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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) GGA [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]. In fact, the original PBE article is the 16th most cited scholarly article of all time (as of 2004) Cite: https://www.nature.com/news/polopoly_fs/1.16224!/menu/main/topColumns/topLeftColumn/pdf/514550a.pdf, to illustrate the application and importance of this method.

5.1.3 Meta-GGA

Meta-GGA functionals is the final level of complexity of the non-empirical approximations to the exchange-correlation functional. In addition to the the constant density (LDA) and local gradient of the density (GGA), meta-GGA methods consider the kinetic energy density of the occupied Kohn-Sham orbitals [4], defined as

$$\tau_{\omega} = \sum_i^{\text{occ}} \frac{1}{2} |\nabla \psi_{i\omega}|^2. \quad (5.3)$$

The role of this quantity on the the calculated band gap is well described in [5]. In this project we employ a meta-GGA functional named *Strongly Constrained Appropriately Normed*, or SCAN. This functional is the only known functional to satisfy all 17 known exact constraints of the XC functional [6]. The initial outcomes of the SCAN functional showed promising improvement over both LDA and PBE at similar computational cost. Studies utilizing the SCNA functional have found results supporting superior accuracy of the band gap and electronic density of states [7], and atomic structures [8]. Moreover can provide high accuracy and comparative outputs to hybrid functionals for geometries and energies in diversely bonded materials [9], compared to LDA and PBE. However drawbacks are also present in the SCAN functional, one of these is opposite to structures with strong binding where SCAN yields superior accuracy of crystal volume, magnetism and band gap, SCAN is observed less reliable and accurate to PBE in weakly-bound structures [10]. Another very popular meta-GGA implementation is the *Modified Becke-Johnson* functional

[11], however we did not manage to converge calculations with this functional in this project.

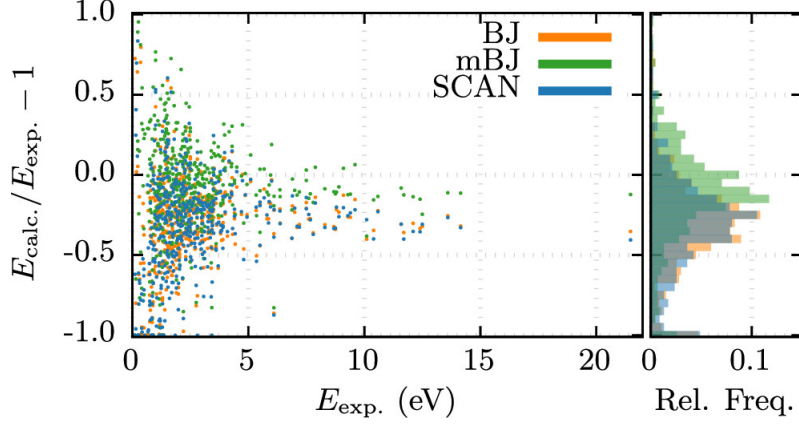


Figure 5.1: Calculated to experimental band gap measurements of Becke-Johnson, modified Becke-Johnson and SCAN functionals [12]

5.1.4 Hybrid functionals

The most precise functional known to DFT belong to the family of *hybrid functionals*. Accordingly this method consist of a hybrid between simpler functionals such as LDA, PBE or even meta-GGA and the exact treatment of exchange energy from Hartree-Fock, for example the global hybrid functional PBE0 [13] described as

$$E_{xc}^{PBE0} = (1 - \alpha)E_x^{PBE} + \alpha E_x^{HF} + E_c^{PBE}, \quad (5.4)$$

where alpha is the mixing parameter to decide the balance between the exchange energy, denoted x of Hartree-Fock with PBE, alike the last term represent the correlation energy from the PBE functional. This parameter alpha is determined empirically, thus making hybrid functional a semi-empirical model. Obviously considering the exact exchange in Hartree-Fock is a computationally challenging prospect. Heyd-Scuseria-Ernzerhof managed to lower the cost by the concept of Screened functionals that separate the Coloumb interaction into long-range and short-range interaction by a function $erfc(\mu r)$. These are known as HSE functionals [14], the overall best functional for accurate band gaps of solids is by many considered to be HSE06 [15] with $\alpha = 0.25$ and $\mu = 0.11$.

5.1.5 Outlook

In many cases LDA and GGA suffice, PBE especially is by most considered the conventional standard for DFT calculations, for its balance of accuracy, cost and wide range applicability. However, distinctly concerning the band gap of a solids, both of these fall short. This is because the band gap of DFT calculations is complicated by the fact that the derivative of the XC-functional is discontinues with respect to the electron concentration [16],

thus the simpler functionals fail to recall the experimental values since the total band gap in DFT is the fundamental gap (valence - conduction) + this contribution. This is corrected in meta-GGA and hybrid functionals in the generalized Kohn-Sham scheme. Lastly, we would like to refer the reader to the work of Borlido, Aull, Huran, Tran, Marques, and Botti whom in 2019 conducted an exhaustive investigation of the band gap of over 470 unique non-magnetic compounds in order to benchmark the relative performance of several of the available and wideley used XC-functionals [12]. In this large-scale project they found overwhelming confirmation that the HSE06 functional followed closely by Modified-Becke Johnson is the superior choice for accurate band-gap measures. Regarding the SCAN functional, in several cases this yielded outputs very comparable to MBJ, and produce much better formation energies than PBE, but tend to overestimate in magnetic alloys. On the other hand the LDA and PBE functional resulted in 50% and 30% under-estimation of the band gap and several cases of miss-classified metals, this was particularly evident in compounds containing Ni and other 3d elements. This result in a limited application to for example narrow gap thermoelectrics or photovoltaics where accurate values of the band gap and states at the band edges is critical.

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

$$\psi_k(\mathbf{r}) = u_k(\mathbf{r})e^{ikr}, \quad (5.5)$$

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

$$g = \frac{V_{\text{cell}}}{(2\pi)^3} \int_{\text{BZ}} g(\mathbf{k})d\mathbf{k}, \quad (5.6)$$

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 $N \times N \times N$. Recalling that reciprocal space is inverse to regular space, supercells with equal and large dimensions converge at smaller values of N , and inversely for cells of small dimension. In supercells with different length axis, such as hexagonal cells, we use the notation $N \times N \times M$, where M relate to the distinctly different axis. The amount of kpoints required can be further reduced by utilizing the symmetry of the cell, in which we can exactly approximate the entire BZ by extending a lesser zone through symmetry. This reduced zone is appropriately named the irreducible Brillouin zone (IBZ).

Metals in particular require a large set of kpoints to achieve accurate results. This is because we encounter discontinuous functions in the Brillouin zone around the Fermi surface where the states discontinuously change from occupied to non-occupied. To reduce the cost of this operation, there are two primary methods, tetrahedron and smearing. The idea behind the tetrahedron method is to use the discrete set of k-points to fill the reciprocal space with tetrahedra and interpolate the function within each tetrahedron such that the function can be integrated in the entire space rather than at discrete points. The latter approach for solving discontinuous integrals is to smear out the discontinuity and thus transforming the integral to a continuous one. A good analogy to this method is the Fermi-Dirac function, in which a small variable σ transform a step-function into a continuous 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 parameter arises from the Bloch function described previously. 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

$$u_k(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{G}} e^{i\mathbf{G}\mathbf{r}}, \quad (5.7)$$

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

$$\psi_k(\mathbf{r}) = \sum_{\mathbf{G}} c_{k+\mathbf{G}} e^{i(k+\mathbf{G})\mathbf{r}} \quad (5.8)$$

The consequence from this expression is that evaluating the wavefunction of an electron at a single 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

$$E = \frac{\hbar^2}{2m} |\mathbf{k} + \mathbf{G}|^2. \quad (5.9)$$

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

$$E_{\text{cut}} = \frac{\hbar^2}{2m} G_{\text{cut}}^2. \quad (5.10)$$

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

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{|\mathbf{k}+\mathbf{G}| < G_{\text{cut}}} c_{\mathbf{k}+\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G})\mathbf{r}} \quad (5.11)$$

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 [17], [18].

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 it's practical ability to model various materials. In figure 5.2 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 on the effective potential again. The clever approach, as seen in figure 5.2 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.

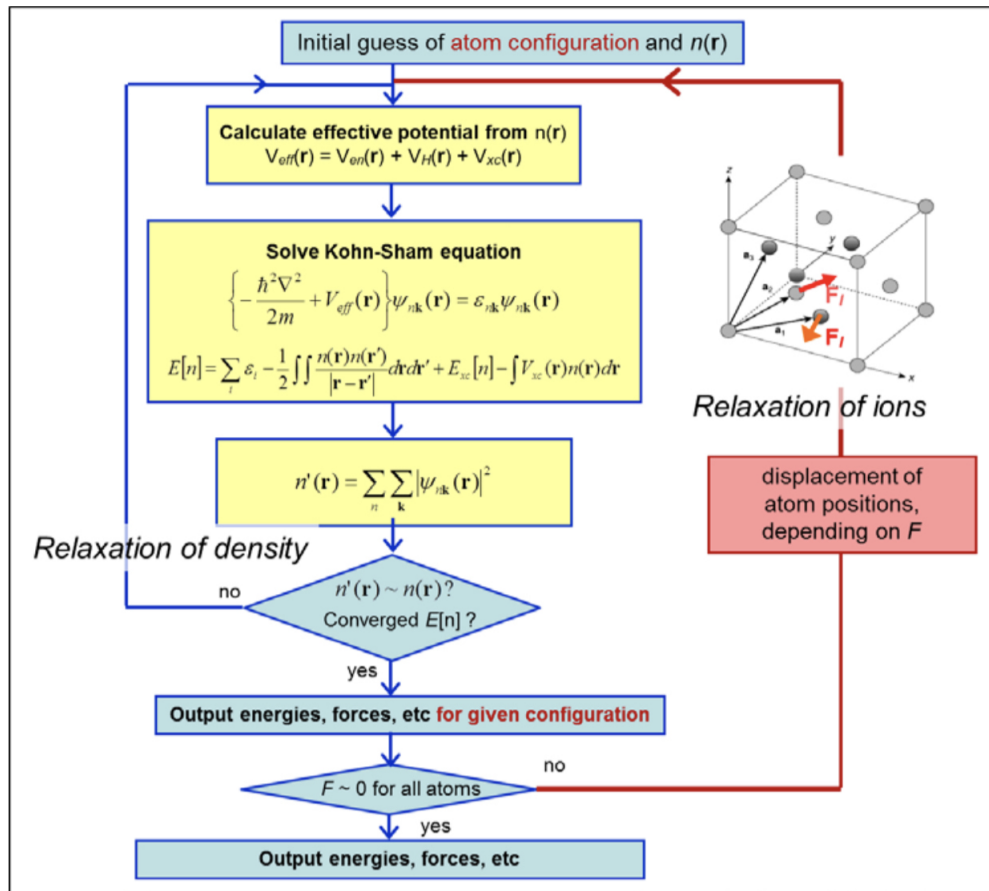


Figure 5.2: Self consistent iteration of a DFT calculation. Figure adopted from lecture notes [fys-mena4111](#) cite

Part III

Results and Discussion

Part IV

Conclusion

Write conclusion here

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