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Thesis Title

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Abstract

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Preface

Chapter 1

Introduction

The technological revolution the last decades have been based largely on the discovery and application of new materials and alloys. Alloying materials reach back into the old civilization. But the difference today is the method of which we can apply to research and produce materials. One of which is high-entropy alloys, a novel class of materials based on alloying multiple components as opposed to the more traditional binary alloys. This offers many new possibilities, and recently there have been discovered HEA with unexpected and superior properties from the original components, such as increased strength and tear resistance **cite**. Along with the recent advancements in material informatics and numerical methods such as density functional theory, this makes for a promising foundation for researching this new class of materials. **More on the use of DFT and developments in the field.**

In this thesis, we will mainly look at the physical and electrical properties of high-entropy alloys. The primary goal of this thesis could be formulated as a search for semiconducting high-entropy alloys. Semiconductors have w wide range of applications in today's world, ranging from optical and electrical devices to renewable energy sources such as solar and thermoelectricity. Given the economic and sustainable factors concerning silicon, in addition to its role in relevant applications such as microelectronics and solar power. Silicon emerges as a natural selection to build our alloys around **Point to Mari's master and the article on HEA silicide**. Furthermore, the development and research on both high entropy alloys and metal silcides have been heavily centered around 3d transition metals. Keeping in line with the economic and environmental properties of silicon, we will thus continue this direction in this study by focusing on high entropy stabilized 3d metal silicides. Adding to this, the alloys will be based on the well known and researched silicides CrSi2, FeSi2, Fe2Si and MnSi175, as these offer a decent range of different starting properties, such as band gap, crystal structure and metal to silicon ratios.

An additional point is that most of the recent progress and studies on high-entropy alloys have been solely directed at the mechanical properties, while the physical landscape is mostly left unexplored. Building on this idea comes the overarching philosophy behind this thesis, as an attempt to

employ the technology and methods we have developed today to explore the unknown, and in that image, explore materials that does not fall under any known material class.

Another key aspect of this thesis, will be to trial the ability and progress of ab inito and other numerical methods to perform qualitative studies of such complex materials. This is a key contributor to why high-entropy alloys have only emerged the last decade or so, without the aid of computational methods, would make the research of complex disordered structures very challenging. Mainly, we will observe the applicability of DFT to perform accurate measure of the band gap and structure, which historically have been a shortcoming of this theory. In addition we will apply a method called special quasi-random structures, an algorithm based on Monte Carlo simulations, to correctly model these disordered materials. And evaluate both the accuracy, reliability and the computational feasibility of this method and ab initio simulations in general.

Something on the structure of the project and what topics will be covered. Write in particular, that this thesis will assume the reader is somewhat familiar with materials science and semiconductor physics, thus not include it in the theory section. I think? Maybe I will add it later More on recent research and findings in both silicides and HEA, as well DFT based studies, basically just the introduction of many articles placed here! Also mention the use of VASP and the term "composistional complex alloys", as this make the latter sections mores sensible

Part I

Theory

Chapter 2

Background

2.1 Solid-state physics

Contents are band-theory, dos, reciprocal space, BZ

2.2 Silicides

This section should contain a brief overview of the silicides used in this project, ie crystal structure and electronic properties of Fe2Si, FeSi2, MnSi175, CrSi2

Chapter 3

High-Entropy alloys

To begin this project, we will start by giving a brief description of high-entropy alloys. This will include an introduction covering the basics and definitions, as well some more advanced topics relating to the physical properties of HEA's. This section will be largely based on the fantastic description of HEA's in "High-Entropy Alloys - Fundamentals and Application" [1] and the references therein, it's an excellent read.

3.1 Fundamentals

High-Entropy Alloys are a quickly emerging field in materials science due to the infinitely many possibilities and the fascinatingly observed properties. Since it's original discovery by Jin in 2004, as of 2015 there have been over 1000 published journal articles on the field. In its simplicity, a high-entropy alloy can be compared to a smoothie. By combining an assortment of fresh fruit and vegetables one can produce unique combinations of flavors and nutritional values based on both the properties of the distinct items, and their interplay in the mixture. In materials science, this exact procedure can be applied to generate a large range of materials with tunable properties depending on the intended application. In the topic of HEA's, this can be increased strength or ductility, corrosive resistance or lowered thermal conductivity, all of which have been observed in actual researched high-entropy alloys. Moving on from the rather banal fruit analogy, a high-entropy alloy typically falls under the two conditions.

1. The material consist of at least 5 distinct elements, where each element contribute between 5-35% of the composition

2. The total configurational entropy is greater than 1.5R, where R is the gas constant.

The latter in particular is an especial case for high-entropy alloys. Typically the configurational entropy, eq .. for a solid solution increases with a higher number of components in the mix. For example, the ideal configurational entropy of binary alloy is 0.69R, while a 5-component alloy is 1.61R **ref**

5

book. If we neglect other factors that influence the formation of solid solutions (will be covered later), from Gibbs free energy (eq ..) the two primary factors in impacting the formation of solid solution is the mixing enthalpy, which is the driving force to form compounds, and the mixing entropy which is the driving force to form random solid solutions. At elevated temperatures especially, it's clear that the energy term related to the entropy of the system becomes comparative to the mixing enthalpy and contribute to the overall equation. In summary, the overall concept of high-entropy alloys is that through alloying a greater number of elements, the increase in the configurational entropy of the system prohibit formation of intermetallic compounds in favor of a random solid solution. The random term simply relate to the various components occupying lattice positions based on probability. All though the mixing entropy as mentioned above plays a central role in the formation, there are many more factors that may oppose the formation of a single disordered phase. One of these is the atomic size effect which is related to the discrepancy in atomic sizes between the various elements in the alloy. **The book** points to a study, and figure illustrating the relationship between ΔH_{mix} and δ, indicating that for very small values of δ, ie similar atomic sizes. The elements have an equal probability to occupy lattice sites to form solid solutions, but the mixing enthalpy is not negative enough to promote formation of solid solution. Increasing δ does result in greater ΔH_{mix}, but leads to a higher degree of ordering. In conclusion, the formation of solid solution high-entropy alloys lie in a narrow range of δ value to satisfy both the enthalpy of mixing and the disordered state. To define this range of formation of HEA, Yang and Zhang introduced the parameter Ω as

$$\Omega = \frac{T_{\mathrm{m}} \delta S_{\mathrm{mix}}}{|\Delta H_{\mathrm{mix}}|} \tag{3.1}$$

, and found that the formation of single disordered solid solution is found for $\Omega \geq 1.1$ and $\delta \leq 6.6\%$. While compounds such as intermetallics form for greater values of δ and lesser values of Ω. Similarly, replacing the atomic size effect constant for the number of elements result in an equivalent condition. Another factor that is strongly related to the crystal structure and physical properties of high-entropy alloys is the total number of electrons VEC (Valence electron concentration). VEC is an important parameter that is strongly related to the crystal structure of the material. For example, in Co_3V, originally a hexagonal structure. Can by increasing the VEC by alloying with Ni transform to a tetragonal structure, or a cubic structure by reducing the VEC with Fe. Altering the crystal structure had a massive impact on the properties of the material, seeing as hexagonal alloys tend to be brittle, while cubic alloys are more ductile. In fact, Mizutani **book, cite?** obtained a clear relationship between physical properties in 3d transition. metals and the VEC. Derived from the work of Guo et al. on the phase stability of a $Al_xCrCuFeNi_2$ HEA, the VEC can be directly related to the crystal structure of high-entropy alloys. A lower VEC stabilize the BCC phase, while higher values stabilize FCC. In between is a mixture of the two. Specifically values greater than 8.0 stabilize FCC, and values bellow

6.87 favor BCC. However, these boundaries is not rigid when including elements outside of transition metals, exceptions has also been found for high-entropy alloys containing "Mn". All though a heavy majority of reported high-entropy alloys that form solid solutions are either FCC or BCC, recent studies have observed HEA's in orthorombic structure like $Ti_{35}Zr_{27.5}Hf_{27.5}Ta_5Nb_5$ and hcp structures, for example $CoFeNiTi$

3.2 Core effects

Next, we will summarize the discussion above into four core elements that distinctly describe high-entropy alloys and their implications on the functional properties. The first of these is the "high-entropy effect", related to the increased configurational entropy due to the amount of elements, that can inhibit the formation of strongly ordered structures. The high-entropy effect is most prominent in Gibbs energy of a system, where the balance between entropy and enthalpy is central and the effects are further emphasized at elevated temperatures, responsible for the high-temperature stability in high-entropy alloys. **This needs work!**. Secondly is "severe lattice distortion effect", that originates from the fact that every element in a high-entropy structure is surrounded by non-homogeneous elements, thus leading to lattice strain and stress. The overall lattice distortion is additionally attributed to the differences in atomic size, bonding energies and crystal structure tendencies between the components. Therefore the total lattice distortion observed in HEA's are significantly greater than that of conventional alloys. This effect mostly affect the strength and conductivity of the material, such that a higher degree of distortion yields greater strength and greatly reduces the electronic and thermal conductivity due to increased electron and phonon scattering. An upside to this is that the scattering and following properties become less temperature dependent given that it originates from the lattice rather than thermal vibrations. The two remaining effects, "sluggish diffusion" and "cocktail effect" can be summarized swiftly. The first is a direct consequence of the multi-component layout of high-entropy alloys, that result in significantly slowed diffusion and phase transformation because of the number of different elements that is demanded in the process. The most notable relation from this effect is an increased creep resistance. Lastly we have the cocktail effect, which is identical to the smoothie analogy mentioned previously, in that the resultant characteristics of such a mixture is a combination of both the elements and their interaction. This is possible the most promising concept behind high-entropy alloys, which fuels researchers with ambition to discover highly optimized materials by meticulously combining and predicting properties from different elements. Examples of this can be the refractory HEA's developed by "Air Force Research Laboratory" severely exceeding the melting points and strength of previous Ni or Co-based superalloys by alloying specifically refractory elements such as Mo. Nb and W. Or the research conducted by Zhang et al. on the high-entropy system $FeCoNi(AlSi_{0-0.8}$ in the intent of unveiling

the optimal combination of magnetic, electric and mechanical properties. Resulting in an excellent soft magnet.

3.3   Physical properties

In the discussion above of the core effects regarding high-entropy alloys, especially the lattice distortion and cocktail effect are responsible for the physical properties because of the former's effect on scattering and the latter on combining properties from various elements. The initial study on the physical properties on high-entropy alloys was conducted on the H-x alloy, referring to the system $Al_x CoCrFeNi$ with $0 \leq x \leq 2$. It was found that the electrical resistivity was higher than that of conventional alloys, and that the conductivity generally decreased with increasing amounts of Al. Going back to the section on lattice distortion, we also know that these properties are relatively temperature insensitivity since the lattice effects outweigh the thermal effects in terms of electron and phonon scattering. To further justify this point, the H-x compound mentioned above exhibited noteworthy low carrier mobility compared to conventional alloys. Similar findings have also been made for the $FeCoNi(AlSi)_x$ system. **Write a small part on magnetic and relate to the cocktail effect, then very briefly conclude by mentioning findings of superconductivity, corrosion resistance, hydrogen storage and other properties/applications.**

Chapter 4

Special quasi-random Structures

There are numerous difficulties involved with modeling of high-entropy alloys, or more general multi-component random alloys. **These are ...** Today, the most popular approaches are the coherent potential approximation (CPA), the virtual crystal approximation (VCA), the cluster expansion method, and special quasi-random structure (SQS). For this project, we exclusively used the latter primarily for it's direct and easy VASP implementation. Compared to the other approaches mentioned above, SQS reliably outperforms MC/MD simulations in terms of DOS calculations, and are significantly easier to implement and interpret. All though especially CPA is considered superior in simulating the electronic character of random alloys, combination with VASP is cumbersome and thus we opted for SQS as the building block of this thesis. **More on this? Cite relevant references on this, and restructure the paragraph to include more specif information and sources.**

4.1 The concept and fundamentals of SQS - Write proper later

Before the arrival of SQS and CPA methods, the common approach of modeling random alloys was to distribute the numerous elements randomly over the lattice sites. This was a costly operation, which either involved averaging a great number of possible configurations, or infeasible large supercells considering the computational efforts required. In the original paper on SQS published in 1990 [3] **Replace this article with the bigger SQS article from 1990**, it was proposed a selective occupation strategy (originally intended at random binary alloys) to design special periodic quasi-random structures that exceed previous methods in accuracy and cost. The key concept was to create a periodic unit cell of the various components in a finite N lattice site single configuration such that the structure most closely resemble the configuration average of an infinite perfect random alloy. In an attempt to work withing the

50 lattice sites boundary of ab initio methods at that time. The working theory was that if one can resemble an infinite perfect random alloy by a periodic finite N cell, also the electronic properties would be similar between the two. The solution to this model was that for each N, ie lattice site, to minimize the difference of structural correlation function between the approximated cell and the perfect random alloy. There are obviously errors involved with approximating a random alloy by a periodic cell, but by the hierarchical relation to the properties of the material, interactions between distant sites only offer a negligible small contribution to the total energy of the system. Thus the aim of the SQS method is focused around optimizing the correlations within the first few shells of a given site. To follow is a review of the mathematics related to the SQS method.

4.2 Mathematical formulation: Might need to expand on the definition and meaning behind terms such as clusters, figures, correlation functions etc (Add in post!)

Before describing the SQS approach, we begin by reviewing the concepts of topics such as cluster expansions, statistics and superposition of periodic structures. These topics are widely covered in the literature, we will simply focus on the summarizing the description given in [3]. Thus, we opt readers to refer to the original article or similar literature for a more comprehensive description of these topics. On a side note regarding the following mathematical derivation, the original concept was devolved for random binary alloys, but the theory have later been successfully extended to multi-component alloys as well.

The different possible atomic arrangements are denoted as "configurations" σ. The various physical properties of a given configuration is $E(\sigma)$, and $< E >$ is the ensemble average over all configurations σ. In practice, this quantity is unfeasible in terms of computational cost, seeing as the average require calculations and relaxations of all possible configurations, for a binary alloy this is 2^N for a fixed N number of lattice sites. A solution to this is to use the theory of cluster expansions and discretize each configuration into "figures" f. A figure in the lattice is defined in terms of the number of atoms it include k, distance in terms of neighbors m, and position in the lattice l. Further we assign spin values for each lattice site i in the figure to denote which element it holds (+1,-1 for a binary alloy). By defining the spin product of spin variables in a figure at lattice position l as $\Pi_f(l, \sigma)$, we can write the average of all locations in the lattice of a given figure f as

$$\vec{\Pi}_f(\sigma) = \frac{1}{ND_f} \sum_l \Pi_f(l, \sigma) \tag{4.1}$$

where D_f is the number of equivalent figures f per site. The brilliance of this notation is that we now can express the physical property $E(\sigma)$ in terms

of the individual contributions ϵ_f of a figure f.

$$E(\sigma) = \sum_{f,l} \Pi_f(l,\sigma)\epsilon_f(l) \tag{4.2}$$

The quantity ϵ_f is called the "effective cluster property" and is defined as (for a random binary alloy $A_{1-x}B_x$)

$$\epsilon_f(l) = 2^{-N} \sum_{\sigma}^{2^N} \Pi_f(l,\sigma)E(\sigma) \tag{4.3}$$

Inserting the equation for $\vec{\Pi}_f$ into that of $E(\sigma)$ we can describe the the previous cluster expansion of $E(\sigma)$ as

$$E = N \sum_f D_f < \vec{Pi}_f > \epsilon_f \tag{4.4}$$

And obtain a simplified expression for $< E(\sigma >)$ in eq 1? Thus we have successfully managed to reduce the expensive task of sampling all $E(\sigma)$ into calculating the effective cluster properties and summing over all types of figures. Remembering that $E(\sigma)$ can relate to many physical properties, the most common and applied case is that $E(\sigma)$ is the total energy, while ϵ_f is many body interaction energies. The cluster expansion above converge rather quickly with increasing number of figures, an effective method is thus to select a set of configurations to evaluate the effective cluster properties. Don't know how to write this, but the next step is to select a finite largest figure denoted F, and "specialize" the cluster expansion to a set of N_s periodic structures $\sigma =$s to obtain the two expressions for $E(s)$ and ϵ_f using matrix inversion to obtain the result for ϵ_f

$$E(s) = N \sum_f^F D_f \vec{\Pi}_f(s)\epsilon_f \tag{4.5}$$

$$\epsilon_f = \frac{1}{ND} \sum_s^{N_s} [\vec{\Pi}_f(s)] - 1E(s) \tag{4.6}$$

Assuming now that the sum of figures F and N_s periodic structures are well converged, $E(\sigma)$ can be rewritten as a superposition of $E(s)$

$$E(\sigma) = \sum_s^{N_s} \xi_s(\sigma)E(s) \tag{4.7}$$

$$\xi_s(\sigma) = \sum_f^F [\vec{\Pi}_f(s)]^{-1}\vec{\Pi}_f(\sigma) \tag{4.8}$$

where ξ is the weights. Thus we have effectively reduced the problem to a convergence problem of the number of figures F and structures N_s. This can be easily solved given that we are dealing with periodic crystal structures s that can employ the general applications of ordered structures from ab initio methods, and increasing F until the truncation error falls

bellow a desired threshold. However, this approach requires that the variance of the observable property is much lower than the sample mean, otherwise one would have to employ a much bigger sample size to reach statistical convergence. Don't how to write this part nicely, but: Because of the different relationship between various physical properties and the correlation functions, one observe different convergence depending on the meaning of E. The idea behind SQS was therefore to design single special structures with correlation functions $\vec{\Pi}_f(s)$ that most accurately match those of the ensemble average of a random alloy $< \vec{\Pi}_f >_R$.

The correlation functions of an perfect random infinite alloy, denoted as R is defined bellow

$$\vec{\Pi}_{k,m}(R) = < \vec{\Pi}_{k,m} >_R = (2x-1)^l \qquad (4.9)$$

with k, m defined as before and x being the composition ratio of the alloy. In the case of an eqvimolar alloy ($x = \frac{1}{2}$), the functions equal 0 for all k except $< \vec{\Pi}_{0,1} >_R = 1$. If we now randomly assign either atom A or B to every lattice site, for a sufficiently large value of N, the goal is then to create a single configuration that best match the random alloy. Keeping with the $x = \frac{1}{2}$ case, the problem is now that even though the average correlation functions of a large set of these structures approaches zero, like for the random alloy. The variance of the average is nonzero meaning that a selected structure of the sample is prone to contain errors. The extent of these errors can be evaluated from the standard deviations

$$v_{k,m}(N) = | < \vec{\Pi}^2_{k,m} > |^{\frac{1}{2}} = (D_{k,m}N)^{-\frac{1}{2}} \qquad (4.10)$$

Given the computational aspects, it's obvious that economical structures with small N are prone to large errors. In fact, in some cases these errors can result in correlation functions centering around 1, as opposed to 0 for a perfect random alloy.

I don't know how to write the prelude to this part! (see section IIIA in [3]). The degree to which a structure s fails to reproduce the property E of the ensemble-averaged property of the random alloy can be described by a hierarchy of figures, see eq .. bellow

$$< E > -E(s) = \sum_{k,m}' D_{k,m}[(2x-1)^k - \vec{\Pi}_{k,m}(s)]\epsilon_{k,m} \qquad (4.11)$$

, the prime is meant symbolize the absence of the value $0,1$ for k, m. The contribution from the figure property ϵ reduces for larger figures. In general, for disordered systems, the physical property "E" at a given point R falls of exponentially as $|R - R'|/L$, where L is a characteristic length scale relating to the specific property. Using this, the approach of SQS is to specify a set of correlation functions that hierarchically mimic the correlation functions of the random alloy. Meaning that it prioritize the nearest neighbor interactions. With the set of functions decided on, the objective it finally to locate the structures that correspond to the selected structures.

Finished :) Write a final conclusion on this SQS derivation and motivate the incredibly bored reader for the coming sections.

4.3 Results and Advances in SQS and application to high-entropy alloys

A big part of this is related to the use of periodic crystal structures, that can employ standard ab initio methods; see article [3]. Write later, Begin with results of original SQS proposed in 1990, move on to mcsqs and finally mcsqs for HEA and results in that field. For references see: see ch 10 book HEA, mcsqs article and later sections in [3]

Following the 1990 paper, in 2013 a team of researchers further developed the concept of SQS to the current method used today, by the addition of monte-carlo algorithms [2]. **Write later**

Today SQS have been successfully applied to study formation energies, elastic properties, bond lengths, density of states, band gaps, plus more for a number of disordered structures, including semiconductors, metals, and high-entropy alloys. **Last section of 10.1, maybe include references from this section?** However, a large portion of SQS studies relate to binary and ternary alloys, with a very limited amount of literature on SQS on high-entropy alloys.

Chapter 5

Density-Functional Theory

5.1 Review of Quantum Mechanics

5.1.1 The Shrödinger equation

The Schrödinger equation composed of the wavefunction $\Psi(\vec{r}, t)$ and Hamiltonian $\hat{H}(\vec{r}, t)$ where $\vec{r}$ and t is the spatial position and time respectfully.

$$i\hbar \frac{\partial}{\partial t} \Psi(\vec{r}, t) = \hat{H}(\vec{r}, t) \Psi(\vec{r}, t) \tag{5.1}$$

The time-independent shrödinger equation for the eigenvalues E_k of the k-th eigenvalue $\psi_k(\vec{r}$

$$\hat{H} \psi_k(\vec{r}) = E_k \psi_k(\vec{r}) \tag{5.2}$$

Extending to a system comprised of multiple particles, we have the many-particle Shrödinger equation, involving the many-body Hamiltonian. This quantity is composed of the kinetic energy of N_e electrons T_e, the interaction energy between electrons U_{ee}, the kinetic energy of N_n nuclei, the coulomb interaction between nuclei U_{nn}, and finally the attractive interaction between nuclei and electrons U_{en}. In the equation bellow for the may-body equation, we use the following symbols and notation: m_e = electron mass, m_n = nuclei mass, ϵ_0 = permittivity in vacuum, q = particle charge, α = nuclei number, Z_a = atom number of nuclei α, r = position of electron, R = position of nuclei.

$$\hat{H} = T_e + T_n + U_{ee} + U_{nn} + U_{en} \tag{5.3}$$

$$= -\sum_{j=1}^{N_e} \frac{\hbar^2 \nabla_j}{2m_e} - \sum_{\alpha=1}^{N_n} \frac{\hbar^2 \nabla_\alpha}{2m_n} + \frac{1}{4\pi\epsilon_0} \sum_{j=1}^{N_e} \sum_{j'<j} \frac{q^2}{|r_j - r_{j'}|}$$

$$+ \frac{1}{4\pi\epsilon_0} \sum_{\alpha=1}^{N_n} \sum_{\alpha'<\alpha} \frac{q^2 Z_\alpha Z_{\alpha'}}{R_\alpha - R_{\alpha'}} - \frac{1}{4\pi\epsilon_0} \sum_{j=1}^{N_e} \sum_{\alpha=1}^{N_n} \frac{q^2 Z_\alpha}{|r_j - R_\alpha|} \tag{5.4}$$

5.1.2 Simplifications and approximations to solve the many-electron Shrödinger equation

Born-Oppenheimer

Challenges with solving many-particle Shrödinger equation is i) computationally expensive, ii) need to know how Ψ depends on single particle wavefunctions ψ_k. To solve this complex problem, we need approximations. Particularly Born-Oppenheimer and Harte-Fock approximations. The first makes the cleaver and reasonable assumption that since the electron mass is negligibly small in comparison to that of a nuclei, we can treat the nuclei as point charges, enabling us to divide the eigenfunction into a separate electronic and nuclear part, ie

$$\Psi_k^{en}(\vec{r}, \vec{R}) \approx \Psi_k(\vec{r}, \vec{R})\Theta_k(\vec{R}) \tag{5.5}$$

where we have written the complete wavefunction in terms of an electronic part $\Psi_k(\vec{r}, \vec{R})$ and nuclear part $\Theta_k(\vec{R})$. The dependencies come from the fact that electrons can respond instantaneously to new positions of the nuclei, therefore the $\vec{R}$ dependence. Writing this in terms of the Hamiltonian we get

$$\left(T_e + U_{ee} + U_{en}\right)\Psi_k(\vec{r}, \vec{R}) = E_k(\vec{R})\Psi_k(\vec{r}, \vec{R}) \tag{5.6}$$

$$\left(T_n + U_{nn} + E_k(\vec{R})\right)\Theta(\vec{R}) = E_k^{en}(\vec{R})\Theta_k(\vec{r}, \vec{R}). \tag{5.7}$$

The two sections are interrelated through the electronic energy eigenvalue $E_k(\vec{R})$. Furthermore, the left hand side of the nuclear part can be simplified to $U_{nn} + E_k(\vec{R})$, assuming that the kinetic energy of point charges is zero. This simplified expression for the nuclear left hand side is called for the potential energy surface (EPS).

Hartree-Fock

The next step in line is to find a wavefunction that can describe all electrons in a system. This was originally done by Hartree, which assumed that electrons can be described independently and suggested the ansatz for a two-electron wavefunction

$$\Psi_k(\vec{r_1}, \vec{r_2}) = A \cdot \psi_1(\vec{r_1})\psi_2(\vec{r_2}), \tag{5.8}$$

where A is the normalization constant. However this approximation does not account for the fact that electrons are indistinguishable and hence does not obey the Pauli exclusion principle for ferminons. This was overcome with the Hartree-Fock approximation that implement an anti-symmetric wavefunction. The full expression is given bellow

$$\Psi_k(\vec{r_1}, \vec{r_2}) = \frac{1}{\sqrt{2}}\left(\psi_1(\vec{r_1})\psi_2(\vec{r_2}) - \psi_1(\vec{r_2})\psi_2(\vec{r_1})\right) \tag{5.9}$$

The Hartree-Fock (HF) approximation makes the electrons distinguishable and hence obey the Pauli exclusion principle, this means that the exchange energy is accounted for. On the other side, HF is not a complete description as it fails to model the electron correlations.

The Variational principle

In materials science, the overarching concern is the ground-state properties of a system. This can be found efficiently and easy by whats known as the variational principle. This states that the energy of any trial wavefunction will always be higher than the ground-state energy E_0, ie

$$E_0 = \langle \psi_0 | H | \psi_0 \rangle \leq \langle \psi | H | \psi \rangle = E \tag{5.10}$$

This enable us to find the ground state energy and corresponding wavefunction by a minimization technique. Next, we will present the basics of the density functional theory for how these equations can be solved numerically and efficiently in order to study real materials and systems.

5.2 Fundamentals of Density-Functional Theory

The density functional theory was developed by Hohenberg and Kohn in 1964 and revolved around the fact that the ground-state density can be expressed in terms of the ground-state wavefunction. We have

$$n_0(r) = |\Psi_0(r)|, \tag{5.11}$$

furthermore the theorem states that all ground-state physical properties can be found as unique functionals of the ground-state density. The biggest upside of this, is that instead of trying to solve the many-body Shrödinger equation to obtain the ground-state wavefunction, we have reduced the computational complexity from $3N_e$ to 3. Thus, the Hohenberg and Kohn density functional theory makes for a promising and effective method to obtain the ground-state properties of a system, given that the exact electron density functional is known. However, this is still 60 years later unknown.

The density functional theory build on two specific theories, called the Hohenberg-Kohn theorems. They are:

1. For any system of interacting particles in an external potential V_{ext}, the density is uniquely determined.

2. There exists a variational principle for the energy density functional such that, if n is not the electron density of the ground-state, them $E[n_0] < E[n]$.

The proof behind both theorems can be found in appendix .. A direct result of the second theorem is the energy can be described as a function of the density

$$E[n] = T[n] + U_{ee}[n] + U_{en}[n], \tag{5.12}$$

where the first two terms $T[n]$ and $U_{ee}[n]$ make up the Hohenberg-Kohn functional.

We know move on to the Kohn-Sham equations, in which Kohn and Sham expressed the exact ground-state density from Hartree type wavefunctions.

$$\Psi(\vec{r}_1, \vec{r}_2, .., \vec{r}N_e) = \psi_1^{KS}(\vec{r}_1)\psi_2^{KS}(\vec{r}_2)...\psi_{N_e}^{KS}(\vec{r}_{N_e}) \tag{5.13}$$

In which, ψ_j^{KS} are auxiliary independent single-particle wavefunctions. We know modify the equation for total energy as a function of density defined by the second theorem, to include the single auxiliary wavefunctions and their corresponding kinetic energy and interaction energy. We get:

$$E[n] = T_s[n] + U_s[n] + U_{en}[n] + (T[n] - T_s[n]) + (U_{ee}[n] - U_s[n]). \tag{5.14}$$

with the s subscript denoting the single particle wavefunctions. The latter two terms are known as the exchange-correlation energy E_{xc}

$$E_{xc}[n] = \Delta T + \Delta U \tag{5.15}$$

This term is responsible for the many-electron interaction. The complete total energy functional can now be expressed as

$$E[n] = \overbrace{\sum_j \int \psi_j^{KS*} \frac{-\hbar^2\nabla^2}{2m} \psi_j^{KS} d\vec{r}}^{T_s[n]} + \overbrace{\frac{1}{2}\frac{1}{4\pi\epsilon_0} \int \int q^2 \frac{n(\vec{r})n(\vec{r}')}{|\vec{r}-\vec{r}'|} d\vec{r}\vec{r}'}^{U_s[n]}$$
$$+ \underbrace{\int V_{en}(\vec{r}n(\vec{r})d\vec{r}}_{U_en[n]} + \underbrace{(T[n]-T_s[n]) + (U_{ee}[n]-U_s[n])}_{E_{xc}[n]} \tag{5.16}$$

Finally we write the complete expression for the Kohn-Sham single-electron equations given an exact exchange-correlation energy and utilizing the variational principle described previously

$$\left\{ -\frac{\hbar^2}{2m_e}\nabla_s^2 + v_H(\vec{r}) + V_{en}(\vec{r}) + V_{xc}(\vec{r}) \right\}\psi_s^{KS}(\vec{r}) = \epsilon_s^{KS}(\vec{r})\psi_s^{KS}(\vec{r}), \tag{5.17}$$

Define V_H and V_{xc} and mention that the former include self interaction that can be accounted for in XC functional. Finally, the total energy of the many-electron system is defined as

$$E[n] = \sum_j \epsilon_j^{KS} - \frac{1}{2}\frac{1}{4\pi\epsilon_0} \int \int q^2 \frac{n(\vec{r})n(\vec{r}')}{|\vec{r}-\vec{r}'|} d\vec{r}d\vec{r}' + E_{xc}[n] - \int V_{xc}(\vec{r})n(\vec{r})d\vec{r}. \tag{5.18}$$

This is the fundamental working principle of the density functional theory and Kohn-Sham equations.

5.3 The exchange-correlation energy

Add references and other fixes later If we can find an expression for $E_{xc}[n]$ as a functional of the density, we have all the tools required to calculate

the total energy of any material. Given that the physical properties of a material is strongly related to the electronic density of said material, the precision of DFT is very dependent on the type of approximation to the density is used. However there exist a compromise here, as a more precise density model is significantly more complex and costly from a computational perspective. In this section we will discuss the extensions of DFT since the original formulation in 1960, and the different approximations one can apply to the electronic density. Thereafter we will discuss the application of DFT, therein the pros and cons, successes and failures.

The exchange-correlation functional is only exactly known for a homogeneous electron gas, however this is of limited use in real materials with a high degree of variation in the electron concentration. An improvement on this is the local density approximation (LDA), in which the electronic density is set at each position according to the homogeneous electron gas at that position, ie

$$V_{xc}(\vec{r}) = V_{xc}^{e\,gas}[n(\vec{r}]$$ (5.19)

This is seen as a successful approximation for the exchange-correlation energy in bulk materials, given that typically the electron density does not vary tremendously. However this method is not without flaws, most notably is the presence/degree of self-interaction induced from this method, from that the self-interaction term does not completely cancel out by only including the local environment of given positions. This may lead to artificial contributions to V_{xc} and an overall inaccurately high electron density. The success behind this method most reliably lies in the low computational cost.

The generalized gradient approximation (GGA) extends on the concept of LDA by also including the gradient of the electron density.

$$V_{xc}^{GGA}(\vec{r}) = V_{xc}[n(\vec{r}), \nabla n(\vec{r})].$$ (5.20)

GGA is good for materials with a slowly varying density, but fails with large gradients. The GGA functional is implemented in two different methods, Perdew-Wang 91 (PW91) and Perdew-Burke-Ernzerhof (PBE).

Both methods underestimate the band gap and wrongly predict the charge localization in cases of narrow bands or lattice distortion. A large part of this comes from the self-interaction of the Hartee potential. By combining the correlations and exchange of LDA/GGA with the exact exchange of the Hartree-Fock approximation, we can obtain much more precise calculations. This method was proposed by Becke and proposed as hybrid functionals, since the functional is a hybrid between the two. This method is superior in describing localized states, but comes at a significant larger computational cost. In order to reduce this cost, Heyd al et. split the Hartree-Fock exchange into short-range and long-range parts, in which calculations can adapt exact Hartree-Fock exchange for short-range (SL) and non-exact for long-range (LR). By introducing the parameter ω to

adjust the order parameter of the method, we can express this method, called HSE (Heyd-Scuseria-Ernzerhof) by

$$E_{xc}^{HSE} = \alpha E_x^{HF,SR}(\omega) + (1 - \alpha)E_x^{PBE,SR}(\omega) + E_x^{PBE,LR}(\omega) + E_c^{PBE} \qquad (5.21)$$

- Explain what the different notations mean, and the success + limitations of HSE compared to LDA and GGA.

- Write a paragraph on meta-GGA, such as SCAN and perhaps MBJ.

5.4   Success and limitation of DFT

- Local minima method

- Not exact V_{xc}, means we must compromise between accuracy and cost, and choose between the different methods for specific application. There is no one best overall method that is superior for all purposes.

Part II

Methodology and Implementation

Chapter 6

Practical application of DFT

In this section we will present how the density functional theory discussed above can be applied and implemented in a computationally feasible manner to model various materials.

Insert section in XC functionals here. With the echange-correlation functionals presented above, we now have everything in order to perform DFT calculations. To begin solving eq .., we need the single-electron wavefunction, for a free electron this is a plane wave $\psi_k = Ae^{ikr}$. In a solid however, there exist a nonzero periodic potential $V(r) = V(r + R)$, the solution to the Shrödinger equation is given by Bloch's theorem wich states that the solution takes the form

$$\psi_k(r) = u_k(r)e^{ikr},\tag{6.1}$$

where $u_k(r$ is a bloch wave with identical periodicity to the supercell. And k is the wavevector. Along with eq(above), problems in DFT are solved in k-space or reciprocal space for convience sake. For instance a great deal of DFT calculations revolve around solving the integral

$$g = \frac{V_{\text{cell}}}{(2\pi)^3} \int_{\text{BZ}} g(k)dk,\tag{6.2}$$

with BZ denoting that the integral be evaluated for all k in the Brillouin zone. This integral can be approximated by evaluating the integral at a set of discrete points and summing over the points with appropriatly assigined weigts. A larger set of points leads to more exact approximations. This method is called Legendre quadrature. The method for selceting these points in reciprocal space was devolped by Monkhorst and Pack in 1976, and simply put requieres a amount of kpoints in each direction in reciprocal space, in the form $NxNxN$. Recalling that reciprocal space is inverse to regular space, supercells with equal and large dimensions converge at smaller values of N, and inversly for cells of small dimsion. In supercells with different length axis, such as hexagonal cells, we use the notation $NxNxM$, where M relate to the distincntly different axis. The amount of kpoints required can be fruther reduced by utulizing the symmetry of the cell, in which we can exactly approximate the entire BZ by extending a

lesser zone through symmertry. This reduced zone is appropriartly named the irreducible Brillouin zone (IBZ).

Metals in particular requiere a large set of kpoints to acchive accurate results. This is becouse we encounter discontinuies functions in the Brillouin zone around the fermi sufrace where the states discontinusly change from occupied to non-occupied. To reduce the cost of this operatin, there are two primary methods, tetrhaedon and smearing. The idea behind the tetrahedon method is to use the discrete set of k-points to fill the reciprocal space with tethraeda and interpolate the function within each tethraeda such that the function can be integrated in the entire space rather than at discrete points. The latter approach for solving discontinuos integrals is to smear out the discontinuity and thus transforming the integral to a continous one. A good analogy to this method is the fermi-dirac function, in which a small variable σ transform a step-functino into a continious function that can be integrated by standard methods.

In addition to the number of kpoints, there is one more distinct parameter that must be specified in DFT calculations, namely the energy cutoff, or E_{cut}. This parameters arise from the Bloch function described previosly. In which $u_k(r)$ was a bloch wave with the same periodicity as the supercell. This implies that the wave can be expanded by a set of special plane waves as

$$u_k(r) = \sum_G c_G e^{iGr}, \tag{6.3}$$

where G is the reciprocal lattice vector. Combining this with eq ..(first eq for blcoh function) we get

$$\psi_k(r) = \sum_G c_{k+G} e^{i(k+G)r} \tag{6.4}$$

The consequense from this expression is that evaluating the wavefunction of an electron at a single k point demand a summation over the entirity of reciprocal space. In order to reduce this computational burden, we can introduce a maximum paramater E_{cut} to cap the calculations. This is possible becouse eq ..(above) is the solution of the Shrödinger equation with kinetic energy

$$E = \frac{\hbar^2}{2m} |k + G|^2. \tag{6.5}$$

Seeing as the solution with lower energies are the most interesting, we can limit the calculations of eq ..(2 above) to solutions with energy less than E_{cut} given bellow

$$E_{cut} = \frac{\hbar^2}{2m} G_{cut}. \tag{6.6}$$

Thus, we can reduce the infinitly large sum above to a much more feasable calculation in

$$\psi_k(r) = \sum_{|k+G|<G_{cut}} c_{k+G} e^{i(k+G)r} \tag{6.7}$$

A summary on kpoints and ENCUT, plus a discussion on nummerical convergence and how to select kpoints and ENCUT

A final consideration to how DFT is applied in practise is how the core electrons are handled. Tightly bound core electrons as opposed to valene electrons demand a greater number of plane-waves to converge. The most efficient method of reducing the expenses of core-electrons are so-called pseudopotentials. This method works by approximating the electron density of the core elecrons by a constant density that mimic the properties of true ion core and core electrons. This density is then remained constant for all subsequent calculations, ie only considering the valence electrons while regarding the core electrons as frozen-in. There are currently two popular types of psudopotentials used in DFT, so-called ultrasoft psudopotentials (USPPs) devoplped by Vanderbilt, and the projecter augmented-wave (PAW) method by Bloch. This project will exclusivly apply the latter.

Self-consistent iteration and relaxation discussion and figure

Chapter 7

Computational details

This section is intended to provide the nescssary details for reproduction of results to be presented later on. First we begin by describing the software used for the project.

7.1 Vienna Ab initio Simulation Package

This software, often referred to as VASP is a package for ab initio quantom mechanics calculations using the projected augmented wave method and plane wave basis set. The intended methodolgy is DFT, but have been extended for methods post the original DFT-formulation. Calculations with VASP was carried out on the supercomputer fram, with a quantity of allocated time and resources provided på Uninett Sigma2,**add reference!**.

The strucutre of VASP rely on a set of input files and output files from the calculation, the input files required to perform a DFT computation in VASP are the following:

- INCAR - this file provide the tags responsible for different methods, algorithms, parameters etc.

- POSCAR - this file is related to the crystal strucure of the system

- POTCAR - What psudopotential that is used

- KPOINTS - A file containing information on what KPOINTS will be used

- jobfile - This file contains information for the supercomputer regarding resources and such.

The capitalization displayed above is directly related to the requierements of the filesystem in the VASP/fram collaboration. Some important output files are:

- CONTCAR - The relaxed crystal strucure after finalized calculation

- CHGCAR - This file contains the electron density after calculation

- EIGENVAL - Contains the solutions to the Kohn-Sham eigenfunctions

- DOSCAR - Infomration on the Density of States

- OUTCAR - Contains a list of all other information.

In this project, we began the calculation of every induvidual structure by testing the convergence of total energy with repsect to the number of k-points and cutoff energy. In VASP, the latter can be specified by setting the tag "ENCUT" in the INCAR file, we found 300 eV to yield producive results in terms of convergence and computation time for total energy calcuations, and 400 for ionic+volume relaxations. Regarding the number of points in the reciprical space, we carried out a great deal of simulations on numerous strucutes with distinct crystal strucutres and corresponding supercells, for this reason we employed a number of different sets of k-points depending on the strucure. Typically the number of points ranged from a 2x2x2 mesh to 4x4x4 mesh. With the smaller being required for hybrid functionals to converge.

Upon realizing the convergence parameters, the strucures were allowed to relax both the ionic posistions, and cell volume with the quas-newton method and a convergence criterion of $1E - 2$ for the forces and $1E - 5$ for the total energy. However, the symmetry of the stucutre was forced constant by the use of vasp-std-noshear. This process was repeated two times before perfoming one final total energy calculation with GGA functional, and one with the SCAN functional, increasing the convergence criterion to $1E - 6$. In certain cases, we also attempted to perform calculations with the hybrid functional HSE06.

The specific tags, algorithms, parameters and options of VASP that was in use throughout this project can be found at our github adress, but in particlar we would like to cover specificlly two factors/tags. Firstly is the tag ISPIN that correspond to the magnetism of the system. Considering this study revolved heavily around magnetic elements such as iron and Nickel, we used ISPIN=2 which allow for colinear spin-polarized calculations. However, there are many more magnetic orientations the system can adopt besided colinear, therfore the final total energies we found may not be the true lowest energies. But given the allocated duration and resources of this project, this is a understood consequence. Secondly is the type of smearing that was used for the different calculations. The preferred method for accurate total energies and density of states in semiconductors is the tethraedon method, and for accurate forces in metals the Methfessel-Paxton method is recommended. However, our system contains both metals and a large portion of Si. For this reason we used a combination of smearing methods. For the relaxation and minimzation of forces, we used gaussian smearing with smearing width $\sigma = 0.05$, as this method provide accurate foces in both metallic and semicondicing materials. And to claculate the total energy and DOS, we used the tetradon method, as recommended. One interesting result of this project, is that we were not able to converge calculations with hybrid functinoals using the tetrahedon

method and was thus forced to adopt the gaussion method in this case additionaly.

Band structure/DOS and band-unfolding?

7.2 Generation of SQS

The generation of special quasi-random structures as described in section .., was done by utilizing the Temperature Dependent Effective Potential (TDEP) method. This package, devolped by Olle Hellman, offers a wide range of tools primarly intended for studies of finite temperature lattice dynamics. In this project we utilize the program generate-strucutre within the TDEP package to contruct SQS's. The work of TDEP is the result of an unpuplished PHD thesis by Nina Shulumba **(Insert citation)**, thus the documentation on the software and generate-structure script is limited, please refer to the original author for more information.

In this project, we constructed SQS's by first transforming the cif-files of a given initial structure, for instance that of *FeSi$_2$*, to a primitive unit cell. The SQS's was genereated by the same principles explained in section .., for each strucure we created 5 distinct SQS's of an equal size under the constraint that the 3d atoms be distributed eqvimolar in the systen. Precise file formats and such can be found at github. Another approach could have been to construct SQS's of specific cell counts instead of total number of atoms, however this quikly lead to extremly large supercells, up to 256 atoms, that simply would not converge to our best efforts. **Insert figure of SQS's before relaxation, for some of the strucures and give a brief summary.**

7.3 Utility scripts

During the course of the projects lifetime, several shell and python scripts was devolped by myself and/or provided to me by my superviosor Ole Martin Løvvik and his team of researchers at Sintef. These can be located at the github adress :...

Part III

Results and Discussion

Chapter 8

Results of SQS

8.1 Something

Compare the results from different SQS in terms of stability and total energy: Factors to include can be bond length, nearest neigbors, density, structure, elementes, size of SQS, initial magnetic settings. ETC

Chapter 9

Band gap results

9.1 Compare and anlayze band gaps

Results here can be a table of the band gaps for different SQS both within one cell, or compare multiple cells. Other results include Density of States, Local DOS, bandgap from eigenval without impurity states. Compare different methods, GGA, SCAN and hybrid. The CHGCAR to evaluate bonding in terms of metallic or covalent. Possibly band-unfolding?

Part IV

Conclusion

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