is  $\tilde{\boldsymbol{P}} = -\tilde{\boldsymbol{P}}$  and a system with a polar symmetry axis. The case corresponds to  $\lambda = 0$  in eq. (5.22) and the second structure to  $\lambda = 1$ . Another option more akin to what is done in experiments is to compute the difference in polarization between energetically degenerate states with a polarization density of similar magnitude pointing in opposite directions. In this case the polarization difference will be  $2\boldsymbol{P}_0$ , with  $\boldsymbol{P}_0$  being the spontaneous polarization. When applying eqs.



Figure 5.2: The figure depicts the steps necessary in calculating the branch fixed in-plane polarization for the two-dimensional material  $As_4Se_6$ . The polarization is given in dimensionless units, such that the quantity 1 corresponds to one polarization quantum. In fig. a) the in-plane polarization of  $As_4Se_6$  is calculated using a polarization path with only 5 points resulting in an incorrect formal polarization. In b) the same calculation is carried out with more points. The final result is depicted in figure c), and it is seen that in this case one branch remains fixed across all calculations. The final figure is taken from [I].

(5.28-5.26) in practice to compute the polarization the  $\lambda$  variable is discretized. Due to the ambiguity in the definition of the polarization density a practical calculation of the spontaneous polarization involves choosing to compute the polarization along some branch. A branch is defined as calculation polarizations for different values of lambda that are matched such that they correspond to the same value of n in eq. 5.29. Such branches are depicted in 5.2, where the polarization is computed for  $As_4Se_6$  a twodimensional ferroelectric found in [I]. As seen in the figure one cannot simply use the end points or a few points between the end points to reliably construct a branch. For each now point, other points along the same polarization lattice are found by adding and subtracting  $n \stackrel{e}{\underline{v}} R$  from the polarization n times. Each value is then compared to the value obtained at the previous point on the branch. The point that is closest is then chosen as the next branch point. By iterating this procedure one can then obtain a full polarization branch and finally subtract the value at the endpoint from the one at the starting point to obtain the total change in polarization along the branch. The necessary number of branch points as well as points shifted points along the polarization lattice generally vary depending on the material in question. If the polarization is many times larger than the polarization quantum the different polarization branches will lie closer to one another and more copies as well as branch points are needed to accurately construct a polarization branch. If the size of the polarization change relative to the polarization quantum is not known, like in a high-throughput study, one has to use a lot of points to be on the safe side.

In addition to the potential computational issues already mentioned, the entire framework of the modern theory of polarization rests on the assumption of the adiabatic approximation. As already mentioned in chapter 2 ferroelectrics are only well defined if they are insulating because polar metals cannot have their polarization switched since any electric field would be screened by charged carriers. Within the framework of the modern theory of polarization the assumption that the system must be ferroelectric is enforced implicitly. If a band gap closes it means some of the energy bands have crossed, and then the assumption that energies were well separated breaks down.

#### 5.3 Coercive fields and switchability

It is not sufficient to know whether a polar material has a polarization, since it may simply be a pyroelectric material. In order to know whether a material is ferroelectric it is necessary to determine whether the polarization is switchable or not. One way to answer this question theoretically is to compute the size of the electric field required to switch the polarization. This is however much more complicated than it sounds. First of all real ferroelectric materials contain many different domains with ferroelectric states pointing in various directions. In addition real materials contain impurities such as defects or grain boundaries and as such it may not be able to switch the polarization in each domain with the same ease. However if we consider a theoretical case where the polarization in all domains are perfectly aligned. What electric field is required to switch the polarization in this case? One can achieve a good answer by considering the monodomain case of switching the polarization within just one unit cell. The polarization can be obtained using the approach outlined in section 5.2. If one can then parameterize the energy landscape in terms of the polarization P:

$$E(\mathbf{P}) = E_0(\mathbf{P}) - \boldsymbol{\mathcal{E}} \cdot \boldsymbol{P},\tag{5.30}$$

the coercive field can be computed as:

$$\mathcal{E}_{\rm c} = \max\left(\frac{dE_0(\mathbf{P}^{\lambda})}{d|\mathbf{P}|}\right). \tag{5.31}$$

By computing the maximal value of the slope of  $E_0(\mathbf{P})$  we are computing the field exactly necessary to switch the polarization from  $\mathbf{P}$  to  $-\mathbf{P}$ . This estimate of the coercive field is an unrealistic estimate for real materials where polarizations are switched by more complicated means like domain wall migration and nucleation, however it serves an upper bound on coercive field. This is useful in high-throughput studies where one is typically concerned with finding materials with smaller coercive fields since these might be the best candidates for certain technological applications. If the upper bound on the coercive field is predicted to be comparatively small for a given material, then the actual coercive field for that material must also be small.

#### 5.4 Born effective charges and polarization densities

So far we have been concerned with calculating the polarization for a periodic system using the berry phase approach. There is however a couple of drawbacks to this approach, the primary one being that some systems that are ferroelectricly ordered, that is the systems contain finite electric dipoles, have electric dipoles that add up to a total polarization density of 0. The most simple example would be a material in an anti-ferroelectric phase with neighbouring unit cells having net electric dipoles that were anti-aligned. In this case the berry phase approach would correctly predict a vanishing polarization density. However this approach fails to capture the local dipole moments and it is therefore impossible to tell apart anti-ferroelectric materials from non-ferroelectric ones. More generally ferroelectric materials contain domains that can have local polarizations aligned in many different directions, and there are antiferrielectric phases where individual electric dipoles have different magnitudes. In order to identify these materials and characterize the origin of electric dipoles, additional analysis tools are needed. One approach is to use so called Born effective charges. These are charges defined such that they describe the effective charge an atom has once it is bonded in a given chemical environment. The Born effective charges are defined as the change in force on a given atom a under the application of an external electric field  $\mathcal{E}$ :

$$F_i^a = \sum_j (Z_{ij}^a)^* \mathcal{E}_j, \tag{5.32}$$

where  $(Z_{ij}^a)^*$  is the Born effective charge tensor on atom a. A more applicable but equivalent definition, is that the Born effective charge tensor of atom a is the change in polarization density given a displacement of said atom:

$$Z_{ij}^{a} = \frac{V}{e} \frac{\partial P^{i}}{\partial u_{j}^{a}} |_{\mathcal{E}=0}, \tag{5.33}$$

where the partial derivative of  $\frac{\partial P^i}{\partial u_g^a}|_{\mathcal{E}=0}$  is the partial derivative of the polarization density with respect to atomic displacement of the a'th atom in the j'th direction. To perform a computation of the Born effective charge tensor using 5.33 one would use the formula for the polarization in eq. 5.22 and then compute the change in polarization under tiny variations in u. The notion of Born effective charge given here can be contrasted with the simple nominal charges that individual atoms have a non-bonded environment. The Born effective charge can then be thought of (as the name suggests) as an effective charge of an atom in a given environment when one includes not only the ionic but also the electronic contribution. Using the definition of polarization from eq. 5.22 the Born effective charges then becomes:

$$Z_{ij}^a = \delta_{ij} Z_{ij}^a + \frac{V}{e} \frac{\partial P_{el}^i}{\partial u_i^a} |_{\mathcal{E}=0},$$
(5.34)

From this equation ne can explicitly see that the Born effective charges of an atom is the sum of the nominal ionic charge as well as a contribution from due to electrons. For this reason Born effective charges can be quite useful to determine how bonded Despite being useful in for example determining how strength of a chemical bonds. Born effective charges can also be utilized to compute the contribution to the electron polarization from individual atoms. If for example one interested in knowing the polarization profile in a ferroelectric domain where the polarization varies as a function of space. In such a scenario one has to divide the domain up into sections and then compute the polarization of each part by adding up contributions in the following way:

$$P_i = \frac{1}{\Omega} \sum_j \sum_a Z^a_{ij} \Delta R^a_j \tag{5.35}$$

where  $P_i$  is the polarization in the i'th direction,  $\Delta R_j$  is the displacement of atom a in the j'th direction relative the structure in a non-polar phase and  $Z_{ij}^a$  is the Born effective charge tensor of atom a.

#### 5.5 Generalalized formula for the polarization

In the theory of King-Smith and Vanderbilt one obtains the polarization from a quantum system under the assumption that the many-body state can be written as the Slater determinant of single particle states. This is however not generally the case. It is possible to derive a conceptually similar theory that doesn't make this assumption [109]. A formula has also been derived that extends the theory to non-crystalline insulators [110]. So far it remains an open question whether or not there are known materials where the approach derived by King-Smith and Vanderbilt fails and one has to apply a many-body variant of the polarization<sup>1</sup>, but one could imagine it would be relevant in for example insulators where electrons are strongly correlated. However little research has been done in trying to carry out such calculations [111].

#### 5.6 Ferroelectricity in metals

Thus far we have only been concerned with definitions of polarization densities that pertain to insulating material systems. It has long been speculated whether metals could be also support ferroelectric[112]. Recently a structural phase transition from a non-polar to a polar phase was observed in  $\text{LiOsO}_3[113]$  reviving the interest in the field. Even if such metals can sustain a finite electric polarization it will not be switchable since any applied field would be ineffectual due to screening, they are therefore referred to as polar metals. Furthermore there is no unified theory of how to calculate the polarization in such a case since metals have no gap and therefore the adiabatic assumption made in the modern theory of polarization is no longer valid. An exception to this is the case of polar metals with lower dimensionality like trilayer WTe<sub>2</sub>[114]. This material is metallic and supports an out of plane polarization, but not an in plane one. This polarization can be switched by applying an external electric

<sup>&</sup>lt;sup>1</sup>At least to the best of my knowledge

field, since the material has a finite extend in the z-direction and therefore also finite screening length.

### CHAPTER 6

## Results

### 6.1 Summary: Two-dimensional ferroelectrics from high-throughput computational screening

Ferroelectric materials already have applications in several important technologies such as sensors, actuators, capacitors as well as several potential future applications including ferroelectric field transistors[11] and ferroelectric random access memory [9]. Two dimensional ferroelectrics also has the advantage that they are not limited by a finite critical thickness in the same way that thin films made from bulk ferroelectrics are[115]. Several two dimensional ferroelectrics have already been experimentally synthesized [30–36] or have been predicted theoretically [21–29]. The purpose of this study has been to construct a computational workflow and use it to search for new two dimensional ferroelectric materials. We have then applied this workflow to polar materials in the computational 2D materials database (C2DB). Materials from the database are



Figure 6.1: The workflow used to search for new ferroelectric materials in [I]. Only gapped, dynamically stable structures are extracted from the C2DB database. The materials that have a well defined adiabatic paths are potential candidates which are analyzed further..

selected according to the criteria stated in the workflow depicted in fig. 6.1. We start by selecting dynamically stable materials, that have a polar point group and a finite band gap. That amounted to 252 materials at the time we began the project. These materials are then relaxed with a tighter criteria than the ones used in the original C2DB workflow. Specifically we require that forces on all atom be smaller than 0.001 eV/Å. This is done to ensure that we get the correct value of polarization and to verify that all structures actually have a polar pointgroup, as some were found not to have one after a close inspection. Subsequently we construct the centrosymmetric structures that are need as references to compute the branch fixed polarization using eqs. (5.26-5.28). Centrosymmetric structures are constructed using evgraf[116]. One should keep in mind that centrosymmetric is not the same as non-polar. Ideally one would find a reference structure that obey that ladder criteria. However the software at our disposal did not have this as a feature. We then construct a switching path between the centrosymmetric and polar structure using linear interpolation. Then we change the atomic positions of the original structure such that the atomic positions of each structure along the path become:

$$\boldsymbol{R}_{\lambda} = \lambda \boldsymbol{R}_f + (1 - \lambda) \boldsymbol{R}_i, \tag{6.1}$$

where  $\lambda \in [0, 1]$  is a reaction coordinate that parameterize different points along the polarization branch,  $\lambda R_f$  and  $R_i$  denote the atomic positions in the polar and non-polar structures respectively. Knowing the polarization itself is not enough to determine whether a polar material is a ferroelectric. If the polarization is not switchable the material is merely pyroelectric not ferroelectric. Linear interpolation may be a good guess for a switching path in some cases. However in many cases the initial guess may in fact be far from the actual path and as a consequence one may get the wrong energy barrier as well as the wrong coercive field. Furthermore it may be the case that the band gap of one of the structures along the path vanishes if they are generated using linear interpolation. In the last case one would not simply get the wrong values, but predict that a material is not switchable and it would be discarded. In order to get more accurate results we use the nudged elastic band (NEB) technique to optimize each of the structures along the switching path [117]. We found that for our particular application the NEB technique worked best in conjunction with the FIRE algorithm used for structural optimization of each NEB image [118]. Results for three representative materials are shown in fig 6.2. For the first material  $Ge_2S_2$  we see that linear interpolation and NEB give almost identical results. Qualitatively one does gain anything by using NEB for materials that fall in this category. In the case of  $F_2Li_2S_2$ the two methods predict qualitatively different results. Simple linear interpolation gives a large energy barrier between the centrosymmetric and polar states and that the centrosymmetric state is a metastable. Whereas the NEB method indicate that there is no such barrier. In the final case of  $In_2Te_4$  both methods indicate a barrier, however the NEB method indicates that it is much lower than what is predicted by simple linear interpolation. We have used the results obtained using the NEB method to compute coercive fields using the approach outlined in section 5.3. The examples given in fig. 6.2 indicate that linear interpolation in many cases are not a reliable method qualitatively as well as quantitatively for predicting energy barriers as well as coercive fields.

We classify the resulting ferroelectrics according to whether they are in-plane ferroelectrics, out of plane ferroelectrics or 3D ferroelectrics who have polarization densities with components in all three directions. We find 49 materials with in plane polarizations, 8 materials with out of plane polarizations and 6 materials with a three dimensional polarization. Ferroelectric materials are classified according to their point group. There are 10 polar point groups in total: 1, 2, m, mm2, 3, 3m, 4, 4mm, 6 and 6mm. The first four pointgroups might have an in plane axis. The remaining 6 point groups cannot have an in-plane polarization.

There is however an exception in the case of out of plane ferroelectrics. Some two dimensional materials may have a so called topological in-plane polarization. This is the



**Figure 6.2:** Energy versus polarization for three representative ferroelectrics, taken from [I]. Left:  $Ge_2S_2$  (in-plane polarization). Middle:  $In_2Te_4$  which has both in-plane and out-of-plane components of the spontaneous polarization. Right:  $F_2Li_2S_2$  (in-plane polarization). In all three cases we show the energy along the linearly interpolated path (LI) and energy along the path optimized by the nudged elastic band method (NEB). The insets show the side views of polar and non-polar states for  $Ge_2S_2$  and  $In_2Te_4$  and top views for  $F_2Li_2S_2$ .

case for all the out-of-plane ferroelectrics depicted in table II in [I]. This is a special type of polarization that is found in so called crystalline topological insulators[119–121]. Here the in plane values of polarization are restricted by crystal symmetries, and therefore are a priori predictable based on symmetry alone. This is still compatible with the theory applied so far and if one uses eq. 5.26-5.28 to compute the polarization in such structures one still finds the correct result. However since the polarization in such structures are fixed by symmetry one has to break the symmetry in order to change the in plane polarization. These materials are therefore not as such in-plane ferroelectrics as this would require that the in-plane polarization be switchable. The out of plane polarization is however still switchable.

As an exception to the case stated above it is possible to switch a topological polarization if the symmetry that protects it is broken. This is the case for  $In_2Se_3$  which is highlighted in the paper, with it's switching path shown in fig. 7 in [I]. Interestingly the in-plane polarization is rotated in such a way that the structure does not cross through a state where  $\mathbf{P} = 0$ .

As explained in section 2 one can classify the ferroelectrics according to whether they are proper or improper ferroelectrics. Knowing the polarization density alone doesn't reveal anything about the origin of ferroelectricity, and while an exact knowledge of this would require an in depth study of each candidate material we find it is worth to try to classify the materials we find as much as possible. If one for example wishes to explore the thermodynamics of two ferroelectrics further it matters a great deal what type of ferroelectric a given material is. Proper and improper ferroelectrics are driven by different mechanisms and it would therefore require different models to predict properties such as the critical temperature.

We have also investigated whether the ferroelectrics are proper or improper. This is done by studying the lowest energy phonon modes of the centrosymmetric reference structures (if they are well defined) at the  $\Gamma$ -point. If the phonon mode with the lowest imaginary frequency is a polar mode, it indicates that the ferroelectric which results from a distortion of the structure is a proper ferroelectric. If this isn't the case we conclude that it is an improper ferroelectric. All materials we have investigated are found to be proper ferroelectrics. Our phonon analysis does reveal that some materials appear to have a centrosymmetric state which is metastable. This might have implications for whether the phase transition in the ferroelectric materials are of first- or second-order.

Previous investigations of critical temperatures of two dimensional ferroelectrics have used a model of the form: [21, 26, 28, 122]:

$$E(P) = \sum_{i} \left( \frac{A}{2} P_i^2 + \frac{B}{2} P_i^4 + \frac{C}{2} P_i^6 \right) + \frac{D}{2} \sum_{\langle i,j \rangle} \left( P_i - P_j \right)^2,$$
(6.2)

to model phase transitions and compute critical temperatures. This model considers a supercell where the summation index i represent the cell index and  $P_i$  the polarization of each cell. The parameters A, B, C and D are Landau parameters were the first three terms describe an anharmonic double well potential. The last term represent dipole-dipole interactions, with the sum being limited to sites j that are neighbors to sites i. The parameter D cannot be obtained from the data extracted in this study and require either mean-field treatment or more computationally heavy approaches that require supercell calculations[123]. The parameters A, B and C can be found by fitting the first three terms above to the energy and polarization datasets obtained in the study using DFT. If an expression of the energies in the form presented in eq. 6.2 is used in conjunction with Monte-Carlo simulations it is possible to predict critical temperatures of ferroelectrics. Of course the exact form of the model depends on the specific ferroelectric in question.

The polar materials considered in our study also include magnetic ones. All the magnetic structures in the C2DB have their magnetic moments set to be ferromagnetically aligned by default. This is not because they are all neccessarely ferromagnetic, but a choice made by the database creators. Notably our workflow does not capture ferroelectricity in any one of them. There are two primary reasons for this. The first being that some of the magnetic materials are mabye not actually switchable and that our workflow simply predicts them to be pyroelectric. The other explanation might be that the gaps are mispredicted. This can happen for a number of reasons. The first being that the magnets might be considered in magnetic configuration that is not actually the true groundstate magnetic configuration. Several of the magnets in our study such as VOCl2 and VOBr2 have been shown to be multiferroic, but to have an

antiferromagnetic groundstate [124]. Another explanation is that the PBE functional simply can't correctly predict the band gap. It suffers from the infamous derivative discontinuity. This problem may even also be the case for some of the ferroelectrics that are not magnetic. Furthermore the magnetic compounds contain transition metal atoms with partially filled d orbitals. The correct description of these materials require local correlations to taken into account to avoid the self-interaction error as described in section 3.7. This can be done either by applying a PBE+U approach where Hubbard corrections are added to the d orbitals of transition metal atoms. Another option is to simply use a different functional like what was done for the VOX2 (with X=Cl, Br, F, I) compounds in references [124, 125] where the HSE06 functional was applied. This functional is however much more computationally expensive and therefore the PBE + U approach may be a better future alternative for high-throughput studies of magnetic ferroelectrics. The paper also highlights one polar magnetic material that has been investigated further namely  $VAgP_2Se_6$ . We find the material to have a triply degenerate ferroelectric groundstate, which is switched through rotation The magnetic properties can be characterized using the Heisenberg model:

$$H = -\frac{J_1}{2} \sum_{\langle ij \rangle \angle} \boldsymbol{S}_i \cdot \boldsymbol{S}_j - \frac{J_2}{2} \sum_{\langle ij \rangle \perp} \boldsymbol{S}_i \cdot \boldsymbol{S}_j$$
(6.3)

We find that all the states are ferromagnetic, but an analysis of the excitation spectra using spin-wave theory shows that the the excitation spectra depends on the polar axis. This means that one can actually readout which ferroelectric state the material is in by probing the magnetic excitations.

Despite successfully having found new ferroelectric materials, there are several shortcomings of our workflow. The first one is that our results hinges on the fact that the materials must be gapped in order for a polarization to be computed using the Berry phase approach. Of course some of the polar materials may simply not be switchable. Another reason could be that the PBE functional erroneously predicts a structure along the adiabatic path to be gapless. The PBE famously suffer from the so called derivative discontinuity problem. An alternative approach would therefore be to simply use a better exchange correlation functional. This would come at the expense that calculations would be more computationally heavy. In another high-throughput study on bulk ferroelectrics a slightly different approach was taken [126]. Here the change in volume as the material switches between it's polar and non-polar phase was taken into account. To get the correct polarization the authors instead used the corrected polarization:

$$\tilde{P}_{\lambda,i} = P_{\lambda,i} \frac{\frac{R_i^{\text{polar}}}{\Omega_{\text{polar}}}}{\frac{R_{\lambda,i}}{\Omega_{\lambda}}}$$
(6.4)

for the polarization at each point along the branch. In our study this wasn't an issue because the **evgraf** software didn't modify the unit cell and any relaxations we performed only optimized atomic positions not lattice constants. A potential application of a modifying our workflow would be looking for ferroelectric-ferroelastic multiferroics. In these system one has to investigate changes in polarization in conjunction with changes in strain. In such a case the lattice constants are not fixed and one has to modify the polarization lattice according to eq. 6.4.

The magnetic structures investigated here are all considered in a ferromagnet state. That means that their polar point group stems from the symmetry of the lattice, not the magnetic order. This implicitly limits our search to magnetoelectric multiferroics of type-I. In order to extend the search to type-II multiferroics, the workflow must be extended to include candidate structures where the structural point group is non-polar, but where the magnetic configuration gives rise to a polar magnetic point group. Such work is beyond the scope of this thesis, but recent work has been done for a number of selected two dimensional magnets with non-collinear spin configurations [127].

The workflow presented in this work could easily be applied to another dataset from another database or for C2DB once more materials are added, such that more ferroelectrics might be discovered. Another way to look for new materials would be to use lattice decoration techniques for the prototypes found in this work. One would likely find materials that were qualitatively similar, but differences in chemical composition might yield materials that are more suited for applications. A good example would be ferroelectrics with lower switching barriers or higher spontaneous polarizations than other ferroelectrics from the same material family.

### 6.2 Summary: Recent Progress of the Computational Materials Database (C2DB)

Ever since it was discovered that graphene could successfully be exfoliated from bulk graphite [19], the interest in two dimensional materials within the materials science community has exploded. Not long after other two dimensional materials were successfully exfoliated. These include, among others, the transition metal dichalcogenides like  $MoS_2$ , noble metal dichalcogenides like  $PtSe_2$  and elemental 2D materials like black phosphorus [128]. In 2017 the first two dimensional magnet, CrI<sub>3</sub>, was exfoliated from its bulk counterpart [20]. Due to the surge of interest in two dimensional materials, several researchers have aimed to predict many new potentially synthesizeable two dimensional compounds systematically by using computational methods. This has resulted in the creation of several 2D material repositories [95, 99–101]. This paper concerns the addition of new materials and material descriptors to the Computational 2D Materials Database (C2DB). The paper is thus a sequel to the original work were the first materials were added in a freely available online repository among with the most basic mechanical, electronic and magnetic properties, such as dynamic- and thermodynamic stability, bandstructures, electron masses and magnetic configurations[95]. In this paper new materials have been added to the database and the original property workflow has been extended, as depicted in figure 6.3. If a given material passes the criteria listed in the figure, the new features in the property workflow are: exfoliation energies, Bader charges, Born effective charges, polarizabilities (optical and infrared), piezoelectric tensors, Raman, spectra, second harmonic generation, spontaneous polarizations, topological invariants and exchange coupling constants computed from the



Figure 6.3: The workflow used to generate materials found in [93], and compute their properties. This is an updated version of the original workflow, with the addition of new features in the property workflow.

Heisenberg model. The paper also contains a section on machine learning, where the pDOS fingerprint is presented as an example of machine learning applied to the C2DB. The new materials included are monolayers that are exfoliated from experimentally known compounds and Janus monolayers. In addition to new features the paper also included some updates to already existing features such as the dynamical stability, the stiffness tensor, the optical absorbance, the emasses and the magnetic classification. The paper also discusses the possibilities of creating new databases that are extensions of the C2DB database, like a monolayer database where specific atoms are substituted with defects or multilayer databases where homobilayers are created starting from the monolayers found in C2DB. A defect database was later created[129].

My part of the paper was the addition of spontaneous polarizations to the workflow. These are described in section 5.3 of the paper, which I co-wrote. The computational method for finding the spontaneous polarization using the Berry phase is already explained in chapter 5 of the thesis. Figure 15 in [II] illustrates the computation of the spontaneous for  $\text{Ge}_2\text{S}_2$ . The computations were performed for materials that in addition to satisfying the requirements listed in fig. 6.3, had a polar point group and a finite band gap. At the time of publication the database had above 4000 materials, which approximately 2500 more materials than the original 1500 materials. The database is constantly being updated with new materials and new properties. Since the publication of this paper the C2DB has been updated further. In the time of writing it has a total of 15733 materials.

### 6.3 Summary: Oxygen Vacancies Nucleate Charged Domain Walls in Ferroelectrics

Charged domain walls have attracted significant research attention due to their potential applications in areas ranging from non-volatile memory [130] and to photovoltaics [16, 131]. The charge degree of freedom sets these domain walls apart from their neutral counter has been shown to result in a much more rich phenomenology. Research in this area has been focused on understanding the formation, structure, and behavior of charged domain walls in ferroelectrics, as well as their interaction with external stimuli such as electric fields.

In this project we set out to gain a better understanding of the role played by oxygen vacancies in the formation of ferroelectric domains. Previous theoretical and experimental work on charged domain walls indicates that oxygen vacancies act as crucial stabilizing agents for charged domain walls [132–134]. In this work we focus on the role oxygen vacancies plays in the formation of charged domain walls. To investigate this phenomenon we study the perovskite oxide  $BaTiO_3$ . We investigate  $BaTiO_3$  in it's tetragonal structure (P4mm), which has a polarization in the [001] direction. This phase forms at 404K and persist down to 273K. Our focus is on formation of  $180^{\circ}$ degree domain walls where polarizations of opposite alignment meet at the domain wall. This leads to two types of domain walls: positively charged head-to-head (HH) and negatively charged tail-to-tail (TT) walls. The first section of the paper studies defect free charged domain walls in  $BaTiO_3$  as a reference for later calculations with defects. We simulate domain walls by setting up 1x1x16 supercells, with HH domain walls situated at the zone boundaries and TT domain walls situated in the middle of the cell. The polarization profile across the supercells are modelled according to the function:

$$P^{a}(z) = P_{0} \tanh\left(z^{a}/\delta\right) \tag{6.5}$$

where  $P_0$  is the saturated polarization value inside domain which is computed using eq. (5.35) and the approach outline in section 5.4,  $z^a$  is the distance measured from the center of cell a and  $\delta = 1.75$  the domain wall width. Because the domain walls are in fact metallic, we can't calculate the Born effective charges in this state. Instead we have used an average between the converged values obtained for the born effective charges in bulk tetragonal and cubic reference structures. This approach leads to a polarization of  $0.24C/m^2$  which is in good agreement with what has previously been observed. Further analysis of the TT and HH domain walls is done by computing the density of bound charges resulting from the polarization profile and the electrostatic potential using DFT. This is done using the sliding average technique. The full approach is outlined in the appendix of the paper, but the idea is that because nuclear and electronic charge varies rapidly at the atomic scale the charge distribution will oscillate rapidly as a function of distance. In order to determine the charge density (and the potential) we perform integrals (slide averages) over the charge density around the point of interest. We use a Gaussian dampening function for the nuclear charge and integrate over intervals [z - c/2, z + c/2] where c is the length of the unit cell. Our results indicate a linear potential and thus a constant electric field in each domain. Our

computations suggest that free charge almost perfectly compensates the bound charge at the domain walls. Projected density of states calculations provide further evidence that the conduction electrons at the Fermi level are situated at the charged domain walls. Projected bandstructure calculations indicate that electron (hole) doping occur at the HH (TT) walls respectively.

The later part of the paper focuses on the formation of charged domain walls with oxygen vacancies present. The starting point are single domains simulated using a  $3 \times 3 \times 8$  supercell. We then start by adding a single oxygen vacancy and then performing a structural relaxation. Our analysis has revealed that it is more energetically favorable for vacancies to occupy BaO planes as supposed to  $TiO_2$  planes. We compare the total energy of the relaxed structures with an oxygen vacancy with the energy of a vacancy free bulk structure. We then go on to add more than one vacancy compute the energy as function of which BaO plane the vacancy is in for each iteration. Our analysis shows that it is energetically favourable for oxygen vacancies to cluster at different positions in the same BaO plane. This seems counter intuitive at first sight because the vacancies are all positively charged and one would expect them to repel one another. We resolve this by observing that each vacancy indices a polarization, which in turn causes negative charge to migrate to the TT wall in order to compensate for the positive charge of the vacancies. Thus negative TT walls are formed which in turn acts as sinks for any additional vacancy which is added. We also compute profiles for the bound charge density which indicate that concentration of oxygen vacancies seems to saturate once the walls are formed, with our computations suggesting the saturated number of vacancies lie somewhere between two and three. We interpret these results as implying that oxygen vacancies acts to initiate the formation of TT domain walls in  $BaTiO_3$ and not merely stabilize them as previous research seems to indicate.

After the submission of paper [III], new work on Born effective charges outside the adiabatic limit has been done [135, 136]. Those papers attempts to generalize the notion of Born effective charges to the non-adiabatic regime. This may provide a venue to compute the polarization profiles of supercells in a way that is more methodologically correct.

# CHAPTER 7 Anomalous Hall conductivity in magnets

The results presented in this chapter is part of unfinished work, and therefore not found in the list of publications in the introduction of this thesis.

The experimental methods used for investigating magnetic materials are many. One of the most widely used techniques when it comes to magnets is neutron scattering [39]. When it comes to two dimensional materials however neutron scattering often falls short when faced with scattering values on the atomic scale. For such systems different techniques have to be applied such as transport- or magneto-optical measurements. One of the most famous two dimensional transport signatures is the Hall effect. The effect was originally discovered by Edwin Hall, and hinted that current was caused be negative carriers not positive ones<sup>1</sup> [137]. Subsequently the Hall effect has been utilized in order to determine the carrier concentration in semiconductors. After its original discovery the Hall effect was observed in magnetic conductors but at a magnitude much larger than what was observed for the ordinary Hall effect. It was subsequently dubbed the anomalous Hall effect and the theoretical underpinnings of this phenomenon was not properly understood before the later half of the 20'th century. This was a period were various related effects have been discovered such as spin Hall effect[138, 139], an analog of the Hall effect for spin currents. Then came the discovery of the quantized analogs of the Hall effect first in two dimensional electron gases [140–144] and later in topological insulators [145-148]. This era also to a deeper understanding of the anomalous Hall effect in magnets and sparked a renewed interest in the field.

This chapter concerns a computational study into the anomalous Hall effect. First the ordinary Hall effect is briefly introduced and then contrasted with the anomalous Hall effect. Linear response theory is briefly introduced and subsequently used to derive an expression for the intrinsic contribution to the Hall conductivity. Finally results obtained using an implementation of the Hall conductivity in GPAW are presented and compared with results found in literature.

<sup>&</sup>lt;sup>1</sup>The electron was not discovered yet.

#### 7.1 Ordinary Hall Effect

The Hall effect was first discovered in 1879, by Edwin Hall, when he was investigating the relationship between electric current and magnetic fields [137]. The effect is best understood by considering a Hall bar setup, like the one depicted in fig. 7.1. Here a power source provides a finite voltage across a material resulting in a finite current. The material is simultaneously under the influence of an external magnetic field applied perpendicular to the plane. Under such conditions a finite potential difference is generated between each side of the Hall bar in the direction perpendicular to the current. The Hall effect can be understood by applying the classical theory of electromagnetism. A classical charged particle moving in a electromagnetic field is under the influence of the Lorentz force:

$$\boldsymbol{F} = q\left(\boldsymbol{E} + \boldsymbol{v} \times \boldsymbol{B}\right),\tag{7.1}$$

where F is the Lorentz force, q is the particle charge, E the electric field, v the velocity of the charged particle and B represents an external magnetic field. In the Hall bar setup the electric current. J = -ev is caused by electrons with charge q = -e running through it. The first term in 7.1 is what generates the electric current, while the second term is what is responsible for electrons drifting to one side of the material. The system eventually reaches a steady state when the two forces in eq. 7.1 cancel each



Figure 7.1: a). A sketch of a Hall bar setup viewed from above. A power source delivers a finite voltage V across a material resulting in a finite current J. Upon the application of an external magnetic field B, the charged particles (electrons) in the material start to drift to one side due to the Lorentz force, resulting in a finite transverse voltage.

other out. The drift of electrons to one side causes a voltage to develop perpendicularly to the current. As shown by Hall this setup can be used to measure the charge carrier concentration using an expression of the form [137]:

$$R_H = \frac{V_H t}{JB} = \frac{1}{ne}.\tag{7.2}$$

where  $R_H$  is the Hall coefficient,  $V_H$  the Hall voltage i.e. the voltage that develops from the drift component of the electric field, B is the magnetic field, J the current, t the material thickness, e the electron charge and n the charge carrier concentration. This effect is still widely applied to determine the electron (or hole) concentration in semiconductors. Not long after its discovery, the Hall effect was observed in magnetic conductors. Here the effect was much stronger, and later it was discovered that the effect persisted in magnetic systems even in the absence of an external magnetic field. For this reason it was given the name the anomalous Hall effect. This effect will be the main topic for the remainder of this chapter.

#### 7.2 Anomalous Hall effect

The anomalous Hall effect (AHE) is similar to the ordinary Hall effect, in that the observed physics is the same. The underlying cause is however quite different. While the ordinary Hall effect occur in materials under the application of an external magnetic field, the anomalous Hall effect refers to analogous phenomena but without any external magnetic field present. Instead it happens for materials where time-reversal symmetry is broken by different means, namely by the material having an finite internal magnetization. A finite magnetization is not enough however, as the material must in addition have a finite spin-orbit coupling. The fact that the (AHE) requires ferromagnetism, stems from the fact that time-reversal symmetry breaking is necessary in order to obtain a finite Hall conductivity. The characteristic feature the Hall conductivity is defined as the anti-symmetric component of the linear conductivity which is defined through the relation:

$$J(\boldsymbol{r},t)_{\alpha} = \int_{-\infty}^{\infty} d\boldsymbol{r}' \int_{-\infty}^{\infty} dt' \sigma_{\alpha\beta}(\boldsymbol{r},\boldsymbol{r}',t,t') E_{\beta}(\boldsymbol{r}',t'), \qquad (7.3)$$

where  $J(\mathbf{r}, t)_{\alpha}$  denotes the current in the  $\alpha$ 'th direction and  $E_{\beta}(\mathbf{r}', t')$  the electric field in the  $\beta$ 'th direction. The fact that time-reversal symmetry breaking is necessary follows directly from the Onsager relation for response functions [149]:

$$\sigma_{\alpha\beta}(\omega, M) = \sigma_{\beta\alpha}(\omega, -M) \tag{7.4}$$

The Hall conductivity therefore obeys the equation:

$$\sigma_{xy}^{A}(\boldsymbol{M}) = \sigma_{xy}(\boldsymbol{M}) - \sigma_{yx}(\boldsymbol{M}) = \sigma_{xy}(\boldsymbol{M}) - \sigma_{xy}(-\boldsymbol{M}).$$
(7.5)

As indicated by eq. 7.5 the Hall conductivity is only non-zero if time-reversal symmetry is broken by either an external magnetic field or an internal magnetization.

There are generally three terms that contribute to the anomalous Hall conductivity[149]:

$$\sigma_{\alpha\beta}^{\rm AH} = \sigma_{\alpha\beta}^{\rm AH-int} + \sigma_{\alpha\beta}^{\rm int-skew} + \sigma_{\alpha\beta}^{\rm int-sj}$$
(7.6)

The first contribution is the intrinsic contribution, which is also sometimes referred to as Karplus-Luttinger contribution [150]. The contribution is intrinsic in the sense that it does not external factors such as impurities. The proposed theory by Karplus and Luttinger was that when electrons in magnetic solids with strong spin-orbit coupling are subject to an external electric field they acquire a transverse contribution to their group velocity that was not previously recognised. This is analogous to the role of the Lorentz force for the ordinary Hall effect. A Hall bar exhibiting the AHE is depicted in figure 7.2.

The second contribution is the skew scattering term which is directly proportional to the lifetime of the scattering electrons  $\tau$  physically its involves scattering asymmetry effects in materials with impurities.

The third contribution to the anomalous Hall conductivity is the side-jump contribution. This is sometimes defined merely as the contribution which doesn't fall into the two other categories. In physical terms it arises during electron impurity scattering due to the spin-orbit coupling of the impurity. This contribution, unlike the skew scattering part, is independent of the scattering time.

In concrete experiments one has to try to separate the different contributions to the anomalous Hall conductivity. Experimentalists usually measure the resistivity, not the conductivity. A method that has been frequently applied is to see how the Hall component  $\rho_{xy}$  of the resistivity varies as a function of the longitudinal component  $\rho_{xx}$ . Because the different Hall components depend on electron scattering rates at different orders one can extrapolate the contributions from the data [149]. There has been some debate among experimentalists regarding the accuracy of this method when measurements are performed over a range of temperatures. Some of the recent developments have provided more accurate schemes for separating the three different contributions [151][152].

Most of the theoretical work attempting to describe the (AHE) from first-principles has focused on the intrinsic component. However some work has also been done for the side-jump contribution [153]. For the remainder of this chapter our focus will be the intrinsic contribution.

#### 7.3 Linear response theory

A useful framework for computing inherently non-equilibrium response functions, like the conductivity tensor, is linear response theory [154]. The general philosophy is to express the response function of interest, using only information about the system in equilibrium. This description works well if the response to a weak external perturbation is also weak. Consider a system described by a Hamiltonian:

$$H(t) = H_0 + H'(t) \tag{7.7}$$

where  $H_0$  is the Hamiltonian in equilibrium, H'(t) is a time-dependent contribution that stems from some external perturbation. In equilibrium the system is simply governed by  $H_0$ . In this case the thermodynamic average of a quantity represented by



Figure 7.2: A sketch of a Hall bar setup similar to the one displayed in 7.1, but without an external magnetic field. Instead the material under consideration is a ferromagnetic metal with spin-orbit coupling. The magnetic moments give rise to an finite internal magnetization M which breaks time-reversal symmetry. Combined with spin-orbit coupling this gives rise to a drift of electrons to one side, giving rise to a finite Hall conductivity.

the operator A is given by:

$$\langle \hat{A} \rangle_0 = \operatorname{Tr}\left(\rho_0 \hat{A}\right) = \sum_n \frac{e^{-\beta E_n}}{Z} \langle n | A | n \rangle, \qquad (7.8)$$

where

$$\rho_0 = \frac{1}{Z} \sum_n |n\rangle \langle n|, \qquad (7.9)$$

is the density matrix, Z denotes the partition function,  $\beta = \frac{1}{k_B T}$  is the inverse temperature, Tr denotes the trace and the bracket  $\langle \cdot \rangle$  indicates that a thermodynamic average is taken. We now consider the same average but at some time t after the application of an external perturbation. Now the density matrix from the equation above has acquired time dependence:

$$\rho(t) = \frac{1}{Z} \sum_{n} |n(t)\rangle \langle n(t)|, \qquad (7.10)$$

and the thermodynamic average is given by:

$$\langle \hat{A}(t) \rangle = \operatorname{Tr}\left(\rho(t)\hat{A}\right) = \sum_{n} \frac{e^{-\beta E_{n}}}{Z} \langle n(t) | \,\hat{A} \, | n(t) \rangle \,. \tag{7.11}$$

Here an assumption was made, namely that the states of the system described by the Hamiltonian 7.7 are distributed according to the equilibrium distribution function, even at later times. All the time dependence is therefore packed into the states  $|n(t)\rangle$ . These can be obtained from the time-dependent Schrödinger equation:

$$i\hbar\frac{\partial}{\partial t}|n(t)\rangle = \hat{H}(t)|n(t)\rangle \tag{7.12}$$

In the interaction picture the time evolution can be described as:

$$|n(t)\rangle = e^{-\frac{iH_0t}{\hbar}} \hat{U}(t,0) |n\rangle, \qquad (7.13)$$

where U(t, 0) is the time evolution operator [106]:

$$\hat{U}(t,0) = 1 + \sum_{n} \left(\frac{-i}{\hbar}\right)^{n} \int_{0}^{t} dt_{1} \int_{0}^{t_{1}} dt_{2} \dots \int_{0}^{t_{n-1}} dt n \hat{H}(t_{1}) \hat{H}(t_{2}) \dots \hat{H}(t_{n})$$
(7.14)

Within linear response theory one includes only the time-evolution to linear order. Therefore the time-evolution operator can be written as:

$$\hat{U}(t,0) = 1 - \frac{i}{\hbar} \int_0^t dt' \hat{H}'(t').$$
(7.15)

The thermodynamic average at time t:

$$\langle \hat{A} \rangle = \langle \hat{A} \rangle_0 - i \int_t^\infty \theta(t - t') dt' \langle [\hat{A}(t), \hat{H}'(t')] \rangle_0$$
(7.16)

or equivalently:

$$\langle \Delta A(t) \rangle = \langle \hat{A} \rangle_0 = \tag{7.17}$$

$$\int_{-\infty}^{\infty} dt' C(t,t') \tag{7.18}$$

where  $\langle \Delta A(t) \rangle$  is the response function and where the correlation function C(t,t') is given by:

$$C(t,t') = -i\theta(t-t') \left\langle [A(t), H(t')] \right\rangle$$
(7.19)

Here A(t) is the operator for the relevant physical observable and H(t') is the Hamiltonian describing the external perturbation. The formula in eq. 7.19 is known as the Kubo formula [155]. If the external perturbations are such that the perturbing Hamiltonian can be written:

$$\hat{H}'(t) = \hat{B}f(t) \tag{7.20}$$

Here  $\hat{B}$  denotes an operator and f(t) a function which is time-dependent. In this scenario all the time dependence is packed into the scalar function and not the operator. Because the scalar is perfectly commutative it can be shown that in this scenario the correlation function C(t, t') only depends on the time difference t - t'.
## 7.4 Intrinsic contribution to the Hall conductivity

To obtain an expression for the Hall conductivity, we will first start of by finding a general expression for the conductivity and then separate out the Hall contribution from the any other components. The linear conductivity tensor is defined through the relation:

$$J(\boldsymbol{r},t)_{\alpha} = \int_{-\infty}^{\infty} d\boldsymbol{r}' \int_{-\infty}^{\infty} dt' \sigma_{\alpha\beta}(\boldsymbol{r},\boldsymbol{r}',t,t') E_{\beta}(\boldsymbol{r}',t')$$
(7.21)

The Fourier transformed version reads:

$$J^{\alpha}(\boldsymbol{q},\omega) = \sigma^{\alpha\beta}(\boldsymbol{q},\omega)E^{\beta}(\boldsymbol{q},\omega)$$
(7.22)

The electric field can be expressed in terms of fields:

$$E^{\alpha}(\boldsymbol{r},t) = -\left(\nabla\phi(\boldsymbol{r},t)\right)^{\alpha} - \frac{dA^{\alpha}(\boldsymbol{r},t)}{dt}$$
(7.23)

We pick the Landau gauge where  $\nabla \phi(\mathbf{r}, t) = 0$ . Next we Fourier transform the remaining expression to obtain:

$$E^{\alpha}(\boldsymbol{q},\omega) = -i(\omega + i\eta)A^{\alpha}(\boldsymbol{q},\omega)$$
(7.24)

here we have made use of the generalized Fourier transform, where the frequency has an imaginary component. We are using this transform instead of an ordinary Fourier transform, in order to be consistent since a generalized Fourier transform is necessary in the treatment of response functions. We are now going to derive an expression for the averaged current as a function of applied electric field such the the conductivity in eq. (7.21) can be inferred. In order to apply the machinery of linear response theory we need to add a perturbation. An applied electric field leads to (using the Landau gauge) a perturbing Hamiltonian of the form:

$$H_{\text{ext}}(t) = e \int d\mathbf{r} \mathbf{J}(\mathbf{r}) \cdot \mathbf{A}_{\text{ext}}(\mathbf{r}, t)$$
(7.25)

The current operator generally has two contributions:

$$\boldsymbol{J}(\boldsymbol{r},t) = \boldsymbol{J}^{\text{para}}(\boldsymbol{r}) + \frac{e}{m}\rho(\boldsymbol{r})\boldsymbol{A}_{\text{ext}}(\boldsymbol{r},t).$$
(7.26)

The first of these is usually referred to as the paramagnetic term and the second the diamagnetic. Only the second term contains external fields. The thermodynamic average of the current becomes:

$$\langle \boldsymbol{J}(\boldsymbol{r},t)\rangle = \langle \boldsymbol{J}^{\text{para}}(\boldsymbol{r})\rangle + \frac{e}{m} \langle \rho(\boldsymbol{r})\boldsymbol{A}_{\text{ext}}(\boldsymbol{r},t)\rangle$$
(7.27)

We evaluate these within the assumptions of linear response that is we assume that the external vector potential can be evaluated in the equilibrium state, such that

$$\frac{e}{m} \left\langle \rho(\boldsymbol{r}) \boldsymbol{A}_{\text{ext}}(\boldsymbol{r}, t) \right\rangle \approx \frac{e}{m} \left\langle \rho(\boldsymbol{r}) \right\rangle_0 \boldsymbol{A}_{\text{ext}}(\boldsymbol{r}, t)$$
(7.28)

The Fourier transformed expression becomes:

$$\frac{e}{m} \langle \rho(\boldsymbol{r}) \rangle_0 \boldsymbol{A}_{\text{ext}}(\boldsymbol{r}, \omega) = \frac{e}{im(\omega + i\eta)} \langle \rho(\boldsymbol{r}) \rangle_0 \boldsymbol{E}_{\text{ext}}(\boldsymbol{r}, \omega)$$
(7.29)

The paramagnetic term is evaluated using linear response theory:

$$\langle J^{\text{para}}(\boldsymbol{r},t)_{\alpha}\rangle = -ie \int_{t}^{\infty} dt' \theta(t-t') \left\langle \left[J_{\alpha}(\boldsymbol{r},t),H_{\text{ext}}(t')\right]\right\rangle_{0}$$
(7.30)

$$= -ie \sum_{\beta=x,y,z} \int d\mathbf{r}' \int_{-\infty}^{\infty} dt' \theta(t-t') \left\langle \left[ J_{\alpha}(\mathbf{r},t), J_{\beta}(\mathbf{r}') \right] \right\rangle_{0} A_{\beta}(\mathbf{r}',t')$$
(7.31)

$$=\sum_{\beta=x,y,z} \int d\mathbf{r}' \int_{-\infty}^{\infty} dt' e C_{J\alpha J\beta}(t-t') A_{\beta}(\mathbf{r}',t')$$
(7.32)

here we used that the current in equilibrium is zero and that we are only including linear orders in electric field such that the term proportional to  $A_{\text{ext}} \cdot A_{\text{ext}}$  is neglected. We consider the Fourier transformed version of the equation above:

$$\langle \boldsymbol{J}^{\text{para}}(\boldsymbol{r},\omega)\rangle = \sum_{\beta=x,y,z} \int d\boldsymbol{r}' C_{J\alpha,J\beta}(\omega) \frac{1}{i(\omega+i\eta)} E_{\beta}(\boldsymbol{r}',\omega)$$
(7.33)

The physical quantity of interest is the electric current which is just the number current times the electron charge -e. By including this and comparing the results above with the expression for the linear conductivity tensor in eq. 7.22 we see that:

$$\sigma_{\alpha\beta}(\boldsymbol{r},\boldsymbol{r}',\omega) = \frac{e^2}{i(\omega+i\eta)} C_{J\alpha J\beta}(\boldsymbol{r},\boldsymbol{r}',\omega) + \delta_{\alpha\beta} \frac{e^2}{m(i\omega-\eta)} \langle \rho(\boldsymbol{r}') \rangle_0 \,\delta(\boldsymbol{r}-\boldsymbol{r}') \tag{7.34}$$

Additional Fourier transform in the spatial domains yields

$$\sigma_{\alpha\beta}(\boldsymbol{q},\omega) = \frac{e^2}{i(\omega+i\eta)} C_{J\alpha J\beta}(\boldsymbol{q},\omega) + \delta_{\alpha\beta} \frac{e^2}{m(i\omega-\eta)} \left\langle \rho(\boldsymbol{q}) \right\rangle_0 \tag{7.35}$$

The Hall conductivity is a phenomenon that occur under the application of a spatial homogeneous constant electric field. Therefore we consider the limit where  $\omega = 0$ , q = 0:

$$\sigma_{\alpha\beta} = \lim_{\omega \to 0} \left( \frac{e^2}{i(\omega + i\eta)} C_{J\alpha J\beta}(\omega) \right) - \delta_{\alpha\beta} \frac{e^2 \langle \rho \rangle_0}{m\eta}$$
(7.36)

The second term is an Ohmic contribution. It is an fact simply the Drude expression for the conductivity. This effect occur in conductors were the time between electronion collisions is  $\tau$ . At a quantum level this corresponds to the lifetime of a conduction electron in a particular state. This life time is roughly the inverse of the imaginary frequency in eq. 7.36  $\tau \sim \frac{1}{\eta}$ . The second term is then  $\delta_{\alpha\beta} \frac{e^2 \langle \rho \rangle_0 \tau}{m}$  which we recognize as the Drude conductivity [156]. The Hall conductivity is the anti-symmetric component of the conductivity tensor in eq. 7.36:

$$\sigma_{\alpha\beta}^{A} = \sigma_{\alpha\beta} - \sigma_{\beta\alpha} = e^{2} \lim_{\omega \to 0} \left( \frac{1}{i(\omega + i\eta)} \left( C_{J\alpha J\beta}(\omega) - C_{J\beta J\alpha}(\omega) \right) \right).$$
(7.37)

Thus finding an expression for the anomalous Hall conductivity amounts to deriving an expression for the Fourier transform of the current-current correlation function. An exact expression for this function cannot be obtained analytically in all cases. If one however considers a system of non-interacting particles as is for example the case for the free electron gas or for a Kohn-Sham system, it is possible to derive an analytic expression for the correlation function and also for the conductivity. A direct calculation of the current-current correlation function is given in detail in Appendix B. Furthermore the conductivity is also obtained using eq. (7.37). The result is [157]:

$$\sigma_{\alpha\beta}^{A} = \frac{e^{2}}{h} \int_{\mathrm{BZ}} \frac{d\boldsymbol{k}}{(2\pi)^{d-1}} \sum_{n,m}^{N} \left( f(E_{n\boldsymbol{k}}) - f(E_{m\boldsymbol{k}}) \right) \left( \frac{\mathrm{Im}\left( \left\langle n\boldsymbol{k} \right| \frac{dH}{dk_{\alpha}} \left| m\boldsymbol{k} \right\rangle \left\langle m\boldsymbol{k} \right| \frac{dH}{dk_{\beta}} \left| n\boldsymbol{k} \right\rangle \right)}{(E_{n\boldsymbol{k}} - E_{m\boldsymbol{k}})^{2}} \right).$$

$$(7.38)$$

Here the matrix elements  $\langle n\mathbf{k} | \frac{dH}{dk_{\alpha}} | m\mathbf{k} \rangle = \hbar v_{\alpha}$  denotes the matrix elements stemming from the velocity operator,  $f(E_{n\mathbf{k}})$  denote the Fermi-Dirac distribution function and  $E_{n\mathbf{k}}$  the eigenenergies of n'th band at  $\mathbf{k}$ . The form presented here is one where the band indices n, m are treated on equal footing. A less computationally practical, but very illuminating form of eq. 7.38 is given by:

$$\sigma_{\alpha\beta}^{A} = -\frac{e^2}{h} \int_{\mathrm{BZ}} \frac{d\mathbf{k}}{(2\pi)^{d-1}} \sum_{n}^{N} f(E_{n\mathbf{k}}) \Omega_n^{\alpha\beta}(\mathbf{k})$$
(7.39)

where the term under the integrand:

$$\Omega_{n}^{\alpha\beta}(\boldsymbol{k}) = i \left\langle \partial_{\alpha} n \boldsymbol{k} \right| \times \left| \partial_{\beta} n \boldsymbol{k} \right\rangle = -\sum_{m \neq n}^{N} \frac{2 \mathrm{Im} \left( \left\langle n \boldsymbol{k} \right| \frac{dH}{dk_{\alpha}} \left| m \boldsymbol{k} \right\rangle \left\langle m \boldsymbol{k} \right| \frac{dH}{dk_{\beta}} \left| n \boldsymbol{k} \right\rangle \right)}{(E_{n\boldsymbol{k}} - E_{m\boldsymbol{k}})^{2}}$$
(7.40)

is known as the Berry curvature. It is a geometric quantity related to the Berry phase introduced back in section 5.2. Unlike the Berry phase which is defined for a closed loop, the Berry curvature is geometrically local it nature. While the Berry phase is explicitly gauge dependent, the Berry curvature is a gauge-invariant quantity that is expressed solely in terms of the wavefunctions [158]. With this expression in mind, it is easier to see why the expression in eq. 7.38 is referred to as the intrinsic contribution, since it depends solely on the local properties of the wavefunction without reference to sample size, scattering or any other relevant transport quantities. A closer look at eq. 7.38 also reveal that the primary contribution to the integrand comes from the areas where the denominator  $(E_{nk} - E_{mk})^2$  is close to zero. This explicitly shows the importance of spin-orbit coupling since small energy differences between different bands at the same k-point are often the result of lifted degeneracies that result from spin-orbit coupling.

In order to compute the anomalous Hall conductivity numerically it is more convenient to convert the k-point integral in eq. 7.38 into a sum such that the expression becomes:

$$\sigma_{\alpha\beta}^{A} = \frac{e^{2}}{h} \frac{2\pi}{N_{\boldsymbol{k}}V} \sum_{\boldsymbol{k}\in\mathrm{BZ}} \sum_{n,m}^{N} \left(f(E_{n\boldsymbol{k}}) - f(E_{m\boldsymbol{k}})\right) \left(\frac{\mathrm{Im}\left(\langle n\boldsymbol{k} | \frac{dH}{dk_{\alpha}} | m\boldsymbol{k} \rangle \langle m\boldsymbol{k} | \frac{dH}{dk_{\beta}} | n\boldsymbol{k} \rangle\right)}{(E_{n\boldsymbol{k}} - E_{m\boldsymbol{k}})^{2}}\right),$$

(7.41)

where  $N_k$  denotes the number of k-points and V the unit cell volume. Evaluating the expression in eq. 7.41 requires numerical evaluation of the matrix elements  $\langle n \mathbf{k} | \frac{dH}{dk_{\alpha}} | m \mathbf{k} \rangle$ . Here the states are eigenstates with spin-orbit coupling. However the response code in GPAW used for computations presented in this thesis does not have an implementation that can compute such matrix elements for spinors. Instead we will express the spinors in terms of the Kohn-Sham eigenstates found without spin-orbit coupling as shown in eq. 3.26. In such a case the integrand in eq. 7.41 takes the form:

$$\Omega_{\alpha\beta}(\boldsymbol{k}) = -\sum_{n,m}^{N} \frac{(f(E_{n\boldsymbol{k}}) - f(E_{m\boldsymbol{k}}))}{(E_{n\boldsymbol{k}} - E_{m\boldsymbol{k}})^2}$$
(7.42)

$$\times 2\mathrm{Im}\left(\left(\sum_{l,p}^{N}\sum_{s1=\uparrow,\downarrow}C_{\boldsymbol{k},m,s1,p}C^{*}_{\boldsymbol{k},n,s1,l}\left\langle l^{0}_{s1,\boldsymbol{k}}\right|\frac{\partial H}{\partial\boldsymbol{k}_{\alpha}}\left|p^{0}_{s1,\boldsymbol{k}}\right\rangle\right)$$
(7.43)

$$\times \left(\sum_{q,r}^{N}\sum_{s2=\uparrow,\downarrow} C^*_{\boldsymbol{k},m,s2,r} C_{\boldsymbol{k},n,s2,q} \left( \left\langle q^0_{s2,\boldsymbol{k}} \right| \frac{\partial H}{\partial \boldsymbol{k}_{\beta}} \left| r^0_{s2,\boldsymbol{k}} \right\rangle \right)^* \right) \right)$$
(7.44)

With these changes the expression for the anomalous Hall conductivity in eq. 7.41 can be written in the form:

$$\sigma_{\alpha\beta}^{A} = \frac{e^{2}}{h} \frac{2\pi}{N_{k}V} \sum_{k \in \text{BZ}} \sum_{n,m}^{N} \frac{(f(E_{nk}) - f(E_{mk}))}{(E_{nk} - E_{mk})^{2}}$$
(7.45)

$$\times \operatorname{Im}\left(\left(\sum_{l,p}^{N}\sum_{s1=\uparrow,\downarrow}C_{\boldsymbol{k},m,s1,p}C_{\boldsymbol{k},n,s1,l}^{*}\left\langle l_{s1,\boldsymbol{k}}^{0}\right|\frac{\partial H}{\partial k_{\alpha}}\left|p_{s1,\boldsymbol{k}}^{0}\right\rangle\right)$$
(7.46)

$$\times \left(\sum_{q,r}^{N}\sum_{s2=\uparrow,\downarrow} C^*_{\boldsymbol{k},m,s2,r} C_{\boldsymbol{k},n,s2,q} \left( \langle q^0_{s2,\boldsymbol{k}} | \frac{\partial H}{\partial k_\beta} | r^0_{s2,\boldsymbol{k}} \rangle \right)^* \right) \right).$$
(7.47)

This version of the Hall conductivity has been implemented using the GPAW software package and henceforth all computations are carried out using the expression in eq. (7.45). Numerically the denominator in eq. (7.45) does pose some challenges since one has to get the k-point sampling right in order to compute capture all the relevant regions of the Brillioun zone.

### 7.5 Adaptive k-point refinement

The expression for the anomalous Hall conductivity given in eq. 7.45 does come with some practical issues. The integrand is inversely proportional to the difference in band energies to the second power. As mentioned previously band splittings form the main contributions to the anomalous Hall conductivity. However since we are dealing with contributions from non-filled bands in metals, the results are very sensitive to how the k-points entering in the sum in eq. 7.45 are sampled. Practical calculations reveal

that it is very computational expensive, and in some cases practically impossible, to converge the anomalous Hall conductivity with respect to the number of k-points by simply using a more dense k-point grid. An approach that has been popular is to refine certain points in the k-point grid, namely those where the integrand in eq. 7.45 are largest. In order to do so, one must first know where such points reside in the Brillouin zone in the first place. Leaving aside the special case where one has a priori knowledge of the system in question, the only way to do this is to first compute the integrand in equation 7.45 for a k-point grid sufficiently dense to capture the points of interest. Subsequently one can then construct k-point grids nested inside the initial grid around the points of interest. It is then possible to evaluate the Berry curvature on the new nested k-point grids and then finally add these contributions to the ones from the initial k-point grid to get more accurate result. This method of selectively adding k-points is known as adaptive refinement and has previously been successfully applied to reduce the number of k-points required to compute the anomalous Hall conductivity. The caveat to the adaptive refinement procedure is that the new k-point grid no longer



**Figure 7.3:** Depicted is a sketch the adaptive refinement procedure for a two dimensional k-point grid. On the left side is a equidistant k-point grid. The right side contains a similar figure but where the point at the center has been replaced with a 5x5 refinement grid.

has all of its points uniformly spaced. When carrying out an integral or a summation one therefore has to attach different weight to the evaluated integrand, in this case the Berry curvature.

To be more concrete lets assume we wish to refine a k-point grid with  $N_{k} = N_{kx} \times N_{ky} \times N_{kz}$  points, where  $N_{kx}$ ,  $N_{ky}$ ,  $N_{kz}$  are the number of k-points in the initial k-point grid  $\mathcal{K}$ . We now apply a refinement grid consisting of  $N_{kx}^{\text{ref}} \times N_{ky}^{\text{ref}} \times N_{kz}^{\text{ref}}$  points, at a selected point  $k_0 \in \mathcal{K}$ . We denote the set of points introduced by refinement as  $\mathcal{K}^*$ . In order to evaluate the Berry curvature on the refined grid a new weight has to be assigned the Berry curvature at the new points which have been introduced. The value of the Berry curvature at the old points  $k_0$  then has to be replaced according to:

$$\Omega(\boldsymbol{k}_{0}) \to \frac{1}{N_{\boldsymbol{k}x}^{\text{ref}} \times N_{\boldsymbol{k}y}^{\text{ref}} \times N_{\boldsymbol{k}z}^{\text{ref}}} \sum_{i \in \mathcal{K}^{*}} \Omega(\boldsymbol{k}_{i}) \forall \boldsymbol{k}_{0} \in \mathcal{K}$$
(7.48)

This procedure can then be iterated for all points that are found to be relevant, i.e. the ones which large contributions to the Berry curvature. Since these k-points are only a small subset of the total grid, the resulting refined grid tends to contain fewer points than the original. Therefore this scheme is much more numerically efficient then simply increasing the k-point density. When it comes to the selection of points there is no straightforward way to do it. Usually one starts by evaluating the integrand in equation 7.45 on an initial grid and subsequently select the point where absolute value of the integrand is largest. Performing refinement around one point is rarely sufficient, and therefore it is necessary to pick points according to some principle, like taking all points where the integrand is within 10% of the maximal value. Such algorithms have been extensively used to compute anomalous Hall conductivities from first-principles [159, 160]. Unfortunately we currently do not have an implemented version of this algorithm that works in conjunction with the implementation of 7.45.

### 7.6 Results

In this part results obtained using an implementation of the anomalous Hall conductivity in eq. 7.45 are presented. We start by performing calculations for bcc Fe, fcc Ni, hcp Co and fcc Co as these are some of the most studied examples of bulk metals. These will serve as benchmarks and they have the advantage that the unit cell contain only one or two atoms making system size less of a computational bottleneck. All calculations for bcc Fe have been done with the lattice constant a = 5.42 Bohr



Figure 7.4: The figures show a computation of the anomalous Hall conductivity as a function of number of k-points used in each direction for bcc Fe on the left and fcc Co on the right respectively. The dashed blue and green line in the plot to the left represent converged results obtained in [159] and [157] respectively. The dashed blue and green line in the plot to the right represent converged results obtained in [161] and [159] respectively.

= 2.87 Å which is the experimental lattice constant as well as the one used in all references where numerical computations where carried out. The same thing goes for Co and Ni, only here the relevant parameters are different. Calculations for hcp Co have been done with the lattice constant a = 4.73 Bohr = 2.50 Å and a hcp ratio of

1.633. Calculations for fcc Co have been done with the lattice constant = 6.69 Bohr = 3.54 Å. Calculations for fcc Ni have been done with the lattice constant a = 6.65 Bohr = 3.52 Å. All of these lattice constants coincide with the experimental value for each respective material. Throughout this section all results that are presented have



Figure 7.5: The figures show a computation of the anomalous Hall conductivity as a function of the number of k-points used in each direction for hcp Co on the left and fcc Ni on the right respectively. The dashed blue line in the plot to the left represent the converged result obtained in [161]. The dashed blue and green line in the plot to the right represent converged results obtained in [162] and [163] respectively.

been computed with the following set of computational parameters unless otherwise stated: a plane-wave cutoff of 800 eV, a Fermi-smearing of 0.001 eV is used for occupation factors. Furthermore all k-point grids used are  $\Gamma$ -centered. We use grids of the form  $N_k = N \times N \times N$  for 3D materials and  $N_k = N \times N \times 1$  for 2D materials, with N denoting the number of k-points along each direction. All calculations have been carried out using the PBE functional unless otherwise stated. It has been shown that Hubbard corrections are necessary to get accurate results for the anomalous Hall conductivity in Ni. Previous work by Fuh. et. al. have shown that applying an effective Hubbard parameter U= 0.7 eV leads to an anomalous Hall conductivity  $\sigma_{xy}^A = 1046$ [S/cm] in good agreement with experiments performed at low temperatures [152, 163]. For this chapter we are primarily concerned with comparing the results of our calculations with those obtained by other researchers. But we have included the results obtained with PBE + U as well to have more data to compare our results with. Our primary concern is to assess how well converged our results are with respect to the total of k-points. Calculations are performed by first performing a DFT calculation at high k-point sampling to ensure that the density is converged with respect to the number of k-points. For the calculations shown have we have used a  $40 \times 40 \times 40$  grid. Then the Kohn-Sham equations are solved using the converged result for the density in previous calculations. This is repeated for in an increasing number of k-points. In this way we keep the density constant while only varying the number of k-points. This is because the converged Kohn-Sham density is itself a function of the choice of k-point grid. This approach ensures that we are using the same fixed density and that any



Figure 7.6: The figure on the left show computations of the anomalous Hall conductivity as a function of number of k-points used in each direction for Ni using an effective Hubbard U correction of 0.7 eV and 1.3 eV respectively. The dashed blue and green line in the plot to the left represent converged results obtained in [163]. The figure on the right is a plot of the anomalous Hall conductivity for Fe using different Fermi smearings for the occupation factors in eq. 7.45.

$\sigma^A_{xy}[\frac{S}{cm}]$	Fe (bcc)	Co~(fcc)	Co~(hcp)	Ni (fcc)
This work	$700^{(*)}$	$223^{(*)}$	$408^{(*)}$	$1952^{(*)}$
Previous Theo.	751 [157], 750 [162]	249 [161]	477 [159]	2203[159]
	753[159]		481 [161]	2275[159]
This work $(U=0.7)$	-	-	_	1228
Previous theo. $(U=1.3)$	-	-	-	1064[163]
This work $(U=1.3)$	-	-	-	937
Previous theo. $(U=1.3)$	-	-	-	946[163]
Exp. $(T = 0K)$	1032 [164]	$727^{(**)}[165]$	813[161]	646 [166]
Exp. $(T = 5K)$				1100 [152]

Table 7.1: Comparative table of the anomalous Hall conductivity for transition metals. The table contains values that are theoretically predicted as well as those that are experimentally observed. The functional used for the theoretical calculations is PBE, and PBE + U in the case of Ni. (\*) The values produced using GPAW are not fully converged as evident from figures (7.4-7.6). Instead they are the values obtained at the largest of the k-point grids presented in the plots in figures (7.4-7.6). (\*\*) This is the experimental value for the intrinsic contribution only. In the paper analysis was applied to separate it from extrinsic contributions.

lack of convergence in the anomalous Hall conductivity with respect to the number of k-points is due to poor sampling and not due to the density not being converged. In practice it turns out to only make a big difference for low k-point densities, but it is more methodologically clean. Results for Fe, Co and Ni are shown in figures 7.4-7.6. We have used 20, 11, 40, and 18 bands for bcc Fe, fcc Co, hcp Co and fcc Ni respectively. The hardest material to converge is by far Fe. Even at k-point grids as large as  $125 \times 125 \times 125$  corresponding to almost 2 million points in total, the anomalous Hall

$m{m}_{ m spin} \; [\mu_{ m B}/{ m atom}]$	Fe (bcc)	Co~(fcc)	Co (hcp)	Ni (fcc)
This work PBE	2.22	1.66	1.62	0.65
Previous Theory (PBE)	2.22 [159]	-	1.60 [159]	0.62 [159]
Exp.	2.13 [167]	-	1.59 [167]	0.56 [167]

Table 7.2: Comparative table of the spin magnetic moments for the transition metals. The table contains values that are theoretically predicted using GPAW as well as those obtained theoretically in [162] and experimentally in [167].

conductivity as still not converged. The inset figure also indicates that the result still vary between 650-700 [S/cm] The results look better in the case of hcp Co where only up to one million k-points are used. Here the results are also not perfectly converged but there are fewer oscillations in the plot. For fcc Ni and fcc Co the results also seem to have the correct order of magnitude but they are like the first two cases not converged. The results shown for fcc Co, hcp Co and fcc Ni does seem to indicate that anomalous Hall conductivity for these three materials have a lower convergence radius. For all 4 materials we seem to get a lower number for the Hall conductivity compared to others. This might of cause be becomes the results are not fully converged. We haven't managed to fully converge any of the 4 examples given so far by sampling increasing the k-point density. Numerically very large grids become more and more expensive. Performing ground state calculations alone becomes a bottleneck at this point. We would like to applied the adaptive refinement scheme mentioned in sec 7.5. However as mentioned in the previous section we do not have a working code for the adaptive refinement yet. A summary of comparisons between our results and the those found in the relevant literature on the anomalous Hall conductivity is given in table 7.1.Besides k-point sampling there are a couple of other parameters that impact



Figure 7.7: The figures show a computation of the anomalous Hall conductivity for bcc Fe and hcp Co respectively as a function of the total number of bands used.

the value of the anomalous Hall conductivity to some extend. The anomalous Hall conductivity is implicitly a function of the magnetization of the material, as discussed in section 7.2. Therefore it is worth comparing our results to those obtained by others as well as the actual experimental values. The results for all the transition metals are listed in table 7.2. We obtain good agreement with previous results.

Another relevant factor to take into account is the finite Fermi smearing used for calculation the occupation factors in eq. 7.45. Calculations have been performed using different values of Fermi smearing for the occupation factors in eq. 7.45 and using a fixed  $100 \times 100 \times 100$  k-point grid. We have shown results for Fe in figure 7.6 as this is the material where the choice of smearing seems to have the largest effect. The results are depicted in fig. 7.6. For small smearings of the occupation factors the anomalous Hall conductivity does not change much. At a large smearing of 0.273 eV the convergence of the anomalous Hall conductivity improves significantly as expected, it does come at the cost that the converged value of the anomalous Hall conductivity is reduced far below what is found otherwise. This makes good sense physically because the occupation numbers follow a Fermi-Dirac distribution which is a step function if the smearing is zero and gets smeared out more at higher values, effectively reducing the value of occupation factors that are otherwise 1. This lowers the total value of the integrand in eq. 7.45 and thus the final value of the anomalous Hall conductivity. We have also performed convergence calculations for Fe, Co and Ni with respect to



Figure 7.8: The figures show a computation of the anomalous Hall conductivity for fcc Co and fcc Ni respectively as a function of the total number of bands used.

the number of bands. These are depicted in figures 7.6 and 7.6. The overall trend is the same, which is that the conductivity is more or less converged if the total number of bands exceeds the number of occupied bands. The number of occupied bands are 8, 9, 18, 16 for bcc Fe, hcp Co, fcc Co and fcc Ni respectively. The results show that a few extra bands in addition to the number of occupied bands are needed to get exact convergence. Furthermore the convergence radius is in some cases larger than in others. Generally speaking however the conductivity is seen to change very little on the order of magnitude once enough bands are added. Having to add many bands could easily become a computational bottleneck. The results presented here seems to indicate that a moderate number of bands is sufficient to achieve results that would be satisfactory for high-throughput computations. In such scenarios an error margin like that shown here is acceptable. In summary these results clearly indicate that k-point convergence matters most in terms of reducing the error margin when computing the anomalous Hall conductivity followed by occupation factor smearing and the number of bands used. Occupation factor smearing is not a computational bottleneck and we have shown that the number of bands necessary to achieve satisfactory results are within reasonable limits. The primary bottleneck that prevents us from applying the current implementation of the code for high-throughput studies is therefore k-point sampling. As mentioned previously we unfortunately do not have a working version of the adaptive refinement scheme described in section 7.5. There are many codes that can currently compute the anomalous Hall conductivity. The most prominent example would be using Wannier90 [159, 160]. In such cases one applies Wannier90 to construct Wannier functions for a material and then compute the anomalous Hall conductivity as a post processing step, using the obtained functions. The drawback of this method is that the wannierization process cannot be easily be automated  $^2$ , therefore this method is not well suited for high-throughput studies at the moment. Such methods could of course still be useful if one had obtained results from a high-throughput study and wanted to study one material more thoroughly. The approach taken here however does have the advantage that computations are easy to automate. We now turn



Figure 7.9: The figures show a computation of the anomalous Hall conductivity as a function of the number of k-points used in each direction for  $FeCl_2$  in the T-phase on the left and the  $Fe_3GeTe_2$  on the right. The dashed blue line in the left plot to the left is the converged result obtained in [169]. The dashed green line in the right plot is the converged result obtained in [170].

our attention towards two dimensional systems. From a computational vantage point investigating two dimensional magnets should pose less of a challenge since the total number k-points used will be significantly smaller compared to computations performed for three dimensional magnets. In order to assess the applicability of our code we have applied it to a select number of two dimensional magnets.

 $<sup>^{2}</sup>$ At least not to a sufficient accuracy [168].

The first materials under consideration are FeCl<sub>2</sub> in the (T-phase) and Fe<sub>3</sub>GeTe<sub>2</sub> since these are materials for which comparisons can be made [169, 170]. The results are depicted in figure 7.6. For FeCl<sub>2</sub> we achieve results that are actually fairly close to that which was obtained by others. In this case our result also look nearly converged. At large k-points the anomalous Hall conductivity vary on the order  $0.0001e^2/h$ . We do however use a different lattice constant than the one used by Sawahata et. al. [169].

We have also performed calculations for Fe<sub>3</sub>GeTe<sub>2</sub> using the LDA functional. This material also seems somewhat difficult to converge but the variation is not as large as for the bulk materials considered previosuly. We do however get a result which is much larger than what was obtained by Lin et. al. [170]. Our result for the anomalous Hall conductivity at a k-point grid of  $100 \times 100 \times 1$  is  $0.57 \ e^2/h$  while the reference have found it to be  $0.37 \ e^2/h$ . There is some discrepancy between the magnetic moment we have computed for Fe<sub>3</sub>GeTe<sub>2</sub> and the one found by Lin et al. We find a magnetic moment of 5.12 moment  $\mu_B$  and in the reference a magnetic moment of 4.71  $\mu_B$  is found[170]. This might explain a large part of the difference between our results for the anomalous Hall conductivity. It is however hard to say since structural details are missing from the reference. The calculations performed for FeCl<sub>2</sub> and Fe<sub>3</sub>GeTe<sub>2</sub> were done using a total of 26 and 45 bands respectively. and an occupation number smearing of 0.05 eV for FeCl<sub>2</sub> and 0.001 eV for Fe<sub>3</sub>GeTe<sub>2</sub>.



Figure 7.10: The figures show a computation of the anomalous Hall conductivity as a function of the number of k-points used in each direction for  $Br_2Cu_2S_2$  in the T-phase.

To further test the capability of the implemented code we also the van der Waals magnet  $Br_2Cu_2S_2$ . The calculations performed for  $Br_2Cu_2S_2$  were done using a total of 54 bands and an occupation number smearing of 0.05eV. The results are depicted in figure 7.6. The anomalous Hall conductivity computed for the vdW magnet  $Br_2Cu_2S_2$  seems easier to converge although there is still an error margin of about  $\pm 0.02 \ e^2/h$  according to the inset in fig. 7.6. All relevant details regarding crystal structure and atomic positions can be found in appendix B. Since we are not ready to perform a full high-throughput study, no further results are presented. There are however many candidates who would be interesting to investigate further once the aforementioned

problems are fixed. Examples include other nodal semimetals similar to  $Fe_3GeTe_2$  [170], Kagome metals [171] and other vdW-magnets [172].

## 7.7 Future directions

There are several ways to improve upon the results presented in this chapter as well as several potential future directions of research. One option would be to extend the current features that are implemented in the code such that the anomalous Hall conductivity can be computed for shifted Fermi levels. In this case our result could be compared to experiments where the electron filling is tuned using voltage gates. Another more computationally demanding option would be to compute the more general frequency dependent conductivity.

There are also related areas where the anomalous Hall conductivity plays a crucial role. Within the field of thermoelectrics the anomalous Nernst effect is an analogy of the anomalous Hall conductivity, but for the heat conductivity as supposed to the electric conductivity. It has been shown that one can compute the anomalous Nernst conductivity by first computing the anomalous Hall conductivity in a relevant energy range [172, 173]. This is straightforward if one simple shifts the Fermi level of the system under investigation. Another application is within magneto-optical effects the so called magneto optical Kerr effect (MOKE), which describes the change in direction of light reflected of a magnetic surface [174]. It has several applications among them, the ability to determine the magnetic structure of materials without destroying them. The so called Kerr angle can be determined from the Hall conductivity alone [172, 173]. In this thesis we only discussed the linear contribution to the Hall effect. By going to non-linear order one can derive expressions for various non-linear terms [175]. Such effects can be dominant in the cases were the linear terms vanish, and have recently been observed [176].

# CHAPTER 8

# Outlook

The main topic covered in this thesis has been multiferroics. The main results in particular being those summarized in section 6.1 and discussed in detail in paper [I]. There are several improvements which could increase the numerical accuracy and potentially lead to additional ferroelectric materials being discovered. The most obvious being the shortcomings of the PBE functional due to the derivative discontinuity problem as well as the self-interaction error discussed in sections 3.5, 3.7 and 6.1. This is not merely an issue of getting the correct quantitative results. Mispredicting a material to be gap less means it will get discarded in a high-throughput context. In order to correct this better functionals have to be applied such as PBE + U or HSE. The fact that our workflow didn't find any magnetic ferroelectrics suggest that another functional than PBE might be needed in this particular case. In addition one could extend the types of magnetic order considered to states beyond ferromagnetic ones.

There are several spin off projects one could try. One would be thermodynamic properties, as discussed in section 6.1 this would require further analysis than what was done in paper [I], specifically one would need to compute dipole interactions between electric dipoles at different sites. This does require relatively large supercells and it is not something that is computationally feasible for many materials in a high-throughput context. It is possible to look for other multiferroic orders than the ones we focused on in this thesis. For example one could try to look at ferroelectric-ferroelastic multiferroics, by trying to search for states with different strains. It would similarly be viable to look at ferromagnetic-ferroelastic compounds by focusing on strain analysis in magnets.

Chapter 7 was devoted to one topic alone: the anomalous Hall conductivity. The focus was on the intrinsic components and how to compute this from first principles. Benchmark results were shown from an implementation of the anomalous Hall conductivity in GPAW. Due to difficulties related to k-point convergence it was not possible to fully validate our results. Although we did get results in some cases that were in good agreement with results previously obtained by others. We conclude that some form of adaptive refinement scheme is necessary in order to consistently achieve converged results. There are several other improvements of the code which could be made and many related research topics one could investigate. A straightforward implementation would be to compute the anomalous Hall conductivity over a range of Fermi levels, or to try to make the more general frequency dependent conductivity computationally feasible. One could also try to extend the theory of chapter 7 to incorporate non-linear effects or try to investigate transport phenomena involving scattering effects since these are not included in the intrinsic contribution to the anomalous Hall effect. As mentioned in the end of chapter 7 there are several interesting physical quantities that can be

derived from the anomalous Hall conductivity such as the anomalous Nernst effect and the magneto-optical Kerr effect.

Of course high-throughput studies on their own won't suffice in discovering new material properties. Many materials have to be studied more thoroughly in depth both theoretically as well as experimentally. It will be interesting to see what new discoveries will be made within the field of two dimensional materials in the years to come.



# Papers

9.1 Paper I: Two-dimensional ferroelectrics from high throughput computational screening

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arXiv: 2209.13911.

# ARTICLE OPEN (R) Check for updates Two-dimensional ferroelectrics from high throughput computational screening

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We report a high throughput computational search for two-dimensional ferroelectric materials. The starting point is 252 pyroelectric materials from the computational 2D materials database (C2DB) and from these we identify 63 ferroelectrics. In particular we find 49 materials with in-plane polarization, 8 materials with out-of-plane polarization and 6 materials with coupled inplane and out-of-plane polarization. Most of the known 2D ferroelectrics are recovered by the screening and the far majority of the predicted ferroelectrics are known as bulk van der Waals bonded compounds, which makes them accessible by direct exfoliation. For roughly 25% of the materials we find a metastable state in the non-polar structure, which may imply a first order transition to the polar phase. Finally, we list the magnetic pyroelectrics extracted from the C2DB and focus on the case of VAgP<sub>2</sub>Se<sub>6</sub>, which exhibits a three-state switchable polarization vector that is strongly coupled to the magnetic excitation spectrum.

npj Computational Materials (2023)9:45; https://doi.org/10.1038/s41524-023-00999-5

#### INTRODUCTION

Ferroelectric materials are characterized by having a spontaneous electric polarization that is switchable by means of an external field<sup>1</sup>. This property makes them suitable for non-volatile memory applications, which may be based on ferroelectric tunnel junctions, ferroelectric random access memory or ferroelectric field effect transistors<sup>2-5</sup>. While the large dielectric constant of ferroelectrics makes them ideal constituents of standard capacitors, it has also been demonstrated that ferroelectrics can acquire a negative capacitance under particular circumstances and this property may be utilized to reduce the energy consumption of conventional electronics significantly<sup>6–8</sup>. Finally, the inherent pyroelectric and piezoelectric properties of ferroelectrics make them useful for a wide range of sensor and actuator applications<sup>2,9</sup>. The recent discovery of monolayer ferroelectrics<sup>10</sup> has initiated fundamental interest in the basic properties of 2D ferroelectricity and spurred hope that devices based on ferroelectrics may undergo a dramatic size reduction. There is currently an intense effort to discover new 2D ferroelectrics with optimized properties and the list of materials that have been characterized experimentally includes In<sub>2</sub>Se<sub>3</sub><sup>11,12</sup>, CuInP<sub>2</sub>Se<sub>6</sub><sup>13,14</sup>, MoTe<sub>2</sub><sup>15</sup>, Nil<sub>2</sub><sup>16</sup>, SnTe<sup>10</sup>, SnSe<sup>17,18</sup> and SnS<sup>19</sup>

Devoid of the challenges that the synthesis of new 2D materials usually present, density functional theory (DFT) has emerged as an important tool to predict new ferroelectrics and characterize their properties. The compounds studied by DFT include in-plane ferroelectrics such as the group-IV monochalcogenides GeSe, GeS, SnS, SnSe, GeTe, SiTe, SnTe<sup>20,21</sup>, the niobium oxyhalides (NbOl<sub>2</sub>, NbOCr<sub>2</sub>, NbOBr<sub>2</sub>)<sup>22</sup>, the magnetic vanadium oxyhalides VOX<sub>2</sub> (X = I, Cl, Br, F)<sup>23,24</sup> as well as ClGaTe and y-SbX (X = As, P)<sup>25,26</sup>. In addition, the transition metal phosphorus chalcogenides ABP<sub>2</sub>X<sub>6</sub> (A = Cu/Ag, B = In/Bi/Cr/V, X = 5/Se)<sup>14,27-29</sup> have been predicted to exhibit out-of-plane polarization and thus overcome the fundamental thickness limit below which out-of-plane polarization vanishes in standard perovskite thin film<sup>30</sup>. Other compounds, such as  $\alpha$ -In<sub>2</sub>S<sub>3</sub> and related III<sub>2</sub>-IV<sub>3</sub> compounds have been predicted to have both in-plane and out-of-plane components of polarization, which are strongly intercorrelated<sup>31</sup>. The strong

confinement of electrons in 2D materials makes screening of outof-plane polarization inefficient and have led to the prediction of the ferroelectric metals CrN and CrB<sup>32</sup>. Finally, the notion of sliding ferroelectrics have recently emerged as a new type of ferroelectrics in 2D, where the polarization of bilayer ferroelectrics is coupled to the stacking configuration<sup>33,34</sup>.

For three-dimensional compounds there has been a vivid search for new ferroelectrics with optimal properties. For example with respect to lead-free energy storage materials  $^{35}$  or low switching barriers for memory applications  $^{36}.$  To this end, high throughput DFT calculations has proven a powerful strategy that can be used to rapidly screen thousands of materials for desired properties. For the case of ferroelectrics, however, it is not always straightforward to identify good candidate materials in a high throughput framework, since one has to demonstrate the existence of an a priori unknown switching path. In ref. 37 , 16 ferroelectrics were identified from 2750 polar materials taken from the Inorganic Crystal Structure Database (ICSD). More recently, a high throughput project based on 67,000 materials from the Materials Project database<sup>38</sup> identified 126 new ferroelectrics. The primary success criterion of such search strategies is the subsequent experimental demonstration of ferroelectric properties of the predicted materials. Such validation may pose major experimental challenges and in some cases predicted ferroelectrics have been shown to condense into non-polar phases during synthetization<sup>39</sup>. Regarding 2D materials, there seems to be a lack of systematic high throughput search for new ferroelectrics. One exception is a recent study where 60 new 2D ferroelectrics were identified from lattice decoration of a certain prototype<sup>40</sup>, but it is again not completely clear whether such an approach actually leads to experimentally realizable materials. In the present work, we present a high throughput screening for 2D ferroelectrics based on the C2DB, which contains materials obtained from lattice decoration as well as materials that are expected to be easily exfoliable from bulk van der Waals bonded materials. In addition to well-known 2D ferroelectrics we find a wide range of new 2D ferroelectric materials with both in-plane, out-of-plane and mixed polarization. The far majority of the

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materials are known experimentally in their 3D bulk form and it is reasonable to expect that several of these may be validated experimentally in the future.

The paper is organized as follows. We start by describing the workflow used to obtain ferroelectric materials from C2DB and discuss the results. In particular, we provide a detailed description of the adiabatic path required to assign a polar insulator as ferroelectric and classify materials according to the direction of polarization with respect to the atomic plane and the stability of phonons in the non-polar reference state. We then list the magnetic polar materials in C2DB and discuss the ferromagnetic and ferroelectric compound VAgP<sub>2</sub>Se<sub>6</sub>, which was not found by our workflow. In section "Discussion" we provide a discussion and outlook.

#### RESULTS

#### Polar insulators in the C2DB

The starting point of the calculations performed in this work is all dynamically stable 2D insulators from the C2DB<sup>41</sup> that have a polar point group. There are 252 materials satisfying these criteria, but many of these are not expected to be ferroelectric. For example, the Janus monolayers where a single transition metal atom is sandwiched between two different chalcogenides always have an out-of-plane dipole, which are not switchable by an external electric field. Such materials can obviously not be regarded as being ferroelectric, but one may easily calculate the spontaneous polarization, by simply integrating the electronic density weighted by a coordinate orthogonal to the layer over the entire system. For polar materials with an in-plane polar axis, this approach cannot be applied and we may only define the spontaneous polarization if an adiabatic path that connects the structure to a non-polar phase can be identified. In Fig. 1 we show examples of various prototypical compounds in the C2DB exhibiting polar point groups.

For 2D ferroelectrics it is natural to distinguish between materials where the symmetries forbid components of the polarization in the plane, materials where the polarizations out of plane is forbidden and those where the polar axis is neither constrained to the in-plane or our-of-plane directions. For the ten crystallographic polar point groups 1, 2, *m*, *mm*2, 3, *3m*, 4, *4mm*, 6 and 6*mm* only the first four may have an in-plane polar axis. In the cases of 2 and *mm*2 the polarization is parallel to the two-fold axis, which may be either in-plane or out-of-plane. For 1 there is

no constraints on the polarization and for m the polarization is confined to be in-plane if the mirror coincides with the atomic plane. As mentioned above, it is possible to calculate the spontaneous polarization for out-of-plane polar materials even if they are not ferroelectric, but we will not go into detail with these since this group is dominated by Janus monolayers, which have been studied elsewhere<sup>42</sup>. In Fig. 2 we outline the workflow applied to classify the polar and gapped materials in C2DB.

#### Definition of the adiabatic path

For materials that do not have an out-of-plane polar axis one needs a non-polar reference state that can be adiabatically connected with the polar states in order to calculate the spontaneous polarization. We have used the module evgraf<sup>43</sup> to generate the centrosymmetric structure of highest similarity to the polar structure<sup>44</sup> of all materials. This structure is then relaxed under the constraint of inversion symmetry and the result is taken as our reference ( $\lambda = 0$ ) non-polar structure. We then check if there is an adiabatic path connecting the two points by performing nudged elastic band (NEB) calculations<sup>45</sup> connecting the polar and non-polar structures. In all calculations the unit cell of the polar structure is conserved. If the band gap remains finite along the path there is a well-defined adiabatic path and we regard the material as being ferroelectric. We then proceed by performing single-shot DFT calculations for each structure on the path including the two endpoints and evaluate the formal polarization from the Berry phase formula Eq. (2) and for each point on the path we choose the polarization branch which deviates the least from the former point on the path. With this procedure the spontaneous polarization is calculated as the (branch fixed) change in polarization along the path. In Fig. 3 we show an example of such a calculation for As<sub>2</sub>Se<sub>3</sub>, where the polarization is shown in units of the polarization quantum  $ea_1/A$  $(\mathbf{a}_1$  is the unit cell vector which is parallel to the polarization and A is the unit cell area). This represents a rather extreme case where the spontaneous polarization is 3.5 times larger than the polarization quantum and highlights the importance of branch fixing on the adiabatic path. A naive single-shot calculation of the polarization in the polar phase will yield an arbitrary point in the infinite polarization lattice. Moreover, in general the polarization is not guaranteed to vanish at  $\lambda = 0$ , since non-polar structures may acquire a finite topological polarization with certain discrete values dictated by the symmetry of the polarization lattice<sup>46,47</sup>.



Fig. 1 Prototypes of polar materials. The first column depicts the 2 non-ferroelectric pyroelectrics TiClBr and  $Cr_2Mo_2S_8$ . The second column depicts two in-plane ferroelectrics  $As_2Sb_2O_6$  and  $Sn_2S_2$ . The third column depicts the ferroelectric  $In_2Te_4$ , which has polarization with both in-plane and out-of-plane components and  $AgBiP_2Se_6$ , which has purely out-of-plane polarization.

Published in partnership with the Shanghai Institute of Ceramics of the Chinese Academy of Sciences



Fig. 2 Summary of the workflow used in the study. We pick out all dynamically stable gapped materials with a polar point group. The materials for which an adiabatic polarization path exists are classified as ferroelectric and the ones where it is ill defined are classified as pyrolelectric. For ferroelectric materials additional computations are performed and the materials are further classified according to the direction of polarization (see main text).



Fig. 3 Polarization branches for As<sub>2</sub>Se<sub>3</sub> in units of the lattice vector divided by unit cell area. For the adiabatic path we choose one branch (in this case the one that crosses zero polarization at  $\lambda = 0$ ) and the spontaneous polarization is defined as the change in polarization between  $\lambda = 0$  and  $\lambda = 1$ .

We note that a linear interpolation between the polar and nonpolar structures is sufficient for calculating the spontaneous polarization as long as the system remains insulating along the path. The NEB is therefore only required for extracting energy barriers between the non-polar and polar structures and for the calculation of the coercive field.

#### Ferroelectrics in C2DB

From the 252 stable and gapped polar materials in C2DB we have identified 63 materials with a well-defined adiabatic path connecting the polar structure to a non-polar structure. The remaining 189 compounds are classified as non-ferroelectric pyroelectrics. Except for the magnetic materials, which are discussed below, the non-ferroelectric pyroelectrics will not be analyzed further in the present work. We will just mention that 63 of these have an in-plane polar axis that is neither constrained to the atomic plane or the direction orthogonal to the atomic plane. In the Supplementary tables we have included unit cells and atomic positions of all the ferroelectrics found in the present work.

There are two main reasons why one may fail to define a proper adiabatic path in the remaining materials. (1) Some point along the path becomes metallic. (2) The calculation breaks down because the centrosymmetric structure is unphysical with atoms situated on top of each other (for example in the case of Janus monolayers). We cannot exclude the existence of an adiabatic path in either of these cases since we always consider the nonpolar phase to be centrosymmetric, which does not need to be the case. For example, for the Janus layers one may define a path from P to -P that does not involve a centrosymmetric structure emerges along such a path, the energy barrier for the transition would be rather large and is not likely to be switchable under realistic conditions. Nevertheless, there may be other materials where we miss a relevant adiabatic path between P and -P that

does not involve a centrosymmetric state. It may also happen that the path passing through a centrosymmetric point is adiabatic and may be used to extract the spontaneous polarization, but the path is not necessarily the minimum energy path. This situation is realized in most of the out-of-plane ferroelectrics as will be discussed below.

The spontaneous polarization of the 63 predicted ferroelectrics are summarized in Table 1 (in-plane polarization), Table 2 (out-ofplane polarization) and Table 3 (both in-plane and out-of-plane polarization). In Fig. 4 we show three examples of the energy as a function of polarization along the adiabatic path obtained by linear interpolation as well as the NEB optimized path. The first one is Ge<sub>2</sub>S<sub>2</sub>, which have been subjected to extensive theoretical scrutiny as a prototypical example of a 2D ferroelectric<sup>20,48–50</sup>. In that case the linear interpolation and NEB paths largely coincide, which reflect the simplicity of the ferroelectric transition that involves a small displacement of atoms long the polarization direction. The second example is  $Li_2F_2S_2$ , which exhibits a somewhat more complicated path where the different elements undergo displacements in various directions along the path. This is reflected in a large difference between the linearly interpolated path and the NEB path.

Finally, the case In2Te4 has in-plane as well as out-of-plane components of the polarization. Here the switching barrier is lowered by an order of magnitude compared to the linear interpolation. The centrosymmetric state is seen to reside in a local minimum and is thus metastable, which could have important implications for the thermodynamical properties. In fact, for these three examples it is only the case of  $Ge_2S_2$  that appears to be representable by the Landau free energy type of expression  $F = \alpha P^2 + \beta P^4$  with  $\alpha < 0$  relevant for second order phase transitions. When the centrosymmetric phase is metastable (like In<sub>2</sub>Te<sub>4</sub>) the path may be (roughly) fitted to a sixth order polynomial of the form  $F = \alpha P^2 + \beta P^4 + \gamma P^6$  with  $\alpha > 0$  and  $\beta < 0$  and the local minimum might indicate a first order phase transition to the ferroelectric phase if the free energy of the metastable state is lowered more rapidly than the polar minimum with increasing temperature. This could be estimated by comparing the entropy originating from phonons in the two minima.

We have divided all the ferroelectrics into two classes depending on whether the non-polar state is metastable or not. As a sanity check we have calculated the phonon spectrum in the non-polar phase for all materials and compared with the NEB curvature. The results are shown in Fig. 5 and it is confirmed that materials with a positive NEB curvature in the non-polar phase are characterized by a lack of imaginary phonon frequencies (represented as negative phonon energies in Fig. 5). We find a total of 16 materials with metastable centrosymmetric phases. For the materials that are unstable in the non-polar phase we have analyzed the symmetry of the lowest imaginary phonon mode. In all cases we find the mode to be polar and all the materials in this work can thus be regarded as proper ferroelectrics.

Next, we distinguish between materials having in-plane polarization, out-of-plane polarization and materials where the polarization has both in-plane and out-of-plane components. npj

Name	Space group	$P_{\rm w}$ [pC m <sup>-1</sup> ]	$\Delta E  [meV Å^{-2}]$	$\mathcal{E}_{r}$ [V nm <sup>-1</sup> ]	Gap [eV]	ω [meV]	FH [eV/atom]	ID
		,    [pe iii ]				w [iiicv]	-	
As <sub>4</sub> O <sub>6</sub>	P21	191	42.2	45.8	3.9	-36.1	0	4513280
Zn <sub>2</sub> As <sub>4</sub> O <sub>8</sub>	P2 <sub>1</sub>	313	30.7	4.51	3.0	0.00	0	9001071
W <sub>2</sub> O <sub>12</sub> Sb <sub>4</sub>	P2 <sub>1</sub>	238	9.82	1.08	1.7	-30.1	0.02	/5595
Ag <sub>2</sub> Cl <sub>2</sub> Se <sub>4</sub>	P2 <sub>1</sub>	359	14.4	-	1.3	0.00	0	-
Ag <sub>2</sub> Cl <sub>2</sub> Ie <sub>4</sub>	P2 <sub>1</sub>	45.1	20.0	-	1.3	-5.33	0	-
Ag <sub>2</sub> Br <sub>2</sub> Se <sub>4</sub>	P2 <sub>1</sub>	126	13.0	-	1.2	0.00	0	-
Ag <sub>2</sub> l <sub>2</sub> Te <sub>4</sub>	P2 <sub>1</sub>	119	19.8	-	1.0	0.00	0.01	-
Au <sub>2</sub> Cl <sub>2</sub> Te <sub>4</sub>	P2 <sub>1</sub>	18.3	3.88	-	0.98	0.00	0.1	-
Au <sub>2</sub> Br <sub>2</sub> Te <sub>4</sub>	P2 <sub>1</sub>	25.7	5.27	-	1.0	0.00	0.05	-
Au <sub>2</sub> I <sub>2</sub> Te <sub>4</sub>	P2 <sub>1</sub>	60.4	8.57	-	0.71	0.00	0.06	-
Na <sub>2</sub> Nb <sub>2</sub> Cl <sub>12</sub>	P2 <sub>1</sub>	32.2	2.26	1.66	2.3	-3.55	0	8103950
$Zn_2Te_2(N_2H_4)_2$	P2 <sub>1</sub>	202	9.12	-	1.8	0.00	0.1	4113794
K <sub>2</sub> (CHO <sub>3</sub> ) <sub>2</sub>	P21	44.4	0.172	-	4.5	0.00	0	9016039
As <sub>2</sub> O <sub>8</sub> Te <sub>2</sub> (OH) <sub>2</sub>	P21	395	2.68	-	3.4	0.00	0	425501
HgH <sub>2</sub> S <sub>2</sub>	C2	323	10.8	-	2.4	-13.6	0	-
NiZrF <sub>6</sub>	C2	281	31.1	18.0	0.41	-10.1	0.2	-
As <sub>4</sub> O <sub>6</sub>	Pc	502	48.3	-	4.3	-13.8	0	9014252
As <sub>2</sub> O <sub>6</sub> Sb <sub>2</sub>	Pc	783	197	-	4.0	-57.5	0	9015432
Sn <sub>2</sub> H <sub>2</sub> O <sub>6</sub> P <sub>2</sub>	Pc	301	313	-	4.3	-48.9	0	4328407
$Zn_2O_6Se_2(H_2O)_2$	Pc	710	166	-	4.5	-52.0	0	78916
Nb <sub>2</sub> Cl <sub>4</sub> O <sub>2</sub>	Pmm2	213	0.739	0.816	1.0	0.00	0	-
Nb <sub>2</sub> Br <sub>4</sub> O <sub>2</sub>	Pmm2	199	0.626	0.811	1.0	0.00	0	416669
Nb <sub>2</sub> l <sub>4</sub> O <sub>2</sub>	Pmm2	183	5.17	-	1.0	-38.9	0	36255
Mo <sub>2</sub> Br <sub>4</sub> O <sub>4</sub>	Pmc2 <sub>1</sub>	240	11.7	2.59	1.4	-44.4	0	422483
W <sub>2</sub> Cl <sub>4</sub> O <sub>4</sub>	Pmc2 <sub>1</sub>	191	5.97	1.16	2.2	-31.1	0	28510
Sr <sub>2</sub> H <sub>8</sub> O <sub>6</sub>	Pmc2 <sub>1</sub>	234	45.0	-	4.4	-22.8	0	15366
Cu <sub>2</sub> Hq <sub>2</sub> Cl <sub>2</sub> Se <sub>2</sub>	Pmc2 <sub>1</sub>	453	50.3	-	0.83	-7.91	0.009	1001109
Hf <sub>2</sub> Zr <sub>2</sub> S <sub>8</sub>	Pma2	601	-48.9	3.79	1.1	0.00	0.2	-
Hf <sub>2</sub> Zr <sub>2</sub> Se <sub>8</sub>	Pma2	579	-36.7	5.00	0.84	0.00	0.2	-
Pb <sub>4</sub> O <sub>4</sub>	Pca2 <sub>1</sub>	290	10.8	0.860	2.6	-20.8	0	36250
As <sub>4</sub> S <sub>6</sub>	Pmn2 <sub>1</sub>	530	19.9	-	2.3	0.00	0.0002	9008211
As <sub>4</sub> Sec	Pmn2	494	15.7	2 69	1.7	0.00	0.002	9011471
GaalnaSc	Pmn2	922	139	3.56	2.0	-21.7	0	62340
GapClaTea	Pmn2	580	113	5.29	2.2	-18.0	0	7221395
	Pmn2	252	31.6	7.85	2.5	-12.1	0.09	63490
a-Go S	Pmn2	490	30.5	1.63	17	25.2	0.03	2107064
a Ge <sub>2</sub> 5 <sub>2</sub>	Pmn2.	357	6.66	0.482	1.7	_14.4	0.03	9008783
	Pmn2	31/	2.30	0.190	0.81	11.0	0.02	638005
a Sp 0	Pmn2	205	2.50	2.00	2.5	-11.0	0.05	20624
		303	25.4	2.09	2.5	-25.4	0.05	20024
a-sn <sub>2</sub> s <sub>2</sub>	Pmn2 <sub>1</sub>	292	3.55	0.300	1.4	-13.2	0.04	152/220
		219	0.960	0.109	0.92	-7.29	0.04	1557075
	Pmn2 <sub>1</sub>	138	0.0900	0.0147	0.60	-3.64	0.06	652743
$\beta$ -Ge <sub>2</sub> S <sub>2</sub>	Pmn2 <sub>1</sub>	201	2.10	0.238	1.8	-13.0	0.05	-
β-Ge <sub>2</sub> Se <sub>2</sub>	Pmn2 <sub>1</sub>	161	0.589	0.0925	1./	-7.68	0.05	-
$\beta$ -Sn <sub>2</sub> S <sub>2</sub>	Pmn2 <sub>1</sub>	123	0.3/4	0.0750	1.8	-8.07	0.06	-
β-Sn <sub>2</sub> Se <sub>2</sub>	Pmn2 <sub>1</sub>	107	0.148	0.0345	1.6	-4.93	0.07	-
As <sub>2</sub> Sb <sub>2</sub>	Pmn2 <sub>1</sub>	382	7.50	-	0.75	-18.3	0.09	-
P <sub>2</sub> Sb <sub>2</sub>	Pmn2 <sub>1</sub>	346	6.56	0.678	0.80	-23.0	0.2	-
$Cd_2O_6Se_2(H_2O)_2$	Pmn2 <sub>1</sub>	722	178	-	4.1	-52.3	0	2007038

The columns show the stoichiometry, space group, magnitude of spontaneous polarization ( $P_{\parallel}$ ), energy difference between the polar and the non-polar structures ( $\Delta E$ ), coercive field ( $\mathcal{E}_c$ ), band gap in the polar structure, lowest phonon energy of the non-polar structure at the  $\Gamma$ -point ( $\omega$ ), energy above the convex hull (EH) and finally the ICSD or COD identifier (ID).

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Name	Space group	$P_{\perp}$ [pC m <sup>-1</sup> ]	P <sub>top</sub>	$\Delta E \text{ [meV Å}^{-2}\text{]}$	$\mathcal{E}_{c}$ [V nm <sup>-1</sup> ]	Gap [eV]	EH [eV/atom]	ID
CulnP <sub>2</sub> S <sub>6</sub>	P3	4.99	(2/3, 1/3)	14.7	58.2	1.5	0	-
CulnP <sub>2</sub> Se <sub>6</sub>	P3	3.67	(2/3, 1/3)	8.17	13.7	0.49	0	71969
CuBiP <sub>2</sub> Se <sub>6</sub>	P3	2.51	(1/3, 2/3)	8.14	27.3	1.0	0	4327329
AgBiP <sub>2</sub> Se <sub>6</sub>	P3	1.39	(2/3, 1/3)	0.336	3.84	1.1	0	4327327
InP	P3m1	12.5	(0, 0)	3.45	1.69	1.1	0.4	-
CSiF <sub>2</sub>	P3m1	0.656	(0, 0)	295	10.7	1.9	0.6	-
CSiH₂	P3m1	19.4	(0, 0)	544	-	3.8	0	-
In <sub>2</sub> Se <sub>3</sub>	P3m1	16.9	(1/3, 2/3)	70.0	9.01	0.75	0.008	-

Table 3.	Materials with in-p	lane polarization	$(P_{\parallel})$ as well as c	ut-of-plane polariz	ation ( $P_{\perp}$ ).				
Name	Space group	$P_{\parallel}$ [pC m <sup>-1</sup> ]	$P_{\perp}  [pC  m^{-1}]$	$\Delta E \text{ [meV Å}^{-2}\text{]}$	$\mathcal{E}_{c}[V nm^{-1}]$	Gap [eV]	ω [meV]	EH [eV/atom]	ID
In <sub>2</sub> Te <sub>4</sub>	P1	253	5.98	0.496	0.0935	0.49	0.00	0.2	501
TiZr <sub>3</sub> S <sub>8</sub>	P1	608	0.140	-42.8	-	1.0	0.00	0.2	-
HfZr <sub>3</sub> S <sub>8</sub>	P1	600	0.411	-46.9	-	1.2	0.00	0.2	-
$Li_2F_2S_2$	P1	114	1.70	1.87	1.31	1.7	-2.13	0.5	-
$Hf_3ZrS_8$	Pm	602	0.230	-51.2	-	1.1	0.00	0.2	-
Hf <sub>3</sub> ZrSe <sub>8</sub>	Pm	580	0.261	-38.7	3.66	0.84	0.00	0.2	-



Fig. 4 Energy versus polarization for three representative ferroelectrics. a (Left):  $Ge_2S_2$  (in-plane polarization). b (Middle):  $F_2Li_2S_2$  (in-plane polarization). c (Right):  $I_2Te_4$ , which has both in-plane and out-of-plane components of the spontaneous polarization. In all three cases we show the energy along the linearly interpolated path (LI) and energy along the path optimized by the nudged elastic band method (NEB). The insets show the side views of polar and non-polar states for  $Ge_2S_2$  and  $In_2Te_4$  and top views for  $F_2Li_2S_2$ .



Fig. 5 Lowest phonon frequency (imaginary modes represented as negative numbers) versus energy curvature of the NEB energy potential surface calculated in the non-polar phase. The points are color coded according to the direction of polarization with respect to the atomic plane.

In Fig. 6 we present a scatter plot of the polarization versus energy difference between the polar and centrosymmetric states color coded according to the direction of polarization with respect to the atomic plane. In Tables 1–3 we list all of the materials including space groups, magnitude of spontaneous polarization, band gap, coercive field and energy above convex hull. For the materials that are known in bulk form as layered van der Waals bonded structures we also state the identifier of the bulk material from either ICSD<sup>51</sup> (ID < 10<sup>6</sup>) or COD (ID > 10<sup>6</sup>). We note that we find a few materials with a negative energy difference signifying that the centrosymmetric phase is more stable. These are Hf/Zr alloys of transition metal dichalcogenides and and their Janus structures. The present calculations simply show that the (centrosymmetric) T-phase is more stable than the polar H-phase, which is the one appearing in the C2DB.

In Table 1 we display the 2D ferroelectrics with an in-plane polar axis. Most of the materials are situated within 0.1 eV per atom of the convex hull and can thus be regarded as being thermodynamically stable (with the exceptions of  $Hf_2Zr_2S_8$  and  $Hf_2Zr_2Se_8$ 



Fig. 6 Magnitude of polarization versus the energy difference between the polar and non-polar phases. The points are color coded according to the direction of polarization with respect to the atomic plane.

discussed above). It should also be noted that the far majority of the structures are derived from layered bulk materials (implied by the presence of the ID reference) and are thus expected to be exfoliable from known bulk materials. The spontaneous 2D polarization is generally on the order of a few hundred pC/m. The largest polarization is found for Ga<sub>2</sub>In<sub>2</sub>S<sub>6</sub> with a value of 922 pC/m, but it also exhibits a rather high barrier of 139 meV/Å<sup>2</sup>, which could imply that it is not switchable under realistic conditions. We emphasize again that in the present work we have defined materials to be ferroelectric if an adiabatic path exists that connects the structure to the closest centrosymmetric phase. There may be several other pyroelectric materials in the C2DB where an adiabatic path to a non-polar phase exists that we have not found in the present study. In addition, for a given material identified as ferroelectric there may exist a different path that lowers the barrier by circumventing the centrosymmetric structure. This has, for example been found to be the case for Ge<sub>2</sub>Se<sub>2</sub><sup>49</sup> and the stated values for barriers and coercive fields in this work should be regarded as upper limits. However this does not affect the reported value of the spontaneous polarization as discussed above. Compounds in Table 1 with low barriers are of particular interest, since these are expected to be easily switchable. Besides the Ge and Sn chalcogenides, which have already been discussed extensively in literature<sup>10,17-21,49,52</sup>, we find C<sub>2</sub>H<sub>2</sub>K<sub>2</sub>O<sub>6</sub>, Nb<sub>2</sub>Na<sub>2</sub>Cl<sub>12</sub> and As<sub>2</sub>H<sub>2</sub>Te<sub>2</sub>O<sub>10</sub> as interesting candidates that are easily switchable. In addition, the niobium oxide dihalides  $Nb_2O_2X_4$  (X = CLBr.I) have low switching barriers and large spontaneous polarization. These have, however, been shown to exhibit an anti-ferroelectric ground state<sup>22</sup>, which has not been considered here. While the barrier itself does not yield a quantitative estimate of the ease with which a ferroelectric may switch polarization state it is expected to constitute a rough qualitative estimate. For a more precise estimate one may calculate the coercive field for coherent monodomain switching. For the materials where we succeeded in converging the NEB calculation we have calculated this field according to Eq. (4).

From Table 1 it is clear that the calculated coercive fields largely correlate with the barrier and the lowest fields are found for materials with small barriers. We have not put additional effort into converging all NEB calculations since the actual switching mechanism in ferroelectrics typically involve migration of domain walls rather than coherent monodomain switching and the estimated coercive fields may thus be orders of magnitude larger than experimentally relevant coercive fields<sup>52</sup>. Nevertheless, for the Ge and Sn monochalcogenides the fields required for switching the polarization state through domain wall migration have been shown to be largely correlated with the energy barrier for switching<sup>52</sup> and the *relative* values of coercive fields in Table 1

may be regarded as a rough measure of the hardness with which the materials can be switched by an external electric field.

For the out-of-plane ferroelectrics stated in Table 2 there exist simple adiabatic paths that do not pass through inversion symmetric structures. Referring to the example of AgBiP<sub>2</sub>Se<sub>6</sub> in Fig. 1 it is easy to see that there is a path connecting states of opposite polarity without passing through an inversion symmetric point. This involves shifting the Ag atom from the top Se layer to the bottom Se layer. The path passes through a structure with the non-polar point group 32, which does not have inversion symmetry. For most of the materials there exists another adiabatic path passing through a inversion symmetric point, but the energy barrier along the 32 path is much lower. Our general workflow only identifies paths involving a centrosymmetric point, but we have recalculated the barriers along the simple paths (not passing through centrosymmetric structures) for all the materials in Table 2.

In general, we find that the magnitude of polarization is significantly smaller in materials with purely out-of-plane polarization compared to those with in-plane polarization. The experimentally known structures  $\mathsf{ABP}_2\mathsf{Se}_6$  (A = Ag, Cu and B = In, Bi) in Table 2 have a small out-of-plane dipole originating from the A atom being displaced from the center of the layer towards the top or bottom (see. Fig. 1) and the remaining materials are buckled honeycomb structures with inequivalent atoms that naturally gives rise to a small dipole. The polar state in these materials involves a significant displacement of the atoms, but the magnitudes of polarization are rather small due to small values (~0.1e) of the z-components of Born effective charge tensors<sup>53</sup> for the displaced atoms. We note that CulnP<sub>2</sub>Se<sub>6</sub> and CulnP<sub>2</sub>S<sub>6</sub> have previously been predicted to have anti-ferroelectric ground states by DFT<sup>27,5</sup> <sup>4</sup>. but these are not found in the present study since they can only be extracted by investigating larger super cells.

All of the materials are classified as purely out-of-plane ferroelectrics due to a three-fold rotational symmetry in the plane. However, since the formal polarization Eq. (2) is not single valued, the in-plane polarization is allowed to be non-vanishing. In particular, for the case of three-fold rotational symmetry the allowed values are (0, 0), (1/3, 2/3) and (2/3, 1/3) in units of cell vectors divided by cell area (for a hexagonal cell with 120° angle between vectors). Such a "topological polarization" is not switchable, but enforces gapless states at any zigzag terminated ribbon or nanoflake<sup>47,55,56</sup>. Interestingly, all of the experimentally known materials in Table 2 exhibit non-trivial topological polarization.

The case of In2Se3 deserves a brief discussion in terms of topological properties. In contrast to the remaining materials in Table 2, this material breaks the three-fold rotational symmetry along the adiabatic path. This allows for a coupling of the out-ofplane polarization to the in-plane polarization, since the in-plane polarization is only protected by topology in the relaxed polar structures. In Fig. 7 we show the in-plane and out-of-plane polarization of In<sub>2</sub>Se<sub>3</sub> along the adiabatic path and indeed observe that both components of polarization are switched simultaneously. While the out-of-plane components vanishes halfway along the path, the magnitude of the in-plane component only varies marginally, and simply rotates from one high symmetry point to another. It thus changes topology from (1/3, 2/3) to (2/3, 1/3) along the path. We note that the coupling of polarization components has been observed experimentally in thin films of In<sub>2</sub>Se<sub>3</sub>,<sup>12</sup> but to our knowledge the topological properties of the polarization has not been unraveled prior to the present work.

In Table 3 we list all materials that have in-plane as well as outof-plane components of the spontaneous polarization. The only point groups that allow for this are 1 and *m*. In the latter case the mirror plane has to be orthogonal to the atomic plane to allow for a polarization that is not purely in-plane. Again, we find a few alloys of transition metal dichalcogenides in the H-phase that are



Fig. 7 Polarization switching of  $\ln_2$ Se<sub>3</sub>. Left: Magnitude of the out-of-plane ( $P_{\perp}$ ) and in-plane ( $P_{\parallel}$ ) polarization along a path that switches between two inversion related high symmetry points in the Wigner-Seitz cell. Right: the angle of in-plane polarization along the switching path.

found to be more stable in the T-phase (as implied by negative values of  $\Delta E$ ). These are probably not switchable under realistic conditions and it is dubious if it is even possible to synthesize any of them. Instead we wish to highlight the case of  $\ln_2 Te_4$ , which is the only material with mixed polarization that is experimentally known as a van der Waals bonded bulk material and thus may be easy to exfoliate. The out-of-plane component of polarization is much smaller than the in-plane component, but since the components are coupled along the switching path the in-plane polarization can be switched by application of a purely out-of-plane field. This could have significant practical consequences for the operation of ferroelectric devices based on 2D materials since a large out-of-plane field can be implemented by rather simple means using top and bottom gates.

#### Magnetic polar materials

The magnetic polar materials warrant a special treatment for several reasons. First of all, the interest in 2D magnetism has exploded in recent years and novel 2D magnets are interesting in their own right - polar or not. Since polar materials are pyroelectric by definition all the polar magnetic materials from C2DB can be regarded as being multiferroic and these compounds may exhibit coupling between magnetic order and polar order. In Table 4 we list all dynamically stable 2D magnetic materials that are polar and have a finite band gap. In addition to the gap and energy above the convex hull, we also state the spin state of the magnetic transition metal atoms and the nearest neighbor exchange coupling obtained from collinear energy mapping<sup>57,58</sup>. The sign of the nearest neighbor exchange coupling (positive for ferromagnetic interaction) in Table 4 indicates whether the true ground state is expected to have ferromagnetic or anti-ferromagnetic order.

A few of the materials in Table 4 have already been discussed prior to this work. For example, the vanadium oxyhalides  $VOX_2$  (X = F, Cl, Br, I) have been shown to be switchable multiferroics<sup>23,24</sup>. VOCl<sub>2</sub> and VOBr<sub>2</sub> exhibit anti-ferromagnetic order in the gapped ground state while the ferromagnetic state is metallic. As a consequence, they are not captured by our workflow since all materials in C2DB are reported in their ferromagnetic state. Furthermore, it has been argued that it is necessary to apply beyond-PBE approaches such as HSE or PBE+U in order to calculate the band gap accurately for these materials.  $VOF_2$  and  $VOI_2$  may thus be predicted to be gapped and switchable in the ferromagnetic state if a more accurate functional is applied<sup>23</sup>.

None of the materials in Table 4 have an adiabatic switching path that passes through a centrosymmetric point why they are not present in Tables 1–3. This does not, however, imply that none of the compounds are ferroelectric and due to the intriguing possibility of having coexistence of ferromagnetic and ferroelectric orders it is worthwhile to investigate whether any of these may be switched through an alternative path. Here we will just

focus on two examples—VAgP\_2Se\_6 and Cr\_2P\_2Se\_6—and leave a systematic study of 2D multiferroics to future work.

Bulk VAgP<sub>2</sub>Se<sub>6</sub> was synthesized and characterized in ref. <sup>59</sup>, where it was found to have space group C2 and to order ferromagnetically below 18 K. The vanadium atoms are in the oxidation state  $V^{3+}$ , which implies a  $d^2$  configuration with a magnetic moment of 2  $\mu_{\rm B}$ . The basic structure of the individual layers can be envisioned as a distorted honeycomb lattice of alternating Ag and V atoms as shown in Fig. 8. Each V atom thus has one nearest neighbor Ag atom (distance 3.21 Å) and two next nearest neighbors (distance 3.96 Å), which produces a polar axis along the short bond. Since each V atom may form three equivalent short bonds the compound has three polarization states where the polarization vectors are rotated by 120°. The PBE relaxed monolayer in C2DB is dynamically stable and has the same space group as the bulk material. In Fig. 8 we show the switching path obtained from a NEB calculations between two such rotated polarization states. The barrier is rather low with a value of 1.2 meV/Å<sup>2</sup> and the structure is thus expected to be easily switchable by application of an external electric field. We also calculate the spontaneous polarization along the path and find that the magnitude is nearly constant, but with an abrupt change in direction at the point where the Ag atom is exactly between the two V atoms. The material thus comprises an example of a system with a switchable discrete three-state polarization, which may be of relevance for non-volatile memory applications. The V atoms constitute the magnetic lattice, which is hexagonal and each V atom thus have six nearest neighbors. These are, however not equivalent due to the polarization and the two exchange constants  $(J_1)$  orthogonal to the polar axis are distinct from the four exchange constants  $(J_2)$  along bonds that are at a 30° angle with respect to the polar axis as illustrated in Fig. 8. We have calculated the two exchange constants by an energy mapping approach<sup>60,61</sup> using three magnetic configurations in a  $2 \times 2$  repetition of the unit cell. One ferromagnetic state and two states with ferromagnetic chains that are anti-ferromagnetically aligned with neighboring chains and at different angle with respect to the polarization direction. The three energies can be mapped to the nearest neighbor isotropic Heisenberg model

$$H = -\frac{1}{2}J_1 \sum_{\langle ij \rangle_{\perp}} \mathbf{S}_i \cdot \mathbf{S}_j - \frac{1}{2}J_2 \sum_{\langle ij \rangle_{\perp}} \mathbf{S}_i \cdot \mathbf{S}_j, \tag{1}$$

where **S**<sub>i</sub> denotes the spin of vanadium site *i*,  $\langle ij \rangle_{\perp}$  denotes sum over nearest neighbors perpendicular to polarization and  $\langle ij \rangle_{\perp}$ denotes sum over the remaining nearest neighbors. We then find that  $J_1 = 5.5$  meV and  $J_2 = -1.6$  meV. It should be noted that the nearest neighbor exchange coupling stated in Table 4 differs from  $J_1$  calculated here, since the former value was obtained from simple high throughput calculations where only two magnetic configurations were considered. It is rather interesting that the exchange path perpendicular to the polarization direction is npj

Table 4. Dynamic	ally stable 2D polar ma	ignetic materials th	at exhibits a band	d gap.			
Name	Space group	Gap [eV]	J [meV]	Spin [ħ]	Axis	EH [eV/atom]	ID
ReAu <sub>2</sub> F <sub>6</sub>	P1	0.18	-	1/2	3D	0.2	-
NiPS₃	P1	0.075	5.9	1/2	3D	0.3	646140
$Cu_2I_4O_{12}$	P21	0.73	3.3	1/2	11	0.03	4327
$Cr_2Cu_2P_4S_{12}$	P21	1.1	1.2	3/2	11	0	1000355
CoZrBr <sub>6</sub>	C2	0.39	-	1/2	Ш	0	-
VAgP <sub>2</sub> Se <sub>6</sub>	C2	0.35	1.9	1	11	0.004	1509506
$Mn_2H_4O_8S_2$	Pc	2.1	-2.1	2	Ш	0.08	74810
VF <sub>2</sub> O	Pmm2	0.76	13	1/2	11	0.001	-
VCl₂O	Pmm2	0.81	-26	1/2	Ш	0	24380
VBr <sub>2</sub> O	Pmm2	0.77	-14	1/2	Ш	0	24381
VI <sub>2</sub> O	Pmm2	0.50	6.8	1/2	11	0	-
NiC <sub>6</sub> Cl <sub>2</sub> H <sub>4</sub> N <sub>2</sub>	Pmm2	0.86	9.1	1	11	0.2	7227895
$Mn_2Cl_2Sb_2S_4$	Pmc2 <sub>1</sub>	0.35	-3.0	2	Ш	0.08	151925
Mn <sub>2</sub> Br <sub>2</sub> Sb <sub>2</sub> Se <sub>4</sub>	Pmc2 <sub>1</sub>	0.26	-3.2	2	Ш	0.09	1528451
Ti <sub>4</sub> Cl <sub>4</sub> Se <sub>4</sub>	Pmn2 <sub>1</sub>	0.042	-	1/2	Ш	0.1	-
Ti <sub>4</sub> Br <sub>4</sub> Se <sub>4</sub>	Pmn2 <sub>1</sub>	0.063	-	1/2	11	0.1	-
VCIBr	P3m1	1.3	-4.1	3/2	$\perp$	0.01	-
VCII	P3m1	1.1	-2.5	3/2	$\perp$	0.06	-
VBrl	P3m1	1.2	-1.5	3/2	$\perp$	0.02	-
VSSe	P3m1	0.013	58	1/2	$\perp$	0	-
VSeTe	P3m1	0.12	74	1/2	$\perp$	0.01	-
Nb <sub>3</sub> Cl <sub>8</sub>	P3m1	0.21	-	1/6	$\perp$	0	408645
Nb <sub>3</sub> Br <sub>8</sub>	P3m1	0.29	-	1/6	$\perp$	0	1539108
Nb <sub>3</sub> I <sub>8</sub>	P3m1	0.19	-	1/6	$\perp$	0	1539109
CrHO <sub>2</sub>	P3m1	0.092	3.0	3/2	$\perp$	0.2	9012135
Cr <sub>2</sub> P <sub>2</sub> Se <sub>6</sub>	P31m	0.43	11	3/2	T	0.01	626521

In addition to the columns shown in Table 1, we also state the nearest neighbor exchange constant (positive for ferromagnets) and the spin carried by the magnetic atoms. The polar axis follows from the point group symmetries and is stated for convenience.

anti-ferromagnetic whereas the remaining paths are ferromagnetic. These exchange couplings yield a ferromagnetic ground state, but the sign of  $J_2$  introduces magnetic frustration in the system. The polar axis also introduces a small in-plane magnetic anisotropy (roughly 0.06 meV per formula unit), but this will not be easily observable since we predict (a weak) out-of-plane easy axis in this material. The ground state magnetization is therefore not expected to change when the polarization direction is switched between the three discrete states. Nevertheless, the polarization will be observable from the magnetic excitations, which will have a dispersion that is strongly influenced by the direction of the polar axis. In Fig. 8 we show the magnon dispersion calculated from linear spin-wave theory<sup>62</sup> along two different paths that would be equivalent without the polar axis. Due to the large difference between  $J_1$  and  $J_2$  one observes a magnon energy at the Brillouin zone boundary (the M-point) that is more than two times smaller in the direction parallel to the polarization compared to the directions that are not parallel (the M'-point). Such a switchable magnon dispersion could perhaps find applications in information processing based on magnonics<sup>63</sup>.

The second case of  $Cr_2P_2Se_6$  has space group P31m, which implies a polar axis out-of-plane. The material exhibits a rather large ferromagnetic nearest neighbor exchange constant of 11 meV and weak out-of-plane easy axis. The structure is similar to the P3 materials of Table 2, but the Cr atoms are centered in the atomic plane and the P atoms are shifted slightly to the top or bottom of the layer. Again, the switching path involves a simple shift of the P atoms in the direction orthogonal to the plane, which does not pass through a centrosymmetric point. We have calculated the NEB energy along the path connecting the two states of opposite polarization and find an energy barrier of 8.24 meV/Å<sup>2</sup>. However, the material has a rather small gap of 0.43 eV, which closes along the path and Cr<sub>2</sub>P<sub>2</sub>Se<sub>6</sub> is therefore not switchable according to the criterion of an adiabatic path. Nevertheless, the out-of-plane polarization is easily calculated by integrating the dipole density over the z-direction, which yields  $P_{\perp} = 5.4$  pC/m. Although the gap closes along the path, it is highly likely that one may still switch the state of polarization by an external electric field, since the metallic states confined in the 2D layer will not be able to fully screen a transverse field.

We finally mention, that all the present calculations of magnetic materials are collinear and cannot capture potential type-II multi-ferroics where non-collinear magnetic order introduces a polar axis. This has, for example been found in Nil<sub>2</sub><sup>16</sup> and Hf<sub>2</sub>VC<sub>2</sub>F<sub>2</sub><sup>64</sup>.

#### DISCUSSION

The starting point of the present work has been the 252 polar insulators in the C2DB. For pyroelectric applications all of these are interesting in their own right and may easily be filtered from the C2DB by the point group alone. The main interest here has been the ferroelectric properties and we have thus calculated the spontaneous polarization of all materials where an adiabatic path that pass through a centrosymmetric structure in close proximity to the polar phase could be identified. These materials are expected to be switchable by an external electric field and we



Fig. 8 Polar states and magnetic excitations of VAgP<sub>2</sub>Se<sub>6</sub>. Left: Polarization and energy along the adiabatic path that switches the polarization by 120°. The top shows a schematic view of the Ag/V lattice with the two inequivalent nearest neighbor exchange interactions indicated in the two polarization states. Right: Magnon energies along different directions in the Brillouin zone (polar axis indicated by dashed line) derived from nearest neighbor interactions. We note that K and K' are equivalent but are given different labels here to distinguish the ΓK and ΓK' directions.

found 49 materials with purely in-plane polarization, 8 materials with purely out-of-plane polarization and 6 materials with mixed components of polarization. In particular, we have recovered most of the well-known 2D ferroelectrics, but have extended the list by a large number of new 2D ferroelectrics. We emphasize that most of the discovered compounds are known as bulk van der Waals bonded materials and are expected to be easily exfoliable. Each of the materials in Tables 1–3 thus warrants a more detailed study of ferroelectric properties with respect to stability under ambient conditions, domain wall formation, Curie temperatures etc, but this is out of scope for the present work.

It is worth stressing that the present study is by no means exhaustive. The requirement of having a centrosymmetric nonpolar phase that is adiabatically connected to the polar structure is not in general fulfilled for all ferroelectrics. The case of CulnP2Se6 comprises an example where the polar structure has point group 3 and the non-polar structure has the non-centrosymmetric point group 32. It is possible to filter materials where a noncentrosymmetric non-polar structure may exist in a systematic way. For example, if the polar structure contains a two-fold axis and an orthogonal mirror plane (this is the case for half of the materials in Table 1) it is expected that the non-polar state (roughly) conserves the mirror and the non-polar state thus cannot reside in a chiral point group, which leaves only five possible noncentrosymmetric points groups that will typically be inconsistent with the Bravais lattice. We have not attempted to perform such analysis here, but merely point at possible future directions for a more systematic search for 2D ferroelectrics.

Finally, we have allocated special attention to the magnetic polar materials present in the C2DB. While none of these are switchable through an adiabatic path passing through a centrosymmetric point, the materials are inherently multiferroic even if they are not ferroelectric and are expected to exhibit non-vanishing Dzyaloshinskii-Moriya interactions, magnetoelectric coupling and a range of other properties that are dependent on broken timereversal and broken inversion symmetry. We have highlighted the case of VAgP<sub>2</sub>Se<sub>6</sub> (point group 2) where the non-polar structure is in close proximity to a structure of 32 symmetry, which lacks inversion symmetry. It is, however, straightforward to identify three equivalent polar structures and calculate the spontaneous polarization as well as the barrier for switching. We found that the structural space for switching comprises nearly discrete states of polarization, which situates the material rather far from a Landau free energy type of description (at low temperatures). Moreover, we showed that the polar axis introduces highly anisotropic nearest neighbor exchange interactions, which introduces a strong coupling of the magnetic excitations spectrum to the polar state of the material. Again, we believe that all of the compounds listed in Table 4 warrant a more detailed study and there could be several additional materials that allow for an adiabatic switching path that does not involve a centrosymmetric point.

#### METHODS

#### **Formal polarization**

The defining property of ferroelectric materials is the presence of a spontaneous electrical polarization, which is switchable by application of an external electric field. While the polarization is not well defined in bulk materials one may define the spontaneous polarization as the change in polarization with respect to a non-polar state that can be adiabatically connected to the polar phase. According to the modern theory of electrical polarization<sup>65–67</sup>, one can calculate the formal 2D polarization for a system in a given configuration as

$$\mathbf{P} = e\left(\frac{1}{A}\sum_{a} Z_{a}\mathbf{r}_{a} - \sum_{n} \int_{BZ} \frac{d\mathbf{k}}{(2\pi)^{2}} \langle u_{n\mathbf{k}} | i\nabla_{\mathbf{k}} | u_{n\mathbf{k}} \rangle\right)$$
(2)

where *e* denotes the electron charge, *A* is the unit cell area,  $Z_a$  is the charge of nucleus *a* (including core electrons),  $u_{nk}$  are Bloch states represented in a smooth gauge such that the *k*-space derivative is well defined and the sum runs over occupied states.

The formal polarization is only defined modulo  $e\mathbf{R}_i/A$ , where  $\mathbf{R}_i$  is an arbitrary lattice vector. This is due to the fact that the nuclei positions can be chosen in any unit cell and the Brillouin zone integral may change by  $\mathbf{R}_i/A$  by a gauge transformation of the Bloch states. Nevertheless, differences in polarization along any adiabatic path (continuous change of atomic positions where the system remains insulating) is well defined since one may track the polarization along a particular branch. One can therefore define the spontaneous polarization as

$$\mathbf{P}_{\rm S} = \int_{\lambda=0}^{\lambda=1} d\lambda \frac{d\mathbf{P}^{\lambda}}{d\lambda}.$$
(3)

where  $\lambda$  parameterizes an adiabatic path between a non-polar reference structure ( $\lambda = 0$ ) and the polar ground state ( $\lambda = 1$ ).

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#### **Coercive field**

The coercive field is defined as the electric field required to switch a ferroelectric material between two different polarization states. In reality this is likely to involve complicated structural reorganization, which is typically dominated by migration of domain walls<sup>19,52,68-70</sup>. In the present work we simply calculate the field required for coherent monodomain switching, which may be orders of magnitude larger than the actual field required for polarization switching mediated by domain wall motion. Nevertheless, the field provides a rough measure of the polarization stiffness in the material and yields an upper bound for the true coercive field.

The coercive field for monodomain switching can be estimated by finding the minimum energy path connecting the two structures corresponding to  $\lambda = 0$  (non-polar) and  $\lambda = 1$  (polar), which may be obtained by the nudged elastic band method<sup>45</sup>. In the presence of an electric field the energy will acquire a term proportional to  $\mathcal{E} \cdot \mathbf{P}$  and the the system will change polarization state when the force originating from the field matches the maximal slope of the energy along the path. If the field is applied parallel to the polarization the magnitude of the coercive field may then be calculated according to

$$\mathcal{E}_{c} = \max\left(\frac{d\mathcal{E}(\mathbf{P}^{\lambda})}{d|\mathbf{P}|}\right),\tag{4}$$

where  $E(\mathbf{P}^{\lambda})$  is the energy per unit area along the path. We note that even in the realm of strict monodomain switching, this is an approximate approach since the true minimal path in the presence of an electric field may differ from that found without a field.

#### **Computational details**

All the calculations in the present work were carried out using the electronic structure package GPAW<sup>71,72</sup>, which applies the projector-augmented wave (PAW) method and a plane wave basis set. We have used the Perdew-Burke-Ernzerhof (PBE) functional, a plane wave cutoff of 800 eV, a k-point density of 12 Å and a Fermi smearing of 0.05 eV. All structures were relaxed with a force tolerance of 1 meV/Å. For details on the implementation of Eq. (2) we refer to ref. <sup>53</sup>.

#### DATA AVAILABILITY

The authors declare that the data supporting the findings of this study are available within the paper and at https://cmrdb.fysik.dtu.dk/c2db/.

#### CODE AVAILABILITY

The authors declare that the applied software supporting the findings of this study are available in the GPAW software package. https://gitlab.com/gpaw/gpaw/-/tree/master/gpaw.

Received: 5 October 2022; Accepted: 7 March 2023; Published online: 29 March 2023

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#### ACKNOWLEDGEMENTS

M.K. and T.O. were supported by the Danish Independent Research Foundation, Grant number 9040-00269B. U.P. and T.O. were supported by the Villum foundation, Grant No. 00028145.

#### AUTHOR CONTRIBUTIONS

M.K. and U.P. have performed calculations and data analysis. M.N.G. and K.S.T developed the code for calculating spontaneous polarization. K.W.J. contributed to the development of ideas and methodology. T.O. supervised the project. M.K. and T.O. wrote the manuscript.

#### **COMPETING INTERESTS**

The authors declare no competing interests.

#### ADDITIONAL INFORMATION

Supplementary information The online version contains supplementary material available at https://doi.org/10.1038/s41524-023-00999-5.

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# Supplemental Material: Two-dimensional ferroelectrics from high throughput computational screening

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#### ADDITIONAL TABLES WITH STRUCTURAL DETAILS

Below we state the structural details of the materials presented in tables I, II and III in the main text. The structures are also available at  $\frac{https://cmrdb.fysik.dtu.dk/c2db/}{https://cmrdb.fysik.dtu.dk/c2db/}$ 

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$ \begin{array}{c c} \text{Li}_{12}\text{F}_2\text{S}_2 & \text{al}_{1}(5.161, -0.0, 0.0) & \text{Li}_{1}(0.459, 0.849, 9.825) \\ \text{A}_{2}(0.0, 5.797, -0.0) & \text{A}_{3}(0.0, 0.0, 18.615) & \text{S}_{2}(3.134, 0.394, 9.726) \text{F}_{2}(3.001, 1.323, 8.171) \\ \hline \text{A}_{3}(0.0, 0.0, 18.615) & \text{S}_{2}(3.134, 0.394, 9.726) \text{F}_{2}(3.001, 1.323, 8.171) \\ \hline \text{A}_{3}(0.0, 0.0, 3.97, -0.0) & \text{A}_{3}(0.0, 0.0, 32.19) & \text{A}_{3}(2.058, 0.706, 15.022) \text{A}_{3}(.471, 5.502, 15.612) \text{A}_{3}(4.044, 6.544, 17.132) \\ \hline \text{A}_{3}(0.0, 0.0, 32.19) & \text{A}_{3}(2.058, 2.481, 15.058) \text{O}_{2}(3.089, 0.59, 16.724) \text{O}_{3}(4.404, 6.544, 17.132) \\ \hline \text{A}_{3}(0.0, 0.0, 32.19) & \text{A}_{3}(2.058, 2.481, 15.058) \text{O}_{2}(3.089, 0.59, 16.724) \text{O}_{3}(4.404, 6.544, 17.132) \\ \hline \text{A}_{3}(2.00, 0.0, 32.19) & \text{A}_{3}(2.00, 0.0, 32.19) & \text{A}_{3}(2.058, 2.481, 15.058) \text{O}_{2}(3.089, 0.59, 16.724) \text{O}_{3}(4.404, 6.544, 17.132) \\ \hline \text{A}_{3}(2.00, 0.0, 32.19) & \text{A}_{3}(2.2058, 2.481, 15.058) \text{O}_{2}(3.089, 0.59, 16.724) \text{O}_{3}(4.404, 6.544, 17.132) \\ \hline \text{A}_{3}(2.00, 0.0, 32.19) & \text{O}_{1}(1.929, 3.036, 20.8) \text{A}_{5}(-0.0, 0.014, 15.128) \text{A}_{5}(2.488, 4.794, 20.729) \\ \hline \text{A}_{3}(2.2058, 2.481, 15.017) \text{O}_{3}(4.259, 4.332, 20.887) \text{O}_{4}(0.536, 1.711, 14.92) \\ \hline \text{O}_{1}(1.929, 3.036, 20.8) \text{A}_{2}(-0.0, 0.014, 15.128) \text{A}_{3}(2.488, 4.794, 20.729) \\ \hline \text{A}_{3}(2.205, 2.453, 18.9) \text{O}_{6}(0.083, 5.014, 16.917) \text{O}_{1}(2.2378, 4.994, 18.939) \\ \hline \text{O}_{2}(2.866, 0.474, 15.017) \text{O}_{3}(4.259, 4.332, 20.887) \text{O}_{4}(0.536, 1.771, 14.99) \\ \hline \text{O}_{1}(2.917, 3.205, 18.489) \text{I}_{1}(0.814, 4.373, 16.057) \text{O}_{2}(1.055, 2.534, 16.447) \\ \hline \text{O}_{1}(2.917, 3.205, 18.49) \text{I}_{1}(0.814, 4.373, 16.057) \text{O}_{2}(1.055, 2.534, 16.447) \\ \hline \text{O}_{3}(2.365, 8.533, 20.206) \text{O}_{4}(5.153, 5.044, 17.825) \text{O}_{5}(3.29, 5.714, 19.867) \\ \hline \text{O}_{1}(2.917, 3.205, 18.439) \text{I}_{1}(0.814, 4.373, 16.057) \text{O}_{2}(1.055, 2.574, 10.275) \\ \hline \text{I}_{3}(2.365, 8.533, 20.206) \text{O}_{4}(5.153, 5.044, 17.825) \text{O}_{5}(3.29, 5.714, 19.867) \\ \hline \text{O}_{1}(2.917, 3.205, 18.439) \text{I}_{1}(0.232, 2.6, 5, 18.16$	
$ \begin{array}{c c} \text{Li}_2\text{F}_2\text{S}_2 & \text{a}_2^{(2)}(0, 5, 797, -0.0) \\ \text{a}_3^{(0,0)}(0, 0, 0, 18.615) & \text{Li}_2^{(2)}(2.472, 3.043, 8.94) \text{S1:}(4.31, 4.628, 9.368) \text{F1:}(1.001, 2.515, 9.757) \\ \text{a}_3^{(0,0)}(0, 0, 0, 18.615) & \text{S2:}(3.134, 0.394, 9.726) \text{F2:}(3.001, 1.323, 8.171) \\ \text{As}_4\text{O}_6 & \text{a}_2^{(2)}(0, 0, 8.397, -0.0) \\ \text{a}_2^{(0,0)}(0, 0, 0, 32.19) & \text{As}_2^{(2)}(2.386, 0.706, 15.022) \text{As}_3^{(2)}(4.471, 5.502, 15.612) \text{As}_4^{(2)}(2.124, 3.524, 16.53) \\ \text{O}_1^{(0,742, 8.436, 15.466)} \text{O}_2^{(2)}(3.089, 0.59, 16.724) \text{O}_3^{(4)}(4.04, 6.544, 17.133) \\ \text{O}_4^{(2)}(2.058, 2.481, 15.058) \text{O}_5^{(3)}(3.884, 4.0, 16.477) \text{O}_6^{(1)}(1.537, 5.025, 15.713) \\ \text{O}_4^{(2)}(2.058, 2.481, 15.058) \text{O}_5^{(3)}(3.884, 4.0, 16.477) \text{O}_6^{(1)}(1.537, 5.025, 15.713) \\ \text{O}_4^{(2)}(2.058, 2.481, 15.058) \text{O}_5^{(3)}(3.884, 4.0, 16.477) \text{O}_6^{(1)}(1.537, 5.025, 15.713) \\ \text{O}_4^{(2)}(2.058, 2.481, 15.058) \text{O}_5^{(3)}(3.884, 4.0, 16.477) \text{O}_6^{(1)}(1.537, 5.025, 15.713) \\ \text{O}_4^{(2)}(2.058, 2.481, 15.058) \text{O}_5^{(3)}(3.894, 1.5, 15.7946) \text{Zn}_2^{(1)}(2.956, 3.711, 17.86) \\ \text{O}_1^{(1)}(1.929, 3.036, 20.8) \text{As}_2^{(2)}(-0.0, 0.014, 15.128) \text{As}_3^{(2)}(2.486, 0.474, 15.017) \text{O}_3^{(3)}(4.259, 4.332, 20.887) \text{O}_4^{(1)}(0.536, 1.771, 14.99) \\ \text{O}_5^{(0)}(0.7, 2.453, 18.9) \text{O}_6^{(0)}(0.83, 5.014, 16.917) \text{O}_7^{(2)}(2.378, 4.994, 18.939) \\ \text{O}_5^{(0)}(0.7, 2.453, 18.9) \text{O}_6^{(0)}(0.83, 5.014, 16.917) \text{O}_2^{(1)}(1.552, 2.534, 16.44) \\ \text{O}_3^{(3)}(3.56, 4.415, 15.416) \text{Cu}_2^{(3)}(3.292, 6.5, 18.164) 12^{(3)}(3.5, 3.876, 20.257) \\ \text{I}_3^{(2)}(2.365, 8.533, 20.206) \text{O}_4^{(5)}(5.153, 5.044, 17.825) \text{O}_5^{(3)}(3.29, 5.714, 19.867) \\ \end{array}$	
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$ \begin{array}{c c} As1: (0.154, 2.575, 20.689) \\ As1: (4.641, -0.0, 0.0) \\ a2: (-0.0, 5.123, -0.0) \\ a3: (0.0, 0.0, 35.817) \end{array} \begin{array}{c} As1: (0.154, 2.575, 20.689) \\ O1: (1.929, 3.036, 20.8) \\ As2: (-0.0, 0.014, 15.128) \\ As2: (-0.0, 0.014, 15.128) \\ As3: (2.307, 2.232, 15.088) \\ As4: (2.307, 2.232, 15.088) \\ Cu: (2.866, 0.474, 15.017) \\ O3: (4.259, 4.332, 20.887) \\ O4: (0.536, 1.771, 14.92) \\ O5: (0.07, 2.453, 18.9) \\ O6: (0.083, 5.014, 16.917) \\ O7: (2.378, 4.994, 18.939) \\ O8: (2.418, 2.432, 16.878) \\ Cu: (1.686, 1.749, 18.15) \\ O1: (2.917, 3.205, 18.489) \\ I1: (0.814, 4.373, 16.057) \\ O2: (1.055, 2.534, 16.447) \\ O3: (3.56, 4.415, 15.416) \\ Cu: (2.392, 6.5, 18.164) \\ I2: (3.05, 3.876, 20.257) \\ I3: (2.365, 8.533, 20.206) \\ O4: (5.153, 5.044, 17.825) \\ O5: (3.29, 5.714, 19.867) \\ O5: (3$	3)
$ \begin{array}{c} a_{1:}(4.641, -0.0, 0.0) \\ a_{2:}(-0.0, 5.123, -0.0) \\ a_{3:}(0.0, 0.0, 35.817) \end{array} \begin{array}{c} O1:(1.929, 3.036, 20.8) \ As2:(-0.0, 0.014, 15.128) \ As3:(2.488, 4.794, 20.728 \\ As4:(2.307, 2.232, 15.088) \ Zn1:(3.539, 1.15, 17.946) \ Zn2:(1.256, 3.711, 17.86) \\ O2:(2.866, 0.474, 15.017) \ O3:(4.259, 4.332, 20.887) \ O4:(0.536, 1.771, 14.99) \\ O5:(0.07, 2.453, 18.9) \ O6:(0.083, 5.014, 16.917) \ O7:(2.378, 4.994, 18.939) \\ O5:(0.07, 2.453, 18.9) \ O6:(0.083, 5.014, 16.917) \ O7:(2.378, 4.994, 18.939) \\ O5:(0.07, 2.453, 18.9) \ O6:(0.083, 5.014, 16.917) \ O7:(2.378, 4.994, 18.939) \\ O5:(0.07, 2.453, 18.9) \ O6:(0.083, 5.014, 16.917) \ O7:(2.378, 4.994, 18.939) \\ O3:(3.56, 4.415, 15.416) \ Cu2:(3.922, 6.5, 18.164) \ I2:(3.05, 3.876, 20.257) \\ I3:(2.365, 8.533, 20.206) \ O4:(5.153, 5.044, 17.825) \ O5:(3.29, 5.714, 19.867) \\ O3:(3.26, 8.533, 20.206) \ O4:(5.153, 5.044, 17.825) \ O5:(3.29, 5.714, 19.867) \\ O3:(3.26, 8.533, 20.206) \ O4:(5.153, 5.044, 17.825) \ O5:(3.29, 5.714, 19.867) \\ O3:(3.26, 8.533, 20.206) \ O4:(5.153, 5.044, 17.825) \ O5:(3.29, 5.714, 19.867) \\ O3:(3.26, 8.533, 20.206) \ O4:(5.153, 5.044, 17.825) \ O5:(3.29, 5.714, 19.867) \\ O3:(3.26, 8.533, 20.206) \ O4:(5.153, 5.044, 17.825) \ O5:(3.29, 5.714, 19.867) \\ O3:(3.26, 8.533, 20.206) \ O4:(5.153, 5.044, 17.825) \ O5:(3.29, 5.714, 19.867) \\ O3:(3.26, 8.533, 20.206) \ O4:(5.153, 5.044, 17.825) \ O5:(3.29, 5.714, 19.867) \\ O3:(3.26, 8.533, 20.206) \ O4:(5.153, 5.044, 17.825) \ O5:(3.29, 5.714, 19.867) \\ O3:(3.26, 8.533, 20.206) \ O4:(5.153, 5.044, 17.825) \ O5:(3.29, 5.714, 19.867) \\ O3:(3.26, 8.533, 20.206) \ O4:(5.153, 5.044, 17.825) \ O5:(3.29, 5.714, 19.867) \\ O3:(3.26, 8.533, 20.206) \ O4:(5.153, 5.044, 17.825) \ O5:(3.29, 5.714, 19.867) \\ O3:(3.26, 8.533, 20.206) \ O4:(5.153, 5.044, 17.825) \ O5:(3.29, 5.714, 19.867) \\ O3:(3.26, 8.533, 20.206) \ O4:(5.153, 5.044, 17.825) \ O5:(3.29, 5.714, 19.867) \\ O3:(3.26, 8.533, 20.206) \ O4:(5.153, 5.044, 17.825) \ O5:(3.29, 5.714, 19.867) \\ O3:(3.26, 8.533, 20.206) \ O4:(5.153, 5.044, 17.825) \ O5:(3.29, $	0)
$ \begin{array}{c c} Zn_2As_4O_8 & a2:(-0.0, 5.123, -0.0) \\ a3:(0.0, 0.0, 35.817) & As4:(2.307, 2.232, 15.088) Zn1:(3.539, 1.15, 17.946) Zn2:(1.256, 3.711, 17.85) \\ O2:(2.866, 0.474, 15.017) O3:(4.259, 4.332, 20.887) O4:(0.536, 1.771, 14.93) \\ O2:(2.866, 0.474, 15.017) O3:(4.259, 4.332, 20.887) O4:(0.536, 1.771, 14.93) \\ O5:(0.07, 2.453, 18.9) O6:(0.083, 5.014, 16.917) O7:(2.378, 4.994, 18.939) \\ O8:(2.418, 2.432, 16.878) \\ O1:(2.917, 3.205, 18.489) I1:(0.814, 4.373, 16.057) O2:(1.055, 2.534, 16.44') \\ O3:(3.56, 4.415, 15.416) Cu2:(3.922, 6.5, 18.164) I2:(3.05, 3.876, 20.257) \\ I3:(2.365, 8.533, 20.206) O4:(5.153, 5.044, 17.825) O5:(3.29, 5.714, 19.867) \\ O3:(3.56, 8.533, 20.206) O4:(5.153, 5.044, 17.825) O5:(3.29, 5.714, 19.867) \\ O3:(3.56, 8.533, 20.206) O4:(5.153, 5.044, 17.825) O5:(3.29, 5.714, 19.867) \\ O3:(3.56, 8.533, 20.206) O4:(5.153, 5.044, 17.825) O5:(3.29, 5.714, 19.867) \\ O3:(3.56, 8.533, 20.206) O4:(5.153, 5.044, 17.825) O5:(3.29, 5.714, 19.867) \\ O3:(3.56, 8.533, 20.206) O4:(5.153, 5.044, 17.825) O5:(3.29, 5.714, 19.867) \\ O3:(3.56, 8.533, 20.206) O4:(5.153, 5.044, 17.825) O5:(3.29, 5.714, 19.867) \\ O3:(3.56, 8.533, 20.206) O4:(5.153, 5.044, 17.825) O5:(3.29, 5.714, 19.867) \\ O3:(3.56, 8.533, 20.206) O4:(5.153, 5.044, 17.825) O5:(3.29, 5.714, 19.867) \\ O3:(3.56, 8.533, 20.206) O4:(5.153, 5.044, 17.825) O5:(3.29, 5.714, 19.867) \\ O3:(3.56, 8.533, 20.206) O4:(5.153, 5.044, 17.825) O5:(3.29, 5.714, 19.867) \\ O3:(3.56, 8.533, 20.206) O4:(5.153, 5.044, 17.825) O5:(3.29, 5.714, 19.867) \\ O3:(3.56, 8.533, 20.206) O4:(5.153, 5.044, 17.825) O5:(3.29, 5.714, 19.867) \\ O3:(3.56, 8.533, 20.206) O4:(5.153, 5.044, 17.825) O5:(3.29, 5.714, 19.867) \\ O3:(3.56, 8.533, 20.206) O4:(5.153, 5.044, 17.825) O5:(3.29, 5.714, 19.867) \\ O3:(3.56, 8.533, 20.206) O4:(5.153, 5.044, 17.825) O5:(3.29, 5.714, 19.867) \\ O3:(3.56, 8.533, 20.206) O4:(5.153, 5.044, 17.825) O5:(3.29, 5.714, 19.867) \\ O3:(3.56, 8.533, 20.206) O4:(5.153, 5.044, 17.825) O5:(3.29, 5.714, 19.867) \\ O3:(3.56, 8.533, 20.206) O4:(5.153, 5.044, 17.825) O5:(3.29, 5.714,$	9)
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	87)
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$\begin{array}{c c c c c c c c c c c c c c c c c c c $	")
$\begin{array}{c c} & & & & & \\ & & & & & \\ & & & & \\ & & & & & \\ & & & & & \\ & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & \\$	
$ \begin{array}{c} \text{O}1(2.917, 3.205, 18.489) 11: (0.814, 4.373, 16.057) O2: (1.055, 2.534, 16.48) 03: (3.56, 4.415, 15.416) Cu2: (3.922, 6.5, 18.164) 12: (3.05, 3.876, 20.257) \\ \text{O}2(4.00, 9.453, 0.0) \\ \text{O}3: (3.56, 8.533, 20.206) O4: (5.153, 5.044, 17.825) O5: (3.29, 5.714, 19.867) 03: (3.56, 8.533, 20.206) O4: (5.153, 5.044, 17.825) O5: (3.29, 5.714, 19.867) \\ \text{O}3: (3.56, 8.533, 20.206) O4: (5.153, 5.044, 17.825) O5: (3.29, 5.714, 19.867) \\ \text{O}3: (3.56, 8.533, 20.206) O4: (5.153, 5.044, 17.825) O5: (3.29, 5.714, 19.867) \\ \text{O}3: (3.56, 8.533, 20.206) O4: (5.153, 5.044, 17.825) O5: (3.29, 5.714, 19.867) \\ \text{O}3: (3.56, 8.533, 20.206) O4: (5.153, 5.044, 17.825) O5: (3.29, 5.714, 19.867) \\ \text{O}3: (3.56, 8.533, 20.206) O4: (5.153, 5.044, 17.825) O5: (3.29, 5.714, 19.867) \\ \text{O}3: (3.56, 8.533, 20.206) O4: (5.153, 5.044, 17.825) O5: (3.29, 5.714, 19.867) \\ \text{O}3: (3.56, 8.533, 20.206) O4: (5.153, 5.044, 17.825) O5: (3.29, 5.714, 19.867) \\ \text{O}3: (3.56, 8.533, 20.206) O4: (5.153, 5.044, 17.825) O5: (3.29, 5.714, 19.867) \\ \text{O}3: (3.56, 8.533, 20.206) O4: (5.153, 5.044, 17.825) O5: (3.29, 5.714, 19.867) \\ \text{O}3: (3.56, 8.533, 20.206) O4: (5.153, 5.044, 17.825) O5: (3.29, 5.714, 19.867) \\ \text{O}3: (3.56, 8.533, 20.206) O4: (5.153, 5.044, 17.825) O5: (3.29, 5.714, 19.867) \\ \text{O}3: (3.56, 8.533, 20.206) O4: (5.153, 5.044, 17.825) O5: (3.29, 5.714, 19.867) \\ \text{O}3: (3.56, 8.533, 20.206) O4: (5.153, 5.044, 17.825) O5: (3.29, 5.714, 19.867) \\ \text{O}3: (3.56, 8.533, 19.864) \\ \text{O}3: (3.56, 8.534) \\ \text{O}3: (3.56, 8.$	477)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	±()
$ \cup 1214 \cup 122 =   a2.(-0.0, 3.433, 0.0)   13.(2.303, 0.033, 20.200) \cup 4.(3.133, 3.044, 17.023) \cup 3.(3.23, 3.114, 13.00)$	) 7)
(2, 1, 2, 2, 3, 3, 3, 3, 3, 3, 3, 3, 3, 3, 3, 3, 3,	<i>()</i> (2)
$\begin{array}{c} \textbf{a5.} (0.0, 0.0, 0.0.014) \\ \textbf{b6.} (1.524, 3.534, 20.563) (J.(2.306, 0.944, 19.503) (S.(2.01, 1.639, 16.445) \\ \textbf{b6.} (1.524, 3.534, 20.563) (J.(0.100, 0.104, 544, 7.305, 16.46) \\ \textbf{b6.} (1.524, 3.534, 20.563) (J.(0.104, 544, 7.305, 16.46) \\ \textbf{b6.} (1.524, 3.534, 20.563) (J.(0.104, 544, 7.305, 16.46) \\ \textbf{b6.} (1.524, 3.534, 20.563) (J.(0.104, 544, 7.305, 16.46) \\ \textbf{b6.} (1.524, 3.534, 20.563) (J.(0.104, 544, 7.305, 16.46) \\ \textbf{b6.} (J.(0, 0.01, 104, 544, 7.305, 16.46) \\ \textbf{b6.} (J.(0, 0, 01, 104, 544, 7.305, 16.46) \\ \textbf{b6.} (J.(0, 0, 01, 104, 544, 7.305, 16.46) \\ \textbf{b6.} (J.(0, 0, 01, 104, 544, 7.305, 16.46) \\ \textbf{b6.} (J.(0, 0, 01, 104, 544, 7.305, 16.46) \\ \textbf{b6.} (J.(0, 0, 01, 104, 544, 7.305, 16.46) \\ \textbf{b6.} (J.(0, 01, 104, 7.305, 16.46) \\ \textbf{b6.} (J.(0, 01, 104, 7.305, 16.46) \\ \textbf{b6.} (J.(0, 01, 104, $	39)
(110, 037, 035, 10, 037, 10, 10, 10, 10, 10, 10, 10, 10, 10, 10	,2)
011.(0.504, 11.011) 012.(11.04, 0.115, 10.102)	
$W_{2}/(3.703, 1.670, 18, 886)$ Sh $^{+}/(4.984, 4.907, 15, 862)$ Sh $^{+}/(4.038, 2.051, 15, 8)$	800)
$(0.1)^{(2)}(61$	2)
$ \begin{array}{c} \text{Gr}(2.657, 0.647, 0.647, 0.657, 0.677, 0.466, 14.877, 0.667, 14.87, 0.466, 14.877, 0.667, 14.87, 0.667, 14.87, 0.667, 14.87, 0.667, 0.677, 0.466, 14.879, 0.667, 0.677, 0.466, 14.879, 0.667, 0.677, 0.466, 0.678, 0.467, 0.466, 0.468$	1)
$a_2(0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,$	
$O_{8}(3,202,1,714,20,712), O_{9}(2,992,0,071,23,103), O_{10}(22,69,2,916,23,00), O_{10}(22,69,2,916,23,00)$	(-)
O11-(0.168, 3.06, 19.559) O12-(0.106, 0.165, 19.542)	(00)
Br1:(0.214, 0.179, 7.273)	
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	(39)
$\begin{vmatrix} Ag_2Br_2Se_4 \\ a2:(0.0, 8.245, 0.0) \end{vmatrix} = \begin{vmatrix} a_2:(0.0, 8.245, 0.0) \\ Se_4:(2.011, 2.918, 8.124) \\ Ag_2:(3.05, 1.006) \\ Se_4:(2.011, 2.918, 8.124) \\ Ag_1:(3.825, 1.227, 9.09) \\ Se_4:(3.05, 1.006) \\ Se_4:(2.011, 2.918, 8.124) \\ Ag_1:(3.825, 1.227, 9.09) \\ Se_4:(3.05, 1.006) \\ Se_4:($	)5)
a3:(0.0, 0.0, 18.17) Ag2:(1.185, 6.768, 9.074)	- /
Cli:(4.998, 7.911, 7.51)	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	(27)
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$42)^{'}$
a3:(0.0, 0.0, 18.17) Ag2:(1.476, 6.914, 9.127)	/

	a1.(5 505 0 0 0 0)	Cl1:(0.223, 0.135, 7.583)
Ag-Cl-To-	22:(0.0, 8.61, 0.0)	Cl2:(3.02, 7.974, 10.587) Te1:(3.123, 5.195, 7.91) Te2:(0.325, 2.914, 10.26)
Ag2012164	a2.(-0.0, 0.01, 0.0) a3.(0.0, 0.0, 18, 17)	Te3:(4.793, 5.398, 10.212) $Te4:(1.996, 2.711, 7.958)$ $Ag1:(3.985, 1.234, 9.16)$
	a5.(0.0, 0.0, 10.17)	Ag2:(1.188,  6.874,  9.01)
	21:(5.612.0.0.0.0)	I1:(5.494, 8.389, 7.151)
Ag-L-To-	22:(0.0, 8.77, 0.0)	I2: $(2.689, 8.026, 11.019)$ Te1: $(3.023, 5.027, 7.957)$ Te2: $(0.217, 2.618, 10.213)$
Ag2121e4	a2.(-0.0, 0.17, 0.0)	Te3:(4.695, 5.106, 10.25) Te4:(1.889, 2.539, 7.92) Ag1:(3.864, 0.945, 9.088)
	as.(0.0, 0.0, 18.17)	Ag2:(1.058,  6.7,  9.082)
	0.1:(5.607.0.0.0.0)	Br1:(0.185, 0.035, 7.462)
An Dr. To	a1.(5.097, 0.0, 0.0)	Br2: $(3.036, 8.022, 10.709)$ Te1: $(3.093, 5.157, 7.912)$ Te2: $(0.245, 2.901, 10.26)$
Au <sub>2</sub> Dr <sub>2</sub> 1e <sub>4</sub>	a2.(-0.0, 8.709, 0.0)	Te3:(4.917, 5.44, 10.16) Te4:(2.069, 2.618, 8.013) Au1:(3.916, 1.363, 9.518)
	as:(0.0, 0.0, 18.17)	Au2:(1.067,  6.694,  8.652)
	s1:(5.674_0.0_0.0)	Cl1:(0.359, 0.238, 7.581)
Au Cl To	a1.(5.074, 0.0, 0.0)	Cl2:(3.197, 8.039, 10.586) Te1:(3.14, 5.234, 7.88) Te2:(0.303, 3.044, 10.286)
Au <sub>2</sub> O <sub>12</sub> 1e <sub>4</sub>	a2.(-0.0, 8.051, 0.0)	Te3:(4.963, 5.579, 10.127) Te4:(2.126, 2.7, 8.04) Au1:(3.962, 1.49, 9.606)
	as:(0.0, 0.0, 18.17)	Au2:(1.124,  6.787,  8.559)
	01.(5.607.00.00)	I1:(5.626, 8.61, 7.301)
An I To	a1:(5.097, 0.0, 0.0)	I2:(2.778, 8.163, 10.871) Te1:(3.039, 5.139, 7.962) Te2:(0.19, 2.74, 10.21)
Au <sub>2</sub> 1 <sub>2</sub> 1e <sub>4</sub>	$a_{2:}(-0.0, 8.894, 0.0)$	Te3:(4.872, 5.27, 10.212) Te4:(2.023, 2.609, 7.961) Au1:(3.937, 1.178, 9.196)
	a3:(0.0, 0.0, 18.17)	Au2:(1.088, 6.7, 8.975)
		Zn1:(2.676, 2.931, 19.329)
	a1.(4.101 0.002 0.0)	Zn2:(0.644, 6.384, 18.723) Te1:(2.746, 0.366, 20.034) Te2:(0.577, 3.82, 18.019)
7. T. (N.H.)	a1:(4.191, -0.003, 0.0)	N1: (2.575, 3.799, 21.298) N2: (0.748, 0.348, 16.755) H1: (2.757, 4.809, 21.199)
$2n_2 1e_2(N_2 \Pi_4)_2$	$a_{2:}(-0.002, 0.905, -0.0)$	H2:(0.566, 1.358, 16.854) N3:(3.555, 3.242, 22.205) N4:(3.956, 6.695, 15.849)
	as:(0.0, 0.0, 38.055)	H3:(3.952, 5.681, 16.037) H4:(1.605, 3.684, 21.641) H5:(1.717, 0.232, 16.412)
		H6:(3.558, 2.229, 22.016) H7:(3.23, 3.363, 23.17) H8:(0.092, -0.088, 14.883)
		Cl1:(-0.139, 0.227, 19.248)
	s1:(6.655.0.0.0.0)	Cl2:(5.155, 3.74, 20.094) Cl3:(5.531, 5.47, 16.618) Cl4:(6.139, 1.957, 22.725)
N. M. CI	a1:(0.055, 0.0, -0.0)	Nb1:(0.734, 6.812, 16.953) Nb2:(4.281, 3.298, 22.39) Cl5:(6.366, 1.714, 16.221)
Na2ND2CI122	$a_{2:}(0.0, 7.020, 0.0)$	Cl6:(5.304, 5.227, 23.122) Cl7:(1.726, 6.354, 14.94) Cl8:(3.289, 2.841, 24.403)
	as:(0.0, 0.0, 59.545)	Na1:(3.887, 6.237, 19.55) Na2:(1.128, 2.724, 19.793) Cl9:(1.893, 4.886, 17.959)
		Cl10: (3.122, 1.373, 21.384) Cl11: (2.641, 1.085, 17.713) Cl12: (2.374, 4.598, 21.63)
		K1:(0.018, 0.057, 19.6)
	a1:(3.78, -0.0, -0.0)	K2:(0.877, 2.949, 17.002) H1:(1.571, 3.64, 21.781) H2:(3.105, 0.749, 14.821)
$K_2(CHO_3)_2$	a2:(-0.0, 5.782, 0.0)	C1:(2.306, 2.853, 20.193) $C2:(2.369, 5.744, 16.408)$ $O1:(2.915, 3.129, 19.128)$
	a3:(0.0, 0.0, 36.6)	O2:(1.76, 0.238, 17.474) O3:(1.926, 1.748, 20.645) O4:(2.749, 4.639, 15.956)
		O5:(2.021, 3.991, 20.99) O6:(2.654, 1.1, 15.611)
		Te1:(0.002, 0.001, 19.069)
	21.(4.773, 0.0, 0.0)	Te2:(2.389, 1.691, 17.03) As1:(3.851, 4.821, 16.092) As2:(1.464, 3.186, 20.007)
AsaOaToa(OH)a	a1.(4.775, 0.0, 0.0) a2.(0.0, 6.314, 0.0)	O1:(3.27, 3.226, 15.83) $O2:(0.883, 4.78, 20.269)$ $O3:(4.598, 4.855, 17.683)$
A5208162(011)2	a2.(0.0, 0.014, 0.0)	O4: (2.211, 3.152, 18.416) O5: (1.79, 0.401, 18.561) O6: (4.176, 1.291, 17.538)
	45.(0.0, 0.0, 50.1)	O7:(2.583, 5.955, 15.887) O8:(0.196, 2.051, 20.212) O9:(0.298, 5.12, 14.893)
		O10: (2.685, 2.887, 21.206) H1: (1.184, 5.388, 15.314) H2: (3.571, 2.618, 20.786)
	a1:(6 747 -3 373 0 0)	Bi1:(6.747, 0.0, 16.57)
AgBiPaSec	a2:(0.0, 5.843, 0.0)	Se1:(2.096, 3.65, 14.987) $Se2:(-1.26, 2.203, 14.987)$ $Se3:(-0.836, 5.833, 14.986)$
118DH 2000	a2:(0.0, 0.0, 33, 563)	Se4:(4.301, 3.844, 18.573) $Se5:(4.551, 0.196, 18.573)$ $Se6:(1.268, 1.803, 18.573)$
	40.(0.0, 0.0, 00.000)	P1:(3.373, 1.948, 17.872) P2:(3.373, 1.948, 15.582) Ag1:(0.0, 3.895, 17.25)
	a1:(6.642 -3.321 -0.0)	Bi1:(6.643, -0.0, 17.107)
BiCuPoSee	a2:(-0.0, 5, 754, 0.0)	Se1:(2.104, 3.558, 18.604) $Se2:(5.351, 2.152, 18.605)$ $Se3:(2.51, 0.042, 18.605)$
210 al 2000	a3:(0,0,0,0,0,33,515)	Se4: $(1.145, 5.627, 14.98)$ Se5: $(0.978, 1.948, 14.98)$ Se6: $(-2.124, 3.932, 14.981)$
	401(010; 010; 001010)	P1:(0.0, 3.835, 15.716) P2:(0.0, 3.835, 18.012) Cu1:(3.321, 1.917, 15.413)
	a1:(6,167, -3.083, -0.0)	Cu1:(0.004, 0.003, 18.097)
CuInP <sub>2</sub> S <sub>6</sub>	a2:(0.0, 5.341, -0.0)	In1: $(3.087, 1.783, 16.396)$ P1: $(0.004, 3.564, 17.74)$ P2: $(0.003, 3.563, 15.483)$
2.00	a3:(0.0, 0.0, 33,465)	S1:(0.858, 5.352, 18.358) $S2:(1.126, 1.929, 18.358)$ $S3:(-1.972, 3.409, 18.359)$
	401(010; 010; 001100)	S4:(1.964, 3.629, 14.943) S5:(-0.92, 1.832, 14.944) S6:(-1.035, 5.229, 14.944)
	a1:(6.449, -3.224, 0.0)	Cu1:(-0.0, -0.0, 18.212)
CuInP <sub>2</sub> Sec	a2:(-0.0, 5 585 -0.0)	In1:(3.224, 1.861, 16.499) P1:(-0.0, 3.723, 17.891) P2:(-0.0, 3.723, 15.608)
2.000	a3:(0.0, 0.0, 33,465)	Sel: $(0.894, 5.661, 18.582)$ Se2: $(1.231, 1.98, 18.582)$ Se3: $(-2.126, 3.529, 18.582)$
		Se4:(2.114, 3.865, 15.012) Se5:(-0.934, 1.821, 15.012) Se6:(-1.181, 5.483, 15.012)
	a1:(4.097, -2.048, 0.0)	In1:(1.882, 1.162, 20.924)
$In_2Se_3$	a2:(0.0, 3.546, -0.0)	Se1: $(3.931, -0.019, 22.242)$ In2: $(-0.166, 2.345, 16.701)$ Se2: $(-0.166, 2.344, 19.244)$
	a3:(0.0, 0.0, 36.367)	Se3:(3.931, -0.019, 15.456)

$CF_2Si$	$\begin{array}{c} a1:(3.161,-1.58,0.0)\\ a2:(0.0,2.737,0.0)\\ a3:(0.0,0.0,18.625) \end{array}$	Si1:(0.0, 0.0, 9.117) C1:(-0.0, 1.825, 9.689) F1:(0.0, 0.0, 7.5) F2:(-0.0, 1.825, 11.126)
InP	$\begin{array}{c} a1:(4.215,\ -2.108,\ 0.0)\\ a2:(0.0,\ 3.65,\ 0.0)\\ a3:(0.0,\ 0.0,\ 15.495) \end{array}$	$ \begin{array}{c} {\rm In1:}(0.0,2.434,7.504)\\ {\rm P1:}(2.108,1.217,7.991) \end{array} $
$As_4O_6$	$\begin{array}{c} a1{:}(4.651,-0.375,-0.0)\\ a2{:}(0.032,5.625,-0.0)\\ a3{:}(0.0,0.0,33.864)\end{array}$	$\begin{array}{c} \qquad \qquad$
$\mathrm{Zn_2O_6Se_2(H_2O)_2}$	a1:(4.867, -0.222, -0.0) a2:(-0.115, 5.768, 0.0) a3:(0.0, 0.0, 33.865)	$\begin{array}{c} {\rm Zn1:} (1.591,4.924,16.668)\\ {\rm Zn2:} (4.136,1.983,17.197){\rm Se1:} (2.068,2.077,14.971){\rm Se2:} (4.39,4.904,18.894)\\ {\rm O1:} (2.79,0.841,16.006){\rm O2:} (0.246,3.783,17.859){\rm O3:} (0.424,0.602,18.02)\\ {\rm O4:} (2.746,3.429,15.845){\rm O5:} (2.743,4.87,18.482){\rm O6:} (0.42,2.044,15.383)\\ {\rm O7:} (2.708,2.084,18.782){\rm H1:} (1.939,1.48,18.613){\rm H2:} (2.342,3.001,18.748)\\ {\rm O8:} (0.164,5.026,15.083){\rm H3:} (4.262,4.307,15.252){\rm H4:} (0.02,0.175,15.117)\\ \end{array}$
$As_2O_6Sb_2$	$\begin{array}{c} a1{:}(4.657,\ -0.46,\ -0.0)\\ a2{:}(0.021,\ 5.638,\ -0.0)\\ a3{:}(0.0,\ 0.0,\ 34.073) \end{array}$	$\begin{array}{c} {\rm As1:} (0.016,\ 0.04,\ 19.117)\\ {\rm As2:} (2.115,\ 2.87,\ 14.956)\ {\rm Sb1:} (2.252,\ 2.362,\ 18.39)\ {\rm Sb2:} (-0.307,\ 5.17,\ 15.683)\\ {\rm O1:} (1.762,\ 0.526,\ 19.047)\ {\rm O2:} (3.861,\ 3.355,\ 15.026)\ {\rm O3:} (2.011,\ 1.862,\ 16.47)\\ {\rm O4:} (4.109,\ 4.692,\ 17.602)\ {\rm O5:} (4.162,\ 1.716,\ 18.529)\ {\rm O6:} (1.603,\ 4.525,\ 15.544) \end{array}$
$\mathrm{Sn_2H_2O_6P_2}$	$\begin{array}{l} a1{:}(4.776,-1.264,-0.0)\\ a2{:}(-0.153,6.599,0.0)\\ a3{:}(0.0,0.0,34.237) \end{array}$	$\begin{array}{c} {\rm Sn1:}(-0.113,\ 0.137,\ 18.482)\\ {\rm Sn2:}(-0.745,\ 3.437,\ 15.755)\ {\rm P1:}(2.262,\ 2.442,\ 18.566)\ {\rm P2:}(1.63,\ 5.741,\ 15.672)\\ {\rm O1:}(3.108,\ 1.322,\ 19.221)\ {\rm O2:}(2.476,\ 4.621,\ 15.016)\ {\rm O3:}(3.052,\ 3.415,\ 17.653)\\ {\rm O4:}(3.684,\ 0.116,\ 16.584)\ {\rm O5:}(1.003,\ 1.883,\ 17.831)\ {\rm O6:}(0.371,\ 5.182,\ 16.406)\\ {\rm H1:}(1.81,\ 3.251,\ 19.633)\ {\rm H2:}(2.442,\ -0.048,\ 14.604)\end{array}$
$Pb_4O_4$	$\begin{array}{c} a1{:}(5.724,\ 0.0,\ 0.0)\\ a2{:}(0.0,\ 5.24,\ 0.0)\\ a3{:}(0.0,\ 0.0,\ 32.37) \end{array}$	$\begin{array}{c} {\rm Pb1:}(-0.063,-0.175,14.858)\\ {\rm Pb2:}(0.222,2.445,17.511){\rm Pb3:}(3.084,2.445,14.859){\rm Pb4:}(2.799,-0.175,17.512)\\ {\rm O1:}(5.213,1.966,15.45){\rm O2:}(0.671,4.586,16.92){\rm O3:}(3.533,4.586,15.45)\\ {\rm O4:}(2.351,1.966,16.92)\end{array}$
$\mathrm{Hf}_{3}\mathrm{ZrS}_{8}$	$\begin{array}{c} a1{:}(7.097,\ 0.0,\ 0.0)\\ a2{:}(0.0,\ 6.153,\ 0.0)\\ a3{:}(0.0,\ 0.0,\ 18.249) \end{array}$	$\begin{array}{c} & Zr1:(0.006,\ 0.009,\ 8.841)\\ Hf1:(3.554,\ 0.006,\ 9.221)\ Hf2:(1.781,\ 3.082,\ 9.172)\ Hf3:(5.327,\ 3.082,\ 9.174)\\ S1:(0.005,\ 2.147,\ 7.5)\ S2:(1.735,\ 5.149,\ 10.651)\ S3:(0.006,\ 1.998,\ 10.633)\\ S4:(1.85,\ 5.1,\ 7.517)\ S5:(3.554,\ 2.03,\ 7.615)\ S6:(5.373,\ 5.149,\ 10.652)\\ S7:(3.554,\ 2.08,\ 10.749)\ S8:(5.258,\ 5.1,\ 7.518)\end{array}$
$\mathrm{Hf_3ZrSe_8}$	a1:(7.365, 0.0, 0.0) a2:(0.0, 6.379, 0.0) a3:(0.0, 0.0, 18.428)	$\begin{array}{c} {\rm Zr1:}(0.004,\ 0.009,\ 9.029)\\ {\rm Hf1:}(3.687,\ 0.005,\ 9.278)\ {\rm Hf2:}(1.847,\ 3.196,\ 9.243)\ {\rm Hf3:}(5.526,\ 3.196,\ 9.243)\\ {\rm Se1:}(0.004,\ 2.196,\ 7.492)\ {\rm Se2:}(1.817,\ 5.332,\ 10.871)\ {\rm Se3:}(0.004,\ 2.1,\ 10.858)\\ {\rm Se4:}(1.895,\ 5.298,\ 7.503)\ {\rm Se5:}(3.687,\ 2.114,\ 7.568)\ {\rm Se6:}(5.556,\ 5.332,\ 10.871)\\ {\rm Se7:}(3.687,\ 2.147,\ 10.931)\ {\rm Se8:}(5.478,\ 5.298,\ 7.503)\\ \end{array}$
$\mathrm{Hf_2Zr_2S_8}$	a1:(7.105, 0.0, 0.0) a2:(0.0, 6.169, 0.0) a3:(0.0, 0.0, 18.28)	$\begin{array}{c} {\rm Zr1:}(0.008,\ 0.012,\ 8.896)\\ {\rm Zr2:}(3.56,\ 0.012,\ 9.386)\ {\rm Hf1:}(1.784,\ 3.094,\ 9.136)\ {\rm Hf2:}(5.337,\ 3.094,\ 9.144)\\ {\rm S1:}(0.007,\ 2.142,\ 7.5)\ {\rm S2:}(1.709,\ 5.132,\ 10.706)\ {\rm S3:}(0.009,\ 2.014,\ 10.632)\\ {\rm S4:}(1.859,\ 5.135,\ 7.573)\ {\rm S5:}(3.562,\ 2.014,\ 7.649)\ {\rm S6:}(5.412,\ 5.134,\ 10.709)\\ {\rm S7:}(3.559,\ 2.143,\ 10.78)\ {\rm S8:}(5.261,\ 5.133,\ 7.575)\end{array}$
$\mathrm{Hf_{2}Zr_{2}Se_{8}}$	$\begin{array}{c} a1{:}(7.374,\ 0.0,\ 0.0)\\ a2{:}(0.0,\ 6.395,\ 0.0)\\ a3{:}(0.0,\ 0.0,\ 18.465) \end{array}$	$\begin{array}{c} {\rm Zr1:}(0.006,\ 0.007,\ 9.063)\\ {\rm Zr2:}(3.693,\ 0.007,\ 9.405)\ {\rm Hf1:}(1.849,\ 3.206,\ 9.233)\ {\rm Hf2:}(5.536,\ 3.206,\ 9.234)\\ {\rm Se1:}(0.006,\ 2.196,\ 7.501)\ {\rm Se2:}(1.794,\ 5.321,\ 10.919)\ {\rm Se3:}(0.006,\ 2.107,\ 10.864)\\ {\rm Se4:}(1.904,\ 5.322,\ 7.549)\ {\rm Se5:}(3.693,\ 2.107,\ 7.603)\ {\rm Se6:}(5.591,\ 5.321,\ 10.919)\\ {\rm Se7:}(3.693,\ 2.196,\ 10.966)\ {\rm Se8:}(5.481,\ 5.322,\ 7.549)\end{array}$
$Mo_2Br_4O_4$	$\begin{array}{c} a1:(3.984,-0.0,-0.0)\\ a2:(-0.0,7.767,0.0)\\ a3:(0.0,0.0,34.767) \end{array}$	$\begin{array}{c} {\rm Mo1:}(2.27,\ 3.704,\ 17.386)\\ {\rm O1:}(0.0,\ 3.858,\ 17.386)\ {\rm O2:}(2.053,\ 1.976,\ 17.386)\ {\rm Mo2:}(1.753,\ 7.588,\ 17.386)\\ {\rm O3:}(1.97,\ 5.86,\ 17.386)\ {\rm Br1:}(2.128,\ 0.164,\ 14.969)\ {\rm Br2:}(1.895,\ 4.048,\ 14.969)\\ {\rm Br3:}(2.128,\ 0.164,\ 19.802)\ {\rm Br4:}(1.895,\ 4.048,\ 19.802)\ {\rm O4:}(0.039,\ -0.026,\ 17.386)\\ \end{array}$
W <sub>2</sub> Cl <sub>4</sub> O <sub>4</sub>	$ \begin{array}{c} a1:(3.92,\ 0.0,\ -0.0)\\ a2:(0.0,\ 7.736,\ -0.0)\\ a3:(0.0,\ 0.0,\ 34.434) \end{array} $	$\begin{array}{c} W1: (0.172,\ 3.602,\ 17.217)\\ O1: (-0.009,\ 1.834,\ 17.217)\ O2: (1.929,\ 3.735,\ 17.217)\ W2: (3.678,\ 7.47,\ 17.217)\\ O3: (1.92,\ -0.133,\ 17.217)\ O4: (3.859,\ 5.702,\ 17.217)\ C11: (3.801,\ 3.874,\ 19.491)\\ C12: (3.801,\ 3.874,\ 14.943)\ C13: (0.048,\ 0.006,\ 14.943)\ C14: (0.048,\ 0.006,\ 19.491) \end{array}$

$\mathrm{Sr}_{2}\mathrm{H}_{8}\mathrm{O}_{6}$	$\begin{array}{l} a1: (3.621, \ -0.0, \ -0.0)\\ a2: (0.0, \ 6.923, \ 0.0)\\ a3: (0.0, \ 0.0, \ 35.702) \end{array}$	$\begin{array}{c} {\rm Sr1:}(-0.0,\ -0.141,\ 18.493)\\ {\rm Sr2:}(-0.0,\ 3.32,\ 17.209)\ {\rm O1:}(-0.0,\ 0.662,\ 15.971)\ {\rm O2:}(-0.0,\ 4.123,\ 19.731)\\ {\rm O3:}(1.811,\ 6.018,\ 20.201)\ {\rm O4:}(1.811,\ 2.57,\ 15.501)\ {\rm O5:}(1.811,\ 5.261,\ 17.305)\\ {\rm O6:}(1.811,\ 1.8,\ 18.397)\ {\rm H1:}(0.775,\ 1.224,\ 15.654)\ {\rm H2:}(2.846,\ 1.224,\ 15.654)\\ {\rm H3:}(2.846,\ 4.686,\ 20.048)\ {\rm H4:}(0.775,\ 4.686,\ 20.048)\ {\rm H5:}(1.811,\ 2.176,\ 19.297)\\ {\rm H6:}(1.811,\ 2.84,\ 14.573)\ {\rm H7:}(1.811,\ 5.637,\ 16.405)\ {\rm H8:}(1.811,\ 2.176,\ 19.297)\\ \end{array}$
$\mathrm{Cu_2Hg_2Cl_2Se_2}$	$\begin{array}{c} a1{:}(4.158,0.0,0.0)\\ a2{:}(-0.0,7.047,0.0)\\ a3{:}(0.0,0.0,39.524) \end{array}$	$\begin{array}{c} {\rm Hg1:}(2.079,\ 7.681,\ 20.268)\\ {\rm Hg2:}(2.079,\ 4.157,\ 19.255)\ {\rm Se1:}(2.079,\ 1.916,\ 17.963)\ {\rm Se2:}(2.079,\ 5.44,\ 21.561)\\ {\rm Cu1:}(0.0,\ 0.745,\ 18.071)\ {\rm Cu2:}(0.0,\ 4.268,\ 21.453)\ {\rm Cl1:}(0.0,\ 2.036,\ 21.744)\\ {\rm Cl2:}(0.0,\ -1.487,\ 17.78)\end{array}$
$Nb_2Br_4O_2$	$\begin{array}{c} a1{:}(3.944,0.0,0.0)\\ a2{:}(0.0,7.07,0.0)\\ a3{:}(0.0,0.0,34.045) \end{array}$	$\begin{array}{c} {\rm Nb1:}(2.147,\ 3.957,\ 17.023)\\ {\rm Br1:}(1.911,\ 1.941,\ 15.25)\ {\rm Br2:}(1.948,\ 5.476,\ 14.923)\ {\rm Nb2:}(2.147,\ 6.996,\ 17.023)\\ {\rm Br3:}(1.911,\ 1.941,\ 18.795)\ {\rm Br4:}(1.948,\ 5.476,\ 19.123)\ {\rm O1:}(-0.019,\ 3.918,\ 17.023)\\ {\rm O2:}(-0.019,\ -0.035,\ 17.023)\end{array}$
$\mathrm{Nb_2I_4O_2}$	$\begin{array}{c} a1:(3.969,\ 0.0,\ -0.0)\\ a2:(0.0,\ 7.581,\ -0.0)\\ a3:(0.0,\ 0.0,\ 34.533) \end{array}$	$\begin{array}{c} {\rm Nb1:}(-0.051,\ 4.406,\ 17.266)\\ {\rm O1:}(2.129,\ 4.377,\ 17.266)\ 11:(0.176,\ 2.196,\ 15.387)\ 12:(0.146,\ 5.987,\ 14.968)\\ {\rm Nb2:}(-0.051,\ -0.013,\ 17.266)\ {\rm O2:}(2.129,\ 7.596,\ 17.266)\ 13:(0.176,\ 2.196,\ 19.146)\\ {\rm I4:}(0.146,\ 5.987,\ 19.565)\end{array}$
$Nb_2Cl_4O_2$	$\begin{array}{c} a1{:}(3.942,\ 0.0,\ -0.0)\\ a2{:}(0.0,\ 6.739,\ -0.0)\\ a3{:}(0.0,\ 0.0,\ 34.045)\end{array}$	$\begin{array}{c} {\rm Nb1:}(2.147,\ 3.74,\ 17.023)\\ {\rm Cl1:}(1.908,\ 1.85,\ 15.35)\ {\rm Cl2:}(1.949,\ 5.22,\ 15.079)\ {\rm Nb2:}(2.147,\ 6.7,\ 17.023)\\ {\rm Cl3:}(1.908,\ 1.85,\ 18.695)\ {\rm Cl4:}(1.949,\ 5.22,\ 18.966)\ {\rm O1:}(-0.021,\ 3.693,\ 17.023)\\ {\rm O2:}(-0.021,\ 0.008,\ 17.023)\end{array}$
$ m As_4S_6$	$\begin{array}{c} a1{:}(4.618,-0.075,0.0)\\ a2{:}(0.027,11.354,0.0)\\ a3{:}(0.0,0.0,32.82) \end{array}$	$ \begin{array}{c} {\rm As1:}(4.664,-0.036,15.697)\\ {\rm As2:}(2.317,5.628,17.123){\rm As3:}(2.294,8.936,17.124){\rm As4:}(0.023,3.245,15.696)\\ {\rm S1:}(1.56,9.736,15.115){\rm S2:}(3.907,4.072,17.705){\rm S3:}(3.864,10.511,17.707)\\ {\rm S4:}(1.593,4.821,15.113){\rm S5:}(1.33,1.6,16.647){\rm S6:}(3.601,7.291,16.173) \end{array} $
$As_4Se_6$	$\begin{array}{c} a1{:}(4.531,-0.052,0.0)\\ a2{:}(0.018,12.079,0.0)\\ a3{:}(0.0,0.0,33.177) \end{array}$	$\begin{array}{c} \qquad \qquad$
$\mathrm{Cd}_2\mathrm{O}_6\mathrm{Se}_2(\mathrm{H}_2\mathrm{O})_2$	$\begin{array}{l} a1:(5.042,-0.0,0.0)\\ a2:(-0.0,6.049,-0.0)\\ a3:(0.0,0.0,34.123)\end{array}$	$\begin{array}{c} {\rm Cd1:}(2.232,5.365,16.734)\\ {\rm Cd2:}(4.753,2.341,17.39){\rm Se1:}(2.69,2.341,14.959){\rm Se2:}(0.169,5.365,19.165)\\ {\rm O1:}(3.609,5.365,18.649){\rm O2:}(1.088,2.341,15.474){\rm O3:}(3.45,1.033,15.865)\\ {\rm O4:}(0.929,0.625,18.259){\rm O5:}(3.45,3.649,15.865){\rm O6:}(0.929,4.057,18.259)\\ {\rm O7:}(0.561,5.365,15.088){\rm O8:}(3.082,2.341,19.036){\rm H1:}(2.482,3.119,18.918)\\ {\rm H2:}(2.482,1.563,18.918){\rm H3:}(-0.039,4.588,15.206){\rm H4:}(-0.039,0.094,15.206)\\ \end{array}$
$\rm Ga_2 In_2 S_6$	a1:(3.813, 0.0, 0.0) a2:(-0.0, 6.252, 0.0) a3:(0.0, 0.0, 37.098)	$\begin{array}{c} {\rm In1:}(0.0,0.007,16.914)\\ {\rm In2:}(1.907,3.133,20.184)\ {\rm Ga1:}(1.907,3.484,15.924)\ {\rm Ga2:}(0.0,0.358,21.174)\\ {\rm S1:}(1.907,4.659,17.975)\ {\rm S2:}(0.0,1.533,19.122)\ {\rm S3:}(0.0,4.427,14.934)\\ {\rm S4:}(1.907,1.301,22.164)\ {\rm S5:}(0.0,4.342,21.42)\ {\rm S6:}(1.907,1.216,15.678)\end{array}$
$Ga_2Cl_2Te_2$	$\begin{array}{c} a1:(4.165,-0.0,-0.0)\\ a2:(0.0,5.943,-0.0)\\ a3:(0.0,0.0,35.15) \end{array}$	$\begin{array}{c} {\rm Ga1:}(-0.0,\ 0.014,\ 18.504)\\ {\rm Ga2:}(2.083,\ 2.985,\ 16.646)\ {\rm Cl1:}(-0.0,\ 1.411,\ 20.23)\ {\rm Cl2:}(2.083,\ 4.382,\ 14.92)\\ {\rm Te1:}(-0.0,\ 1.35,\ 16.202)\ {\rm Te2:}(2.083,\ 4.322,\ 18.948) \end{array}$
$\mathrm{Cu}_2\mathrm{C}_2\mathrm{Cl}_2\mathrm{O}_2$	$\begin{array}{c} a1:(3.702,-0.0,0.0)\\ a2:(0.0,5.042,-0.0)\\ a3:(0.0,0.0,37.181) \end{array}$	$\begin{array}{c} \text{Cu1:}(-0.0,4.034,17.387)\\ \text{Cl1:}(1.851,2.548,17.662) \ \text{Cu2:}(1.851,1.513,19.794) \ \text{Cl2:}(-0.0,5.069,19.519)\\ \text{C1:}(1.851,2.459,21.348) \ \text{O1:}(1.851,3.014,22.352) \ \text{C2:}(0.0,-0.061,15.832)\\ \text{O2:}(0.0,0.493,14.829)\end{array}$
$\alpha$ -Ge <sub>2</sub> Se <sub>2</sub>	$\begin{array}{c} a1{:}(4.274,\ 0.0,\ -0.0)\\ a2{:}(0.0,\ 3.973,\ -0.0)\\ a3{:}(0.0,\ 0.0,\ 17.11) \end{array}$	$\begin{array}{c} {\rm Se1:}(0.231,-0.0,7.252)\\ {\rm Se2:}(2.368,1.986,9.857) {\rm Ge1:}(0.597,-0.0,9.765) {\rm Ge2:}(2.734,1.986,7.344) \end{array}$
$\alpha$ -Ge <sub>2</sub> S <sub>2</sub>	$\begin{array}{c} a1:(4.482,\ 0.0,\ -0.0)\\ a2:(0.0,\ 3.652,\ 0.0)\\ a3:(0.0,\ 0.0,\ 17.11) \end{array}$	$\begin{array}{c} {\rm S1:}(0.136,-0.0,7.487)\\ {\rm S2:}(2.377,1.826,9.623) {\rm Ge1:}(0.731,-0.0,9.837) {\rm Ge2:}(2.972,1.826,7.273) \end{array}$
$\alpha$ -Ge <sub>2</sub> Te <sub>2</sub>	$\begin{array}{c} \text{a1:}(4.376, -0.0, -0.0) \\ \text{a2:}(-0.0, 4.23, 0.0) \\ \text{a3:}(0.0, 0.0, 17.11) \end{array}$	$\begin{array}{c} {\rm Te1:}(0.29,\ -0.0,\ 7.037)\\ {\rm Te2:}(2.478,\ 2.115,\ 10.073)\ {\rm Ge1:}(0.561,\ -0.0,\ 9.756)\ {\rm Ge2:}(2.749,\ 2.115,\ 7.354) \end{array}$
$\alpha$ -Sn <sub>2</sub> O <sub>2</sub>	$\begin{array}{c} a1{:}(5.025,\ 0.0,\ 0.0)\\ a2{:}(0.0,\ 3.339,\ 0.0)\\ a3{:}(0.0,\ 0.0,\ 32.15)\end{array}$	$\begin{array}{c} {\rm Sn1:}(0.2,\ 0.0,\ 17.26)\\ {\rm O1:}(1.059,\ 1.67,\ 16.212) \ {\rm Sn2:}(2.712,\ 1.67,\ 14.89) \ {\rm O2:}(3.572,\ 0.0,\ 15.938) \end{array}$
$\alpha$ -Sn <sub>2</sub> Se <sub>2</sub>	a1:(4.411, -0.0, 0.0) a2:(-0.0, 4.285, 0.0) a3:(0.0, 0.0, 17.11)	Se1:(0.299, -0.0, 7.225) Se2:(2.504, 2.142, 9.884) Sn1:(0.549, -0.0, 9.935) Sn2:(2.755, 2.142, 7.175)

$\alpha$ -Sn <sub>2</sub> Te <sub>2</sub>	$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	$\begin{array}{c} {\rm Te1:}(0.372,-0.0,6.977)\\ {\rm Te2:}(2.663,2.273,10.133){\rm Sn1:}(0.507,-0.0,9.895){\rm Sn2:}(2.797,2.273,7.215) \end{array}$
$\alpha$ -Sn <sub>2</sub> S <sub>2</sub>	$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	$\begin{array}{c} {\rm S1:}(0.236,-0.0,7.421)\\ {\rm S2:}(2.399,2.032,9.689){\rm Sn1:}(0.598,-0.0,9.986){\rm Sn2:}(2.761,2.032,7.124) \end{array}$
$\beta$ -Sn <sub>2</sub> Se <sub>2</sub>	$\begin{array}{c} a1:(6.181,0.0,0.0)\\ a2:(0.0,3.909,0.0)\\ a3:(0.0,0.0,18.0) \end{array}$	$\begin{array}{c} {\rm Sn1:}(-0.083,-0.0,7.98)\\ {\rm Sn2:}(3.008,1.954,10.02){\rm Se1:}(0.083,1.954,9.879){\rm Se2:}(3.173,-0.0,8.121) \end{array}$
$\beta$ -Sn <sub>2</sub> S <sub>2</sub>	$\begin{array}{c} a1:(5.856,-0.0,0.0)\\ a2:(-0.0,3.787,-0.0)\\ a3:(0.0,0.0,18.0) \end{array}$	$\begin{array}{c} {\rm Sn1:(-0.103,\ -0.0,\ 7.891)} \\ {\rm Sn2:(2.825,\ 1.894,\ 10.109)\ S1:(0.103,\ 1.894,\ 9.67)\ S2:(3.03,\ 0.0,\ 8.33)} \end{array}$
$P_2Sb_2$	$\begin{array}{c} a1:(5.949,\ 0.0,\ 0.0)\\ a2:(0.0,\ 3.721,\ -0.0)\\ a3:(0.0,\ 0.0,\ 18.0)\end{array}$	Sb1:(-0.165, -0.0, 7.988) Sb2:(2.809, 1.861, 10.012) P1:(0.165, 1.861, 9.726) P2:(3.14, 0.0, 8.274)
$As_2Sb_2$	$\begin{array}{c} a1:(6.234,\ 0.0,\ 0.0)\\ a2:(-0.0,\ 3.841,\ -0.0)\\ a3:(0.0,\ 0.0,\ 18.0)\end{array}$	Sb1:(-0.174, -0.0, 8.103) Sb2:(2.943, 1.92, 9.897) As1:(0.174, 1.92, 9.935) As2:(3.291, -0.0, 8.065)
$\beta$ -Ge <sub>2</sub> S <sub>2</sub>	$\begin{array}{c} a1:(5.679, -0.0, -0.0)\\ a2:(-0.0, 3.499, -0.0)\\ a3:(0.0, 0.0, 18.0) \end{array}$	$\begin{array}{c} {\rm Ge1:(-0.154,\ -0.0,\ 8.074)}\\ {\rm Ge2:(2.685,\ 1.75,\ 9.926)\ S1:(0.154,\ 1.75,\ 9.718)\ S2:(2.994,\ 0.0,\ 8.282)} \end{array}$
$\beta$ -Ge <sub>2</sub> Se <sub>2</sub>	$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	$ \begin{array}{c} {\rm Ge1:(-0.11,\ -0.0,\ 8.182)} \\ {\rm Ge2:(2.837,\ 1.83,\ 9.818) \ Se1:(0.11,\ 1.83,\ 9.937) \ Se2:(3.057,\ -0.0,\ 8.063)} \end{array} $

# 9.2 Paper II: Recent Progress of the Computational Materials Database (C2DB)

M. N. GJERDING A. TAGIZADEH A. RASMUSSEN S. ALI F. BERTOLDO T. DEILMANN N. R. KNØSGAARD M. KRUSE A. H. LARSEN S. MANTI T. G. PEDERSEN U. PETRALANDA T. SKOVHUS M. K. SVENDSEN J. J. MORTENSEN T. OLSEN K. S. THYGESEN

2D Mater. 2021, 8, 044002.

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# Recent progress of the Computational 2D Materials Database (C2DB)

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RECEIVED 18 January 2021

REVISED 31 May 2021

ACCEPTED FOR PUBLICATION 30 June 2021

PUBLISHED 15 July 2021

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Recent progress of the Computational 2D Materials Database (C2DB)

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Keywords: 2D materials, high-throughput, ab-initio, database, density functional theory

#### Abstract

The Computational 2D Materials Database (C2DB) is a highly curated open database organising a wealth of computed properties for more than 4000 atomically thin two-dimensional (2D) materials. Here we report on new materials and properties that were added to the database since its first release in 2018. The set of new materials comprise several hundred monolayers exfoliated from experimentally known layered bulk materials, (homo)bilayers in various stacking configurations, native point defects in semiconducting monolayers, and chalcogen/halogen Janus monolayers. The new properties include exfoliation energies, Bader charges, spontaneous polarisations, Born charges, infrared polarisabilities, piezoelectric tensors, band topology invariants, exchange couplings, Raman spectra and second harmonic generation spectra. We also describe refinements of the employed material classification schemes, upgrades of the computational methodologies used for property evaluations, as well as significant enhancements of the data documentation and provenance. Finally, we explore the performance of Gaussian process-based regression for efficient prediction of mechanical and electronic materials properties. The combination of open access, detailed documentation, and extremely rich materials property data sets make the C2DB a unique resource that will advance the science of atomically thin materials.

#### 1. Introduction

The discovery of new materials, or new properties of known materials, to meet a specific industrial or scientific requirement, is an exciting intellectual challenge of the utmost importance for our environment and economy. For example, the successful transition to a society based on sustainable energy sources and the realisation of quantum technologies (e.g. quantum computers and quantum communication) depend critically on new materials with novel functionalities. First-principles quantum mechanical calculations, e.g. based on density functional theory (DFT) [1], can predict the properties of materials with high accuracy even before they are made in the lab. They provide insight into mechanisms at the most fundamental (atomic and electronic) level and can pinpoint and calculate key properties that determine the performance of the material at the macroscopic level. Powered by high-performance computers, atomistic quantum calculations in combination with data science approaches, have the potential to revolutionise the way we discover and develop new materials.

Atomically thin, two-dimensional (2D) crystals represent a fascinating class of materials with exciting perspectives for both fundamental science and technology [2–5]. The family of 2D materials has been growing steadily over the past decade and counts about a hundred materials that have been realised
in single-layer or few-layer form [6-10]. While some of these materials, including graphene, hexagonal boron nitride (hBN), and transition metal dichalcogenides (TMDCs), have been extensively studied, the majority have only been scarcely characterised and remain poorly understood. Computational studies indicate that around 1000 already known layered crystals have sufficiently weak interlayer (IL) bonding to allow the individual layers to be mechanically exfoliated [11, 12]. Supposedly, even more 2D materials could be realised beyond this set of already known crystals. Adding to this the possibility of stacking individual 2D layers (of the same or different kinds) into ultrathin van der Waals (vdW) crystals [13], and tuning the properties of such structures by varying the relative twist angle between adjacent layers [14, 15] or intercalating atoms into the vdW gap [16, 17], it is clear that the prospects of tailor made 2D materials are simply immense. To support experimental efforts and navigate the vast 2D materials space, first-principles calculations play a pivotal role. In particular, FAIR<sup>5</sup> [18] databases populated by high-throughput calculations can provide a convenient overview of known materials and point to new promising materials with desired (predicted) properties. Such databases are also a fundamental requirement for the successful introduction and deployment of artificial intelligence in materials science.

Many of the unique properties exhibited by 2D materials have their origin in quantum confinement and reduced dielectric screening. These effects tend to enhance many-body interactions and lead to profoundly new phenomena such as strongly bound excitons [19–21] with nonhydrogenic Rydberg series [22-24], phonons and plasmons with anomalous dispersion relations [25, 26], large dielectric band structure renormalisations [27, 28], unconventional Mott insulating and superconducting phases [14, 15], and high-temperature exciton condensates [29]. Recently, it has become clear that long range magnetic order can persist [30, 31] and (in-plane) ferroelectricity even be enhanced [32], in the single layer limit. In addition, first-principles studies of 2D crystals have revealed rich and abundant topological phases [33, 34]. The peculiar physics ruling the world of 2D materials entails that many of the conventional theories and concepts developed for bulk crystals break down or require special treatments when applied to 2D materials [26, 35, 36]. This means that computational studies must be performed with extra care, which in turn calls for well-organised and welldocumented 2D property data sets that can form the basis for the development, benchmarking, and consolidation of physical theories and numerical implementations.

The Computational 2D Materials Database (C2DB) [6, 37] is a highly curated and fully open database containing elementary physical properties of around 4000 2D monolayer crystals. The data has been generated by automatic high-throughput calculations at the level of DFT and many-body perturbation theory as implemented in the GPAW [38, 39] electronic structure code. The computational workflow is constructed using the atomic simulation recipes (ASR) [40]—a recently developed Python framework for high-throughput materials modelling building on the atomic simulation environment (ASE) [41]—and managed/executed using the MyQueue task scheduler [42].

The C2DB differentiates itself from existing computational databases of bulk [43–45] and lowdimensional [11, 12, 46–50] materials, by the large number of physical properties available, see table 1. The use of beyond-DFT theories for excited state properties (GW band structures and Bethe–Salpeter equation (BSE) absorption for selected materials) and Berry-phase techniques for band topology and polarisation quantities (spontaneous polarisation, Born charges, piezoelectric tensors), are other unique features of the database.

The C2DB can be downloaded in its entirety or browsed and searched online. As a new feature, all data entries presented on the website are accompanied by a clickable help icon that presents a scientific documentation ('what does this piece of data describe?') and technical documentation ('how was this piece of data computed?'). This development enhances the usability of the database and improves the reproducibility and provenance of the data contained in C2DB. As another novelty it is possible to download all property data pertaining to a specific material or a specific type of property, e.g. the band gap, for all materials thus significantly improving data accessibility.

In this paper, we report on the significant C2DB developments that have taken place during the past two years. These developments can be roughly divided into four categories: (1) General updates of the workflow used to select, classify, and stability assess the materials. (2) Computational improvements for properties already described in the 2018 paper. (3) New properties. (4) New materials. The developments, described in four separate sections, cover both original work and review of previously published work. In addition, we have included some outlook discussions of ongoing work. In the last section we illustrate an application of statistical learning to predict properties directly from the atomic structure.

# 2. Selection, classification, and stability

Figure 1 illustrates the workflow behind the C2DB. In this section we describe the first part of the workflow

<sup>&</sup>lt;sup>5</sup> FAIR data are data which meet principles of findability, accessibility, interoperability, and reusability.

Table 1. Properties calculated by the C2DB monolayer workflow. The computational method and the criteria used to decide whether the property should be evaluation for a given material is also shown. A '\*' indicates that spin–orbit coupling (SOC) is included. All calculations are performed with the GPAW code using a plane wave basis except for the Raman calculations, which employ a double-zeta polarised basis of numerical atomic orbitals [51].

Property	Method	Criteria	Count
Bader charges	PBE	None	3809
Energy above convex hull	PBE	None	4044
Heat of formation	PBE	None	4044
Orbital projected band structure	PBE	None	2487
Out-of-plane dipole	PBE	None	4044
Phonons ( $\Gamma$ and BZ corners)	PBE	None	3865
Projected density of states	PBE	None	3332
Stiffness tensor	PBE	None	3968
Exchange couplings	PBE	Magnetic	538
Infrared polarisability	PBE	$E_{\rm gap}^{\rm PBE} > 0$	784
Second harmonic generation	PBE	$E_{\text{gap}}^{\text{PBE}} > 0$ , non-magnetic,	375
, i i i i i i i i i i i i i i i i i i i		non-centrosymmetric	
Electronic band structure PBE	PBE*	None	3496
Magnetic anisotropies	PBE*	Magnetic	823
Deformation potentials	PBE*	$E_{\rm gap}^{\rm PBE} > 0$	830
Effective masses	PBE*	$E_{\text{sap}}^{\text{PBE}} > 0$	1272
Fermi surface	PBE*	$E_{\text{sap}}^{\text{PBE}} = 0$	2505
Plasma frequency	PBE*	$E_{\text{gap}}^{\text{PBE}} = 0$	3144
Work function	PBE*	$E_{\text{gap}}^{\text{PBE}} = 0$	4044
Optical polarisability	RPA@PBE	None	3127
Electronic band structure	HSE06@PBE*	None	3155
Electronic band structure	$G_0W_0@PBE^*$	$E_{\text{sap}}^{\text{PBE}} > 0, N_{\text{atoms}} < 5$	357
Born charges	PBE, Berry phase	$E_{\text{sap}}^{\text{PBE}} > 0$	639
Raman spectrum	PBE, LCAO basis set	Non-magnetic, dyn. stable	708
Piezoelectric tensor	PBE, Berry phase	$E_{\text{gap}}^{\text{PBE}}$ , non-centrosym.	353
Optical absorbance	BSE@G <sub>0</sub> W <sub>0</sub> *	$E_{\text{gap}}^{\text{PBE}} > 0, N_{\text{atoms}} < 5$	378
Spontaneous polarisation	PBE, Berry phase	$E_{\text{gap}}^{\text{PBE}} > 0$ , nearly centrosym.	151
* *	7 I	polar space group	
Topological invariants	PBE*, Berry phase	$0 < E_{\text{gap}}^{\hat{\text{PBE}}} < 0.3 \text{ eV}$	242



**Figure 1.** The workflow behind the C2DB. After the structural relaxation, the dimensionality of the material is checked and it is verified that the material is not already present in the database. Next, the material is classified according to its chemical composition, crystal structure, and magnetic state. Finally, the thermodynamic and dynamic stabilities are assessed from the energy above the convex hull and the sign of the minimum eigenvalues of the dynamical matrix and stiffness tensor. Unstable materials are stored in the database; stable materials are subject to the property workflow. The C2DB monolayer database is interlinked with databases containing structures and properties of multilayer stacks and point defects in monolayers from the C2DB.

until the property calculations (red box), focusing on aspects related to selection criteria, classification, and stability assessment, that have been changed or updated since the 2018 paper.

## 2.1. Structure relaxation

Given a prospective 2D material, the first step is to carry out a structure optimisation. This calculation is performed with spin polarisation and with the symmetries of the original structure enforced. The latter is done to keep the highest level of control over the resulting structure by avoiding 'uncontrolled' symmetry breaking distortions. The prize to pay is a higher risk of generating dynamically unstable structures.

#### 2.2. Selection: dimensionality analysis

A dimensionality analysis [52] is performed to identify and filter out materials that have disintegrated into non-2D structures during relaxation. Covalently bonded clusters are identified through an analysis of the connectivity of the structures where two atoms are considered to belong to the same cluster if their distance is less than some scaling of the sum of their covalent radii, i.e.  $d < k(r_i^{cov} + r_i^{cov})$ , where *i* and *j* are atomic indices. A scaling factor of k = 1.35 was determined empirically. Only structures that consist of a single 2D cluster after relaxation are further processed. Figure 2 shows three examples (graphene, Ge<sub>2</sub>Se<sub>2</sub>, and Pb<sub>2</sub>O<sub>6</sub>) of structures and their cluster dimensionalities before and after relaxation. All structures initially consist of a single 2D cluster, but upon relaxation Ge<sub>2</sub>Se<sub>2</sub> and Pb<sub>2</sub>O<sub>6</sub> disintegrate into two 2D clusters as well as one 2D and two 0D clusters, respectively. On the other hand, the relaxation of graphene decreases the in-plane lattice constant but does not affect the dimensionality. According to the criterion defined above only graphene will enter the database.

#### 2.3. Selection: ranking similar structures

Maintaining a high-throughput database inevitably requires a strategy for comparing similar structures and ranking them according to their relevance. In particular, this is necessary in order to identify different representatives of the same material e.g. resulting from independent relaxations, and thereby avoid duplicate entries and redundant computations. The C2DB strategy to this end involves a combination of structure clustering and Pareto analysis.

First, a single-linkage clustering algorithm is used to group materials with identical reduced chemical formula and 'similar' atomic configurations. To quantify configuration similarity a slightly modified version of PyMatGen's [53] distance metric is employed where the cell volume normalisation is removed to make it applicable to 2D materials surrounded by vacuum. Roughly speaking, the metric measures the maximum distance an atom must be moved (in units of Å) in order to match the two





atomic configurations. Two atomic configurations belong to the same cluster if their distance is below an empirically determined threshold of 0.3 Å.

At this point, the simplest strategy would be to remove all but the most stable compound within a cluster. However, this procedure would remove many high symmetry crystals for which a more stable distorted version exists. For example, the well known T-phase of MoS<sub>2</sub> would be removed in favour of the more stable T'-phase. This is undesired as highsymmetry structures, even if dynamically unstable at T = 0, may provide useful information and might in fact become stabilised at higher temperatures [54]. Therefore, the general strategy adopted for the C2DB,



Figure 3. Illustration of the Pareto analysis used to filter out duplicates or irrelevant structures from the C2DB. All points represent materials with the same reduced chemical formula (in this case  $ReS_2$ ) that belong to the same cluster defined by the structure metric. Only structures lying on the  $(N, \Delta H)$ -Pareto front are retained (black circles) while other materials are excluded (red circles). The philosophy behind the algorithm is to keep less stable materials if they contain fewer atoms per unit cell than more stable materials and thus represent structures of higher symmetry.

is to keep a material that is less stable than another material of the same cluster if it has fewer atoms in its primitive unit cell (and thus typically higher symmetry). Precisely, materials within a given cluster are kept only if they represent a defining point of the (N,  $\Delta H$ )-Pareto front, where N is the number of atoms in the unit cell and  $\Delta H$  is the heat of formation. A graphical illustration of the Pareto analysis is shown in figure 3 for the case of ReS<sub>2</sub>.

#### 2.4. Classification: crystal structure

The original C2DB employed a *crystal prototype* classification scheme where specific materials were promoted to prototypes and used to label groups of materials with the same or very similar crystal structure. This approach was found to be difficult to maintain (as well as being non-transparent). Instead, materials are now classified according to their *crystal type* defined by the reduced stoichiometry, space group number, and the alphabetically sorted labels of the occupied Wyckoff positions. As an example, MoS<sub>2</sub> in the H-phase has the crystal type: AB2-187-bi.

#### 2.5. Classification: magnetic state

In the new version of the C2DB, materials are classified according to their magnetic state as either *non-magnetic* or *magnetic*. A material is considered magnetic if any atom has a local magnetic moment greater than 0.1  $\mu_{\rm B}$ .

In the original C2DB, the *magnetic* category was further subdivided into ferromagnetic (FM) and antiferromagnetic (AFM). But since the simplest antiferromagnetically ordered state typically does not represent the true ground state, all material entries with an AFM state have been removed from the C2DB and replaced by the material in its FM state. Although the latter is less stable, it represents a more well defined state of the material. Crucially, the nearest neighbour exchange couplings for all magnetic materials have been included in the C2DB (see section 5.8). This enables a more detailed and realistic description of the magnetic order via the Heisenberg model. In particular, the FM state of a material is not expected to represent the true magnetic ground if the exchange coupling J < 0.

#### 2.6. Stability: thermodynamic

The heat of formation,  $\Delta H$ , of a compound is defined as its energy per atom relative to its constituent elements in their standard states [55]. The thermodynamic stability of a compound is evaluated in terms of its energy above the *convex hull*,  $\Delta H_{\text{hull}}$ , which gives the energy of the material relative to other competing phases of the same chemical composition, including mixed phases [6], see figure 4 for an example. Clearly,  $\Delta H_{\text{hull}}$  depends on the pool of reference phases, which in turn defines the convex hull. The original C2DB employed a pool of reference phases comprised by 2807 elemental and binary bulk crystals from the convex hull of the Open Quantum Materials Database (OQMD) [55]. In the new version, this set has been extended by approximately 6783 ternary bulk compounds from the convex hull of OQMD, making a total of 9590 stable bulk reference compounds.

As a simple indicator for the thermodynamic stability of a material, the C2DB employs three labels (low, medium, high) as defined in table 2. These indicators are unchanged from the original version of the C2DB. In particular, the criterion  $\Delta H_{\text{hull}} < 0.2 \text{ eV} \text{ atom}^{-1}$ , defining the most stable category, was established based on an extensive analysis of 55 experimentally realised monolayer crystals [6].



Figure 4: Collect full diagram for  $(B_1, E_2)$ -composition. Green (red) colouring indicate materials that have a convex hull energy of less than (greater than) 5 meV. The monolayers  $BI_3$ ,  $Bi_2Te_3$  and BiTe lie on the convex hull. The monolayers are degenerate with their layered bulk parent because the vdW interactions are not captured by the PBE xc-functional.

**Table 2.** Thermodynamic stability indicator assigned to all materials in the C2DB.  $\Delta H$  and  $\Delta H_{\text{hull}}$  denote the heat of formation and energy above the convex hull, respectively.

Thermodynamic stability indicator	Criterion (eV atom <sup>-1</sup> )
Low	$\Delta H > 0.2$
Medium	$\Delta H < 0.2$ and $\Delta H_{ m hull} > 0.2$
High	$\Delta H < 0.2$ and $\Delta H_{\rm hull} < 0.2$

It should be emphasised that the energies of both monolayers and bulk reference crystals are calculated with the Perdew-Burke-Ernzerhof (PBE) xc-functional [56]. This implies that some inaccuracies must be expected, in particular for materials with strongly localised *d*-electrons, e.g. certain transition metal oxides, and materials for which dispersive interactions are important, e.g. layered van der Waals crystals. The latter implies that the energy of a monolayer and its layered bulk parent (if such exists in the pool of references) will have the same energy. For further details and discussions see reference [6].

#### 2.7. Stability: dynamical

Dynamically stable materials are situated at a local minimum of the potential energy surface and are thus stable to small structural perturbations. Structures resulting from DFT relaxations can end up in saddle point configurations because of imposed symmetry constraints or an insufficient number of atoms in the unit cell.

In C2DB, the dynamical stability is assessed from the signs of the minimum eigenvalues of (1) the stiffness tensor (see section 3.1) and (2) the  $\Gamma$ -point Hessian matrix for a supercell containing  $2 \times 2$  repetitions of the unit cell (the structure is not relaxed in the  $2 \times 2$  supercell). If one of these minimal eigenvalues is negative the material is classified as dynamically unstable. This indicates that the energy can be reduced by displacing an atom and/or deforming the unit cell, respectively. The use of two categories for dynamical stability, i.e. stable/unstable, differs from the original version of the C2DB where an intermediate category was used for materials with negative but numerically small minimal eigenvalue of either the Hessian or stiffness tensors.

## 3. Improved property methodology

The new version of the C2DB has been generated using a significantly extended and improved workflow for property evaluations. This section focuses on improvements relating to properties that were already present in the original version of the C2DB while new properties are discussed in the next section.

## 3.1. Stiffness tensor

The stiffness tensor, *C*, is a rank-4 tensor that relates the stress of a material to the applied strain. In Mandel notation (a variant of Voigt notation) *C* is expressed as an  $N \times N$  matrix relating the *N* independent components of the stress and strain tensors. For a 2D material N = 3 and the tensor takes the form:

$$\mathbf{C} = \begin{bmatrix} C_{\text{XXXX}} & C_{\text{XXYY}} & \sqrt{2}C_{\text{XXXY}} \\ C_{\text{XXYY}} & C_{\text{YYYY}} & \sqrt{2}C_{\text{YYXY}} \\ \sqrt{2}C_{\text{XXXY}} & \sqrt{2}C_{\text{YYXY}} & 2C_{\text{XXXY}} \end{bmatrix}, \quad (1)$$

where the indices on the matrix elements refer to the rank-4 tensor. The factors multiplying the tensor elements account for their multiplicities in the full rank-4 tensor. In the C2DB workflow, C is calculated as a finite difference of the stress under an applied strain with full relaxation of atomic coordinates. A negative eigenvalue of C signals a dynamical instability, see section 2.7.

In the first version of the C2DB only the diagonal elements of the stiffness tensor were calculated. The new version also determines the shear components such that the full  $3 \times 3$  stiffness tensor is now available. This improvement also leads to a more accurate assessment of dynamical stability [57].

## 3.2. Effective masses with parabolicity estimates

For all materials with a finite band gap the effective masses of electrons and holes are calculated for bands within 100 meV of the conduction band minimum and valence band maximum, respectively. The Hessian matrices at the band extrema (BE) are determined by fitting a second order polynomium to the PBE band structure including SOC, and the effective masses are obtained by subsequent diagonalisation of the Hessian. The main fitting-procedure is unaltered



**Figure 5.** Left: The PBE band structures of  $Rh_2Br_6$  and  $MoS_2$  (coloured dots) in regions around the conduction band minimum. The dashed red line shows the fit made to estimate the effective masses of the lowest conduction band. The shaded grey region highlights the error between the fit and the true band structure. The mean absolute relative error (MARE) discussed in the main text is calculated for energies within 25 meV of the band minimum. For  $MoS_2$  the fit is essentially on top of the band energies. Right: The distribution of the MARE of all effective mass fits in the C2DB. The inset shows the full distribution on a log scale. As mentioned in the main text, very large MAREs indicate that the band minimum/maximum was incorrectly identified by the algorithm and/or that the band is very flat. Only three materials have MAREs > 1000% but these each have several bands for which the fit fails.

from the first version of C2DB, but two important improvements have been made.

The first improvement consists in an additional kmesh refinement step for better localisation of the BE in the Brillouin zone. After the location of the BE has been estimated based on a uniformly sampled band structure with k-point density of 12 Å, another oneshot calculation is performed with a denser k-mesh around the estimated BE positions. This ensures a more accurate and robust determination of the location of the BE, which can be important in cases with a small but still significant spin-orbit splitting or when the band is very flat or non-quadratic around the BE. The second refinement step is the same as in the first version of C2DB, i.e. the band energies are calculated on a highly dense k-mesh in a small disc around the BE, and the Hessian is obtained by fitting the band energies in the range up to 1 meV from the BE.

The second improvement is the calculation of the mean absolute relative error (MARE) of the polynomial fit in a 25 meV range from the BE. The value of 25 meV corresponds to the thermal energy at room temperature and is thus the relevant energy scale for many applications. To make the MARE independent of the absolute position of the band we calculate the average energy of the band over the 25 meV and compare the deviation of the fit to this energy scale. The MARE provides a useful measure of the parabolicity of the energy bands and thus the validity of the effective mass approximation over this energy scale.

Figure 5 shows two examples of band structures with the effective mass fits and corresponding fit errors indicated. Additionally, the distribution of MARE for all the effective mass fits in the C2DB are presented. Most materials have an insignificant MARE, but a few materials have very large errors. Materials with a MARE above a few hundreds of percentages fall into two classes. For some materials the algorithm does not correctly find the position of the BE. An example is  $Ti_2S_2$  in the space group C2/m. For others, the fit and BE location are both correct, but the band flattens away from the BE which leads to a large MARE as is the case for Rh<sub>2</sub>Br<sub>6</sub> shown in the figure or Cl<sub>2</sub>Tl<sub>2</sub> in the space group P-1. In general a small MARE indicates a parabolic band while materials with large MARE should be handled on a case-bycase basis.

#### 3.3. Orbital projected band structure

To facilitate a state-specific analysis of the PBE Kohn– Sham wave functions, an orbital projected band structure (PBS) is provided to complement the projected density of states (PDOS). In the PAW methodology, the all-electron wave functions are projected onto atomic orbitals inside the augmentation spheres centred at the position of each atom. The PBS resolves these atomic orbital contributions to the



wave functions as a function of band and *k*-point whereas the PDOS resolves the atomic orbital character of the total density of states as a function of energy. The SOC is not included in the PBS or PDOS, as its effect is separately visualised by the spin-PBS also available in the C2DB.

As an example, figure 6 shows the PBS (left) and PDOS (right) of monolayer  $MoS_2$  calculated with PBE. The relative orbital contribution to a given Bloch state is indicated by a pie chart symbol. In the present example, one can deduce from the PBS that even though Mo-*p* orbitals and S-*p* orbitals contribute roughly equally to the DOS in the valence band, the Mo-*p* orbital contributions are localised to a region in the BZ around the *M*-point, whereas the S-*p* orbitals contribute throughout the entire BZ.

#### 3.4. Corrected G<sub>0</sub>W<sub>0</sub> band structures

The C2DB contains  $G_0W_0$  quasiparticle (QP) band structures of 370 monolayers covering 14 different crystal structures and 52 chemical elements. The details of these calculations can be found in the original C2DB paper [6]. A recent in-depth analysis of the 61.716  $G_0W_0$  data points making up the QP band structures led to several important conclusions relevant for high-throughput  $G_0W_0$  calculations. In particular, it identified the linear QP approximation as a significant error source in standard  $G_0W_0$  calculations and proposed an extremely simple correction scheme (the *empirical Z* (empZ) scheme), that reduces this error by a factor of two on average.

The empZ scheme divides the electronic states into two classes according to the size of the QP weight, Z. States with  $Z \in [0.5, 1.0]$  are classified as QP consistent (QP-c) while states with  $Z \notin [0.5, 1.0]$ are classified as QP inconsistent (QP-ic). With this definition, QP-c states will have at least half of their spectral weight in the QP peak. The distribution of the 60.000+ Z-values is shown in figure 7. It turns out that the linear approximation to the self-energy, which is the gist of the QP approximation, introduces significantly larger errors for QP-ic states than for QP-c states. Consequently, the empZ method replaces the calculated Z of QP-ic states with the mean of the Z-distribution,  $Z_0 \approx 0.75$ . This simple replacement reduces the average error of the linear approximation from 0.11 to 0.06 eV.

An illustration of the method applied to  $MoS_2$  is shown in figure 7. The original uncorrected  $G_0W_0$ band structure is shown in blue while the empZ corrected band structure is shown in orange.  $MoS_2$  has only one QP-ic state in the third conduction band at the *K*-point. Due to a break-down of the QP approximation for this state, the  $G_0W_0$  correction is greatly overestimated leading to a local discontinuity in the band structure. The replacement of *Z* by  $Z_0$  for this particular state resolves the problem. All  $G_0W_0$  band structures in the C2DB are now empZ corrected.

#### 3.5. Optical absorbance

In the first version of the C2DB, the optical absorbance was obtained from the simple expression [6]

$$A(\omega) \approx \frac{\omega \mathrm{Im}\alpha^{\mathrm{2D}}(\omega)}{\epsilon_0 c},$$
 (2)

where  $\alpha^{2D}$  is the long wavelength limit of the in-plane sheet polarisability density (note that the equation is written here in SI units). The sheet polarisability is related to the sheet conductivity via  $\sigma^{2D}(\omega) =$  $-i\omega\alpha^{2D}(\omega)$ . The expression (2) assumes that the electric field inside the layer equals the incoming field (i.e. reflection is ignored), and hence, it may overestimate the absorbance.

In the new version, the absorbance is evaluated from A = 1 - R - T, where *R* and *T* are the reflected and transmitted powers of a plane wave at normal



**Figure 7.** Top: Distribution of the 61 716 QP weights (*Z*) contained in the C2DB. The blue part of the distribution shows QP-consistent (QP-c) *Z*-values while the orange part shows QP-inconsistent (QP-ic) *Z* values. In general, the linear expansion of the self-energy performed when solving the QP equation works better for *Z* closer to 1. About 0.3% of the *Z*-values lie outside the interval from 0 to 1 and are not included in the distribution. Bottom:  $G_0W_0$  band structure before (blue) and after (orange) applying the emp*Z* correction, which replaces *Z* by the mean of the distribution for QP-ic states. In the case of MoS<sub>2</sub> only one state at *K* is QP-ic.

incidence, respectively. These can be obtained from the conventional transfer matrix method applied to a monolayer suspended in vacuum. The 2D material is here modelled as an infinitely thin layer with a sheet conductivity. Alternatively, it can be modelled as quasi-2D material of thickness *d* with a 'bulk' conductivity of  $\sigma = \sigma^{2D}/d$  [58], but the two approaches yield very similar results, since the optical thickness of a 2D material is much smaller than the optical wavelength. Within this model, the expression for the absorbance of a suspended monolayer with the sheet conductivity  $\sigma^{2D}$  reads:

$$A(\omega) = \operatorname{Re}\left\{\sigma^{2\mathrm{D}}(\omega)\eta_{0}\right\} \left|\frac{2}{2 + \sigma^{2\mathrm{D}}(\omega)\eta_{0}}\right|^{2}, \quad (3)$$

where  $\eta_0 = 1/(\epsilon_0 c) \approx 377~\Omega$  is the vacuum impedance.

If the light–matter interaction is weak, i.e.  $|\sigma^{2D}\eta_0| \ll 1$ , equation (3) reduces to equation (2).

Nonetheless, due the strong light–matter interaction in some 2D materials, this approximation is not reliable in general. In fact, it can be shown that the maximum possible absorption from equation (3) is 50%, which is known as the upper limit of light absorption in thin films [59]. This limit is not guaranteed by equation (2), which can even yield an absorbance above 100%.

As an example, figure 8 shows the absorption spectrum of monolayer  $MoS_2$  for in- and out-ofplane polarised light as calculated with the exact equation (3) and the approximate equation (2), respectively. In all cases the sheet polarisability is obtained from the BSE to account for excitonic effects [6]. For weak light–matter interactions, e.g. for the *z*-polarised light, the two approaches agree quite well, but noticeable differences are observed in regions with stronger light–matter interaction.

# 4. New materials in the C2DB

In this section we discuss the most significant extensions of the C2DB in terms of new materials. The set of materials presented here is not complete, but represents the most important and/or well defined classes. The materials discussed in sections 4.1 and 4.2 (MXY Janus monolayers and monolayers extracted from experimental crystal structure databases) are already included in the C2DB. The materials described in sections 4.3 and 4.4 (homo-bilayers and monolayer point defect systems) will soon become available as separate C2DB-interlinked databases.

#### 4.1. MXY Janus monolayers

The class of TMDC monolayers of the type MX<sub>2</sub> (where M is the transition metal and X is a chalcogen) exhibits a large variety of interesting and unique properties and has been widely discussed in the literature [60]. Recent experiments have shown that it is not only possible to synthesise different materials by changing the metal M or the chalcogen X, but also by exchanging the X on one side of the layer by another chalcogen (or halogen) [61-63]. This results in a class of 2D materials known as MXY Janus monolayers with broken mirror symmetry and finite out-of-plane dipole moments. The prototypical MXY crystal structures are shown in figure 9 for the case of MoSSe and BiTeI, which have both been experimentally realised [61-63]. Adopting the nomenclature from the TMDCs, the crystal structures are denoted as H- or T-phase, depending on whether X and Y atoms are vertically aligned or displaced, respectively.

In a recent work [64], the C2DB workflow was employed to scrutinise and classify the basic electronic and optical properties of 224 different MXY Janus monolayers. All data from the study is available in the C2DB. Here we provide a brief discussion of the Rashba physics in these materials and refer the



**Figure 8.** Optical absorption of standalone monolayer  $MoS_2$  for *x/y*-polarisation (left) and *z*-polarisation (right) at normal incident in the BSE framework, obtained using equation (2) (blue) or equation (3) (orange). The crystal structure cross-sectional views are shown in the inset with the definition of directions.



interested reader to [64] for more details and analysis of other properties.

A key issue when considering hypothetical materials, i.e. materials not previously synthesised, is their stability. The experimentally synthesised MoSSe and BiTeI are both found to be dynamically stable and lie within 10 meV of the convex hull confirming their thermodynamic stability. Out of the 224 initial monolayers 93 are classified as stable according to the C2DB criteria (dynamically stable and  $\Delta H_{hull} <$ 0.2 eV atom<sup>-1</sup>). Out of the 93 stable materials, 70 exhibit a finite band gap when computed with the PBE xc-functional.

The Rashba effect is a momentum dependent splitting of the band energies of a 2D semiconductor in the vicinity of a band extremum arising due to the combined effect of spin–orbit interactions and a broken crystal symmetry in the direction perpendicular to the 2D plane. The simplest model used to describe the Rashba effect is a 2D electron gas in a perpendicular electric field (along the *z*-axis). Close to the band extremum, the energy of the two spin bands is described by the Rashba Hamiltonian [65, 66]:

$$H = \alpha_R(\boldsymbol{\sigma} \times \mathbf{k}) \cdot \hat{\mathbf{e}}_z, \qquad (4)$$

where  $\sigma$  is the vector of Pauli matrices,  $\mathbf{k} = \mathbf{p}/\hbar$  is the wave number, and the Rashba parameter is proportional to the electric field strength,  $\alpha_R \propto E_0$ .

Although the Rashba Hamiltonian is only meant as a qualitative model, it is of interest to test its validity on the Janus monolayers. The electric field of the Rashba model is approximately given by  $E_0 = \Delta V_{\text{vac}}/d$ , where  $\Delta V_{\text{vac}}$  is the shift in vacuum potential on the two sides of the layer (see left inset of figure 10) and *d* is the layer thickness. Assuming a similar thickness for all monolayers, the electric field is proportional to the potential shift. Not unexpected, the latter is found to correlate strongly with the difference in electronegativity of the X and Y atoms, see left panel of figure 10.

The Rashba energy,  $E_R$ , can be found by fitting  $E(k) = \hbar^2 k^2 / 2m^* \pm \alpha_R k$  to the band structure (see right inset of figure 10) and should scale with the electric field strength. However, as seen from the right panel of figure 10, there is no correlation between the two quantities. Hence we conclude that the simple Rashba model is completely inadequate and that the strength of the perpendicular electric field cannot be used to quantify the effect of spin–orbit interactions on band energies.

# 4.2. Monolayers from known layered bulk crystals

The C2DB has been extended with a number of monolayers that are likely exfoliable from experimentally known layered bulk compounds. Specifically, the Inorganic Crystal Structure Database (ICSD) [67] and Crystallography Open Database (COD) [68]



**Figure 10.** Left: Correlation between the electronegativity difference of *X* and *Y* in MXY Janus monolayers and the vacuum level shift across the layer. Right: Correlation between the Rashba energy and the vacuum level shift. Structures in the H-phase (e.g. MoSSe) are shown in black while structures in the T-phase (e.g. BiTeI) are shown in orange. The linear fit has the slope  $1.35 \text{ eV}/\Delta\chi$  (Pauling scale). The insets show the definition of the vacuum level shift and the Rashba energy, respectively. Modified from [64].

have first been filtered for corrupted, duplicate and theoretical compounds, which reduce the initial set of 585.485 database entries to 167.767 unique materials. All of these have subsequently been assigned a 'dimensionality score' based on a purely geometrical descriptor. If the 2D score is larger than the sum of 0D, 1D and 3D scores we regard the material as being exfoliable and we extract the individual 2D components that comprise the material (see also section 2.2). We refer to the original work on the method for details [52] and note that similar approaches were applied in [11, 12] to identify potentially exfoliable monolayers from the ICSD and COD.

The search has been limited to bulk compounds containing less than six different elements and no rare earth elements. This reduces the set of relevant bulk materials to 2991. For all of these we extracted the 2D components containing less than 21 atoms in the unit cell, which were then relaxed and sorted for duplicates following the general C2DB workflow steps described in sections 2.1-2.3. At this point 781 materials remain. This set includes most known 2D materials and 207 of the 781 were already present in the C2DB prior to this addition. All the materials (including those that were already in C2DB) have been assigned an ICSD/COD identifier that refers to the parent bulk compound from which the 2D material was computationally exfoliated. We emphasise that we have not considered exfoliation energies in the analysis and a subset of these materials may thus be rather strongly bound and challenging to exfoliate even if the geometries indicate van der Waals bonded structures of the parent bulk compounds.

Figure 11 shows the distribution of energies above the convex hull for materials derived from

parent structures in ICSD or COD as well as for the entire C2DB, which includes materials obtained from combinatorial lattice decoration as well. As expected, the materials derived from experimental bulk materials are situated rather close to the convex hull whereas those obtained from lattice decoration extend to energies far above the convex hull. It is also observed that a larger fraction of the experimentally derived materials are dynamically stable. There are, however, well known examples of van der Waals bonded structures where the monolayer undergoes a significant lattice distortion, which will manifest itself as a dynamical instability in the present context. For example, bulk MoS2 exists in van der Waals bonded structures composed of either 2 H-MoS<sub>2</sub> or 1 T-MoS<sub>2</sub> layers, but a monolayer of the 1 T phase undergoes a structural deformation involving a doubling of the unit cell [69] and is thus categorised as dynamically unstable by the C2DB workflow. The dynamically stable materials derived from parent bulk structures in the ICSD and COD may serve as a useful subset of the C2DB that are likely to be exfoliable from known compounds and thus facilitate experimental verification. As a first application the subset has been used to search for magnetic 2D materials, which resulted in a total of 85 ferromagnets and 61 anti-ferromagnets [70].

#### 4.3. Outlook: multilayers

The C2DB is concerned with the properties of covalently bonded monolayers (see discussion of dimensionality filtering in section 2.2). However, multilayer structures composed of two or more identical monolayers are equally interesting and often have properties that deviate from those of the monolayer. In fact, the synthesis of layered vdW structures with a



for the 2D materials extracted from bulk compounds in ICSD and COD (top) and for the entire C2DB including those constructed from combinatorial lattice decoration (bottom). Dynamically stable materials are indicated in blue.

controllable number of layers represents an interesting avenue for atomic-scale materials design. Several examples of novel phenomena emerging in layered vdW structures have been demonstrated including direct-indirect band gap transitions in MoS<sub>2</sub> [71, 72], layer-parity selective Berry curvatures in few-layer WTe<sub>2</sub> [73], thickness-dependent magnetic order in CrI<sub>3</sub> [74, 75], and emergent ferroelectricity in bilayer hBN [76].

As a first step towards a systematic exploration of multilayer 2D structures, the C2DB has been used as basis for generating homobilayers in various stacking configurations and subsequently computing their properties following a modified version of the C2DB monolayer workflow. Specifically, the most stable monolayers (around 1000) are combined into bilayers by applying all possible transformations (unit cell preserving point group operations and translations) of one layer while keeping the other fixed. The candidate bilayers generated in this way are subject to a stability analysis, which evaluates the binding energy and optimal IL distance based on PBE-D3 [77] total energy calculations keeping the atoms of the monolayers fixed in their PBE relaxed geometry, see figures 12 and table 3.



Figure 12. An illustration of the optimisation of the interlayer (IL) distance for  $MoS_2$  in the AA stacking. The black crosses are the points sampled by the optimisation algorithm while the blue curve is a spline interpolation of the black crosses. The inset shows the  $MoS_2$  AA stacking and the definition of the IL distance is indicated with a black double-sided arrow.

**Table 3.** Exfoliation energies for selected materials calculated with the PBE+D3 xc-functional as described in section 4.3 and compared with the DF2 and rVV10 results from [11]. The spacegroups are indicated in the column 'SG'. All numbers are in units of meV  $Å^{-2}$ .

Material	SG	PBE + D3	DF2	rVV10
MoS <sub>2</sub>	P-6m2	28.9	21.6	28.8
MoTe <sub>2</sub>	P-6m2	30.3	25.2	30.4
ZrNBr	Pmmn	18.5	10.5	18.5
С	P6/mmm	18.9	20.3	25.5
Р	Pmna	21.9	38.4	30.7
BN	P-6m2	18.9	19.4	24.4
WTe <sub>2</sub>	P-6m2	32.0	24.7	30.0
РЬТе	P3m1	23.2	27.5	33.0

The calculated IL binding energies are generally in the range from a few to a hundred meV Å<sup>-2</sup> and IL distances range from 1.5 to 3.8 Å. A scatter plot of preliminary binding energies and IL distances is shown in figure 13. The analysis of homobilayers provides an estimate of the energy required to peel a monolayer off a bulk structure. In particular, the binding energy for the most stable bilayer configuration provides a measure of the *exfoliation energy* of the monolayer. This key quantity is now available for all monolayers in the C2DB, see section 5.1.

# 4.4. Outlook: point defects

The C2DB is concerned with the properties of 2D materials in their pristine crystalline form. However, as is well known the perfect crystal is an idealised model of real materials, which always contain defects in smaller or larger amounts depending on the intrinsic materials properties and growth conditions. Crystal defects often have a negative impact on





physical properties, e.g. they lead to scattering and life time-reduction of charge carriers in semiconductors. However, there are also important situations where defects play a positive enabling role, e.g. in doping of semiconductors, as colour centres for photon emission [78, 79] or as active sites in catalysis.

To reduce the gap between the pristine model material and real experimentally accessible samples, a systematic evaluation of the basic properties of the simplest native point defects in a selected subset of monolayers from the C2DB has been initiated. The monolayers are selected based on the stability of the pristine crystal. Moreover, only non-magnetic semiconductors with a PBE band gap satisfying  $E_{gap} > 1$  eV are currently considered as such materials are candidates for quantum technology applications like single-photon sources and spin qubits. Following these selection criteria around 300 monolayers are identified and their vacancies and intrinsic substitutional defects are considered, yielding a total of about 1500 defect systems.

Each defect system is subject to the same workflow, which is briefly outlined below. To enable point defects to relax into their lowest energy configuration, the symmetry of the pristine host crystal is intentionally broken by the chosen supercell, see figure 14 (a). In order to minimise defect–defect interaction, supercells are furthermore chosen such that the minimum distance between periodic images of defects is larger than 15 Å. Unique point defects are created based on the analysis of equivalent Wyckoff positions for the host material. To illustrate some of the properties that will feature in the upcoming point defect database, we consider the specific example of monolayer  $CH_2Si$ .

First, the formation energy [80, 81] of a given defect is calculated from PBE total energies. Next,

Slater-Janak transition state theory is used to obtain the charge transition levels [82, 83]. By combining these results, one obtains the formation energy of the defect in all possible charge states as a function of the Fermi level. An example of such a diagram is shown in figure 14 (b) for the case of the  $V_C$  and  $C_{Si}$ defects in monolayer CH2Si. For each defect and each charge state, the PBE single-particle energy level diagram is calculated to provide a qualitative overview of the electronic structure. A symmetry analysis [84] is performed for the defect structure and the individual defect states lying inside the band gap. The energy level diagram of the neutral VSi defect in CH2Si is shown in figure 14 (c), where the defect states are labelled according to the irreducible representations of the  $C_{\rm s}$  point group.

In general, excited electronic states can be modelled by solving the Kohn-Sham equations with non-Aufbau occupations. The excited-state solutions are saddle points of the Kohn-Sham energy functional, but common self-consistent field (SCF) approaches often struggle to find such solutions, especially when nearly degenerate states are involved. The calculation of excited states corresponding to transitions between localised states inside the band gap is therefore performed using an alternative method based on the direct optimisation (DO) of orbital rotations in combination with the maximum overlap method (MOM) [85]. This method ensures fast and robust convergence of the excited states, as compared to SCF. In figure 14 (d), the reorganisation energies for the ground and excited state, as well as the zero-phonon line (ZPL) energy are sketched. For the specific case of the Si vacancy in CH2Si, the DO-MOM method yields  $E_{\text{ZPL}} = 3.84 \text{ eV}, \lambda_{\text{gs}}^{\text{reorg}} = 0.11 \text{ eV} \text{ and } \lambda_{\text{exc}}^{\text{reorg}} = 0.16 \text{ eV}.$ For systems with large electron-phonon coupling (i.e. Huang–Rhys factor > 1) a one-dimensional approximation for displacements along the main phonon mode is used to produce the configuration coordinate diagram (see figure 14 (d)). In addition to the ZPL energies and reorganisation energies, the Huang-Rhys factors, photoluminescence spectrum from the 1D phonon model, hyperfine coupling and zero field splitting are calculated.

#### 5. New properties in the C2DB

This section reports on new properties that have become available in the C2DB since the first release. The employed computational methodology is described in some detail and results are compared to the literature where relevant. In addition, some interesting property correlations are considered along with general discussions of the general significance and potential application of the available data.

#### 5.1. Exfoliation energy

The exfoliation energy of a monolayer is estimated as the binding energy of its bilayer in the most stable



orbital symmetry of the localised single-particle states of the V<sub>Si</sub> defect for both spin channels (left and right). The Fermi level is shown by the dotted line. (d) Schematic excited state configuration energy diagram. The transitions corresponding to the vertical absorption and the zero-phonon emission are indicated.

stacking configuration (see also section 4.3). The binding energy is calculated using the PBE + D3 xcfunctional [86] with the atoms of both monolayers fixed in the PBE relaxed geometry. Table 3 compares exfoliation energies obtained in this way to values from Mounet et al [11] for a representative set of monolayers.

#### 5.2. Bader charges

For all monolayers we calculate the net charge on the individual atoms using the Bader partitioning scheme [87]. The analysis is based purely on the electron density, which we calculate from the PAW pseudo density plus compensation charges using the PBE xcfunctional. Details of the method and its implementation can be found in Tang et al [88]. In section 5.4 we compare and discuss the relation between Bader charges and Born charges.

## 5.3. Spontaneous polarisation

The spontaneous polarisation  $(\mathbf{P}_s)$  of a bulk material is defined as the charge displacement with respect to that of a reference centrosymmetric structure [89, 90]. Ferroelectric materials exhibit a finite value

of **P**<sub>s</sub> that may be switched by an applied external field and have attracted a large interest for a wide range of applications [91-93].

The spontaneous polarisation in bulk materials can be regarded as electric dipole moment per unit volume, but in contrast to the case of finite systems this quantity is ill-defined for periodic crystals [89]. Nevertheless, one can define the formal polarisation density:

$$\mathbf{P} = \frac{1}{2\pi} \frac{e}{V} \sum_{l} \phi_l \mathbf{a}_l,\tag{5}$$

where  $\mathbf{a}_l$  (with  $l \in \{1, 2, 3\}$ ) are the lattice vectors spanning the unit cell, V is the cell volume and e is the elementary charge.  $\phi_l$  is the polarisation phase along the lattice vector defined by:

$$\phi_l = \sum_i Z_i \mathbf{b}_l \cdot \mathbf{u}_i - \phi_l^{\text{elec}},\tag{6}$$

where  $\mathbf{b}_l$  is the reciprocal lattice vector satisfying  $\mathbf{b}_l$ .  $\mathbf{R}_l = 2\pi$  and  $\mathbf{u}_i$  is the position of nucleus *i* with charge  $eZ_i$ . The electronic contribution to the polarisation phase is defined as:



**Figure 15.** Depicted in the blue plot is the formal polarisation calculated along the adiabatic path for GeSe, using the methods described in the main text. The orange plot shows the energy potential along the path as well as outside. Figure inset: The structure of GeSe in the two non-centrosymmetric configurations corresponding to  $-\mathbf{P}_s$  and  $\mathbf{P}_s$  and the centrosymmetric configuration.

$$\phi_l^{\text{elec}} = \frac{1}{N_{k\perp \mathbf{b}_l}} \text{Im} \sum_{\substack{k \in BZ_{\perp \mathbf{b}_l}}} \\ \times \ln \prod_{j=0}^{N_{k\parallel \mathbf{b}_l} - 1} \det_{occ} \left[ \left\langle u_{n\mathbf{k}+j\delta\mathbf{k}} \right\rangle \left| u_{m\mathbf{k}+(j+1)\delta\mathbf{k}} \right], \right]$$
(7)

where  $BZ_{\perp \mathbf{b}_l} = \{\mathbf{k} | \mathbf{k} \cdot \mathbf{b}_l = 0\}$  is a plane of **k**-points orthogonal to  $\mathbf{b}_l$ ,  $\delta \mathbf{k}$  is the distance between neighbouring k-points in the  $\mathbf{b}_l$  direction and  $N_{k||\mathbf{b}_l}$  ( $N_{k\perp \mathbf{b}_l}$ ) is the number of **k**-points along (perpendicular to) the  $\mathbf{b}_l$  direction. These expression generalise straightforwardly to 2D.

The formal polarisation is only well-defined modulo  $e\mathbf{R}_n/V$  where  $\mathbf{R}_n$  is any lattice vector. However, changes in polarisation are well defined and the spontaneous polarisation may thus be obtained by:

$$\mathbf{P}_{\rm s} = \int_0^1 \frac{d\mathbf{P}(\lambda)}{d\lambda} d\lambda, \tag{8}$$

where  $\lambda$  is a dimensionless parameter that defines an adiabatic structural path connecting the polar phase  $(\lambda = 1)$  with a non-polar phase  $(\lambda = 0)$ .

The methodology has been implemented in GPAW and used to calculate the spontaneous polarisation of all stable materials in the C2DB with a PBE band gap above 0.01 eV and a polar space group symmetry. For each material, the centrosymmetric phase with smallest atomic displacement from the polar phase is constructed and relaxed under the constraint of inversion symmetry. The adiabatic path connecting the two phases is then used to calculate the spontaneous polarisation using equations (5)-(8). An example of a calculation for GeSe is shown in figure 15 where the polarisation along the path connecting two equivalent polar phases via the centrosymmetric phase is shown together with the total energy. The spontaneous polarisation obtained from the path is  $39.8 \text{ nC m}^{-1}$  in good agreement with previous calculations [94].

#### 5.4. Born charges

The Born charge of an atom *a* at position  $\mathbf{u}_a$  in a solid is defined as:

$$Z_{ij}^{a} = \frac{V}{e} \frac{\partial P_{i}}{\partial u_{aj}} \bigg|_{F=0}.$$
 (9)

It can be understood as an effective charge assigned to the atom to match the change in polarisation in direction *i* when its position is perturbed in direction *j*. Since the polarisation density and the atomic position are both vectors, the Born charge of an atom is a rank-2 tensor. The Born charge is calculated as a finite difference and relies on the Modern theory of polarisation [95] for the calculation of polarisation densities, see reference [96] for more details. The Born charge has been calculated for all stable materials in C2DB with a finite PBE band gap.

It is of interest to examine the relation between the Born charge and the Bader charge (see section 5.2). In materials with strong ionic bonds one would expect the charges to follow the atoms. On the other hand, in covalently bonded materials the hybridisation pattern and thus the charge distribution, depends on the atom positions in a complex way, and the idea of charges following the atom is expected to break down. In agreement with this idea, the (in-plane) Born charges in the strongly ionic hexagonal hBN ( $\pm 2.71e$ for B and N, respectively) are in good agreement with the calculated Bader charges  $(\pm 3.0e)$ . In contrast, (the in-plane) Born charges in MoS<sub>2</sub> (-1.08e and 0.54e for Mo and S, respectively) deviate significantly from the Bader charges (1.22e and -0.61e for)Mo and S, respectively). In fact, the values disagree even on the sign of the charges underlining the nonintuitive nature of the Born charges in covalently bonded materials.

Note that the out-of-plane Born charges never match the Bader charges, even for strongly ionic insulators, and are consistently smaller in value than the in-plane components. The smaller out-of-plane values are consistent with the generally smaller out-ofplane polarisability of 2D materials (for both electronic and phonon contributions) and agrees with the intuitive expectation that it is more difficult to polarise a 2D material in the out-of-plane direction as compared to the in-plane direction.

Figure 16 shows the average of the diagonal of the Born charge tensor,  $\text{Tr}(Z^a)/3$ , plotted against the Bader charges for all 585 materials in the C2DB for which the Born charges have been computed. The data points have been coloured according to the ionicity of the atom *a* defined as  $I(a) = |\chi_a - \langle \chi \rangle|$ , where  $\chi_a$  and  $\langle \chi \rangle$  are the Pauling electronegativity of atom *a* and the average electronegativity of all atoms in the



**Figure 16.** Born charges, Tr(Z)/3, vs. Bader charges for 3025 atoms in the 585 materials for which the Born charges are calculated. The colors indicate the ionicity of the atoms (see main text).



unit cell, respectively. The ionicity is thus a measure of the tendency of an atom to donate/accept charge relative to the average tendency of atoms in the material. It is clear from figure 16 that there is a larger propensity for the Born and Bader charges to match in materials with higher ionicity.

Figure 17 plots the average (in-plane) Born charge and the Bader charge versus the band gap. It is clear that large band gap materials typically exhibit integer Bader charges, whereas there is no clear correlation between the Born charge and the band gap.

#### 5.5. Infrared polarisability

The original C2DB provided the frequency dependent polarisability computed in the random phase approximation (RPA) with inclusion of electronic interband and intraband (for metals) transitions [6]. However, phonons carrying a dipole moment (socalled IR active phonons) also contribute to the polarisability at frequencies comparable to the frequency of optical phonons. This response is described by the IR polarisability:



**Figure 18.** Total polarisability, including both electrons and phonons, of monolayer hBN in the infrared (IR) frequency regime. The resonance at around 180 meV is due to the  $\Gamma$ -point longitudinal optical phonon. At energies above all phonon frequencies (but below the band gap) the polarisability is approximately constant and equal to the static limit of the electronic polarisability,  $\alpha_{\infty}$ .

$$\alpha^{\mathrm{IR}}(\omega) = \frac{e^2}{A} \mathbf{Z}^T \mathbf{M}^{-1/2} \left( \sum_i \frac{\mathbf{d}_i \mathbf{d}_i^T}{\omega_i^2 - \omega^2 - i\gamma\omega} \right) \mathbf{M}^{-1/2} \mathbf{Z},$$
(10)

where **Z** and **M** are matrix representations of the Born charges and atomic masses,  $\omega_i^2$  and  $d_i$  are eigenvectors and eigenvalues of the dynamical matrix, *A* is the inplane cell area and  $\gamma$  is a broadening parameter representing the phonon lifetime and is set to 10 meV. The total polarisability is then the sum of the electronic polarisability and the IR polarisability.

The new C2DB includes the IR polarisability of all monolayers for which the Born charges have been calculated (stable materials with a finite band gap), see section (5.4). As an example, figure 18 shows the total polarisability of monolayer hexagonal hBN. For details on the calculation of the IR polarisability see reference [96].

## 5.6. Piezoelectric tensor

The piezoelectric effect is the accumulation of charges, or equivalently the formation of an electric polarisation, in a material in response to an applied mechanical stress or strain. It is an important material characteristic with numerous scientific and technological applications in sonar, microphones, accelerometers, ultrasonic transducers, energy conversion, etc [97, 98]. The change in polarisation originates from the movement of positive and negative charge centres as the material is deformed.

Piezoelectricity can be described by the (proper) piezoelectric tensor  $c_{ijk}$  with  $i, j, k \in \{x, y, z\}$ , given by [99]:

$$c_{ijk} = \frac{e}{2\pi V} \sum_{l} \frac{\partial \phi_l}{\partial \epsilon_{jk}} a_{li}, \qquad (11)$$

which differs from equation (5) only by a derivative of the polarisation phase with respect to the strain tensor

Table 4. Comparison of computed piezoelectric tensor versus experimental values and previous calculations for hexagonal BN and a selected set of TMDCs (space group 187). All numbers are in units of nC/m. Experimental data for MoS<sub>2</sub> is obtained from [102].

Material	Exp.	Theory [101]	C2DB	
BN	_	0.14	0.13	
MoS <sub>2</sub>	0.3	0.36	0.35	
MoSe <sub>2</sub>	_	0.39	0.38	
MoTe <sub>2</sub>	_	0.54	0.48	
WS <sub>2</sub>	_	0.25	0.24	
WSe <sub>2</sub>	_	0.27	0.26	
WTe <sub>2</sub>	_	0.34	0.34	

 $\epsilon_{jk}$ . Note that  $c_{ijk}$  does not depend on the chosen branch cut.

The piezoelectric tensor is a symmetric tensor with at most 18 independent components. Furthermore, the point group symmetry restricts the number of independent tensor elements and their relationships due to the well-known Neumann's principle [100]. For example, monolayer MoS2 with point group  $D_{3h}$ , has only one non-vanishing independent element of cijk. Note that cijk vanishes identically for centrosymmetric materials. Using a finitedifference technique with a finite but small strain (1% in our case), equation (11) has been used to compute the proper piezoelectric tensor for all noncentrosymmetric materials in the C2DB with a finite band gap. Table 4 shows a comparison of the piezoelectric tensors in the C2DB with literature for a selected set of monolayer materials. Good agreement is obtained for all these materials.

## 5.7. Topological invariants

For all materials in the C2DB exhibiting a direct band gap below 1 eV, the *k*-space Berry phase spectrum of the occupied bands has been calculated from the PBE wave functions. Specifically, a particular *k*-point is written as  $k_1\mathbf{b}_1 + k_2\mathbf{b}_2$  and the Berry phases  $\gamma_n(k_2)$ of the occupied states on the path  $k_1 = 0 \rightarrow k_1 = 1$  is calculated for each value of  $k_2$ . The connectivity of the Berry phase spectrum determines the topological properties of the 2D Bloch Hamiltonian [103, 104].

The calculated Berry phase spectra of the relevant materials are available for visual inspection on the C2DB webpage. Three different topological invariants have been extracted from these spectra and are reported in the C2DB: (1) The Chern number, C, takes an integer value and is well defined for any gapped 2D material. It determines the number of chiral edge states on any edge of the material. For any non-magnetic material the Chern number vanishes due to time-reversal symmetry. It is determined from the Berry phase spectrum as the number of crossings at any horizontal line in the spectrum. (2) The mirror Chern number,  $C_M$ , defined for gapped materials with a mirror plane in the atomic layer [105]. For such materials, all states may be chosen as mirror eigenstates with eigenvalues  $\pm i$  and the Chern numbers  $C_{\pm}$  can be defined for each mirror sector separately. For a material with vanishing Chern number, the mirror Chern number is defined as  $C_M = (C_+ - C_+)$  $(C_{-})/2$  and takes an integer value corresponding to the number of edge states on any mirror symmetry preserving edge. It is obtained from the Berry phase spectrum as the number of chiral crossings in each of the mirror sectors. (3) The  $Z_2$  invariant,  $\nu$ , which can take the values 0 and 1, is defined for materials with time-reversal symmetry. Materials with  $\nu = 1$ are referred to as quantum spin Hall insulators and exhibit helical edge states at any time-reversal conserving edge. It is determined from the Berry phase spectrum as the number of crossing points modulus 2 at any horizontal line in the interval  $k_2 \in [0, 1/2]$ .

Figure 19 shows four representative Berry phase spectra corresponding to the three cases of nonvanishing *C*,  $C_M$  and  $\nu$  as well as a trivial insulator. The four materials are: OsCl<sub>3</sub> (space group 147) a Chern insulator with C = 1, OsTe<sub>2</sub> (space group 14)—a mirror crystalline insulator with  $C_M = 2$ , SbI (spacegroup 1)—a quantum spin Hall insulator with  $\nu = 1$  and BiITe (spacegroup 156)—a trivial insulator. Note that a gap in the Berry phase spectrum always implies a trivial insulator.

In [106] the C2DB was screened for materials with non-trivial topology. At that point it was found that the database contained 7 Chern insulators, 21 mirror crystalline topological insulators and 48 quantum spin Hall insulators. However, that does not completely exhaust the the topological properties of materials in the C2DB. In particular, there may be materials that can be topologically classified based on crystalline symmetries other than the mirror plane of the layer. In addition, second order topological effects may be present in certain materials, which imply that flakes will exhibit topologically protected corner states. Again, the Berry phase spectra may be used to unravel the second order topology by means of nested Wilson loops [107].

#### 5.8. Exchange coupling constants

The general C2DB workflow described in sections 2.1-2.3 will identify the FM ground state of a material and apply it as starting point for subsequent property calculations, whenever it is more stable than the spin-paired ground state. In reality, however, the FM state is not guaranteed to comprise the magnetic ground state. In fact, AFM states often have lower energy than the FM one, but in general it is non-trivial to obtain the true magnetic ground state. We have chosen to focus on the FM state due to its simplicity and because its atomic structure and stability are often very similar to those of other magnetic states. Whether or not the FM state is the true magnetic ground state is indicated by the nearest neighbour exchange coupling constant as described below.



When investigating magnetic materials the thermodynamical properties (for example the critical temperatures for ordering) are of crucial interest. In two dimensions the Mermin–Wagner theorem [108] comprises an extreme example of the importance of thermal effects since it implies that magnetic order is only possible at T = 0 unless the spin-rotational symmetry is explicitly broken. The thermodynamic properties cannot be accessed directly by DFT. Consequently, magnetic models that capture the crucial features of magnetic interactions must be employed. For insulators, the Heisenberg model has proven highly successful in describing magnetic properties of solids in 3D as well as 2D [109]. It represents the magnetic degrees of freedom as a lattice of localised spins that interact through a set of exchange coupling constants. If the model is restricted to include only nearest neighbour exchange and assume magnetic isotropy in the plane, it reads:

$$H = -\frac{J}{2} \sum_{\langle ij \rangle} \mathbf{S}_i \cdot \mathbf{S}_j - \frac{\lambda}{2} \sum_{\langle ij \rangle} S_i^z S_j^z - A \sum_i \left(S_i^z\right)^2, \quad (12)$$

where *J* is the nearest neighbour exchange constant,  $\lambda$  is the nearest neighbour anisotropic exchange constant and *A* measures the strength of single-ion anisotropy. We also neglect off-diagonal exchange coupling constants that give rise to terms proportional to  $S_i^x S_j^y$ ,  $S_j^y S_j^z$  and  $S_i^z S_i^x$ . The out-of-plane direction has been chosen as z and  $\langle ij \rangle$  implies that for each site *i* we sum over all nearest neighbour sites *j*. The parameters *J*,  $\lambda$  and *A* may be obtained from an energy mapping analysis involving four DFT calculations with different spin configurations [70, 110, 111]. The thermodynamic properties of the resulting 'first principles Heisenberg model' may subsequently be analysed with classical Monte Carlo simulations or renormalised spin wave theory [36, 112].

The C2DB provides the values of J,  $\lambda$ , and A as well as the number of nearest neighbours  $N_{nn}$  and the maximum eigenvalue of  $S_z$  (S), which is obtained from the total magnetic moment per atom in the FM ground state (rounded to nearest half-integer for metals). These key parameters facilitate easy post-processing analysis of thermal effects on the magnetic structure. In [113] such an analysis was applied to estimate the critical temperature of all FM materials in the C2DB based on a model expression for  $T_C$  and the parameters from equation (12).

For metals, the Heisenberg parameters available in C2DB should be used with care because the Heisenberg model is not expected to provide an accurate description of magnetic interactions in this case. Nevertheless, even for metals the sign and magnitude of the parameters provide an important qualitative measure of the magnetic interactions that may be used to screen and select materials for more detailed investigations of magnetic properties. A negative value of *J* implies the existence of an AFM state with lower energy than the FM state used in C2DB. This parameter is thus crucial to consider when judging the stability and relevance of a material classified as magnetic in C2DB (see section 2.5). Figure 20 shows the distribution of exchange coupling constants (weighted by  $S^2$ ) of the magnetic materials in the C2DB. The distribution is slightly skewed to the positive side indicating that FM order is more common than AFM order.

The origin of magnetic anisotropy may stem from either single-ion anisotropy or anisotropic exchange and it is in general difficult a priori to determine, which mechanism is most important. There is, however, a tendency in the literature to neglect anisotropic exchange terms in a Heisenberg model description of magnetism and focus solely on the single-ion anisotropy. In figure 20 we show a scatter plot of the anisotropy parameters A and  $\lambda$  for the FM materials (J > 0). The spread of the parameters indicate that the magnetic anisotropy is in general equally likely to originate from both mechanisms and neglecting anisotropic exchange is not advisable. For ferromagnets, the model (equation (12)) only exhibits magnetic order at finite temperatures if  $A(2S-1) + \lambda N_{nn} > 0$  [113]. Neglecting anisotropic exchange thus excludes materials with A < 0 that satis fies  $A(2S-1) + \lambda N_{nn} > 0$ . This is in fact the case for 11 FM insulators and 31 FM metals in the C2DB.

#### 5.9. Raman spectrum

Raman spectroscopy is an important technique used to probe the vibrational modes of a solid (or molecule) by means of inelastic scattering of light [114]. In fact, Raman spectroscopy is the dominant method for characterising 2D materials and can yield detailed information about chemical composition, crystal structure and layer thickness. There exist several different types of Raman spectroscopies that differ mainly by the number of photons and phonons involved in the scattering process [114]. The firstorder Raman process, in which only a single phonon is involved, is the dominant scattering process in samples with low defect concentrations.

In a recent work, the first-order Raman spectra of 733 monolayer materials from the C2DB were calculated, and used as the basis for an automatic procedure for identifying a 2D material entirely from its experimental Raman spectrum [115]. The Raman spectrum is calculated using third-order perturbation theory to obtain the rate of scattering processes involving creation/annihilation of one phonon and two photons, see reference [115] for details. The light field is written as  $\mathcal{F}(t) = \mathcal{F}_{in}\mathbf{u}_{in} \exp(-i\omega_{in}t) + \mathcal{F}_{out}\mathbf{u}_{out} \exp(-i\omega_{out}t) + c.c.$  where  $\mathcal{F}_{in/out}$  and  $\omega_{in/out}$  denote the amplitudes and frequencies of the input/output electromagnetic fields, respectively. In addition,  $\mathbf{u}_{in/out} = \sum_i u_{in/out}^i \mathbf{e}_i$  are the corresponding polarisation vectors, where  $\mathbf{e}_i$  denotes the unit



Figure 20. Top: Distribution of exchange coupling constants in C2DB. Bottom: Single-ion anisotropy A vs anisotropic exchange  $\lambda$  for ferromagnetic materials with S > 1/2. The shaded area indicates the part of parameter space where the model (equation (12)) does not yield an ordered state at finite temperatures.

vector along the *i*-direction with  $i \in \{x, y, z\}$ . Using this light field, the final expression for the Stokes Raman intensity involving scattering events by only one phonon reads [115]:

$$I(\omega) = I_0 \sum_{\nu} \frac{n_{\nu} + 1}{\omega_{\nu}} \left| \sum_{ij} u_{in}^{i} R_{ij}^{\nu} u_{out}^{j} \right|^2 \delta(\omega - \omega_{\nu}).$$
(13)

Here,  $I_0$  is an unimportant constant (since Raman spectra are always reported normalised), and  $n_{\nu}$ is obtained from the Bose-Einstein distribution, i.e.  $n_{\nu} \equiv (\exp[\hbar\omega_{\nu}/k_BT] - 1)^{-1}$  at temperature T for a Raman mode with energy  $\hbar\omega_{\nu}$ . Note that only phonons at the Brillouin zone center (with zero momentum) contribute to the one-phonon Raman processes due to momentum conservation. In equation (13),  $R_{ii}^{\nu}$  is the Raman tensor for phonon mode  $\nu$ , which involves electron–phonon and dipole matrix elements as well as the electronic transition energies and the incident excitation frequency. Equation (13) has been used to compute the Raman spectra of the 733 most stable, non-magnetic monolayers in C2DB for a range of excitation frequencies and polarisation configurations. Note that the Raman shift  $\hbar\omega$  is typically expressed in cm<sup>-1</sup> with



**Figure 21.** Comparison of the calculated and experimental (extracted from [62]) Raman spectrum of MoS<sub>2</sub> (left) and MoSSe (right). The excitation wavelength is 532 nm, and both the polarisation of both the incoming and outgoing photons are along the *y*-direction. The Raman peaks are labelled according to the irreducible representations of the corresponding vibrational modes. Adapted from [115].

1 meV equivalent to 8.0655 cm<sup>-1</sup>. In addition, for generating the Raman spectra, we have used a Gaussian  $[G(\omega) = (\sigma\sqrt{2\pi})^{-1} \exp(-\omega^2/2\sigma^2)]$  with a variance  $\sigma = 3$  cm<sup>-1</sup> to replace the Dirac delta function, which accounts for the inhomogeneous broadening of phonon modes.

As an example, figure 21 shows the calculated Raman spectrum of monolayer MoS<sub>2</sub> and the Janus monolayer MoSSe (see section 4.1). Experimental Raman spectra extracted from reference [62] are shown for comparison. For both materials, good agreement between theory and experiment is observed for the peak positions and relative amplitudes of the main peaks. The small deviations can presumably be attributed to substrate interactions and defects in the experimental samples as well as the neglect of excitonic effects in the calculations. The qualitative differences between the Raman spectra can be explained by the different point groups of the materials ( $C_{3\nu}$  and  $D_{3h}$ , respectively), see reference [115]. In particular, the lower symmetry of MoSSe results in a lower degeneracy of its vibrational modes leading to more peaks in the Raman spectrum.

Very recently, the Raman spectra computed from third order perturbation theory as described above, were supplemented by spectra obtained from the more conventional Kramers–Heisenberg–Dirac (KHD) approach. Within the KHD method, the Raman tensor is obtained as the derivative of the static electric polarisability (or equivalently, the susceptibility) along the vibrational normal modes [116, 117]:

$$R_{ij}^{\nu} = \sum_{\alpha l} \frac{\partial \chi_{ij}^{(1)}}{\partial r_{\alpha l}} \frac{v_{\alpha l}^{\nu}}{\sqrt{M_{\alpha}}}.$$
 (14)

Here,  $\chi_{ij}^{(1)}$  is the (first-order) susceptibility tensor,  $r_{\alpha}$  and  $M_{\alpha}$  are the position and atomic mass of atom

 $\alpha,$  respectively, and  $v_{\alpha l}^{\nu}$  is the eigenmode of phonon  $\nu$ . The two approaches, i.e. the KHD and third-order perturbation approach, can be shown to be equivalent [114], at least when local field effects can be ignored as is typically the case for 2D materials [35]. We have also confirmed this equivalence from our calculations. Furthermore, the computational cost of both methods is also similar [115]. However, the KHD approach typically converge faster with respect to both the number of bands and k-grid compared to the third-order perturbation method. This stems from the general fact that higher-order perturbation calculations converge slower with respect to kgrid and they require additional summations over a complete basis set (virtual states) and hence a larger number of bands [118]. Currently, Raman spectra from both approaches can be found at the C2DB website.

#### 5.10. Second harmonics generation

Nonlinear optical (NLO) phenomena such as harmonic generation, Kerr, and Pockels effects are of great technological importance for lasers, frequency converters, modulators, etc. In addition, NLO spectroscopy has been extensively employed to obtain insight into materials properties [119] that are not accessible by e.g. linear optical spectroscopy. Among numerous nonlinear processes, second-harmonic generation (SHG) has been widely used for generating new frequencies in lasers as well as identifying crystal orientations and symmetries.

Recently, the SHG spectrum was calculated for 375 non-magnetic, non-centrosymmetric semiconducting monolayers of the C2DB, and multiple 2D materials with giant optical nonlinearities were identified [120]. In the SHG process, two incident photons at frequency  $\omega$  generate an emitted photon at frequency of  $2\omega$ . Assume that a mono-harmonic electric



Figure 22. (Left panel) SHG spectra of monolayer  $Ge_2 \delta e_2$ , where only non-vanishing independent tensor elements are shown. The vertical dashed lines mark  $\hbar \omega = E_g/2$  and  $\hbar \omega = E_g$ , respectively. The crystal structure of  $Ge_2 Se_2$  structure is shown in the inset. (Right panel) The rotational anisotropy of the static ( $\omega = 0$ ) SHG signal for parallel (blue) and perpendicular (red) polarisation configurations with  $\theta$  defined with respect to the crystal *x*-axis.

field written  $\mathcal{F}(t) = \sum_i \mathcal{F}_i \mathbf{e}^{-i\omega t} + c.c.$  is incident on the material, where  $\mathbf{e}_i$  denotes the unit vector along direction  $i \in \{x, y, z\}$ . The electric field induces a SHG polarisation density  $\mathbf{P}^{(2)}$ , which can be obtained from the quadratic susceptibility tensor  $\chi_{iit}^{(2)}$ ,

$$P_i^{(2)}(t) = \epsilon_0 \sum_{jk} \chi_{ijk}^{(2)}(\omega, \omega) \mathcal{F}_i \mathcal{F}_j e^{-2i\omega t} + \text{c.c.}, \quad (15)$$

where  $\varepsilon_0$  denotes the vacuum permittivity.  $\chi_{ijk}^{(2)}$  is a symmetric (due to intrinsic permutation symmetry i.e.  $\chi_{ijk}^{(2)} = \chi_{ijk}^{(2)}$ ) rank-3 tensor with at most 18 independent elements. Furthermore, similar to the piezo-electric tensor, the point group symmetry reduces the number of independent tensor elements.

In the C2DB, the quadratic susceptibility is calculated using density matrices and perturbation theory [118, 121] with the involved transition dipole matrix elements and band energies obtained from DFT. The use of DFT single-particle orbitals implies that excitonic effects are not accounted for. The number of empty bands included in the sum over bands was set to three times the number of occupied bands. The width of the Fermi-Dirac occupation factor was set to  $k_BT = 50$  meV, and a line-shape broadening of  $\eta = 50$  meV was used in all spectra. Furthermore, time-reversal symmetry was imposed in order to reduce the k-integrals to half the BZ. For various 2D crystal classes, it was verified by explicit calculation that the quadratic tensor elements fulfil the expected symmetries, e.g. that they all vanish identically for centrosymmetric crystals.

As an example, the calculated SHG spectra for monolayer  $Ge_2Se_2$  is shown in figure 22 (left panel).

Monolayer Ge<sub>2</sub>Se<sub>2</sub> has five independent tensor elements,  $\chi^{(2)}_{xxx}$ ,  $\chi^{(2)}_{xyy}$ ,  $\chi^{(2)}_{xzz}$ ,  $\chi^{(2)}_{yyx} = \chi^{(2)}_{yxy}$ , and  $\chi^{(2)}_{zzx} =$  $\chi^{(2)}_{ZVZ}$ , since it is a group-IV dichalcogenide with an orthorhombic crystal structure (space group 31 and point group  $C_{2\nu}$ ). Note that, similar to the linear susceptibility, the bulk quadratic susceptibility (with SI units of mV-1) is ill-defined for 2D materials (since the volume is ambiguous) [120]. Instead, the unambiguous sheet quadratic susceptibility (with SI units of m<sup>2</sup>V<sup>-1</sup>) is evaluated. In addition to the frequency-dependent SHG spectrum, the angular dependence of the static ( $\omega = 0$ ) SHG intensity at normal incidence for parallel and perpendicular polarisations (relative to the incident electric field) is calculated, see figure 22 (right panel). Such angular resolved SHG spectroscopy has been widely used for determining the crystal orientation of 2D materials. The calculated SHG spectra for all nonvanishing inequivalent polarisation configurations and their angular dependence, are available in the C2DB.

Since C2DB has already gathered various material properties of numerous 2D materials, it provides a unique opportunity to investigate interrelations between different material properties. For example, the strong dependence of the quadratic optical response on the electronic band gap was demonstrated on basis of the C2DB data [120]. As another example of a useful correlation, the static quadratic susceptibility is plotted versus the static linear susceptibility for 67 TMDCs (with formula MX<sub>2</sub>, space group 187) in figure 23. Note that for materials with several independent tensor elements, only the largest is shown. There is a very clear correlation between the two quantities. This is not unexpected as both



**Figure 23.** Scatter plot (double log scale) of the static sheet quadratic susceptibility  $|\chi_{ijk}^{(2)}|$  versus the static sheet linear susceptibility  $|\chi_{ij}^{(1)}|$  for 67 TMDCs (with chemical formula MX<sub>2</sub> and space group 187). A few well known materials are highlighted.

the linear and quadratic optical responses are functions of the transition dipole moments and transition energies. More interestingly, the strength of the quadratic response seems to a very good approximation to be given by a universal constant times the linear susceptibility to the power of three (ignoring polarisation indices), i.e.

$$\chi^{(2)}(0,0) \approx A \chi^{(1)}(0)^3, \tag{16}$$

where A is only weakly material dependent. Note that this scaling law is also known in classical optics as semi-empirical Miller's rule for non-resonant quadratic responses [122], which states that the second order electric susceptibility is proportional to the product of the first-order susceptibilities at the three frequencies involved.

# 6. Machine learning properties

In recent years, material scientists have shown great interest in exploiting the use of machine learning (ML) techniques for predicting materials properties and guiding the search for new materials. ML is the scientific study of algorithms and statistical models that computer systems can use to perform a specific task without using explicit instructions but instead relying on patterns and inference. Within the domain of materials science, one of the most frequent problems is the mapping from atomic configuration to material property, which can be used e.g. to screen large material spaces in search of optimal candidates for specific applications [123, 124].

In the ML literature, the mathematical representation of the input observations is often referred to as a fingerprint. Any fingerprint must satisfy a number of general requirements [125]. In particular, a fingerprint must be:

- (a) Complete: The fingerprint should incorporate all the relevant input for the underlying problem, i.e. materials with different properties should have different fingerprints.
- (b) Compact: The fingerprint should contain no or a minimal number of features redundant to the underlying problem. This includes being invariant to rotations, translations and other transformations that leave the properties of the system invariant.
- (c) *Descriptive*: Materials with similar target values should have similar fingerprints.
- (d) Simple: The fingerprint should be efficient to evaluate. In the present context, this means that calculating the fingerprint should be significantly faster than calculating the target property.

Several types of atomic-level materials fingerprints have been proposed in the literature, including general purpose fingerprints based on atomistic properties [126, 127] possibly encoding information about the atomic structure, i.e. atomic positions [125, 128, 129], and specialised fingerprints tailored for specific applications (materials/properties) [130, 131].

The aim of this section is to demonstrate how the C2DB may be utilised for ML-based prediction of general materials properties. Moreover, the study serves to illustrate the important role of the fingerprint for such problems. The 2D materials are represented using three different fingerprints: two popular structural fingerprints and a more advanced fingerprint that encodes information about the electronic structure via the PDOS. The target properties include the HSE06 band gap, the PBE heat of formation  $(\Delta H)$ , the exciton binding energy  $(E_B)$  obtained from the many-body BSE, the in-plane static polarisability calculated in the RPA averaged over the x and y polarisation directions ( $\langle \alpha_i \rangle$ ), and the in-plane Voigt modulus ( $\langle C_{ii} \rangle$ ) defined as  $\frac{1}{4}(C_{11}+C_{22}+2C_{12})$ , where  $C_{ii}$ is a component of the elastic stiffness tensor in Mandel notation.

To introduce the data, figure 24 shows pair-plots of the dual-property relations of these properties. The plots in the diagonal show the single-property histograms, whereas the off-diagonals show dual-property scatter plots below the diagonal and histograms above the diagonal. Clearly, there are only weak correlations between most of the properties, with the largest degree of correlation observed between the HSE06 gap and exciton binding energy. The lack of strong correlations motivates the use of ML for predicting the properties.

The prediction models are build using the Ewald sum matrix and many-body tensor representation (MBTR) as structural fingerprints. The Ewald fingerprint is a version of the simple Coulomb matrix fingerprint [128] modified to periodic systems [125]. The MBTR encodes first, second and third order



**Figure 24.** Pair-plot of selected properties from C2DB. The diagonal contains the single property histograms. Below the diagonal are two-property scatter plots showing the correlation between properties and above the diagonal are two-property histograms. Properties include the HSE06 band gap, the PBE heat of formation ( $\Delta H$ ), the exciton binding energy ( $E_B$ ) calculated from the BSE, the in-plane static polarisability calculated in the RPA and averaged over the *x* and *y* polarisation directions ( $\langle \alpha_n \rangle$ ), and the in-plane Voigt modulus ( $\langle C_{ii} \rangle$ ) defined as  $\frac{1}{4}$  ( $C_{11} + C_{22} + 2C_{12}$ ), where  $C_{ij}$  is a component of the elastic stiffness tensor.

terms like atomic numbers, distances and angles between atoms in the system [129]. As an alternative to the structural fingerprints, a representation based on the PBE PDOS is also tested. This fingerprint<sup>6</sup> encodes the coupling between the PDOS at different atomic orbitals in both energy and real space. It is defined as:

$$\rho_{\nu\nu'}(E,R) = \sum_{a \in \text{cell } a'} \sum_{a'} \rho_{a\nu}(E) \rho_{a'\nu'}(E) G$$
$$\times (R - |R_a - R_{a'}|), \qquad (17)$$

where G is a Gaussian smearing function, a denotes the atoms,  $\nu$  denotes atomic orbitals, and the PDOS is given by:

$$\rho_{a\nu}(E) = \sum_{n} |\langle \psi_n | a\nu \rangle|^2 G(E - \epsilon_n), \quad (18)$$

<sup>6</sup> Details will be published elsewhere.

where n runs over all eigenstates of the system. Since this fingerprint requires a DFT-PBE calculation to be performed, additional features derivable from the DFT calculation can be added to the fingerprint. In this study, the PDOS fingerprint is amended by the PBE band gap. The latter can in principle be extracted from the PDOS, but its explicit inclusion has been found to improve the performance of the model.

A Gaussian process regression using a simple Gaussian kernel with a noise component is used as learning algorithm. The models are trained using 5-fold cross validation on a training set consisting of 80% of the materials with the remaining 20% held aside as test data. Prior to training the model, the input space is reduced to 50 features using principal component analysis (PCA). This step is necessary to reduce the huge number of features in the MBTR fingerprint to a manageable size. Although this is not required for the Ewald and PDOS fingerprints,



Figure 25. Prediction scores (MAE normalised to standard deviation of property values) for the test sets of selected properties using a Gaussian process regression.



we perform the same feature reduction in all cases. The optimal number of features depends on the choice of fingerprint, target property and learning algorithm, but for consistency 50 PCA components are used for all fingerprints and properties in this study.

Figure 25 shows the prediction scores obtained for the five properties using the three different fingerprints. The employed prediction score is the mean absolute error of the test set normalised by the standard deviation of the property values (standard deviations are annotated in the diagonal plots in figure 24). In general, the PDOS fingerprint outperforms the structural fingerprints. The difference between prediction scores is smallest for the static polarisability  $\langle \alpha_i \rangle$  and largest for the HSE06 gap. It should be stressed that although the evaluation of the PBE-PDOS fingerprint is significantly more time consuming than the evaluation of the structural fingerprints, it is still much faster than the evaluation of all the target properties. Moreover, structural fingerprints require the atomic structure, which in turns

requires a DFT structure optimisation (unless the structure is available by other means).

The HSE06 band gap shows the largest sensitivity to the employed fingerprint. To elaborate on the HSE06 results, figure 26 shows the band gap predicted using each of the three different fingerprints plotted against the true band gap. The mean absolute errors on the test set is 0.95 and 0.74 eV for Ewald and MBTR fingerprints, respectively, while the PDOS significantly outperforms the other fingerprints with a test MAE of only 0.21 eV. This improvement in prediction accuracy is partly due to the presence of the PBE gap in the PDOS fingerprint. However, our analysis shows that the pure PDOS fingerprint without the PBE gap still outperforms the structural fingerprints. Using only the PBE gap as feature results in a test MAE of 0.28 eV.

The current results show that the precision of MLbased predictions are highly dependent on the type of target property and the chosen material representation. For some properties, the mapping between atomic structure and property is easier to learn while IOP Publishing

others might require more/deeper information, e.g. in terms of electronic structure fingerprints. Our results clearly demonstrate the potential of encoding electronic structure information into the material fingerprint, and we anticipate more work on this relevant and exciting topic in the future.

# 7. Summary and outlook

We have documented a number of extensions and improvements of the C2DB made in the period 2018-2020. The new developments include: (1) A refined and more stringent workflow for filtering prospective 2D materials and classifying them according to their crystal structure, magnetic state and stability. (2) Improvements of the methodology used to compute certain challenging properties such as the full stiffness tensor, effective masses, G0W0 band structures, and optical absorption spectra. (3) New materials including 216 MXY Janus monolayers and 574 monolayers exfoliated from experimentally known bulk crystals. In addition, ongoing efforts to systematically obtain and characterise bilayers in all possible stacking configurations as well as point defects in the semiconducting monolayers, have been described. (4) New properties including exfoliation energies, spontaneous polarisations, Bader charges, piezoelectric tensors, IR polarisabilities, topological invariants, magnetic exchange couplings, Raman spectra, and SHG spectra. It should be stressed that the C2DB will continue to grow as new structures and properties are being added, and thus the present paper should not be seen as a final report on the C2DB but rather a snapshot of its current state.

In addition to the above mentioned improvements relating to data quantity and quality, the C2DB has been endowed with a comprehensive documentation layer. In particular, all data presented on the C2DB website are now accompanied by an information field that explains the meaning and representation (if applicable) of the data and details how it was calculated thus making the data easier to understand, reproduce, and deploy.

The C2DB has been produced using the ASR in combination with the GPAW electronic structure code and the MyQueue task and workflow scheduling system. The ASR is a newly developed Python-based framework designed for high-throughput materials computations. The highly flexible and modular nature of the ASR and its strong coupling to the well established community-driven ASE project, makes it a versatile framework for both high- and lowthroughput materials simulation projects. The ASR and the C2DB-ASR workflow are distributed as open source code. A detailed documentation of the ASR will be published elsewhere.

While the C2DB itself is solely concerned with the properties of perfect monolayer crystals, ongoing efforts focus on the systematic characterisation of homo-bilayer structures as well as point defects in monolayers. The data resulting from these and other similar projects will be published as separate, independent databases, but will be directly interlinked with the C2DB making it possible to switch between them in a completely seamless fashion. These developments will significantly broaden the scope and usability of the C2DB+ (+ stands for associated databases) that will help theoreticians and experimentalists to navigate one of the most vibrant and rapidly expanding research fields at the crossroads of condensed matter physics, photonics, nanotechnology, and chemistry.

# Data availability statement

The data that support the findings of this study are openly available at the following URL/DOI: https://doi.org/10.11583/DTU.14616660.

## Acknowledgments

The Center for Nanostructured Graphene (CNG) is sponsored by the Danish National Research Foundation, Project DNRF103. This project has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation program Grant Agreement No. 773122 (LIMA) and Grant Agreement No. 951786 (NOMAD CoE). T D acknowledges financial support from the German Research Foundation (DFG Projects No. DE 2749/2-1).

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# 9.3 Paper III: Oxygen Vacancies Nucleate Charged Domain Walls in Ferroelectrics

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Phys. Rev. Lett. **127**, 117601.

## **Oxygen Vacancies Nucleate Charged Domain Walls in Ferroelectrics**

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(Received 17 December 2020; revised 25 June 2021; accepted 12 August 2021; published 9 September 2021)

We study the influence of oxygen vacancies on the formation of charged  $180^{\circ}$  domain walls in ferroelectric BaTiO<sub>3</sub> using first principles calculations. We show that it is favorable for vacancies to assemble in crystallographic planes, and that such clustering is accompanied by the formation of a charged domain wall. The domain wall has negative bound charge, which compensates the nominal positive charge of the vacancies and leads to a vanishing density of free charge at the wall. This is in contrast to the positively charged domain walls, which are nearly completely compensated by free charge from the bulk. The results thus explain the experimentally observed difference in electronic conductivity of the two types of domain walls, as well as the generic prevalence of charged domain walls in ferroelectrics. Moreover, the explicit demonstration of vacancy driven domain wall formation implies that specific charged domain wall configurations may be realized by bottom-up design for use in domain wall based information processing.

DOI: 10.1103/PhysRevLett.127.117601

Domain walls (DWs) in ferroelectric crystals are twodimensional topological defects separating domains of distinct directions of the spontaneous polarization. They are ubiquitous, and significantly affect physical properties [1–3] such as polarization switching [4,5], dielectric permittivity [6,7], and piezoeletric response [8,9]. In addition, DWs are typically highly mobile [10] and their position may be controlled by external electric fields. The versatile properties of DWs [11,12] have thus opened exciting avenues for applications in electronics, such as diodes [13] and nonvolatile memory devices [14,15], and are promising candidates as building blocks for the next generation of photovoltaics [16,17].

The properties of individual DWs strongly depend on the orientation of the spontaneous polarization (**P**) with respect to the DW. When the normal component of **P** changes across the wall, a net bound charge is created in the DW [18], giving rise to electric fields that typically far exceed the coercive field for polarization reorientation. Such a charged domain wall (CDW) would be highly unstable without a mechanism to screen the bound charge [19–21]. As such, unambiguous verification that CDWs are present in proper ferroelectric crystals [18,20,22,23] has led to the conclusion that charged impurities must play a fundamental role in stabilizing CDWs [24].

The role of oxygen vacancies ( $V_{OS}$ ) as a stabilizing agent for CDWs has been studied both experimentally and by simulations [25–31]. In addition, it is known that  $V_{OS}$  may assemble in perovskite lattice planes under certain conditions [32–36]. However, these two effects have generally been regarded as unrelated, as the most widely accepted view is that  $V_{OS}$  serve to stabilize CDWs that have formed spontaneously, or by other means. However, previous studies have also shown that  $V_{OS}$  located at axial sites of TiO<sub>6</sub> octahedra in PbTiO<sub>3</sub> create a displacement of the Ti atom [37] and a corresponding dipole moment. This suggests an alternative view in which vacancies may in fact facilitate the formation of CDWs instead of simply delivering a stabilizing charge distribution. The notion that V<sub>OS</sub> may directly nucleate CDWs has broad implications for the understanding and application of CDWs in general. However, the formation mechanisms of CDWs remain elusive due to the apparent strong instability of CDWs and the technical challenges associated with carrying out *ab initio* studies of CDWs in both pristine and doped ferroelectrics.

In this Letter, we describe results from first-principles calculations of  $180^{\circ}$  domain walls in BaTiO<sub>3</sub> showing that it is favorable for oxygen vacancies to accumulate in planes, and that such accumulation gives rise to CDWs forming spontaneously. In particular, we demonstrate that the screening of the bound charge of head-to-head (HH) CDWs occurs through the filling of local conduction bands, regardless of vacancies. The negative charge at tail-to-tail (TT) CDWs is screened by the positive charge from the vacancies, thus quenching the *p*-type conductivity characterizing TT CDWs in the pristine system.

BaTiO<sub>3</sub> presents a phase transition from cubic  $(Pm\bar{3}m)$  to tetragonal (P4mm) structure at ~404 K, a subsequent first-order transition to an orthorhombic (Amm2) structure at ~273 K and finally another first-order transition at ~183 K to a rhombohedral (R3m) structure with polarization in the (111) direction [38,39]. Here we will focus on the tetragonal phase, but expect that the conclusions will hold true for other phases and similar compounds.

0031-9007/21/127(11)/117601(6)

Our calculations were done in the framework of density functional theory (DFT), implemented in the GPAW electronic structure package [40,41] using the projectoraugmented wave method [42], the local density approximation (LDA) [43] and a plane wave basis. We used a plane-wave cutoff of 700 eV and a  $\Gamma$ -centered Monkhorst-Pack *k*-point grid with a density of 6 Å. Forces were typically relaxed below 0.01 eV/Å (for details on the atomic structure and Born effective charges see the Supplemental Material [44]).

We begin by considering 180° CDWs in BaTiO<sub>3</sub> without any vacancies. This will serve as a reference system that allows us to gain insight into the influence of vacancies on the electronic properties of CDWs. In addition, it is known that a dilute distribution of CDWs in oxide perovskites can be stable and robust in defect-free thin films [22]. We thus construct a  $1 \times 1 \times 16$  supercell of tetragonal BaTiO<sub>3</sub> and divide it into two areas of opposite polarization parallel to the long axis of the supercell. The polarization of the subcell  $\alpha$  can be written as  $P_{i,\alpha} = (1/\Omega) \sum_{j,a \in \alpha} Z_{ij}^{*a} d_j^a$ [47]. Here  $\Omega$  is the unit cell volume,  $d_i^a$  is the displacement of atom a with respect to its position in the centrosymmetric structure in direction j,  $Z_{ij}^{*a}$  is the Born effective charge tensor of atom a and the sum runs over atoms in unit cell  $\alpha$ . Since the  $Z_{ij}^{*a}$  depend on the local electronic structure, we average the tensors obtained for the cubic and tetragonal phases of BaTiO<sub>3</sub> [44]. The atomic displacements of the supercell are smoothed so the polarization profile becomes  $P_{\alpha} = P_0 \tanh(z_{\alpha}/\delta)$ , where  $z_{\alpha}$  is the center position of unit cell  $\alpha$  and  $P_0$  is the magnitude of the calculated bulk polarization,  $0.24 \text{ C/m}^2$ , which is in good agreement with the experimental value of  $0.26 \text{ C/m}^2$ [48,49] and computational works using the LDA [50,51]. We set  $\delta = 1.75$  as the structural width of the wall and adopt BaO centered DWs, since the  $V_{OS}$  used in the simulations described below are more stable at these planes. We did not relax the structure, as it would so be driven into a single domain. Finally, we emphasize that, although this structure is a somewhat artificial representation of a CDW, its primary intention is to unravel the basic principles of screening in the system.

Figure 1 shows a schematic representation of the supercell, including the profile of polarization per unit cell as calculated following the procedure in Ref. [47]. We also show the bound charge density  $\rho_b$  arising from the polarization profile, as well as the electrostatic potential obtained from DFT. As expected, a positive (negative) bound charge density peak is located at the HH (TT) wall and is accompanied by a minimum (maximum) of the potential. The integrated bound charge density at each of the walls has magnitude  $2P_0$  by construction and the potential energy difference ( $\Delta V$ ) between the walls is linear, the electric fields inside the two domains can be



FIG. 1. Properties of the unrelaxed CDWs in a  $1 \times 1 \times 16$  supercell. Top: schematic atomic structure with exagerated displacements. The blue arrows indicate the direction of polarization; green, blue and red spheres indicate Ba, Ti, and O atoms, respectively. The dots indicate positions of Ti atoms in the individual unit cells. Second from top: polarization profile of the supercell. Second from bottom: bound  $\rho_b$  and smoothed free  $\rho_f$  charge density. Bottom: electrostatic potential energy v(z) averaged over the plane orthogonal to z and total charge density  $\rho$  obtained from a sliding window average.

regarded as constant and the *total* charge density at the CDWs are then related to the potential energy difference by Gauss law as

$$\sigma_{\rm tot}(d) = \frac{\varepsilon_0 \Delta V/e}{d},\tag{1}$$

where *d* is the distance between the walls and  $\varepsilon_0$  is the vacuum permittivity. Inserting the values obtained from DFT yields a charge density of  $\sigma_{tot} = 0.0048 \text{ C/m}^2$ . This is 2 orders of magnitude smaller than the bound charge indicating that the bound charge is almost fully compensated by free charge.

The mechanism behind the screening can be envisioned by considering two CDWs in close proximity with bound charge densities  $\pm 2P_0$ . Without any screening mechanism, the electric field between the walls would be determined by the polarization  $P_0$  only. However, if the distance between the walls is increased, the potential difference between the walls increases (due to the constant electric field) and the conduction (valence) bands are lowered (raised) at the HH (TT) until they are aligned [22,23,52]. At this point, charge will be transferred between the walls to align the Fermi levels at the walls, and the potential energy difference will be pinned at the value of the band gap. Thus, when the difference between the walls *d* is increased in Eq. (1),  $\Delta V$  will remain fixed while the electric field and charge density at the walls decrease.

For CDWs at large separation, the charge density will thus be finite, albeit orders of magnitude smaller than the bound charge. In our calculations we obtain a LDA band gap for BaTiO<sub>3</sub> of 1.9 eV, which is in agreement with the potential difference of 2.3 eV. Note that for such a "pristine" CDW structure, the total charge density at the walls is roughly determined by the band gap and the distance between the walls, whenever *d* exceeds the "short-circuit distance"  $d_{\rm sc} = \varepsilon_0 E_{\rm gap}/2eP_0$ . Integrating the charge density through the CDW (obtained from a sliding window average (see Supplemental Material [44] for details) yields 0.005 C/m<sup>2</sup>, which is in agreement with the result obtained from Eq. (1). We have checked that the calculated potential difference is the same for  $1 \times 1 \times 8$  and  $1 \times 1 \times 12$  unit cell systems.

The screening described above is more clearly visualized from the band structure and projected density of states (PDOS) resolved in individual unit cells, shown in Fig. 2. Given the indirect band gap in BaTiO<sub>3</sub>, the electron (hole) doping at the HH (TT) walls occurs at different locations in the 2D Brillouin zone. The band structure shows that the  $\Gamma$ point mediates the electron doping at the HH wall, whereas the hole doping mainly occurs at the M point. Resolving the PDOS in contributions from different unit cells yields a profile reminiscent of the electrostatic potential. For a given unit cell, the PDOS resembles that of bulk BaTiO<sub>3</sub>, but shifted according to the local value of the electrostatic potential. The PDOS also implies that charge carriers in the vicinity of the Fermi level are strictly localized at the two CDWs as expected, which implies that we can calculate the free charge density at the HH (TT) wall by adding the norm-squared wave functions of the conductive states below(above) the Fermi level (see Supplemental Material for details [44]). This procedure yields a free charge density of  $\pm 0.40$  C/m<sup>2</sup> at the two walls, which (almost) cancel the bound charge density at the two walls as anticipated. The smoothed free charge density is shown in Fig. 1 and exhibits a profile that compensates the bound charge.

In order to study the role of  $V_{\Omega}s$  in the formation of CDWs, we use a bulk, single domain represented in a  $3 \times$  $3 \times 8$  supercell as the starting point. We find the most stable position for a planar distribution of oxygen vacancies is the BaO plane (see Fig. S2 in the Supplemental Material [44]), although the formation energies of a single vacancy are similar in both planes [53]. We therefore begin by introducing one vacancy into a BaO plane, and fully relax the supercell (see the top part of Fig. 3). Following this relaxation, we see that the vacancy strongly repels the neighboring Ti atom towards the opposite direction of the initial polarization, thereby decreasing the local polarization, as shown in Fig. 3. This occurs through the breaking of the bonding orbital formed by the emptied O p and the Ti  $t_{2a}$ , in a similar scenario to that described by Park *et al.* for PbTiO<sub>3</sub> [37]. We note that we obtain the same configuration if we set an artificial DW in a  $3 \times 3 \times 8$  supercell, put a vacancy on it and relax it.

We will now show that it is favorable for additional vacancies to migrate to a plane with an initial amount of vacancies. To this aim, we define the energy cost of adding the *i*th vacancy in unit cell  $\alpha$  relative to the energy cost of adding a single vacancy in a bulk BaO plane:

$$\Delta E_{i\alpha} = E_{i\alpha} - E_{(i-1)\alpha_0} - (E_1 - E_{\text{bulk}}), \quad i > 1, \quad (2)$$

where  $E_{\text{bulk}}$  is the energy of a single domain without vacancies,  $E_1$  is the energy of the supercell with a single vacancy in any BaO plane, and  $E_{i\alpha}$  is the energy of the supercell with the *i*th vacancy placed in unit cell  $\alpha$  and i - 1 vacancies at their optimal positions ( $\alpha_0$ ).

We first calculate  $E_{1\alpha}$ , starting with a fully relaxed configuration with a vacancy in the BaO plane, and calculate the energy of the structure with a second vacancy in all the possible BaO planes. The result, shown in Fig. 3, shows that the optimal position of the second vacancy is the plane where the first vacancy was placed. We have checked that vacancies in the TiO<sub>2</sub> plane are always more unfavorable (see Fig S3 in the Supplemental Material [44]). We



FIG. 2. Left: projected band structure of the unrelaxed  $1 \times 1 \times 16$  supercell with no vacancies. Right, the projected density of states resolved in individual unit cells.



FIG. 3. Top: Schematic illustration of the vacancy migration that leads to domain wall formation in a  $3 \times 3 \times 8$  supercell. The crosses indicate the lowest formation energy positions at each BaO plane. Below, we show the energy cost  $\Delta E_{i\alpha}$  for the *i*th vacancy at position  $\alpha$  (see text) given that i - 1 vacancies are situated at their optimal positions.  $P_{z,i\alpha}$  is the polarization profile of the supercell with *i* vacancies at their optimal positions. The bottom panel shows the smoothed free ( $\rho_f$ ) charge density profiles for the relaxed supercell with one, two, and three vacancies at the central BaO plane.

then calculate  $E_{2\alpha}$  by the same procedure starting with the relaxed structure with two vacancies in a single BaO plane. Again, the optimal position is the BaO plane where the other vacancies are located. And the same happens to the fourth vacancy, although we see that it experiences a weaker attraction to the three initial vacancies [see Fig. 3], indicating that once enough vacancies needed to form the wall are assembled, the attraction for further vacancies decreases. This attraction between vacancies may seem counterintuitive, since they present a charge of +2eand should thus repel one another. However, the vacancies induce a polarization that initiates a negatively charged DW, which in turn provides the attractive long-ranged force between the vacancies. This process is evident in Fig. 3, where we show the polarization profiles for 1, 2, and 3 vacancies at their optimal positions in the third panel, starting from the top. The first vacancy introduces a local polarization reminiscent of a negatively charged domain wall, attracting the next vacancy. When additional

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vacancies diffuse to the optimal position at the wall the local polarization is distorted further, until a TT DW is fully formed. This suggests that accumulation of oxygen vacancies in planes occurs naturally in the material. Depending on the initial distribution of vacancies in the crystal, they could potentially accumulate in alternative plane geometries creating other types of DWs such as 90 degree walls [54].

In our simulations a single vacancy corresponds to a 11% oxygen depletion in a single BaO plane. It is natural to ask whether our findings will hold true at realistic vacancy distributions. For a random distribution of vacancies there will inevitably be some planes with a higher concentration than others, which will act as sinks for vacancies of the neighboring environment. The actual accumulation will be mediated through thermally assisted diffusion, however, a quantitative estimation of diffusion rates is beyond the scope of this work.

It is instructive to compare the smoothed free charge density profiles shown in Fig. 3 during the DW formation process, with the case without vacancies shown in Fig. 1. In all cases we see a similar picture at the HH wall, where the negative free charge screens the positive bound charge. In contrast, as the TT wall is formed it presents nearly no free charge since the bound charge already compensates the positive charge of the  $V_{O}s$ . In fact, the apparent finite charge at the TT wall in Fig. 3 is nearly exclusively an artifact of the finite supercell size as shown in the Supplemental Material [44], where we also show the raw charge densities used to calculate smoothed free charge profiles in Fig. 3. Once seeded, the HH-TT DW pair are structurally protected topological defects. As shown in Fig. 1, the HH wall is not fully screened by free charge and this enforces a net negative charge in the TT wall area. Because of charge neutrality we have  $\sigma_f + 2en_{\text{vac}} = 0$ , where  $\sigma_f$  is the total free charge in the supercell and  $n_{\rm vac}$  the vacancy number at the wall. This is verified in the increase of free charge at the TT wall at increasing  $n_{\rm vac}$ , as shown in Fig. 3 and Table S3 in the Supplemental Material [44]. In addition the complete screening for well separated walls implies  $\sigma_{f,HH} \sim \sigma_{b,HH}$  and we conclude that the optimal vacancy density at the wall, when  $\sigma_{f,TT} = 0$ , is given by  $n_{\rm vac.0} \sim (P_0/e)$ . In our system this number lies between two and three vacancies per supercell. Figure 3 suggests the concentration of DW vacancies saturates once the wall is formed. As additional vacancies provide a localized screening charge for the TT bound charge, the ability of the TT wall to conduct is very limited, in agreement with experiments [24]. Moreover, such extra free charge will be manifestly delocalized, unlike the pristine wall free charge (see Fig. S4 in the Supplemental Material [44]), reducing the potential difference between walls (see Fig. S5 [44]) and significantly increasing their stability. Compared to the pristine case, the conductivity mechanism of the HH wall remains essentially unaffected though; Ti  $t_{2q}$  states from the conduction band shift below the Fermi level in the HH wall area, similarly to the pristine system (see Figs. S1 and S6 in Ref. [44]).

In conclusion, we have shown that, having an initial oxygen vacancy cluster in tetragonal BaTiO<sub>3</sub>, it is favorable for other vacancies to migrate to the BaO plane defined by this cluster and that a TT domain wall is formed in the process. The driving force is the negative bound charge emerging at the TT wall. It naturally follows from our calculations that oxygen vacancies are attracted to TT DWs, which has already been suggested in the past [24,32]. However, the fact that oxygen vacancies play a critical role in the formation of CDWs has not been demonstrated previously and provides a significant indication as to why and how CDWs form. Moreover, the implications of this mechanism are potentially far reaching, since it suggests that particular CDW distributions may be accomplished by simply seeding a ferroelectric with a suitable distribution of vacancies. Such control will be a crucial ingredient for the future development of domain wall nanoelectronics.

T.O. and U.P. were supported by the Villum Foundation, Grant No. 00028145.

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## Supplemental Materials for: Vacancy driven nucleation of charged domain walls in ferroelectrics

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#### ADDITIONAL STRUCTURAL DETAILS

As building blocks of our supercells we use a relaxed tetragonal BaTiO<sub>3</sub> unit cell with lattice parameters and the atomic positions indicated in Table S1. The tetragonality of the structure is 1.010, in very good agreement with experimental value of 1.011 [1, 2]. We calculate the Born effective charges for this structure above as well as for the cubic phase with a lattice parameter of a = 3.946 Å, which corresponds to a cubic structure with the same volume of as the relaxed tetragonal structure. The non-vanishing components of the calculated Born effective charge tensors are listed in Table S2. The results are in close agreement with [3]. The Born effective charge tensor applied in the present work is obtained by averaging these two tensors.

#### FREE CHARGE DENSITY CALCULATION METHOD

In order to calculate the free charge density across the supercell long axis plotted in Figs. 1 and 3 of the main text we use the following expression:

$$\rho_f(z) = \rho_{f,\text{TT}}(z) + \rho_{f,\text{HH}}(z) \tag{1}$$

where

$$\rho_{f,\mathrm{TT}}(z) = \frac{e}{AN_k} \sum_{\mathbf{k}} \int dx dy \left( \sum_{n|\epsilon_{\mathrm{F}} < \epsilon_{n\mathbf{k}} < \epsilon_{\mathrm{VBM}}} |\psi_{n\mathbf{k}}^{\mathrm{TT}}(\mathbf{r})|^2 + \sum_{n|\epsilon_{\mathrm{CDM}} < \epsilon_{n\mathbf{k}} < \epsilon_{\mathrm{F}}} |\psi_{n\mathbf{k}}^{\mathrm{TT}}(\mathbf{r})|^2 \right)$$
(2)

and

$$\rho_{f,\text{HH}}(z) = \frac{e}{AN_k} \sum_{\mathbf{k}} \int dx dy \sum_{n|\varepsilon_{\text{CDM}} < \varepsilon_{n\mathbf{k}} < \varepsilon_{\text{F}}} |\psi_{n\mathbf{k}}^{\text{HH}}(\mathbf{r})|^2$$
(3)

here *A* is the supercell area parallel to the walls,  $N_k$  is the number of k points, *x* and *y* are the coordinates parallel to the walls.  $n_{E_F}$ ,  $n_{vBM}^*$  and  $n_{CBM}^*$  represent the Fermi level, valence band maximum and conduction band minimum respectively.  $\psi_{nk}^{TT}$  and  $\psi_{nk}^{TT}$ are wave functions at the  $n^{th}$  band at k point **k**, which satisfy  $\int_{L/2-d}^{L/2+d} \int dx dy \psi_{nk}^{RT}(\mathbf{r})|^2 dz > 0.5$  and  $\int_{-d}^{-d} \int dx dy \psi_{nk}^{HH}(\mathbf{r})|^2 dz > 0.5$ , respectively; *L* is the supercell length in *z* direction and *d* is chosen convienently. In order to ensure an accurate sampling of the Brillouin zone, we calculated it applying eq. 1 on high k point densities. In the pristine case (as in figure 1 in the main text), the right summand in eq. 2 vanishes as there are no free electrons at the TT wall area; while in the case with vacancies (as in figure 3 of the main text or figure S4) it is the left summand on the right side of eq. 2 that vanishes, as all states below the Fermi level are occupied in the TT wall area.

TABLE S1: Relaxed BaTiO<sub>3</sub> tetragonal structure with space group P4mm (no. 99) lattice parameters a = b = 3.933 Å and a = 3.971 Å.

Atom	Wyckoff p.	x	у	z
Ba	1a	0.000	0.000	0.010
Ti	1b	0.500	0.500	0.521
0	1b	0.500	0.500	-0.009
0	2c	0.500	0.000	0.497

Fetragonal					
	xx,yy			zz	
$Z^*_{Ba}$	2.74			2.79	
$Z_{Ti}^{*}$	7.11			6.34	
		$\perp$			
$Z^*_{O_1}$		-2.09			-5.05
	Ι		II		
$Z^*_{O_2}$	-1.94		-2.15		-5.60
Cubic					
	xx,yy,zz				

TABLE S2: Non-vanishing components of Born-effective charge tensors obtained for  $BaTiO_3$  tetragonal and cubic structures. Parallel and perpendicular directions are defined taking as a reference the Ti-O band directions, as done in Ref 3. For the O atoms at 2c positions in the tetragonal structure, we define the perpendicular (to the Ti-O bond) I and II directions as being, in addition, parallel and perpendicular to the tetragonal axis, respectively.

#### TOTAL NET CHARGE AT THE WALLS

 $Z_{Ba}^*$ 

 $Z_{Ti}^{*}$ 

 $Z_0^*$ 

2.75

7.28

-2.16

To gain insight on the charge distribution at the DWs we calculate the charge density per unit length in the supercell, n(z). Within the projector-augmented wave formalism the all electron density  $n_e(z)$  can be obtained, and we can represent the nuclear charges as point charges. Then, after integrating the electronic density over the coordinates parallel to the domain walls we get:

$$\rho(z) = -\rho_e(z) + \sum_i Z_i \delta(z - z_i), \tag{4}$$

where  $n_e(z)$  is the all-electron density,  $z_i$  are the coordinates of the nuclei and  $Z_i$  are the nuclear charges. The charge density is rapidly varying at the atomic scale due to the localized nuclei and core electrons. Any integral of Eq. 4 will thus depend strongly on the domain of integration and the charge residing at the domain walls cannot be obtained in any sensible way. To accommodate this problem we consider the sliding window average for the density and in addition we convolute the nuclear charge with a Gaussian function. We integrate over the directions perpendicular to the wall and then obtain the averaged onedimensional charge density

$$\tilde{\rho}(z) = \frac{1}{c} \int_{z-c/2}^{z+c/2} \left( \rho_e(z') + \sum_i Z_i \delta(z-z_i-z') g(z') \right) dz',$$
(5)

where we defined the Gaussian distribution as  $g(x) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left\{\frac{-x^2}{2\sigma^2}\right\}$  with  $\sigma = 0.0877$ Å and *c* is the unit cell length. This way we obtain the smoothened total charge density shown in Fig. 1 in the main text.

At the bottom part of Fig. 1 in the main text we see wide regions on both sides of the walls where the charge density is constant. This allows for a well-defined computation of the net charge within the wall regions. We find a net charge density of  $-0.005 \text{ C/m}^2$  at the TT wall area and the exact opposite,  $0.005 \text{ C/m}^2$  at the HH area. Note that, if the supercell were insulating we would see, at any region enclosing one domain wall, an absolute net charge density of  $2P_0 \approx 0.48 \text{ C/m}^2$ , where  $P_0$  is the absolute value of the spontaneous polarization of the bulk crystal ( $P_0 = 0.24 \text{ C/m}^2$  for the tetragonal unit cell in our calculations). This indicates nearly full charge compensation of the bound charge by free carriers. In addition, the bound charge enclosed at the walls is  $0.40 \text{ C/m}^2$ . This is expected from the fact that the definition of Born effective charges becomes problematic in metal-ferroelectric interfaces [4]. It is instructuve to transform the charge densities at the walls into atomic units. We have for the net charge at the wall, for  $a=b \approx 3.9$ Å square unit cell parameter (area =  $55.4 a_0^2$ ), and taking into account that  $1 e = 1.602 \times 10^{-16}$  C:  $\sigma_{tori} = \frac{0.05}{0.55} ea_0^{-2}$ , which means that per unit cell area, the CDWs present a net charge of about 0.005 *e*.

Ш

-5.71

-0.1

FIG. S1: PDOS at the HH wall of the 1x1x16 supercell containing a HH and TT wall. Ti  $t_{2g}$  states, Ti non- $t_{2g}$  states and the rest are differentiated with different colors. The Fermi level is set as the origin for the energies.

E-E<sub>F</sub> (eV)

-0.3

Finally, we also apply an analogous sliding window average to the electrostatic potential to obtain the smooth function  $\tilde{v}(z)$ 

$$\tilde{v}(z) = \frac{1}{c} \int_{z-c/2}^{z+c/2} v(z') dz'$$
(6)

where v is the electrostatic potential, which includes the nuclear potential as well as the Hartree potential.

PDOS (eV<sup>-1</sup>)

#### APPLICATION OF THE PSEUDO-CAPACITOR MODEL

In order to apply the Eq. 1 in the main text on the present system, we calculate the electrostatic potential generated by a net charge density of  $\pm 0.005 \text{ C/m}^2$  residing at the two walls. We have

$$\Delta V = \frac{\sigma_{tot}d}{\varepsilon_0} \tag{7}$$

and obtain (in atomic units)  $\sigma_{tat} = \frac{0.005}{55.4} ea_0^{-2}$ ;  $d=63.54 a_0$ ;  $\varepsilon_0 = \frac{1}{4\pi} e^2 a_0^{-1} E_h^{-1}$ . We thus have  $\Delta V \approx 0.007 E_h e^{-1}$ , so  $e\Delta V \approx 2.1$  eV, which is essentially matching the electrostatic energy difference (2.3 eV) between the walls in Fig. 1 of the main text.

#### PDOS OF 1X1X16 SUPERCELL WITHOUT VACANCIES

In Fig. S1 we show the projected density of electronic states (PDOS) at the HH wall in the 1x1x16 system with no vacancies and two charged domain walls. We see that  $t_{2g} d$  orbitals account for the majority of electronic states just below the Fermi level and therefore host the conduction band electrons that account for the conductivity of the HH wall.

#### DETERMINING THE OPTIMAL CRYSTALLOGRAPHIC PLANES FOR THE VACANCIES

We take the 1x1x16 supercell containing a HH and TT wall as described in the main text and distinguish between two cases: one with BaO centered walls and another with TiO<sub>2</sub> centered walls. Then we remove an oxygen atom from the TT wall in each supercell and relax the forces. Both relaxed configurations are shown in Fig. S2. For the Ba centered case, there are no oxygen atoms left at the TT wall, while in the Ti centered case half of the oxygens are present after setting the vacancies. We find that the BaO centered walls with vacancies are more stable by about 0.5 eV. This occurs because the total depletion of oxygens at the TT wall allows for a stronger polarization change at the wall. Hence we select a BaO plane in the bulk supercell for the position of the initial V<sub>0</sub> in our stability calculations. In fact, the TT wall grows naturally from an initial bulk configuration where an oxygen vacancy plane has been placed in a BaO plane. In Fig. S3 we show the energy cost profiles for adding a second oxygen vacancy in Ti planes, once one vacancy has been pinned at a BaO plane. The calculations are repeated for the case with three initial oxygen vacancies at the BaO plane. We see that the potential energy well towards the BaO plane is mimicked by the TiO<sub>2</sub> planes as well, but their energy is higher compared to the BaO planes, and therefore less favourable.


FIG. S2: The two DW configurations in 1x1x16 supercells used in order to determine the crystallographic plane where the oxygen vacancies are placed in the calculations. In a) BaO centered TT wall with vacancies, in b) TiO<sub>2</sub> centered TT wall with vacancies. The forces of both structures have been relaxed.



FIG. S3: Energy cost profiles for the  $i^{th}$  vacancy at  $\alpha$  unit cell within the 3x3x8 supercell (the energies are defined as for Fig. 3 in the main text) at Ba and Ti planes. The case where two (three) vacancies are fixed at a wall position is shown at the top (bottom), and the energies are calculated with respect to that of the relaxed configuration with two and three vacancies at the BaO plane wall, respectively.

#### FREE CHARGE PROFILES ALONG THE WALL FORMATION PROCESS

In table S3 we show the free charges at the relaxed structure in a 2x2x8 supercell, separated by head-to-head and tail-to-tail regions. We calculate the free charges by integrating eqs. 2 and 3 separately.

In figure S4 we illustrate the effect of using a truncated integration in eq.1, wherein we do d = L/6 in the wave functions entering eqs. 2 and 3. The result of the truncated integration for two DW vacancies in a 3x3x8 supercell are shown at the top, while the middle panel shows the full integration (d = L/4) results. We see the truncated integration (which is used for the free charge plots in fig 3 of the main text) avoids the artificial overlap of free charges originated at the different walls due to the small supercell size. In the lower panels we illustrate the effect of using a larger supercell for free charge integration (doing again d = L/4), comparing the HH wall free charge profiles with one DW vacancy in 2x2x8 and 2x2x16 supercells with structures relaxed: we see the HH free charge localizes within the wall, more efficiently the larger the simulation cell. In contrast, the free charge at the TT wall generated to compensate the excess positive charge of vacancies it very delocalized. For the reference we also show at the bottom panel the polarization profile of the relaxed 2x2x16 supercell with a DW vacancy: we see that, despite being a much sharper DW, the free charge of the TT wall tends to spread massively in the supercell.

#### ELECTRONIC PROPERTIES OF RELAXED SUPERCELLS WITH OXYGEN VACANCIES

To demonstrate the influence of the  $V_O$  on the electronic properties of the HH wall, the 1x1x16 above is not sufficient to study the TT wall, since the  $V_O$  concentration is unrealistically large. The bound charge at the wall thus cannot compensate the positive charge and electrons migrate to the conduction band. Therefore, we adopt the 3x3x8 supercell described in the main text to show the influence of vacancies on the full system. In Fig. S5 we show the density of states per TiO<sub>2</sub> plane with two  $V_O$ 



FIG. S4: Free charge densities obtained by integrating the squares of wave functions using eq. 1 (see details in the text). Starting from the top, truncated and non-truncated charge densities in a 3x3x8 system with 2 wall vacancies. In the next two panels, HH and TT wall free charges for relaxed 2x2x8 and 2x2x16 supercells with a DW vacancy. At the bottom, polarization profile of the relaxed 2x2x16 supercell with a DW vacancy

Vacancies at TT wall	HH wall free charge $(e)$	TT wall free charge (e)
0	0	0
1	1.32	0.68
2	3.15	0.85
3	4.28	1.72

TABLE S3: Calculated free charge at head-to-head and tail-to-tail domain wall areas.



FIG. S5: Density of states of the relaxed 3x3x8 supercell with a HH and TT wall, with two vacancies at the latter, projected into the atomic orbitals of TiO<sub>2</sub> planes. The Fermi level is set as the origin for the energies.

at the TT wall plane: there are HH wall states below the Fermi level as in the vacancy-free case, ensuring its *n* type conductivity and showing the little influence of vacancies on its conducting properties. In the TT wall area some delocalized free charge has emerged due to the vacancy positive charge, flattening the electrostatic potential between walls.

To see the pure influence of vacancies on the HH wall we work again with the 1x1x16 supercell containing a single oxygen vacancy at a BaO plane. We then calculate the PDOS at the HH wall, in a similar way as done in the previous section with for the pristine system. As shown in Fig. S6 we find that, again, Ti  $t_{2g}$  states dominate this region of the DOS, suggesting little influence of the V<sub>O</sub> on the (*n* type) conductivity mechanism of the HH walls.



FIG. S6: PDOS at the HH wall of the relaxed  $1 \times 1 \times 16$  supercell containing a HH and TT wall and an oxygen vacancy at the latter. Ti  $t_{2g}$  states, Ti non- $t_{2g}$  states and the rest are differentiated with different colors. The Fermi level is set as the origin for the energies.

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### APPENDIX A

# Appendix A: Berry phase formula for the polarization density

Here we show how to obtain the expression for polarization presented in eqs. (5.26-5.28). Specificially we derive a now expression for the electronic contribution starting from the expression presented eq. 5.24. While the ladder expression is theoretical correct it is not very practical for numerical computations. The expression derived here is implemented in the GPAW code[37] and it is the method used for all computations related to polarization calculations in this thesis. To show the validity eqs. (5.26-5.28) expression we start from eq. 5.24. For purposes that will be clear later we focus on the polarization in the *n*'th direction:

$$\boldsymbol{n} \cdot \boldsymbol{P}_{el}(\lambda) = -\frac{e}{NV} \operatorname{Im}\left(\sum_{m}^{occ} \sum_{\boldsymbol{k} \in \mathrm{BZ}} \langle u_{m\boldsymbol{k}}^{(\lambda)} | \boldsymbol{n} \cdot \nabla_{(\boldsymbol{k})} | u_{m\boldsymbol{k}}^{(\lambda)} \rangle\right)$$
(A.1)

The derivatives can be expanded to first order as:

$$\nabla_{\boldsymbol{k}} |u_{n\boldsymbol{k}}^{\lambda}\rangle = \frac{|u_{\boldsymbol{m}\boldsymbol{k}+\boldsymbol{\delta}\boldsymbol{k}}^{\lambda}\rangle - |u_{\boldsymbol{m}\boldsymbol{k}}^{\lambda}\rangle}{\delta\boldsymbol{k}}$$
(A.2)

where  $\frac{1}{\delta \mathbf{k}} = \hat{\mathbf{k}} \frac{1}{\Delta k}$ . We end up with a product of the form  $\hat{\mathbf{n}} \cdot \frac{1}{\delta \mathbf{k}} = \hat{\mathbf{n}} \cdot \hat{\mathbf{k}} \frac{1}{\Delta k_{\parallel}} = \frac{1}{\Delta k_{\parallel}}$ , where  $\Delta k_{\parallel}$  is the **k**-point spacing in the direction parallel to  $\hat{n}$ . By plugging eq. A.2 into eq. (A.1) we obtain:

$$\boldsymbol{n} \cdot \boldsymbol{P}_{el}(\lambda) = -\frac{e}{NV} \operatorname{Im} \left( \sum_{\boldsymbol{k}_{\perp} \in \mathrm{BZ}} \sum_{\boldsymbol{k}_{\parallel} \in \mathrm{BZ}} \sum_{m} \frac{1}{\Delta k_{\parallel}} \left( \langle u_{m\boldsymbol{k}+\delta \boldsymbol{k}} | u_{m\boldsymbol{k}} \rangle - 1 \right) \right)$$
(A.3)

The **k**-point spacing can be rewritten as  $\Delta k_{\parallel} = \frac{|\mathbf{b}_{\mathrm{BZ}}|}{N_{\parallel}} = \frac{2\pi}{|\mathbf{a}_{\parallel}|N_{\parallel}}$ . Where  $|\mathbf{b}|_{\mathrm{BZ}}$  and  $|\mathbf{a}_{\parallel}|$  are the length in the *n*'th direction of the Brillioun zone and the unit cell respectively.  $N_{\parallel}$  Denotes the total number of **k**-points along the direction parallel to  $\hat{\mathbf{n}}$ . We now substitute the sum over occupied bands with a trace, such that eq. (A.3) becomes:

$$\boldsymbol{n} \cdot \boldsymbol{P}_{el}(\lambda) = -\frac{e|\boldsymbol{a}_{\parallel}|}{2\pi N_{\perp} V} \operatorname{Im}\left(\sum_{\boldsymbol{k}_{\perp} \in \mathrm{BZ}} \sum_{\boldsymbol{k}_{\parallel} \in \mathrm{BZ}} \operatorname{Tr}_{\mathrm{occ}}\left(\langle u_{n\boldsymbol{k}+\delta\boldsymbol{k}} | u_{m\boldsymbol{k}} \rangle - 1\right)\right).$$
(A.4)

Here the trace is in the space of band indices (n, m) and the subscript indicates that only occupied states are included. We will now make use of the following matrix identity  $S - I \approx \ln(S)$ , where I is the identity matrix and S is an matrix where the elements are close to those in the identity matrix. Now eq. (A.4) becomes:

$$\boldsymbol{n} \cdot \boldsymbol{P}_{el}(\lambda) = -\frac{e|\boldsymbol{a}_{\parallel}|}{2\pi N_{\perp} V} \operatorname{Im}\left(\sum_{\boldsymbol{k}_{\perp} \in \mathrm{BZ}} \sum_{\boldsymbol{k}_{\parallel} \in \mathrm{BZ}} \operatorname{Tr}_{\mathrm{occ}}\left(\ln\left(\langle u_{n\boldsymbol{k}+\delta\boldsymbol{k}} | u_{m\boldsymbol{k}} \rangle\right)\right)\right).$$
(A.5)

The equation above can be rewritten by using the identity  $\operatorname{Tr}(\ln(S)) = \ln(\det(S))$ , where det is the determinant. Now eq. A.5 can be written as:

$$\boldsymbol{n} \cdot \boldsymbol{P}_{el}(\lambda) = -\frac{e|\boldsymbol{a}_{\parallel}|}{2\pi N_{\perp} V} \operatorname{Im}\left(\sum_{\boldsymbol{k}_{\perp} \in \mathrm{BZ}} \sum_{\boldsymbol{k}_{\parallel} \in \mathrm{BZ}} \ln\left(\operatorname{det}_{\operatorname{occ}}\left(\langle u_{n\boldsymbol{k}+\delta\boldsymbol{k}} | u_{m\boldsymbol{k}} \rangle\right)\right)\right)$$
(A.6)

We now use the fact that the sum over logarithms is equivalent to take the logarithm of a product to rewrite eq. (A.6) as:

$$\boldsymbol{n} \cdot \boldsymbol{P}_{el}(\lambda) = -\frac{e|\boldsymbol{a}_{\parallel}|}{2\pi N_{\perp} V} \operatorname{Im}\left(\sum_{\boldsymbol{k}_{\perp} \in \mathrm{BZ}} \sum_{\boldsymbol{k}_{\parallel} \in \mathrm{BZ}} \ln \prod_{\boldsymbol{k}} \operatorname{det}_{\operatorname{occ}}\left(\langle u_{n\boldsymbol{k}+\delta\boldsymbol{k}} | u_{m\boldsymbol{k}} \rangle\right)\right)$$
(A.7)

We now change notation with respect to the product over k points to make it explicit that it is a product of states along a string:

$$\boldsymbol{n} \cdot \boldsymbol{P}_{el}(\lambda) = -\frac{e|\boldsymbol{a}_{\parallel}|}{2\pi N_{\perp} V} \operatorname{Im}\left(\sum_{\boldsymbol{k}\perp\in\mathrm{BZ}} \ln\prod_{j=0}^{N_{\boldsymbol{k}\parallel\boldsymbol{b}_{l}}-1} \operatorname{det}_{\operatorname{occ}}\left(\langle u_{n\boldsymbol{k}+j\delta\boldsymbol{k}}|u_{m\boldsymbol{k}+(j+1)\delta\boldsymbol{k}}\rangle\right)\right)$$
(A.8)

The electronic contribution to the polarization can then be written as:

$$\boldsymbol{P}_{\rm el} = -\frac{e}{2\pi V} \sum_{l} \boldsymbol{a}_{l} \phi_{l}^{el} \tag{A.9}$$

$$\phi_l^{el} = \operatorname{Im}\left(\frac{1}{N_\perp} \sum_{\boldsymbol{k}\perp\in\mathrm{BZ}} \ln\prod_{j=0}^{N_{\boldsymbol{k}\parallel\boldsymbol{b}_l}-1} \det_{\mathrm{occ}}\left(\langle u_{n\boldsymbol{k}+j\delta\boldsymbol{k}} | u_{m\boldsymbol{k}+(j+1)\delta\boldsymbol{k}}\rangle\right)\right)$$
(A.10)

The total polarization, with the ionic contribution included then becomes:

$$\boldsymbol{P}(\lambda) = \frac{e}{2\pi V} \sum_{l} \boldsymbol{a}_{l} \phi_{l} \tag{A.11}$$

where

$$\phi_l = \sum_i Z_i \boldsymbol{b}_i \cdot \boldsymbol{R}_i - \phi_l^{el}.$$
(A.12)

# APPENDIX B Appendix B: Linear response and Hall conductivity

This Appendix explains contains two parts. The first part is simply the convetion of Fourier transforms used in the main text and the in later part of this appendix. The second part contains a detailed calculation of the current-current correlation function used to derive the expression for the anomalous Hall conductivity presented in chapter 7 in the main text.

#### B.1 Fourier transforms

We will be applying two types of Fourier transforms in the the main text and in the following section. The first type is Fourier transform in the temporal domain. The temporal Fourier transform is defined as:

$$\tilde{F}(\omega + i\eta) = \int dt F(t) e^{i(\omega + i\eta)t}$$
(B.1)

Here F(t) is a function in the time domain and  $\tilde{F}(\omega + i\eta)$  is the Fourier transform of F(t). The factor  $\eta$  is included to ensure that the Fourier transform is still well defined in cases where F(t) doesn't have a natural dampening build in. (An example of this would be the non-interacting electron gas). This is sometimes referred to as the generalized Fourier transform. The inverse temporal Fourier transform is then given by:

$$F(t) = \lim_{\eta \to 0^+} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} F(\omega + i\eta) e^{-i\omega t}$$
(B.2)

The spatial Fourier transform is defined as:

$$F(\boldsymbol{q}) = \int d\boldsymbol{r} F(\boldsymbol{r}) e^{i\boldsymbol{q}\cdot\boldsymbol{r}}$$
(B.3)

The inverse spatial Fourier transform is defined as:

$$F(\mathbf{r}) = \frac{1}{2\pi} \int d\mathbf{q} F(\mathbf{q}) e^{-i\mathbf{q}\cdot\mathbf{r}}$$
(B.4)

For correlation (two-point) functions the definition can be extended as:

$$F(\boldsymbol{q},\boldsymbol{q}') = \frac{1}{\Omega} \int \int d\boldsymbol{r} d\boldsymbol{r}' e^{-i\boldsymbol{q}\cdot\boldsymbol{r}} F(\boldsymbol{r},\boldsymbol{r}') e^{i\boldsymbol{q}'\cdot\boldsymbol{r}'}$$
(B.5)

We will be dealing exclusively with crystals which are periodic in the spatial coordinate. Due to this symmetry the physically observable variables (correlation functions etc.) satisfy  $F(\mathbf{r}, \mathbf{r}') = F(\mathbf{r} + \mathbf{R}, \mathbf{r}' + \mathbf{R})$ . Where  $\mathbf{R}$  is a lattice vector. From this it follows that:

$$\int d\mathbf{r} \int d\mathbf{r}' g(\mathbf{r}, \mathbf{r}') = \sum_{\mathbf{R}} \int_{\Omega_{\text{cell}}} d\mathbf{r} \int d\mathbf{r}' g(\mathbf{r} + \mathbf{R}, \mathbf{r}' + \mathbf{R})$$
(B.6)

Here we changed the integration volume in the first integral from that of the whole material to that of the unit cell. We will now show what this means for the Fourier transform of the two point function:

$$F(\boldsymbol{q} + \boldsymbol{G}, \boldsymbol{q} + \boldsymbol{G}') = \frac{1}{\Omega} \int d\boldsymbol{r} \int d\boldsymbol{r}' e^{-i(\boldsymbol{q} + \boldsymbol{G}) \cdot \boldsymbol{r}} F(\boldsymbol{r}, \boldsymbol{r}') e^{i(\boldsymbol{q} + \boldsymbol{G}') \cdot \boldsymbol{r}'}$$
(B.7)

$$= \frac{1}{\Omega} \sum_{\boldsymbol{R}} \int_{\Omega_{\text{cell}}} d\boldsymbol{r} \int d\boldsymbol{r}' e^{-i(\boldsymbol{q}+\boldsymbol{G})\cdot(\boldsymbol{r}+\boldsymbol{R})} F(\boldsymbol{r}+\boldsymbol{R},\boldsymbol{r}'+\boldsymbol{R}) e^{i(\boldsymbol{q}+\boldsymbol{G}')\cdot(\boldsymbol{r}'+\boldsymbol{R})}$$
(B.8)

$$=\frac{1}{\Omega_{\text{cell}}}\int_{\Omega_{\text{cell}}} d\boldsymbol{r} \int d\boldsymbol{r}' e^{-i(\boldsymbol{q}+\boldsymbol{G})\cdot\boldsymbol{r}} F(\boldsymbol{r},\boldsymbol{r}') e^{i(\boldsymbol{q}+\boldsymbol{G}')\cdot\boldsymbol{r}'} \left(\frac{\Omega_{\text{cell}}}{\Omega}\sum_{\boldsymbol{R}} e^{i(\boldsymbol{G}'-\boldsymbol{G})\cdot\boldsymbol{R}}\right)$$
(B.9)

$$= \frac{1}{\Omega_{\text{cell}}} \int_{\Omega_{\text{cell}}} d\mathbf{r} \int d\mathbf{r}' e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} F(\mathbf{r},\mathbf{r}') e^{i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'}.$$
(B.10)

In the more general case one gets:

.....

$$F(\boldsymbol{q} + \boldsymbol{G}, \boldsymbol{q}' + \boldsymbol{G}') = \frac{1}{\Omega} \int d\boldsymbol{r} \int d\boldsymbol{r} \int d\boldsymbol{r}' e^{-i(\boldsymbol{q} + \boldsymbol{G}) \cdot \boldsymbol{r}} F(\boldsymbol{r}, \boldsymbol{r}') e^{i(\boldsymbol{q}' + \boldsymbol{G}') \cdot \boldsymbol{r}'}$$
(B.11)

$$= \frac{1}{\Omega} \sum_{\boldsymbol{R}} \int_{\Omega_{\text{cell}}} d\boldsymbol{r} \int d\boldsymbol{r}' e^{-i(\boldsymbol{q}+\boldsymbol{G})\cdot(\boldsymbol{r}+\boldsymbol{R})} F(\boldsymbol{r}+\boldsymbol{R},\boldsymbol{r}'+\boldsymbol{R}) e^{i(\boldsymbol{q}'+\boldsymbol{G}')\cdot(\boldsymbol{r}'+\boldsymbol{R})}$$
(B.12)

$$=\frac{1}{\Omega_{\text{cell}}}\int_{\Omega_{\text{cell}}} d\mathbf{r} \int d\mathbf{r}' e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} F(\mathbf{r},\mathbf{r}') e^{i(\mathbf{q}'+\mathbf{G}')\cdot\mathbf{r}'} \left(\frac{\Omega_{\text{cell}}}{\Omega}\sum_{\mathbf{R}} e^{-i(\mathbf{q}-\mathbf{q}')\cdot\mathbf{R}}\right)$$
(B.13)

$$= \frac{1}{\Omega_{\text{cell}}} \int_{\Omega_{\text{cell}}} d\mathbf{r} \int d\mathbf{r}' e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} F(\mathbf{r},\mathbf{r}') e^{i(\mathbf{q}'+\mathbf{G}')\cdot\mathbf{r}'} (2\pi)^d \delta(\mathbf{q}-\mathbf{q}')$$
(B.14)

$$= F(\boldsymbol{q} + \boldsymbol{G}, \boldsymbol{q}' + \boldsymbol{G}')(2\pi)^d \delta(\boldsymbol{q} - \boldsymbol{q}') = F(\boldsymbol{q} + \boldsymbol{G}, \boldsymbol{q} + \boldsymbol{G}')$$
(B.15)

#### B.2 Conductivity from linear response

The purpose of this appendix is obtain an expression for the anomalous Hall conductivity from the current-current correlation function. The conductivity tensor is related to the current-current correlation function:

$$\sigma_{\alpha\beta}(\boldsymbol{q},\omega) = \frac{1}{i(\omega+i\eta)} C_{J\alpha J\beta}(\boldsymbol{q},\omega), \tag{B.16}$$

and from the anti-symmetric part of the conductivity tensor we can get the Hall conductivity. We are only interested in the conductivity tensor in the limit q = 0,  $\omega = 0$ . It is however easier to start from the more general and then derive the later. In the spatial-temporal domain the current-current correlation function is given by:

$$C_{J\alpha J\beta}(\boldsymbol{r}, \boldsymbol{r}', t, t') = -i\theta(t - t') \left\langle \left[ J_0^{\alpha}(\boldsymbol{r}, t), J_0^{\beta}(\boldsymbol{r}', t') \right] \right\rangle$$
(B.17)

First step is to rewrite the current-current correlation function by Fourier transform:

$$C_{J\alpha J\beta}(\boldsymbol{q},\boldsymbol{q}',t,t') = -i\theta(t-t') \int d\boldsymbol{r} \int d\boldsymbol{r}' e^{-i\boldsymbol{q}\cdot\boldsymbol{r}} \left\langle \left[J_0^{\alpha}(\boldsymbol{r},t), J_0^{\beta}(\boldsymbol{r}',t')\right]\right\rangle e^{i\boldsymbol{q}'\cdot\boldsymbol{r}'}$$
(B.18)  
$$= -i\theta(t-t') \int d\boldsymbol{r} \int d\boldsymbol{r}' \frac{1}{(2\pi)^2} \sum_{\boldsymbol{q}_1,\boldsymbol{q}_2} \left\langle \left[J_0^{\alpha}(\boldsymbol{q}_1,t), J_0^{\beta}(\boldsymbol{q}_2,t')\right]\right\rangle e^{-i\boldsymbol{q}\cdot\boldsymbol{r}} e^{i\boldsymbol{q}\cdot\boldsymbol{r}'} e^{i\boldsymbol{q}_1\cdot\boldsymbol{r}} e^{i\boldsymbol{q}_2\cdot\boldsymbol{r}'}$$
(B.19)

$$= -i\theta(t-t')\sum_{\boldsymbol{q}_{1},\boldsymbol{q}_{2}}\left\langle \left[J_{0}^{\alpha}(\boldsymbol{q}_{1},t),J_{0}^{\beta}(\boldsymbol{q}_{2},t')\right]\right\rangle \frac{1}{(2\pi)}\int d\boldsymbol{r}^{3}e^{i(\boldsymbol{q}_{1}-\boldsymbol{q})\cdot\boldsymbol{r}}\frac{1}{(2\pi)}\int d\boldsymbol{r'}^{3}e^{i(\boldsymbol{q'}+\boldsymbol{q}_{2})\cdot\boldsymbol{r'}}.$$
(B.20)

Finally one obtains:

$$C_{J\alpha J\beta}(\boldsymbol{q}, \boldsymbol{q}', t, t') = -i\theta(t - t') \left\langle \left[J_0^{\alpha}(\boldsymbol{q}, t), J_0^{\beta}(-\boldsymbol{q}', t')\right] \right\rangle.$$
(B.21)

We now use the identity  $C_{J\alpha J\beta}(\boldsymbol{q}, \boldsymbol{q}') = C_{J\alpha J\beta}(\boldsymbol{q}, \boldsymbol{q})$  to define:

$$C_{J\alpha J\beta}(\boldsymbol{q},t,t') = -i\theta(t-t') \left\langle [J_0^{\alpha}(\boldsymbol{q},t), J_0^{\beta}(-\boldsymbol{q},t')] \right\rangle$$
(B.22)

We now turn to the frequency dependence of the conductivity. We will limit further discussion to the q = 0 case, here the correlation function reduces to:

$$C_{J\alpha J\beta}(t,t') = -i\theta(t-t') \left\langle [J_0^{\alpha}(t), J_0^{\beta}(t')] \right\rangle$$
(B.23)

Since the perturbation stemming from the applied electric field fulfills the requirement given in the end of section 7.3, we may use only the time difference  $\tau = t - t'$ :

$$C_{J\alpha J\beta}(\omega) = \int_{-\infty}^{\infty} d\tau C_{\alpha\beta}(\tau) e^{i(\omega+i\eta)\tau}$$
(B.24)

$$= -i \int_{-\infty}^{\infty} d\tau e^{i(\omega+i\eta)\tau} \theta(\tau) \Biggl( \left\langle e^{\frac{iH_0t}{\hbar}} J^{\alpha} e^{-\frac{iH_0t}{\hbar}} e^{\frac{iH_0t'}{\hbar}} J^{\beta} e^{-\frac{iH_0t'}{\hbar}} \right\rangle$$
(B.25)

$$-\left\langle e^{\frac{iH_0t}{\hbar}'}J^{\beta}e^{-\frac{iH_0t'}{\hbar}}e^{\frac{iH_0t}{\hbar}}J^{\alpha}e^{-\frac{iH_0t}{\hbar}}\right\rangle$$
(B.26)

(B.27)

To evaluate the averages in the equation above we will now make use of that fact that the Hamiltonian is that of a single particle system with well defined band indices n

and momenta k:

$$C_{J\alpha J\beta}(\omega) = -\frac{i}{\hbar} \int_0^\infty d\tau e^{i(\omega+i\eta)\tau} \int_{\mathrm{BZ}} \frac{d\mathbf{k}}{(2\pi)^d} \sum_n^N$$
(B.28)

$$\times \left( \left\langle n\boldsymbol{k} \right| \frac{e^{-\beta H_0}}{Z} e^{\frac{iH_0t}{\hbar}} J^{\alpha} e^{-\frac{iH_0t}{\hbar}} e^{\frac{iH_0t'}{\hbar}'} J^{\beta} e^{-\frac{iH_0t'}{\hbar}} \left| n\boldsymbol{k} \right\rangle$$
(B.29)

$$-\left\langle n\boldsymbol{k}\right|e^{\frac{iH_{0}t'}{\hbar}}J^{\beta}e^{-\frac{iH_{0}t'}{\hbar}}e^{\frac{iH_{0}t}{\hbar}}J^{\alpha}e^{-\frac{iH_{0}t}{\hbar}}\left|n\boldsymbol{k}\right\rangle \right) \tag{B.30}$$

$$= -\frac{i}{\hbar} \int_{\mathrm{BZ}} \frac{d\mathbf{k}}{(2\pi)^d} \int_{\mathrm{BZ}} \frac{d\mathbf{k}'}{(2\pi)^d} \sum_{n=1}^{N} f(E_{n\mathbf{k}}) \sum_{m\neq n=1}^{N} \int_{0}^{\infty} d\tau e^{i(\omega+i\eta)\tau}$$
(B.31)

$$\times \left( \left\langle n\boldsymbol{k} \right| e^{\frac{iH_0t}{\hbar}} J^{\alpha} e^{-\frac{iH_0t}{\hbar}} \left| \boldsymbol{m}\boldsymbol{k}' \right\rangle \left\langle \boldsymbol{m}\boldsymbol{k}' \right| e^{\frac{iH_0t'}{\hbar}} J^{\beta} e^{-\frac{iH_0t'}{\hbar}} \left| \boldsymbol{n}\boldsymbol{k} \right\rangle$$
(B.32)

$$-\langle n\boldsymbol{k}| e^{\frac{iH_0t'}{\hbar}} J^{\beta} e^{-\frac{iH_0t'}{\hbar}} |m\boldsymbol{k}\rangle \langle m\boldsymbol{k}| e^{\frac{iH_0t}{\hbar}} J^{\alpha} e^{-\frac{iH_0t}{\hbar}} |n\boldsymbol{k}\rangle \right)$$
(B.33)

$$= -\frac{i}{\hbar} \int_{\mathrm{BZ}} \frac{d\mathbf{k}}{(2\pi)^d} \sum_{n}^{N} \sum_{m \neq n}^{N} f(E_{n\mathbf{k}}) \int_0^\infty d\tau e^{i(\omega+i\eta)\tau}$$
(B.34)

$$\times \left( e^{i\frac{(E_{n\boldsymbol{k}}-E_{m\boldsymbol{k}})}{\hbar}t} e^{i\frac{(E_{n\boldsymbol{k}}-E_{m\boldsymbol{k}})}{\hbar}t'} \langle n\boldsymbol{k} | J^{\alpha} | m\boldsymbol{k} \rangle \langle m\boldsymbol{k} | J^{\beta} | n\boldsymbol{k} \rangle \right)$$
(B.35)

$$-e^{i\frac{(E_{n\boldsymbol{k}}-E_{m\boldsymbol{k}})}{\hbar}t'}e^{i\frac{(E_{n\boldsymbol{k}}-E_{m\boldsymbol{k}})}{\hbar}t}\langle n\boldsymbol{k}|J^{\beta}|m\boldsymbol{k}\rangle\langle m\boldsymbol{k}|J^{\alpha}|n\boldsymbol{k}\rangle \right)$$
(B.36)

$$= -\frac{i}{\hbar} \int_{\mathrm{BZ}} \frac{d\mathbf{k}}{(2\pi)^d} \sum_{n}^{N} \sum_{m \neq n}^{N} f(E_{n\mathbf{k}}) \int_{0}^{\infty} d\tau \left( e^{i(\omega + i\eta + \frac{(E_{n\mathbf{k}} - E_{m\mathbf{k}})}{\hbar})\tau} \langle n\mathbf{k} | J^{\alpha} | m\mathbf{k} \rangle \langle m\mathbf{k} | J^{\beta} | n\mathbf{k} \rangle \right)$$
(B.37)

$$-e^{i(\omega+i\eta-\frac{(E_{n\boldsymbol{k}}-E_{m\boldsymbol{k}})}{\hbar})\tau}\langle n\boldsymbol{k}|J^{\beta}|m\boldsymbol{k}\rangle\langle m\boldsymbol{k}|J^{\alpha}|n\boldsymbol{k}\rangle\right)$$
(B.38)

$$= \int_{\mathrm{BZ}} \frac{d\mathbf{k}}{(2\pi)^d} \sum_{n=1}^{N} \sum_{m\neq n}^{N} f(E_{n\mathbf{k}}) \left( \frac{\langle n\mathbf{k} | J^{\alpha} | m\mathbf{k} \rangle \langle m\mathbf{k} | J^{\beta} | n\mathbf{k} \rangle}{(\hbar\omega + i\hbar\eta + (E_{n\mathbf{k}} - E_{m\mathbf{k}}))} - \frac{\langle n\mathbf{k} | J^{\beta} | m\mathbf{k} \rangle \langle m\mathbf{k} | J^{\alpha} | n\mathbf{k} \rangle}{(\hbar\omega + i\hbar\eta - (E_{n\mathbf{k}} - E_{m\mathbf{k}}))} \right). \tag{B.39}$$

To get an expression for the Hall conductivity we focus in on the anti-symmetric part of the conductivity tensor  $\sigma_{\alpha\beta}^A = \sigma_{\alpha\beta} - \sigma_{\beta\alpha}$ . The components can be found by computing

the anti-symmetric part of the current-current correlation function:

$$C^{A}_{J\alpha J\beta}(\omega) = C_{J\alpha J\beta}(\omega) - C_{J\beta J\alpha}(\omega)$$
(B.40)

$$= \int_{\mathrm{BZ}} \frac{d\mathbf{k}}{(2\pi)^d} \sum_{n}^{N} \sum_{m \neq n}^{N} f(E_{n\mathbf{k}}) \left( \frac{\langle n\mathbf{k} | J^{\alpha} | m\mathbf{k} \rangle \langle m\mathbf{k} | J^{\beta} | n\mathbf{k} \rangle}{(\hbar\omega + i\hbar\eta + (E_{n\mathbf{k}} - E_{m\mathbf{k}}))} \right)$$
(B.41)

$$-\frac{\langle n\mathbf{k}| J^{\beta} | m\mathbf{k} \rangle \langle m\mathbf{k} | J^{\alpha} | n\mathbf{k} \rangle}{(\hbar\omega + i\hbar\eta - (E_{n\mathbf{k}} - E_{m\mathbf{k}}))}$$
(B.42)

$$-\frac{\langle n\mathbf{k}|J^{\beta}|m\mathbf{k}\rangle\langle m\mathbf{k}|J^{\alpha}|n\mathbf{k}\rangle}{(\hbar\omega+i\hbar\eta+(E_{n\mathbf{k}}-E_{m\mathbf{k}}))}+\frac{\langle n\mathbf{k}|J^{\alpha}|m\mathbf{k}\rangle\langle m\mathbf{k}|J^{\beta}|n\mathbf{k}\rangle}{(\hbar\omega+i\hbar\eta-(E_{n\mathbf{k}}-E_{m\mathbf{k}}))}\right)$$
(B.43)

$$= \int_{\mathrm{BZ}} \frac{d\boldsymbol{k}}{(2\pi)^d} \sum_{n=1}^{N} \sum_{m\neq n}^{N} f(E_{n\boldsymbol{k}}) \left( \left\langle n\boldsymbol{k} \right| J^{\alpha} \left| m\boldsymbol{k} \right\rangle \left\langle m\boldsymbol{k} \right| J^{\beta} \left| n\boldsymbol{k} \right\rangle \right.$$
(B.44)

$$\times \left(\frac{1}{(\hbar\omega + i\hbar\eta + (E_{n\boldsymbol{k}} - E_{m\boldsymbol{k}}))} + \frac{1}{(\hbar\omega + i\hbar\eta - (E_{n\boldsymbol{k}} - E_{m\boldsymbol{k}}))}\right)$$
(B.45)

$$-\langle n\boldsymbol{k}| J^{\beta} | \boldsymbol{m}\boldsymbol{k} \rangle \langle \boldsymbol{m}\boldsymbol{k} | J^{\alpha} | \boldsymbol{n}\boldsymbol{k} \rangle \left( \frac{1}{(\hbar\omega + i\hbar\eta - (E_{n\boldsymbol{k}} - E_{\boldsymbol{m}\boldsymbol{k}}))} \right)$$
(B.46)

$$+\frac{1}{(\hbar\omega+i\hbar\eta+(E_{n\boldsymbol{k}}-E_{m\boldsymbol{k}}))}\bigg)\bigg) \tag{B.47}$$

$$= \int_{\mathrm{BZ}} \frac{d\mathbf{k}}{(2\pi)^d} \sum_{n}^{N} \sum_{m \neq n}^{N} f(E_{n\mathbf{k}})$$
(B.48)

$$\times \left( \left\langle n\boldsymbol{k} \right| J^{\alpha} \left| \boldsymbol{m} \boldsymbol{k} \right\rangle \left\langle \boldsymbol{m} \boldsymbol{k} \right| J^{\beta} \left| \boldsymbol{n} \boldsymbol{k} \right\rangle \left( \frac{1}{\left( \hbar \omega + i\hbar \eta \right)^{2} - (E_{n\boldsymbol{k}} - E_{\boldsymbol{m} \boldsymbol{k}})^{2}} \right)$$
(B.49)

$$-\langle n\boldsymbol{k}| J^{\beta} | \boldsymbol{m}\boldsymbol{k} \rangle \langle \boldsymbol{m}\boldsymbol{k} | J^{\alpha} | \boldsymbol{n}\boldsymbol{k} \rangle \left( \frac{1}{\left( \hbar\omega + i\hbar\eta \right)^{2} - (E_{n\boldsymbol{k}} - E_{\boldsymbol{m}\boldsymbol{k}})^{2}} \right) \right)$$
(B.50)

We now use that:  $\langle n\mathbf{k} | J^{\alpha} | m\mathbf{k} \rangle \langle m\mathbf{k} | J^{\beta} | n\mathbf{k} \rangle = \langle n\mathbf{k} | J^{\beta} | m\mathbf{k} \rangle^* \langle m\mathbf{k} | J^{\alpha} | n\mathbf{k} \rangle^*$ . to reduce the expression for the current-current correlation function to:

$$C^{A}_{J\alpha J\beta}(\omega) = \int_{\mathrm{BZ}} \frac{d\mathbf{k}}{(2\pi)^{d}} \sum_{n}^{N} \sum_{m \neq n}^{N} f(E_{n\mathbf{k}}) 2i \mathrm{Im} \left( \langle n\mathbf{k} | J^{\alpha} | m\mathbf{k} \rangle \langle m\mathbf{k} | J^{\beta} | n\mathbf{k} \rangle \right)$$
(B.51)

$$\times \left(\frac{(\hbar\omega + i\hbar\eta)}{(\hbar\omega + i\hbar\eta)^2 - (E_{n\mathbf{k}} - E_{m\mathbf{k}})^2}\right)$$
(B.52)

The relationship between the correlation function and the conductivity is:

$$\sigma^{A}_{\alpha\beta}(\omega) = \frac{e^2}{i(\omega+i\eta)} C^{A}_{J\alpha J\beta}(\omega)$$
(B.53)

The conductivity therefore becomes

$$\sigma_{\alpha\beta}^{A}(\omega) = e^{2}\hbar \int_{\mathrm{BZ}} \frac{d\boldsymbol{k}}{(2\pi)^{d}} \sum_{n}^{N} \sum_{m\neq n}^{N} f(E_{n\boldsymbol{k}}) \left( \frac{2\mathrm{Im}\left( \langle n\boldsymbol{k} | J^{\alpha} | \boldsymbol{m}\boldsymbol{k} \rangle \langle \boldsymbol{m}\boldsymbol{k} | J^{\beta} | \boldsymbol{n}\boldsymbol{k} \rangle \right)}{(\hbar\omega + i\hbar\eta)^{2} - (E_{n\boldsymbol{k}} - E_{\boldsymbol{m}\boldsymbol{k}})^{2}} \right)$$
(B.54)

In the single particle picture the current operator is given by:  $J_{\alpha} = v_{\alpha}$  and the velocity operator is given by:  $v_{\alpha} = \frac{1}{\hbar} \frac{dH}{dk_{\alpha}}$ , where *H* is the Hamiltonian [154]. The conductivity can then be written as:

$$\sigma_{\alpha\beta}^{A}(\omega) = \frac{e^{2}}{h} 2\pi \int_{\mathrm{BZ}} \frac{d\mathbf{k}}{(2\pi)^{d}} \sum_{n}^{N} \sum_{m\neq n}^{N} f(E_{n\mathbf{k}}) \left( \frac{2\mathrm{Im}\left( \langle n\mathbf{k} | \frac{dH}{dk_{\alpha}} | m\mathbf{k} \rangle \langle m\mathbf{k} | \frac{dH}{dk_{\beta}} | n\mathbf{k} \rangle \right)}{(\hbar\omega + i\hbar\eta)^{2} - (E_{n} - E_{m})^{2}} \right)$$
(B.55)

In practical computations it is often helpful to treat the eigenstate indices n and m on equal footing with respect to summation. To this end we use the fact that expressions of the type:

$$\sum_{m}^{N} \sum_{n \neq m}^{N} f(E_n) A(E_n, E_n)$$
(B.56)

can be rewritten as

$$\sum_{m}^{N} \sum_{n}^{N} \frac{1}{2} \left( f(E_n) - f(E_n) \right) A(E_n, E_m)$$
(B.57)

provided that  $A(E_n, E_m) = A(E_m, E_n)$ . Here  $f(E_n)$  denote the Fermi-Dirac distribution function and  $A(E_n, E_m)$  a well-behaved function of both summation variables. The Hall conductivity then takes the form [157]:

$$\sigma_{\alpha\beta}^{A}(\omega) = \frac{e^{2}}{h} \int_{\mathrm{BZ}} \frac{d\boldsymbol{k}}{(2\pi)^{d-1}} \sum_{n,m}^{N} \left( f(\epsilon_{n\boldsymbol{k}}) - f(\epsilon_{n\boldsymbol{k}}) \right) \left( \frac{\mathrm{Im}\left( \langle n\boldsymbol{k} | \frac{dH}{dk_{\alpha}} | m\boldsymbol{k} \rangle \langle m\boldsymbol{k} | \frac{dH}{dk_{\beta}} | n\boldsymbol{k} \rangle \right)}{(\hbar\omega + i\hbar\eta)^{2} - (E_{n\boldsymbol{k}} - E_{m\boldsymbol{k}})^{2}} \right)$$
(B.58)

To get an expression for the Hall conductivity we consider the dc limit where  $\omega \to 0$ and  $\eta \to 0$  to get:

$$\sigma_{\alpha\beta}^{A} = \frac{e^{2}}{h} \int_{\mathrm{BZ}} \frac{d\boldsymbol{k}}{(2\pi)^{d-1}} \sum_{n,m}^{N} \left( f(\epsilon_{n\boldsymbol{k}}) - f(\epsilon_{n\boldsymbol{k}}) \right) \left( \frac{\mathrm{Im}\left( \left\langle n\boldsymbol{k} \right| \frac{dH}{dk_{\alpha}} \left| m\boldsymbol{k} \right\rangle \left\langle m\boldsymbol{k} \right| \frac{dH}{dk_{\beta}} \left| n\boldsymbol{k} \right\rangle \right)}{(E_{n\boldsymbol{k}} - E_{m\boldsymbol{k}})^{2}} \right)$$
(B.59)

converting the integral to a sum we get:

$$\sigma_{\alpha\beta}^{A} = \frac{e^{2}}{h} \frac{2\pi}{N_{\boldsymbol{k}}V} \sum_{\boldsymbol{k}\in\mathrm{BZ}} \sum_{n,m}^{N} \left(f(\epsilon_{n\boldsymbol{k}}) - f(\epsilon_{n\boldsymbol{k}})\right) \left(\frac{\mathrm{Im}\left(\langle n\boldsymbol{k} | \frac{dH}{dk_{\alpha}} | m\boldsymbol{k} \rangle \langle m\boldsymbol{k} | \frac{dH}{dk_{\beta}} | n\boldsymbol{k} \rangle\right)}{(E_{n\boldsymbol{k}} - E_{m\boldsymbol{k}})^{2}}\right) \tag{B.60}$$

### B.3 Supplementary tables

The table contains atomic positions and lattice vectors in units of Å for the relevant two dimensional magnetic materials mentioned in the main text.

Name	Unit cell vectors [Å]	Atomic positions [Å]	
$\rm Fe_3GeTe_2$	a1:(3.909, 0.0, 0.0)	Te1:(2.329, 1.693, 14.575)	
	a2:(-1.954, 3.385, 0.0)	Te2:(2.329, 1.693, 9.425) Ge1:(0.301, 2.864, 12.0) Fe1:(0.301, 0.522, 13.242)	
	a3:(0.0, 0.0, 24.0)	Fe2:(0.301, 0.522, 10.758) Fe3:(2.329, 1.693, 12.0)	
$\mathrm{Br_2Cu_2S_2}$	a1:(4.686, 0.0, 0.0)	Cu1:(2.343, 0.0, 9.537)	
	a2:(-0.0, 3.488, 0.0)	Cu2:(0.0, 1.744, 11.805) S1:(2.343, 1.744, 11.123) S2:(-0.0, 0.0, 10.219)	
	a3:(-0.0, 0.0, 21.342)	Br1:(2.343, 1.744, 7.76) Br2:(-0.0, -0.0, 13.583)	
$FeCl_2$ (T-phase)	a1:(3.556, -0.0, 0.0)	$E_{a1}(0,0,0,0,8,721)$	
	a2:(-1.778, 3.08, 0.0)	Cl1:(1.778, 1.027, 10.111) Cl2:(0.0, 2.053, 7.332)	
	a3:(-0.0, 0.0, 17,443)		

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Bibliography

Ferroic order is a phenomenon of enourmous importance in the field of materials science. The word refers to materials that posses long-range order in specific material properties such as magnetization, polarization or elasticity. A good example is ferromagnetism which occur in magnetic materials where microscopic magnetic dipoles align over long distances to produce a macro-scopic magnetization. In such materials the magnetization can be controlled externally, which has lead to a variety of interesting applications. Recent advances in material science have uncovered a new form a ferroic material, the so called multiferroics. These are materials where several types of ferroic order are simultaneously present. Combining different types of ferroic order may open the possibility for novel applications in wide range of different technologies from new electronics for computing or information storage to new forms of chemical catalysts.

The goal of this thesis is to apply computational methods to uncover new types of multiferroics materials. This is done using first-principles methods, which applies the most fundamental equations of quantum mechanics to materials without prior empirical knowledge of the system in question and using only a minimal set of assumptions. These methods are applied in a highthroughput framework where one attempts to investigate many materials at once by automating the computational process. The thesis presents results from a study of new two-dimensional ferroelectric materials. These are materials that are as thin as one atomic layer and has become an increasingly popular materials platform over the last decade. These materials do not suffer from some of the drawbacks of their bulk counterparts such as limitations on thickness.

Lastly the thesis presents a chapter on the study of the anomalous Hall conductivity in magnetic systems with spin-orbit coupling. Benchmark calculations are presented for Fe, Co and Ni, using software implementation of the Hall conductivity in the GPAW code maintained at DTU. Finally results are shown for selected two dimensional systems.

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