Understanding Physical Reality via Virtual Experiments

SERGIU ARAPAN
Dissertation presented at Uppsala University to be publicly examined in Häggsalen, Ångströmlaboratoriet, Lägerhyddsvägen 1, Uppsala, Friday, October 31, 2008 at 10:15 for the degree of Doctor of Philosophy. The examination will be conducted in English.

Abstract

In this thesis I have studied some problems of condensed matter at high pressures and temperatures by means of numerical simulations based on Density Functional Theory (DFT).

The stability of MgCO$_3$ and CaCO$_3$ carbonates at the Earth's mantle conditions may play an important role in the global carbon cycle through the subduction of the oceanic crust. By performing ab initio electronic structure calculations, we observed a new high-pressure phase transition within the Pmnc structure of CaCO$_3$. This transformation is characterized by the change of the sp-hybridization state of carbon atom and indicates a change to a new crystal-chemical regime. By performing ab initio Molecular Dynamics simulations we show the new phase to be stable at 250 GPa and 1000K. Thus, the formation of sp$^3$ hybridized bonds in carbonates can explain the stability of MaCO$_3$ and CaCO$_3$ at pressures corresponding to the Earth's lower mantle conditions. We have also calculated phase transition sequence in CaCO$_3$, SrCO$_3$, and BaCO$_3$, and have found that, despite the fact that these carbonates are isostructural and undergo the same type of aragonite to post-aragonite transition, their phase transformation sequences are different at high pressures.

The continuous improvement of the high-pressure technique led to the discovery of new composite structures at high pressures and complex phases of many elements in the periodic table have been determined as composite host-guest incommensurate structures. We propose a procedure to accurately describe the structural parameters of an incommensurate phase using ab initio methods by approximating it with a set of analogous incommensurate supercells and exploiting the fact that the total energy of the system is a function of structural parameters. By applying this method to the Sc-II phase, we have determined the incommensurate ratio, lattice parameters and Wyckoff positions of Sc-II in excellent agreement with the available experimental data. Moreover, we predict the occurrence of an incommensurate high-pressure phase in Ca from first-principle calculations within this approach.

The implementation of DFT in modern electronic structure calculation methods proved to be very successful in predicting the physical properties of a solid at low temperature. One can rigorously describe the thermodynamics of a crystal via the collective excitation of the ionic lattice, and the ab initio calculations give an accurate phonon spectra in the quasi-harmonic approximation. Recently an elegant method to calculate phonon spectra at finite temperature in a self-consistent way by using first principles methods has been developed. Within the framework of self-consistent ab initio lattice dynamics approach (SCAILD) it is possible to reproduce the observed stable phonon spectra of high-temperature bcc phase of Ti, Zr and Hf with a good accuracy. We show that this method gives also a good description of the thermodynamics of hcp and bcc phases of Ti, Zr and Hf at high temperatures, and we provide a procedure for the correct estimation of the hcp to bcc phase transition temperature.

Keywords: density functional theory, ab initio calculations, electronic structure, lattice dynamics, high-pressure phase transitions, high-temperature phase transitions, incommensurate structures

Sergiu Arapan, Department of Physics and Materials Science, Ångströmlaboratoriet, Lägerhyddsv. 1, Box 530, Uppsala University, SE-75121 Uppsala, Sweden

© Sergiu Arapan 2008

ISSN 1651-6214
ISBN 978-91-554-7305-1
urn:nbn:se:uu:diva-9314 (http://urn.kb.se/resolve?urn=urn:nbn:se:uu:diva-9314)
to my Teachers
List of Papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals.

I Formation of \(sp^3\) hybridized bonds and stability of CaCO\(_3\) at very high pressure

II High-pressure phase transformations in carbonates
Sergiu Arapan and Rajeev Ahuja, in Manuscript.

III Determination of the structural parameters of an incommensurate phase from first principles: the case of Sc-II

IV Predicted incommensurate crystal structure of Ca at high pressure: An \textit{ab initio} investigation

V Estimation of hcp to bcc transition temperature in Ti, Zr, and Hf from \textit{ab initio} finite-temperature lattice dynamics
Sergiu Arapan, Rajeev Ahuja, Petros Souvatzis, M. I. Katsnelson, and Olle Eriksson, in Manuscript.

Reprints were made with permission from the publishers.

The following papers, accomplished during my PhD studies, are not included in the thesis.

I Conductance of a disordered double quantum wire in a magnetic field: Boundary roughness scattering

II Effect of the boundary roughness on the conductance of double quantum wire in a magnetic field

III Exciton levels and optical absorption in coupled double quantum well structures

**IV Electronic structure of Cu3N films studied by soft x-ray spectroscopy**

Contents

1 Introduction .......................................................... 11
2 Many-body problem .................................................. 17
  2.1 Born-Oppenheimer approximation .......................... 18
  2.2 Electron correlation .......................................... 19
  2.3 Density Functional Theory .................................... 21
  2.4 Kohn-Sham equations .......................................... 23
  2.5 Local Density Approximation ................................ 26
3 Virtual laboratory ..................................................... 29
  3.1 Pseudopotentials ................................................ 31
  3.2 Projector Augmented Waves ................................... 33
  3.3 Hellman-Feynman forces ....................................... 36
4 Pressure induced phase transitions in carbonates ............... 39
  4.1 Crystal structure and equation of state .................... 40
  4.2 Stability of carbonates at high pressure ................... 43
5 Complex composite structures at high pressures ................ 49
  5.1 Incommensurate composite structures ....................... 50
  5.2 Structural parameters of Sc-II phase ....................... 52
6 Structural phase transformations at high temperatures .......... 55
  6.1 Lattice dynamics in the quasi-harmonic approximation .... 55
    6.1.1 Lattice vibrations: classical equations of motion .... 56
    6.1.2 Lattice vibrations: quantum mechanics ................. 58
  6.2 Thermodynamics of the harmonic crystal .................. 59
  6.3 Calculating phonons: the small displacement method ...... 61
  6.4 Calculating phonons at $T \neq 0$: the SCAILD method ...... 64
Bibliography ............................................................. 71
Nobody likes to read a thesis that makes him feel unintelligent.

An "old" Greek saying by Panos
1. Introduction

In the last few decades computer simulations have become a powerful tool in exploring the physical reality and help us expand our understanding of the world [1, 2]. Our image of the real world is based on approximations and is limited by our ability to describe any possible situation or process. Although our knowledge is not complete in that sense, one can, in principle, create a true picture of the physical reality from the knowledge of the laws governing the processes of the real world. These are the laws of physics. Starting from the knowledge of the laws of modern physics one can build theoretical models for an approximate description of the world and be able to give an interpretation of various processes we observe experimentally.

There is also the possibility that some processes go beyond the well-established area of knowledge within a given theoretical model and in these cases experimental observations help us choose the right scenario. On the other hand, the observation of new phenomena enables us to construct a more rigorous theoretical model. As long as this process is self-consistent, the actual laws of physics serve as the fundamentals that give us the true image of the physical reality.

However, the way of acquiring knowledge and approaching the true image of reality as described above has an inherent limitation. A theoretical model can't go beyond a certain degree of analytical complexity, and there are certain constrains on the domain of physical processes and phenomena accessible by experiment. At this point the numerical simulations come into play. The developments in computer technology make it possible to study the physical reality by computer simulations starting from the fundamentals. Thus a virtual reality obeying the laws of the real world gives us the true image of the physical reality, and by performing numerical simulations we explore the real phenomena and processes in a similar way as in a real experiment. That's why one might call performing computer simulations a virtual experiment.

It might seem that we are now able to visualize the image of the real world in all its details, but there are a few basic difficulties that prevent us from doing it. First of all, the power to simulate any possible situation or process is limited by computer technology and furthermore, our ability to understand the physical reality is constrained by the image of the world we perceive through our physical senses.

In this thesis I have studied aspects of a part of the physical reality called condensed matter. Condensed matter refers to systems of interacting atoms, which consist of nuclei and electrons. These systems obey the laws
of quantum mechanics. Within the framework of quantum mechanics we have a complete image of a system that consists of one nucleus interacting with one electron, the hydrogen atom. We call this aspect of the real world one-electron problem. The object of condensed matter is to investigate more complex systems, which represent another aspect of reality called a many-body problem. Although we can numerically simulate this object, our image of this part of the physical reality will be approximate, because we are able to understand this complex object only in terms of the one-electron picture. It turns out that it is possible to some extent to simulate a real object by a less complex fictitious one, which will accurately mimic the real physical processes and will give us the most representative image of the real world.

This thesis is organized as follows. Chapter 2 presents the model which allows us to simulate the real physical system and to what extent this model describes reality. This model is called the Density Functional Theory and it describes complex systems and phenomena through the intuitive notions and quantities of the surrounding world. It also makes the numerical simulation feasible by using modern computers. Chapter 3 describes a practical implementation of the Density Functional Theory on a computer. These two chapters serve as a general introduction to the methods and tools I have been using in the present study. Then I will address several specific problems related with some different aspects of the physical reality and show how we can get a deeper understanding of the world by performing computer experiments.

Chapter 4 introduces us to the high-pressure phase transformations of carbonates. The question of stability of carbonates is closely related with the processes of carbon recycling in the biosphere. MgCO₃ and CaCO₃ carbonates are the dominant carbon bearing compounds within the Earth's mantle and carbon is removed from the atmosphere by the subduction of carbonates. Therefore, it is important to know whether carbon can be stored as some stable carbonate compound at high pressure deep into the Earth's mantle. Computer modeling helps us to study matter at pressures hard to attain in real experiments and to enhance our understanding of the mechanism behind the phase transformation at such extreme conditions.

Chapter 5 focuses on another interesting high-pressure phenomenon related to the formation of complex non-periodic structures in simple elements. Advances in the high-pressure technique led to the discovery of a series of new phases for elements in the periodic table. A series of complex solid structures at high pressure has been identified and determined as incommensurate structures. Their elemental composition includes elements from the alkali and earth-alkaline metals as well as elements of group VA and VIA of the periodic table. These new phases lack periodicity in one or more dimensions, but can be described as periodic structures in an abstract mathematical space with dimensionality higher than 3. They can also be described as a host-guest structure made of two interpenetrating periodic lattices with an incommensurate ratio of the lattice parameters along some
directions in real space. In this chapter I will present a method to accurately describe such structures and make an attempt to predict similar phases in other elements.

Chapter 6 presents some aspects of how matter behaves at high temperatures. In the beginning we find an introduction to the problem of lattice dynamics and how it can be described with phonon theory. This is followed by arguments on how phonons can be used to describe high-temperature phenomena and how we can correctly calculate thermodynamic quantities. This approach is later used to study the high-temperature transition from the hcp to bcc crystal structures in Ti, Zr and Hf.
Svensk Introduction


Det är även möjligt att några processer sker bortom väletablerade kunskapsområden inom ett givet teoretisk modell och i dessa fall hjälper experimentella observationer oss att välja rätt scenario. Å andra sidan, observationer av nya fenomen ger oss möjlighet att skapa mer rigorösa teoretiska modeller. Så länge denna process är självkonsistent så tjänar de gällande fysiska lagar som fundamenten som ger oss den sanna avbilden av den fysiska verkligheten.


Det kan verka som att vi nu har möjlighet att visualisera avbilden av den verkliga världen i alla dess detaljer, men det finns ett fåtal grundläggande svårigheter som hindrar oss från att göra det. Först och främst är förmågan att simulera ett godtyckligt förhållande eller process begränsad av dator- teknologi, dessutom är vår möjlighet att förstå den fysiska verkligheten begränsad av den bild av verkligheten vi förnimmar genom våra fysiska sin- nen.

I den här avhandlingen har jag studerat aspekter av en del av den fysiska verkligheten kallad kondenserad materia. Kondenserad materia syftar till system av växelverkande atomer, som består av kärnor och elektroner. Dessa system lyder under kvantmekanikens lagar. Inom den teoretiska ramen för kvantmekanik har vi en komplett avbild för system som består av
en kärna som växelvekar med en elektron, väteatomen. Vi kallar denna aspekt av den verkliga världen för *enelektontproblem*. Målet för kondenserad materia är utforska mer komplexa system, som representerar en annan aspekt av verkligheten kallad för *mångkropparsproblem*. Även om vi numerisk kan simulera denna objekt, förblir vår avbild av den delen av den fysiska realiteten att vara approximativ, eftersom vi har möjlighet att förstå detta komplexa objekt endast i termer av enelektron bilden. Det visar sig möjligt att till viss del simulera en verklig objekt genom en mindre komplext fiktiv objekt, som noggrant efterliknar de verkliga fysiska processer och ger oss den mest representativa avbilden av den verkliga världen.
2. Many-body problem

The many-body problem is the study of the way that the interaction between particles in a dense system alters the behavior of the isolated noninteracting particles.

David Pines

In modern physics the state of any physical system is described by a mathematical object $\Psi$ called wave function defined in the configurational space of all the independent variables that describe the system [3]. If we consider, for example, a free electron in space, then its wave function $\psi(r, \sigma)$ is a function of electron position and spin. The wave function is not an observable quantity. Instead, the expression $|\psi(r, \sigma)|dr$ gives the probability of finding the electron with spin $\sigma$ in an elementary volume $dr$ in real space. The evolution of the wave function in time is given by the Schrödinger equation

$$-i\hbar \frac{\partial \Psi}{\partial t} = H\Psi, \quad (2.1)$$

where $H$ is another mathematical object called Hamiltonian, which is used to describe interactions in physical systems. For a system consisting of interacting nuclei and electrons, a good description is provided by the non-relativistic Hamiltonian, which describes only the Coulomb interaction between charged particles

$$H = -\frac{\hbar^2}{2m} \sum_i \nabla^2 r_i - \frac{\hbar^2}{2} \sum_I \frac{1}{M_I} \nabla^2 R_I + V(\vec{r}, \vec{R}), \quad (2.2)$$

where $\vec{r} = (r_1, r_2, r_3, \ldots)$ and $\vec{R} = (R_1, R_2, R_3, \ldots)$ are the positions of the electrons and nuclei, respectively.

The first two terms in (2.2) describe the kinetic energy of electrons and nuclei, respectively, and

$$V(\vec{r}, \vec{R}) = \sum_{i<j} \frac{e^2}{|r_i - r_j|} + \sum_{I<J} \frac{Z_I Z_J e^2}{|R_I - R_J|} - \sum_{i,I} \frac{Z_I e^2}{|r_i - R_I|} \quad (2.3)$$

describes the Coulomb interaction between nuclei and electrons. Among the solutions of (2.1) we are mainly interested in the stationary states, in which some observable quantities of the physical system such as the total
energy, for example, have well defined and constant values. Such solutions are provided by a time independent Hamiltonian like (2.2) and the problem is reduced, consequently, to a time independent Schrödinger equation

$$H\Psi = E\Psi.$$  \hfill (2.4)

### 2.1 Born-Oppenheimer approximation

Solving the above equation (2.4) for a large number of interacting particles is an impractical task. The aim of the physical theory is to provide us with well founded approximations, which are both solvable and accurate. For our system we make use of the fact that the mass of a nucleus $M_j$ is much larger than the mass of an electron $m$ and as a result, the motion of the nuclei is much slower than that of electrons. Thus, we can consider the positions of the nuclei as fixed and account only for the electron degrees of freedom. This is known as the Born-Oppenheimer approximation and the wave function of electrons moving in the external field of fixed nuclei is described by the following equation

$$\left(-\frac{\hbar^2}{2m} \sum_i \nabla_{r_i}^2 + V_{ee} + V_{ext}(R)\right)\Psi_R(R) = E(R)\Psi_R(R).$$  \hfill (2.5)

where the nuclei positions are parameters, that both the energy and wave functions of electrons depend on, $V_{ee}$ is the Coulomb interaction between electrons and $V_{ext}$ is the Coulomb interaction between electrons and fixed nuclei. In principle, we can now solve (2.5) with the desired accuracy, by using methods such as Quantum Monte-Carlo or Configuration Interaction. However, in practice, only systems with few interacting constituent particles, such as small molecules and clusters, can be treated with these methods. There is also major difficulty in understanding all the information provided by the wave function, since it refers to an abstract mathematical world. We perceive only its projection onto our approximate image of the physical reality.

To express this in mathematical terms, we calculate the expectation value of the energy $E$ of the many-body system described by (2.5) for an arbitrary state $\Psi(R)$

$$E = \langle \Psi | H | \Psi \rangle = \sum_i \int \left( \prod_i dr_i \right) \Psi^* (R) \left(-\frac{\hbar^2}{2m} \sum_i \nabla_{r_i}^2 + \frac{1}{2} \sum_{j\neq i} \frac{e^2}{|r_i - r_j|} - \sum_I \frac{Z_I e^2}{|r_i - R_I|}\right) \Psi (R).$$  \hfill (2.6)

Since the electrons are indistinguishable particles we can perform the summation in (2.6) and write the above expression in terms of distribution func-


\[ E = E[\rho(\mathbf{r}), \rho_{12}(\mathbf{r}, \mathbf{r}')] = \]
\[ = -\frac{\hbar^2}{2m} \int d\mathbf{r} [\nabla^2 \rho_{12}(\mathbf{r}, \mathbf{r}')]_{r'=r} + \frac{e^2}{2} \int d\mathbf{r} \rho_{12}(\mathbf{r}, \mathbf{r}') \frac{1}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r}' + \int d\mathbf{r} \rho(\mathbf{r}) U(\mathbf{r}). \]

Thus, the energy of the many-electron system is a functional of one-electron density \( \rho(\mathbf{r}) \)
\[ \rho(\mathbf{r}) = N \int \left( \prod_{i=2}^{N} d\mathbf{r}_i \right) |\Psi(\mathbf{r}, \ldots, \mathbf{r}_i, \ldots, \mathbf{r}_N)|^2, \quad (2.8) \]

and two-particle density \( \rho_{12}(\mathbf{r}, \mathbf{r}') \)
\[ \rho_{12}(\mathbf{r}, \mathbf{r}') = N(N-1) \int \left( \prod_{i=3}^{N} d\mathbf{r}_i \right) |\Psi(\mathbf{r}, \mathbf{r}', \ldots, \mathbf{r}_i, \ldots, \mathbf{r}_N)|^2. \quad (2.9) \]

### 2.2 Electron correlation

The two-particle density (2.9) accounts for interactions between electrons and makes the exact solution of (2.5) unattainable. We can rewrite the Hamiltonian of (2.5) in the following form
\[ H = \sum_i H_i + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}, \quad (2.10) \]

where
\[ H_i = -\frac{\hbar^2}{2m} \nabla^2_i + V(\mathbf{r}_i) \quad (2.11) \]

is the Hamiltonian of a single electron interacting with all nuclei. If there was no interaction between electrons, we would be back to a single-electron problem
\[ H = \sum_i H_i, \quad H_i \psi_i = E_i \psi_i, \]
\[ E = \sum_i E_i, \quad \Psi(\mathbf{r}) = \prod_i \psi_i(\mathbf{r}_i), \]

and the two-particle density would be a product of one-electron densities
\[ \rho_{12}(\mathbf{r}, \mathbf{r}') = \rho(\mathbf{r}) \rho(\mathbf{r}'). \quad (2.12) \]

Since the repulsion between electrons becomes very strong when two electrons approach each other, we can not neglect the interaction between electrons. It is possible, however, to account for electron electrostatic repulsion and describe the system within the one-electron picture (2.12). The idea is to replace the electron-electron interaction with an one-electron effective
potential, which describes the interaction between one given electron and the average field due to the rest of the electrons

\[ H \Rightarrow \sum_i \left( H_i + V_{\text{eff}}(r_i) \right) = \sum_i H_i. \quad (2.13) \]

This idea led to the Hartree approximation and the energy of a many-body system becomes a functional of the one-electron density only

\[ E_H[\rho(r)] = -\frac{\hbar^2}{2m} \int d\mathbf{r} \left[ \nabla^2 \rho_{12}(\mathbf{r}, \mathbf{r}') \right]_{\mathbf{r}'=\mathbf{r}} + \frac{e^2}{2} \int d\mathbf{r} \rho(\mathbf{r}) \rho(\mathbf{r}') \frac{d\mathbf{r}'}{|\mathbf{r}'-\mathbf{r}|} + \int d\mathbf{r} \rho(\mathbf{r}) U(\mathbf{r}). \quad (2.14) \]

As mentioned in the beginning, an individual electron is also described by a spin and as fermions they obey the Pauli exclusion principle. According to this, two electrons cannot be in the same quantum state and consequently, two electrons with the same spin cannot be found at the same place. Therefore, the many-body wave function must satisfy the exchange symmetry. For example, for a system consisting only of two interacting electrons, the two-electron wave function within the framework of the one-electron picture will be

\[ \Psi(\mathbf{r}_1, \sigma_1; \mathbf{r}_2, \sigma_2) = \frac{1}{\sqrt{2}} \left( \psi_1(\mathbf{r}_1, \sigma_1) \psi_2(\mathbf{r}_2, \sigma_2) - \psi_1(\mathbf{r}_2, \sigma_2) \psi_2(\mathbf{r}_1, \sigma_1) \right) \]

\[ = \frac{1}{\sqrt{2!}} \begin{vmatrix} \psi_1(\mathbf{r}_1, \sigma_1) & \psi_2(\mathbf{r}_2, \sigma_2) \\ \psi_2(\mathbf{r}_1, \sigma_1) & \psi_1(\mathbf{r}_2, \sigma_2) \end{vmatrix}. \quad (2.15) \]

The Hartree-Fock approximation accounts for the electron spin. The inclusion of exchange symmetry will lower the total energy of the system because it keeps the electrons away from each other and reduces their positive repulsive energy. This energy reduction is called exchange energy. Finally, we are able to replace the many-electron problem by that of a single electron moving in the average potential of other electrons. We account for an effective repulsion between the electrons, but we completely ignore their correlation, that is the change of the quantum state of a given electron due to the instantaneous interaction with other electrons in the system. The electron correlation means that

\[ \rho_{12}(\mathbf{r}, \mathbf{r}') \neq \rho(\mathbf{r}) \rho(\mathbf{r}'). \quad (2.16) \]

To understand some of the effects of the correlation, we introduce the correlation function \( h(\mathbf{r}, \mathbf{r}') \) as

\[ \rho_{12}(\mathbf{r}, \mathbf{r}') = \rho(\mathbf{r}) \rho(\mathbf{r}') \left( 1 + h(\mathbf{r}, \mathbf{r}') \right). \quad (2.17) \]
By integrating (2.17) and (2.9) we get

\[
\int d r' \rho_{12}(r, r') = \left( N + \int d r' \rho(r') h(r, r') \right) \rho(r) = (N - 1) \rho(r) \Rightarrow \int d r' \rho(r') h(r, r') = -1,
\]

(2.18)

and by defining the exchange-correlation hole as

\[
\rho_{xc}(r, r') = \rho(r') h(r, r'),
\]

(2.19)

the energy of the many-electron system can be written as

\[
E[\rho(r)] = -\frac{\hbar^2}{2m} \int d r \left[ \nabla^2 \rho_{12}(r, r') \right]_{r' = r} + \frac{e^2}{2} \int d r' \rho(r) \rho(r') \frac{|r' - r|}{|r' - r|} dr' + \int d r \rho(r) U(r).
\]

(2.20)

We observe that the electron correlation due to exchange symmetry and instantaneous interactions between the electrons gives rise to a non-local distribution of exchange-correlation holes and lowers the energy of the system by reducing the contribution of Coulomb repulsion.

### 2.3 Density Functional Theory

The Hartree-Fock theory describes the many-body system as a system of independent electrons moving in the static potential of fixed nuclei and the average repulsive interaction between electrons by ignoring their correlation. It turns out that it is possible to include the correlation simply by modifying the effective potential and it can in principle be done exactly only for the ground state of the system. Using the Hartree approximation we disregard the effects of the exchange symmetry and the electron correlation, which actually lower the energy of the system. This energy reduction is called the exchange-correlation energy \( E_{xc} \).

The major statement of the **Density Functional Theory** (DFT) is that the exchange-correlation energy can be expressed solely in terms of the electron density \( \rho(r) \). Thus, the many-body physical system is described by a physical object, the electron density in the real 3-dimensional space, instead of an abstract multi-variable mathematical object, the wave function. Hohenberg and Kohn have shown that such a description is exact for the ground state and they developed an exact formal variational principle for the ground-state energy, in which the electron density \( \rho(r) \) is the variable function. Let’s consider the many-body system described by (2.5), which is a collection of \( N \) electrons moving under the influence of an external potential \( U(r) \) and the mutual Coulomb repulsion. Below we quote the original proof of Hohenberg and Kohn [4] (the notation of the quantities as well as the numbering of the equations are adapted to the text).
"We shall in all that follows assume for simplicity that we are only dealing with situations in which the ground state is non-degenerate. We denote the electronic density in the ground state $\Psi_0$ by

$$\rho_0(r) = N \int \left( \prod_{i=2}^{N} dr_i \right) |\Psi_0(r, \ldots, r_i, \ldots, r_N)|^2,$$

which is clearly a functional of $U(r)$. We shall now show that conversely $U(r)$ is a unique functional of $\rho_0(r)$, apart from a trivial additive constant.

The proof proceeds by reductio ad absurdum. Assume that another external potential $U'(r)$, with ground state $\Psi'_0$ gives rise to the same density $\rho_0(r)$. Now clearly, unless $U'(r) - U(r) = \text{const}$, $\Psi'_0$ can not be equal to $\Psi_0$ since they satisfy different Schrödinger equations. Hence, if we denote the Hamiltonian and ground-state energies associated with $\Psi_0$ and $\Psi'_0$ by $H$, $H'$ and $E_0$, $E'_0$, we have by the minimal property of the ground state,

$$E'_0 = \langle \Psi'_0 | H' | \Psi'_0 \rangle < \langle \Psi'_0 | H' | \Psi_0 \rangle = \langle \Psi_0 | H + V_{\text{ext}}' - V_{\text{ext}} | \Psi_0 \rangle,$$

so that

$$E_0 < E_0 + \int dr \left( U'(r) - U(r) \right) \rho_0(r). \quad (2.23)$$

Interchanging primed and unprimed quantities, we find in exactly the same way that

$$E_0 < E'_0 + \int dr \left( U(r) - U'(r) \right) \rho_0(r). \quad (2.24)$$

Addition of (2.23) and (2.24) leads to the inconsistency

$$E'_0 + E_0 < E_0 + E'_0. \quad (2.25)$$

Thus $U(r)$ is (to within a constant) a unique functional of $\rho_0(r)$; since, in turn, $U(r)$ fixes $H$ we see that the full many-particle ground state is a unique functional of $\rho_0(r)$.

A straightforward consequence of the last statement is that the ground-state energy $E_0$ is also uniquely determined by the ground-state charge density or, in mathematical terms, $E_0$ is a functional of $\rho_0(r)$

$$E_0[\rho_0(r)] = \langle \Psi_0 | H | \Psi_0 \rangle = F[\rho_0(r)] + \int dr \rho_0(r) U(r), \quad (2.26)$$

where

$$F[\rho_0(r)] = \langle \Psi_0 | T + V_{\text{ee}} | \Psi_0 \rangle \quad (2.27)$$

is a universal functional of the charge density $\rho_0(r)$, valid for any many-body system. Further, Hohenberg and Kohn have shown that the energy as a functional of electronic density $E[\rho(r)]$, for a system of $N$ particles, assumes its minimum value $E_0$ for the correct ground-state charge density $\rho_0(r)$, with
the constraint
\[ \int d\mathbf{r} \rho_0(\mathbf{r}) = N. \] (2.28)

Quoting again from Hohenberg and Kohn:

"It is well known that for a system of \( N \) particle, the energy functional of \( \Psi \)
\[ \mathcal{E}[\Psi] \equiv \langle \Psi | V_{\text{ext}} | \Psi \rangle + \langle \Psi | T + V_{\text{ee}} | \Psi \rangle \] (2.29)
has a minimum at the correct ground state \( \Psi_0 \), relative to arbitrary variations of \( \Psi \) in which the number of particles is kept constant. In particular, let \( \Psi \) be the ground state associated with a different external potential \( U'(\mathbf{r}) \). Then, by (2.29) and (2.27)
\[ \mathcal{E}[\Psi] = \int d\mathbf{r} \rho(\mathbf{r}) U(\mathbf{r}) + F[\rho(\mathbf{r})] > \int d\mathbf{r} \rho_0(\mathbf{r}) U(\mathbf{r}) + F[\rho_0(\mathbf{r})] = \mathcal{E}[\Psi_0]. \] (2.30)

Thus the minimal property of (2.26) is established relative to all density functions \( \rho(\mathbf{r}) \) associated with some other external potential \( U'(\mathbf{r}) \)."

We can extract from \( F[\rho_0] \) the classical Coulomb energy (Hartree term)
\[ F[\rho_0(\mathbf{r})] = \frac{\epsilon^2}{2} \int d\mathbf{r} \frac{\rho_0(\mathbf{r}) \rho_0(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + G[\rho_0(\mathbf{r})], \] (2.31)
and then the ground-state energy of an interacting inhomogeneous electron gas in a static external potential \( U(\mathbf{r}) \) can be written as
\[ E_0[\rho_0(\mathbf{r})] = \int d\mathbf{r} \rho_0(\mathbf{r}) U(\mathbf{r}) + \frac{\epsilon^2}{2} \int d\mathbf{r} \frac{\rho_0(\mathbf{r}) \rho_0(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + G[\rho_0(\mathbf{r})] \] (2.32)
where \( G[\rho_0(\mathbf{r})] \) is a universal functional of the density. In this way, DFT exactly reduces the \( N \)-body problem to the determination of a 3-dimensional function \( \rho(\mathbf{r}) \), which minimizes the functional \( E[\rho(\mathbf{r})] \). However, the functional \( G[\rho(\mathbf{r})] \) is not known and an exact expression for \( G[\rho(\mathbf{r})] \) is unlikely to be found. At this point we have to make another approximation.

### 2.4 Kohn-Sham equations

Kohn and Sham [5] reformulated the problem addressed by Hohenberg and Kohn, and proposed a procedure on the practical implementation of DFT. The system of interacting electrons is mapped on to an auxiliary system of non-interacting electrons having the same ground-state charge density \( \rho_0(\mathbf{r}) \). The universal functional can be written as
\[ G[\rho_0(\mathbf{r})] = T_s[\rho_0(\mathbf{r})] + E_{xc}[\rho_0(\mathbf{r})], \] (2.33)
where $T_s[\rho_0(\mathbf{r})]$ is the kinetic energy of a system of non-interacting electrons with density $\rho_0(\mathbf{r})$ and $E_{xc}[\rho_0(\mathbf{r})]$ is the exchange-correlation energy of an interacting system with density $\rho_0(\mathbf{r})$. For a system of non-interacting electrons the ground-state charge density can be represented as a sum over one-electron occupied states, described by wave functions $\psi_{i\sigma}(\mathbf{r})$, called the Kohn-Sham orbitals,

$$\rho_0(\mathbf{r}) = \sum_{i\sigma} |\psi_{i\sigma}(\mathbf{r})|^2.$$  \hspace{1cm} (2.34)

We can derive the equations for one-electron orbitals by applying the variational principle to the Kohn-Sham functional with the constraints

$$\int d\mathbf{r} \psi^*_{i\sigma}(\mathbf{r}) \psi_{j\sigma'}(\mathbf{r}) = \delta_{ij}\delta_{\sigma\sigma'}.$$  \hspace{1cm} (2.35)

We start by writing the constrained Kohn-Sham functional as

$$E'[\psi_{i\sigma}(\mathbf{r})] = E[\rho_0(\mathbf{r})] - \sum_{i,j,\sigma\sigma'} \lambda_{ij,\sigma\sigma'} \left( \int d\mathbf{r} \psi^*_{i\sigma}(\mathbf{r}) \psi_{j\sigma'}(\mathbf{r}) - \delta_{ij}\delta_{\sigma\sigma'} \right),$$  \hspace{1cm} (2.36)

where $\lambda_{ij,\sigma\sigma'}$ are the Lagrange multipliers. Finally, we obtain the equations for the Kohn-Sham orbitals by minimizing the functional (2.36) with respect to an arbitrary variation of $\psi_{i\sigma}(\mathbf{r})$

$$\frac{\delta E'[\psi_{i\sigma}]}{\delta \psi_{i\sigma}} = \frac{\delta E'[\psi_{i\sigma}]}{\delta \psi^*_{i\sigma}} = 0.$$  \hspace{1cm} (2.37)

It is useful to write the Kohn-Sham energy functional as follows

$$E[\rho_0(\mathbf{r})] = T_s[\rho_0(\mathbf{r})] + E_H[\rho_0(\mathbf{r})] + E_{xc}[\rho_0(\mathbf{r})] + \int d\mathbf{r} \rho_0(\mathbf{r}) U(\mathbf{r}).$$  \hspace{1cm} (2.38)

The first term is the kinetic energy of non-interacting electrons

$$T_s[\rho_0(\mathbf{r})] = -\frac{\hbar^2}{2m} \sum_{i\sigma} \int d\mathbf{r} \psi^*_{i\sigma}(\mathbf{r}) \nabla^2 \psi_{i\sigma}(\mathbf{r}).$$  \hspace{1cm} (2.39)

The second term, called the Hartree energy, describes the classical electrostatic interaction between clouds of charge

$$E_H[\rho_0(\mathbf{r})] = \frac{e^2}{2} \int d\mathbf{r} \frac{\rho_0(\mathbf{r}) \rho_0(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' = \frac{e^2}{2} \sum_{i\sigma} \sum_{j\sigma'} \int d\mathbf{r} \frac{|\psi_{i\sigma}(\mathbf{r})|^2 |\psi_{j\sigma'}(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'.$$  \hspace{1cm} (2.40)

The third term is the unknown exchange and correlation energy and the last term is the energy due to the external potential. A functional derivative
\( \frac{\delta F[f(x)]}{\delta f(y)} \) is defined implicitly through the expression

\[
\delta F = \int \left( \frac{\delta F[f(x)]}{\delta f(y)} \right) \delta f(y) dy,
\]

(2.41)

where \( \delta F \) is the first order variation of \( F[f(x)] \) produced by an arbitrary variation \( \delta f(y) \) of the function \( f(y) \). Using the definition (2.41) it is easy to show that in the case where \( F[f(x)] \equiv f(x) \),

\[
\frac{\delta f(x)}{\delta f(y)} = \delta(x - y),
\]

(2.42)

and that the functional derivative of the charge density \( \rho_0(r) \) due to the variation of a Kohn-Sham orbital \( \psi_{i\sigma}^*(r') \) is

\[
\frac{\delta \rho_0(r)}{\delta \psi_{i\sigma}^*(r')} = \delta \psi_{i\sigma}(r) \delta(r - r').
\]

(2.43)

Now, we get the following expressions for the kinetic energy and Hartree energy functional derivatives

\[
\frac{\delta T_s}{\delta \psi_{i\sigma}^*(r)} = -\frac{\hbar^2}{2m} \sum_{i\sigma} \nabla^2 \psi_{i\sigma}(r),
\]

(2.44)

\[
\frac{\delta E_H}{\delta \psi_{i\sigma}^*(r)} = e^2 \int d\mathbf{r}' \rho_0(r') \frac{\rho_0(|\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|} \psi_{i\sigma}(r).
\]

(2.45)

We now define the Hartree potential

\[
V_H(r) = e^2 \int d\mathbf{r}' \rho_0(r') \frac{\rho_0(|\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|},
\]

(2.46)

and the exchange-correlation potential

\[
V_{xc}[\rho_0(r)] = \frac{\delta E_{xc}[\rho_0(r)]}{\delta \rho_0(r)} ,
\]

(2.47)

and we obtain the following equations for the one-electron orbitals

\[
 \left( -\frac{\hbar^2}{2m} \nabla^2 + V_H(r) + V_{xc}[\rho_0(r)] + U(r) \right) \psi_{i\sigma}(r) = \sum_{j\sigma'} \lambda_{ij,\sigma\sigma'} \psi_{j\sigma'}(r).
\]

(2.48)

By a unitary transformation we can choose a new basis \( \psi_{i\sigma}(r) \) for which the Lagrange multipliers are diagonal, \( \lambda_{ij,\sigma\sigma'} = \epsilon_{i\sigma} \delta_{ij} \delta_{\sigma\sigma'} \), and within this new basis, we finally get the Kohn-Sham equations

\[
(H_{KS} - \epsilon_{i\sigma}) \psi_{i\sigma}(r) = 0,
\]

(2.49)
where the Kohn-Sham Hamiltonian $H_{KS}$ is defined as

$$H_{KS} \equiv -\frac{\hbar^2}{2m} \nabla^2 + V_{KS}(\mathbf{r}) = -\frac{\hbar^2}{2m} \nabla^2 + V_H(\mathbf{r}) + V_{xc}[\rho_0(\mathbf{r})] + U(\mathbf{r}).$$  \hspace{1cm} (2.50)$$

The set of the Kohn-Sham equations is a set of self-consistent equations that resemble the conventional Hartree and Hartree-Fock equations, but also include exchange and correlation effects. However, we still do not know the analytical expression for the exchange-correlation functional $E_{xc}$.

### 2.5 Local Density Approximation

Kohn and Sham [5] introduced the Local Density Approximation (LDA) to the exchange-correlation energy $E_{xc}[\rho_0(\mathbf{r})]$. We can express the exchange-correlation functional through the exchange-correlation energy density $\epsilon_{xc}[\rho_0(\mathbf{r})]$ as

$$E_{xc}[\rho_0(\mathbf{r})] = \int d\mathbf{r} \epsilon_{xc}[\rho_0(\mathbf{r})] \rho_0(\mathbf{r}).$$  \hspace{1cm} (2.51)$$

Kohn and Sham approximated $\epsilon_{xc}[\rho_0(\mathbf{r})]$ with a function of the local density $\rho(\mathbf{r})$

$$\epsilon_{xc}[\rho_0(\mathbf{r})] \Rightarrow \epsilon_{xc}(\rho(\mathbf{r})), \hspace{1cm} (2.52)$$

and for $\epsilon_{xc}(\rho(\mathbf{r}))$ they used the same dependence on the density as for the homogeneous electron gas (jellium). The exchange-correlation potential in (2.50) is now approximated by

$$V_{xc}[\rho_0(\mathbf{r})] \Rightarrow V^{LDA}_{xc}(\mathbf{r}) = \frac{\delta E^{LDA}_{xc}[\rho_0(\mathbf{r})]}{\delta \rho_0(\mathbf{r})} = \left( \epsilon_{xc}(\rho(\mathbf{r})) + \rho(\mathbf{r}) \frac{d\epsilon_{xc}(\rho(\mathbf{r}))}{d\rho(\mathbf{r})} \right)_{\rho(\mathbf{r})=\rho_0(\mathbf{r})}. \hspace{1cm} (2.53)$$

For a homogeneous gas of electrons the charge density $\rho(\mathbf{r})$ is constant, but even for this simple system the exact analytical form of $\epsilon_{xc}(\rho(\mathbf{r}))$ is unknown. However, numerical results from Monte-Carlo calculations by Ceperley and Alder [6] have been parameterized by Perdew and Zunger [7] with a simple analytical form

$$\epsilon_{xc}(\rho) = \begin{cases} -0.4582/r_s - 0.1423/(1 + 1.0529\sqrt{r_s} + 0.3334r_s), & r_s \geq 1 \\ -0.4582/r_s - 0.0480 + 0.0311\ln r_s - 0.0116r_s + 0.0020r_s\ln r_s, & r_s \leq 1 \end{cases}$$

where $r_s = (3/4\pi n)^{1/3}$ in atomic units ($e^2 = \hbar = m = 1$). Surprisingly, LDA has turned out to be much more successful than expected. It is computationally less demanding than the Hartree-Fock method, which accounts for the exact exchange energy through a non-local effective potential, and it gives qualitatively similar results for atoms and molecules, despite the fact that such systems are highly inhomogeneous. For extended systems like periodic solids, LDA describes accurately their structural and vibrational
properties. In most of the cases the correct crystal structure is found to have the lowest energy. The bulk moduli and phonon frequencies are also accurate within a few percent. We can understand the unexpected success of LDA by considering a system in which the Coulomb interaction between electrons is adiabatically switched on

\[ V_{ee}^\lambda = \lambda V_{ee} = \frac{\lambda}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|}, \]  

(2.54)

where \( \lambda = 0 \) for the non-interacting system, and \( \lambda = 1 \) for the interacting one. The charge density remains equal to that of the interacting system during the adiabatic switching of the electron-electron interaction \( \rho_\lambda(r) = \rho_0(r) \). For a non-interacting system, \( \lambda = 0 \) and the energy functional has the form

\[ E_0 = T_s[\rho_0(r)] + \int d\mathbf{r} \rho_0(r) U_0(r), \]  

(2.55)

where the external potential \( U_\lambda(r) \) establishes the ground-state density of the interacting system.

For the interacting system where \( \lambda = 1 \), the energy functional is

\[ E_1 = F[\rho_0(r)] + \int d\mathbf{r} \rho_0(r) U_1(r) \]  

(2.56)

\[ = T_s[\rho_0(r)] + E_H[\rho_0(r)] + E_{xc}[\rho_0(r)] + \int d\mathbf{r} \rho_0(r) U_1(r). \]

Alternatively, we can write the functional of the interacting system as the integral of the energy derivative with respect to \( \lambda \)

\[ E_1 = E_0 + \int_0^1 \frac{dE_\lambda}{d\lambda} d\lambda. \]  

(2.57)

We can express this derivative using the Hellmann-Feynman theorem

\[ \frac{dE_\lambda}{d\lambda} = \langle \Psi_\lambda | \frac{dH_\lambda}{d\lambda} | \Psi_\lambda \rangle \]  

(2.58)

\[ = \langle \Psi_\lambda | U | \Psi_\lambda \rangle + \langle \Psi_\lambda | \frac{dV_{ext}^\lambda}{d\lambda} | \Psi_\lambda \rangle. \]

Thereafter, from the above equations (2.56) and (2.57) we obtain

\[ E_{xc}[\rho_0(r)] = \int_0^1 d\lambda \langle \Psi_\lambda | U | \Psi_\lambda \rangle - E_H[\rho_0(r)] \]  

(2.59)

\[ = \frac{e^2}{2} \int_0^1 d\lambda \int d\mathbf{r} \int d\mathbf{r}' \frac{\rho_\lambda^A(r, r')}{|r - r'|} dr' - \frac{e^2}{2} \int d\mathbf{r} \rho_0(r) \rho_0(r') \frac{1}{|r - r'|}, \]

and finally arrive to the expression for the energy of the Coulomb interaction between the electron charge density and the exchange-correlation
hole
\[ E_{xc}[\rho_0(\mathbf{r})] = \frac{e^2}{2} \int d\mathbf{r} \frac{\rho_{xc}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \rho_0(\mathbf{r}) d\mathbf{r}'. \] (2.60)

The exchange-correlation hole describes the charge missing around \( \mathbf{r} \) due to Coulomb repulsion between electrons (correlation) and the Pauli exclusion principle (exchange). It can be defined through the electron pair correlation function \( g_\lambda(\mathbf{r}, \mathbf{r}') \), which gives the probability to find an electron at point \( \mathbf{r}' \) when another electron is at point \( \mathbf{r} \)

\[ \rho_{xc}(\mathbf{r}, \mathbf{r}') = \rho_0(\mathbf{r}') \int_0^1 d\lambda \left( g_\lambda(\mathbf{r}, \mathbf{r}') - 1 \right). \] (2.61)

We can express the pair correlation function through two-particle density matrix as

\[ g(\mathbf{r}, \mathbf{r}') = \frac{\rho_{12}(\mathbf{r}, \mathbf{r}')}{\rho_0(\mathbf{r})\rho_0(\mathbf{r}')}. \] (2.62)

By using this relation and the equations (2.17), (2.19), and (2.61) it is easy to get (2.60). In this way, we can justify the integral form (2.51) of the exchange-correlation functional. Furthermore, we see that \( E_{xc}[\rho_0(\mathbf{r})] \) depends only on the spherical part of the exchange-correlation hole

\[ E_{xc}[\rho_0(\mathbf{r})] = \frac{e^2}{2} \int d(\ln s) \tilde{\rho}_{xc}(\mathbf{r}, s) \rho_0(\mathbf{r}) d\mathbf{r}, \] (2.63)

which is described very well within LDA and this can partially explain the good performance of LDA.

Nevertheless, there exist a number drawbacks with the LDA. The band gaps in insulators are highly underestimated and the cohesive energies in molecules and solids, as well as the binding energies are overestimated. (Apparently, LDA does succeed to give good results for the binding energies of systems bound by the van der Waals interactions, which in principle can not be described correctly with LDA). The weaknesses of LDA have motivated the research for better functionals and more accurate gradient-corrected functionals have been proposed and widely established.
3. Virtual laboratory

In the previous chapter we described an approximate, however accurate model to simulate the properties of matter. Now we have to implement this model on the computer and thus obtain a visualization of the true picture of the real world.

In order to get the desired information about the system of interacting electrons and nuclei we have to solve a set of differential equations for the Kohn-Sham orbitals (2.49) in a self-consistent way. Since computers operate with lists of numbers, we need a way to represent mathematical objects (functions, etc.) by numbers, to perform numerical simulations. We do this by using another mathematical object, the Hilbert space of one-electron wave functions. Then we can expand the Kohn-Sham orbital $|\psi\rangle$ in an infinite set of linearly independent basis vectors $|i\rangle$ of that Hilbert space

$$|\psi\rangle = \sum_i c_i |i\rangle,$$

and here we have used the Dirac notations for the wave vectors (functions). In the expansion (3.1) the coefficients $c_i$ are numbers. Within this representation, the Kohn-Sham differential equations become a set of linear equations

$$\sum_j \left( H_{ij} - \epsilon S_{ij} \right) = 0,$$

where

$$H_{ij} \equiv \langle i | H_{KS} | j \rangle$$

is the Kohn-Sham Hamiltonian matrix, and

$$S_{ij} \equiv \langle i | j \rangle$$

is the overlap matrix. As a result of this transformation, we now deal with lists of numbers $c_i$, $H_{ij}$, and $S_{ij}$, that are appropriate for numerical modeling. Since computers can only deal with finite sets of numbers, the exact expansion of the wave function (3.1) must be approximated by a finite set of coefficients $c_i$. Therefore, we have to use a truncated basis set of vectors and solve the matrix equation (3.2) for a finite set of coefficients $c_i$. We can
do this truncation in a controllable way and have the desired accuracy in
the approximation, which is something that, up to this point, has not been
attained with the exchange-correlation functional approximation. Now the
task of practical implementation of DFT is reduced to the methods of solv-
ing the matrix equation (3.2) and to the choice of a suitable basis set. Differ-
ent basis sets gave rise to different electronic structure methods.

There are two kinds of basis sets of vectors that are mostly used in mod-
ern electronic structure calculations. The first emerged from the idea that
the one-electron wave functions $\psi(r)$ of electrons in an assembly of atoms
resemble the wave functions $\phi_\alpha(r)$ of electrons in isolated atoms
\begin{equation}
\psi(r) = \sum_\alpha c_\alpha \phi_\alpha(r). \tag{3.5}
\end{equation} 

The other choice of basis functions originates from the idea that electrons
in condensed matter behave like free particles and consequently, the one-
electron orbital can be expanded in a set of plane waves $\exp(i k r)$
\begin{equation}
\psi(r) = \sum_k c_k \exp(i k r). \tag{3.6}
\end{equation} 

These two quite different basis sets, usually called localized and plane
wave basis sets, respectively, have produced two large classes of widely
used computational methods: (i) the linear augmented-plane-waves \[8, 9\] and
linear muffin-tin orbital \[10, 11\] methods, and (ii) the ab initio
pseudopotential methods \[12, 13, 14\].

For a large number of atoms in condensed matter the plane wave meth-
ods have been much more successful. One reason is that the wave functions
can be made as accurate as necessary by simply increasing the number of
plane waves, which helps the method to be systematically improvable. An-
other reason is that for periodic systems like crystals, plane waves represent
a natural choice for the basic set due to the Bloch theorem.

A perfect crystal represents a periodic arrangement of atoms and is de-
scribed by a periodically repeated unit cell. In a 3-dimensional space the
unit cell is described by a set of three vectors $a_i$. The periodicity is described
by an infinite set of vectors $R_m = \sum_i m_i a_i$, where $m_i$ are integers and it is
called a Bravais lattice. Hence, the Kohn-Sham effective potential is peri-
odic due to the translational symmetry
\begin{equation}
V_{KS}(r + R_m) = V_{KS}(r), \tag{3.7}
\end{equation} 
and the solutions of the Kohn-Sham equation (2.49) are the Bloch functions
\begin{equation}
\psi_{ik}(r) = u_{ik}(r) \exp(i k r), \quad u_{ik}(r + R_m) = u_{ik}(r), \tag{3.8}
\end{equation} 
where $k$ is a vector in the reciprocal space. The periodic systems are rep-
resented by plane waves in the same way as periodic functions are repre-
sented by Fourier series. These are generally easy to deal with on the com-
puter.
However, in real life perfect periodicity is absent and the system is either approximately periodic or periodic in one or two dimensions. In all such cases we can simulate the system with a periodically repeated fictitious supercell. We can neglect the effects of artificial periodicity as the size of the supercell is increased. The reason for this is that in many cases the physical interactions between atoms have a range not larger than a few nearest neighbors. The study of point defects requires that the defect does not interact with its periodic equivalent. For disordered solids the supercell must be large enough to guarantee a significant sampling of the configuration space.

In order to simulate a surface, we use a crystal slab alternated with a slab of empty space and both of them are large enough to ensure that the bulk behavior is recovered inside the crystal slab and the surface is unaffected by the periodic equivalent of the crystal slab. Even finite systems, like molecules and clusters, can be studied by using supercells, providing that the interaction between periodically equivalent structures is negligible. The use of supercells for the simulation of molecular or completely aperiodic systems like liquids, has become quite common in recent years thanks to the development of first principles calculations using a plane wave basis set.

3.1 Pseudopotentials

The key behind the success of the methods that use a plane wave basis set is the concept of pseudopotential. We can consider a Bravais lattice \( \mathbf{R} \) and its reciprocal lattice \( \mathbf{G} \). The Kohn-Sham wavefunctions are classified by a band index \( i \) and a Bloch vector \( \mathbf{k} \) in the Brillouin Zone (3.8). A plane wave basis set is defined as

\[
\langle \mathbf{r} | \mathbf{k} + \mathbf{G} \rangle = \frac{1}{V} e^{i(\mathbf{k}+\mathbf{G})\mathbf{r}},
\]

\[
\frac{\hbar^2}{2m} |\mathbf{k} + \mathbf{G}|^2 \leq E_{\text{cut}},
\] (3.9)

where \( V \) is the system volume, and \( E_{\text{cut}} \) is the cutoff of the kinetic energy of plane waves. Thus, the plane wave basis is defined by the crystal structure and by the cutoff. Unfortunately, the extended character of plane waves makes it difficult to accurately reproduce the localized functions of the core states. When an electron is near the nucleus, it experiences a strong attractive potential, which gives it a large kinetic energy. This means that the wave vector \( \mathbf{k} \) of such an electron is very large and consequently, the basis set must contain a large number of plane waves to correctly describe that electron, which will make the calculations impractical. We can deal with the problem of large plane wave basis set, or large cutoff energy, by replacing the true nucleus potential with a pseudopotential. The interaction between valence electrons and atomic cores is described by a weak effective poten-
tial which gives a correct picture of the electron states and the energy of the system. With this idea we assume that the core electrons do not significantly contribute to chemical bonding and solid state properties. Thus, the core electrons are thought to be exactly in the same states as in the isolated atom, or to be "frozen" in their atomic states. The validity of the frozen core approximation was shown by Von Barth and Gelatt [15]. We can denote the true self-consistent core and valence charge densities as $\rho_c$ and $\rho_v$, and the frozen-core and corresponding valence charge densities as $\tilde{\rho}_c$ and $\tilde{\rho}_v$, respectively. If $E[\rho_c, \rho_v]$ is the frozen core functional, then the error due to the frozen core approximation is

$$\delta = E[\tilde{\rho}_c, \tilde{\rho}_v] - E[\rho_c, \rho_v]$$

(3.10)

$$\simeq \int d\mathbf{r} \frac{\delta E}{\delta \rho_c} (\tilde{\rho}_c - \rho_c) + \int d\mathbf{r} \frac{\delta E}{\delta \rho_v} (\tilde{\rho}_v - \rho_v).$$

In the fully self-consistent calculation the energy functional must be stationary with respect to variations in the core and valence charge densities separately, therefore

$$\frac{\delta E}{\delta \rho_c} = \mu_c, \quad \text{and} \quad \frac{\delta E}{\delta \rho_v} = \mu_v,$$

(3.11)

where $\mu_{c,v}$ are the Lagrangian multipliers associated with the conservation of the core and valence charges. Since the total number of core and valence electrons is the same for both the frozen-core and all-electron calculations, then $\delta$ vanishes.

More accurate calculations of solid-state properties using the plane wave basis functions started with the development of first-principles norm-conserving pseudopotentials [12]. These are atomic potentials derived from accurate atomic calculations and constructed to mimic the scattering properties of the true atom. For a given reference atomic configuration, a norm-conserving pseudopotential must fulfill the following conditions:

1) for a chosen prototype atomic configuration the all-electron and pseudo valence eigenvalues are in agreement.
2) the all-electron and pseudo atomic wave functions are the same beyond a chosen core radius $r_c$.
3) for each valence state, the integrals from 0 to $r$ of the all-electron and pseudo charge densities agree for $r > r_c$.
4) the logarithmic derivatives of all-electron and pseudo wave functions and their first energy derivatives agree for $r > r_c$.

Here, the definition all-electron refers to the solution of the Kohn-Sham equation that includes the core electrons. Condition (3) guarantees, through Gauss's theorem, that the electrostatic potential produced outside $r_c$ is identical for all-electron and pseudo charge distributions. This condition is referred to as norm conservation, since the all-electron and pseudo charge densities inside the region $r < r_c$ must be the same.
Condition (4) guarantees that the scattering properties of the real ion cores are reproduced as the eigenvalues are shifted away from the atomic levels due to bonding and formation of bands. The last two conditions are crucial for the pseudopotential to be transferable among different chemical environments in self-consistent calculations in which the pseudo charge is treated as a real one.

Good transferability for norm-conserving pseudopotentials requires the choice of a value for the core radius around the position of the outermost maximum of the all-electron wave function. This condition results in a large plane wave basis set for elements with strongly localized orbitals (like first-row, rare-earth, and 3d elements). The increase of the core radius significantly beyond the outermost maximum of the all-electron wave function is not a satisfactory solution because it obstructs the transferability of such soft pseudopotential. A solution to this problem was proposed by Vanderbilt [13], who relaxed the norm-conservation constraint and introduced a localized atom-centered augmentation charge, defined as the difference between all-electron and pseudo charge. As a result, the core radius of the pseudopotential can now be assigned a value around half of the nearest-neighbor distance, independently of the maximum of the all-electron wave function. However, we have to define several cutoff radii when constructing such an ultra-soft pseudopotential and the increase of the number of parameters requires extensive tests in order to obtain an accurate and highly transferable pseudopotential.

### 3.2 Projector Augmented Waves

An alternative approach which avoids some of the disadvantages of the ultra-soft pseudopotentials, is the *Projector Augmented Waves* (PAW) method, derived by Blöchl [14]. The idea of PAW method is to find a mapping between the all-electron wave function and the pseudo wave function via a suitable linear operator. In this way arrive to a simple and consistent way for reconstructing the all-electron wave functions from pseudo wave functions. We can rewrite the Kohn-Sham energy functional (2.38) as

$$
E_{KS}[\rho] = -\frac{\hbar^2}{2m} \sum_n f_n \langle \Psi_n | \nabla^2 | \Psi_n \rangle + E_H[\rho + \rho_Z] + E_{xc}[\rho],
$$

(3.12)

where $E_H[\rho + \rho_Z]$ is the Hartree energy of the electronic charge density $\rho$ and the point charge densities $\rho_Z$ of the nuclei, $E_{xc}$ is the electronic exchange-correlation energy and $f_n$ are the orbital occupation numbers. Following the PAW method, we derive the all-electron wave function $\Psi_n$ from the pseudo wave function $\tilde{\Psi}_n$ by means of a linear transformation

$$
|\Psi_n\rangle = \mathcal{T} |\tilde{\Psi}_n\rangle,
$$

(3.13)
and the pseudo wave functions $\bar{\Psi}_n$ are the variational quantities, that we receive from

$$\frac{\delta E_{KS}[\mathcal{T}|\bar{\Psi}_n]}{\delta \langle \bar{\Psi}_n \rangle} = \epsilon \mathcal{T}^\dagger \mathcal{T} |\bar{\Psi}_n\rangle. \quad (3.14)$$

Since we want to replace the all-electron wave function only within the region around the nucleus, we can apply a transformation that differs from the identity transformation only by a sum of local, atom-centered contributions $\mathcal{T}_R$ such as

$$\mathcal{T} = 1 + \sum_R \mathcal{T}_R. \quad (3.15)$$

Each local contribution $\mathcal{T}_R$ acts only within some augmentation region $\Omega_R$ enclosing the atom R and outside this region all-electron and pseudo wave functions coincide. The local transformation $\mathcal{T}_R$ is individually defined for each augmentation region by specifying the partial all-electron $|\phi_i\rangle$ waves and partial pseudo waves $|\tilde{\phi}_i\rangle$ as

$$|\phi_i\rangle = (1 + \mathcal{T}_R)|\tilde{\phi}_i\rangle, \quad (3.16)$$

where $|\tilde{\phi}_i\rangle$ are orthogonal to the core states and complete in the augmentation region.

A natural choice for all-electron partial waves is the solutions of the radial Schrödinger equation for the isolated atom, which are orthogonalized to the core states if necessary. Here the index $i$ is a shorthand for the atomic site $R$, $l$, $m$ are the angular momentum numbers, and we also have an additional index $k$ referring to the energy $\epsilon_{kl}$. The all-electron partial waves $|\phi_i\rangle$ are obtained for a reference atom, and the pseudo partial waves $|\tilde{\phi}_i\rangle$ are equivalent to the all-electron ones outside a core radius $r'_c$, which is usually chosen around half of the nearest-neighbor distance. Now, within the augmentation region any pseudo wave function $|\bar{\Psi}\rangle$ can be expanded into pseudo partial waves

$$|\bar{\Psi}\rangle = \sum_i |\tilde{\phi}_i\rangle c_i, \; \mathbf{r} \in \Omega_R, \quad (3.17)$$

and the corresponding all-electron function has the form

$$|\Psi\rangle = \mathcal{T}|\bar{\Psi}\rangle = \sum_i |\phi_i\rangle c_i, \; \mathbf{r} \in \Omega_R. \quad (3.18)$$

Therefore, we can express the all-electron function as

$$|\Psi\rangle = |\bar{\Psi}\rangle + \sum_i (|\phi_i\rangle - |\tilde{\phi}_i\rangle) c_i. \quad (3.19)$$

For a linear transformation the coefficients $c_i$ must be linear functionals of $|\bar{\Psi}_n\rangle$ and can be defined through the scalar product

$$c_i = \langle \tilde{p}_i | \bar{\Psi} \rangle, \quad (3.20)$$

34
where $\tilde{p}_i$ is a projector function which must fulfill the condition
\begin{equation}
\sum_i |\tilde{\phi}_i\rangle\langle \tilde{p}_i| = 1, \ r \in \Omega_R.
\end{equation}

Here it is presumed that
\begin{equation}
\langle \tilde{p}_i|\tilde{\phi}_i\rangle = \delta_{ij}.
\end{equation}

Thus, the linear transformation that transforms valence wave functions to fictitious pseudo wave functions is given by the following expression
\begin{equation}
\mathcal{T} = 1 + \sum_i (|\phi_i\rangle - |\tilde{\phi}_i\rangle) \langle \tilde{p}_i|.
\end{equation}

With the help of the above transformation we can express the observable quantities in terms of the variational parameters $|\tilde{\Psi}_n\rangle$ of the Kohn-Sham functional. The expectation value of an operator $\mathcal{A}$ is
\begin{equation}
\langle \mathcal{A} \rangle = \sum_n f_n \langle \Psi_n|\mathcal{A}|\Psi_n\rangle = \sum_n f_n \langle \tilde{\Psi}_n|\tilde{\mathcal{A}}|\tilde{\Psi}_n\rangle.
\end{equation}

In order to calculate the total energy and charge density, we need to evaluate the expectation values of the kinetic energy operator $-\frac{\hbar^2}{2m}\nabla^2$ and the real space projection operator $|r\rangle\langle r|$. For such quasi-local operators the expression for the pseudo operator has the following form
\begin{equation}
\tilde{\mathcal{A}} = \mathcal{T}^\dagger \mathcal{A} \mathcal{T}
\end{equation}
\begin{align}
&= \mathcal{A} + \sum_{i,j} |\tilde{p}_i\rangle \left( \langle \phi_i|\mathcal{A}|\phi_j\rangle - \langle \tilde{\phi}_i|\mathcal{A}|\tilde{\phi}_j\rangle \right) \langle \tilde{p}_j|.
\end{align}

We are free to add to the equation above a term of the form
\begin{equation}
\mathcal{B} = \mathcal{B} - \sum_{i,j} |\tilde{p}_i\rangle \langle \tilde{\phi}_i|\mathcal{B}|\tilde{\phi}_j\rangle \langle \tilde{p}_j|,
\end{equation}

where $\mathcal{B}$ is an arbitrary operator localized within the augmentation region. The expectation value of $\mathcal{B}$ is zero for any pseudo wave function $|\tilde{\Psi}_n\rangle$. This freedom can be utilized for example, to cancel the Coulomb singularity of the plane wave extension and obtain an expression that is less sensitive to a truncation of the number of plane waves.

By making use of Eq. (3.25), the all-electron charge density in the PAW method is given by
\begin{equation}
\rho(r) = \tilde{\rho}(r) + \rho_r(r) - \tilde{\rho}_r(r),
\end{equation}

where $\tilde{\rho}(r)$ is the soft pseudo charge density calculated on a plane-wave grid directly from the pseudo wave functions,
\begin{equation}
\tilde{\rho}(r) = \sum_n f_n \langle |\tilde{\Psi}_n| r \rangle \langle r | \tilde{\Psi}_n \rangle.
\end{equation}
Here, $\rho_r(\mathbf{r})$ and $\tilde{\rho}_r(\mathbf{r})$ are the on-site charge densities calculated on a radial grid, which extends up to $r_{rad}$ around each ion and are defined as

$$
\rho_r(\mathbf{r}) = \sum_{ij} \rho_{ij} \langle |\phi_i| \mathbf{r} \rangle \langle \mathbf{r} | \phi_j \rangle,
$$

$$
\tilde{\rho}_r(\mathbf{r}) = \sum_{ij} \rho_{ij} \langle |\tilde{\phi}_i| \mathbf{r} \rangle \langle \mathbf{r} | \tilde{\phi}_j \rangle,
$$

where $\rho_{ij}$ are the occupancies of each augmentation channel ($i, j$),

$$
\rho_{ij} = \sum_n f_n \langle |\tilde{\Psi}_n\rangle \tilde{\phi}_i \rangle \langle \tilde{\phi}_j | \tilde{\Psi}_n \rangle.
$$

The use of radial support grids around each ion is another advantage of the PAW method because the augmentation charge is treated with the full all-electron functions (the charge density $\tilde{\rho}_r(\mathbf{r})$ is exactly the same as $\tilde{\rho}(\mathbf{r})$ inside the augmentation region for a complete set of projectors). We can show that ultra-soft and norm-conserving pseudo potentials can be derived from the PAW method [14].

The results presented in the next chapters, were obtained by using an implementation of the PAW method, the Vienna Ab Initio Simulation Package (VASP) [16, 17].

### 3.3 Hellman-Feynman forces

Within the framework of the Born-Oppenheimer approximation (2.5) we solve the many-body problem of interacting electrons in the potential of fixed nuclei. In crystals with simple structure the positions of the atoms are fixed by the symmetry, but for more complex systems the equilibrium atomic positions are not known and we need to calculate them. The nuclei are considered as classical objects and at zero temperature the equilibrium atomic positions $\overline{R}_0$, are determined by the minimum of the total energy $E_{tot}$ of the system, which is the sum of the electronic energy $E$ (the minimum of the Kohn-Sham energy functional) and the electrostatic energy $E_{II}$ of the ion-ion interaction.

If we consider the electrons in their ground state for any given configuration of ions $\overline{R}$, the total energy will be a function of the atomic positions

$$
E_{tot}(\overline{R}) = E(\overline{R}) + E_{II}(\overline{R}).
$$

The procedure to find the atomic configuration that yields the minimum total energy is called structural optimization or relaxation. For infinite periodic structure there is a distinction between atomic displacements that change the shape and volume of the unit cell (elastic modes) and atomic displacements internal to the unit cell (phonon modes). Usually, the optimization of the lattice and of the atomic positions is done using different procedures.

If the unit cell is fixed, then the problem of finding the minimum of the total energy as a function of atomic positions can be solved by calculating
the gradients of the energy (forces) with respect to the variables (the positions of nuclei in the unit cell). There is one thing we must account for when finding the equilibrium configuration by minimizing forces: gradient algorithms are very likely to bring the system to the closest local minimum (a zero gradient point), rather than to the global minimum (the lowest energy minimum).

The derivatives of the total energy $E_{tot}$ with respect to the atomic positions $\mathbf{R}_i$ are called Helmann-Feynman forces. The Hellmann-Feynman theorem states that for the many body Hamiltonian and wave function, only terms containing explicit derivatives in the Hamiltonian contribute, while the terms containing implicit derivatives through the wave functions must vanish:

$$F_i = -\frac{dE}{d\mathbf{R}_i} = -\frac{d}{d\mathbf{R}_i} \langle \Psi | H | \Psi \rangle \quad (3.32)$$

$$= -\langle \Psi | \frac{\delta H}{\delta \mathbf{R}_i} | \Psi \rangle - \bar{F}_i,$$

where

$$\bar{F}_i = \langle \frac{d\Psi}{d\mathbf{R}_i} | H | \Psi \rangle + \langle \Psi | H | \frac{d\Psi}{d\mathbf{R}_i} \rangle \quad (3.33)$$

$$= E \left( \langle \frac{d\Psi}{d\mathbf{R}_i} | \Psi \rangle + \langle \Psi | \frac{d\Psi}{d\mathbf{R}_i} \rangle \right) = E \frac{d}{d\mathbf{R}_i} \langle \Psi | \Psi \rangle = 0.$$

The Hellman-Feynman theorem must also apply to the DFT approximation of a many-body problem. By using the expression (3.31), we can write the force as

$$F_i = - \int d\mathbf{r} \rho(\mathbf{r}) \frac{\delta U(\mathbf{r})}{\delta \mathbf{R}_i} - \frac{\delta E_{II}}{\delta \mathbf{R}_i} - \bar{F}_i, \quad (3.34)$$

where the first two terms explicitly depend on ionic positions (the first is due to Coulomb interaction between the electrons and the nuclei and is the external potential term in the Kohn-Sham energy functional) and the last term $\bar{F}_i$ contains implicit derivatives through the Kohn-Sham orbitals:

$$\bar{F}_i = \sum_k \int d\mathbf{r} \left( \frac{\partial \psi^*_k(\mathbf{r})}{\partial \mathbf{R}_i} \frac{\delta E}{\delta \psi^*_k(\mathbf{r})} + \frac{\partial \psi_k(\mathbf{r})}{\partial \mathbf{R}_i} \frac{\delta E}{\delta \psi_k(\mathbf{r})} \right). \quad (3.35)$$

The functional derivative yields the Kohn-Sham Hamiltonian

$$\frac{\delta E}{\delta \psi_k^*(\mathbf{r})} = H_{KS} \psi_k(\mathbf{r}), \quad (3.36)$$

and we can write $\bar{F}_i$ as

$$\bar{F}_i = \sum_k \int d\mathbf{r} \left( \frac{\partial \psi^*_k(\mathbf{r})}{\partial \mathbf{R}_i} H_{KS} \psi_k(\mathbf{r}) + \frac{\partial \psi_k(\mathbf{r})}{\partial \mathbf{R}_i} H_{KS} \psi^*_k(\mathbf{r}) \right). \quad (3.37)$$
Furthermore, using the fact that the total number of electrons in the system is conserved, we obtain the following identity

$$\frac{d}{dR_i} \int dr \rho(r) = \sum_k \int dr \left( \frac{\partial \psi^*_k(r)}{\partial R_i} \psi_k(r) + \frac{\partial \psi_k(r)}{\partial R_i} \psi^*_k(r) \right) = 0$$  \hspace{1cm} (3.38)$$

and we can also rewrite the expression for $\tilde{F}_i$ as

$$\tilde{F}_i = \sum_k \int dr \left( \frac{\partial \psi^*_k(r)}{\partial R_i} (H_{KS} - \epsilon_k) \psi_k(r) + \frac{\partial \psi_k(r)}{\partial R_i} (H_{KS} - \epsilon_k) \psi^*_k(r) \right)$$  \hspace{1cm} (3.39)$$

which becomes zero in the ground state. Consequently, as in the exact many-body case, the forces acting on the atoms are expressed through the ground state matrix elements of the gradient of the external potential $U(r, \mathbf{R})$, plus the gradient of the electrostatic potential due to interactions between nuclei, $E_{II}(\mathbf{R})$:

$$F_i = -\int d\rho(r) \frac{\delta U(r)}{\delta R_i} - \frac{\delta E_{II}}{\delta R_i}.$$  \hspace{1cm} (3.40)$$
4. Pressure induced phase transitions in carbonates

The study of the properties of matter at high pressure became a field of a successful application of electronic structure calculation methods. Apart from the fundamental aspects of understanding the behavior of matter at high pressure, there are also some practical applications, like predicting new materials or new physical properties, or finding a way to tune some desirable properties by applying high pressure. One important area of application of computer modeling of matter within the framework of the DFT is the study of the interior of the Earth [18]. There is a fundamental difficulty to get a complete knowledge of the physics of the Earth’s interior based on traditional methods of study, because the system of interest is inaccessible for direct observation. We have fairly precise information about the density and elastic properties of materials within the Earth’s interior deduced from seismic data, and detailed knowledge of the magnetic field of the Earth, which is related to its interior structure. As for the chemical composition, we have a complete knowledge of the chemistry of the Earth’s crust, which can be sampled directly, and a less complete information about the composition of the Earth’s mantle is available from the study of the inclusions and products that are brought to the surface by volcanic eruptions.

However, our understanding of the deep interior of the earth relies on indirect data provided by the composition of chondritic meteorites [19, 20]. It is difficult to extract useful and reliable information by performing experiments at pressures and temperatures relevant to the Earth’s interior. There are few techniques for performing experiments at such critical conditions [21], among which the Diamond Anvil Cells (DACs) based experiments give the most detailed information. By coupling a DACs with a laser beam it is possible to attain pressures up to 200-250 GPa and temperatures up to 6000 K. DACs can also be used with synchrotron x-ray radiation to perform in situ characterization of the a sample. However, the challenge for such studies is the accuracy with which pressure and temperature can be measured. On the other hand, numerical simulations of matter based on quantum mechanics can accurately describe the properties of materials under extreme conditions. Furthermore, computer simulations allow us easily to go beyond the pressure and temperature range accessible in laboratory experiments.
4.1 Crystal structure and equation of state

The state of matter under certain physical conditions is described by a thermodynamic equation of state (EOS). The thermodynamic state of a system at equilibrium is described by a set of thermodynamic quantities, like pressure, volume, temperature, entropy, internal energy, and other thermodynamic potentials, which describe the macroscopic state of matter. The equation of state provides a mathematical relationship between different thermodynamic quantities and allows us to compare the stability of different phases of matter in general and different crystal structures in particular as a function of thermodynamic variables. DFT is an exact theory of the ground state of a physical system, hence, within the Kohn-Sham approach, we can accurately calculate the properties of matter at the temperature $T = 0K$. The state of a crystalline phase at $T = 0K$ and different values of pressure $P$ is described by the enthalpy of the system:

$$H(P) = E(V) + PV,$$

where the pressure $P$ is defined by

$$P(V) = -\left(\frac{\partial E(V)}{\partial V}\right)_T.$$

Thus, by performing a series of total energy calculations for a set of given volumes $E_i = E(V_i)$, we can determine the dependence of the total energy of the system on its volume $E = E(V)$, and to calculate the enthalpy as a function of pressure via (4.2). With the change of pressure, a given material will experience a sequence of structural phase transformations, and at a given pressure, the stable structure is the one which has the lowest enthalpy. The transition pressure $P_{1 \rightarrow 2}$ from phase 1 to phase 2 is found from the condition $H_1(P) = H_2(P)$ or

$$\Delta H(P) = 0.$$

For simple crystals, in which the positions of atoms are completely fixed by symmetry, the calculations are straightforward, since the same kind of calculations is repeated at different unit cell volumes. For less symmetrical crystals, the equilibrium unit cell parameters and the position of atoms in the unit cell must be determined via a structure optimization procedure at each volume.

A particular attention must be paid to the determination of the mathematical form of the dependence of energy on volume or the zero-temperature equation of state $P = P(V)$. There are many ways to fit a curve $E = E(V)$ from a finite set of values $\{V_i, E_i\}$. If there are many calculated points, and no extrapolation over the range of the calculated data is required, than a polynomial interpolation gives the best fitting for $E = E(V)$ curve. However, in the most cases, experimental data are scarce and the range of the pressure variation is very limited, especially when a given high-pressure phase exists within a narrow pressure interval. In
such cases, $E = E(V)$ or $P = P(V)$ curves are fitted to an appropriate EOS, which form is deduced from general physical considerations. Thus, one should use this kind of the EOS when comparing the results of calculations with empirical data. In my work, I have been using the Murnaghan, Birch-Murnaghan, and Vinet equations of state.

Murnaghan [22] obtained an EOS from the elastic theory of an isotropic medium under finite hydrostatic pressure. The Murnaghan EOS is used to fit a $P = P(V)$ curve by using only three free parameters, namely the equilibrium volume $V_0$, the equilibrium bulk modulus $B_0$ and its pressure derivative evaluated at equilibrium $B'_0$. The bulk modulus is defined as

$$B = -V \left( \frac{\partial P}{\partial V} \right)_T,$$  \hspace{1cm} (4.4)

and its pressure derivative as

$$B' = \left( \frac{\partial B}{\partial P} \right)_T.$$

(4.5)

Assuming that the bulk modulus pressure derivative does not change with pressure, that is $B' = B'_0$, we can write

$$B(P) \approx B_0 + B'_0 P,$$  \hspace{1cm} (4.6)

and combining this expression with the definition (4.4), we get

$$\frac{dV}{V} = - \frac{dP}{B_0 + B'_0 P}.$$  \hspace{1cm} (4.7)

By performing the integration we obtain the Murnaghan EOS for $P = P(V)$

$$P(V) = \frac{B_0}{B'_0} \left( \frac{V_0}{V} \right)^{B'_0} - 1.$$  \hspace{1cm} (4.8)

If we substitute Eq.(4.8) in Eq.(4.2) and integrate, we obtain the Murnaghan EOS for $E = E(V)$

$$E(V) = E_0 + \frac{B_0}{B'_0} \left( \frac{V_0}{V} \right)^{B'_0} \left( \frac{V_0}{B'_0 - 1} + 1 \right) V - \frac{B_0 V_0}{B'_0 - 1},$$  \hspace{1cm} (4.9)

where $E_0$ is the total energy of the system at equilibrium. Birch [23] have extended the Murnaghan theory of finite strain for system of cubic symmetry subjected to finite hydrostatic pressure and obtained the so-called third-order Birch-Murnaghan EOS

$$P(V) = \frac{3 B_0}{2} \left[ \left( \frac{V_0}{V} \right)^{\frac{3}{2}} - \left( \frac{V_0}{V} \right)^{\frac{5}{2}} \right] \left[ 1 + \frac{3}{4} (B'_0 - 4) \left( \left( \frac{V_0}{V} \right)^{\frac{3}{2}} - 1 \right) \right].$$  \hspace{1cm} (4.10)
Vinet et al have [24] discovered a universal form for pressure as a function of volume for all classes of solids, starting from the universal relation between the binding energy $E$ and the separation between atoms:

$$E(a^*) = E_0 E^*(a^*), \quad a^* = (r_{WS} - r_{WS}^0)/l,$$  
(4.11)

where $r_{WS}^0$ is the equilibrium value of the Wigner-Seitz radius $r_{WS}$, and $l$ is a scaling length. The pressure is obtained from the volume derivative of Eq.(4.11) by making use of $V \equiv 4\pi r_{WS}^3/3$:

$$P(a^*) = -\frac{E_0}{4\pi l(la^* + r_{WS}^0)^2} \frac{\partial E^*(a^*)}{\partial a^*},$$  
(4.12)

but, because of the presence of $a^*$ in the denominator, it cannot be scaled to the universal form $E^*(a^*)$. However, the force

$$F(a^*) = 4\pi r_{WS}^2 P(a^*) = -\frac{E_0}{l} \frac{\partial E^*(a^*)}{\partial a^*}$$  
(4.13)

can be scaled in the same manner as the binding energy. One can define a universal pressure function $G^*(a^*)$ [25]

$$G^*(a^*) = -\frac{1}{a^*} \frac{\partial E^*(a^*)}{\partial a^*} = \frac{4\pi l(la^* + r_{WS}^0)^2}{a^* E_0} P(a^*),$$  
(4.14)

which is constant near equilibrium. One can further define a specific form for the universal function by requiring $\frac{\partial^2 E^*(a^*)}{\partial a^{*2}} = 1$, and fixing the scaling parameter to $l = \sqrt{E_0/12\pi B_0 r_{WS}^0}$. Thus, the universal function $G^*$ can be written in terms of pressure and volume as:

$$B_0 G^*(a^*) = H(V) \equiv \frac{1}{3} \left( \frac{V}{V_0} \right)^{2/3} P(V),$$  
(4.15)

where the dependence of $\ln H(V)$ versus $1 - (V/V_0)^{1/3}$ is linear and has the same slope for all solids. From a detailed examination of a large number of experimental data, Vinet et al have obtained that

$$a^* = -\frac{3}{2} (B_0' - 1) \left[ \left( \frac{V}{V_0} \right)^{\frac{1}{3}} - 1 \right],$$  
(4.16)

and the universal dependence of pressure on volume is given by

$$P(V) = \frac{3 B_0}{(V/V_0)^{2/3}} \left[ 1 - \left( \frac{V}{V_0} \right)^{\frac{1}{3}} \right] \exp \left[ -\frac{3}{2} (1 - B_0') \left[ 1 - \left( \frac{V}{V_0} \right)^{\frac{1}{3}} \right] \right].$$  
(4.17)

The corresponding universal EOS for the energy as a function of volume is

$$E(x) = E_0 + \frac{4 B_0 V_0}{(B_0' - 1)^2} [1 - (1 + x)e^{-x}],$$  
(4.18)
where
\[ x = \frac{3}{2} (B'_0 - 1) \left[ 1 - \left( \frac{V}{V_0} \right)^\frac{1}{3} \right]. \]

This equation of state can be used also at finite temperatures \( T \neq 0 \) [26] with a temperature dependent bulk modulus \( B = B(T) \).

### 4.2 Stability of carbonates at high pressure

A question of stability of MgCO₃ and CaCO₃ carbonates has aroused appreciable interest of scientists from different fields of physics, like geophysics, chemistry and materials science. These carbonates are found in abundance at the surface of the Earth and within the Earth's crust, but they are minor components of the Earth's interior. What would be the cause of such an interest, apart from an academic study? The reason is that these carbonates are believed to be the major carbon bearing minerals within the Earth's mantle, and they play an important role in the global carbon cycle. The issue of the CO₂ content in the atmosphere has become very important recently, and great efforts are made to reduce its emission and find efficient mechanisms to reduce its content. However, earlier studies have shown that the amount of carbon in the exosphere is small, and that most of it is kept within the Earth's interior. The carbon present in the Earth's mantle has probably been included during the period of Earth's accretion from the primordial nebular carbon. However, it is possible that carbon is delivered into the mantle through the subduction of the carbonate sediments. Therefore, if the carbonates are stable at the temperatures and pressures under the Earth's mantle conditions, then the subduction of MgCO₃ and CaCO₃ carbonates is a natural way to lower the carbon content.

A series of experimental investigations have been carried out during the last decades and the question wether the carbonates survive the subduction or not is still open. Although recent experiments impose some constraints on the subduction of carbonates deep into the Earth's interior, there are experimental evidences that MgCO₃ is stable under the Earth's lower mantle conditions, and that carbonates could be recycled into the lower mantle by a subducted oceanic crust. At ambient conditions, stable forms of Mg- and Ca- carbonates are *magnesite* MgCO₃, *calcite* CaCO₃, and *dolomite* CaMg(CO₃)₂. Calcite transforms to *aragonite* at pressures corresponding to the Earth's upper mantle, and this phase can be quenched to ambient conditions, the presence of the aragonite mineral at the surface being a vivid example. Dolomite breaks to magnesite and aragonite at the pressures corresponding to Earth's crust conditions, thus in the uppermost part of the mantle magnesite and aragonite are stable polymorphs of MgCO₃ and CaCO₃, respectively. However, with the increase of pressure, both magnesite and aragonite might transform to some other stable crystalline structures. Magnesite has a large stability
field and is stable up to 115 GPa, above which it undergoes a structural phase transition to a post-magnesite. The structure of the high-pressure phase could not be resolved from experimental data and its determination has become a challenge for materials scientists. Aragonite has also been found to transform to a post-aragonite phase above 40 GPa, but the structure of this phase remained a controversial issue. Santillán and Williams reported a trigonal phase in the space group $P\bar{3}1c$, while Ono et al reported an orthorhombic structure for post-aragonite.

Skorodumova et al have reported a transition from the magnesite to a pyroxene post-magnesite structure in the space group $C2/c$ at a pressure of 113 GPa, in close agreement with experimental observations. They predicted also a subsequent transformation of the post-magnesite into a CaTiO$_3$-type structure (space group $Pmcn$) above 200 GPa. The search of a possible post-magnesite phase has been done within perovskite-type and pyroxene-type structures based on the similarity between carbon and silicon. We can call this a traditional way to predict new possible structures and it has obvious limits of applications: (i) it is subjective, since the choice of a set of candidate structures is based on scientist's intuition and knowledge, (ii) candidate structures are only the phases known to occur in nature, thus, there is a little chance that a completely new structure will be predicted. Although this approach is not a systematic one, in many cases it gives correct answers.

However, very recently, new methods to predict crystal structure based on a systematic approach have been developed and seem to be very promising. Oganov et al have determined the correct structure of the post-aragonite phase, and predicted a new pyroxene-type structure (space group $C222_1$) for the post-magnesite above 117 GPa and the post-post-aragonite above 137 GPa. Moreover, the prediction for the post-post-aragonite phase has been confirmed by Ono et al [27]. At about the same time, in Paper I, we have found that the $Pmcn$ structure of CaCO$_3$ becomes again a stable phase over 235 GPa. The phase sequence of CaCO$_3$ with pressure is shown in Fig. 4.1. Both structures, $C2/c$ predicted by Skorodumova et al for MgCO$_3$, and $C222_1$ predicted by Oganov et al for both, MgCO$_3$ and CaCO$_3$, show a new crystal-chemical regime. Carbonates represent a classical example of a compound with triangular CO$_2^-$ groups aligned in parallel planes, which determine the strong anisotropy of their physical properties. In contrast to magnesite, aragonite and post-aragonite, the new pyroxene-type high-pressure phase contains CO$_4^-^4$ tetrahedra. The high-pressure $Pmcn$ phase is also different from the aragonite structure, and the difference is due to the transition from triangular to tetrahedral bonded carbon ion. Actually, during our simulations, we have been able to observe the transition from the phase with carbon atom in the $sp^2$ hybridization state to the phase with carbon in the $sp^3$ hybridized state within the same $Pmcn$ space group. In Fig. 4.2, the projections of the charge density onto two mutually perpendicular planes crossing at a C atom site are shown for two different $Pmcn$ phases.
In Paper II we have studied the sequence of phase transitions in SrCO₃ and BaCO₃. These carbonates are isostructural to CaCO₃ and at ambient conditions crystallize in the structure of aragonite. Since the ionic radii of Sr and Ba are larger than the ionic radius of Ca, SrCO₃ and BaCO₃ are expected to undergo the same sequence of phase transformation as in CaCO₃ but at lower pressure. And indeed, at moderate pressures all three carbonates undergo the same kind of aragonite to post-aragonite transition. However, at high pressures the phase transition sequence of SrCO₃ and BaCO₃ differ from that of CaCO₃. The pyroxene-type structure found in CaCO₃ do not exist in SrCO₃ and BaCO₃, and the change of carbon hybridization state from \( sp^2 \) to \( sp^3 \) within the \( Pmcn \) structure occurs at larger pressures for carbonates with larger cation radius. Therefore, we cannot predict the phase transformations sequence in all compounds by generalizing the results obtained for the compound with the largest cation radius at all pressures. Thus, we show that the concept that isostructural compounds with different cations undergo the same phase transition sequence can be applied only within a certain range of pressures.
Figure 4.1: High-pressure phase sequence of CaCO$_3$: $Pmcn \rightarrow Pmmn \rightarrow C222_1 \rightarrow Pmcn$.

Figure 4.2: Projections of the charge density onto two mutually perpendicular planes crossing at carbon atom site.
5. Complex composite structures at high pressures

At ambient conditions the great majority of the metallic elements have simple high-symmetry crystal structures, such as body-centered (bcc), face-centered cubic (fcc) and hexagonal close-packed (hcp). Under high pressure, we might expect the close-packed elements to merely compress. We also expect the elements that do not have a closed-packed or bcc structure at ambient pressure, to obtain such a structure in the high-pressure conditions.

The structural changes with pressure are determined by the change in the electronic structure. The stability of the crystal structure of metals is known to be determined by the intricate interplay between the electrostatic contribution of ions $E_{\text{latt}}$ and the band structure energy of the valence electrons $E_{\text{band}}$. These two main contributions to the energy of the crystal depend on the volume in different ways. The Madelung energy $E_{\text{latt}}$ depends on volume as $V^{-1/3}$, while the band energy $E_{\text{band}}$ depends on volume as $V^{-2/3}$ [28]. At normal conditions, the electrostatic contribution prevails and it stabilizes the metallic elements in close-packed, high-symmetry structures, such as fcc, hcp, and bcc. As the pressure increases, there will be a change in the balance between the energy contributions that will favor the energy of the valence band electrons. The change in the electronic structure can influence the nature of the bonding in such a way that there may be structural transitions to phases with lower symmetry and less close packing than those found at the ambient pressure.

Structural changes and changes in the electronic band structure can also give rise to dramatic changes in the physical properties. Of considerable interest is the quantum phenomenon of superconductivity, which some metallic elements exhibit at low temperature. Certain metallic elements that do not exhibit superconductivity at normal pressure undergo phase transitions at high pressures accompanied by the onset of superconductivity. Even elements that are insulators at ambient pressure can exhibit structural phase transitions accompanied by metallization and the onset of superconductivity and so, by high-pressure studies, the number of elements that manifest the phenomenon of superconductivity has increased by over 70% [29].

Long-term studies of the phenomenon of structural phase transitions with pressure have established general structural trends within the different groups of the periodic table [30]. In particular, it has been established that the heavier elements within a group of the periodic table tend to follow...
the same general sequence of structural changes as the lighter members of the group but at lower pressures. These trends have also been proven by \textit{ab initio} computational studies of changes in the electronic structure with pressure [31, 32]. The majority of the high-pressure phases studied prior to 1999 exhibited phase transitions to simple structures with cubic, tetragonal or hexagonal symmetry. Besides that, there was a significant number of high-pressure phases that were already known to occur in more complex structures but up to this point in time, they resisted attempts at identification.

The difficulty in solving complex structures at high pressures had two principal reasons. First, the powder diffraction methods were used for crystal structure characterization. Second, energy-dispersive diffraction techniques with intense polychromatic x-ray radiation were used to overcome the weak signal given by the small volume of the measured samples. Although these techniques enabled us to understand the high-pressure behavior of many elements at pressures above 100 GPa, the modest resolution and unreliable peak intensities of the energy-dispersive powder diffraction data prevented the solution of more complex phases. The introduction of image-plate area detectors and the use of synchrotron radiation led to the development of angle-dispersive powder-diffraction methods with higher resolution [33] and the use of 2-D powder patterns of diffraction data [34].

An unexpected outcome with these optimized angle-dispersive methods was the discovery of new structures that were still too complex to solve. One of the factors that still limited the effectiveness of powder-diffraction methods was the tendency of complex phases to form large crystallites and give "spotty" powder diffractions patterns, and this required the further development of the use of single-crystal methods. As a conclusion, recent powder and single-crystal diffraction studies have revealed a large number of previously unidentified phases, and uncovered a number of completely new complex structure types previously unknown in the elements [35].

5.1 Incommensurate composite structures

The new complex structures in the metallic and semi-metallic elements fall naturally into 4 categories: incommensurate composite structures, incommensurately modulated structures, modulated layer structures, and other complex structures [35]. In the following only the first category of complex structures will be discussed.

Incommensurate composite structures consist of two interpenetrating substructures, a \textit{host} and a \textit{guest} structure. These two substructures are incommensurate with each other along one or more axes. This type of structure is very unexpected in elements due to its two-component nature and is not known for any element at ambient conditions. However, after a composite incommensurate structure was first found in Ba at 12 GPa [36], it has
Figure 5.1: Composite structure of Sc-II shown in projection down the c-axis. The structure consists of two interpenetrating sublattices: a body-centered tetragonal host lattice and a C-face centered tetragonal guest lattice.

also been observed in high-pressure phases of other elements [37, 38, 39, 40, 41].

The host structure of Ba-IV is a tetragonal body-centered structure in the space group \( I4/mcm \), with 8 atoms on the \( 8h \) Wickoff site at \((x, x + 1/2, 0)\). The Wickoff and tetragonal lattice parameters at 12.1 GPa are \( x = 0.1486, a_1 = b_1 = 8.4207\) Å and \( c_1 = 4.7369\) Å, respectively [36]. The guest structure is a C-face centered monoclinic in the space group \( C2/m \) with \( a_2 = 8.4623\) Å, \( b_2 = b_1, c_2 = 3.4269\) Å, and \( \beta_2 = 96.151^\circ \). The host and guest structures are commensurate with each other in the \( a-b \) plane, but they are incommensurate with each other along their common \( c \) axis. Ba-IV also exhibits a second coexisting metastable guest structure, which is C-face centered tetragonal in the space group \( C4/mmm \) with lattice parameters \( a_2 = a_1 \) and \( c_2 = 3.4117\) Å. Structures with the same 8-atom tetragonal host framework have also been found in Sr, Sc, and Bi. The incommensurate structure of Sc-II is shown in Fig. 5.1.

Another composite incommensurate structure of the same type was first discovered in Rb [38] and later in K [39]. The host structure of Rb-IV is tetragonal body-centered in the same space group \( I4/mcm \) as in Ba, Sr, Sc and Bi but is made up of 16 atoms on 16k site at \((x, y, 1/2)\). At a pressure of 16.8 GPa, the Wyckoff and unit cell lattice parameters are \( x = 0.7903, y = 0.0851, a_1 = b_1 = 10.3503\) Å, and \( c_1 = 5.1865 \), respectively [38]. The guest structure is body-centered tetragonal in the space group \( I4/mmm \) with \( a_2 = a_1 \) and \( c_2 = 3.1797\) Å. In the K-III structure the guest structure is also tetragonal but C-face centered.
One important aspect of these composite incommensurate structures is that the host unit cell contains a non-integer number of atoms. Since the host and guest structures are incommensurate along the \( c \) axis, the total number of atoms is \( 8 + 2(c_1/c_2) \) in Ba, Sr, Sc and Bi, and \( 16 + 2(c_1/c_2) \) in Rb and K.

Another aspect, that makes it difficult to investigate these structures by using ab initio calculations, is the lack of periodicity in the 3-D space. From a crystallographic perspective, a rigorous treatment of these structures can be obtained within the formalism of 4-D superspace, in which the periodicity of these incommensurate structures is recovered \([42, 43]\). We can index the diffraction peaks using four Miller indices \((hklm)\) instead of three and the symmetry is described by using 4-D superspace groups. The reflections from the host sublattice are indexed as \((hkl0)\) and the reflections from the guest substructure are indexed as \((hk0m)\).

The superspace group notations represent the symmetry operations of the composite structure and the superspace Bravais lattice. Thus, for a composite incommensurate structure with superspace group \( I\bar{4}/mcm(00q_3)000s \), \( 4/mcm \) refer to the symmetry operations of the host component, \( I(00q_3) \) refer to \((3+1)\)-D Bravais lattice and \( 000s \) refer to the glide-translational operations along the incommensurate directions, where the letter \( s \) stands for 1/2 glide-translation fractional component. Such is the case for K-III, where the guest structure is \( C \)-face centered tetragonal with space group \( C4/mmm \) and the resulting superspace group is \( I\bar{4}/mcm(00q_3)000s \) with \( q_3 = 1.603 \) at 22.1 GPa.

The superspace group of the Ba-IV phase with \( C \)-face centered tetragonal guest structure is \( I\bar{4}/mcm(00q_3)0000 \) with \( q_3 = c_1/c_2 = 1.3884 \). Sr-V and Sc-II also have \( C \)-face centered tetragonal guest structures and their superspace group is \( I4/mcm(00q_3)0000 \) with \( q_3 = 1.404 \) at 56 GPa and with \( q_3 = 1.2804 \) at 23 GPa, respectively. The Bi-III phase has a body-centered tetragonal guest structure and the incommensurate structure is described by the superspace group \( I'/4/mcm(00q_3)0000 \), where \( I' \) denotes the centering \((1/2,1/2,1/2,1/2)\) in superspace and \( q_3 = 1.309 \) at 6.8 GPa. The guest structure of Rb-IV is body-centered tetragonal in the space group \( I4/mmm \) and the superspace group of the composite structure is \( I'/4/mcm(0q_3)000s \) with \( q_3 = 1.631 \) at 16.8 GPa.

5.2 Structural parameters of Sc-II phase

The high-pressure phase of Sc-II was first observed about three decades ago in high-pressure resistivity measurements \([44]\). These studies revealed resistance anomalies at around 17 GPa accompanied by the onset of superconductivity. Energy-dispersive x-ray diffraction experiments on Sc have also shown that at around 20 GPa it undergoes a structural phase transition \([45]\). Surprisingly, Sc did not follow the high-pressure transformation sequence \( hcp \to aSm \to dhcp \to fcc \) predicted for rare-earth elements.
and experimentally confirmed in La and Y [46]. None of the known crystal structures could fit the x-ray diffraction pattern and the exact structure of Sc-II remained a puzzle for more than two decades. Only with the recent development of the angle-dispersive single crystal technique has the structure of Sc-II phase been identified as a composite incommensurate structure.

Initially, the complex phase of Sc-II was determined to be an incommensurate host-guest structure in the superspace group $I4/mcm(00q_3000)$ with the incommensurate ratio of $q_3 = 1.5028$ at 23 GPa [47]. But this solution gives too short guest-guest distance along the chains and thus, a new incommensurate structure in the space group $I4/mcm(00q_3000)$ with $q_3 = 1.2804$ has been proposed [41]. For the first structure that has a tetragonal body-centered guest, the incommensurate ratio was found to increase with pressure up to 1.6 at 104 GPa. If this pressure dependence is corresponded also to $I4/mcm(00q_3000)$ structure, then $q_3$ would increase up to 1.36 with pressure, passing through a commensurate value of $4/3$ at 72 GPa [41].

The incommensurate nature of composite structures prevents the exact electronic structure calculations of these complex phases. However, we can approximate a composite structure with a commensurate analogue (a periodic supercell) and perform ab initio calculations for the approximate structure. Such calculations reproduce the reported transition sequence quite well and can provide us with some insight into the composite structure [48, 49, 50, 51].

In Paper III we describe a procedure that enables us to obtain the total energy of the incommensurate structure and determine the structural parameters of the composite phase by means of first-principle electronic structure calculations for periodic systems. The idea is to approximate the composite structure with a set of commensurate analogues, with a host to guest ratio near the incommensurate one and use the fact that the total energy is a function of the structural parameters and has a minimum for the parameters corresponding to the composite phase. We apply this approach to obtain the structural parameters of the Sc-II phase and we see that the calculated values for the incommensurate ratio, lattice parameters and Wyckoff positions are in excellent agreement with the measured values at 23 GPa [41]. Moreover, we calculated the dependence of the incommensurate ratio on the applied pressure and show that it is qualitatively different from the one predicted from the experimental data. We also show the importance of the structural optimization procedure for the total energy calculations for the commensurate analogues.

The procedure of determining the structural parameters of an incommensurate composite phase by performing ab initio calculations enables us to predict incommensurate structures with numerical simulations. In Paper IV we apply this procedure to predict an incommensurate phase in Ca at high pressures.
6. Structural phase transformations at high temperatures

We solve the Schrödinger equation Eq.(2.4) for an interacting many-particle system via the Born-Oppenheimer approximation Eq.(2.5) which decouples degrees of freedom of electrons and ions. Within this approximation, we freeze the motion of ions and solve the quantum equation of motion for the ground state of the electronic subsystem. For a given structure we can optimize the unit cell parameters and the position of atoms in this cell via Hellmann-Feynman forces and bring the structure to equilibrium at \( T = 0 \text{K} \). Within the framework of the static lattice model, which neglect the thermal motion of atoms and consider them fixed at some average positions, we can still explain a large number of material properties, such as the electronic structure and chemical properties, shapes and symmetry of crystals, material hardness, low temperature structural phase transformations, x-ray, electron and ion beams Bragg scattering, etc [53]. We know, however, that atoms actually move around inside the crystal and this motion gives rise to the concept of temperature. And even at \( T = 0 \text{K} \), atoms are not frozen in fixed positions due to the uncertainty principle [52]. There are a number of properties of matter that cannot be explained by a static model, such as thermal expansion, structural phase transition at finite-temperature, including melting, sound propagation and thermal conductivity, the phenomenon of superconductivity and interaction of radiation with matter, etc [53]. Thus, we need to find an accurate description for the dynamics of the crystal lattice to account for the thermal motions of ions. In many cases such a description is possible due to a classical nature of the ionic motion.

6.1 Lattice dynamics in the quasi-harmonic approximation

The motion of a classical object such as an atom as a whole is determined accurately by the second Newton's law of mechanics:

\[
M \frac{\partial^2 \mathbf{R}(t)}{\partial t^2} = -\nabla U(\mathbf{R}(t), t), \tag{6.1}
\]

where \( M \) is the atomic mass and \( U(\mathbf{R}, t) \) is the instantaneous potential energy of the atom at a position \( \mathbf{R}(t) \). Equation (6.1) is a key equation to de-
scribe the lattice dynamics, and to solve this equation the knowledge of the interatomic interactions or forces in a crystal is needed. Therefore, the concept Hellmann-Feynman forces plays an important role in the description of matter at finite temperature and accurate values of these forces are provided by DFT based \textit{ab initio} calculations.

6.1.1 Lattice vibrations: classical equations of motion

In the following, we assume that at finite temperatures ions oscillate about the equilibrium positions of a static lattice at $T=0K$, and the atomic displacements are small compared to the interatomic distances. Hence, we can unambiguously label each ion with a Bravais lattice site $\mathbf{R}_0 \sigma l$ about which it oscillates, and the instantaneous position of this ion can be written as:

$$\mathbf{R}_\sigma l(t) = \mathbf{R}_0 \sigma l + \mathbf{u}_\sigma l(t), \quad (6.2)$$

where $\mathbf{u}_\sigma l$ is the displacement of an atom $\sigma$ in a unit cell $l$. The total energy $E_{tot}^0$ of the system of interacting electrons and nuclei at $T=0K$, with nuclei fixed at equilibrium positions $\mathbf{R}_0 = (\mathbf{R}_0^1, \ldots, \mathbf{R}_0^i, \ldots, \mathbf{R}_0^N)$ is given by:

$$E_{tot}^0 = E_{KS}(\mathbf{R}_0) + E_{II}(\mathbf{R}_0), \quad (6.3)$$

where $E_{KS}$ is the Kohn-Sham ground state energy of the electronic system in the external potential of fixed nuclei, and $E_{II}$ is the energy due to the electrostatic interaction between ions. The total energy of the system with atoms displaced from their mean equilibrium positions due to thermal agitation can be expanded for small displacements $\mathbf{u}$ as [54]

$$E_{tot}(\mathbf{R}_0 + \mathbf{u}) = E_{tot}^0 + \frac{1}{2} \sum_{\sigma l, \sigma' l'} \Phi_{\sigma l, \sigma' l'}^{\alpha \beta} (\mathbf{u}_\sigma l \mathbf{u}_{\sigma' l'}), \quad (6.4)$$

$$+ \frac{1}{3!} \sum_{\sigma l, \sigma' l', \sigma'' l''} \Phi_{\sigma l, \sigma' l', \sigma'' l''}^{\alpha \beta \gamma} (\mathbf{u}_\sigma l \mathbf{u}_{\sigma' l'} \mathbf{u}_{\sigma'' l''} + \ldots),$$

where, in particular, $\Phi_{\sigma l, \sigma' l'}^{\alpha \beta}$ is the force-constant matrix, given by $\delta^2 E_{tot}/\delta \mathbf{u}_\sigma l \delta \mathbf{u}_{\sigma' l'}$ evaluated at $\mathbf{R}_0$. Thus, for a distorted lattice, the total energy of the system (with frozen ions) differs from that of an ideal lattice by the potential energy of the displaced atoms, which is exactly the quantity required to solve the Newton's equations of motion. If we consider only small displacements, such that we can neglect higher order anharmonic terms in the expansion (6.4), then the problem of the lattice dynamics is reduced to the problem of a system of independent harmonic oscillators, which has an exact solution.
The equations of motion describing the lattice dynamics within the approximation of harmonic motion are:

\[ M_\sigma \ddot{u}_\sigma l = - \frac{\partial E_{tot}(\mathbf{R})}{\partial u_\sigma l} = - \sum_{\sigma', h} \Phi_{\sigma l, \sigma' l + h}^\alpha \beta \dot{u}_{\sigma', l + h}^\beta \]  \hspace{1cm} (6.5)

where \( h = l' - l \), and \( \Phi_{\sigma l, \sigma' l + h}^\alpha \beta = \Phi_{\sigma l, \sigma' l'}^\alpha \beta \), which expresses the fact that the force matrix depends on relative positions of atoms only. One can see that Eqs.(6.5) are invariant under the lattice translations within the quasi-harmonic approximation, thus the displacements of atoms should satisfy the Bloch theorem:

\[ u_{\sigma l}(t) = e^{i q \mathbf{R}_0^0} u_{\sigma}(q, t), \]  \hspace{1cm} (6.6)

where \( q \) is a wave vector defined in the same reciprocal space of wave vectors \( \mathbf{k} \) that describes the electronic states, and the problem of the lattice dynamics reduces to the following eigenvalue problem:

\[ \sum_{\sigma' \beta} \left( D_{\sigma \sigma'}^{\alpha \beta}(q) - \left( \omega_{s q}^0 \right)^2 \delta_{\sigma \sigma'} \delta_{\alpha \beta} \right) u_{\sigma'}^\beta(q) = 0, \]  \hspace{1cm} (6.7)

where \( D_{\sigma \sigma'}(q) \) is the Fourier transform of the force constant matrix known as the dynamical matrix. \( \omega_{s q}^0 \) are the frequencies of the lattice vibrations about the equilibrium positions at \( T = 0K \). The approximation is called quasi-harmonic since the phonon frequencies might depend on volume through the dynamical matrix. For a crystal structure with \( n \) atoms in the unit cell, the system of equations (6.7) has \( 3n \) solutions, labeled \( s \) for each reciprocal vector \( q \). Thus, the displacement of an atom in a crystal can be written as:

\[ u_{\sigma l}(t) = \sum_{q} u_{\sigma s}(q) e^{i q \mathbf{R}_0^0 - \omega_{s q}^0 t}, \]  \hspace{1cm} (6.8)

where \( u_{\sigma s}(q) \) is the amplitude vector that tells us how the atom \( \sigma \) moves under the influence of the wave with frequency \( \omega_{s q}^0 \). It is usual to define a set of new quantities \( Q_{s q} \), referred to as normal mode coordinates, by rewriting Eq.(6.8) as

\[ u_{\sigma l}(t) = \frac{1}{\sqrt{N M_\sigma}} \sum_{q} e_{\sigma s}(q) e^{i q \mathbf{R}_0^0} Q_{s q}(t). \]  \hspace{1cm} (6.9)

Since an atomic displacement is always a real quantity, \( Q_{s q}(t) \) are subject to the following constraint \( Q^*_s \mathbf{q} = Q_{s - \mathbf{q}} \). Vectors \( e_{\sigma s}(q) \) give the direction in which each atom \( \sigma \) moves and is called the displacement vectors or the polarization vectors. On the other hand, these vectors are the eigenvectors of the eigenvalue equations (6.7) and, in order that the normal modes \( Q_{s q} \) to be orthogonal, these eigenvectors satisfy the following orthogonality con-
\[ \sum_{\sigma} e_{\sigma s}(q)e_{\sigma s'}(-q) = \delta_{ss'}. \]  

(6.10)

With the use of the normal mode coordinates, the total (dynamical) energy of a harmonic lattice can be written as

\[ E_{latt} = \frac{1}{2} \sum_{sq} \left( Q_{sq} \dot{Q}_{s-q} + \left( \omega_{sq}^0 \right)^2 Q_{sq} Q_{s-q} \right). \]

(6.11)

Hence, we have got that the energy of oscillating atoms in the crystal is a sum of the energies of independent harmonic oscillators. We can now define the normal mode momenta \( P_{sq} \)

\[ P_{sq} = \frac{\partial E_{latt}}{\partial \dot{Q}_{sq}}, \]

(6.12)

and write the Hamiltonian of the harmonic lattice as

\[ H_{latt} = \frac{1}{2} \sum_{sq} \left( P_{sq} P_{s-q} + \left( \omega_{sq}^0 \right)^2 Q_{sq} Q_{s-q} \right). \]

(6.13)

### 6.1.2 Lattice vibrations: quantum mechanics

Although we considered ions classical objects and made use of Newtonian mechanics to derive the lattice equations of motion, the real behavior of Nature is described by quantum physics. Thus, the dynamical lattice will be described by a wave function \( |\Psi\rangle \), which is the solution of the Schrödinger equation with the lattice Hamiltonian \( H_{latt} \) (6.13):

\[ \mathcal{H} |\Psi\rangle = \frac{1}{2} \sum_{sq} \left( \rho_{sq} \rho_{s-q} + \omega_{sq}^0 \delta_{sq} \rho_{s-q} - i \rho_{sq} \right) |\Psi\rangle = \mathcal{E} |\Psi\rangle, \]

(6.14)

where \( \rho_{sq} \) and \( \delta_{sq} \) are the operators corresponding to normal mode momenta and coordinates, respectively (the frequency superscript "0" is omitted for simplicity throughout this subsection). As has already been mentioned, we can exactly solve the quantum mechanical problem for the harmonic oscillator, and an elegant way to solve it is through the formalism of annihilation and creation operators, defined as:

\[ a_{sq} = \frac{1}{\sqrt{2\hbar \omega_{sq}}} \left( \omega_{sq} \delta_{sq} + i \rho_{sq} \right), \]

(6.15)

\[ a_{sq}^{\dagger} = \frac{1}{\sqrt{2\hbar \omega_{sq}}} \left( \omega_{sq} \delta_{sq}^{\dagger} - i \rho_{sq}^{\dagger} \right). \]

(6.16)

With the help of the new operators, the Schrödinger equation for the harmonic lattice can be written as

\[ \mathcal{H} |\Psi\rangle = \sum_{sq} \hbar \omega_{sq} \left( a_{sq}^{\dagger} a_{sq} + \frac{1}{2} \right) |\Psi\rangle, \]

(6.17)
and within the *quasi-particles* formalism, its solutions are obtained in a straightforward way. In a complete analogy with *photons*, which is a quantum concept that describes the electromagnetic waves in the particle representation, we can describe the elastic waves of oscillating atoms in terms of *phonons*. Thus, the creation and annihilation operators create and, respectively, annihilate a phonon. The ground state of the crystal is the static lattice \( |0\rangle \) with no thermally excited atoms at all. Since we have no quasi-particles, \( a_{sq}|0\rangle = 0 \), and for the ground state of the crystal lattice we have:

\[
\mathcal{H}|0\rangle = \sum_{sq} \hbar \omega_{sq} \left( a_{sq}^{\dagger} a_{sq} + \frac{1}{2} \right) |0\rangle = \frac{1}{2} \sum_{sq} \hbar \omega_{sq} |0\rangle.
\] (6.18)

This extraordinary result means that the energy of the static lattice \( \mathcal{E}_0 \) is not zero, but equal to

\[
\mathcal{E}_0 = \frac{1}{2} \sum_{sq} \hbar \omega_{sq}.
\] (6.19)

This energy is called a *zero-point energy* and implies that atoms cannot be frozen even at absolute zero. Now, an excited lattice with \( n \) phonons with frequency \( \omega_{sq} \) is described by a state \( |n_{sq}\rangle \), which is the eigenvector of the *number operator* \( a_{sq}^{\dagger} a_{sq} \):

\[
a_{sq}^{\dagger} a_{sq} |n_{sq}\rangle = n_{sq} |n_{sq}\rangle,
\] (6.20)

and a corresponding energy of this state is

\[
\mathcal{E}_{n_{sq}} = \hbar \omega_{sq} \left( n_{sq} + \frac{1}{2} \right).
\] (6.21)

### 6.2 Thermodynamics of the harmonic crystal

If a many-particle system is at thermal equilibrium and the macroscopical state of the system can be realized through \( N \) microscopical states, then the probability of that the system is in a state \( |n\rangle \) with the energy \( E_n \) is given by

\[
P_n = \frac{1}{\mathcal{Z}} \exp \left( - \frac{E_n}{k_B T} \right),
\] (6.22)

where

\[
\mathcal{Z} = \sum_{n} \exp \left( - \frac{E_n}{k_B T} \right),
\] (6.23)

is the *partition function* and \( k_B \) is the Boltzmann constant. If \( A \) is the quantum mechanical operator of an observable quantity, then the average or expectation value of that quantity for a system at thermal equilibrium is given by

\[
\langle A \rangle = \frac{1}{\mathcal{Z}} \sum_{n} \langle n|A|n\rangle \exp \left( - \frac{E_n}{k_B T} \right),
\] (6.24)
and this expression is a paramount relation of the statistical mechanics [55]. The main principle of the statistical mechanics states that the knowledge of the partition function $\mathcal{Z}$ determines all the thermodynamic properties of the system. The free energy $F$ is defined as

$$F = -k_B T \ln \mathcal{Z} = -k_B T \ln \left( \sum_n \exp \left( -\frac{E_n}{k_B T} \right) \right), \quad (6.25)$$

the entropy $S$ of the system is defined as

$$S = -k_B \sum_n P_n \ln P_n, \quad (6.26)$$

and the internal energy $E$ is given by a fundamental expression (6.27):

$$E = \frac{1}{\mathcal{Z}} \sum_n E_n \exp \left( -\frac{E_n}{k_B T} \right). \quad (6.27)$$

It is easy to show that for a system built of several independent subsystems, such that $E_n = \sum_i E_{n_i}$, where $E_{n_i}$ is the energy of the subsystem $i$, the total free energy is a sum of subsystem free energies:

$$F = -k_B T \ln \left( \sum_n \exp \left( -\frac{E_n}{k_B T} \right) \right) = -k_B T \ln \left( \sum_i \exp \left( -\frac{\sum E_{n_i}}{k_B T} \right) \right) \quad (6.28)$$

$$= -k_B T \ln \prod_i \left( \sum_{n_i} \exp \left( -\frac{E_{n_i}}{k_B T} \right) \right) = -k_B T \sum_i \left[ \ln \left( \sum_{n_i} \exp \left( -\frac{E_{n_i}}{k_B T} \right) \right) \right] = \sum_i F_i.$$

Now, for a system of harmonic oscillators at thermal equilibrium, the partition function $\mathcal{Z}_i$, the free energy $F_i$, and the internal energy $E_i$ of an oscillator $i$ in a quantum state $|n_i\rangle$ and energy $E_{n_i} = \hbar \omega_i (n_i + 1/2)$, are given by

$$\mathcal{Z}_i = \sum_{n_i} \exp \left[ -\frac{\hbar \omega_i (n_i + 1/2)}{k_B T} \right] = \frac{e^{-\hbar \omega_i / 2k_B T}}{1 - e^{-\hbar \omega_i / k_B T}}, \quad (6.29)$$

$$F_i = -k_B T \ln \mathcal{Z}_i = \frac{\hbar \omega_i}{2} + k_B T \ln \left( 1 - e^{-\hbar \omega_i / k_B T} \right), \quad (6.30)$$

and

$$E_i = \frac{\partial}{\partial (1/T)} \left( \frac{F_i}{T} \right) = \frac{\hbar \omega_i}{2} + \frac{\hbar \omega_i}{e^{\hbar \omega_i / k_B T} - 1}. \quad (6.31)$$

Hence,

$$F = \sum_i \left[ \frac{\hbar \omega_i}{2} + k_B T \ln \left( 1 - e^{-\hbar \omega_i / k_B T} \right) \right], \quad (6.32)$$

$$E = \sum_i \left[ \frac{\hbar \omega_i}{2} + \frac{\hbar \omega_i}{e^{\hbar \omega_i / k_B T} - 1} \right]. \quad (6.33)$$
An important quantity, the average occupation number $\bar{n}_i$ of states $|n_i\rangle$ is defined through the following relation:

$$E_i = \left(\bar{n}_i + \frac{1}{2}\right)\hbar\omega_i,$$

(6.34)

and is given by the following distribution:

$$\bar{n}_i(T) = \frac{1}{e^{\hbar\omega_i/k_BT} - 1}.$$  

(6.35)

Equations (6.32-6.35) with $i = (sq)$ allow us to completely describe the lattice dynamics of the harmonic crystal. Since, for a large periodic system, the reciprocal vectors are quasi-continuous, it is of practical convenience to use the integral expressions for $F$ and $E$:

$$F = \int_0^\infty d\omega g(\omega) \left[ \frac{\hbar\omega}{2} + k_B T \ln \left(1 - e^{-\hbar\omega/k_BT}\right) \right],$$

(6.36)

$$E = \int_0^\infty d\omega g(\omega)\hbar\omega \left[ \frac{1}{2} + \bar{n} \left(\frac{\hbar\omega}{k_BT}\right) \right],$$

(6.37)

where $g(\omega)$ is the phonon density of states.

6.3 Calculating phonons: the small displacement method

Within the quasi-harmonic approximation, the relation between the Hellmann-Feynman forces, $F_{\sigma l}$, acting on atom $\sigma$ in a unit cell $l$, and the displacements $u_{\sigma'l'}$ is given by the force-constant matrix $\Phi_{\sigma\alpha l,\sigma'\beta l'}$:

$$F_{\sigma l}^\alpha = -\frac{\partial E(u)}{\partial u_{\sigma l}^\alpha} = -\sum_{\sigma'\beta l'} \Phi_{\sigma l,\sigma'\beta l'}^\alpha u_{\sigma' l'}^\beta,$$

(6.38)

and the vibrational frequencies $\omega_{sq}^0$ are the eigenvalues of the dynamical matrix $D_{\sigma\sigma'}(q)$, defined as:

$$D_{\sigma\sigma'}^{\alpha\beta}(q) = \frac{1}{\sqrt{M_{\sigma}M_{\sigma'}}} \sum_l \Phi_{\sigma l,\sigma' l'}^{\alpha\beta} \exp \left[i q (R_{\sigma l}^0 - R_{\sigma' l'}^0)\right].$$

(6.39)

If the complete force-constant matrix is known, then the dynamical matrix $D_{\sigma\sigma'}(q)$, and the phonon frequencies $\omega_{sq}^0$ can be obtained at any $q$.

There are basically two elegant approaches to calculate phonons in a crystal by means of ab initio electronic structure calculations. One strategy, called linear response method, calculates the dynamical matrix in the framework of the Density Functional Perturbation Theory (DFPT) [56]. The main idea to calculate the phonon dispersion in DFPT is based on the fact that the linear order variation in the electron charge density upon the appli-
cation of a perturbation to the crystal induces a variation in energy up to a third order of the perturbation [57]. Thus, using the standard perturbation theory, the linear order variation of the electronic charge density can be calculated using only the ground state wave-functions of the crystal, which are provided by DFT calculations. If the perturbation is a vibrational wave with wave-vector $\mathbf{q}$, then the dynamical matrix at that wave-vector $D_{\sigma\sigma'}(\mathbf{q})$ can be obtained by calculating the change of the charge density to linear order in the perturbation theory.

Another approach to calculate phonon frequencies, called small displacement method [59], is based on the fact that for small displacements, the relation between forces and displacements is linear (Eq.(6.38)). All that has to be done is to displace a single atom $\sigma'$ from the equilibrium position $\mathbf{R}_0^{\sigma'}$ in the unit cell $l'$ in the Cartesian direction $\beta$ by a small displacement $u_\beta^{\sigma',l'}$, providing that all other atoms are held fixed at their equilibrium positions $\mathbf{R}_0^\sigma$. Then, the forces $F_{\sigma l}^\alpha$ acting on all other atoms give directly the elements of the force-constant matrix $\Phi_{\sigma l,\sigma' l'}^{\alpha\beta}$ for the given $(\sigma' l').$ In a general case, we have to repeat this procedure $3n$ times, where $n$ is the number of atoms in the unit cell, however the 3D space group symmetry of the lattice reduces this number substantially. The small displacement method gives the exact force-constant matrix in the limit of infinite crystal. In practical calculations, a crystal is replaced by a super-cell, and in order to get accurate results, the super-cell must be large enough so that the elements $\Phi_{\sigma l,\sigma' l'}^{\alpha\beta}$ vanish at the boundaries. Because of the periodic boundary conditions, the dynamical matrix is exactly calculated at reciprocal wave vectors commensurate with the supercell lattice vectors. The reason is that moving one atom in the supercell also means moving all its periodic images, and consequently, the relation between the force is not linear any more:

$$F_{\sigma l}^\alpha = -\sum_{L} \frac{\partial E(\mathbf{U})}{\partial u_{\sigma,l+L}^{\alpha}} = -\sum_{L} \sum_{\sigma' l'} \Phi_{\sigma,l+L;\sigma' l'}^{\alpha\beta} u_{\sigma',l'+L}^{\beta},$$

$$=-\sum_{L} \sum_{\sigma' l'} \Phi_{\sigma,l+L;\sigma' l'}^{\alpha\beta} u_{\sigma',l'},$$

(6.40)

where $l$ labels the unit cell position in the supercell, $L$ labels all possible images of the supercell. The corresponding dynamical matrix is given by

$$D_{\sigma\sigma'}^{\alpha\beta}(\mathbf{q}) = \frac{1}{\sqrt{M_\sigma M_{\sigma'}}} \sum_{L} \sum_{l} \Phi_{\sigma,l+L;\sigma' l'}^{\alpha\beta} \exp\left[i\mathbf{q}\left(\mathbf{R}_0^{\sigma' l'} - \mathbf{R}_0^{\sigma l}\right)\right],$$

(6.41)

where $\mathbf{R}_L$ is a vector connecting two supercells. One can see, that for reciprocal vectors $\mathbf{q}$ such that $\mathbf{q}\mathbf{R}_L = 2n\pi$ the above expression gives the exact dynamical matrix (6.39).
Figure 6.1: (Color online) Phonon spectra of bcc Mo calculated by using 6x6x6 supercell for a set of different k-meshes in the Brillouin zone. Symbols denote the experimentally measured phonon frequencies for the transverse (T₁,T₂) and longitudinal (L) acoustic branches.

The advantage of the small displacement method is that it works as an add-on to any DFT code that provides forces. However, the need to use large supercells makes it computationally less efficient. The advantage of the linear response method is that it is capable to give the exact phonon frequencies at requested points, which is suitable for systems with anomalies in the phonon dispersion.

In Fig.6.1 and Fig.6.2, phonon dispersion relations for the bcc phase of Mo at ambient pressure are shown as an example of phonon calculations using the small displacements method. Forces have been calculated with the aid of the VASP code, with the electron exchange-correlation described within the LDA, and phonon spectra have been calculated by the PHON code [60]. Total energy calculations have been performed at the calculated equilibrium volume for a static lattice with the temperature of the electronic system $T_{el} = 300K$, and calculated phonon frequencies are compared with the experimental spectrum at $T = 300K$. Calculations have been done for different supercell sizes and different k-meshes in the Brillouin zone. The results of phonon calculations are in a very good agreement with the experimental data, except for the vicinity of high symmetry points H and N at the boundary of the Brillouin zone, where the phonon spectrum shows some anomalies. The accuracy of the phonon calculations strongly depends in this case on the amount of k-points used to sample the Brillouin zone, since, despite the large size of the supercell, we need a large number of k-points to account for the complex Fermi surface of the bcc Mo.
Figure 6.2: (Color online) Phonon spectra of bcc Mo calculated by using 7x7x7 supercell for a set of different k-meshes in the Brillouin zone. Symbols denote the experimentally measured phonon frequencies for the transverse (T₁, T₂) and longitudinal (L) acoustic branches.

6.4 Calculating phonons at $T \neq 0$: the SCAILLD method

The assumption of small displacements appears to be reasonable in most solids for temperatures well below the melting point. However, some equilibrium properties of the crystal, like the thermal expansion and the dependence of the elastic constants on volume and temperature can be explained only by the presence of anharmonic terms in the expansion of the ionic interaction energy about the equilibrium value. In a real crystal, the force-constant matrix does depend on the equilibrium lattice about which the harmonic expansion of the potential energy is made, and, thus, the vibration frequencies have an implicit volume dependence. One can express the change of the normal-mode frequencies when the equilibrium lattice vectors are changed from $R^0_{\sigma l}$ to $(1 + \epsilon)R^0_{\sigma l}$, via the coefficients of the anharmonic terms in the expansion of the potential energy about the equilibrium positions $R^0_{\sigma l}$ [58]. From the thermodynamic relations

$$F = E - TS, \quad P = -\left(\frac{\partial F}{\partial V}\right)_T, \quad T\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial E}{\partial T}\right)_V,$$

we can express the pressure $P$ entirely in terms of internal energy as:

$$P(V, T) = -\frac{\partial}{\partial V} \left( E(V, T) - T \int_0^T dT' \frac{1}{T'} \frac{\partial E(V, T')}{\partial T'} \right), \quad (6.42)$$

64
and using the expression for the internal energy $E$ of the dynamical lattice, given by Eq.(6.33), one finds that

$$P(V, T) = -\sum_{s q} \frac{\partial (\hbar \omega_{s q}^0(V))}{\partial V} \left[ \frac{1}{2} + n(\hbar \omega_{s q}^0(V)) \right].$$  (6.43)

According to (6.43), the equilibrium pressure depends on temperature only because the phonon frequencies depend on the equilibrium volume of the crystal. For an isotropic crystal the coefficient of thermal expansion is given by

$$\alpha = \frac{1}{3 V} \left( \frac{\partial V}{\partial T} \right)_p = \frac{1}{3 B} \left( \frac{\partial P}{\partial T} \right)_V,$$  (6.44)

where $B = -V(\partial P/\partial V)_T$ is the *bulk modulus*. Substituting the expression for pressure into the above equation, we find that the coefficient of the thermal expansion in the quasi-harmonic approximation can be written as

$$\alpha = -\frac{1}{3B} \sum_{s q} \frac{\partial (\hbar \omega_{s q}^0(V))}{\partial V} \frac{\partial n(\hbar \omega_{s q}^0(V))}{\partial T}.$$  (6.45)

We can see that the phonon picture of the lattice dynamics provides a good description of the thermal effects at moderate temperatures and *ab initio* methods of electronic structure and phonon calculations can accurately describe thermodynamics of the system of interacting electrons and vibrating ions. One can account for thermal excitations of the electronic subsystem providing that the Helmholtz free energy $F$ is the variational functional in the Kohn-Sham approach [61]. Thus, the free energy of the electrons $F_{el}^0$ at finite temperature $T$ and equilibrium volume $V$, is given by

$$F_{el}^0(T, V) = E_{tot}^0(V, T) - T S_{el}^0,$$  (6.46)

where the electronic entropy $S_{el}^0$ is expressed in terms of an occupation number $f_i$ of the Kohn-Sham orbital $i$, given by the Fermi-Dirac distribution at finite temperature as,

$$S_{el}^0 = -2k_B T \sum_i (f_i \ln f_i + (1 - f_i) \ln(1 - f_i)).$$  (6.47)

The superscript "0" in the above equations indicates that the considered quantities are evaluated for a static lattice with atoms fixed at their equilibrium lattice positions $\mathbf{R}_{\sigma l}^0$, at electronic temperature $T$. Hence, the total free energy $F^0$ of the system of electrons and vibrating atoms at a given temperature $T$ can be written as

$$F^0(V, T) = F_{el}^0(V, T) + F_{ph}^0(V, T),$$  (6.48)
where the phonon contribution to the free energy $F_{ph}^0$ is given by (6.32)

$$F_{ph}^0(V, T) = k_B T \sum_{s q} \ln \left( \frac{2 \sinh (\hbar \omega_{sq}^0 / 2 k_B T)}{2 \sinh (\hbar \omega_{sq}^0 / 2 k_B T)} \right),$$

(6.49)

and the phonon frequencies are calculated within the quasi-harmonic approximation of the lattice with atoms vibrating about the equilibrium lattice positions $\mathbf{R}_{q\ell}^0$. At finite temperature, the total free energy $F^0$ might not be minimal for atoms oscillating about the equilibrium configuration $\overline{\mathbf{R}}_0$, and the crystal will change its volume until the minimum of the free energy is reached. We can calculate the free energy for a set of given volumes at fixed temperature and, by fitting to an equation of state, obtain properties of the solid at finite temperature, like the equilibrium volume, bulk modulus, Grüneisen parameter, linear thermal expansion coefficient $\alpha$, etc.

The knowledge of the phonon spectrum provides also valuable information about the dynamical stability of a crystalline structure at a certain thermodynamic state. The dynamical stability means that under an external perturbation, atoms will move around the equilibrium positions of the unperturbed lattice $\overline{\mathbf{R}}_0$, and that the ionic interaction energy is minimal at the equilibrium lattice positions $\overline{\mathbf{R}}_0$. In this case, all the phonon frequencies are positive (except the acoustic phonons at $\Gamma$ point) real numbers. If, however, phonon calculations yield imaginary frequencies, then this might be a sign that the structure is dynamically unstable and under a perturbation, the atoms will prefer to move about a new equilibrium lattice $\overline{\mathbf{R}}_0$. The study of dynamical stability is closely related to the study of structural phase transitions. The knowledge of the thermodynamic functions describing the system under consideration helps us to understand the mechanism behind the structural phase transition. The knowledge of the phonon dispersion allows us to accurately calculate the lattice contribution to the free energy. However, within the quasi-harmonic approximation, we can calculate only the phonon frequencies $\omega_{sq}^0$ corresponding to zero lattice temperature. If a given crystal structure is dynamically unstable at low temperature, but becomes stable at finite temperature, then we cannot use the quasi-harmonic lattice dynamics model, since a phonon calculation would yield imaginary frequencies. We have to go beyond the harmonic expansion in the lattice energy, which makes the problem of lattice dynamics less tractable.

Recently, Souvatzis et al have developed an elegant self-consistent ab initio lattice dynamics approach (SCAILD) to calculate the phonon spectrum at finite temperature [62]. The idea of the SCAILD method is to calculate the re-normalization of the phonon frequencies $\omega_{sq}^0$ due to the effect of temperature and account for the anharmonic terms in the expansion (6.4) within the framework of harmonic formalism. The system of interacting phonons with frequencies $\omega_{sq}^0$ is substituted by a system of independent phonons with re-normalized frequencies $\omega_{sq}$, described by a mean-field Hamilto-
\[ \mathcal{H} = \frac{1}{2} \sum_{\mathbf{q}} \left( \mathcal{D}_{\mathbf{s}} \mathcal{D}_{\mathbf{s} - \mathbf{q}} + \omega^2_{\mathbf{s}} \mathcal{D}_{\mathbf{s}} \mathcal{D}_{\mathbf{s} - \mathbf{q}} \right). \]  

(6.50)

The re-normalized frequencies \( \omega_{\mathbf{s}} \) are the eigenvalues of a re-normalized dynamical matrix \( \tilde{\mathbf{D}}_{\sigma\sigma'}(\mathbf{q}) \), and the forces are calculated for a configuration of atoms displaced around the equilibrium positions \( \mathbf{R}^0_{\sigma l} \) according to the phonon distribution \( n(h \omega_{\mathbf{s}}/k_B T) \) at finite \( T \). The practical implementation of SCAILD is done within the framework of the small displacement method, and the displacement of an atom \( \sigma \) in the unit cell \( l \) at a given temperature is a superposition of all phonons with wave vectors \( \mathbf{q} \) commensurate with the supercell:

\[ u_{\sigma l}(T) = \frac{1}{\sqrt{N}} \sum_{\mathbf{q}} e^\sigma_{\mathbf{s} \mathbf{q}} \mathcal{F}_{\mathbf{s} \mathbf{q}}^\sigma(T) e^{\mathbf{q} \mathbf{R}^0_{\sigma l}}, \]

(6.51)

where \( e^\sigma_{\mathbf{s} \mathbf{q}} \) are the eigenvectors of the dynamical matrix \( \tilde{\mathbf{D}}_{\sigma\sigma'}(\mathbf{q}) \), and the displacement amplitudes \( \mathcal{F}_{\mathbf{s} \mathbf{q}}^\sigma \) are given by

\[ \mathcal{F}_{\mathbf{s} \mathbf{q}}^\sigma(T) = \pm \sqrt{\left( \mathcal{D}_{\mathbf{s}} \mathcal{D}_{\mathbf{s} - \mathbf{q}} \right) / M_\sigma} = \pm \sqrt{\frac{\hbar}{M_\sigma \omega_{\mathbf{s}}} \left[ \frac{1}{2} + n \left( \frac{\hbar \omega_{\mathbf{s}}}{k_B T} \right) \right]]. \]

(6.52)

The above expression is correct in the classical limit, thus the method can be applied only at elevated temperatures. The SCAILD method alternates between setting up atomic displacements based on phonon frequencies and evaluating the phonon frequencies from \textit{ab initio} calculated forces acting on the displaced atoms in a self-consistent way. For the first iterative step zero temperature phonon frequencies \( \omega^0_{\mathbf{s}} \) and corresponding eigenvectors serve to calculate a finite temperature atomic configuration, and a new set of phonon frequencies are obtained from the Fourier transform \( \mathbf{F}_{\sigma \mathbf{q}} \) of the Hellmann-Feynman forces,

\[ \overline{\omega^2_{\mathbf{s}}} = \sum_{\sigma} e^\sigma_{\mathbf{s} \mathbf{q}} \mathbf{F}_{\sigma \mathbf{q}} / M_\sigma \mathcal{F}_{\mathbf{s} \mathbf{q}}^\sigma. \]

(6.53)

Symmetry of different \( \mathbf{q} \) vectors is restored by

\[ \Omega^2_{\mathbf{s} \mathbf{q}} = \frac{1}{m_\mathbf{q}} \sum_{S \in S(\mathbf{q})} \overline{\omega^2_{\mathbf{s} S^{-1} \mathbf{q}}}, \]

(6.54)

where \( S(\mathbf{q}) \) is the symmetry group of the wave vector \( \mathbf{q} \), and \( m_\mathbf{q} \) is the number of group elements. Finally, the re-normalized frequencies at the iteration step \( N_I \) are calculated according to the expression

\[ \omega^2_{\mathbf{s}} = \frac{1}{N_I} \sum_{i} \Omega^2_{\mathbf{s} i}, \]

(6.55)
and these frequencies are used to generate a new set of atomic displacements $\mathbf{u}$ [63]. Within the SCAILD approach, Souvatzis et al have been able to reproduce the measured phonon spectrum of the high-temperature bcc phase of group IVB elements Ti, Zr and Hf. Now, since there is a reliable method to calculate phonons at high temperature, we can make use of the phonon formalism to describe accurately the thermodynamics of the crystal at elevated temperatures. We can use Eq.(6.49), for example, to calculate the free energy of the lattice by substituting $\omega_{sq}$ with $\omega_{sq}$:

$$F_{ph}(V, T) = k_B T \sum_{sq} \ln \left( 2 \sinh \left( \frac{\hbar \omega_{sq}}{2 k_B T} \right) \right). \quad (6.56)$$

In Paper V, we show how to calculate in a correct way the total free energy of the system of interacting electrons and nuclei at high temperatures by using the SCAILD method.

In the quasi-harmonic approximation for a given volume $V$ and temperature $T$, the phonon free energy $F_{ph}^0(V, T)$, calculated within the linear-response or small displacement methods, is evaluated at the same pressure $P$ as the free energy of the electronic system $F_{el}^0(V, T)$, and therefore Eq.(6.48) applies for the total free energy calculation. In the SCAILD method, all atoms are displaced from the equilibrium lattice positions according to the temperature distribution of phonons, and, therefore, such a system will have an equilibrium volume $V'$ different than that of the ideal lattice. But, since we keep the volume constant during our simulations, the system with a dynamical lattice will experience an external pressure $P' \neq P$. Therefore, we cannot combine $F_{el}^0(V, T)$ and $F_{ph}(V, T)$ to obtain the total free energy $F(V, T)$ at fixed $(V, T)$. However, we have a possibility to estimate the electronic free energy of the ideal lattice at the same pressure as the phonon spectrum is calculated, all the necessary ingredients being implemented within the SCAILD approach. The self-consistent iterative procedure implies that total energy $ab\ initio$ calculations are performed over an ensemble of $N_I$ randomly generated configuration of ions, and the free electronic energy of the perturbed system, $F_{el}(V, T, \mathbf{u})$,

$$F_{el}(V, T, \mathbf{u}) \equiv E_{tot}(V, T, \mathbf{u}) - TS_{el} \quad \text{(6.57)}$$

$$= E_{tot}(V, T) - TS_{el} + U_{latt}(V, T, \mathbf{u}) \approx F_{el}(V, T) + U_{latt}(V, T, \mathbf{u}),$$

is calculated at each iterative step $i$. In the above expression, $U_{latt}(V, T, \mathbf{u})$ is the potential energy of the distorted lattice. We can evaluate the free electronic energy $F_{el}(V, T)$ of the undistorted lattice by averaging (6.57) over the ensemble of a large number of configurations,

$$\langle F_{el}(V, T, \mathbf{u}) \rangle_{\mathbf{u}} \approx F_{el}(V, T) + \langle U_{latt}(V, T, \mathbf{u}) \rangle_{\mathbf{u}} \quad \text{(6.58)}$$

assuming that $\langle U_{latt} \rangle \approx (1/2)E_{ph}(V, T)$, where $E_{ph}(V, T)$ is the phonon internal energy. Thus, we can calculate the free energy of the entire system at
a given volume $V$ and temperature $T$ as

$$F(V, T) = F_{el}(V, T) + F_{ph}(V, T).$$  \hspace{1cm} (6.59)

Finally, we have to calculate $F(V, T)$ over a set of volumes in order to obtain the equilibrium volume at a given temperature $T$. 
Acknowledgment

Lilia asked me one day:
“Do you want to go to Sweden?”
“I have to think about it ...”
“You have nothing to think about, you are going!”
(Guess what? She was right!)

So I want to thank Prof. M. A. Liberman for inviting me here and also for giving me a few life lessons.

When I arrived in Sweden I had a guardian angel. His name is Börje Johansson and although he has no wings, he made my PhD take off and fly. Without him it would still be on the ground.

After some time I met my current supervisor, Rajeev Ahuja whom I thank for introducing me to the methods of electronic structure calculations, giving me the opportunity to study some interesting topics of high-pressure physics, paying my salary and above all, letting me do things MY way.

We’ve spent many hours wondering about the nature of science, the science of nature and of course Science and Nature with Anatoly Belonoshko, Natalia Skorodumova and Oleg Peil. Many more hours are to come with Anatoly especially. Thank you guys for the great ideas.

Thank you Jailton Almeida for guiding me through my first steps with calculations and Arkady Mikhaylushkin for challenging me in calculation battles!

I also met some hard working guys from the Theoretical Magnetism group, Olle Eriksson, Petros Souvatzis and Dominik Legut and got to do some great science with them as well.

Other inquiring minds that I met along the way respond to the names Eyvas Isaev, Anden Blomqvist, Moyses Araújo, Kim Duck Young, Andrea Taroni, Vitalie Boțan and Slava Korepov.

Wei is especially acknowledged for all the times we’ve disagreed!

I am also very thankful to Susan Mirbt for listening, advising and offering her support when I most needed help. Many thanks to Gunnel Ingelög and Elisabeth Bill for administrative assistance.

While writing this thesis, the following people offered to help. I want to thank Carlos Ortiz for the swedish translation of the Introduction, Oleg Peil for taking care of mathematical expressions and Panos Korelis for making the text of this thesis a bit more fun to read.

The last place on this list (but not in my heart) belongs to the following people: Moreno Marcellini, Panos Korelis, Vasili Hauryliuk, Oleg Peil, Damir Valiev, Andrey & Julia Smerechuk, Yuri Khotyaintsev & Tanya Leonova, Natalia Fedulova, Leonid Mokrushin.

And the first place in my heart belongs to these two people: Lilia and Alex.
Bibliography


[22] F. D. Murnaghan, PNAS 30, 244 (1944).


[60] Dario Alfè, http://chianti.geol.ucl.ac.uk/~dario/


A doctoral dissertation from the Faculty of Science and Technology, Uppsala University, is usually a summary of a number of papers. A few copies of the complete dissertation are kept at major Swedish research libraries, while the summary alone is distributed internationally through the series Digital Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology. (Prior to January, 2005, the series was published under the title “Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology”.)