Theoretical Modeling of Hydrides

by
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To my Family

Don’t interrupt me
while I’m interrupting
-Winston S. Churchill
Preface

George Gurdjieff.

I feel an immense pleasure to submit my thesis for the degree of Dr. Scient. at the Department of Physics, Faculty of Mathematics and Natural Sciences, University of Oslo, Norway. I have registered my doctor project at the Department of Physics, but the actual work has mainly been carried out at the Department of Chemistry. In the four years of my study period (2001 – 2004) most of the computer modelling has been carried out using Norwegian Supercomputer facilities and I would like to mention that I have used more than 2,000,000 CPU hours during my study period. I express my gratitude for being provided with good infrastructure facilities to carry out my research work effectively. I acknowledge Institute for Energy Technology (IFE; a part of 2001) and the Research Council of Norway (NFR; 2002 – 2004) for their financial support during my study period.

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CHAPTER 1

Introduction

Arise!! Awake!!
and stop not till the goal is reached
Swami Vivekanantha

Stone, bronze, iron; civilization periods have been defined by Man’s relationship to materials. The utilization of materials for feeding, clothing, and protection not only distinguishes human beings from other animals, but ensures the survival and ascendency of our species. Materials have now become so thoroughly ingrained into society that they are often overlooked or underappreciated. When we turn on a light switch, the fact that we are effectively employing hundreds of different materials is hardly apparent to the casual observer. From the glass, metals, and polymers that make up the light bulb to the wires that connect it, via switches and meters, to the power plant that generates the electricity, we are intimately dependent on a wide range of materials which we ordinarily take for granted.

One of the great achievements of the past century has been the rapid growth in the use of energy by a significant fraction of the world’s population. This has been the dominant driver for industrialization and economic growth. A ready supply of varied and cheap food; access to comfort amenities such as hot water, lighting, heating, and increasingly air-conditioning; and access to a range of transport options has become benchmarks for civilized life. All of this is resulting in an inexorable growth in the global demand for energy, raising fundamental problems of resource limitations and environmental pollution. A major challenge for the 21st century is to obtain sustainable solutions to these problems in a way that does not discriminate against the least wealthy part of the world’s population.

It is widely believed that within few decades hydrogen will become the fuel that powers most vehicles and portable devices, i.e., hydrogen will become the means of storing and transporting energy. The reason is the depletion of oil on one hand and on the other hand the relatively facile production of hydrogen from
various renewable sources of energy (hydroelectric, wind, solar, geothermal) with water as the only raw material needed. To release the energy, hydrogen can be burned back to water in an efficient and clean way in a fuel cell, or made to derive an electrochemical cell as in the commonly used nickel hydride battery. It is also emphasized that hydrogen can be used with very high efficiency in fuel cells to generate electrical energy, the estimated efficiency is twice that of the automobile engines used currently. The automobile industry is under pressure to reduce emission substantially and most car makers are engaged in research programs which include fuel cell technology and there has been a number of successful vehicular demonstration projects in which hydrogen fuel cells have provided the power. [1, 2] As concerns over air pollution and global warming increase, the incentive to switch to clean and efficient “hydrogen economy” has increased and the transition may occur well before oil reserves are depleted (after all, the Stone Age did not end because mankind ran out of stones!).

While hydrogen has many obvious advantages, there remains a problem with storage and transportation. Pressurized hydrogen gas takes a great deal of volume compared with, for example, gasoline with equal energy content – about 30 times larger volume at 100 atm gas pressure. Condensed hydrogen is about ten times denser, but it is too expensive to produce and maintain. Chemical conversion of molecular hydrogen into a reversible metal hydride represents an alternative, attractive, and safe method of hydrogen storage. This form of storage has received a lot of attention in the past 30 years. Metals can absorb hydrogen in atomic form and thereby act as hydrogen “sponges”. [3] The hydrogen density in metal hydrides is very high; in fact, higher in some hydrides than in liquid or even solid hydrogen. The number of hydrogen atoms/cm$^3$ in VH$_2$, for example, is $11.4 \times 10^{22}$. This is more than twice than that in solid hydrogen at 4.2 K. [4]

1.1 Metallic and complex hydrides

Around 50 metals of The periodic table can absorb hydrogen in great quantity and the possible choices of hydrogen storage materials are, therefore, very large. It is unfortunate, however, that most metal hydrides are heavy and or expensive in relation to the amount of hydrogen they contain. The crystal structures of these phases are often complex and there are several potential interstices that might accommodate the hydrogen depending on factors like the size and shape of the cavity, chemical nature of the surrounding atoms, and the distances to coordinating atoms and hydrogen neighbors. [5, 6]

However, the solid-state storage also has drawbacks. If one compares the weight fraction of hydrogen in hydrogen storage materials with that of liquid carbohydrates, e.g., oil, the latter have much lower mass density per energy unit than that of most hydrogen storing solids. This parameter must be improved before solid-state storage of hydrogen can become practical. In order to identify potential hydrogen storage materials, different classes of hydrides have been intensively studied for several decades. The hitherto known hydrides with high

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1Hydrogen economy implies a world where pollution problems are solved and where the need for abundant and affordable energy is secured.
1.2. COMPUTATIONAL EXPERIMENTS

capacity for potential reversible hydrogen storage are hampered by thermodynamic and kinetic limitations. For the on-board vehicular applications metal hydrides which accommodate more than 3 wt.% hydrogen have been targeted in the Japanese WE-NET project MITI. [7] The parallel international cooperative project under IEA Task-12 is initiated to develop storage materials which can store more than 5 wt.% hydrogen. [8] Several interstitial metal hydrides operate at around room temperature, but their reversible hydrogen storage capacity is limited to at most 2.5 wt.%. [8] In contrast, MgH$_2$ and LiH have a high relative H content (7 – 13 wt.%), but owing to the presence of strong ionic/covalent bonding interactions, the desorption temperature is high (> 250°C). In the search for suitable materials for reversible hydrogen storage, complex hydrides are other alternatives where one can store high wt.% of hydrogen. A much studied family of such storage materials is alkali aluminum hydrides. NaAlH$_4$ and LiAlH$_4$ have attracted interest mainly due to the high relative weight of stored hydrogen (7.5 and 10.6 wt.% theoretical hydrogen content, respectively). However, a serious problem in this type of materials is poor kinetics and lacking reversibility with respect to hydrogen absorption/desorption. Improved understanding of the processes which occur in these hydrogen-containing materials during uptake and release of hydrogen are of considerable interest. Recent experimental evidences show that NaAlH$_4$ and LiAlH$_4$ after being subjected to mechano-chemical processing under ambient conditions in the presence of certain transition-metal “catalysts” [9, 10, 11, 12] rapidly release 5.6 and 7.9 wt.% of H, respectively. This represents nearly four to five times more stored hydrogen than LaNi$_5$-based alloys which are presently used in nickel-based hydride batteries. This invention motivated us to find other potential candidates in this family, and it is one of the main objectives of the present doctoral project.

1.2 Computational experiments

Whenever we see a material, we observe that nature solve some fundamental equation of physics in order to arrange the atoms. In the same way, in a “computer experiment”, the system under study (atomic nuclei and electrons) is evolved based on the same equations, but this time in the space of the computer world.

Nature has to be an incredibly fast computer to be able to solve the involved coupled nonlinear equations in more than $10^{23}$ variables, self-consistently, and in “real time”. Real computers are of course much slower to calculate the approximate state of any relevant system in a reasonable time limit. However, approximations have made some problems tractable.

“Computer experiments” have many advantages over real experiments. Extreme environmental conditions (e.g., pressure, temperature, toxicity) are usually as easy to study as any other conditions. An exact control over all the variables of the “computer experiment” is always possible and thus the interpretation of the results can be made as clear as desired. Moreover, materials can be studied under conditions which cannot be obtained in nature. For example, to understand the stability trends of a given system in different structures not only any metastable structures can be simulated, but also phases that are yet unknown due to sluggish
CHAPTER 1. INTRODUCTION

kinetics.

The properties of matter are governed by the electrons surrounding the atomic nuclei and their interactions with one another by forming chemical bonding. The ground-state properties of a material are completely determined by the electronic charge density \( n(\mathbf{r}) \), viz. the real space distribution of electrons around the atoms. If one has access to this charge density then one can correctly predict almost all materials properties, like bulk modulus, magnetism, etc. These calculations are said to be the *ab initio* or *first principle* calculations, because they do not contain any input from experiment. The only required information is the species in the form of the constituent atoms and their approximate geometric positions. An approach of the type: Just feed it; tell me What it is, Where it is and I will tell you How it will behave. We can come one step forward if we have powerful enough computers: “Just tell me the chemical composition and I will tell you: What it is, How it is, and Why it is.”

Density-functional theory (DFT) is a quantum mechanical treatment of complicated interactions in an \( N \)-electron system leading to effective one-electron equations which form the basis for current electronic-structure calculations. Walter Kohn received the 1998 Nobel price in Chemistry for his work on DFT. It allows handling of fairly large systems, \( N \) from 100 to 1000, but the computational effort rises linearly (roughly \( N^{2-3} \)) with the increasing number of atoms.

During the past decades, major progress has been achieved in the calculation of structural, chemical, electrical, optical, and magnetic properties of materials. The development of new theoretical approaches based on quantum mechanics, their implementation in the form of efficient computer programs combined with the rapid growth in advanced computer hardware have been the major factors for this evolution. Therefore, the calculation of materials properties has gained an increasingly important role in any scientific and engineering activities related to material science for guiding experimentalists to identify potential interesting materials. The calculation of electronic, structural or magnetic properties of crystals from first principle, i.e., with only knowledge of the constituent elements as input, has become a very successful field in solid-state physics during the last 15 years. Several efficient computational methods based on the local density-functional approximation (LDA) as well as powerful computers including parallel processing are available nowadays to calculate complex properties of single crystals and compounds across The periodic table in a quantitative manner.

1.3 Thesis outline

Today, it is for some cases possible to perform *ab initio* calculations, to tailor make materials for specific application. The thesis presented here deals with theoretical calculations of properties like phase stability, electronic structure, chemical bonding, hydrogen site occupancy, structural prediction, and high pressure behavior of some metal hydrides and complex hydrides. The objective of the study is of a threefold cross-disciplinary nature: The first objective is to gain future knowledge on a fundamental scientific level of the properties of the matter and how these are governed by the electronic structure. Secondly, the findings presented here demonstrate the versatility and increased applicability of theoret-
1.3. THESIS OUTLINE

Theoretical calculations as a complement to experiments (viz. a new tool) for the material scientist in his/her search for novel materials. A third objective is one of direct applicability where the materials studied have been of such a nature that they hopefully, provide answers of immediate concern and interest to a broader audience in the scientific community.

This thesis consists of two main parts. In the first part, an introduction to the work and its background is discussed. The second part deals with a collection of individual papers. This Chapter aims to present general background information to the readers. Chapter 2 and 3 give a brief note to solid-state-physics and material-science community with theoretical background on the topics covered in this project. Chapter 4 presents a brief introduction about various hydrogen storage materials. Chapters 5 to 8 deal with detailed analyses of the results obtained from the theoretical studies, which can then be further complemented by direct access to the articles and publications themselves together with relevant references. The publications are listed in Chapter 9 and the important findings for the hydrogen-storage field are summarized in Chapter 10.

The main aim of the study is to identify potential candidates for hydrogen-storage purpose using advanced density-functional tools. The theoretical investigations have been of a cross-disciplinary nature, made in close collaboration with experimental inorganic chemists, and the research has addressed the electronic structure of both metal hydrides and complex hydrides. The theoretical studies presented in this thesis spans over a number of topics and systems. A brief outline of the research conducted is presented in a logical order to the readers to understand how and why the studies were made in the order that is found.

The search for efficient hydrogen-storage metal hydrides [13] is hampered to some extent by the mental barriers which empirical rules have put on the thinking. For example, the interstitial hole size where hydrogen is expected to occupy should be \( > 0.40 \text{ Å} \). Switendick [14] observed from a compilation of experimental structure data that the minimum \( \text{H}^-\text{H} \) separation in ordered metal hydrides is \( > 2 \text{ Å} \) (the “2-Å rule”). This empirical pattern is later supported by band-structure calculations [15] which ascribe the effect to repulsive interaction generated by the partially charged hydrogen atoms. A practical consequence of this repulsive \( \text{H}^-\text{H} \) interactions in metal hydrides is that it puts a limit to the amount of hydrogen which can be accommodated within a given structural framework. So, if \( \text{H}^-\text{H} \) separations can be less than \( 2 \text{ Å} \) it would open for new efforts to identify potential intermetallics with higher hydrogen-storing capacity. The extensive review by Yvon and Fischer [16] points out that only \( \text{K}_2\text{ReH}_6 \) and \( \text{Th}_2\text{AlH}_4 \) violate the ‘2-Å rule”, where \( \text{Th}_2\text{AlH}_4 \) is a metallic hydride and \( \text{K}_2\text{ReH}_6 \) is a non-metallic complex hydride. Recent experimental [17] and theoretical results for \( \text{Th}_2\text{AlH}_4 \) agreed on a closest \( \text{H}^-\text{H} \) separation of around 1.95 Å (Publication I). However, there are indeed metal hydrides which do violate the “2-Å rule” and we have identified the origin for such behavior (Publications II and III). However, just to reproduce experimental results and explain unusual behaviors of materials are not our main aim, because from the gained knowledge one can predict new hydrides materials. This is found in Publications II, III, and IV and we predict an extremely short \( \text{H}^-\text{H} \) separation of 1.45 Å to occur in \( \text{LaPtInH}_{1.33} \). Examination of the effect of the metal matrix on the \( \text{H}^-\text{H} \) separation in \( RT\text{InH}_{1.33} \).
convinced us that, on a proper choice of alloying element one may be able to reduce the H–H separation below 1.45 Å (Publication IV). In order to verify the above facts we have systematically studied more than 95 compounds with the ZrNiAl-type structure and we found that it should be possible to reduce H–H separation below 1.45 Å (1.40 Å in ThCoInH$_1$$_{333}$). The stability (viz. whether a particular phase will form or not) of these systems is also considered (Publication V). We also demonstrate in Publication V how one can identify the H position in ZrNiAl-type compounds using the electron-localization function as a tool, which otherwise a tough job for experimentalists.

The hitherto discussed investigations have all been concerned with metal hydrides where the decomposition temperature is low, whereas in complex hydrides the decomposition temperature is higher, but at the same time hydrogen content is also high. MgH$_2$ is one of such compound, for which the structural stability is systematically studied up to 20 GPa. Within this pressure range we found five pressure induced structural transitions (Publication VI). In order to verify the theoretical prediction the cooperating experimentalist have made a high pressure study on this compound and confirmed the theoretical prediction. Similarly in BeH$_2$ we identified several pressure induced structural transitions and found a huge volume collapse at the α-to-β transition point (Publication VII).

The structural stability of the entire $AMH_4$ ($A = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}; M = \text{B, Al, Ga}$) series has been studied and equilibrium structures for these phases are identified (Publications IX - XIV). Similarly in the $A_3\text{AlH}_6$ series we have investigated the structural stability and bonding nature systematically (Publications XV-XVII). In Publication XVIII we give examples of how one can use DFT to predict crystal structure, bonding nature, and high pressure behavior of hydrogen-storage materials.
CHAPTER 2

Many body problem

Is simplicity best,
Or simply the easiest?

Martin L. Gere

The properties of matter under normal conditions depend very much on the behavior of the almost mass-less electrons which move around much heavier nuclei. Finding an appropriate description for such a system was one of the big tasks in physics in the beginning of the 20th century. Many people contributed to the solution of the problem, among them in particular Schrödinger, Dirac, Heisenberg, and Bohr made large contributions in the development of a theory they named Quantum Mechanics. Today quantum mechanics has become the basic tool that solid-state theorists work with. If one wants a theoretical model describing matter, then it is necessary to solve a system dealing with the interactions of a very large number of particles, in most macroscopic cases of the order of many moles, i.e., multiples of $10^{23}$ ingredients. This means that in order to deal with a real system some approximations and several simplifications have to be made. In the present work focus is restricted to bulk materials, implying that possible surface effects are excluded and the bulk is considered to be an infinite crystal. To study the properties of a given material, the so-called Schrödinger equation has become the basic tool. The time-independent Schrödinger equation has the form \[ H\psi = E\psi \] (2.1)

where $H$ is the Hamiltonian operator, $E$ energy, and $\psi$ is the wave function. This equation 2.1 can be exactly solved in the case of one nucleus and one electron, viz for hydrogen and hydrogen-like systems. However, a more realistic setup comprises a many-electron wave function $\psi(r_1, r_2, \ldots r_N)$, where $r_i$ denotes the position and spin of particle $i$. The $10^{23}$ ingredients of a typical solid make the problem complicated. The Hamiltonian for the whole bulk system is
In this Hamiltonian $\hbar$ is the Planck constant $h$ divided by $2\pi$, $m$ and $r_k$ denotes the electron mass and coordinates, $M_k$ and $R_k$ nuclear masses and coordinates, and $Z$ is the charge of the constituent nuclei. The indices $i$ and $j$ number the electrons and $k$ and $l$ the nuclei. The first term in Eq. 2.2 is the kinetic energy term for the nuclei, the second term the Coulomb energy term between the nuclei ($V_{NN}$), the third term the kinetic energy term for the electrons, the forth term is the interaction between the electrons ($V_{el}$) and the last term the Columbic interaction between the electrons and the nuclei which can be regarded as an external potential ($V_{ext}$) acting upon the electrons. Since the nuclei are much heavier, and therefore slower than the electrons, we can make the so-called “Born-Oppenheimer approximation” and say that the nuclei are stationary, and that Eq. 2.2 has to be solved for the electrons around these stationary nuclei. This allows us to remove the first term in Eq. 2.2. The second term is only a constant (since the nuclear positions are known), and is not considered until we actually calculate the total energy. Now, the total energy Hamiltonian can be expressed as

$$H = -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 + \sum_{i\neq j} \frac{1}{|r_i - r_j|} - \sum_{i,k} \frac{2Z_k}{|r_i - R_k|}. \quad (2.3)$$

Here we have also introduced Rydberg atomic units, i.e., $\epsilon^2 = 2$, $\hbar = 1$, and $m = \frac{1}{2}$.

### 2.1 The Hartree approximation

In order to simplify Eq. 2.2 we introduce the Hartree approximation which we can solve somewhat easily. In Eq. 2.2, the potential which a certain electrons feels depends on the location of all the other electrons. However, this potential can be approximated by an average single-particle potential

$$V_d(r_i) = \epsilon^2 \sum_{j \neq i} \frac{n_j |\psi_j(r_j)|^2}{|r_i - r_j|} \quad (2.4)$$

where $n_j$ are the orbital occupation numbers and $\psi_j(r_j)$ is a single-particle wave equation, i.e., a solution to the one-particle wave-equation:

$$\left[ -\frac{\hbar^2}{2m} \nabla^2 + V_{ext} + V_d(r_i) \right] \psi_i(r_i) = \epsilon i \psi_i(r_i) \quad (2.5)$$

with this simplification the set of equations now becomes separable. However, the equations are still non-linear and have to be solved self consistently by iteration.

According to the Pauli exclusive principle, two electrons can not be in the same quantum state. However, the wave function in Hartree theory
2.2 HARTREE-FOCK APPROXIMATION

\[
\Psi(r_1\sigma_1, r_2\sigma_2, \ldots, r_N\sigma_N) = \prod_i^N \psi_i(r_i, \sigma_i)
\]  

(2.6)

is not antisymmetric under the interchange of electron coordinates and accordingly does not follow the Pauli principle. Furthermore, the Hartree approximation fails to represent how the configuration of the \(N-1\) electrons affects the remaining electrons. This defect has been rectified by Hartree-Fock theory.

2.2 Hartree-Fock approximation

We assert that a solution to \(H\Psi = E\Psi\) is given by any state \(\Psi\) that makes the following quantity stationary:

\[
E = \frac{\langle\Psi, H\Psi\rangle}{\Psi, \Psi}
\]  

(2.7)

According to variational principle [19], the normalized expectation value of energy is minimized by the ground-state wave function \(\Psi\).

A better description is to replace the wave function in Eq. 2.6 by a Slater determinant of one-electron wave functions:

\[
\Psi(r_1\sigma_1, r_2\sigma_2, \ldots, r_N\sigma_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \Psi_1(r_1\sigma_1) & \Psi_1(r_2\sigma_2) & \cdots & \Psi_1(r_N\sigma_N) \\ \Psi_2(r_2\sigma_2) & \Psi_2(r_2\sigma_2) & \cdots & \Psi_2(r_N\sigma_N) \\ \vdots & \vdots & \ddots & \vdots \\ \Psi_N(r_N\sigma_N) & \Psi_N(r_N\sigma_N) & \cdots & \Psi_N(r_N\sigma_N) \end{vmatrix}
\]  

(2.8)

This is a linear combination of products of the form given by Eq. 2.6 and all other products obtainable from the permutation of the \(r_i\sigma_i\) among themselves. The Hartree-Fock equation which follows from an energy-minimization is given by:

\[
\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{ext} + V_d(r_i)\right] \psi_i(r_i) - \sum_j \int \frac{e^2}{|r - r'|}\psi_j(r')\psi_i(r)\delta_{\sigma_i\sigma_j} = \varepsilon_i\psi_i(r_i)
\]  

(2.9)

The last term on the left hand side is due to exchange and originates from the wave function (Slater determinant). This term only operates between electrons with the same spin, and is called the exchange term. In addition, there should also be a correlation interaction between the electrons, which is not included here. Consequently, the correlation energy can be described as the difference between the exact energy and the Hartree-Fock energy. Another more effective approach to treat the electrons in a solid will be introduced in the following sections.

2.3 Density-functional theory

One of the most successful modern theories for calculating the properties of matter, for which the founder was rewarded the Nobel prize in 1998, is Density-
Functional Theory (DFT). [20] In DFT the basic variable is the electron charge density $n(r)$. The theory was initially formulated as theorems by Hohenberg and Kohn, but has since grown and is now one of the main theoretical tools for understanding the properties of matter. However, the idea to use the electron density as the basic variable when describing the properties of matter did not originate from Hohenberg and Kohn. The Thomas-Fermi theory (Fermi 1928) proposed a scheme based on $n(r)$ but assumed uncorrelated motion of the electrons. This theory was latter improved by Dirac (1930) to include exchange by a term derived from the exchange energy in a homogeneous system. The exchange potential in a system with variable electron density can be approximated by a term $\frac{\partial^2}{\partial r^2}$, where $\frac{\partial^2}{\partial r^2}$ is the local electron density. The $\frac{\partial}{\partial r}$ dependence is a consequence of the “exchange hole” or “Fermi hole”. This hole is the region near an electron which is avoided by electrons of the same spin. Modern DFT approximates the full non-local exchange with a term based on the local electron density, hence called the local density approximation (LDA). The LDA has a widespread use in solid-state physics, but there are more modern terms to treat the full non-local exchange such as the Generalized Gradient Approximation (GGA), where the term is more complex including the contributions from the gradients of the local electron density or higher orders of derivatives such as the Laplacians, (known as meta-GGAs. [21]) The main motivation for these approximations (LDA, GGA, meta-GGA, LDA+U etc.) is that they allow us to solve Schrödinger-type equations with local effective potentials.

One can speculate why DFT is so successful. One of the main reason is that DFT and local approximations to the exchange term work well and another reason may be that the approximations made in the LDA and GGAs to the non-local exchange is fairly good.

2.4 Single-particle equations

After these introductory remarks about the physics of many-electron systems, we are now in the position to formulate the main statements of DFT, which is based on two fundamental theorems introduced by Hohenberg and Kohn [22], and later extended by Kohn and Sham. [23]

Theorem 1

The ground-state expectation value of any observable, including the total energy, is a unique functional of the exact ground-state density $n(r)$.

Theorem 2

The exact ground-state density minimizes the total energy functional $E[n]$. The total energy functional that needs to be minimized in order to find the true ground state is [23]:

$$E[n] = T_0[n] + \int dr^3 n(r)[V_{ext} + \Phi(r)] + EXC[n].$$  \hspace{1cm} (2.10)
2.4. SINGLE-PARTICLE EQUATIONS

where \( T_0[n] \) is the kinetic energy of a non-interacting electron system with density \( n(r) \), \( V_{\text{ext}} \) is the potential from the nuclei, \( \Phi(r) \) is the Coulomb potential from the electron, and \( E_{XC} \) is the exchange-correlation energy. We can regard this as an effective potential

\[
V_{\text{eff}}(r) = V_{\text{ext}} + \Phi(r) + \frac{\delta E_{XC}[n]}{\delta n(r)}.
\]  

(2.11)

which enters the one-particle Schrödinger equations. In the practical implementation of the Kohn-Sham scheme only \( E_{XC} \) requires approximation. For more general systems the spin is also included in the above formulation in a quite simple manner (at least conceptually). The charge density is replaced as variable by the density matrix \( \rho_{\alpha\beta} \) defined by:

\[
\rho_{\alpha\beta}(r) = \langle \Psi | \psi^+_\beta(r) \psi^+_\alpha(r) | \Psi \rangle
\]  

(2.12)

where

\[
\sum_\alpha \int d r \rho_{\alpha\alpha} = N,
\]  

(2.13)

and \( N \) is the number of electrons. All ground-state properties are now functionals of the density matrix \( \rho_{\alpha\beta} \), and the energy \( E \) is required to be stationary with respect to variations in \( \rho_{\alpha\beta} \). The potentials are also allowed to be spin-dependent so

\[
V_{\text{ext}} \rightarrow V^{\alpha\beta}_{\text{ext}}
\]  

(2.14)

and

\[
V^{\alpha\beta}_{\text{XC}} = \frac{\delta E_{XC}}{\delta \rho_{\alpha\beta}}.
\]  

(2.15)

This is called Local Spin-Density Approximation (LSDA).

### 2.4.1 Exchange-correlation energy and the electron hole

The exchange-correlation term in the Eq. 2.10 is to some extent approximated in the current theoretical framework. Since the electrons interact with each other, viz. correlate their motion so that they tend to avoid each other. An electron at \( r \) reduces the probability of finding another electron at \( r' \), and every electron is surrounded by a hole in the electron density of equal and opposite charge. [24] In LDA (LSDA) the exchange-correlation energy is written as

\[
E^{LDA}_{XC} = \int d r n(r) \epsilon_{XC}[n_\uparrow(r), n_\downarrow(r)].
\]  

(2.16)

where \( \epsilon_{XC} \) is the exchange-correlation energy per particle in a homogeneous spin-polarized electron gas. We can also write an exact term for the exchange-correlation energy using exchange-correlation hole [24]:
\[ E_{XC} = \frac{1}{2} \int d(\mathbf{r}) n(\mathbf{r}) \int d\mathbf{r'} \frac{1}{|\mathbf{r} - \mathbf{r'}|} n_{XC}(\mathbf{r}, \mathbf{r'} - \mathbf{r}), \quad (2.17) \]

where \( n_{XC}(\mathbf{r}, \mathbf{r'} - \mathbf{r}) \) is the exchange correlation hole (obeys the sum rule; charge = -1):

\[ \int d\mathbf{r'} n_{XC}(\mathbf{r}, \mathbf{r'} - \mathbf{r}) = -1. \quad (2.18) \]

It can be shown that on making a variable substitution \( R = \mathbf{r'} - \mathbf{r} \), \( E_{XC} \) can be written as [24]:

\[ E_{XC} = \frac{1}{2} \int d(\mathbf{r}) n(\mathbf{r}) \int_0^\infty dRR^2 \frac{1}{R} \int d\Omega n_{XC}(\mathbf{r}, R), \quad (2.19) \]

which in turn implies that the exchange depends only on the spherical average of \( n_{XC} \). Herein lies the answer to why the LDA approximation works so well. The point is that even if LDA does not gives the right form for the exchange-correlation hole it does give a spherical average which is very close to the real one. [24]

### 2.5 Limitations of density-functional theory

There are fundamental limits to what a hypothetical exact density functional, in combination with the Kohn-Sham approach, can predict in terms of ground-state properties. For instance, the exact Kohn-Sham eigenvalue surface and the true Fermi surface are generally not identical for systems that are both interacting and inhomogeneous. [25] In fact, it is at present an open question whether the Kohn-Sham DFT approach is in principle valid for interacting systems with inhomogeneous electron density. Fundamentally, DFT only concerns the electronic ground-state structure and underestimates band gaps, which in semiconductors comes out incorrect by several factors. A famous error is also found for transition metal oxides that are predicted to be metallic, whereas they are often insulators. Other traditional short-comings of the DFT have later been attributed to failures of the specific exchange-correlation functions used, e.g., the failure to predict the bcc ground-state structure of Fe. To be corrected, GGA instead of LDA has to be used. In practice, it is a complicated matter to single out the exact reason for a failure of a certain type of calculation, since there are a number of approximations involved. It is important to be aware that although there are limitations to the applicability of the DFT (and the exchange-correlation functions used), one should perhaps not to be too pessimistic, and instead view these procedures as experimental computational exercises and simply try to push the limits of the theory, of course always seeking to validate the findings with experimental facts.
CHAPTER 3

The computational methods

All the mathematical sciences are founded on relations between physical laws and laws of numbers, so that the aim of exact science is to reduce the problems of nature to the determination of quantities by operations with numbers.

James Clerk Maxwell

This is the stage to consider the actual computational procedures. The solving of equations specified by DFT is not as straightforward as may be presumed on principal grounds. Many choices on various levels of approximations and technical details have to be made along the way. Like in many other modern computational research disciplines, this means solving equations with the help of comprehensive computer codes and massive computational power. In this chapter, we will briefly explain some of the techniques for solving the single-particle equations for crystalline solids and outline the difference between methods that have been used in this thesis to solve the equations. In Chapter 2, we have introduced an effective one-electron equation which can be solved in a self-consistent way,

\[-\nabla^2 + V_{\text{eff}}(r)]\psi_i(r) = \varepsilon_i \psi_i(r). \tag{3.1}\]

From this equation we can find the electron charge density \(n(r)\)

\[n(r) = \sum_{j=1}^{N} |\psi_j|^2. \tag{3.2}\]

Because both \(\Phi\) and \(V_{XC}\) depend on \(n(r)\) we can calculate a new \(V_{\text{eff}}(r)\) using the local density approximation, GGA etc. for the exchange-correlation and the Poisson equation for the electrostatic contribution:

\[\nabla^2 \Phi(r)_i = -4\pi \sum_{j=1, j \neq i}^{N} |\psi_j|^2. \tag{3.3}\]
We repeat this process until self-consistency (viz. the difference between $V_{eff}(r)$ in the $m$ and $m-1$ iterations is less than a predetermined value; the difference being the only chosen convergence criterion) is reached. When self-consistency has been reached, we calculate the total energy of the thus defined system of electrons and nuclei using the total energy expression of the functionals (Eq. 2.10).

### 3.1 Periodicity and crystal symmetry

It would have been an impossible task to solve the equations if we had to perform the calculations for all electrons in a given material. Fortunately the potential is periodic for an infinite crystal, i.e., invariant under lattice translation $T$ and hence solving the equations in some reduced part of the system will provide the solution for the entire system since the solution will necessarily repeat itself with the translational symmetry of the crystal.

\begin{equation}
V(r + T) = V(r),
\end{equation}

\begin{equation}
T = m_1 \mathbf{a}_1 + m_2 \mathbf{a}_2 + m_3 \mathbf{a}_3.
\end{equation}

The vectors $\{\mathbf{a}_i\}$ are the real-space Bravais lattice vectors that span the crystal network and $\{m_i\}$ are integers. According to the Bloch theorem, the eigenstates can be chosen to take the form of a plane wave times a function with the periodicity of the Bravais lattice;

\begin{equation}
\psi_k(r + T) = e^{i \mathbf{k} \cdot \mathbf{T}} \psi_k(r)
\end{equation}

where $\mathbf{k}$ is the Bloch wave vector. Now, the one-electron function can be characterized by the Bloch vector $\mathbf{k}$. As a consequence, Eq. (3.1) can be rewritten as

\begin{equation}
H_{eff}(r)\psi_n(\mathbf{k}; r) = \varepsilon_n(\mathbf{k}) \psi_n(\mathbf{k}; r),
\end{equation}

where the index $i$ in Eq. (3.1) has been replaced by the quantum number $n$. The one-electron wave function $\psi_n$ and the corresponding eigenvalues $\varepsilon_n$ are now characterized by the Bloch wave vector $\mathbf{k}$.

The phase factor take the value 1 for some electronic states. This happens when the wave-vector corresponds to a reciprocal lattice vector defined by

\begin{equation}
g = 2\pi(n_1 \mathbf{b}_1 + n_2 \mathbf{b}_2 + n_3 \mathbf{b}_3)
\end{equation}

where $n_i$ are integers and $\mathbf{b}_i$ are the basis vectors of the reciprocal lattice, i.e.,

\begin{equation}
(\mathbf{a}_i, \mathbf{b}_j) = \delta_{ij}
\end{equation}

for $\mathbf{k} = g$

\begin{equation}
e^{i \mathbf{k} \cdot T} = e^{i \mathbf{g} \cdot T} = e^{2\pi i n_i} = 1.
\end{equation}

Thus a periodicity in real space also introduces a periodicity in reciprocal space ($\mathbf{k}$), and an electron state with wave vector $\mathbf{k}' = \mathbf{k} + \mathbf{g}$ will consequently
satisfy the Block condition. To describe the electronic structure of a solid it is thus not necessary to consider the vectors, we can consider only the wave vectors contained inside the region of the reciprocal space known as Brillouin zone (BZ). In addition to the translation symmetry, the crystal also obeys symmetries under rotations, implying that there are symmetry operations which transform one wave vector into another wave vector and that reduces our problem further. The smallest possible zone which defines a complete set of symmetry independent wave vectors is called the irreducible part of the BZ. For example, in a simple cubic lattice, the irreducible part of the BZ is only 1/48 of the full BZ and this is the only part we need to find a solution for in such an electronic structure problem.

Following the energy principle (minimizing the total energy), and the Pauli exclusion principle, eigenstates with eigenvalues \( \varepsilon_i(k) \) are filled starting from the energetically lowest eigenvalue. The energy of the highest filled eigenstate is called the Fermi energy (\( E_F \)). The Fermi energy is given from

\[
N = \int_{-\infty}^{\varepsilon_F} D(\varepsilon) d\varepsilon, \tag{3.11}
\]

where \( N \) is the number of valence electrons and \( D(\varepsilon) \) is the density of the states (DOS),

\[
D(\varepsilon) = \frac{2}{8\pi^3} \int_{S(\varepsilon)} dS \frac{dS}{|\nabla_{S(\varepsilon)}(\mathbf{K})|}. \tag{3.12}
\]

This integration is carried out all over a surface of constant energy, \( S(\varepsilon) \), in the first BZ. The one-electron states most relevant for physical properties are those with energies around the Fermi level. These states are important for the stability of the crystal structure, transport properties, magnetic susceptibility, etc.

### 3.2 Electronic structure methods

In order to solve Eq. 3.7 we need to expand it in a basis of known functions, and we have to resort to one of the available electronic structure methods.

The choice of basis-functions is crucial for the efficiency of a given computational method and the first step in the implementation of a DFT method is to find a suitable basis set. Different types of basis sets are used for the different methods, but in general the basis sets can be divided into two groups:

<table>
<thead>
<tr>
<th>Table 3.1: Basis set classification and computational methods.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fixed basis set</strong></td>
</tr>
<tr>
<td>Plane wave</td>
</tr>
<tr>
<td>Tight binding</td>
</tr>
<tr>
<td>Pseudo-potential</td>
</tr>
<tr>
<td>Orthogonalized plane wave (OPW)</td>
</tr>
<tr>
<td>Linear combination of atomic orbital (LCAO)</td>
</tr>
</tbody>
</table>

(1) Basis sets that obey the Bloch condition explicitly, viz. the expansion involves basis functions that are fixed and the coefficients \( c_n \) are chosen to minimize the energy.
\[ \psi(\mathbf{r}) = \sum_n c_n \phi_n(\mathbf{r}) \quad (3.13) \]

One disadvantage of this approach is that the wave functions are fixed, which often leads to considerable difficulties in obtaining a sufficiently converged basis set.

(2) The other group involves wave functions that can be varied. The variation is promoted by introducing energy-dependent wave functions \( \phi_n(\varepsilon, \mathbf{r}) \) of the form

\[ \psi(\varepsilon, \mathbf{r}) = \sum_n c_n \phi_n(\varepsilon, \mathbf{r}), \quad (3.14) \]

However, the Bloch conditions is no longer automatically fulfilled. The solutions in one unit cell are now chosen to fit smoothly to those of the neighbor cells, thus fulfilling the Bloch condition “indirectly”. As the wave function can be modified to the problem at hand, these techniques converge very fast for the number of required basis functions. In APW and KKR, the price for this favorable feature is the additional parameter \( \varepsilon \). Every \( \mathbf{k} \) point of the band structure must be solved for a large number of \( \varepsilon \). Solutions only exist when \( \varepsilon \) are actual eigenvalues. While computation based on these methods are accurate, they are also time consuming. A solution to this problem is to linearize the energy dependent orbital basis as done in LAPW, LMTO, and ASW. The basis is introduced in the form of a Taylor expansion in \( \varepsilon \) so that the orbitals themselves are energy independent, although the expansion retains the energy dependence. The variational equation (3.7) thus has to be solved only once for each \( \mathbf{k} \) point. Such methods are extremely rapid and slightly less accurate than other non-linear methods.

3.3 The LMTO method

During the last decades, the linear-muffin-tin-orbital (LMTO)[26] method has become very popular for the calculation of the electronic structure for crystalline systems. The LMTO method combines the following advantages: (a) It uses a minimal basis, which leads to high efficiency and makes calculations possible for large unit cells. (b) In this method all elements are treated in the same way, so that atoms with a large number of core states can be considered (say, phases containing \( d \) and \( f \) metals). (c) This method is very accurate, due to the augmentation procedure which gives the wave function the correct shape near the nucleus. (d) It uses atom-centered basis functions with well-defined angular momentum, which makes the calculation transparent. [27]

3.3.1 Muffin-tin orbitals

The crystal is divided into non-overlapping muffin-tin spheres surrounding the atomic sites and an interstitial region outside the spheres. Inside the muffin-tin sphere the potential is assumed to be spherically symmetric while in the interstitial region the potential, \( V_{MTZ} \), is assumed to be constant or slowly varying.
3.3. THE LMTO METHOD

Because the potential in the interstitial is constant we can shift the energy scale and set it to zero. In the following overview of the method we consider a crystal with only one atom per primitive cell. Within a single muffin-tin well we define the potential by

\[ V_{MT}(r) = \begin{cases} 
V(r) - V_{MTZ}, & |r| < S_{MT} \\
0, & |r| > S_{MT}
\end{cases} \]  

(3.15)

Here \( V(r) \) is the spherically symmetric part of the crystal potential. The radii of the muffin-tin spheres are chosen such that they do not touch each other. In the following \( S_{MT} \) is expressed by \( S \).

To solve the Schrödinger equation for the muffin-tin potential

\[ [-\nabla^2 + V_{MT}]\psi(\epsilon, r) = (\epsilon - V_{MTZ})\psi(\epsilon, r) \]  

(3.16)

one introduces the kinetic energy \( \kappa^2 \) in the interstitial region by

\[ \kappa^2 = (\epsilon - V_{MTZ}) \]  

(3.17)

For an electron moving in the potential from an isolated muffin-tin well embedded in the flat potential \( V_{MTZ} \), the spherical symmetry can extend throughout all space and the wave functions become

\[ \psi_L(\epsilon, r) = i^j Y^m_l(\hat{r})\psi_\beta(\epsilon, r) \]  

(3.18)

using the convention that \( r = |r| \) and \( \hat{r} \) is the direction of \( r \) and including a phase factor \( i^j \).

To obtain basis functions which are approximately independent of energy, reasonably localized, and normalizable for all values of \( \kappa^2 \), Anderson [28] used

**Figure 3.1**: The muffin-tin approximation. a) the muffin-tin sphere with radius \( S_{MT} \), and the describing sphere of radius \( S_E \). b) the radial part of the wave function. c) the muffin-tin part of the crystal potential \( V(r) \). d) the muffin-tin potential \( V_{MT}(r) \).
muffin-tin orbitals. Spherical Bessel functions that cancels the divergent part of $\psi_l(\varepsilon, k, r)$ and simultaneously reduce the energy and potential dependence at the tails, hence, the muffin-tin orbitals can be in the form

$$
\chi_{lm}(\varepsilon, r) = i^l Y_l^m(\hat{r}) \left\{ \begin{array}{ll}
\psi_l(\varepsilon, r) + P_l(\varepsilon) \frac{(r/S)^l}{2(l+1)} , & |r| < S \\
(r/S)^{l-1} , & |r| > S
\end{array} \right.
$$

(3.19)

where $\psi_l(\varepsilon, r)$ is a solution of the radial Schrödinger equation inside the atomic sphere.

$$
P_l(\varepsilon) = 2(2l + 1) \frac{D_l(\varepsilon) + l + 1}{D_l(\varepsilon) - l}
$$

(3.20)

The potential function and the normalization of $\psi_l(\varepsilon, r)$ are determined by satisfying differentiability and continuity of the basis function on the sphere boundary. Here the $D_l(\varepsilon)$ is the logarithmic derivative of the wave function. The tail of the basis function, $\chi_{l}(\varepsilon, r)$, the part outside the muffin-tin sphere are in general introduced by Neumann function, but in Eq. (3.17) the kinetic energy of this tail (known as $k^2$) is simply chosen to be zero. Therefore the Neumann function has a simple form like above.

### 3.3.2 The LMTO-atomic sphere approximation method

In the atomic sphere approximation (ASA), LMTO-ASA, the muffin-tin spheres are overlapping in a way that makes the total volume of the muffin-tin sphere to become equal to the atomic volume. This means that the muffin-tin radius $S$ is equal to the Wigner–Seitz radius $S_{WS}$ where the total volume per atom is given by $V = (4\pi/3)S_{WS}^3$. In the ASA, the potential is also assumed to be spherically symmetric inside each muffin-tin sphere, and the kinetic energy of the basis functions in the interstitial is restricted to be constant, actually zero in the calculation.

In order to construct a linear method, the energy dependent terms in the muffin-tin spheres of Eq. (3.19) are replaced by the energy independent function $\Phi$. The function is defined as a combination of radial functions and their energy derivative

$$
\Phi(D, r) = \phi_l(r) + \omega(D) \dot{\phi}_l(r),
$$

(3.21)

where $\omega(D)$ is a function of the logarithmic derivative. $\omega(D)$ should make the energy dependent orbitals $\chi_{lm}(\varepsilon, r)$, defined in Eq. (3.19), continuous and differentiable at the sphere boundary $S$. The boundary condition is determined as $D = -(l + 1)$. The thus obtained energy independent orbital can now be written as

$$
\chi_{lm}(\varepsilon, r) = i^l Y_l^m(\hat{r}) \left\{ \begin{array}{ll}
\Phi_l(D, r) \frac{(r/S)^l}{2(l+1)} , & |r| < S \\
(r/S)^{l-1} , & |r| > S
\end{array} \right.
$$

(3.22)

### 3.4 Full potential LMTO method

The FP-LMTO calculations are all electron, fully relativistic, without shape approximation to the charge density or potential. The crystal is divided into non-
overlapping muffin-tin spheres and interstitial regions outside the spheres. The wave function is then represented differently in the two types of regions. Inside a muffin-tin spheres, the basis functions are as in the LMTO-ASA method, viz. a Bloch sum of linear muffin-tin orbitals are expanded by structure constants $\frac{\phi(k)}{\Phi(D_k)}$. Unlike the ASA approximation (where kinetic energy is restricted to zero in the interstitial region) the kinetic energy is not a constant. For simplicity, here we only consider a mono-atomic solid and suppress the atomic site index. The $\kappa$ dependent linear muffin-tin orbitals can now be written as

$$\psi_{klm}(k, r) = \chi_{klm}(r) + \sum_{lm} J_{klm}(r) S_{klm'l'm'}(k).$$  \hspace{1cm} (3.23)

where

$$\chi_{klm}(r) = i^l Y^m_l (\hat{r}) \left\{ \begin{array}{ll} -i k h_0(\kappa S) \Phi(D_k, r) \frac{\phi(k)}{\Phi(D_k, S)} & , |r| < S \\
-i k h_0(\kappa r) & , |r| > S \end{array} \right.$$  \hspace{1cm} (3.24)

and

$$J_{klm}(r) = i^l Y^m_l (\hat{r}) \left\{ \begin{array}{ll} J_h(\kappa S) \frac{\phi(D_k, r)}{\Phi(D_k, S)} & , |r| < S \\
J_h(\kappa r) & , |r| > S \end{array} \right.$$  \hspace{1cm} (3.25)

Inside the muffin-tin sphere at $r$, we can also expand the electron density and potential in spherical harmonics times a radial function,

$$n_\tau(r)|_\tau = \sum_h n_\tau(h; r_\tau) D_h(\hat{r}_\tau).$$  \hspace{1cm} (3.26)

$$V_\tau(r)|_\tau = \sum_h V_\tau(h; r_\tau) D_h(\hat{r}_\tau).$$  \hspace{1cm} (3.27)

where $D_h$ are linear combinations of spherical harmonics, $Y^m_l(\hat{r})$. $D_h$ are chosen here because we need an invariant representation of the local point group of the atomic site contained in the muffin-tin. The expansion coefficients $n_\tau(h; r_\tau)$ and $V_\tau(h; r_\tau)$ are numerical functions given on a radial mesh.

In the interstitial region, the basis function, charge density and potential are expressed as Fourier series,

$$\psi(k; r)|_I = \sum_G e^{i(k + \mathbf{G}) \cdot \mathbf{r}} \psi(k + \mathbf{G}),$$  \hspace{1cm} (3.28)

$$n_I(r)|_I = \sum_G n_G e^{i(k + \mathbf{G}) \cdot \mathbf{r}},$$  \hspace{1cm} (3.29)

$$V_I(r)|_I = \sum_G V_G e^{i(k + \mathbf{G}) \cdot \mathbf{r}},$$  \hspace{1cm} (3.30)

where $\mathbf{G}$ are reciprocal lattice vectors spanning the Fourier space.
3.4.1 The basis set

Envelope functions form a suitable basis in interstitial regions. By choosing the appropriate envelope function, e.g., plane waves, Gaussians, and spherical waves (Hankel functions), one can utilize various electronic structure methods (LAPW, LCGO, LMTO, etc.). The LMTO envelope function is represented as,

\[ K_{lm}(\kappa; r) = -\kappa^{l+1}Y^m(l) \begin{cases} -h_l^m(\kappa r) & \kappa^2 \leq 0 \\ n_l(\kappa r) & \kappa^2 > 0 \end{cases} \]  

(3.31)

where \( n_l \) is a spherical Neumann function and \( h_l^m \) is a spherical Hankel function of the first kind. The envelope function is singular Hankel or Neumann functions with regards to the sign of the kinetic energy. This introduces a \( \kappa \) dependence for the basis functions inside the muffin-tin sphere through the matching conditions at the sphere boundary. This is not a problem. Using variational method, the ground state still has several basis functions with the same quantum numbers, \( n, l, \) and \( m \), but different \( \kappa^2 \). This is called a double-basis approach.

The basis can always contain different basis sets corresponding to the atomic quantum number \( l \), but with different principle quantum numbers \( n \). A basis constructed in this way form a fully hybridizing basis set, rather than a set of separate energy panels.

To illustrate the way the basis set is constructed, we use fcc Ce [29] as an example a similar approach was used in Ref. IIIIIIV. The ground-state configuration for Ce is \( 4f^1 5d^1 6s^2 \). Thus we include \( 6s, 6p, 5d, \) and \( 4f \) as valence states. To reduce core leakage at the sphere boundary, the core states \( 5d^1 \) and \( 5p^2 \) are treated as semicore states. By this kind of construction, the basis set has become more complete.

3.4.2 The LMTO matrix

We now introduce a convenient notation for the basis functions:

\[ |\chi_i(k)\rangle = |\phi_i(k)\rangle + |\psi_i(k)\rangle, \]  

(3.32)

where \(|\phi\rangle\) is the basis function inside the muffin-tin spheres and \(|\psi_i(k)\rangle\) represents the basis-function tails outside the spheres.

A wave function \( \Psi_{l,n}(k) \) is then constructed by a linear combination of the LMTO basis functions, \( \chi_i \). The linear combination can be written as

\[ |\Psi\rangle = \sum_i A_i |\chi_i\rangle \]  

(3.33)

The Hamiltonian operator is

\[ H = H_0 + V_{mmt} + V_I \]  

(3.34)

where \( H_0 \) is the Hamiltonian operator containing the kinetic energy operator and the spherical part of the muffin-tin potential, \( V_{mmt} \) represents the nonspherical part of the muffin-tin potential, and \( V_I \) is the interstitial potential. Then
by using the variational principle for the one-electron Hamiltonian, the LMTO secular matrix follow as

\[
\sum_j [\langle \chi_i(\mathbf{k}) | H_0 + V_{nt} + V_I | \chi_j(\mathbf{k}) \rangle - \varepsilon(\mathbf{k}) \langle \chi_i(\mathbf{k}) | \chi_j(\mathbf{k}) \rangle] A_j = 0 \quad (3.35)
\]

which can be reduced it to

\[
\sum_j [H_{ij}^0 + H_{ij}^1 - \varepsilon(\mathbf{k}) O_{ij}] A_j = 0 \quad (3.36)
\]

where

\[
H_{ij}^0 = \langle \phi_i(\mathbf{k}) | H_0 | \phi_j(\mathbf{k}) \rangle \quad (3.37)
\]

\[
O_{ij} = \langle \phi_i(\mathbf{k}) | \phi_j(\mathbf{k}) \rangle + \langle \psi_i(\mathbf{k}) | \psi_j(\mathbf{k}) \rangle \quad (3.38)
\]

and

\[
H_{ij}^1 = \langle \phi_i(\mathbf{k}) | V_{nt} | \phi_j(\mathbf{k}) \rangle + \frac{1}{2}(\kappa_{ij}^2 + \kappa_{ij}^3) \langle \psi_i(\mathbf{k}) | \psi_j(\mathbf{k}) \rangle + \langle \psi_i(\mathbf{k}) | V_I | \psi_j(\mathbf{k}) \rangle \quad (3.39)
\]

where \(| \psi_j(\mathbf{k}) \rangle\) is an eigenfunction to \(\nabla^2\) with eigenvalue \(\kappa_{ij}^2\), \(H_{ij}^0\) is the spherical muffin-tin part of Hamiltonian matrix, \(O_{ij}\) is the overlap between the orbitals inside the sphere as well as in the interstitial region, and \(H_{ij}^1\) contains the corrections to the Hamiltonian matrix coming from the muffin-tin and interstitial regions. The first term in Eq. (3.39) is the non-spherical potential matrix, the next term is the expectation value of the kinetic energy operator in the interstitial region, and the last term is the interstitial potential matrix.

**Total energy**

The total energy for the whole crystal can be expressed as [30]

\[
E_{tot} = E_{val} + E_{cor} + E_{c} + E_{xc} \quad (3.40)
\]

where \(E_{val}\) and \(E_{cor}\) are the kinetic energy for the valence and core electrons, respectively, \(E_c\) is the electrostatic energy including electron–electron, electron–nucleus, and nucleus–nucleus contributions, and \(E_{xc}\) is an exchange energy term. The kinetic energy is usually expressed as the expectation value of the kinetic operator \(-\nabla^2\). By using the eigenvalue equation the expectation value can be expressed as a sum over one-electron energies minus the effective potential energy. The core eigenvalues \(\varepsilon_{ir}\) are obtained as an exact solution to the Dirac equation with the spherical part of the muffin-tin potential

\[
E_{tot} = \sum_{\mathbf{k} \mathbf{n}} w_{\mathbf{k} \mathbf{n}} \varepsilon_{\mathbf{k} \mathbf{n}} + \sum_{\mathbf{j} \mathbf{\tau}} f_{\mathbf{j} \mathbf{\tau}} \varepsilon_{\mathbf{j} \mathbf{\tau}} + \int_{V_v} n(\mathbf{r}) \left[ \frac{1}{2} V_c(\mathbf{r}) - V_{in}(\mathbf{r}) \right] d\mathbf{r} - \frac{1}{2} \sum_{\mathbf{j}} Z_{\mathbf{j} \mathbf{j}} V_c(\mathbf{r}_j; 0) + \int_{V_v} n(\mathbf{r}) \varepsilon_{xc}(n(\mathbf{r})) d\mathbf{r}, \quad (3.41)
\]
where the integral run over the unit cell. The term with summation over \( j \) cover the core states. The density \( n(r) \) is the total charge density, including valence as well as core electrons. \( V_{\text{in}} \) is the input potential obtained from LDA. The Madelung term \( V_{\text{M}}(\tau, 0) \) describes the Coulomb potential at the nucleus less (excluding the \( Z/r \) self contribution) and \( \varepsilon_{\text{xc}} \) is the exchange-correlation energy.

3.5 Full potential LAPW method

![Figure 3.2: Partitioning of the unit cell into atomic spheres and interstitial region.](image)

Some of the calculations in the present project have been carried out with the DFT FP-LAPW program package WIEN97. The LAPW method is a very accurate calculational scheme for electronic structure investigations. This approach is characterized by the use of a basis set which is especially adapted to the problem. The method is basically derived from the APW approach of Slater where the space is divided into regions that are described by different basis expansions in different domains (Fig. 3.2). In particular, radial solutions of the Schrödinger equation are employed inside non-overlapping atom-centered spheres and plane waves in the remaining interstitial regions. The introduction of such a basis set is motivated by the fact that close to the nucleus the potential and wave functions are very similar to those in an atom, while between the atoms the potential is smoother,

\[
\varphi(r) = \begin{cases} 
\frac{1}{\Omega \sqrt{2\pi}} \sum_{G} C_G e^{i(k+\Omega)^G} & r \in \text{interstitial} \\
\sum_{lm} A_{lm} u_l(r) Y_{lm}(r) & r \in \text{inside sphere}
\end{cases}
\]  

(3.42)

where \( \varphi \) is the wave function, \( \Omega \) the cell volume and \( u_l \) the regular solution of the following equation. Here \( C_G \) and \( A_{lm} \) are expansion coefficients, \( E_l \) is a parameter (introduced equal to the band energy) and \( V \) is the spherical component of the potential inside the sphere:

\[
\left[-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + V(r) - E_l\right] r u_l(r) = 0
\]  

(3.43)

The use of these functions has been motivated by Slater in pointing out that plane waves are the solutions of the Schrödinger’s equation in a constant potential and radial functions are solutions in a spherical potential. This approximation to the potential called the muffin-tin (MT) description, will give very good results
3.5. FULL POTENTIAL LAPW METHOD

for close-packed materials like fcc and hcp metals and alloys. Since the continuity on the sphere boundaries needs to be guaranteed on such a dual representation (defined in Eq. 3.42), constraint must be imposed. In the APW method this is done by defining the $A_{lm}$ in terms of $C_G$ in a spherical harmonic expansion of the plane waves.

$$A_{lm} = \frac{4\phi_d}{\Omega^{1/2} u_l (R)} \sum_G C_G j_l (|k + g(R)|) Y_{lm}^* (k + G) \quad (3.44)$$

The coefficient of each $lm$ is matched at the sphere boundary and the origin is taken at the center of the sphere ($R$ is the sphere radius). The expression for $A_{lm}$ are determined by the plane wave coefficients ($C_G$) and the energy parameters $E_l$, which are the variational coefficients in the APW method. The functions labelled by $G$ are the augmented plane waves (APWs) and consist of single plane waves in the interstitial zone which are matched to the radial functions inside the spheres. A more flexible and accurate band structure calculational scheme introduced by the LAPW method where the basis functions and their derivatives are made continuous by matching to a radial function at fixed $E_l$ plus its derivative.

3.5.1 The LAPW basis

The basis functions inside the spheres are linear combinations of a radial functions $u_l (r) Y_{lm} (r)$ and their energy derivatives. The $u_l$ are defined as in the APW method (Eq. 3.43) and the energy derivative, $\dot{u}_l (r) Y_{lm} (r)$, satisfies the following equation:

$$\left[ -\frac{d^2}{dr^2} + \frac{1}{r^2} (l(l + 1)) + V(r) - E_l \right] r \dot{u}_l (r) = r u_l (r) \quad (3.45)$$

These functions are matched to the values and derivatives of the plane waves on the sphere boundaries. Such augmented plan waves are the LAPW basis (LAPWs),

$$\varphi (r) = \left\{ \begin{array}{ll} \frac{1}{\Omega^{1/2}} \sum_G C_G e^{i(G + k) r} & r \in \text{interstitial} \\ \sum_m [ A_{lm} u_l (r) + B_{lm} \dot{u}_l (r)] Y_{lm} (r) & r \in \text{inside sphere} \end{array} \right. \quad (3.46)$$

where the $B_{lm}$ are coefficients for the energy derivative analogous to the $A_{lm}$. The LAPWs are plane waves in the interstitial region of the unit cell, and they match the numerical radial functions inside the spheres with the requirement that the basis functions and their derivatives are continuous at the boundary. In this method no shape approximations are made and consequently such a procedure is often called "full-potential LAPW" (FP-LAPW). The much older muffin-tin approximation corresponds to retaining only the $L = 0$ and $M = 0$ component in Eq. 3.46. A spherical average inside the spheres and a volume average in the interstitial region is thus taken. Inside the atomic sphere a linear combination of radial functions multiplied with the spherical harmonics ($Y_{lm} (r)$) is used. The linear combination of $u_l (r)$ and $\dot{u}_l (r)$ constitutes the so-called "linearization" of

\[ u_l (r) Y_{lm} (r) \] and \[ \dot{u}_l (r) Y_{lm} (r) \] are the augmenting functions.
the radial function. \( u_1(r) \) and \( \tilde{u}_1(r) \) being obtained by numerical integration of the radial Schrödinger equation on a radial mesh inside the sphere.

The LAPWs have more variational freedom inside the spheres than the APWs, a flexibility which is due to the use of two radial functions instead of one, and non-spherical potentials inside the spheres can be now treated without difficulty. There is however, a price to be paid for the additional flexibility of the LAPW, since the basis functions must have continuous derivatives and consequently higher plane wave cut-offs are required to achieve a given level of convergence (i.e. require higher computational efforts). The asymptote problem experienced with the APW method is overcome by the presence of the non-zero \( \tilde{u}_{\text{non}}(R) \) value. According to this combined basis the solution of the KS equations are expanded by the linear variation method:

\[
\chi_k = \sum_n c_n \phi_{kn} \quad (3.47)
\]

where the coefficients \( c_n \) are determined by the Rayleigh–Ritz variational principle. In the WIEN97 package the total energy is calculated according to the Weinert scheme. [34] The convergence of the basis set is controlled by the cut-off parameter \( R_{\text{max}} K_{\text{max}} \) (determining the size of the matrix of the system), which usually assumes values in between 6 and 9. The \( R_{\text{max}} \) represents the smallest of all atomic sphere radii in the unit cell and \( K_{\text{max}} \) is the magnitude of the largest \( K \) vector (plane-wave cut-off).

### 3.6 Projected augmented wave method

Blöchl [35] developed the projected augmented wave method (PAW) by combining ideas from the pseudo potential and linear augmented-plane-wave (LAPW) methods. The PAW method is an all-electron electronic-structure method. It describes the wave functions by a superposition of different terms: the plane wave part, the so-called pseudo wave function, and expansions into atomic and pseudo-atomic orbitals at each atom.

The plane-wave part has the flexibility to describe the bonding and tail regions of the wave functions, but if used alone it would require large basis sets to describe correctly all the oscillations of the wave function near the nucleus. The expansions into atomic orbitals can, on the other hand, describe correctly the nodal structure of the wave function near the nucleus, but lack the variational degrees of freedom for the bonding and tail regions. The PAW method combines the virtues of both numerical representations in one well-defined basis set.

To avoid the dual efforts of performing two electronic structure calculations (for plane waves and atomic orbitals) the PAW method does not determine the coefficients of the atomic orbitals variationally. Instead, the coefficients are treated as unique functions of the plane wave coefficients. The total energy, and most of other observable quantities can be broken into three almost independent contributions; one from the plane wave part and a pair of expansions associated with

\[^2K_{\text{max}}^2\text{ represents the plane wave cut-off parameter (in Ry) used in the pseudo-potential calculation.}\]
3.6. PROJECTED AUGMENTED WAVE METHOD

the atomic orbitals on each atom. The contributions from the atomic orbitals can be broken further down into contributions from each atom, so that strictly there is no overlap between atomic orbitals on different sites to be computed.

In principle, the PAW method is able to recover rigorously the DFT total energy, thus the plane wave and atomic orbital expansions are complete. This provides us with a systematic way to improve the basis-set errors. The present implementation uses the frozen core approximation, which provides the correct densities and wave functions, and thus allows us to calculate other parameters of the system. By making the unit cell sufficiently large and decoupling the long-range interactions, the limitations of the plane-wave-basis sets to periodic systems (crystals) are overcome. Thus this method can be used to study molecules, surfaces, and solids within the same approach.

3.6.1 Wave function

Let us recall that there are two Hilbert spaces, one called the all-electron (AE) Hilbert, and an other the pseudo (PS) Hilbert. We need to map AE valence wave functions on to PS wave functions.

Every PS wave function can be expanded into PS partial waves

\[ |\Psi\rangle = \sum_i |\phi_i\rangle c_i \] (3.48)

The corresponding AE wave function is of the form

\[ |\Psi\rangle = \tau|\bar{\Psi}\rangle = \sum_i |\phi_i\rangle c_i \] (3.49)

From the above two equations, we derive

\[ |\Psi\rangle = |\bar{\Psi}\rangle - \sum_i |\phi_i\rangle c_i + \sum_i |\phi_i\rangle c_i \] (3.50)

and as we require the transformation matrix \( \tau \) to be linear, the coefficients must be linear functions of the PS wave functions. Therefore the coefficients are scalar products of the PS wave function with projector functions \( \langle \tilde{p}_i |, \langle \tilde{p}_i | \bar{\Psi} \rangle \), where the projector functions must fulfill the condition

\[ \sum_i |\tilde{p}_i\rangle \langle \tilde{p}_i | = 1 \] (3.51)

within the augmentation region \( \Omega_R \), implying that

\[ \langle \tilde{p}_i | \tilde{p}_j \rangle = \delta_{ij} \] (3.52)

Finally, the transformation matrix can be deduced from Eqs. (3.49) and (3.50); on introducing the definition \( c_i = \langle \tilde{p}_i | \bar{\Psi} \rangle \)

\[ \tau = 1 + \sum_i (|\phi_i\rangle - |\phi_i\rangle \langle \tilde{p}_i |). \] (3.53)
3.6.2 Charge density

Using this transformation matrix, the AE valence wave functions can be obtained from the PS wave function as

\[ |\Psi\rangle = |\tilde{\Psi}\rangle + \sum_i (|\phi_i\rangle - |\tilde{\phi}_i\rangle) \langle \tilde{\phi}_i | \tilde{\Psi}\rangle \]  \hspace{1cm} (3.54)

The core-state wave functions \(|\Psi|^c\) are decomposed in a similar way giving the three contributions:

\[ |\Psi|^c = |\tilde{\Psi}|^c + |\phi|^c - |\tilde{\phi}|^c \]  \hspace{1cm} (3.55)

where \(|\tilde{\Psi}|^c\) represents a PS core wave function, \(|\phi|^c\) is an AE-core-potential wave, and \(|\tilde{\phi}|^c\) the PS-core-partial wave. Compared to the valence-wave functions no projector functions are needed for the core states, and the coefficients of the one-center expansion are always unity.

![Figure 3.3: Schematic illustration of the PAW method](image)

### 3.6.2 Charge density

The charge density at a point \(\mathbf{r}\) in space is composed of three terms:

\[ n(\mathbf{r}) = \tilde{n}(\mathbf{r}) + n'(\mathbf{r}) - \tilde{n}'(\mathbf{r}) \]  \hspace{1cm} (3.56)

The soft pseudo-charge density \(\tilde{n}(\mathbf{r})\) is the expectation value for the real-space projection operator \(|\mathbf{r}\rangle \langle \mathbf{r}|\) on the pseudo-wave functions.

\[ \tilde{n}(\mathbf{r}) = \sum_n f_n \langle \tilde{\Psi}_n | \mathbf{r} \rangle \langle \mathbf{r} | \tilde{\Psi}_n \rangle \]  \hspace{1cm} (3.57)

The on-site charge densities \(n'(\mathbf{r})\) and \(\tilde{n}'(\mathbf{r})\) are treated on a radial support grid. They are given as:

\[ n'(\mathbf{r}) = \sum_n f_n \langle \tilde{\Psi}_n | \tilde{\phi}_i \rangle \langle \phi_i | \mathbf{r} \rangle \langle \mathbf{r} | \tilde{\phi}_j \rangle \langle \tilde{\phi}_j | \tilde{\Psi}_n \rangle = \rho_{ij} \langle \phi_i | \mathbf{r} \rangle \langle \mathbf{r} | \phi_j \rangle \]  \hspace{1cm} (3.58)

where \(\rho_{ij}\) is the occupancy of each augmentation channel \((i, j)\) which is obtained from the pseudo-wave functions on applying the projector functions:

\[ \rho_{ij} = \sum_n f_n \langle \tilde{\Psi}_n | \tilde{\phi}_i \rangle \langle \tilde{\phi}_j | \tilde{\Psi}_n \rangle. \] Similarly for \(\tilde{n}'(\mathbf{r})\):

\[ \tilde{n}'(\mathbf{r}) = \sum_n f_n \langle \tilde{\Psi}_n | \tilde{\phi}_i \rangle \langle \tilde{\phi}_i | \mathbf{r} \rangle \langle \mathbf{r} | \tilde{\phi}_j \rangle \langle \tilde{\phi}_j | \tilde{\Psi}_n \rangle = \rho_{ij} \langle \tilde{\phi}_i | \mathbf{r} \rangle \langle \mathbf{r} | \tilde{\phi}_j \rangle \]  \hspace{1cm} (3.59)
3.6. PROJECTED AUGMENTED WAVE METHOD

We will focus on the frozen core case, where \( \hat{n} \), \( \hat{n}' \), and \( n' \) are restricted to the valence quantities. Besides that, we introduce four quantities that will be used to describe the core charge density: \( n_c \), \( \hat{n}_c \), \( n_{Zc} \), and \( \hat{n}_{Zc} \). \( n_c \) denotes the charge density of the frozen core all-electron wave function at the reference atom. The partial-core density \( \hat{n} \) is introduced to calculate the nonlinear core corrections. \( n_{Zc} \) is defined as the sum of the point charge of the nucleus \( n_z \) and the frozen core AE charge density \( n_c : n_{Zc} = n_z + n_c \).

The pseudized core density is a charge distribution that is equivalent to \( n_{Zc} \) inside the core region. A compensation charge \( \hat{n} \) is added to the soft charge densities \( \hat{n} + \hat{n}_{Zc} \) and \( \hat{n}' + \hat{n}_{Zc} \) to reproduce the correct multiple moments of the AE charge density \( n' + n_{Zc} \) in each augmentation region. Because \( n_{Zc} \) and \( \hat{n}_{Zc} \) have exactly the same monopole \(-Z_{ion}\) (the charge of an electron being new \(+1\)), the compensation charge must be chosen such that \( \hat{n}' + \hat{n} \) has the same moments as the AE valence charge density \( n' \) within each augmentation sphere.

3.6.3 Total energy

The final expression for the total energy can also be split into three terms:

\[
E(r) = \tilde{E}(r) + E'(r) - \tilde{E}'(r)
\]  

(3.62)

where \( \tilde{E}(r) \), \( E'(r) \), and \( \tilde{E}'(r) \) are given by

\[
\tilde{E}(r) = \sum_n f_n \langle \Psi_n | - \frac{1}{2} \Delta | \Psi_n \rangle + E_{xc}[\hat{n} + \hat{n} + \hat{n}_c] + E_H[\hat{n} + \hat{n}] + \int v_H[\hat{n}_{Zc}][\hat{n}(r) + \hat{n}(r)]dr + U(R, Z_{ion})
\]  

(3.63)

where \( U(R, Z_{ion}) \) is the electrostatic energy of the point charges \( Z_{ion} \) in an uniform electrostatic background.

\[
E'(r) = \sum_{ij} \rho_{ij} \langle \phi_i | - \frac{1}{2} \Delta | \phi_j \rangle + E_{xc}[n' + n_c] + E_H[n'] + \int v_H[n_{Zc}][n'(r)]dr
\]  

(3.64)
where \( \int v_H[\hat{n} Z_e] n' (r) \, dr \) is the electrostatic interaction between core and valence electrons and \( E_H \) is electrostatic energy

\[
E_H[n] = \frac{1}{2} \langle n | n \rangle = \frac{1}{2} \int dr \int dr' \frac{n(r)n(r')}{|r - r'|}
\]  

(3.65)

\[
\hat{E}^1(r) = \sum_{ij} \rho_{ij} \langle \tilde{\phi}_i | - \frac{1}{2} \Delta | \tilde{\phi}_j \rangle + \tilde{E}_{xc} [\hat{n'} + n + \hat{n}_c] + E_H[\hat{n'} + n] + \int v_H[\hat{n} Z_e] [\hat{n'}(r) + \hat{n}(r)] \, dr
\]  

(3.66)

The overlining signalizes that the corresponding terms must be evaluated on the radial grid within each augmentation region.

### 3.7 Ultrasoft pseudopotential

It is unaffordable to treat first-row elements, transition metals, and rare earth elements by standard norm-conserving pseudopotentials (NC-PP). Therefore, various attempts have been made to generate so-called soft potentials, of which Vanderbilt [37] ultrasoft pseudopotentials (US-PP) have proved to be the most successful. There are possible improvements to the original US-PP method: (1) Introduction of nonlinear core corrections. (2) Lower cut-off energies, viz. a reduced number of plane waves compared with NC-PP. This enables us to perform molecular dynamics simulations for systems containing first-row elements and transition metals.

Because \( \hat{E} \) is exactly the same in the PAW and US-PP methods, we only need to consider the linearization of \( E' \) and \( \hat{E}' \). We obtain an approximate \( E' \) by linearization of \( E' \) from the PAW total-energy functional around the atomic reference with occupancy \( \rho_{ij} \)

\[
E^1 \approx \hat{C} + \sum_{ij} \rho_{ij} \langle \tilde{\phi}_i | - \frac{1}{2} \Delta | \tilde{\phi}_j \rangle + \nu_{\text{eff}}[\hat{n'} + n + \hat{n}_c]
\]  

(3.67)

with \( \nu_{\text{eff}} = v_H[n_{a} + n_{Z_e}] + V_{XC}[n_{a} + n_{c}] \) and \( C \) as a constant. A similar linearization can also be performed for \( \hat{E}' \)

\[
\hat{E}^1 \approx \hat{C} + \sum_{ij} \rho_{ij} \langle \tilde{\phi}_i | - \frac{1}{2} \Delta | \tilde{\phi}_j \rangle + \tilde{\nu}_{\text{eff}}[\hat{n'} + n + \hat{n}_c] + \int \tilde{Q}_{ij}^L(r) \tilde{\nu}_{\text{eff}}(r) \, dr
\]  

(3.68)

with

\[
\tilde{\nu}_{\text{eff}} = v_H[(\hat{n} + \hat{n}_a + \hat{n}_{Z_e}) + v_{xc}(\hat{n}' + \hat{n}_a + \hat{n}_{Z_e})]
\]  

(3.69)

\( \tilde{Q}_{ij}^L(r) \) is a pseudized augmentation charge in the US-PP approach. Given \( \tilde{Q}_{ij}^L(r) = Q_{ij}^L(r) = \phi_i^L(r) \tilde{\phi}_j(r) - \tilde{\phi}_i^L(r) \phi_j(r) \), one obtains:
3.8. PAW AND US-PP

\[ E_1 - E_1 = \sum_{ij} \rho_{ij} (\langle \phi_i | - \frac{1}{2} \Delta | \phi_j \rangle - \langle \tilde{\phi}_i | - \frac{1}{2} \Delta | \tilde{\phi}_j \rangle). \]  

(3.70)

We can now compare the PAW functional with the US-PP functional. In the PAW method, where the sum of compensation charge and pseudo-charge density \( n'/n \) is equivalent to the onsite AE charge density \( n'/n \), and \( \tilde{n}_{Ze} = n_{Ze}, \tilde{n}_c = n_c \), we can derive the same \( E_1 - E_1 \) from Eq. (3.64) and Eq. (3.66). In such a limiting case, the PAW method is equivalent to the US-PP method.

3.8 PAW and US-PP

The general rule in the Vienna \textit{ab initio} simulation package (VASP)[38] is to use PAW potential whenever possible, the PAW potentials are especially generated for improving the accuracy in dealing with magnetic materials, alkali and alkaline-earth elements, 3d transition metals, lanthanides and actinides. For such materials, the treatment of semi-cores states as valence states are desirable. The PAW method is then as efficient as the FLAPW method, and it is easy to defreeze the lower lying core states including only one partial wave for the semi-core states.

The essential difference between PAW and US-PP is related to the pseudization of the augmentation charges. By choosing very accurate pseudized augmentation functions, the discrepancies of both methods can be removed. However, augmentation charges must be represented on a regular grid with the US-PP approach. Therefore, hard and accurate pseudized augmentation charges are expensive in terms of computer time and memory. The PAW method avoids these drawbacks by introducing radial support grids on which the rapidly varying functions can be elegantly and efficiently treated.

The PAW potentials are generally slightly harder than the US-PP and they retain the hardness across The periodic table. On the other hand, the US-PP become progressively softer when one moves down The periodic table. For multi-component phases with very different radii, the PAW potentials are clearly superior. For one-component systems, US-PP might be slightly faster at the price of reduced precision. Most PAW potential were optimized to work at a cut-off of 250–300 eV, which is only slightly higher than in US-PP.
CHAPTER 4

Hydrogen storage materials

Available energy is the main object
at stake in the struggle for existence
and the evolution of the world.
Ludwig Boltzmann.

Hydrogen is the most abundant element in the universe and a great potential energy carrier. Unlike petroleum, it can be easily generated from renewable energy sources. It is moreover non-polluting, and forms water as a harmless reaction product during use. Yet it is so difficult to store that its use as fuel has been limited. Hydrogen can be made available for on-board vehicles as compressed gas or as liquid in suitable containers, or in the form of metal hydrides or complex hydrides, or by gas-on-solid adsorption. Hydrogen can also be generated on-board by reaction or decomposition of hydrogen-containing species. Although each method possesses desirable characteristics, none of these approaches satisfy all requirements with respect to efficiency, size, weight, cost, and safety for transportation usages. This chapter deals with how one can store hydrogen in different forms in reservoirs and give a closer description of the aims of the present project. The following sections are written as a brief note for readers generally interested in hydrogen-storage material.

4.1 Gaseous and liquid hydrogen

A gram of H₂ gas occupies about 11 liters (2.9 gallons) of space at atmospheric pressure. Hence, for convenient utilization, the H₂ gas must be intensely pressurized to several hundred atmospheres and stored in pressure containers. The gravimetric energy density of a loaded pressure container depends very much on the material in the container. The traditional steel bottles achieve an energy density of about 0.45 kWh/kg [39], which is equivalent to 1.1 wt. % of hydrogen stored. Through optimal design of the container and choice of materials 1.5 – 2.6 wt. % of stored hydrogen can be achieved. Using ultra-light containers manufactured with permeation-resistant seamless liner and high-performance carbon-composite over-wrap, and tough impact-resistant shell, Quantum Technologies,
Inc. [40] has increased the capacity for hydrogen storage to 5.02 kWh/kg (11.3 wt. %).

Liquid hydrogen has been used as a fuel in space technology for several years. [41] It is light and has less potential risks related to storage pressure compared with compressed gas units. However, liquid hydrogen has a boiling point of 20.25 K and thus the storage containers require sophisticated insulation techniques. The gravimetric energy density of liquid hydrogen in storage containers is about 13.8 kWh/kg (25.9 wt.) and the volumetric energy density is about 2760 kWh/m³. [42] The main problem is boil-off losses, which vary from 0.06 % per day in large containers to 3 % per day in smaller vessels. [43] The boil-off losses can be reduced through proper insulation. In conclusion the compressed and liquid options are not practical for everyday use.

4.2 Metallic hydrides

A possible solution to the difficulties outlined in Section 4.1 is storage of hydrogen in the form of hydrides. This method uses an intermetallic phase that can absorb and hold large amounts of hydrogen by chemical bonding. A suitable hydrogen-storage matrix should be capable of absorbing and releasing hydrogen without compromising the matrix structure. Metal hydrides are prepared by reaction between an intermetallic phase and hydrogen. When exposed to hydrogen at certain pressures and temperatures, these phases absorb large quantities of hydrogen gas and form the corresponding metal (viz. intermetallic) hydrides. If this happens, the hydrogen is distributed compactly throughout the intermetallic lattice. Metal hydrides represent an exciting way of hydrogen storage which are inherently safer than the compressed-gas or liquid storing. Also, some intermetallics (including metals and alloys) store hydrogen at a higher volume density than liquid hydrogen.

Qualities needed to make these intermetallics useful include the ability to absorb and release large amounts of hydrogen gas, often without deteriorating the storage material and with good selectivity with respect to only hydrogen absorption. In addition, favorable metal hydrides absorb and release hydrogen at rates that can be controlled by adjusting temperature and/or pressure.

In chemical shorthand, a typical reaction can be expressed as:

\[ M + \frac{x}{2}H_2 \rightleftharpoons MH_x + \text{Heat} \tag{4.1} \]

where \( M \) represents the intermetallic matrix and \( H \) is hydrogen. The reaction is reversible and the direction is determined by the pressure (and temperature) of the hydrogen gas. If the pressure is above a certain level (the equilibrium pressure), the reaction proceeds to the right to form the hydride; whereas below the equilibrium pressure, hydrogen is liberated and the intermetallic matrix returns to its original state. The equilibrium pressure, itself, depends upon temperature; viz. increases with increasing temperature (and vice versa).

The hydrogen absorbing behavior of a metal hydride is characterized by equilibrium pressure–temperature–composition (PTC) data. These data are determined by keeping a sample of a intermetallic phase at constant temperature while
measuring the quantity of hydrogen desorbed and the pressure at which desorption occurs. The quantity of hydrogen desorbed is expressed in terms of the hydrogen content, either as the number of hydrogen atoms per formula unit of the base alloy, or as the incorporated amount of hydrogen in the alloy on a weight percent basis. The main disadvantages of hydrides is their high weight, which hitherto has made this storage form uneconomical for the transportation sector.

The hydrogen-storage intermetallics in common use may be grouped in four classes: $AB$ (e.g., FeTi), $AB_5$ (e.g., LaNi$_5$), $A_2B$ (e.g., Mg$_2$Ni), and $AB_2$ (e.g., ZrV$_2$) where $A$ denotes a strongly hydride-forming element and $B$ is an element with weaker hydride forming properties.

Research is presently aiming at modifying the compositions of such matrix bases by alloying with various other elements. Such modifications can enhance the stability during cycles of charging and discharging, allow the hydrides to undergo charging/discharging cycles at ambient pressure and temperature, increase the hydrogen storage capacity, increase their hydrogen absorption/desorption rate etc. [44] One of the goals of the thesis has been to identify potential hydrogen-storage materials with high hydrogen content. Another goal is to identify hydrogen positions in the matrices and describe the packing efficiency.

### Solid-solution phases

A solid-solution phase means a primary element into which other elements are dissolved. The dissolved element(s) can form an ordered or disordered substitutional or interstitial (additional) distribution. One promising, but quite expensive group of such phase is based on vanadium. Especially, the combination V–Ti–Fe is currently viewed as an attractive alternative. For example, (V$_{0.9}$Ti$_{0.1}$)$_{0.95}$Fe$_{0.05}$ has a maximum hydrogen capacity of 3.7 wt. % and a reversible hydrogen storage capacity of 1.8 wt. % with good PTC properties. [45]

### 4.3 Complex hydrides

Complex transition-metal hydrides constitute a relatively new class of compounds. The first fully characterized member was K$_2$ReH$_5$ which was reported [16] in 1964, but is now a textbook example. Since then interest in these materials has grown considerably, largely driven by their potential for hydrogen-storage applications because of the high hydrogen contents by weight. Certain transition metals form hydrides together with elements from Groups 1 and 2 of the periodic table in which the transition metal takes a complex-ion configuration. For example, Mg$_2$NiH$_4$ is formed when Mg donates two electrons to the [NiH$_4$]$^{1-}$ complex. As mentioned in the introduction, the kinetics of hydride complexes tends to be slower compared to the traditional intermetallic hydrides where hydrogen takes interstitial lattice sites, whereas the formation and decomposition of the complex ion [NiH$_4$]$^{1-}$ requires metal atom diffusion.

Due to the high hydrogen content of these complex hydrides interest in these materials has grown considerably. The features of such compounds are largely unexplored. A simple complex hydride has the general formula $A_x M H_y$ where
A may be an alkali or alkaline-earth metal, and \( M \) can be almost any of the transition metals from the right-hand side of the periodic table. The stoichiometries of such compounds are quite variable, \( x = 1-4 \) and \( y = 2-9 \). In addition, some quaternary compounds which include two different \( A \) elements (counter-ions) are also known. This means that there is a considerable number of such possible complexes to this day around 100 examples have been structurally characterized using mostly the powerful neutron diffraction technique. [46] Complex hydride of Group 1 with \( \text{Al} \) (e.g., \( \text{LiAlH}_4 \), ...) \( \text{B} \) (\( \text{LiBH}_4 \), ...), or \( \text{Ga} \) (\( \text{LiGaH}_4 \), ...) have received special attention. Recently Bogdanovic and co-workers [9, 47] have established that \( \text{NaAlH}_4 \), (which was earlier considered in actual practice as irreversible with respect to hydrogen absorption/desorption) can be made reversible by doping with Ti. Efforts [10, 48] have also been made to improve the hydrogen reversibility of \( \text{NaAlH}_4 \) by ball milling with or without additives.

The present study has focused on the \( \text{AH}_2 \) (\( A = \text{Be}, \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba} \), \( \text{AMH}_4 \) (\( A = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}; \text{M} = \text{B}, \text{Al}, \text{Ga} \), \( \text{A}_2\text{MH}_6 \) (\( A = \text{Li}, \text{Na}, \text{K} \) series, where one obtains the theoretical hydrogen contents of 1.96 (in \( \text{CsGaH}_4 \)) to 18.28 (in \( \text{BeH}_2 \)) wt. %.

### 4.4 Carbon nanotubes and other carbon-based materials

Hydrogen can be stored as molecular hydrogen in single-wall or multi-wall nanotubes by chemisorption or physisorption, which represents a new direction for solid hydrogen storage especially, if these materials can be altered to store large amounts of hydrogen at room temperature. Most aspects of trapping hydrogen in such nanophase materials are largely un-known [49, 50], but density-functional calculations have given some insights into the mechanisms involved. [49, 51] The advantage of hydrogen-storage in carbon nanotubes is similar to that in complex hydrides where one can store more hydrogen by weight percentage than that in metal hydrides. Moreover the hydrogen absorptin/desorbtion kinetics for hydrogen in nanophase materials are better than for the complex hydrides with kinetics similar to that of metal hydrides. Carbon nanotubes are expected to be able to store anywhere from 4.2 % to 65 % of their own weight of hydrogen. Much excitement had arisen on recent reports on the use of carbon nanofibers [52] and carbon nanotubes [53], now the excitement appears to have calmed down to some extent. [54]

Other forms of carbon may also be considered for hydrogen storage purpose, like graphite nanofibers [52], fullerenes [45, 55], and activated carbon. Among these options hydrogen storage properties of high-surface-area "activated" carbon have been extensively studied. [53, 56] However, activated carbon is regarded as somewhat ineffective for hydrogen-storage systems because only a small fraction of the pores in the typically wide pore-size distribution are small enough to interact strongly with hydrogen molecules.
4.5. OTHER HYDROGEN STORAGE MATERIALS

4.5 Other Hydrogen storage materials

Apart from the above approaches a few other possibilities for storing of hydrogen should be mentioned.

Glass spheres

Tiny hollow glass spheres are warmed (which gives increased permeability through the walls), and filled by exposure to hydrogen gas at high-pressure. [57] The spheres are then cooled, which locks the hydrogen inside the glass balls on A subsequent increase in temperature the hydrogen trapped inside the spheres will be release. [58] This may be useful for one-time use of hydrogen for different purposes, but does not really represent a proper hydrogen-storage alternative.

Zeolites

Zeolites are microporous inorganic compounds with effective pore sizes of some 0.3 to 1.0 nm. These pore sizes are sufficient to permit diffusion of small molecules, such as hydrogen, under elevated temperatures and pressures. However, most of the pores are smaller than the kinetic size of a hydrogen molecule at ambient temperature and this feature thus reduced the trapping ability for hydrogen in the cavities of zeolites. [59, 60]

Metal-organic frameworks

Metal-organic frameworks (MOF) compounds are entirely new classes of materials in which one can store H in frameworks that consist of metal and organic parts. Eddaoudi et al. [61, 62, 63] has reported adsorption of nitrogen and methane in such frameworks. Recently, there has been demonstrated 0.5 wt.% hydrogen uptake in a so-called MOF-5 compound. [64] Solvent molecules captured by the framework pores during crystallization can be removed while retaining the framework which has a remarkable structural stability among known crystalline molecular materials. The storage capacities for these materials are not yet sufficiently high for practical applications, but the ability to modify the organic components of the frameworks offers a unique opportunity for increasing the hydrogen uptake. The hydrogen uptake for, say, MOF-7 is reported to be increased to 2 wt.% when a naphthalene connector is used instead of a benzene connector. Hydrogen adsorption is fast and indefinitely reversible, as may be expected from a pore structure that is continuous in three dimensions.

At present, there is no specific application area marked for activated carbon, zeolites, or glass spheres because of the unpractical operating conditions or poor hydrogen storage capacity. However, more special applications, in which high temperatures and pressures are involved, may exist for activated carbon and glass spheres. In short, metal and complex hydrides have hitherto dominated the hydrogen-storage field more than the other alternatives.
CHAPTER 5

Chemical bonding

Truth is ever to be found in the simplicity and not in the multiplicity and confusion of things.

Sir Isaac Newton.

The properties of a compound are determined by the chemical bonds that hold the constituents together. A chemical bond is an attractive force that exists between certain atoms in a substance. However, in addition to these attractive forces there must be repulsive forces because solids are not easily compressed. The attractive forces between the constituents in solids are basically of an electronic origin and the classification of the different types of bonding are strongly dependent on the electronic structure.

In most of the publications included in this thesis, the bonding characteristics of compounds are explored in order to get insight into the anisotropic volume variation of materials by hydrogenation and reason for the violation of the “2-A rule” or to rationalize hydrogen decomposition temperatures. The bonding in hydrides are quite complex, hence in the following section we try to understand the chemical bonding behavior microscopically, first for some simple systems and then apply the same approach to more complicated real systems.

According to the strength and directionality, chemical bonds are grouped into primary and secondary. By virtue of their nature, primary bonds are interatomic and secondary bonds are intermolecular. Experience from numerous studies of solids has revealed that there are three strong principal types of primary bonds: ionic, covalent, and metallic.

In the idealized ionic bonding, electrons are completely transferred from one atom to another. The electron transfer process go from electro-positive atoms to electro-negative atoms. The electronegativity difference between the constituents commonly taken as a measure of the ionicity in solids. In the process of either losing or gaining negatively charged electrons, the reacting atoms form ions. The oppositely charged ions are attracted to each other by electrostatic forces which constitute the basis of the ionic bond. The often considered example of this type of bonding is NaCl, where Na donates one electron to Cl (see Fig. 5.1a,d,g). An-
other major type of bonding is the covalent category where electrons are equally shared between atoms. As opposite to ionic bonding in which a complete transfer of electrons occurs, covalent bonding occurs when two (or more) atoms share electrons. An example of this type of bonding is found in diamond (Fig. 5.1b,e,h). The covalent bonding has a quantum mechanical origin and occurs because the atoms in a given compound have a similar “desire” for electrons. In order to have covalent interaction between electrons they should be energetically and spatially degenerate and also their spins should be “opposite”. The third type of bonding is called metallic, where the valence electrons are delocalized, i.e., homogeneously distributed in the space in between the atoms. Examples of this type of bonding is found most typically in alkali metals where each atom contributes only one electron to the common pool (see Fig. 5.1c,f,i for Na as an example), Cu, etc.

The bonding nature of materials generally becomes more complex when the number of constituents increases. For binary compounds one can easily calculate the approximate degree of ionic character from their electronegativities using Gordy’s approximation. [65] For ternary and quaternary systems it is usually very hard to estimate the approximate ionic character. When we consider hydrides, it is even more complicated, because of the small atomic size and the only one valence electron of the hydrogen. Moreover, hydrogen takes the valence of $+1$, $0$, or $-1$ depending upon the chemical environment which complicates further attempts to quantify the ionicity in hydrides. There have been several attempts to more rigorous, quantifiable, theories for classifying the bonding in materials, using, e.g., the electronegativity scale of Pauling [66], the population analysis of Mulliken [67], to the classification scheme using gradient regions of the electron density by Bader [68], Born effective charges [69], visualization by electron localization function (ELF) [70], and bond strengths according to the crystal orbital Hamiltonian population (COHP) [71] etc.

When one considers hydrides, bonding analyzes are very important to understand unusual behaviors, like anisotropic volume expansion during the hydrogenation, hydrogen induced structural transitions, hydrogen induced amorphization, hydrogen induced metal-to-insulator or insulator-to-metal transition, hydrogen induced magnetic transitions, etc. By applying a single analysis tool (DOS, charge distribution, charge transfer, ...) one can not expect to obtain the full picture. In order to get a more precise impression of the bonding nature in hydrides several approaches have to be involved. Examples are to be found in publications II, III, IV, and XVI.

5.1 Classification of the hydrides

In general, hydrides are classified according to the nature of the bonding of hydrogen to the host lattice as covalent or volatile, saline or ionic, and metallic, each of these classes bearing distinct characteristics. Such a classification does not always clarify the typical features of the compound in question. For example, lithium hydride, is classified as a saline hydride, whereas it actually exhibits some covalent characteristics. The rare-earth hydrides are usually classified with the metallic hydrides, whereas they exhibit some characteristics similar to those of volatile and saline hydrides (e.g., high heat of formation).
5.2. BONDING NATURE OF HYDRIDES EXPLORED BY THEORETICAL TOOLS

Ionic Hydrides

Ionic hydrides are formed by reaction between a strongly electro-positive alkali (or alkaline-earth) metal and hydrogen, which becomes strongly electronegative because of the electron transfer. In contrast to the covalent hydrides, the bonding in the ionic hydrides results from the strong electrostatic forces between the dissimilar charges of the two kinds of ions. The ionic hydrides are usually well crystalline, exhibit high heats of formation and high melting points. The ionic alkali and alkaline earth hydrides are denser than the pure alkali (45 to 75%) and alkaline-earth metals (20 to 25%).

Covalent Hydrides

Covalent hydrides are found in the solid, liquid or gaseous phases. The bonding between hydrogen and the other constituent(s) is characterized by sharing of then valence electrons on a fairly equal basis. In general molecules with covalent bonding are not strongly attracted to each other, and this absence of strong intermolecular forces results in a degree of volatility and a low melting point. Covalent hydrides are generally somewhat thermally unstable, and this instability increases with increasing atomic weight of the non-hydrogen element(s). Typical covalent hydrides are carbon hydrides, boron hydrides, germanium hydrides, etc. Covalent hydrides generally exhibit low symmetric structures.

Metallic Hydrides

Metallic hydrides are normally formed by the transition metals (e.g., ScH2). They generally exhibit the characteristic metallic properties like high thermal and electrical conductivity, hardness, luster etc. Because of the wide homogeneity ranges adopted by metallic hydrides, they have sometimes been considered as solid solutions of hydrogen in the interstitials of metal, alloy or intermetallic matrices. The crystal structures of metallic hydrides may also be distinctly different from those of the parent matrices.

5.2 Bonding nature of hydrides explored by theoretical tools

The chemical bond arises in reality from a redistribution of the valence electrons of the constituent atoms in a way that it is energetically favorable (nature seeks to minimize energy).

As mentioned in the previous section, the real bonding nature of hydrides is quite complex. In order to strengthen our arguments, we will start with an analysis of well-known classical examples: NaCl for the ionic case, C in the diamond structure for the covalent case, and Na for the metallic case and then extend the analysis to simple hydrogen containing compounds. In the hydride cases, we have chosen LiH for ionic, B3H8 for the covalent, and ScH2 for metal hydride.
5.2.1 Charge density

An understanding of the nature of the chemical bond can be aided by the studies of the distribution of charges in real space. The real space charge density can also be used to understand features of the electronic properties in a real material. One has to remember that the charge density very much depends on the crystal structure, and different characteristics may be formed for one and the same compound in different structural arrangements.

The charge-density distribution in the model substances NaCl, C, and Na are shown in Fig. 5.1a, b, and c, respectively. The charge-density distribution for the simple hydrides LiH (ionic), B$_2$H$_6$ (covalent), and ScH$_2$ (metallic) are also shown in Fig. 5.2a, b, and c, respectively, which clearly reflect the overall picture of ionic, covalent and metallic bonding, respectively. However, the charge-density distribution in ScH$_2$ can not be simply viewed as that for a pure metallic phase as Fig. 5.2c conveys significant ionic and covalent bonding contributions.

In publication I we have used charge density analysis along with structure analysis to explain the anisotropic volume expansion. The experimental [72, 17] and theoretical studies showed high anisotropic changes in lattice expansion on hydrogenation of Th$_2$Al. The interatomic distance between the interstitial regions
5.2. BONDING NATURE OF HYDRIDES EXPLORED BY THEORETICAL TOOLS

Figure 5.2: Calculated valence-electron-density maps (a), (b), and (c); charge transfer plots (d), (e), and (f); and ELF plots (g), (h), and (i) for LiH, B, B/EH, and ScH2. Atoms are labelled on the illustration and scales are given in the right hand side.

in the crystal structure of Th2Al where hydrogen can be accommodated. Hence, there is a large flexible space for accommodation of H atoms in the ab plane without a need to expand the lattice. In contrast, the interatomic distance between the interstitial regions in the ac plane is only 1.65 Å. So, a large expansion of the lattice along c is necessary to accommodate H atoms within the ac plane. As a result, even with a short H–H separation of 1.95 Å, a lattice expansion of 12.41% along c is required when Th2AlH4 is formed from Th2Al. The experimental observation of 0.105% lattice expansion along a and 12.15% along c is found to be in excellent agreement with these considerations. The bonding between Th and H is predominantly covalent as evidenced by the finite charge between these atoms. The H–s electrons are tightly bound to the Th–d states, and arrangement of the Th and H atoms forms an H–Th–H dumb-bell pattern.

5.2.2 Charge transfer

The charge density displays the chemical bonds in a given system, but remains rather featureless, with charge maxima around the atoms, similar to the charge density of overlapping free atoms. The charge-density-transfer contour is
the self-consistent electron density in a particular plane, \( \rho_{\text{comp.}} \), minus the electron density of the corresponding overlapping free atoms, \( \rho_{\text{o.f.a.}} \), i.e.,

\[
\Delta \rho(r) = \rho(r)_{\text{comp.}} - \rho(r)_{\text{o.f.a.}},
\]

which allows one to visualize how electrons are redistributed in a particular plane of the compound compared to free atoms.

If one now (instead of charge density) displays the difference between the electron density of the compound and the electron density of the constituent atoms (viz. the charge transfer), one obtains an impression of how electrons are shifted around when the solid is formed. This allows one to see how the actual chemical bond is formed in real space. Fig. 5.1d, e, and f displays the charge transfer density of the test compounds NaCl, C, and Na. Similarly, Fig. 5.2a, b, and c show the charge redistribution in the hydrides LiH, B\(_2\)H\(_6\) and ScH\(_2\) respectively. In these figures, we clearly see the difference between the three principle types of bonding. In the Figs. 5.1d and 5.2d we see the nature of the ionic bond with large charge transfer from the Na/Li to Cl/H atoms. In Fig. 5.1e we can see the covalent bonding in diamond, with charges from surrounding atoms placed in between the atoms with the characteristics of directional bonds. Similarly, in B\(_2\)H\(_6\) the charges are shared in B–B and B–H bonds. In Figs. 5.1f and 5.2f one can see the spreading of electrons around the metal atoms and there somewhat “even” distribution in the interstitial regions. In Fig. 5.2f charges are also depleted from Sc site which clearly indicate that a finite degree of ionicity is also present in this material. A similar type of bonding nature was identified in the studied RNiInH\(_{1.333}\) (\(R = \text{La, Ce, Pr, Nd}\)) metal hydride systems.

### 5.2.3 Electron localization function

ELF is a ground-state property which discriminates between different kinds of bonding interaction for the constituents of a solid. [70, 73, 74] In the implementation for DFT, this quantity depends on the excess of local kinetic energy \( t_p \) originating from the Pauli principle.

\[
ELF = \{1 + [t_{p(\rho)}/t_p,\delta(\rho(r))]^2\}^{-1}
\]

where:

\[
t_p = \tau - 1/8[(\nabla \rho)^2/\rho]
\]

is the Pauli kinetic energy density of a closed-shell system. \( (\nabla \rho)^2/(8\rho) \) is the kinetic energy density of a bosonic-like system, where orbitals proportional to \( \sqrt{\rho} \) are occupied. \( t_p \) is always positive, and for an assembly of fermions, it describes the additional kinetic energy density required to satisfy the Pauli principle. The total electron density \( \rho \)

\[
\rho = \sum_i^n |\psi_i|^2
\]

as well as the kinetic energy density \( \tau \)

\[
\tau = 1/2 \sum_i^n |\nabla \psi_i|^2
\]
are computed from the orbitals, \( \psi_i \). In both equations, the index \( i \) runs over all occupied orbitals.

According to Eqn. 5.2, the ELF takes the value one either for a single-electron wave function or for a two-electron-singlet wave function. In a many-electron system ELF is close to one in regions where electrons are paired such as covalent bonds, or for unpaired lone electrons of dangling bonds, while the ELF is small in low-density regions. In a homogeneous electron gas ELF equals 0.5 at any electron density, and ELF values of this order in homogeneous systems indicates regions where the bonding has a metallic character. The ELF distribution of typical examples for the bonds in the three test cases are given in Fig. 5.1g–i. For the NaCl case ELF is around 0.9 at the Cl site and only a non-significant ELF value is found at the Na site, thus clearly reflecting ionic bonding. In the C case, a ELF value of around one is found where the shared electrons are present (in between the C atoms). In the third case, maximum values of ELF is present around the interstitial region where the delocalized electrons are found. From the above examples, one can clearly visualize different bonding nature in solids. We extended the corresponding analyzes to hydrides and found almost similar ELFs for LiH as NaCl and for B\(_2\)H\(_6\) like C. In the metallic ScH\(_2\) hydrides, we obtain low ELFs compare to Na. We like to note that our test calculations for the metals Ni, Co, and Cu also show such low ELF values and this is the general characteristic for transition metals (d electrons). We have used ELF to interpret the short H–H separation in the \( R\)InH\(_{1.33}\) (\( R = \) La, Ce, Pr, Nd; \( T = \) Ni, Pd, Pt) series (publications II, III, and IV). We have also conducted such type of analysis for the complex hydrides in order to identify the reason for their high decomposition temperature.

### 5.2.4 Density of states

Density of states (DOS) show how the electrons are distributed in different energy levels. From the electron distribution on the various energy levels one can deduce information about the bonding nature in a solid and whether the particular system is insulator, metal, semiconductor or semi-metal. Materials with an energy band gap (separation between the valence band and conduction band; \( E_g \)) in the range \( 0 < E_g \leq 4 \text{ eV} \) are called semiconductors and those where having a gap \( E_g > 4 \text{ eV} \) are classified as an insulators. Semiconductors with gaps below or near 0.5 eV are called narrow-gap semiconductors; materials with gaps between 2 and 4 eV are called wide-gap semiconductors. In an insulator or semiconductor there should be no electrons at the Fermi level (\( E_F \)) at 0K and the valence and conduction bands are separated by a finite \( E_g \). Material with \( E_g \) close to zero are called semi-metals. In an insulator or semiconductor there should be no electrons at the \( E_F \) and the valence and conduction bands are separated by a finite \( E_g \). With regard to bonding interaction, covalent type of interactions manifest (usually found in semiconducting phases) themselves as localized and energetically degenerated energy levels in certain region of the DOSs. In an ionic compound, the DOS feature is energetically well separated (often insulators). In a metallic compound the DOS will have non-localized electron viz. a finite number of electrons at \( E_F \).

The calculated total DOS for the studied test cases are shown in Fig.5.3. The
magnitude of the $E_g$ for these systems shows that both ionic (NaCl, LiH) and the covalent compounds (C, B$_2$H$_6$) are of the non-metallic type (the valence band and conduction bands are separated by 3.2 eV for B$_2$H$_6$ and 4.5 eV for the LiH). In the Na and ScH$_2$ systems there is a finite number of electrons at the $E_F$ in accordance with their metallic character. In the present thesis we are dealing with both metallic and non-metallic hydrides. A typical example for the metallic case is found in LaNiInH$_{1.33}$ and such results are presented in publications II, III, and IV. The typical example for the non-metallic case from the present project is LiAlH$_4$, where the valence and conduction bands are separated by 4.7 eV. In fact complex hydrides considered in the present projects are non-metallic with $E_g$ between 3.5 and 5.5 eV.

![Figure 5.3: The calculated total density of states for NaCl, C, Na, LiH, B$_2$H$_6$, and ScH$_2$. The valence bands are shaded, the Fermi levels are set at zero energy and marked by dotted vertical lines.](image)

### 5.2.5 Crystal orbital Hamiltonian population

COHP is an extremely useful tool to analyze bonding, antibonding and non-bonding interaction between atoms. The simplest approach is to investigate the complete COHP between the atoms concerned, taking all valence orbitals into account. For a detailed description of the COHP method, the reader is referred to
the original literature. [71] Implications of COHP is that a negative value indicates bonding, positive antibonding and zero value together with a finite DOS represent nonbonding states. The COHP contours depend on the number of states in a particular energy interval. The integrated COHP (ICOHP) curve up to the $E_F$ represents the total overlap population of the bonds in question. The calculated COHP curve for the model cases and the simple hydrides are shown in Fig.5.5. Even though, the ionic and covalent type of interactions are stronger, the COHP study gave maximum ICOHP for covalent compounds, e.g., in the studied model systems, C have a maximum ICOHP; similarly, in hydride case $B\text{H}_2$ have maximum. This is due to non-directional nature of the ionic bonding because overlap between the orbital is very small in the ionic compounds.

In this study, the bond strength of the $R\text{TInH}_{1.333}$ ($R = \text{La, Ce, Pr, Nd}; T = \text{Ni, Pd, Pt}$) series have been examined to see how efficiently one can pack hydrogen in the $R\text{TIn}$ matrix (Publication II-IV). An interesting observation from this project is that, when one includes hydrogen in the $R\text{TIn}$ matrix the estimated ICOHP value for the $T-$In bond is changed from ca. $-0.8$ to $-1.1$ eV. This appears to reflect transfer of electrons from both $T$ and In to the H site which considerably reduces the ionic interaction between $T$ and In. Moreover, we explain the reason for the short H–H separation in the $R\text{TInH}_{1.333}$ matrix and quantitatively evaluated different type of bonding situations in these phases using this approach.

We also extensively studied the COHP in complex hydrides in order to find suitable hydride phases with low decomposition temperature (Publication XI). The most notable feature from this study is the remarkable strength of the Ga–H.
interaction \([-2.6 \text{ to } -3.4 \text{ eV in ICOHP, similar for all } B-H (B = B, Al, Ga) \text{ interactions in these series}]\) compared to the other interactions. Moving from \(A = \text{Li} \) to Cs the \(B-H\) interaction (covalent bond strength) is reduced (both in the Al and Ga series). According to the calculated ICOHP for these phases, the strength of the Al-H bond is stronger than that of the Ga-H bond. This indicates that the stability (the decomposition temperature) in the Al series is higher than in the Ga series. It implies that the partial substitution of Li by other alkaline elements to materials like \(\text{Li}_{1-x} \text{Na}_x \text{AlH}_4\), \(\text{Li}_{1-x} \text{K}_x \text{AlH}_4\), or \(\text{Li}_{1-x} \text{K}_x \text{Al}_{1-y} \text{Ga}_y \text{H}_4\) may give phases with lower decomposition temperatures.

5.2.6 Mulliken population

In order to make a quantitative conclusion, it would be useful if one could identify the amount of electrons on a particular atom and the population of electrons between all atoms concerned. Although there is no unique definition of how
to extract how many electrons that are associated with an atom in a molecule or a sub-unit of a solid it has nevertheless proved useful in many cases to perform population analyzes. Due to its simplicity the Mulliken [75] population scheme has become the most familiar approach to count electrons associated with a given atom. However, also this method is more quantitative than qualitative, the results obtained from this approach are sensitive to the atomic basis. Mulliken charges are listed in Table 5.1 for examples of materials which may provide benchmarks for systems with well recognized chemical bonding. LiH is a reasonably pure ionic compound and the calculated Mulliken charges reflect nearly the expected ionic picture with Li\(^+\) and H\(^-\). The overlap population between Li\(^+\) and H\(^-\) is also close to zero, as expected for an ionic compound. Similarly, in MgH\(_2\), BeH\(_2\), and AlH\(_3\) the bonding interaction is mainly ionic, but the degree of ionicity is reduced from MgH\(_2\) to BeH\(_2\) and further to AlH\(_3\), viz. these compounds exhibit some covalent character as evidenced by the non-zero overlap population. For the CH\(_4\) molecule, the overlap population takes a value of 0.384 consistent with the well known covalent character of this molecule. The Mulliken effective charges for Li, Al, and H in LiAlH\(_4\) and Li\(_3\)AlH\(_6\) indicate that the interaction between the Li and AlH\(_4\)/AlH\(_6\) is ionic (one electron transferred from Li to AlH\(_4\)/AlH\(_6\)).

We thus find that the bonding nature of the hydrides (both metallic and complex) does not exhibit a simple ionic or covalent character. In fact the bonding situation in these compounds quite complex. In the complex hydrides like LiAlH\(_4\) and Li\(_3\)AlH\(_6\) the interaction between Li and AlH\(_4\)/AlH\(_6\) is ionic whereas the interaction and that between Al and H comprises both ionic and covalent character. We believe that similar type of bonding situation prevails in all similar complex hydrides, but the magnitude of the ionic/covalent mixture will exhibit considerable individual variation.

In conclusion the present study shows that for metal and complex hydrides several analysis tools must be consulted in order to make more firm conclusions regarding the bonding nature.
Table 5.1: Mulliken population analysis for selected hydrogen containing compounds. The Mulliken effective charges (MEC) are given in terms of $e$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Atom</th>
<th>MEC</th>
<th>Overlap population</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiH</td>
<td>Li</td>
<td>+0.98</td>
<td>-0.003 (Li–H)</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>-0.98</td>
<td></td>
</tr>
<tr>
<td>CH$_4$</td>
<td>C</td>
<td>-0.26</td>
<td>0.384 (C–H)</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>+0.06</td>
<td></td>
</tr>
<tr>
<td>MgH$_2$</td>
<td>Mg</td>
<td>+1.87</td>
<td>-0.040 (Mg–H)</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>-0.93</td>
<td></td>
</tr>
<tr>
<td>BeH$_2$</td>
<td>Be</td>
<td>+1.63</td>
<td>0.045 (Be–H)</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>-0.82</td>
<td></td>
</tr>
<tr>
<td>AlH$_3$</td>
<td>Al</td>
<td>+2.22</td>
<td>0.091 (Al–H)</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>-0.74</td>
<td></td>
</tr>
<tr>
<td>LiAlH$_4$</td>
<td>Li</td>
<td>+1.01</td>
<td>0.172 (Al–H)</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>+2.01</td>
<td>-0.021 (Li–H)</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>-0.75</td>
<td></td>
</tr>
<tr>
<td>KAlH$_4$</td>
<td>K</td>
<td>+1.08</td>
<td>0.171 (Al–H)</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>+1.88</td>
<td>-0.044 (Li–H)</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>-0.75</td>
<td></td>
</tr>
<tr>
<td>Li$_2$AlH$_6$</td>
<td>Li</td>
<td>+1.01</td>
<td>0.105 (Al–H)</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>+2.08</td>
<td>-0.020 (Li–H)</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>-0.85</td>
<td></td>
</tr>
</tbody>
</table>
CHAPTER 6

Structural exploration

Prediction is very difficult, especially about the future.

Niels Bohr

The crystal structures of the pure elements and most of the binary compounds have been frequently studied and are well characterized. On turning to ternary compounds, however, the amount of knowledge is considerably less extensive (an estimated 10% coverage of structural information) and for quaternary and multi-component phases the structural knowledge is extremely poor.

The knowledge on hydrides fits nicely into this general picture, but it must be recalled that structure determination of hydrides is confronted with an additional complexity that hydrogen is by far the lightest element. X-Ray diffraction (XRD) techniques are suitable for determining the dimensions of the unit cell and the positions of the non-hydrogen atoms, but it is a poor technique to identify the hydrogen positions in hydrides. Neutron diffraction (ND) is also a poor tool to locate hydrogen in crystal lattices, however if one uses deuterated compounds it is very powerful. The problem to use deuterated sample is that the deuterium isotope is quite expensive and its scarcity has so far limited the application of this technique. Neutron diffraction is indeed suitable method for locating the position of both metal and deuterium atoms in deuterides. Neutrons are scattered by nuclei, and thus the scattering factors for light and heavy atoms are of the same magnitude. The schematic structural arrangement obtained from powder XRD and ND for LiAlH$_4$ is illustrated in Fig. 6.1. Note that unit-cell dimensions as well as space groups sometimes vary between investigations based on XRD and PND.

A further important point is to note that, most atomic arrangements are determined on powders owing to synthetical difficulties which may have poor crystallinity and show presence of impurity phases (often not detected directly by XRD). For example, the structurally complicated case Mg$_6$Co$_2$D$_{11}$ [16] has 63 positional parameters, it exhibits structural disorder, and the experimental data have limited resolution when collected with conventional XRD technique. High
resolution measurements (say, with synchrotron XRD) are rare. The data are usually analyzed by the Rietveld method. For improved convergence, the number of refinable parameters, in particular those referring to the atomic displacement amplitudes are reduced.

For all these reasons, hydride (deuteride) structures may rightfully be said to be less well characterized than other compounds. In this situation, theoretical investigations are also a valuable supplementary tool for the experimentalists by suggesting possible structural arrangements with unit-cell parameters and atomic positions.

![Figure 6.1: Schematic structural representation by XRD (a) and PND (b) for LiAlH$_4$. Legends for the different kinds of atoms are given in the illustration.](image)

### 6.1 Structure prediction

From a DFT total energy study, one can reliably reproduce/predict the crystal structure of compounds in general and hydrides in particular. For instance, technologically interesting materials like alkali-metal aluminum and alkali-metal gallium tetrahydrides can be explored although only NaAlH$_4$, LiAlH$_4$, NaGaH$_4$, and KGaH$_4$ are structurally well characterized. For the structures of KAlH$_4$ and LiGaH$_4$, the unit-cell volumes are only experimentally available in the literature and virtually no structural information exists for $ABH_4$ with $A = $ Rb and Cs and $B = $ Al and Ga. By conducting total-energy calculation of different possible structural arrangements one can find (from the minimum-energy configuration since nature always seeks the lowest energy configuration) the stable crystal structure of a system at ground state and high pressures. Another approach is to identify the equilibrium crystal structure by a simulated annealing procedure where one begins with a guess structure with only triclinic $P1$ symmetry (the guess structure may be an experimentally known structure stripped from it symmetry elements to only translation lattice symmetry) and “heat up” the structure from 0 to 1000 K in steps of 50 K. At each temperature the structure is allowed to evolve for 1 ps.
The minimum-energy structural configuration will then be trapped by minimization of forces. Once one reaches the highest temperature the system is cooled back to 0 K, also in 50 K steps. The final parameters of thus processed guess structure is then analyzed for possible symmetry. These procedures are repeated until a satisfactory structure solution is found. Usually a simulated annealing is most efficient if all masses are equal, since then the energy dissipates more quickly between different vibrational modes. It is also important to note that sometimes this method may trapped into a possible metastable phase. From this point of view, the first method is best suited for finding the exact ground state but its limitation is, that one has to consider many possible structural arrangements in order to ensure that one does not end up with a wrong solution. The simulated annealing method is most useful for smaller systems, but sometimes it also ends up with wrong solutions or does not obtain properly converged results. [76] The present project has adopted the minimum-energy configuration method to establish the ground-state structures.

For an example, one may chose KAlH₄ where unit-cell dimensions at room temperature have been reported [77], but a more complete experimental-based structural description is lacking. We have considered seven closely related potential structure types for these simulations: LiAlH₄ (monoclinic; P2₁/c), α-NaAlH₄ (tетragonal; I₄₁/a), β-LiBH₄ (hexagonal; P6₃mc), NaGaH₄ (orthorhombic; Cmcm), NaBH₄ (cubic, Fm3m), SrMgH₄ (orthorhombic; Cmce2₁), and KGaH₄ (orthorhombic; Pnma). Among them the orthorhombic KGaH₄-type arrangement is seem to have the lowest total energy (Fig. 6.2) with unit-cell dimensions \( a = 9.009, b = 5.767, c = 7.399 \) Å at ambient pressure. A recent powder neutron diffraction study [78] on KAlH₄ confirms these predictions.

Using similar type of theoretical approach, we have successfully reproduced or predicted the crystal structures of the entire \( A \)M₃H₈ (\( A = \)alkali metal; \( M = \)B, Al, Ga), A₂H₃ (\( A = \)Be, Mg, Ca, Sr, Ba), and A₃M₃H₈ (\( A = \)Li, Na, K; \( M = \)B, Al) series. This indicates that, DFT is a powerful tool to predict structural properties of hydrides at ambient and high pressures (previously this method is applied only to quite simple compounds). For more complex structural arrangements such theoretical simulations demanded huge computer resources; but the development in the computer technology and efficient program packages have made it possible to handle such computations on available machines within a reasonable time limit.

The temperature effects have not been included in the calculations (i.e., the calculated structural parameters are valid for 0 K) and zero-point energy contributions to the total-energy are also not taken into account. However, the theoretically derived and experimentally observed structural arrangements agree very well and variable structural parameters are matching within the accuracy of the DFT (1 to 3 %). This indicates that, zero-point effects have very little influence on the structural properties. If one really wants to calculate the contributions to the total energy from zero-point-motions, information about the phonon modes are required. These are difficult to extract from DFT calculations, not to mention that they are time consuming. Our experience suggests that the neglect of zero point motion effects does not invalidate the conclusions on phase stability.

Different theoretical tools, e.g., use of different basis sets and various level of
approximations determines the efficiency of the actual computations. Although, the level of approximations may vary one obtains nearly the same equilibrium structure and structural parameters for a given system with different theoretical approaches. In order to illustrate this point, we have displayed the calculated unit-cell volume vs total energy curves for MgH$_2$ in the $\alpha$ and $\gamma$ modifications (Fig. 6.3) as obtained from the VASP and FP-LMTO methods. Both methods correctly reproduce the experimentally known $\alpha$-phase as the ground-state phase and the calculated unit-cell volumes also fit very well with the experimentally measured volume (30.52 and 30.64 Å$^3$/f.u. from FP-LMTO, and VASP, respectively; according to experiment 30.49 Å$^3$/f.u.). The experimentally identified metastable $\gamma$ phase (unit-cell volume 29.99 Å$^3$/f.u.) is predicted as the next stable phase (equilibrium volume 29.94 and 30.01 Å$^3$/f.u. for FP-LMTO, and VASP, respectively). The $\alpha$-to-$\gamma$ transition pressure for MgH$_2$ came out as 0.385 and 0.387 GPa from FP-LMTO and VASP, respectively. As both methods yielded almost same ground-state properties, throughout the present project (in all publications on complex hydrides) the VASP code has been preferred because of its better computational efficiency.

### 6.1.1 Anisotropic behavior

For compounds which maintain the same basic structural framework, the occupancy of hydrogen in interstitial sites is determined by its chemical environment (different chemical affinity for the elements in the coordination sphere also results in different occupancy). Although the hydrogen atom is small and be-
6.2 Tailor made complex hydrides

As mentioned in Section 4.3 the hypothetical combination of elements from the periodic table to form complex hydrides is almost infinite. To date over a 100 of such complexes have been structurally characterized. [46] The present project has focused on the series $A\text{H}_2$ ($A = \text{Be, Mg, Ca, Sr, Ba}$), $AM\text{H}_4$ ($A = \text{Li, Na, K, Rb, Cs}$; $M = \text{B, Al, Ga}$), $A_3M\text{H}_6$ ($A = \text{Li, Na, K}$), where one can obtain theoretical hydrogen contents from 1.96 (in BaGaH$_4$) to 18.28 wt. % (in BeH$_2$). Moreover, the theoretical calculations suggest that the $A$ and $B$ atoms in the $ABH_4$ series can be partially replaced by other $A$ and $B$ atoms (example: in LiAlH$_4$, partial substitution of Li by other alkali elements such as Li$_{1-x}$Na$_x$AlH$_4$ and Li$_{1-x}$K$_x$AlH$_4$ or Li$_{1-y}$K$_y$Al$_{1-y}$Ga$_y$H$_4$ where Al is partially replaced by Ga) and perhaps lower the...
decomposition temperatures. By each substitution one can tailor the hydrogen absorption/desorption properties and wt. % of hydrogen in complex hydrides.

From the light weight and efficient hydrogen storage point of view, alkali- and alkaline-earth-metal based hydrides along with Group 4 elements (especially B, Al, and Ga) have obtained special attention. Using the simple chemical picture one can identify several hypothetical series of phases, e.g., $AH (A = \text{alkali})$, $BH_2 (B = \text{alkaline-earth element})$, $ABH_3$, $ACH_4 (C = \text{Group 4 element})$, $BBH_4$, $A_2BH_4$, $BCH_5$, $AB_2H_5$, $A_2BH_6$, $A_2B_3H_6$, $A_2B_3H_8$, $A_1B_3H_{10}$, etc. The $AH$ and $BH_2$ phases are structurally well characterized and for the $ABH_3$, and $ACH_4$ series most of the compounds are identified. On the other hand, in the remaining series (e.g., in the $BCH_5$ series BaAlH$_5$ [Ref. [80]]; in the $A_2BH_4$ series Cs$_2$MgH$_4$ [Ref. [81]]) only very few compounds are experimentally identified and these are often synthesized via high-pressure routes. So far all established complex hydrides have high decomposition temperatures (usually close to the melting point). However, experimental evidences showed that it is possible to reduce the decomposition temperature by controlling the particle size or by addition of suitable "catalytic" material. These findings clearly tell us that, it is not unlikely than some other compounds, by some synthesis technique and/or with some additives one may obtain materials with more useful operating temperatures and better kinetics. However, one may have to go a long way to find such materials. From amount of stored hydrogen point of view (regardless of whether the absorption/desorption is reversible) one can today tune the H content by varying the chemical composition of the storing system.
CHAPTER 7

Application of pressure on hydrides

I never came upon any of my discoveries through the process of rational thinking.
Albert Einstein

As indicated in Chapter 6, exploration of crystal structures for hydrogen-containing compounds is difficult even at ambient pressure and temperature conditions. When one wants to explore the situation at elevated pressure the challenge has increased considerably and for this reason experimental high-pressure structural studies on hydrides are very limited. In this situation, computational methods provide valuable tools to probe high-pressure phases of hydrides.

Knowledge about the stability of a materials is very important for judging its use in practical applications. [82, 83] Some high-pressure/metastable phases may have superior properties compared to their ambient-pressure parent phases. For example, the high-pressure form of TiO$_2$ should be much harder than diamond. [82, 83] In fact, we found that high-pressure hydride phases have some novel properties compared to ground state phases.

The utilization of high-pressure technology, which can reach the range of hundreds of GPa, has made considerable progress in experimental studies of hydrogen storage materials. For a number of metal–hydrogen systems, it has been demonstrated that application of high pressures efficiently produce vacancies in the host metallic matrix, which in turn lead to altered properties. [84] Recently, a large number of ternary metal hydrides with the general formula $A_xM_yH_z$ ($A =$ alkali- or alkaline-earth-metals; $M =$ transition metal) have been synthesized and characterized. Many of these compounds were prepared via high-temperature, high-pressure routes. [85, 81] The conduction of such studies by theoretical means is a way to probe the various stable/metastable forms before preparation and testing, thus saving time, manpower, running costs, etc.
7.1 Static total energy calculations

The static total energy approach is still the main method in \textit{ab initio} simulations. These calculations evaluate the energy and stability of an ideal, zero-temperature crystal in which all atoms are located on their lattice positions. Pressure induced phase transitions can be reliably predicted by evaluating the enthalpy (total energy plus $PV$) for each phase as a function of pressure. The phase-transition pressure can also be deduced from the common tangent between curves on a total energy versus volume plot corresponding to the two phases. The transition pressure is given by $P_T = (V_2 - V_1)/(V_1 - V_2)$ where $F_1$ and $F_2$ are the Gibb’s free energy for phase 1 and 2, respectively (viz. identical to the total energies at $T = 0$). This free energy is minimized with respect to positional and unit-cell parameters in each phase. One can not evaluate $P_T$ directly from the above equation. So one has to calculate equations of states for two phases separately, and then compute it.

The electronic structure and structural stability of the technologically interesting material NaAlH$_4$ are studied in publication IX. After the establishment of hydrogen reversibility in NaAlH$_4$ by introduction of additives, this particular material has obtained special attention. Our motivation is to search for the formation of other metastable phases for this compound. The calculated structural parameters for $\alpha$-NaAlH$_4$ are in good agreement with the experimental values. Application of pressure converts $\alpha$-NaAlH$_4$ into $\beta$-NaAlH$_4$ at 6.43 GPa with a 4% volume contraction (Fig. 7.1), the co-ordination number of Al in $\beta$-NaAlH$_4$ is six as compared with four in $\alpha$-NaAlH$_4$. The reason for the transition appears to be that the Al-$p$ states of $\beta$-NaAlH$_4$ are more delocalized and also the maximum in the Al-$p$ DOSs is in the lower energy side of the valence band than that in $\alpha$-NaAlH$_4$.

![Figure 7.1: Structural stability of $\alpha$-NaAlH$_4$ relative to $\beta$-NaAlH$_4$ in terms of pressure.](image)

\[\text{Pressure (GPa)}\]
\[\Delta G (\text{kJ/mol})\]
7.2 Cohesive properties

The calculation of cohesive properties is the classical application of DFT based methods, since such properties derive from the behavior of the total energy. Cohesive properties include the cohesive energy, heat of formation, the equilibrium volume, and elastic properties such as the bulk modulus. The usual approach is to calculate the total energy for a number of volumes and then fit these to an equation of state, from which the cohesive properties are extracted.

7.3 Equation of state

The functional relationship for pressure versus volume is called equation of state (EOS). The high-pressure EOS has been represented in various functional forms, for example, the Murnaghan (M) equation, Birch-Murnaghan (BM) equation, universal (U) equation and recently a new EOS appropriate to strong compressions has been put forward by Holzapfel. They all give very similar results.

7.3.1 Murnaghan equation

The Murnaghan EOS [86] is based on the assumption that the pressure derivative $B'$ of the bulk modulus $B$ is a constant.

The $E - V$ form of Murnaghan EOS can be represented as,

$$ E(V) = \frac{B_0 V_0}{B'_0} \left[ \frac{1}{B'_0 - 1} \left( \frac{V_0}{V} \right)^{B'_0 - 1} + \frac{V}{V_0} - \frac{B'_0}{B'_0 - 1} \right] + E_{coh}. \quad (7.1) $$

where $E_{coh}$ is the cohesive energy and is treated as an adjustable parameter. Since the pressure can be obtained from $P(V) = \partial E(V)/\partial V$, the Murnaghan equation can be expressed in its usual form

$$ P(V) = \frac{B_0}{B'_0} \left[ \left( \frac{V_0}{V} \right)^{B'_0} - 1 \right]. \quad (7.2) $$

The bulk modulus is derived through the volume derivative of the Eq. 7.2,

$$ B = -V(\partial P/\partial V), $$

$$ B(V) = B_0 \left( \frac{V_0}{V} \right)^{B'_0}. \quad (7.3) $$

7.3.2 Birch-Murnaghan equation

The BM [87, 88] approach expands the Gibb's free energy in terms of Eulerian strain $\epsilon$, with $V_0/V = (1-2\epsilon)^{3/2}$. The integrated energy volume form of the third order BM-EOS becomes
7.3.3 Universal equation

\[
E(V) = -\frac{9}{10}\beta_0 \left[ (4 - B_0') \left( \frac{V_0}{V} \right)^{\frac{3}{2}} - \left( 14 - 3 B_0' \right) \left( \frac{V_0}{V} \right)^{\frac{5}{2}} \right] + (16 - 3 B_0') \left( \frac{V_0}{V} \right)^{\frac{5}{2}} + E_0.
\]

(7.4)

Using the obtained \( B_0, B_0' \) and \( V_0 \) from a least-square fit of the calculated \( V-E \) curves to Eq. 7.4, the hydrostatic pressure \( P \) is established from the \( P-V \) form of the BM-EOS, which is the volume derivative of the Eq. 7.4. The second order BM-EOS can be written as

\[
P(V) = 1.5 B_0 \left[ \left( \frac{V_0}{V} \right)^{\frac{5}{2}} - \left( \frac{V_0}{V} \right)^{\frac{3}{2}} \right].
\]

(7.5)

While the third order BM-EOS [89] has the analytical form;

\[
P(V) = 1.5 B_0 \left[ \left( \frac{V_0}{V} \right)^{\frac{5}{2}} - \frac{5}{3} \left( \frac{V_0}{V} \right)^{\frac{3}{2}} \right] \left\{ 1 + \frac{3}{4} (B_0' - 4) \left[ \left( \frac{V_0}{V} \right)^{\frac{5}{2}} - 1 \right] \right\}
\]

(7.6)

The bulk modulus corresponding to Eq. (7.6) is

\[
B(V) = 1.5 B_0 \left[ \frac{7}{3} \left( \frac{V_0}{V} \right)^{\frac{5}{2}} - \frac{5}{3} \left( \frac{V_0}{V} \right)^{\frac{3}{2}} \right] \left\{ 1 + \frac{3}{4} (B_0' - 4) \left[ \left( \frac{V_0}{V} \right)^{\frac{5}{2}} - 1 \right] \right\} + 1.5 B_0 \left[ \left( V_0^3 \right)^{\frac{5}{2}} - \left( V_0^3 \right)^{\frac{3}{2}} \right] \left[ \frac{1}{2} (B_0' - 4) \left( \frac{V_0}{V} \right)^{\frac{5}{2}} \right].
\]

(7.7)

### 7.3.3 Universal equation

Vinet et al. [90] have advanced a universal (U) form of the EOS for all classes of solids, such as ionic, metallic, covalent and van der Waals solid, under compression. The Vinet equation of state relies on the existence of a universal scaling of energy relation. The \( P-V \) form in U-EOS can be represented as [91]

\[
P(V) = \left[ 3B_0 \left( 1 - \frac{x}{x^2} \right) \right] exp[\eta(1 - x)]
\]

(7.8)

Here \( \eta \) is fixed in term of \( B_0' \)

\[
\eta = \frac{3}{2} (B_0' - 1)
\]

(7.9)

and \( x = (V/V_0)^{1/3} \). Poirier [92, 93] has pointed out that the universal EOS can be obtained by the same derivation as the BM-EOS, using a strain parameter \( \epsilon = (V_0/V)^{1/3} - 1 \) and the free energy \( F = F_0 (1 + \alpha \epsilon) \exp(-\alpha \epsilon) \). Where \( F_0 \) and \( \alpha \) are constants.

In the present study the U-EOS has been used to calculate the bulk modulus (which is inverse of the compressibility). Hard materials, like diamond, have bulk modulus around 400–500 GPa. Compared to that, the hydrides are very soft, with bulk moduli ranging between 10 and 60 GPa.
7.4 Comparison of different equation of states for NaH

The alkali-metal hydrides represent a series of partly ionic materials whose high-pressure behavior is expected to be parallel with that of the alkali-metal halides. Specifically, the NaCl-to-CsCl-type transition pressures, which is for the alkali-metal halides (except Li) range from 0.4 to 30 GPa, are expected to be within the present days range of the diamond-anvil-cell technology. In this section, we are going to compare the theoretical and experimental EOS for NaH in order to document the validity of our approach. At ambient condition NaH crystallizes in NaCl-type structure with the unit-cell parameter 4.89 Å (calculated 4.83). This NaCl-type phase transforms to CsCl-type at 29.3 ± 0.9 with volume ratio $V/V_0 = 0.61 \pm 0.01$ ($V$ and $V_0$ refer to high pressure volume and equilibrium volume, respectively) [94]. Similarly, the calculated transition pressure for the NaCl-to-CsCl-type phase is 28.8 GPa and the volume ratio $V/V_0 = 0.59$. This implies that, one can reliably reproduce the experimental findings by conducting such theoretical simulations. The calculated and experimentally derived [94, 95] EOS for NaH in the NaCl-type structure is shown in Fig. 7.2, which clearly indicates that the experimentally derived and theoretically simulated EOS agree very well. The above mentioned three EOS give rise to similar equilibrium volumes (28.38, 28.18, and 28.12 Å$^3$/f.u. for M-EOS, BM-EOS, and U-EOS, respectively), $B_0$ (23.5, 23.15, and 23.09 GPa M-EOS, BM-EOS, and U-EOS respectively) and $B_0'$ values (3.16, 3.8, and 4.1 for M-EOS, BM-EOS, and U-EOS respectively) are also very well fitted to experimental findings ($V = 17.83$ Å$^3$/f.u., $B_0 = 19.4$ GPa, $B_0' = 4.4$). [94, 95] However, the Vinet EOS shows the best agreement with the experimental data of Hochheimer et al. [95] and Duclos et al. [94]

![Figure 7.2: Comparison between experimental and theoretical EOS for NaCl-type NaH. Experimental data are taken from Ref. [95] (filled circle) and Ref. [94] (open square).](image-url)
7.5 The cohesive and formation energies

The cohesive energy is a measure of the force that binds atoms together in the solid state. If the cohesive energy for a given compound is negative it means that the constituent atoms will gain energy by reacting to form a compound (solid or a molecule). The cohesive energy of a system is defined as the sum of the total energy of the constituent atoms at infinite separation minus the total energy in the actually formed configuration. The cohesive energy of a material is a fundamental property which has long been a subject of theoretical and computational approaches. The chemical bonding is a mixture between covalent, ionic, and metallic bonding and therefore the cohesive energy cannot be determined reliably from simple models. Thus, first principles calculations based on DFT have become a useful tool to determine the cohesive energy of the solids. In the present project, cohesive energy of Th\(_2\)Al and Th\(_2\)AlH\(_4\) are calculated by using the expression,

\[ E_{cooh}^{A_2B} = [2E_{atom}^A + E_{atom}^B] - E_{total}, \]  

(7.10)

where \(E_{cooh}^{A_2B}\) refers to the total-energy of the compound at equilibrium lattice parameters and \(E_{atom}^A\) and \(E_{atom}^B\) are the atomic energies of the pure constituents calculated semi-relativistically. From cohesive-energy calculations we obtained \(E_{cooh} = 0.15\) and 0.19 eV/atom for Th\(_2\)Al and Th\(_2\)AlH\(_4\), respectively, indicating that hydrogenation enhances the bond strength in Th\(_2\)Al.

To determine the heat of formation, we first calculated the total energies of Th, Al, and H (molecular H\(_2\)/2) corresponding to their respective equilibrium lattice parameters. At zero temperature, there is no entropy contribution to the free energy, therefore the free energy of formation, or the heat of formation (\(\Delta H\)) can be obtained from the following relation for binary case

\[ \Delta H^{A_2B} = E_{total}^{A_2B} - [2E_{solid}^A + E_{solid}^B], \]  

(7.11)

where \(E_{total}^{A_2B}\) refers to the total energy of Th\(_2\)Al at equilibrium lattice constants and \(E_{solid}^A\) and \(E_{solid}^B\) are total energy of the pure elemental constituents. The calculated \(\Delta H\) for Th\(_2\)Al and Th\(_2\)AlH\(_4\) indicate that these are stable compounds (negative \(\Delta H\) value). Since \(\Delta H\) is more negative and \(E_{cooh}\) is higher for Th\(_2\)AlH\(_4\) than for Th\(_2\)Al, we conclude that Th\(_2\)AlH\(_4\) is more stable than Th\(_2\)Al. However, no experimental \(\Delta H\) values for Th\(_2\)Al and Th\(_2\)AlH\(_4\) are available. A similar type of approach was used to find whether a particular system is stable or not in publication XVII.

In publication V we introduce a little different approach to calculate the hydrogen formation energy for 95 ZrNiAl-type compounds. It would indeed have been a quite time-consuming process to perform calculations for such a huge number of systems from the above method. Hence, we used the following simple method to evaluate the hydrogen formation energy.

\[ \Delta E = \frac{1}{x}[E(RT M H_x) - E(RT M)] - \frac{1}{2}E(H_2), \]  

(7.12)

where \(x\) refers to the hydrogen content per formula unit (viz. 0.6667, 1.333 or 2.333 depending on the site(s) considered), \(T\) is a transition metal, \(M\) an el-

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7.5. THE COHESIVE AND FORMATION ENERGIES

Element in the periodic table, $E(\text{RT} M \text{H}_n)$ represents the energy of the hydride phase, $E(\text{RT} M)$ the energy of the intermetallic phase, and $E(\text{H}_2)$ the energy of the dihydrogen molecule ($-6.795 \text{ eV}$ [96]). From this, one can identify whether a particular chosen site for H in the ZrNiAl-type matrix is stable one or not.
CHAPTER 8

Site preference of hydrogen in metal, alloy, and intermetallic matrices

Physics is much too hard for physicists.
David Hilbert

The storage capacity of dissolved hydrogen in metal, alloy, and intermetallic matrices depend on where and how the hydrogen occupies the available interstitial sites. The number of interstices in a given structure generally exceeds the number of hydrogen atoms that can be incorporated. It is therefore important to understand the site preference of hydrogen atoms in metal, alloy and intermetallic frameworks if one wants to improve the hydrogen storage capacity. Several attempts have been made to find/explain the H position in such frameworks. According to Jacob et al. [97] and Giessen and Riesteres [3] the occupancy of the interstitial sites is determined by the heat of formation of the imaginary hydride (the embedded hydride cluster) formed between the host and the hydrogen atoms in the configuration under consideration. On the other hand, Westlake [98] and Magee et al. [99] have claimed that the size of the interstitial hole (minimum required hole radii 0.4 Å) and the hydrogen-hydrogen interatomic distance (minimum distance 2.1 Å; see also the following section) can be used to predict which site(s) the hydrogen may take. In general, the rigid ball model has been used to calculate the available free size at the given interstice, where the atoms surrounding the site are assumed to be hard spheres with fixed radii (say, tabulated ionic radii). In real case hard sphere assumption may not hold as atoms will not have spherically symmetric shape owing to, e.g., directional bonding, large polarizability, etc. There is no unique way to find the correct hole size in metal, alloy, and intermetallic materials. Therefore some additional method/model is needed to guide one to find the locations of the hydrogen atoms.

In order to advance further steps toward an improved understanding about factors which limit the hydrogen absorption capacity, we must gain insight into the factors that determine site preference. From the electronic structure (band structure, DOS, charge density and ELF) studies on intermetallics with hydrogen in different interstitial sites, one can gain such an insight. From the total energy
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Figure 8.1: Calculated ELF plot for (a) ZrNiAl, (b) ZrNiAlH\textsubscript{0.007}, (c) LaNiIn, (d) LaNiInH\textsubscript{1.333} in (001) plane. Arrows guide to the different crystallographic sites (2d, 4h, and 3g) under consideration. The iso-surface values corresponding to 0.6 ELF value.

calculation one can identify the likely hydrogen position. In a particular framework which contains two or more possible sites for location of hydrogen, we must perform total energy calculations for all alternatives. The solution with the lowest total energy will locate the actual H position in the framework under consideration. The electron localization function is another useful tool to spot hydrogen positions in a particular matrix. [73] Recently we have investigated hydrogen position in ZrNiAl-type structures, where H occupies different interstitial positions depending upon the chemical environment (see Fig. 8.1). For example, H occupies the 2d position in ZrNiAl (Fig. 8.1a) with the composition ZrNiAlH\textsubscript{0.007} whereas H occupies the 4h position in LaNiIn (Fig. 8.1b) with the composition LaNiInH\textsubscript{1.333}. We have correctly reproduced the experimental findings for these phases and also predicted hydrogen position in several other compounds of the ZrNiAl series. This type of theoretical exploration is sometimes very useful for experimentalists working with crystal structure determination (or to settle contradictions between different experiments).

In publication V we have reported on attempts to identify the H position in some 100 actual or hypothetical ZrNiAl type phases and we have advanced a site-preference rule which states that, wherever charge (viz. surplus or freed valence electrons) localizes in a matrix, these excess charge regions represent potential locations for hydrogen atoms (for more information see publication V).

8.1 \textbf{H—H separation in metal hydrides}

One of the challenging tasks in the research on hydrogen storage materials is to pack hydrogen atoms or molecules as closely as possible. Structural studies of intermetallic hydrides have provided empirical rules that can be used to predict features of the hydrogen sublattice in a given matrix. [100, 14] The distances between hydrogen atoms occupying interstices in a metal, alloy or intermetallic phases are affected by the H-to-H repulsion and as a result of this the hydrogen atoms cannot actually come closer than certain value which has been stipulated by 2.0 Å. [14] This regularity is true for a majority of precisely determined structures of hydrides. This experience has been formulated into “2-Å rule” which
many believe has general validity.

It is known that molecular hydrogen can be bonded to metal complexes and it has been speculated that (molecular-like) hydrogen pairs may occur in metal hydride systems and give rise to H–H distances considerably shorter than 2.0 Å. [101] Two H atoms in a metal hydride would also come very close together if (strongly destabilized) H–H antibonding states are shifted above the Fermi level and leave behind their electrons to bonding or nonbonding (metallic) levels. The resulting structure with H₂ “dimers” located inside a metallic matrix might appear highly unusual, but Halet [101] points out that H₂ could act as a simple two-electron ligand.

The extensive review by Yvon and Fischer [16] points out only K₂ReH₆ and Th₂AlH₄ violate the “2-Å rule”, where Th₂AlH₄ is a metallic and K₂ReH₆ is a non-metallic complex hydride. Recent experimental[17] and theoretical results for Th₂AlH₄ agree on a closest H–H separation of around 1.95 Å, but the ultimate conclusion is that H–H pairing does not occur in Th₂AlH₄. Hydrides based on the RNiIn (R = La, Ce, Nd) [102] series violate this empirical “2-Å rule” with the H–H separation of some 1.6 Å. The present theoretical calculations suggest that the short H–H separation may be reduced further by choosing proper element combinations (publication II, III, and IV).
CHAPTER 9

Publications included in the thesis

Work, finish, publish
knowledge at our disposal.
Michael Faraday

9.1 List of Publications

I. Electronic structure, phase stability and chemical bonding in Th$_2$Al and Th$_2$AlH$_4$
   P. Vajeeston, R. Vidy, P. Ravindran, H. Fjellvåg, A. Kjekshus, and A. Skjeltorp

II. Violation of the minimum H-H separation “Rule” for Metal Hydrides
    P. Ravindran P. Vajeeston, R. Vidy, A. Kjekshus, and H. Fjellvåg

III. Short hydrogen-hydrogen separation in $R$NiInH$_{1.33}$ ($R$=La, Ce, Nd)
     P. Vajeeston, P. Ravindran, R. Vidy, A. Kjekshus, H. Fjellvåg, and V.A. Yartys

IV. Search for metal hydrides with short hydrogen-hydrogen separation:
    Ab initio calculations
    P. Vajeeston, P. Ravindran, H. Fjellvåg, and A. Kjekshus

V. Indicator for site preference of hydrogen in metal, alloy, and intermetallic frameworks
   P. Vajeeston, P. Ravindran, R. Vidy, H. Fjellvåg, and A. Kjekshus
VI. Pressure-induced structural transitions in MgH\textsubscript{2}
   P. Vajeeston, P. Ravindran, A. Kjekshus, and H. Fjellvåg

VII. Structural stability of BeH\textsubscript{2} at high pressures
   P. Vajeeston, P. Ravindran, A. Kjekshus, and H. Fjellvåg

VIII. Huge-pressure-induced volume collapse in LiAlH\textsubscript{4} and its implications to hydrogen storage
   P. Vajeeston, P. Ravindran, R. Vidya, H. Fjellvåg, and A. Kjekshus

IX. Pressure-induced phase of NaAlH\textsubscript{4} : A potential candidate for hydrogen storage?
   P. Vajeeston, P. Ravindran, R. Vidya, H. Fjellvåg, and A. Kjekshus

X. Crystal structure of KAlH\textsubscript{4} from first principle calculation
   P. Vajeeston, P. Ravindran, A. Kjekshus, and H. Fjellvåg

XI. Design of potential hydrogen-storage material using first-principle density-functional calculations
   P. Vajeeston, P. Ravindran, R. Vidya, H. Fjellvåg, and A. Kjekshus

XII. Structural stability of alkali boron tetrahydrides ABH\textsubscript{4} (A = Li, Na, K, Rb, Cs) from first principle calculation
   P. Vajeeston, P. Ravindran, A. Kjekshus, and H. Fjellvåg

XIII. Chemical-bonding and high-pressure studies on hydrogen-storage materials
   P. Ravindran, P. Vajeeston, A. Kjekshus, and H. Fjellvåg

XIV. A new high-pressure phases of lithium and sodium aluminum tetrahydrides and their implication to hydrogen storage
   P. Vajeeston, P. Ravindran, H. Fjellvåg, and A. Kjekshus
   15\textsuperscript{th} WHEC A1386, (2004).

XV. Structural stability and electronic structure for Li\textsubscript{3}AlH\textsubscript{6}
   P. Vajeeston, P. Ravindran, A. Kjekshus, and H. Fjellvåg

XVI. Reply to “Comment on structural stability and electronic structure for Li\textsubscript{3}AlH\textsubscript{6}"
   P. Vajeeston, P. Ravindran, A. Kjekshus, and H. Fjellvåg
XVII. First principles investigations of complex $M_3\text{AlH}_6$ ($M = \text{Na, K}$) hydrides
P. Vajeeston, P. Ravindran, H. Fjellvåg, and A. Kjekshus

XVIII. Theoretical modeling of hydrogen storage materials: prediction of structure, chemical bond character and high pressure behaviour
P. Vajeeston, P. Ravindran, H. Fjellvåg, and A. Kjekshus
CHAPTER 10

Scientific highlights of the present project

_Now this is not the end._
_It is not even the beginning of the end._
_But it is, perhaps, the end of the beginning._

_Sir Winston Churchill (1942)._

MATERIALS have different types of bonding interactions and therefore some computational approximations are better suited for theoretical simulations than others for a given system of interest. Hydrogen is a very small element which comprises only one electron and a proton and these features makes challenges for theoreticians to handle systems of hydrogen in combination with heavy elements. The present project has therefore chosen different advanced density-functional tools like TB-LMTO, FP-LMTO, WIEN2K, VASP-PAW, and CRYSTAL03 to explore the properties of hydrides. The actual tools to be used depend upon the problem.

10.1 Our contributions to new knowledge about the "Hydride family"

The present project has mainly focused on two classes of hydrogen storage materials. One comprises metal hydrides where the hydrogen can be removed easily below 100°C, such hydrides have a relatively low weight percentage of stored hydrogen (1.5 to 2.5 wt.%). The other class deals with so-called complex hydrides where one can store more hydrogen (up to 18.2 wt.% in BeH₂), but here the problem is high operating temperatures and slow absorption/desorption kinetics.

10.1.1 Aims of the present study

- The main motivation has been to identify potential candidates for hydrogen storage purpose with high hydrogen content and low decomposition
temperature.

- To identify materials that pack the H atoms efficiently in metal matrices, in-
ter alia trying to find metal hydrides with very short H–H separation and
identify the reasons for the presence of such short H–H separation.

- To design potential hydrogen storage materials and try to understand the
stability of these materials from theoretical simulations which helps the ex-
perimentalists to develop synthesis routes to prepare such materials in real.

During the project 18 research articles have been published in well reputed
etc. In this chapter we now try to summarize the important findings/conclusions
arrived from the theoretical simulations.

### 10.1.2 Metal Hydrides

- Two different experimental studies gave different H–H separations in Th$_2$AlH$_4$.
In order to shed light on the discrepancy, an electronic structure study has
been made for this compound which shows that the H–H separation is
1.95 Å, viz. consistent with the findings by high-resolution PND experi-
ments. When the Th$_2$Al matrix is hydrogenated, the volume expansion
is highly anisotropic; which is quite opposite to the findings for other hy-
drides with the same crystal structure. The probable reasons for the anisotropic
volume expansion have been established with the help of charge density
distribution, density of state, and crystal orbital Hamiltonian population
analyzes (Publication I).

- A recent experimental study on $R$NiInH$_{1.33}$ ($R$ = La, Ce, Nd) has shown
that this series of compounds violate the 2 Å rule (H–H separation 1.64–1.56 Å).
Systematic studies of the electronic structure and chemical bonding in these
compounds explain the reason for this unusual behavior. From this type
of theoretical simulation we not only reproduced the experimental results
but also gained some understanding of the possible mechanism behind the
short H–H separations and from this insight other materials are in turn
explored (Publication II).

- From systematic examination of series of compounds we conclude that by
proper choice of alloying element one may be able to reduce the H–H sep-
aration even below 1.56 Å mentioned above. Moreover, we have predicted
several such types of compounds and in some of these phases H–H sepa-
rations around 1.45 Å have been established (Publication II–IV).

- Identification of H position(s) in metal matrixes is a challenging task. For
example, even though the crystal structure can be the same for two com-
ounds, different chemical environments can make H to occupy different
atomic positions. From theoretical simulations of the electron localization function we have demonstrated why H occupies different interstitial sites in ZrNiAl-type metal matrices with different chemical ingredients. More than 300 compounds are formed in the ZrNiAl-type structure and for a selection of 95 potential candidates we systematically examined the site preference of H atoms in different chemical environment. From this study we have correctly located the H positions for compounds where such data are known from experiment. For the other compounds we have predicted H positions. From this type of theoretical simulation we found that one can pack the H more closely (H−H separation below 1.4 Å) in some of these compounds (e.g., ThCoAl, ThNiIn, etc.) than in the RNiInH\textsubscript{1.33} series (Publication V). From the systematic study on this series of compounds we propose a “site-preference rule” which says, Accumulation of electronic charge in a certain interstitial region of a given structural framework gives prominence to that site as a likely location for hydrogen occupation.

10.1.3 Complex Hydrides

- The stability of MgH\textsubscript{2} has for the first time been theoretically investigated up to 20 GPa. Within the explored pressure range we have established four high-pressure forms of MgH\textsubscript{2} and these phases are very sensitive to external pressure and temperature. This is the first report on hydrides showing several pressure induced structural transitions within a limited pressure range. The calculated structural data for α- and γ-MgH\textsubscript{2} are in very good agreement with the experimental findings. The total-energy study suggests that some (if not all) of these high-pressure phases can be prepared by appropriate synthesis methods. This could increase the volume storage capacity by ca. 19.5% compared with α-MgH\textsubscript{2}. In agreement with experiments, the calculations show that α-MgH\textsubscript{2} is an insulator, and we found that all high-pressure modifications also should exhibit insulating behavior. (Publication VI)

- In order to verify the theoretical predictions we have conducted a high-pressure experimental study on MgH\textsubscript{2}. The experiment confirms the theoretical predictions and several pressure induced structural transitions were identified. The bonding nature is systematically studied and the results are compared with experimental findings for the ground-state structure.[103] According to charge density and charge transfer plots MgH\textsubscript{2} is not to be regarded as purely ionic, but rather as a mixture with appreciable covalent character.

- The structural stability of BeH\textsubscript{2} has been investigated and we have identified several pressure induced structural transition for this material. At the first transition point the estimated volume discontinuity is 19% between the involved structures. Density of states studies revealed that BeH\textsubscript{2} remains an insulator up to 100 GPa. Hence the possibility of obtaining high-pressure phases with superconducting properties is ruled out. However, we found
anomalous changes of variation in band-gap with increasing pressure (Publication VII).

- Electronic structure and structural stability of LiAlH$_4$ and NaAlH$_4$ have been investigated (Publications VIII and IX). On application of pressure, the $\alpha$-LiAlH$_4$ phase is transformed into the $\beta$ and $\gamma$ modification at 2.6 and 33.8 GPa, respectively. At the $\alpha$-to-$\beta$ transition point we observe a 17% volume collapse and this abnormal behavior is associated with an electronic transition between Al-$s$ to $-p$ states. The high weight percent of hydrogen; around 22% smaller equilibrium volume, and the drastically different bonding behavior of $\beta$-LiAlH$_4$ than $\alpha$ phase indicate that the $\beta$ modification may be considered as a potential hydrogen storage material. On the other hand, in NaAlH$_4$ we observed only one pressure induced phase transition at 6.43 GPa. (Publication IX). Ongoing experiments confirm the presence of such a pressure-induced structural transition in LiAlH$_4$, but owing to insufficient resolution in the high-pressure data the structural characterization has not yet been made.

- The ground state crystal structure of KAlH$_4$ has been predicted (Publication X) and subsequent experiments have confirmed the prediction. [78] In this case DFT is proved to be a powerful tool to predict an unknown crystal structure.

- We have predicted the equilibrium crystal structures for the entire $AMH_4$ ($A = $ Li, Na, K, Rb, Cs; $M = $ B, Al, Ga) series (Publications VIII-XII) for which most of the involved crystal structures are not yet established experimentally.

- From a systematic study on the $AMH_4$ compounds, we found that the $B-H$ bond strength is reduced when we move from the top to the bottom of the alkali metals in The periodic table. This suggests that substitution of Li by other alkali elements in LiAlH$_4$ may reduce the decomposition temperature (i.e., Li$_{1-x}$Na$_x$AlH$_4$, Li$_{1-x}$K$_x$AlH$_4$ etc.) and provide materials [say (Li, Na, K)AlH$_4$] with considerable hydrogen absorption/desorption at a desirable temperature (Publication XI).

- From the theoretical high-pressure study on $ABH_4$ ($A = $ Li, Na, K, Rb, Cs; $B = $ B, Al, Ga), we found that most of these compounds are not stable at high pressures and we predict several pressure-induced structural transitions.

- From the systematic study on the $AH_2$ and $AAH_4$ ($A = $ Li, Na, K, Rb, Cs) compounds we found that for the smallest $A^+$ cation one can expect several consecutive pressure-induced structural transitions with huge volume collapses at the first phase transition point (Publication XV).

- The structural stability and chemical bonding in Li$_3$AlH$_6$ have been explored. From charge density, charge transfer, electron localization function, crystal orbital Hamilton, and Mulliken population analyzes, we found that the interaction between Li and [AlH$_6$] is purely ionic, whereas the bonding within the [AlH$_6$] unit is partially ionic and partially covalent. Owing
to the close similarities in charge-density distribution and DOS one can expect a similar type of mixed bonding in the whole complex hydride family (Publication XVI-XVIII).

- The structural stability of $\text{Na}_3\text{AlH}_6$ and $\text{K}_3\text{AlH}_6$ has been systematically investigated. The experimentally known crystal structure of $\text{Na}_3\text{AlH}_6$ is reproduced and the structure of $\text{K}_3\text{AlH}_6$ has been predicted. At ambient conditions, $\alpha$-$\text{Na}_3\text{AlH}_6$ and $\alpha$-$\text{K}_3\text{AlH}_6$ stabilize with the same structure type ($\alpha$-$\text{Na}_3\text{AlF}_6$ type). We have predicted that the $\alpha$ modifications of these compounds will not be stable at higher pressures. On application of pressure to $\text{Na}_3\text{AlH}_6$, the $\alpha$ phase transforms into a $\beta$ modification with $\text{Cs}_3\text{NdCl}_6$-type structure at 19.1 GPa. Similarly, $\alpha$-$\text{K}_3\text{AlH}_6$ transforms into two high-pressure forms: (1) $\alpha$ transforms into $\beta$ with $\text{Rb}_3\text{TIF}_6$-type structure at 53.4 GPa and (2) $\beta$ transforms to $\gamma$ with $\text{U}_3\text{ScS}_6$-type structure at 60.2 GPa (Publication XVII).

- Our detailed theoretical studies on several series of hydrides with various computational tools showed that several theoretical methods are needed in order to characterize the chemical bonding correctly, otherwise one will end up with wrong conclusions (Publication II and XVIII).
CHAPTER 10. SCIENTIFIC HIGHLIGHTS OF THE PRESENT PROJECT


[40] Inc. www.qtww.com, webpage of Quantum Technologies.


