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Abstract

Contents

1	Introduction	1
I	Theory	3
2	Background	4
2.1	Overview of sold-state physics	4
2.2	3d Silicides	4
3	High-Entropy alloys	5
3.1	Fundamentals	5
3.2	Core effects and properties of high-entropy alloys	8
4	Modeling of random alloys	10
4.1	The Special Quasi-random Structure model	10
4.1.1	Mathematical description	11
4.2	Applications and limitations of SQS in modeling high-entropy alloys	13
5	Density Functional Theory	17
5.1	Review of Quantum Mechanics	18
5.1.1	The Shrödinger equation	18
5.1.2	Simplifications and approximations to solve the many-electron Shrödinger equation	19
5.2	Fundamentals of Density-Functional Theory	21
5.3	Limitations of DFT	22
II	Methodology and Implementation	24
6	Practical application of DFT	23
6.1	The Exchange-Correlation functional	23
6.2	Fundamental aspects of practical DFT calculations	24
6.3	Self-consistent field calculation	26
7	Computational details	28
7.1	Vienna Ab initio Simulation Package	28
7.2	Generation of SQS	30

7.3	Figures	31
7.3.1	Density of states	31
7.3.2	Probability distribution functions	31
7.3.3	Charge density	31
7.4	Band gap	31
7.5	Utility scripts	31
III	Results and Discussion	33
8	The results of (CrFeMnNi)Si₂ in the β-FeSi₂ structure	33
8.1	Eqvimolar SQSs	33
8.1.1	Introduction	33
8.1.2	The band gap	34
8.1.3	Local and Projected density of states	36
8.1.4	Meta-GGA and hybrid functional	40
8.1.5	Probability distribution functions and charge density	44
8.2	Permutations of the Cr ₄ Fe ₄ Mn ₄ Ni ₄ Si ₃₂ high-entropy silicide	46
9	Changing the elements	52
10	Overview and Relevance	57
10.1	Cr ₄ Fe ₄ Mn ₄ Ni ₄ Si ₃₂ in different crystal structures	57
10.2	Overview	59
IV	Conclusion	60
A	Density of states	56
B	PDFs	57
C	Charge density	58

List of Figures

3.1	Formation of HEA based on δ and N . Figures adopted from [hea2016_ch2]	7
3.2	A schematic illustration of lattice distortion in high-entropy alloys. Figure from [owen_jones_2018]	9
4.1	PDFs of (a) 20 and (b) 250 atom SQS models of CrFeMnNi [hea2016_ch10]	14
4.2	Density of states with SQS and MC/MD of FCC CoCrFeNi, figure from [hea2016_ch10]	15
4.3	Probability distribution functions with SQS and MC/MD of HCP CoOsReRu [hea2016_ch10]	15
5.1	Number of DFT studies per year from 1980 to 2021. Add reference?	17
6.1	Self consistent iteration of a DFT calculation. Figure adopted from lecture notes fys-mena4111 cite	27
7.1	48 atom SQS based on eqvimolar distribution of Cr, Fe, Mn and Ni in and $FeSi_2$ cell.	32
8.1	Density of states SQS D CFMN (fesi2) from PBE calculation .	35
8.2	Density of states SQS B CFMN (fesi2) from PBE calculation .	36
8.3	Local density of states of Si (SQS D)	37
8.4	Local density of states of TMs (SQS D), (a) Cr, (b) Mn, (c) Fe, (d) Ni	37
8.5	Projected density of states SQS D CFMN (fesi2) from PBE calculation	38
8.6	Projected density of states of SQS D and B around E_F	38
8.7	Density of states of SQS C with 2501 points vs 20000 points in the density of states.	39
8.8	Density of states of SQS E illustrating the different band gap from calculations with (a) PBE and (b) SCAN functional . . .	41
8.9	Total density of states of SQS (a) B and (b) E from calculations with HSE06	42
8.10	Probability distribution function of SQS D (top) and B (bottom)	45
8.11	Charge density of SQS D and B from PBE calculations. Illustrated by VESTA	46

8.12	Projected density of states of (a) $\text{Cr}_3\text{Fe}_3\text{Mn}_7\text{Ni}_3\text{Si}_{32}$ (SQS B), (b) $\text{Cr}_5\text{Fe}_5\text{Mn}_3\text{Ni}_3\text{Si}_{32}$ (SQS C), (c) $\text{Cr}_5\text{Fe}_3\text{Mn}_5\text{Ni}_3\text{Si}_{32}$ (SQS A), (d) $\text{Cr}_3\text{Fe}_5\text{Mn}_5\text{Ni}_3\text{Si}_{32}$ (SQS D)	49
8.13	Density of states around E_F of SQS D and E $\text{Cr}_5\text{Fe}_5\text{Mn}_3\text{Ni}_3\text{Si}_{32}$	50
8.14	Projected density of states of $\text{Cr}_3\text{Fe}_3\text{Mn}_3\text{Ni}_7\text{Si}_{32}$ around E_F .	50
8.15	Probability distribution functions to $\text{Cr}_3\text{Fe}_5\text{Mn}_5\text{Ni}_3\text{Si}_{32}$ SQS D, Maybe make larger	51
9.1	Projected density of states of $\text{Cr}_4\text{Fe}_4\text{Co}_4\text{Ni}_4\text{Si}_{32}$	54

List of Tables

8.1	Total energy per atom, final magnetic moment, band gap (GGA) and formation enthalpy of $Cr_4Fe_4Mn_4Ni_4Si_{32}$ SQSs based on $FeSi_2$	34
8.2	Band gap transition of CFMN (fesi2) SQSs with PBE functional	35
8.3	Band gap (eV) with PBE in spin up and spin down channels of CFMN (fesi2) SQSs	36
8.4	Band gap of CFMN ($FeSi_2$) SQSs with GGA (PBE), meta-GGA (SCAN) and hybrid-functionals (HSE06).	40
8.5	Mean and stadard deviation of the total energy and magnetic moment per atom, plus enthalpy of formation of the listed mean energies ($FeSi_2$).	47
8.6	Total and spin dependent band gap of 4 permutations of CFMN (fesi2) with PBE GGA calculation. The structures that are excluded from this list either failed in calculations, or does not show any band gap.<	48
9.1	Summary of the total energy, enthalpy of formation and magnetization of several compositionally different SQS high-entropy alloys based on the β - $FeSi_2$ unit cell.	52

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

Chapter 5

Density Functional Theory

The density functional theory (DFT) is recognized as a overwhelmingly successful method in quantum chemistry and the overall study and understanding of matter. As illustrated in figure 5.1 this is a tremendously popular method with rapid growth to this day due to improvements to both the method and computational power. **More elaborate introduction, write later.**

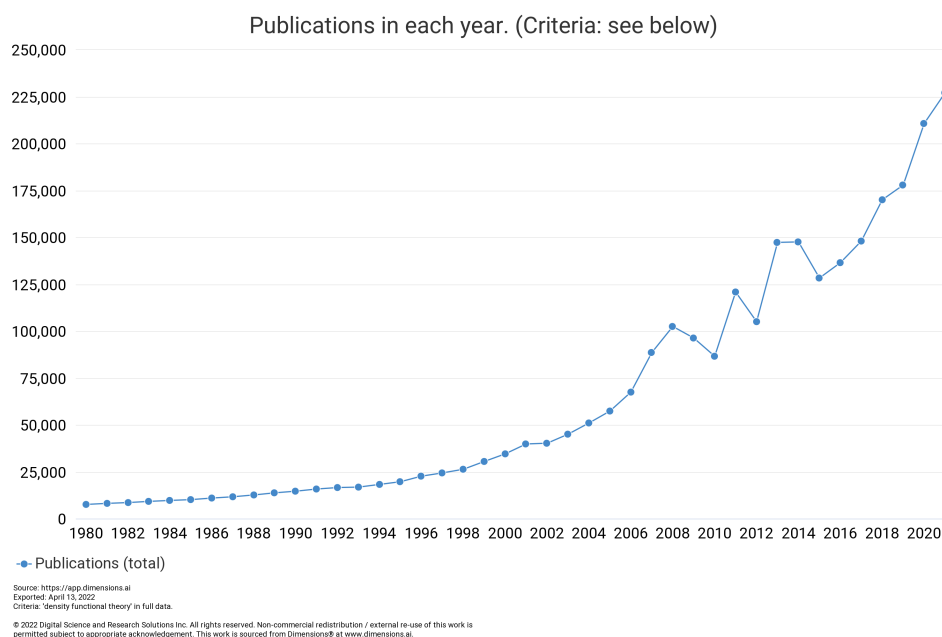


Figure 5.1: Number of DFT studies per year from 1980 to 2021. **Add reference?**

The concept of the density functional theory is to efficiently solve the problems posed by quantum physics, most notably the many-particle Schrödinger equation. Thus in this section we will begin by reviewing some central concepts of quantum physics before presenting the main Hohenberg-Kohn formulation of DFT. The content in this part is inspired from the lecture notes [REF] written by Clas Persson in the course FYS-

MENA4111 at the University of Oslo. **References for theory: fys-mena4111 lecture notes and book**

Quantum mechanics is the engine of density functional theory and to truly understand the method and it's limitations a knowledge of the engines is necessary.

5.1 Review of Quantum Mechanics

5.1.1 The Shrödinger equation

All theoretical information of a material can be derived from the Shrodinger equation, which came to the world in 1926. Since this the major question how been how this equation can be solved. The time-dependent Schrödinger equation for one electron is given bellow

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

This equation consists of the the wavefunction $\Psi(\vec{r}, t)$ which describe the electron, and the Hamiltonian $\hat{H}(\vec{r}, t)$ where \vec{r} and t is the spatial position and time respectively. The Hamiltonian describes the systems total energy by a kinetic part $T = \frac{-\hbar^2 \nabla^2}{2m_e}$, where m_e is the electron mass and \hbar is the constant, and a potential energy operator U , typically an external potential denoted $V_{ext}(\vec{r}, t)$. Wavefunctions of stationary states are eigenfunctions of the Hamiltonian and are denoted as $\psi_\kappa(\vec{r}, t)$ with an energy eigenvalue ϵ_κ . The subscript κ indicate that the wavefunction correspond to the κ eigenstate. Above we included the time-dependent Shrodinger equation, but almost all cases involving Quantum physics employ rather the time-independent Shroidinger eqaution in which the external potential is independent of time. Bellow we show the time-independent Shrodinger equation for the eigenvalues E_k of the k -th eigenfunction $\psi_k(\vec{r})$

Talk about general wavefunctions vs eigenfunctions or skip this?)

$$\left(-\frac{\hbar^2 \nabla^2}{2m_e} + V_{ext}(\vec{r}) \right) \psi_\kappa(\vec{r}) = E_\kappa \psi_\kappa(\vec{r}) \quad (5.2)$$

Solving the single electron time-independent equation often results in infinite eqienstates that the electron can occupy. The most probable state the electron occupy is the lowest energy state called the ground state, this state is indicated by $\kappa = 0$. Extending to a system comprised of multiple particles we have the many-body Shrödinger equation with the many-body wavefunction

The many-body wavefunction is defined as

$$\Psi^{en}(\vec{r}, \vec{R}) = \Psi^{en}(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_{N_e}, \vec{R}_1, \vec{R}_2, \dots, \vec{R}_{N_n}), \quad (5.3)$$

where r_j denote the coordinates of the j :th electron and likewise R_α describe the coordinates of the α :th nucleus, and the subscript "en" subscript means

that we consider both the electrons and nuclei. Furthermore we have the many-body Hamiltonian H^{en} , 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 many-body Hamiltonian the following notations are used m_n = nuclei mass, q = particle charge, α = nuclei number, Z_α = atom number of nuclei α . In final we get

$$\hat{H} = T_e + T_n + U_{ee} + U_{nn} + U_{en} \quad (5.4)$$

$$\begin{aligned} &= - \sum_{j=1}^{N_e} \frac{\hbar^2 \nabla_j^2}{2m_e} - \sum_{\alpha=1}^{N_n} \frac{\hbar^2 \nabla_\alpha^2}{2m_n} + \sum_{j=1}^{N_e} \sum_{j'=1}^{N_e} \frac{q^2}{|r_j - r_{j'}|} \\ &+ \sum_{\alpha=1}^{N_n} \sum_{\alpha'=1}^{N_n} \frac{q^2 Z_\alpha Z_{\alpha'}}{|R_\alpha - R_{\alpha'}|} - \sum_{j=1}^{N_e} \sum_{\alpha=1}^{N_n} \frac{q^2 Z_\alpha}{|r_j - R_\alpha|}, \end{aligned} \quad (5.5)$$

and the many body Schrodinger equation with total energy eigenvalue E_κ^{en} of the whole system in eigenstate κ

$$H^{en} \Psi_\kappa^{en}(\vec{r}, \vec{R}) = E_\kappa^{en} \Psi_\kappa^{en}(\vec{r}, \vec{R}). \quad (5.6)$$

The first step to solving the many-body problem is to obtain an exact expression for the many particle wavefunction $\Psi^{en}(\vec{r}, \vec{R})$ in order to apply the single-particle operators in equation (5.4). If we consider a simplified system consisting of just two electrons, the problem is reduced to finding $\Psi_\kappa(\vec{r}_1, \vec{r}_2)$ that is a function of $\psi_{i1}(\vec{r}_1)$ and $\psi_{i2}(\vec{r}_2)$. In the Hartree approach this is solved by considering the two electrons to be independent of each-other, and employ variable separation to express the two particle wavefunction as

$$\Psi_\kappa(\vec{r}_1, \vec{r}_2) = \psi_{i1}(\vec{r}_1) \psi_{i2}(\vec{r}_2). \quad (5.7)$$

The limitation of the Hartree approach is that the electrons, which are fermions, in this formulation are distinguishable and hence does not obey the Pauli exclusion principle of fermions. This is corrected by the Harte-Fock approximation which introduces a spin function $\chi_{mp}(s_1, s_2)$ to equation (5.4) to make it anti-symmetric with respect to the particle coordinates. The Hartree-Fock approximation is expressed as

$$\Psi_\kappa(\vec{r}_1, \vec{r}_2) = \frac{1}{2} \{ \psi_1(\vec{r}_2) \psi_2(\vec{r}_2) \pm \psi_1(\vec{r}_2) \psi_2(\vec{r}_1) \} \chi_\mp(s_1, s_2). \quad (5.8)$$

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

$$\Psi_k^{en}(\vec{r}, \vec{R}) \approx \Psi_k(\vec{r}, \vec{R}) \Theta_k(\vec{R}) \quad (5.9)$$

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

$$(T_e + U_{ee} + U_{en}) \Psi_k(\vec{r}, \vec{R}) = E_k(\vec{R}) \Psi_k(\vec{r}, \vec{R}) \quad (5.10)$$

$$(T_n + U_{nn} + E_k(\vec{R})) \Theta_k(\vec{R}) = E_k^{en}(\vec{R}) \Theta_k(\vec{R}). \quad (5.11)$$

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

$$\Psi_k(\vec{r}_1, \vec{r}_2) = A \cdot \psi_1(\vec{r}_1) \psi_2(\vec{r}_2), \quad (5.12)$$

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 fermions. This was overcome with the Hartree-Fock approximation that implement an anti-symmetric wavefunction. The full expression is given bellow

$$\Psi_k(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}} (\psi_1(\vec{r}_1) \psi_2(\vec{r}_2) - \psi_1(\vec{r}_2) \psi_2(\vec{r}_1)) \quad (5.13)$$

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 what's 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

$$E_0 = \langle \psi_0 | H | \psi_0 \rangle \leq \langle \psi | H | \psi \rangle = E \quad (5.14)$$

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

$$n_0(r) = |\Psi_0(r)|, \quad (5.15)$$

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 Schrödinger 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, then $E[n_0] < E[n]$.

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

$$E[n] = T[n] + U_{ee}[n] + U_{en}[n], \quad (5.16)$$

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

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

$$\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_{N_e}) = \psi_1^{KS}(\vec{r}_1) \psi_2^{KS}(\vec{r}_2) \dots \psi_{N_e}^{KS}(\vec{r}_{N_e}) \quad (5.17)$$

In which, ψ_j^{KS} are auxiliary independent single-particle wavefunctions. We now 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:

$$E[n] = T_s[n] + U_s[n] + U_{en}[n] + (T[n] - T_s[n]) + (U_{ee}[n] - U_s[n]). \quad (5.18)$$

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

$$E_{xc}[n] = \Delta T + \Delta U \quad (5.19)$$

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

$$\begin{aligned} E[n] = & \underbrace{\sum_j \int \psi_j^{KS*} \left(-\frac{\hbar^2 \nabla^2}{2m} \right) \psi_j^{KS} d\vec{r}}_{T_s[n]} + \underbrace{\frac{1}{2} \frac{1}{4\pi\epsilon_0} \int \int q^2 \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}d\vec{r}'}_{U_s[n]} \\ & + \underbrace{\int V_{en}(\vec{r})n(\vec{r})d\vec{r}}_{U_{en}[n]} + \underbrace{(T[n] - T_s[n]) + (U_{ee}[n] - U_s[n])}_{E_{xc}[n]} \end{aligned} \quad (5.20)$$

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

$$\left\{ -\frac{\hbar^2}{2m_e} \nabla_s^2 + v_H(\vec{r}) + V_{en}(\vec{r}) + V_{xc}(\vec{r}) \right\} \psi_s^{KS}(\vec{r}) = \epsilon_s^{KS}(\vec{r}) \psi_s^{KS}(\vec{r}), \quad (5.21)$$

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

$$E[n] = \sum_j \epsilon_j^{KS} - \frac{1}{2} \frac{1}{4\pi\epsilon_0} \int \int q^2 \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}d\vec{r}' + E_{xc}[n] - \int V_{xc}(\vec{r})n(\vec{r})d\vec{r}. \quad (5.22)$$

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

5.3 Limitations 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.
- kohn-sham eigenfunctions are not the exact eigenfunctions.
- DFT in its original formulation is only valid for the ground state. Thus excited state application of DFT, all though very possible have a lesser theoretical footing.
- The band-gap calculation is also complicated by the self-interaction error which arises in the occupied states in standard DFT, and in the unoccupied states in Hartree-Fock. If you consider the "true" band-structure, then semi-local DFT has a spurious self-interaction in the occupied states, which over-delocalises them and forces them up in energy, thus reducing the band-gap; Hartree-Fock has the same problem but for the *unoccupied* states, so they are over-delocalised and forced up in energy, which increases the band-gap. [1]
- References on the band gap with DFT based methods [3], [2]

Part II

Methodology and Implementation

Part III

Results and Discussion

Part IV

Conclusion

Write conclusion here

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