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Abstract

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Preface

Chapter 1

Introduction

some introduction on the importance of discovering new materials and alloying.

Need something on thermoelectricity related to both the band gap and high-entropy alloys.

High-entropy alloys is a novel class of materials based on alloying multiple components, as opposed to the more traditional binary alloys. This results in an unprecedented opportunity for discovery of new materials with a superior degree of tuning for specific properties and applications. Recent research on high-entropy alloys have resulted in materials with exceedingly strong mechanical properties such as strength, corrosion and temperature resistance, etc **find references**. Meanwhile, the functional properties of high-entropy alloys is vastly unexplored. In this study, we attempt to broaden the knowledge of this field, the precise formulation of this thesis would be an exploration on the possibilities of semiconducting high-entropy alloys.

A key motivation of this thesis is the ability to perform such a broad study of complex materials in light of the advances in material informatics and computational methods. In this project, we will employ Ab initio methods backed by density functional theory on top-of the line supercomputers and software. 20 years ago, at the breaking point of these methods, this study would have been significantly narrower and less detailed firstly, but secondly would have totaled ... amount of CPU hours to complete (**Calculate this number**). In the addition to the development in computational power, is also the progress of modeling materials, specifically we will apply a method called Special Quasi-random Structures (SQS) to model high-entropy alloys or generally computationally complex structures. Together with the open landscape of high-entropy alloys described above, these factors produce a relevant study in the direction of applying modern computational methods to progress the research of a novel material class and point to promising directions for future research.

In specifics, this thesis revolve around the electrical properties of high-entropy alloys, mainly the band gap as this is the key indicator for a semiconducting material and it's applicability. Semiconductors are the building blocks in many different 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. Furthermore, the development and research on both high entropy alloys and metal silicides have been heavily centered around 3d transition metals. Keeping in line with the economic and environmental factors, we will continue this direction by focusing on high entropy stabilized sustainable and economic 3d metal silicides **Not happy with this writing**. Throughout the study we will analyze a great number of permutations of 3d silicides, from different initial metal silicides such as $CrSi_2$, $FeSi_2$, $MnSi_{1.75}$, Fe_2Si , each with distinct properties relating to the band gap, crystal structure and metal to silicon ratio. In addition, the permutations include numerous metal distributions and elements within the 3d-group of metals. Examples are Co, Cr, Fe, Mn, and Ni.

Given a background in high-entropy alloys, one could ask if this study is truly sensible. In the later sections we will cover the details of this field, and it quickly become clear that the materials investigated in this study does not fall under the precise definition of high-entropy alloys, nor do we intend to explore the properties and factors relating to high-entropy stabilized alloys such as the configurational entropy, phase stability and finite temperature studies. However this study is motivated from the discovery of these materials and promising properties, and venture into a more hypothetical space of materials, enabled by the computational methods available to study the potential properties of such materials. On the other hand, very recent studies **Mari, and other HEA silicide study** have experimentally synthesized high-entropy disilicides, thus in some way justifying the direction of this project.

We begin this project by reviewing key concepts of solid-state physics for readers lacking a background in materials science, and an introduction to the base 3d silicides of the experimental work. Later follows a theoretic walk-through of the relevant concepts of this thesis, these topics include high-entropy alloys, special quasi-random structures, and density functional theory. Next we shine light on the implementation of DFT in this project, and other computational details required to reproduce the results in this thesis, such as the use of the Vienna Ab Initio Simulation Package (VASP) and implementation of SQS. Finally we present the results of our study, these include the band gap and electronic properties of various structures and the success and challenges of the computational methods applied throughout the study.

Part I

Theory

Part II

Methodology and Implementation

Chapter 5

Practical application of DFT

In this section we will present the practical application and implementation of density functional theory in the study of materials science.

5.1 The Exchange-Correlation functional

From the former section, we know that the one piece of information missing of the density functional theory is the complex exchange-correlation energy $E_{xc}[n]$ that must account for all the simplifications and approximations employed in Kohn-Sham DFT. In this section we will explore some of the options do include the exchange-correlation functional, they operate in 4 levels of complexity. First is the local density approximation (LDA), followed by the generalized gradient approximation (GGA). These two are the least complex and computationally affording methods of calculating E_{xc} . Next is the methods such as meta-GGA implementations and finally the very accurate, but equally demanding hybrid-functionals. We will begin this section by describing the local density approximation.

5.1.1 Local density approximation

A homogeneous electron gas (HEG) is the sole case we know of where the exchange-correlation functional can be determined exactly, because in the simple example the electron density is constant. The LDA works by setting the exchange-correlation potential $V_{xc}(\mathbf{r})$ at every position equal to that of the homogeneous electron gas, in other words

$$V_{xc}(\mathbf{r}) = V_{xc}^{\text{HEG}}[n(\mathbf{r})]. \quad (5.1)$$

Obviously the LDA is of limited use given that a large part of what makes materials interesting is the change in the electronic density, for example LDA is known to overestimate binding energies and underestimate the band gap in semiconductors and insulators. On the other hand, LDA provide generally adequate results in bulk materials with slowly varying charge density, for example equilibrium distances and vibrational frequencies. The biggest upside of LDA however comes from the low computational cost, and was one of the first big success-stories of DFT.

5.1.2 Generalized gradient approximation

A natural succession to the local density approximation is the family of generalized gradient approximation (GGA) that also include the gradient of the electron density

$$V_{\text{XC}}^{\text{GGA}}(\mathbf{r}) = V_{\text{XC}}[n(\mathbf{r}), \nabla n(\mathbf{r})]. \quad (5.2)$$

The way one can implement the gradient are plenty-full and complicated. Two of the most common methods are the Perdew-Wang 91 (PW91) [1] and the Perdew-Burke-Ernzerhof (PBE) GGE[2]. This project will utilize the latter which came to fruition in 1996 in an article by Perdew, Burke and Ernzerhof appropriately named "Generalized Gradient Approximation Made Simple". The key point regarding the PBE functional is that it's a non-empirical method thus providing reliable and adequate accuracy over a wide range of systems, as compared to for instance the BLYP functional that provide excellent accuracy of organic molecules but fails in other cases [3]

Further, we can extended this idea to include the Laplacian ∇^2 of the density. This range of methods is called meta-GGA, in this project we use a meta-GGA functional called *Strongly Constrained Appropriately Normed*, or SCAN [4]. **Write a brief discussion of these, see for example [5].**

5.1.3 Hybrid functionals

Very precise calculations can be obtained from combining LDA/GGA with the exact Hartree-Fock exchange energy. This method was proposed by Becke as hybrid functionals, since the functional is a hybrid between the two. **Insert eq for hybrid functionals?** 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) [6] as

$$E_{xc}^{\text{HSE}} = \alpha E_x^{\text{HF},\text{SR}}(\omega) + (1 - \alpha) E_x^{\text{PBE},\text{SR}}(\omega) + E_x^{\text{PBE},\text{LR}}(\omega) + E_c^{\text{PBE}} \quad (5.3)$$

Explain what the different notations mean Write more/better on hybrid functionals and HSE06, see references [7], [8]. [9] and write a summary of the different approximations

5.2 Fundamental aspects of practical DFT calculations

Needs work, see mainly DFT book ch 3 With the exchange-correlation functionals presented above, we now have everything in order to perform DFT calculations. To begin solving eq .., we need the single-electron wave-function, for a free electron this is a plane wave $\psi_k = Ae^{ikr}$. In a solid

however, there exist a nonzero periodic potential $V(\mathbf{r}) = V(\mathbf{r} + \mathbf{R})$, the solution to the Shrödinger equation is given by Bloch's theorem wich states that the solution takes the form

$$\psi_k(\mathbf{r}) = u_k(\mathbf{r})e^{i\mathbf{k}\mathbf{r}}, \quad (5.4)$$

where $u_k(\mathbf{r})$ is a bloch wave with the periodicity of the supercell, and \mathbf{k} is the wavevector. Similar to eq(above), k-space, or reciprocal space is useful to solve the numerous mathematical problems posed by DFT. For instance a great deal of DFT calculations revolve around solving the integral

$$g = \frac{V_{\text{cell}}}{(2\pi)^3} \int_{\text{BZ}} g(\mathbf{k}) d\mathbf{k}, \quad (5.5)$$

with BZ denoting that the integral be evaluated for all \mathbf{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 appropriately assigned weights. 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 $N_x N_x N_x$. 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 dimnsion. In supercells with different length axis, such as hexagonal cells, we use the notation $N_x N_x M$, 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 suface 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 $u_k(\mathbf{r})$ 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

$$u_k(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{G}} e^{i\mathbf{G}\mathbf{r}}, \quad (5.6)$$

where \mathbf{G} is the reciprocal lattice vector. Combining this with eq ..(first eq for Bloch function) we get

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{k}+\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G})\mathbf{r}} \quad (5.7)$$

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

$$E = \frac{\hbar^2}{2m} |\mathbf{k} + \mathbf{G}|^2. \quad (5.8)$$

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 below

$$E_{\text{cut}} = \frac{\hbar^2}{2m} G_{\text{cut}}^2. \quad (5.9)$$

Thus, we can reduce the infinitely large sum above to a much more feasible calculation in

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{|\mathbf{k}+\mathbf{G}| < G_{\text{cut}}} c_{\mathbf{k}+\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G})\mathbf{r}} \quad (5.10)$$

A summary on kpoints and ENCUT, plus a discussion on numerical 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 valence 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 electrons 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 pseudopotentials used in DFT, so-called ultrasoft pseudopotentials (USPPs) developed by Vanderbilt, and the projector augmented-wave (PAW) method by Bloch [10], [11].

5.3 Self-consistent field calculation

Needs work, see lecture notes ch 8, book ch1 Preceding this section, we have considered the fundamental theory of DFT and its practical ability to model various materials. In figure 5.1 we present the self-consistent field calculation scheme for how DFT calculations are performed. The initial problem posed by dft is that all properties rely on the density, and are dependent on each other. For instance, the effective potential is dependent on the density, which again is dependent on the eigenfunctions, that rely

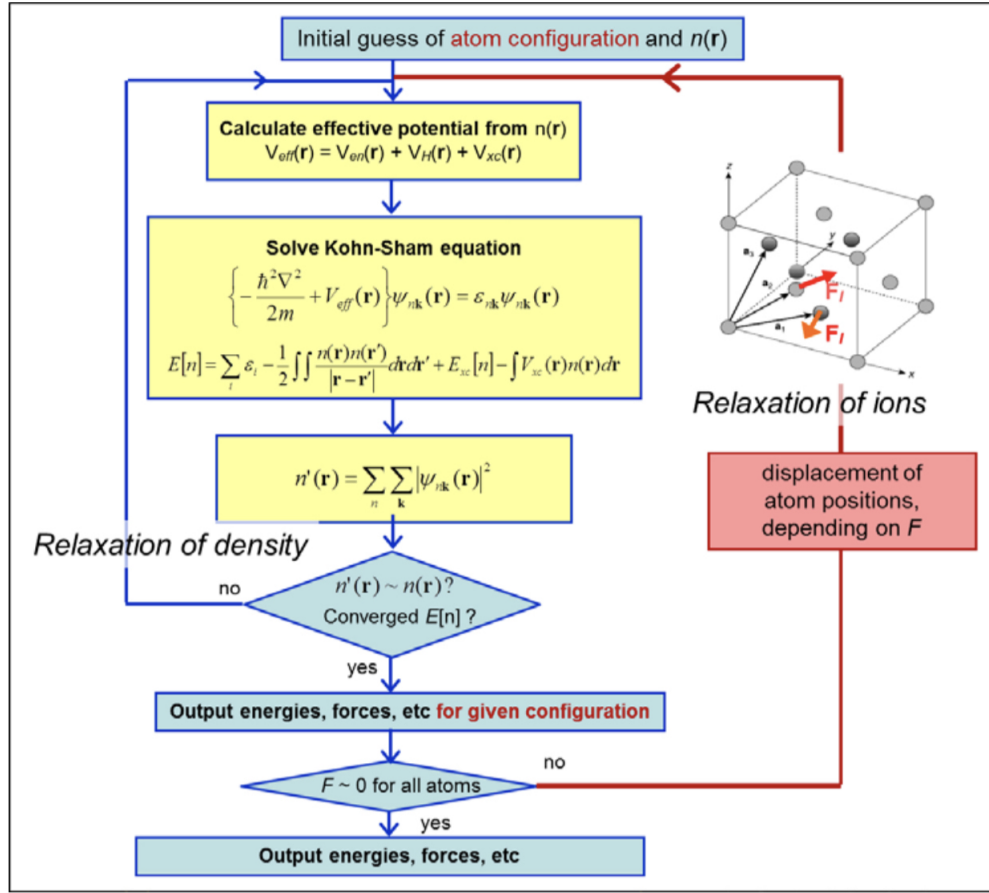


Figure 5.1: Self consistent iteration of a DFT calculation. Figure adopted from lecture notes [fys-mena4111](#) cite

on the effective potential again. The clever approach, as seen in figure 5.1 begin with an initial guess to the density from which we can solve the Kohn-Sham equation and obtain the corresponding eigenfunctions. Following is an iterative method where we apply the recently calculated eigenfunctions to determine a new density and repeat the procedure above. This is repeated until the total energy is converged, by an own-defined criterion. Equivalently, the optimal ionic positions can be found by a similar approach. This method is based on quasi-Newton algorithms to minimize the forces between ions.

Part III

Results and Discussion

Part IV

Conclusion

Write conclusion here

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