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Density Functional Theory and *a Simulation of Water absorption on a Germanium Surface.*

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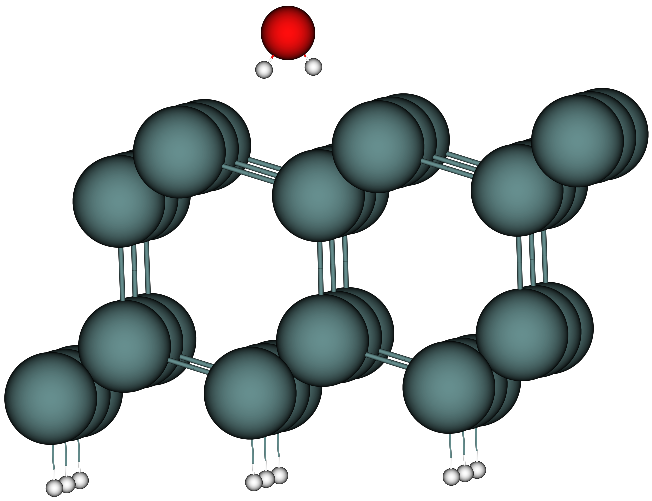

MATHEMATICAL PROJECT COURSE MAM209
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Abstract

This project has to main goals, one leading to the other. To simulate the effects, when a molecule interacts with a surface, one has to understand the underlying theory. When modeling on atomic level, one has to use quantum theory. Schrödingers equation, which is a corner stone of quantum physics, is not possible to solve for our problem. So we have to find an approximation. The method we have used in this project is called Density Functional Theory. In our report we are going to present some basic mathematical and physical concepts, which are importent to be able to understand DFT. At the end of this report we present the results of our simulations. The aims of the simulations is to study the effects on a Germanium when a water molecule interacts with the surface. The simulations was done, using the ab initio software AIMPro.

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CHAPTER

ONE

Introduction

At our present time, we know much more about atoms and nature than Democritos did. We know, for example, that the core of the atom contains protons and neutrons and that there is a cloud of electrons surrounding the atom kernel. The protons and neutrons can be divided to even smaller pieces of matter called quarks. We know this because our knowledge and curiosity for doing experiments and explaining nature with mathematics is greater then before. We use mathematics as a tool to model our experiments. To describe and model the subatomic world we use the mathematical language - quantum physics, with it the Schrödinger equation to solve systems of atoms. Classical and modern physics fail on a microscopic level because the behavior of nuclei and electrons is governed by quantum theory. Nobody knows why and when the quantum effects cease to act on our world - the macroscopic level because our current physical theory is not fully developed yet. But as we speak, scientists are trying to solve the problem by searching for a unified theory that can describe all physical phenomena. This of course is not that easy, and far from being solved.

For example a microscopic piece of solid contains so many atoms that the number of variables and interactions makes the Schrödinger equation impossible to solve analytically or numerically. Even a very tiny object, hardly visible by the naked eye contains thousands of billions of electrons, and the complexity of their motion is enormous. Because electrons are charged and repel one another, the motion of each electron depends on the motion of all others. Trying to calculate the system of this complexity exactly is beyond the capacity of the most powerful computers. But the good news is that if we solve a microscopic system up to a thousand atoms, we get an approximate, often valid system on a macroscopic system about 10^{23} atoms. So we attack

the problem using special methods based on various approximations.

To make calculations easier we create a cluster of atoms where we either terminate the atoms at the boundary with hydrogen atoms [1] or apply boundary conditions.

One of the approximation method is the *The Born-Oppenheimer Approximation*. It makes the assumption that the electronic motion and the nuclear motion in molecules can be separated. It leads to a molecular wave function in terms of electron positions $\mathbf{r}_i$ and nuclear positions $\mathbf{R}_j$.

$$\Psi_{molecule}(\mathbf{r}_i, \mathbf{R}_j) = \Psi_{electrons}(\mathbf{r}_i, \mathbf{R}_j) + \Psi_{nuclei}(\mathbf{R}_j)$$

We assume that the electronic wave function depends upon the nuclear positions $\mathbf{R}_j$ but not upon their velocities. The nuclear motion is so much slower than electron motion that they can be considered to be fixed.

Another approximation is *The Pseudopotential Approximation*. The study of Physics and Chemistry shows that the core electrons of different atoms are almost independent of the environment surrounding the atom and that only the valence electrons participate strongly in interactions between atoms. Thus, the core electron states may be assumed to be fixed and a pseudopotential may be constructed for each atomic species which takes into account the effects of the nucleus and core electrons. The pseudo wave functions corresponding to this modified potential do not exhibit the rapid oscillations of the true wave functions, dramatically reducing the number of plane waves needed for their representation. The calculations then need only explicitly consider the valence electrons, offering a further saving in effort.

We can use methods like empirical[2], semi empirical or *ab initio*[3] to generate our results. Quantum Monte Carlo, Hartree-Fock and Density Functional are all techniques that are *ab initio* methods. The advantage of using *ab initio* methods is that we are not dependent on experimental data. These methods will in the future have a positive impact on for example the farmaceutical industry and materials science. But the methods require fast supercomputers and take a lot of calculation time. The good news, as most of us know, is that computers are getting faster. With the upcoming introduction of the Cell Processor with multiple kernels, we can even push the limit further. But with todays computers we can simulate very accurately a system of atoms composed of about one thousand atoms in a reasonable time (i.e., a couple of days).

The *Hartree-Fock* method was developed in the 1930's and is today widely used in electronic structure calculations. The chemists love this method because it makes it possible to calculate the characteristics of small molecules with high accuracy. The method can be thought as a variational method in

[1] Shown on the front page of this report

[2] Experimental

[3] From the beginning

which the multi-electron wave function has the form of an anti-symmetrized product of one electron wave-functions defined by the Slater determinant. The *Hartree-Fock* method has been demonstrated as successful *ab initio* method by comparing calculations to experimental values, but the values of total energies are not very accurate.

The method for dealing with larger systems with more atoms is called *Density Functional Theory (DFT)*. It was developed in the 1960's and due to the methods high computational efficiency and good accuracy, it has become a very popular and widely spread *ab initio* method. DFT does not provide a prescription how to calculate truth. It only provides the existance proof for possibility of obtaining accuare results, but no prescriptions for systematic improvements. The DFT is accurate if we know how to derive necessary relations between density and energy. Unfortunately energy functionals relating electronic density to energy are unknown. There is no general way to improve them besides trying new ones and judging their quality by the results.

Our work is to understand Density Functional Theory, and to study what happens on a (111) germanium surface when a water molecule interacts with the surface. We use an *ab initio* software called AIMPro[4] (Ab Initio Modeling PROgram) to simulate and calculate the interaction to get a reasonable outcome using the DFT method. The electronic structure of the system of interacting electrons in an external potential $V_{ext}(\mathbf{r})$ are determined by the electronic charge density $\rho(\mathbf{r})$ which is a function of only three variables. The total energy of the system is a kinetic, energy, a Coulomb energy and a term called the exchange-correlation energy. The expressions for the many-body exchange and correlation interactions are unknown. By using an approximation called *The Local Density Approximation* (LDA) we get fairly accurate results.

As mentioned earlier we use *AIMPro*, developed by Professor Sven Öberg and co-workers, to simulate the surface with the interacting molecule. We simulate the system on a supercomputer at HPC2N with parallel processors working on each node. We have done the simulations with different sets of base functions and different approximations to the exchange-correlation energy. We have also change the size of the super-cell by increasing the number of layers on the model.

In the next chapter, we are going to introduce the mathematical and physical tools, that are needed to understand the concept of DFT.

[4] http://aimpro.ncl.ac.uk/

CHAPTER

TWO

Basic Mathematical and Physical Concepts

2.1 Mathematics

2.1.1 Operator

We have used operators many times without thinking of it when we calculate something. Let us say that we have a function and we for example square its value, calculate the Laplace transform or just calculate the second derivative. Then we map one function to another function i.e. we have used an operator. For example if the operator is

$$\mathscr{F} = \frac{\partial^2}{\partial x^2} \tag{2.1}$$

and we apply it on $f(x)$ we get

$$\mathscr{F} f(x) = \frac{\partial^2}{\partial x^2} f(x) = \frac{\partial^2 f(x)}{\partial x^2} \tag{2.2}$$

A commonly used operator in 3 dimensions in vector calculus is the nabla operator also knows as the Del operator, which is a collection of partial derivatives operators.

$$\nabla = \left(\mathbf{i}\frac{\partial}{\partial x} + \mathbf{j}\frac{\partial}{\partial y} + \mathbf{k}\frac{\partial}{\partial z} \right) \tag{2.3}$$

The square of the nabla or Del operator is called the Laplacian and is extremely important in mechanics, electro magnetics, wave theory and quan-

tum mechanics. It appears in Laplace equation as $\nabla^2\psi = 0$ where

$$\Delta = \nabla^2 = \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \tag{2.4}$$

2.1.2 Calculus of Variation - Functional Analysis

A functional is nothing but an operator mapping between two function spaces with a range on the real line or in the complex line. You can also say that it is a rule that assigns a real number to each function y in a well defined class. Like a function, a functional is a rule of association, but its domain is some set of functions rather than a subset of real numbers. To understand this better, let A be a set of functions $y, z, w, \ldots$; then a functional J on A is a rule that associates to each $y \in A$ a real number denoted by $J(y)$ (sometimes written as $J[y]$) as shown in [8].

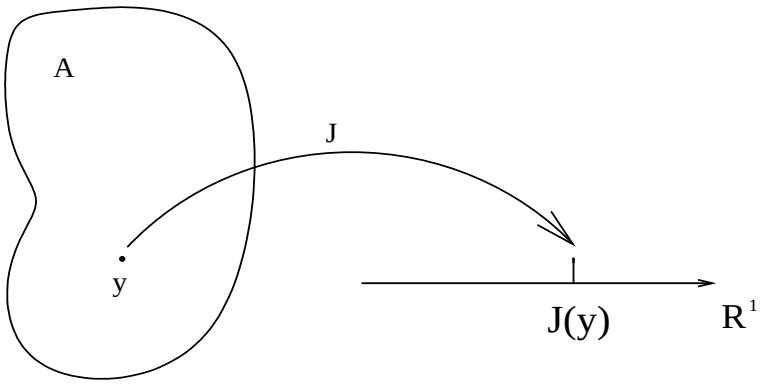

Figure 2.1: A is a set of functions where $J : A \to R^1$

Functional Derivative

We know from calculus that the definition of derivative of a function is the limit of the Newton quotient. So the derivative of a function $f(x)$ at a point x_0 is

$$f'(x_0) = \lim_{\varepsilon \to 0} \frac{f(x_0 - \varepsilon) + f(x_0)}{\varepsilon} \tag{2.5}$$

and the directional derivative of a scalar function $f(\mathbf{x}) = f(x_0, x_1, \ldots, x_n)$ along a unit vector $\mathbf{u} = u(u_0, u_1, \ldots, u_n)$ is defined by

$$D_{\mathbf{u}} f \equiv \lim_{\varepsilon \to 0} \frac{f(\mathbf{x} + \varepsilon \mathbf{u}) - f(\mathbf{x})}{\varepsilon} \equiv \frac{d}{d\varepsilon} f(\mathbf{x} + \varepsilon \mathbf{u})|_{\varepsilon = 0} \tag{2.6}$$

or

$$D_{\mathbf{u}} f \equiv \nabla(f) \cdot \mathbf{u} \tag{2.7}$$

So the derivative of a functional or the first variation $\delta J(y_0, h)$ is nothing but a generalization of directional derivative according to [7]. The difference is that we differentiate in the direction of a function h and not of a vector.

$$\delta J(y_0, h) = \lim_{\varepsilon \to 0} \frac{J(y_0 + \varepsilon h) - J(y_0)}{\varepsilon} = \frac{d}{d\varepsilon} J(y_0 + \varepsilon h)|_{\varepsilon=0} \tag{2.8}$$

Extremals or Stationary Functions

The key theorem of calculus of variation is the Euler-Lagrange equation. This corresponds to the stationary condition on a functional. If $\delta J(y_0, h) = 0$, we say that J is stationary at y_0 in the direction h and we can find the local maximum or minimum value. Given a functional $L(x, y(x), y'(x))$ with continuous first partial derivatives we can find a local minimum by

$$J(y) = \int_\Omega L(x, y, y')dx \tag{2.9}$$

and this must also satisfy the (Euler-Lagrange) ordinary differential equation

$$L_y(x, y, y') - \frac{d}{dx} L_{y'}(x, y, y') = 0, \qquad x \in \Omega \tag{2.10}$$

or for higher derivatives we get

$$\frac{\partial L}{\partial y} - \frac{d}{dx}\left(\frac{\partial L}{\partial y'}\right) + \ldots + (-1)^n \frac{d^n}{dx^n}\left(\frac{\partial L}{\partial y^{(n)}}\right) = 0 \tag{2.11}$$

where $L = L(x, y, y', \ldots, y^{(n)})$.

We can use all these methods to minimize, for example the energy in a system containing atoms. When we reach *The Density Functional Theorem* (DFT) further on in our work, we realize how powerful and important functional analysis is as a tool in solving the different equations.

2.2 Classical Physics

In classical physics it's well known that the total energy of the system is given by the sum of the kinetic energy and the potential energy. The kinetic energy can be written as

$$T = \frac{m\mathbf{v}^2}{2} = \frac{\mathbf{p}^2}{2m} \tag{2.12}$$

where $\mathbf{p} = m\mathbf{v}$ and $\mathbf{p}$ describes the momentum. The potential energy is $V(\mathbf{r}, t)$. The sum of the total energy E in the system is represented by the Hamilton function H

$$H = \frac{\mathbf{p}^2}{2m} + V(\mathbf{r}, t) \tag{2.13}$$

2.3 Quantum Mechanics

2.3.1 Introduction

In 1923-24, L. de Broglie made a great unifying hypothesis that "material particles might also posses wave-like properties", so that like radiation, they would exhibit a dual nature. This is directly related to the existence of a universal constant, called Planck's constant $h \approx 6.62618 \cdot 10^{-34}$ J s, derived through the *the black body radiation experiment*. Just as the velocity c of light plays a central role in relativity, so does Planck's constant in quantum physics. Because Planck's constant is so small, we never notice the quantum effects in our world.

The idea of quantization of energy in which the energy of a system can only take certain discrete values, was totally at variance with classical physics. In 1905, Einstein was able to understand *the photo electric effect* by extending Planck's idea of quantization of energy. He assumed that the electro magnetic field itself was quantized and that light consists of corpuscles, called light quanta or photons. Each photon travels with the speed of light and has an energy

$$E = hf = \frac{hc}{\lambda} \tag{2.14}$$

where f is the frequency, c is the speed of light and λ is the wave length. The magnitude p of momentum of the photon is given by

$$p = \frac{h}{\lambda} \tag{2.15}$$

We introduce the angular frequency $\omega = 2\pi f$, the wave number $k = 2\pi/\lambda$ and the reduced Planck's constant $\hbar = h/2\pi$. We can now write (2.14) and (2.15) in a more symmetric form

$$E = \hbar\omega, \qquad p = \hbar k \tag{2.16}$$

2.3.2 The Wavefunction

We know that some phenomena cannot be explained within the framework of classical physics. As a result of this, revolutionary concepts had to be introduced such as those of quantization and of wave-particle equality. A new theory, called quantum physics[1], was elaborated in two formulations between the years 1925 and 1930. One form of quantum physics is called wave mechanics and was proposed in 1925 by Erwin Schrödinger.

In quantum physics a *wave function* or *state function*

$$\Psi(\mathbf{r}, t) \qquad \text{where} \quad \mathbf{r} = (x, y, z) \tag{2.17}$$

[1] Also called quantum mechanics

can be introduced, which plays the role of a *probability amplitude*. In general the wave function Ψ is a complex quantity. All the information we can possibly have about a given system is contained in the system's wave function. The probability $P(\mathbf{r},t)$ of finding the particle at a particular point within a volume V about the point $\mathbf{r}$ at time t is proportional to $|\Psi|^2$ as shown in experiments in [1]

$$P(\mathbf{r},t) \propto |\Psi(\mathbf{r},t)|^2 \tag{2.18}$$

2.3.3 Interpreting the Wave Function

Imagine a very large number of identical, independent systems, each of them consisting of a single particle moving under the influence of some given external force. If measurements of the position of the particle are made on each of the systems, the probability of finding the particle within the volume V about the point $\mathbf{r}$ at the time t is

$$\int_V P(\mathbf{r},t)d\mathbf{r} = \int_V |\Psi(\mathbf{r},t)|^2 d\mathbf{r} \tag{2.19}$$

so that our first postulate, the *position probability density* becomes

$$P(\mathbf{r},t) = |\Psi(\mathbf{r},t)|^2 = \Psi^*(\mathbf{r},t)\Psi(\mathbf{r},t) \tag{2.20}$$

Hence our interpretation of the wave function is a statistical one.

We normalize the wave function to unity since the probability of finding the particle somewhere in space is 100% so that

$$\langle\Psi|\Psi\rangle = \int_{-\infty}^{+\infty} |\Psi(\mathbf{r},t)|^2 d\mathbf{r} = 1 \tag{2.21}$$

This implies that the wave function is continuous, finite and single-valued because for each point in the domain it has a unique value in the range.

A free particle of mass m, moving in space with a definite momentum $\mathbf{p}$ with a fixed wave vector $\mathbf{k}$ (or propagation vector) can be associated with a plane wave as

$$\Psi(\mathbf{r},t) = Ae^{i(\mathbf{k}\cdot\mathbf{r}-\omega(k)t)} \tag{2.22}$$

$$= Ae^{i(\mathbf{p}\cdot\mathbf{r}-E(p)t)/\hbar} \tag{2.23}$$

The wave function satisfies the two relations

$$-i\hbar\nabla\Psi(\mathbf{r},t) = \mathbf{p}\Psi(\mathbf{r},t) \tag{2.24}$$

and

$$i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r},t) = E\Psi(\mathbf{r},t) \tag{2.25}$$

where ∇ is the gradient operator from (2.3). The two relations show that for a free particle the energy and momentum can be represented by the differential operators

$$E \rightarrow \widehat{E} = i\hbar\frac{\partial}{\partial t}, \qquad \mathbf{p} \rightarrow \widehat{\mathbf{p}} = -i\hbar\nabla \tag{2.26}$$

acting on the wave function $\Psi(\mathbf{r}, t)$. When the particle is not free the dynamic variables E and $\mathbf{p}$ are still represented by these differential operators.

2.3.4 The Hamilton Operator

The Hamilton $\widehat{H}$ is the sum of the total kinetic energy operator $\widehat{T}$ and the potential energy operator $\widehat{V}$ of the particles as

$$\widehat{H} = \widehat{T} + \widehat{V} = \frac{\widehat{\mathbf{p}}^2}{2m} + \widehat{V}(\mathbf{r}, t) \tag{2.27}$$

Substituting (2.26) into (2.27) gives

$$\widehat{H} = -\frac{\hbar^2}{2m}\nabla^2 + \widehat{V}(\mathbf{r}, t) \tag{2.28}$$

In real world, physical systems contain often more than two particles. The Hamiltonian operator $\widehat{H}$ for an atomic system for many particles becomes (To make a clean equation we use atomic units, i.e $\hbar = e = m_e = 4\pi\epsilon_0 = 1$)

$$\widehat{H}_{tot} = \widehat{T}_{nucl} + \widehat{T}_e + \widehat{V}_{nucl-e} + \widehat{V}_{e-e} + \widehat{V}_{nucl-nucl} \tag{2.29}$$

$\widehat{T}_{nucl}$ represents the total kinetic energy operator of the nuclei and is given by

$$\widehat{T}_{nucl} = -\frac{1}{2}\sum_i \frac{\nabla_i^2}{M_i} \tag{2.30}$$

where M is the mass of the nuclei.

$\widehat{T}_e$ represents the total kinetic energy operator of the electron given by

$$\widehat{T}_e = -\frac{1}{2}\sum_i \nabla_i^2 \tag{2.31}$$

$\widehat{V}_{nucl-e}$ is the nuclei-electron interaction energy operator given by

$$\widehat{V}_{nucl-e} = -\sum_{i,j} \frac{Z_i}{|(\mathbf{r}_i - \mathbf{R}_j|} \tag{2.32}$$

where Z_i is the charge of the i-th nucleus (atomic number), $|(\mathbf{r}_i - \mathbf{R}_j|$ is the distance between electron i and the nucleus j. It can also be expressed in Cartesian coordinates

$$|(\mathbf{r}_i - \mathbf{R}_j| = \sqrt{(x_i - X_j)^2 + (y_i - Y_j)^2 + (z_i - Z_j)^2} \tag{2.33}$$

$\widehat{V}_{e-e}$ represents the electron-electron interaction energy operator given by

$$\widehat{V}_{e-e} = \frac{1}{2}\sum_{i\neq j}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \tag{2.34}$$

The factor $\frac{1}{2}$ is added so that the interaction won't be counted twice.

Finally, the $\widehat{V}_{N-N}$ nuclei-nuclei interaction energy operator is given by

$$\widehat{V}_{nucl-nucl} = \sum_{i\neq j}\frac{1}{2}\frac{Z_i Z_j}{|\mathbf{R}_i - \mathbf{R}_j|} \tag{2.35}$$

The total Hamiltonian becomes

$$\widehat{H} = -\frac{1}{2}\sum_i \frac{\nabla_i^2}{M_i} - \frac{1}{2}\sum_i \nabla_i^2 - \sum_{i,j}\frac{Z_i}{|\mathbf{r}_i - \mathbf{R}_j|} + \frac{1}{2}\sum_{i\neq j}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{1}{2}\sum_{i\neq j}\frac{Z_i Z_j}{|\mathbf{R}_i - \mathbf{R}_j|} \tag{2.36}$$

This is obviously a very complicated Hamilton operator equation and when we let it act on the wave function it becomes impossible to solve for more than one atom with one electron. One have to do several approximations to be able to solve real material science problems of at least $N \sim 10^{24}$ particles.

2.3.5 The Born-Oppenheimer Approximation

In material science, one of the most important approximations is the *Born-Oppenheimer approximation*. The idea of this approximation is that the nuclei is much heavier then the electron, and moves much slower. Hence, the nuclei can be treated as a stationery particle while the electron moves rapidly relative to the fix particle. This gives the equation for the electrons.

$$\widehat{H}_e\psi(\mathbf{r}) = (\widehat{T}_e(\mathbf{r}) + \widehat{V}_{e-nucl}(\mathbf{r},\mathbf{R}) + \widehat{V}_{e-e}(\mathbf{r}))\psi(\mathbf{r}) \tag{2.37}$$

2.3.6 The Schrödinger Equation

We would like to find an equation that satisfies the wave function $\Psi(\mathbf{r},t)$. The equation should be *linear* and *homogeneous* so that the *superposition principle* holds. The results obtained by using the equation should agree with those of classical physics in macroscopic situations.

The Time-Dependent Schrödinger Equation

Substituting (2.26) into (2.28) and letting the operators act on the wave function (2.23) we get get the *three-dimensional time-dependent Schrödinger equation for a free particle*

$$i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r},t) = -\frac{\hbar^2}{2m}\nabla^2\Psi(\mathbf{r},t) + \Psi(\mathbf{r},t)V(\mathbf{r},t)$$

$$= \left(-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r},t)\right)\Psi(\mathbf{r},t)$$
$$= \widehat{H}\Psi(\mathbf{r},t) \tag{2.38}$$

The Schrödinger equation, also called the Schrödinger wave equation was proposed by physicist Erwin Schrödinger in 1925 and describes the time-dependence of quantum mechanical systems.

The Time-Independent Schrödinger Equation

By variable separation of the time-dependent Schrödinger equation we can separate the wave function $\Psi(\mathbf{r},t)$ into space and time-dependent coordinates. So we put

$$\Psi(\mathbf{r},t) = \psi(\mathbf{r})v(t) \tag{2.39}$$

Substituting (2.39) into (2.38) gives

$$i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r})v(t) = \widehat{H}\Psi(\mathbf{r})v(t) \qquad \text{and making simple transformations}$$
$$i\frac{\hbar}{v}\frac{dv}{dt} = \frac{1}{\psi(\mathbf{r})}\widehat{H}\psi(\mathbf{r}) \tag{2.40}$$

Equation (2.40) is reduced to a constant with the dimensionality of an energy.

$$i\frac{\hbar}{v}\frac{dv}{dt} = E \tag{2.41}$$

$$\frac{1}{\psi(\mathbf{r})}\widehat{H}\psi(\mathbf{r}) = E \tag{2.42}$$

Solving equation (2.41) and substituting it into (2.39) gives

$$v(t) = e^{-i(E/\hbar)t} \tag{2.43}$$

Finally this gives us the total wave function

$$\Psi(\mathbf{r},t) = \psi(\mathbf{r})e^{-i(E/\hbar)t} \tag{2.44}$$

and the time-independent stationary Schrödinger equation or eigenvalue equation

$$\widehat{H}\psi(\mathbf{r}) = E\psi(\mathbf{r}) \tag{2.45}$$

The task here is to determine the eigenvalues E and eigenfunctions ψ of the Hamilton operator $\widehat{H}$. The general solution $\Psi(\mathbf{r},t)$ of the time-dependent Schrödinger equation (2.38) can be expanded in terms of the energy eigenfunctions as

$$\Psi(\mathbf{r},t) = \sum_k^n e_k(t)\psi_k(\mathbf{r}) \tag{2.46}$$

2.3.7 Quantum Many Body System

A quantum mechanical system of N particles is dependent of many variables. The n:th particle have a position vector $\mathbf{r}_n$ and momentum $\mathbf{p}_n$. If the particle possesses spin, it generates an angular momentum $\mathbf{S}_n$. Let

$$Q_n = \{\mathbf{r}_n, \mathbf{p}_n, \mathbf{S}_n | n \in Z^+\}$$

then the system is described by the wave function $\Psi(Q_1, Q_2, \ldots, Q_N, t)$ which satisfies the time-dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \Psi(Q_1, Q_2, \ldots, Q_N, t) = \widehat{H} \Psi(Q_1, Q_2, \ldots, Q_N, t) \tag{2.47}$$

and the time-independent stationary Schrödinger equation

$$\widehat{H} \psi(Q_1, Q_2, \ldots, Q_N, t) = E \psi(Q_1, Q_2, \ldots, Q_N, t) \tag{2.48}$$

2.3.8 Variational Principle

If we take an approximation to the wave function Ψ then the variation principle states that the expectation value of the energy E for the approximation will be greater or equal than to the true expectation value or the ground state energy E_0 for the system.

$$E = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \geq E_0 = \frac{\langle \Psi_0 | \hat{H} | \Psi_0 \rangle}{\langle \Psi_0 | \Psi_0 \rangle} \tag{2.49}$$

if

$$E = E_0 \Leftrightarrow \Psi_0 \equiv \Psi \tag{2.50}$$

otherwise

$$E \geq E_0 \tag{2.51}$$

This theorem provides us with the prescription how to find a good wave function.

2.4 Solid State Physics

2.4.1 Introduction

Solid state physics is the study of rigid matter or solids. The theory began in the early years of the twentieth century following the discovery of x-ray diffraction by crystals. The theory and research is focused on crystals because of the periodicity of atoms in a crystal, the mathematical modeling of the structure and also because crystalline materials often have optical, electrical, magnetical or mechanical properties.

2.4.2 Crystal Structure

Crystals are composed of a periodic array of atoms and grows by identical building blocks added together. But in reality, solids have defects like vacancies, interstitial atoms, impurities and surfaces which is present in any realistic crystal. The structure of all crystals can be described in terms of a lattice, with a group of atoms attached to every lattice point. The group of atoms is called the basis. When repeated in space it forms the crystal structure.

$$\text{Lattice} + \text{Basis} = \text{Crystal Structure} \tag{2.52}$$

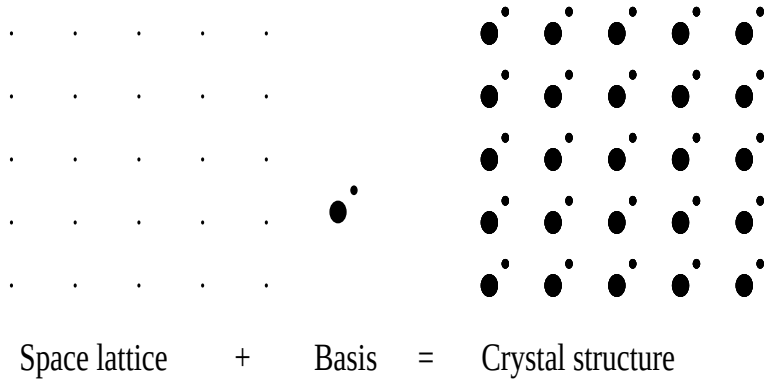

Figure 2.2: A two dimensional figure of a crystal formed by adding a basis to the space lattice.

2.4.3 Lattice Translation Vectors

Three fundamental translation vectors $\mathbf{v}_x$, $\mathbf{v}_y$ and $\mathbf{v}_z$ define the atomic arrangement. If we observe the atomic arrangement from point $\mathbf{P}$ then the crystal will look exactly the same in every point of view, or to a different observer at point $\mathbf{P'}$. We say that the translation vectors are primitive, provided that the vector $\mathbf{T}$ which connects $\mathbf{P}$ and $\mathbf{P'}$ may be expressed as an integral multiple of the translation vectors. A lattice translation operation is the displacement of a crystal by a crystal translation vector shown in [5] as

$$\mathbf{T} = a_x\mathbf{v}_x + a_y\mathbf{v}_y + a_z\mathbf{v}_z \quad \text{where } a_x, a_y \text{ and } a_z \text{ are arbitrary integers} \tag{2.53}$$

2.4.4 Primitive Lattice Cell

The primitive cell is a type of cell or unit cell that is defined by the primitive axes or vectors $\mathbf{v}_x$, $\mathbf{v}_y$ and $\mathbf{v}_z$. There is always one lattice point per primitive cell. The volume $\mathbf{V}_{cell}$ of the primitive cell is given by

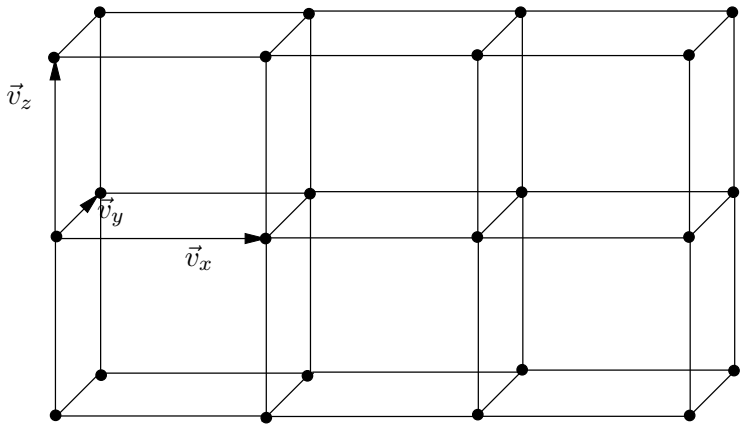

Figure 2.3: The primitive cell with lattice points in three dimensions.

$$\mathbf{V}_{cell} = |\mathbf{v}_x \cdot \mathbf{v}_y \times \mathbf{v}_z| \tag{2.54}$$

Another way of choosing a primitive cell is by first picking a lattice point and draw lines to all nearby closest lattice points. At the midpoint of each, draw another line normal to each of the first set of lines. In the case of the three-dimensional lattice, a perpendicular plane is drawn at the midpoint of the lines between the lattice points. By using this method, the smallest area or volume is enclosed. This is called the *Wigner-Seitz* primitive cell.

2.4.5 Lattice Types

There exists infinitely many possible lattices because the length of the lattice translation vectors can be chosen in infinitely many ways as the angle between the vectors. A general lattice that is invariant under rotation π and 2π about any lattice point is called an oblique lattice. Some special lattices of the oblique type can be invariant under rotation of $\frac{2\pi}{3}$, $\frac{2\pi}{4}$ or $\frac{2\pi}{6}$ or under mirror reflection. Lattices that are invariant under one or more of these special symmetries are called *special lattices*. There are 14 distinct lattice types in the tree dimensional space by the point symmetry group. A distinct lattice type is also called a *Bravis lattice*. Some of the most common crystal structures are shown in figure 2.4.

2.4.6 Reciprocal Lattice

We know that a crystal is invariant under any translation of the form (2.53). Then any local physical property of the crystal is invariant under $\mathbf{T}$, because every physical aspect is repeated throughout the crystal. Mathematically the electron density number is

$$n(\mathbf{r} + \mathbf{T}) = n(\mathbf{r}) \tag{2.55}$$

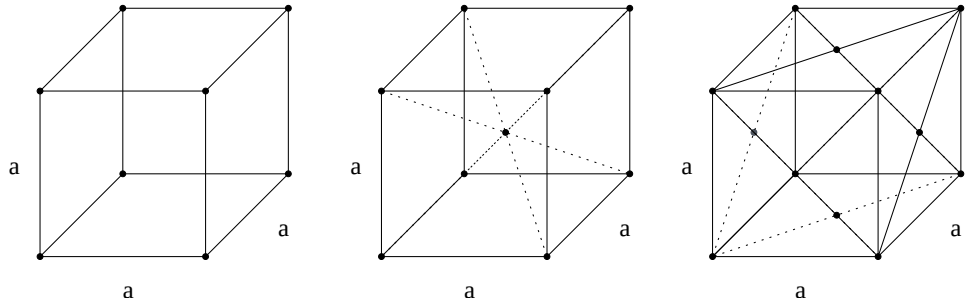

Figure 2.4: A cubic (isometric) simple (sc), body-centered (bcc) and face-centered (fcc) Bravais lattices.

Since the electron number density is periodic it can be written as a Fourier series

$$n(x) = n_0 + \sum_{p>0}(C_p \cos\frac{2\pi px}{a} + S_p \sin\frac{2\pi px}{a}), \quad \text{where} \quad p \in Z^+ \; C_p, \; S_p \in R \tag{2.56}$$

C_p and S_p are the Fourier coefficients according to [10]. The $\frac{2\pi p}{a}$ factor is a point in the reciprocal lattice, the Fourier space or sometimes called the frequency space. The factor $2\pi/a$ in the arguments ensures that $n(x)$ has the period a:

$$\begin{aligned} n(x+a) &= n_0 + \sum_{p>0} C_p \cos(\frac{2\pi px}{a} + 2\pi p) + S_p \sin(\frac{2\pi px}{a} + 2\pi p) \\ &= \sum_{p>0} C_p \cos\frac{2\pi px}{a} + S_p \sin\frac{2\pi px}{a} = n_0 \end{aligned} \tag{2.57}$$

We can also write (2.56) in a more compact way shown also in [10]

$$n(x) = \sum_p n_p e^{(2\pi px/a)i} \tag{2.58}$$

or in three dimensions

$$n(\mathbf{r}) = \sum_{\mathbf{G}} n_{\mathbf{G}} e^{(\mathbf{G}\cdot\mathbf{r})i} \tag{2.59}$$

When $n(\mathbf{r}+\mathbf{T}) = n(\mathbf{r})$ we get

$$e^{i\mathbf{G}\cdot\mathbf{T}} = 1 \quad \text{and} \quad \mathbf{G}\cdot\mathbf{T} = 2\pi m, \quad \text{where } m \text{ is an integer.} \tag{2.60}$$

2.4.7 Reciprocal Lattice Vectors

We must find the vectors $\mathbf{G}$ of the Fourier sum (2.59). To do this we assume that the points in the reciprocal lattice are mapped by the set of vectors

$$\mathbf{G} = b_x \mathbf{w}_x + b_y \mathbf{w}_y + b_z \mathbf{w}_z \tag{2.61}$$

We construct the axes vectors $\mathbf{w}_x$, $\mathbf{w}_y$ and $\mathbf{w}_z$ as:

$$\mathbf{w}_x = 2\pi \frac{\mathbf{v}_y \times \mathbf{v}_z}{\mathbf{v}_x \cdot \mathbf{v}_y \times \mathbf{v}_z}; \quad \mathbf{w}_y = 2\pi \frac{\mathbf{v}_z \times \mathbf{v}_x}{\mathbf{v}_x \cdot \mathbf{v}_y \times \mathbf{v}_z}; \quad \mathbf{w}_z = 2\pi \frac{\mathbf{v}_x \times \mathbf{v}_y}{\mathbf{v}_x \cdot \mathbf{v}_y \times \mathbf{v}_z} \tag{2.62}$$

where $\mathbf{v_x}$, $\mathbf{v_y}$ and $\mathbf{v_z}$ are primitive vectors of the crystal lattice and $\mathbf{w_x}$, $\mathbf{w_y}$ and $\mathbf{w_z}$ are primitive vectors of the reciprocal lattice. Every vector in equation (2.62) is orthogonal to two axis vectors of the crystal lattice. With this properties and vector algebra we get

$$\mathbf{v}_i \cdot \mathbf{w}_j = 2\pi\delta_{ij} \quad \text{where } \delta_{ij} \text{ is Kroneckers delta function.} \tag{2.63}$$

2.4.8 Brillouin zone

The Brillouin zone is something that exists in the Reciprocal space (see section 2.4.6). The first Brillouin zone is defined to be the Wigner-Seitz primitive cell, or a another definition, all the points that can reached from origo without crossing a Bragg plane. In figure 2.5, we see the first Brillouin zone as the smallest area enclosed by lines orthogonal to the vector pointing from origo to the nearest points in Reciprocal space. The figure 2.5, can be seen as a 2-D model of a simple cubic Al lattice (see figure 2.4a)

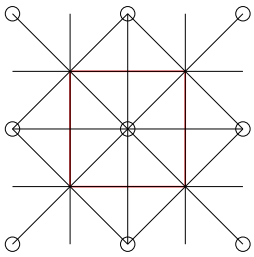

Figure 2.5: The First Brillouin zone, is the smallest area around origo.

Figure 2.6, shows the first Brillouin zone for 2-D model of a FCC lattice (see figure 2.4c)

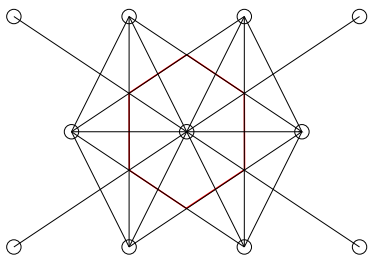

Figure 2.6: The first Brillouin zone

In the first Brillouin zones, all the eigenvalues of the Hamiltonian are plotted along the **k**.

Using the Brillouin zone

Since all the eigenvalues of the electronic Hamiltonian are plotted along the **k** vector, there are some technices in AIMPro to test which of the k-points who contrebuties most.

If we increase the volume of the supercell the volume of the Brillouin zone decreases like

$$V_{Brillouin} = \frac{(2\pi)^3}{V_{supercell}} \tag{2.64}$$

That means, that if we increase the size of the supercell, we have fewer k-points to evaluate.

2.4.9 Germanium

Germanium $Ge^{32}_{72.64}$ was predicted by Mendelev in 1871 as ekasilicon and discovered by Clemins Winkler in 1886. The element is a grey-white metalloid, and in its pure state is crystalline and brittle. Germanium has the same crystal structure as diamond and is an important semiconductor material used in transistors.

CHAPTER

THREE

Density Functional Theory

3.1 Introduction

Density functional theory is one of the most spread *ab initio* [1] method for calculations in material science and solid state physics. Much of what we know about the electrical, magnetical and structural properties of materials has been calculated using DFT. The founding father of DFT, Walter Kohn, was awarded the Nobel Prize 1998 in chemistry and John Pople who was instrumental in implementing DFT in computational chemistry [6].

As shown in [2] the density functional approach can be summarized by the sequence

$$\rho(\mathbf{r}) \Rightarrow \Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N) \Rightarrow v(\mathbf{r})$$

Knowledge of the particle density $\rho(\mathbf{r})$ implies knowledge of the wave function $\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ and the potential $v(\mathbf{r})$.

3.2 Concept of Electron Density

In DFT, electron density is very important. The main idea of this concept is to look at the number of electrons per volume at some point in space. In this approach the electrons are treated as particles forming an electron gas.

[1] Latin: from the beginning

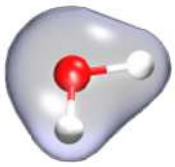

Figure 3.1: The electron density of a water molecule.

3.3 Hartree

One can rarely solve the Schrödinger equation exactly i.e. analytical, so we need approximations for the wave function. The first person who derived a working approximation was Hartree in 1928. He's approach was that the many body wave function Ψ could be approximated by a product of one-electron wave functions ϕ , called orbitals like

$$\Psi(\mathbf{r}_1, \mathbf{r}_1, \cdots, \mathbf{r}_N) = \phi(\mathbf{r}_1)\phi(\mathbf{r}_2)\cdots\phi(\mathbf{r}_N) \tag{3.1}$$

where $\mathbf{r}_i$ is the position of the i:th electron. The Hamiltonian can be written as

$$\hat{H} = \hat{T}_N + \hat{T}_e + \hat{V}_N + \hat{V}_{ext} + \hat{V}_{ee} \tag{3.2}$$

since the nuclei is much heavier than the electron, we can use the Born-Oppenheimer[2] approximation. This results in the electronic Hamiltonian

$$\hat{H}_{el} = \hat{T}_e + \hat{V}_{ext} + \hat{V}_{ee} \tag{3.3}$$

where the kinetic energy operator $\hat{T}_e$ is define as

$$\hat{T}_e = \sum_{i=1}^{N} -\frac{1}{2}\nabla_i^2 \tag{3.4}$$

and the external potential operator $\hat{V}_{ext}$ is define as

$$\hat{V}_{ext} = \sum_{i=1}^{N} \hat{v}_i = \sum_{i=1}^{N} \left(\sum_{\alpha=1}^{N_N} \frac{-Z_\alpha}{|r_i - R_\alpha|} \right) \tag{3.5}$$

and the electron-electron repulsion is define as

$$\hat{V}_{ee} = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \tag{3.6}$$

[2]see chapter 3

Now we can rewrite the electronic Hamiltonian as

$$\hat{H}_{el} = \sum_{i=1}^{N} \hat{h}_i + \hat{V}_{ee} \tag{3.7}$$

where

$$\hat{h}_i = -\frac{1}{2}\nabla_i^2 + \hat{v}_i \tag{3.8}$$

where $\hat{h}_i$ does only depend on the position of the i:th electron, but since $\hat{V}_{ee}$ depends on electron pairs, we can not separate the variables. So Hartree found a approximation, that the electrons does not interact with other electrons, but with an average electron density. The total electron density can be written as

$$\rho_{tot}(\mathbf{r}) = \sum \rho_i(\mathbf{r}) = \sum_{i=1}^{N} |\phi(\mathbf{r})|^2 \tag{3.9}$$

But now, the k:th electron interacts with it self, and that is not true. So, if we define the electron density that the k:th electron interacts with like

$$\rho^{(r)}(\mathbf{r}) = \rho_{tot}(\mathbf{r}) - \rho_k(\mathbf{r}) \tag{3.10}$$

and let $e_k(\mathbf{r})$ be the energy of the k:th electron, interacting with the average electron density be define by

$$\hat{e}_k(\mathbf{r}) = \int \rho^k(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \tag{3.11}$$

now we can write

$$\hat{U}_{ee} \approx \sum_{i=1}^{N} e_i(\mathbf{r}) \tag{3.12}$$

now we can get a approximation to the many body Schrödinger equation as

$$\left(-\frac{1}{2}\nabla_i^2 + \hat{v}_i + \hat{e}_i\right) \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}) \tag{3.13}$$

This equation is solve as a self consistent equation[3], we solve it by guessing a solution, and get a better one and so on until $\phi^{(n)} - \phi^{(n-1)} = \beta$ where β is as small as we like. But the total energy of the ground state E can not be written as a sum of orbital energy

$$E \neq \sum_{i=1}^{N} \epsilon_i \tag{3.14}$$

since, when we solve for ϕ_1, we get interaction between $(1,2)$, $(1,3)$, $(1,3)$ $\cdots$ $(1,N)$, and when we solve ϕ_2 we get interaction between $(2,1)$,

[3]The solution depends on the solution

$(2,3)$, $(2,3)\cdots(2,N)$, and $(1,2)=(2,1)$, so we counted the interaction two times. So we have to write the ground state energy E as

$$E=\sum_{i=1}^{N}\epsilon_i+\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}J_{ij} \tag{3.15}$$

where

$$J_{ij}=\int\int\phi_i^*(\mathbf{r}_1)\phi_j^*(\mathbf{r}_2)\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}\phi_i(\mathbf{r}_1)\phi_j(\mathbf{r}_2)d\mathbf{r}_1d\mathbf{r}_2 \tag{3.16}$$

Hartrees approximation work for small systems, like atoms and small molecules, but for bigger systems, Hartree gets problem. Hartrees method does not take in count the Pauli-principle, that two electrons, can't be described by the same function.

Fock and independently, by Slater, Hartees method was improved by introducing the Slater determinant.

$$\Psi(\mathbf{r}_1,\mathbf{r}_1,\cdots,\mathbf{r}_N)=\frac{1}{\sqrt{N!}}\begin{vmatrix}\phi_1(\mathbf{r}_1) & \phi_2(\mathbf{r}_1) & \cdots & \phi_N(\mathbf{r}_1)\\ \phi_1(\mathbf{r}_2) & \phi_2(\mathbf{r}_2) & \cdots & \phi_N(\mathbf{r}_2)\\ \vdots & \vdots & \ddots & \vdots\\ \phi_1(\mathbf{r}_N) & \phi_2(\mathbf{r}_N) & \cdots & \phi_N(\mathbf{r}_N)\end{vmatrix} \tag{3.17}$$

If we examine the properties of the Slater determinant for a 2-electron case we see that

$$\Psi(\mathbf{r}_1,\mathbf{r}_2)=\frac{1}{\sqrt{2}}\begin{vmatrix}\phi_1(\mathbf{r}_1) & \phi_2(\mathbf{r}_1)\\ \phi_1(\mathbf{r}_2) & \phi_2(\mathbf{r}_2)\end{vmatrix}=\frac{1}{\sqrt{2}}\left[\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)-\phi_2(\mathbf{r}_1)\phi_1(\mathbf{r}_2)\right] \tag{3.18}$$

If we change place of two electrons $\mathbf{r}_1\rightarrow\mathbf{r}_2$ and $\mathbf{r}_2\rightarrow\mathbf{r}_1$

$$\Psi(\mathbf{r}_2,\mathbf{r}_1)=\frac{1}{\sqrt{2}}\begin{vmatrix}\phi_1(\mathbf{r}_2) & \phi_2(\mathbf{r}_2)\\ \phi_1(\mathbf{r}_1) & \phi_2(\mathbf{r}_1)\end{vmatrix}=\frac{1}{\sqrt{2}}\left[\phi_1(\mathbf{r}_2)\phi_2(\mathbf{r}_1)-\phi_2(\mathbf{r}_2)\phi_1(\mathbf{r}_1)\right] \tag{3.19}$$

i.e $\Psi(\mathbf{r}_1,\mathbf{r}_2)=-\Psi(\mathbf{r}_2,\mathbf{r}_1)$

if we now let the two electrons be described by same orbital $\phi_1=\phi_2=\phi$

$$\Psi(\mathbf{r}_1,\mathbf{r}_2)=\frac{1}{\sqrt{2}}\begin{vmatrix}\phi(\mathbf{r}_2) & \phi(\mathbf{r}_2)\\ \phi(\mathbf{r}_1) & \phi(\mathbf{r}_1)\end{vmatrix}=\frac{1}{\sqrt{2}}\left[\phi(\mathbf{r}_2)\phi(\mathbf{r}_1)-\phi(\mathbf{r}_2)\phi(\mathbf{r}_1)\right]\equiv 0 \tag{3.20}$$

The expectation value of the total energy for the single determinant wave function are given by

$$E=\langle\Psi|H|\Psi\rangle=\sum_{i=1}^{N}H_i+\frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}(J_{ij}-K_{ij}) \tag{3.21}$$

where

$$H_i=\int\phi_i^*(\mathbf{r})\left[-\frac{1}{2}\nabla_i^2+\hat{v}_i\right]\phi_i(\mathbf{r})d\mathbf{r} \tag{3.22}$$

The new term K_{ij} is called *exchange integral* which is define by

$$K_{ij} = \int\int \phi_i^*(\mathbf{r}_1)\phi_j(\mathbf{r}_1)\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}\phi_i(\mathbf{r}_2)\phi_j^*(\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2 \tag{3.23}$$

note that if $i = j$, than $J_{ij} = K_{ij}$, that means that there are no contribution from self interacting electrons.

$$\left(-\frac{1}{2}\nabla_i^2 + \hat{v}_i + \hat{e}_i\right)\phi_i(\mathbf{r}) - \int\int \phi_i^*(\mathbf{r}_1)\phi_j(\mathbf{r}_1)\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}\phi_i(\mathbf{r}_2)\phi_j^*(\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2 = \epsilon_i\phi_i(\mathbf{r}) \tag{3.24}$$

Before we can formulate the Density Functional Theory in detail, we need some importent theormes.

3.4 Hohnberg-Kohn

There are two theorems by Hohnberg-Kohn that is important to DFT-calculations. Here we are going to formulate[4] the two theorems and prove them.

3.4.1 Formulation of the Hohnberg-Kohn theorems

First theorem

> *For any system of electrons in an external potential $V_{ext}(\vec{r})$, that potential is determined uniquely, except for a constant, by the ground state density $n(\vec{r})$.*

Second theorem

> *A universal functional for the energy $E[n]$ of the density $n(\vec{r})$ can be defined for all electron systems. The exact ground state energy is the global minimum for a given $V_{ext}(\vec{r})$, and the density $n(\vec{r})$ which minimizes this functional is the exact ground state density.*

Proof of the first Theorem

Suppose that there were two different external potentials $V_{ext}^{(1)}(\vec{r})$ and $V_{ext}^{(2)}(\vec{r})$ whit the same ground state density $n(\vec{r})$. The two external potentials lead to two different Hamiltonians, $\hat{H}^{(1)}$ and $\hat{H}^{(2)}$, which have different ground state wave functions, $\Psi^{(1)}$ and $\Psi^{(2)}$, which are hypothesized to have the same density $n(\vec{r})$. Then:

$$E^1 = \langle\Psi^{(1)}|H^{(1)}|\Psi^{(1)}\rangle < \langle\Psi^{(2)}|H^{(1)}|\Psi^{(2)}\rangle \tag{3.25}$$

[4]Richard M. Martin

which leads to

$$E^{(1)} < E^{(2)} + \int d^3r\{V_{ext}^{(1)}(\vec{r}) - V_{ext}^{(2)}(\vec{r})\}n(\vec{r}) \tag{3.26}$$

But changing the labels leads to

$$E^{(2)} < E^{(1)} + \int d^3r\{V_{ext}^{(2)}(\vec{r}) - V_{ext}^{(1)}(\vec{r})\}n(\vec{r}) \tag{3.27}$$

which is a contradiction. □

3.5 Kohn-Sham

In DFT-theory, the Schrödinger equation is replaced with Kohn-Sham's equation, were the ground state energy and density are obtained[5] by minimizing $E[n]$ with respect to the electron density $n(\vec{r})$. The Kohn-Sham equation is often formulated as

$$[-\frac{\nabla^2}{2} + v_{ks}[n](\vec{r})]\varphi(\vec{r}) = \epsilon_i\varphi_i(\vec{r}) \tag{3.28}$$

where v_{ks} is the Kohn-Sham potential, and itt's defined as

$$v_{ks}[n](\vec{r}) = v_{ext}(\vec{r}) + v_{Hartree}[n](\vec{r}) + v_{xc}[n](\vec{r}) \tag{3.29}$$

where the external potential is defined as

$$v_{ext}(\vec{r}) = \sum_{\alpha} v_\alpha(\vec{r} - \vec{R_\alpha}) \tag{3.30}$$

where v_α is the coulomb attraction between the electron and the nucleus α.

The next term is the Hartree potential, and itt's defined as

$$v_{Hartree}(\vec{r}) = \int \frac{n(\vec{r'})}{|\vec{r} - \vec{r'}|} d^3r'. \tag{3.31}$$

This term describes the interaction between electrons, it can also be written as a ODE of Poissont's type

$$\nabla^2 v_{Hartree}(\vec{r}) = -4\pi n(\vec{r}). \tag{3.32}$$

The last term of the Kohn-Sham potential is the xc (exchange-correlation) potential, and itt's define by the functional derivative of the xc energy as

$$v_{xc}(\vec{r}) = \frac{\delta E_{xc}}{\delta n(\vec{r})} \tag{3.33}$$

This terms includes all the energy which were not accounted for in the previous terms.

[5] Honberg-Kohn second theorem

3.6 Derivation of Kohn-Shams equation

Hohnberg-Kohn provides that, by minimizing the $E[n](\vec{r})$ by variating $n(\vec{r})$ over all density that contains N electrons

$$\frac{\delta}{\delta n(\vec{r}}[E[n(\vec{r})] - \mu \int n(\vec{r})d\vec{r} - N] = 0 \Leftrightarrow \tag{3.34}$$

$$\Leftrightarrow \frac{\delta}{\delta n(\vec{r}}E[n(\vec{r})] = \mu \tag{3.35}$$

$$E[n(\vec{r})] = T_s[n(\vec{r})] + \frac{1}{2}\int\int \frac{n(\vec{r})n(\vec{r'})}{|\vec{r} - \vec{r'}|} + E_{xc}[n(\vec{r})] + \int n(\vec{r})V_{ext}(\vec{r})d\vec{r} \tag{3.36}$$

where T_s is the kinetic energy of the non-interacting electrons of the system which have the same density as the real system. Now let T_s be

$$T_s[n(\vec{r})] = -\frac{1}{2}\sum_{i=1}^{N}\int \psi_i^*(\vec{r})\nabla^2\psi_i(\vec{r})d\vec{r} \tag{3.37}$$

then if

$$v_{ks}(\vec{r}) = v_{ext}(\vec{r}) + \int \frac{n(\vec{r'})}{|\vec{r} - \vec{r'}|}dr' + v_{xc}(\vec{r}) \tag{3.38}$$

equation (4.11) becomes

$$\frac{\delta T_s}{\delta n(\vec{r})} + v_{ks} = \mu \tag{3.39}$$

which can be written in the form of

$$[-\frac{\nabla^2}{2} + v_{ks}[n(\vec{r})]]\varphi(\vec{r}) = \epsilon_i\varphi_i(\vec{r}) \tag{3.40}$$

where

$$\sum_{i}^{N}|\varphi(\vec{r})|^2 = n(\vec{r}) \tag{3.41}$$

3.6.1 Solving Kohn-Shams Equation

When we solve Kohn-Shams equation, we start by guessing a electron density. With this electron density we evaluate the Hartree potential 3.31 and the exchange-correlation potential 3.33. Then we solves Kohn-Shams equation 3.28, and from that, we can get a new value of the electron density from 3.41. This flowchart can be seen in figure 3.2 and [3], [4], [9]

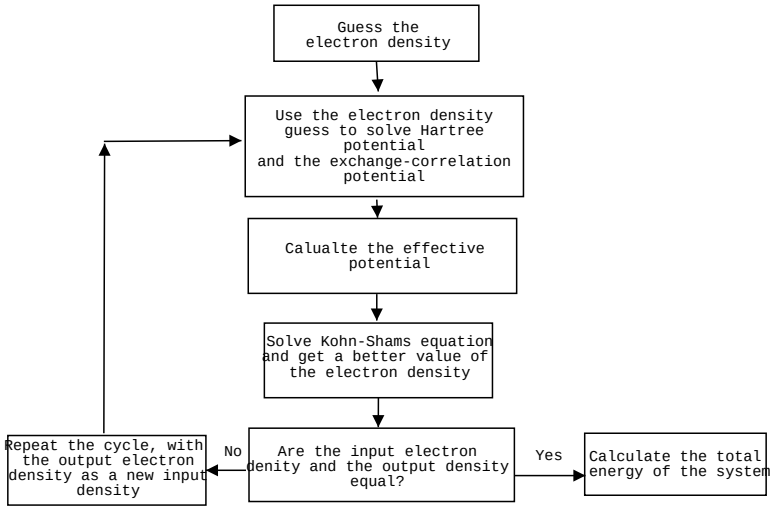

Figure 3.2: Flow chart for how to solve Kohn-Shams equation

3.7 Exchange-correlation energy

$T[n]$ is decomposed into two different parts, one that represents the kinetic energy of noninteracting particles, and the other part, represents the rest of the kinetic energy.

$$T[n] = T_s[n] + T_c[n] \tag{3.42}$$

where the index s stands for "single-particle" and index c stands for "correlation". $T_s[n]$ can be expressed in terms of single-particle orbitals $\phi_i(\mathbf{r})$. Since ϕ_i is non-interacting, the total kinetic energy can just be written as a sum of all single-particle orbitals kinetic energy.

$$T_s[n] = T_s[\phi_i[n]] \tag{3.43}$$

The exchange-correlation term is the last thing we need to solve Kohn-Shams equation. The exchange-correlation functional exist, but is unknown. $E_{xc}[\mathbf{r}]$ is often decomposed into two different parts, i.e $E_{xc}[\mathbf{r}] = E_x + E_c$, where E_x is the exchange energy due to Pauli, and it can be written in terms of single-particle orbitals as

$$E_x[\phi_i[n]] = -\frac{1}{2}\sum_{jk}\int d^3r \int d^3r' \frac{\phi_j^*(\mathbf{r})\phi_k^*(\mathbf{r'})\phi_j(\mathbf{r'})\phi_k(\mathbf{r})}{|\mathbf{r}-\mathbf{r'}|} \tag{3.44}$$

In the $E_{xc}[\mathbf{r}]$ term, we put everything we do not know, such as

- electron exchange
- electron correlation
- kinetic energy, $T - T_s[\mathbf{r}] = T_c[\mathbf{r}]$ is the contribution to E_c.

3.7.1 Local density approximation

There are some good approximations to the real functional such as Local density approximation (LDA). As the name states, the local density approximation, approximates the exchange-correlation energy $E_{xc}[\mathbf{r}]$ by the energy contribution of every small elements $d\mathbf{r}$ in space, if the entire space was of the same density

$$E_{xc}[\mathbf{r}] = \int \epsilon_{xc}(\mathbf{r}) d^3\mathbf{r} \tag{3.45}$$

3.7.2 Gradient corrected approximation

In the gradient corrected approximation, we correct the energy whit the $\nabla\mathbf{r}$

3.8 Pseudopotential

When we are doing calculations on physical systems of many atoms, the complexity of the model is very high. If we divided the electrons into two different groups, valence- and core electrons. The electrons in the inner shell are strongly bond to the core, and do not interact in the procedure of making and splitting chemical bounds. Binding properties are all due to valence electrons. Hence, the core electrons can be ignored, and replaced by a potential. On way of doing this is to use a concept called Pesudopotential. The main idea of the Pesudopotential is like we sade before, that, only the valence electrons are interacting when making and breaking chemical bonds. Hence, we don't need to use all electrons in our wave function. We can replace the core electrons with a pseudopotential and the valence electrons with a pseudo wave function, which is equal to the full wave function outside some radius. In mathematical terms, the pseudopotential can be generated as follows

$$\Psi = \psi + \sum_i a_i \psi_i \tag{3.46}$$

where

$$a_i = -\langle \psi_i | \psi \rangle \tag{3.47}$$

this gives us

$$\Psi = \psi - \sum_i \langle \psi_i | \psi \rangle \psi_i \tag{3.48}$$

using the Hamiltonian

$$H\Psi = E\Psi \tag{3.49}$$

gives

$$H(\psi - \sum_i \langle \psi_i | \psi \rangle \psi_i) = E(\psi - \sum_i \langle \psi_i | \psi \rangle \psi_i) \tag{3.50}$$

$$H\psi - \sum_i \langle \psi_i | \psi \rangle E_i \psi_i = E\psi - E\sum_i \langle \psi_i | \psi \rangle \psi_i \tag{3.51}$$

$$\Leftrightarrow$$

$$H\psi + \sum_i (E - E_i)\langle\psi_i|\psi\rangle\psi_i = E\psi \tag{3.52}$$

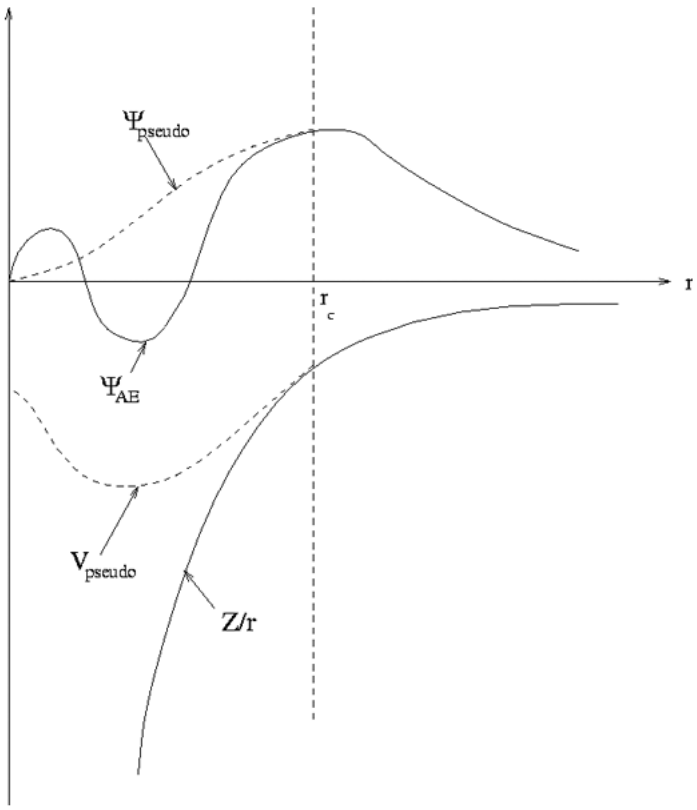

Figure 3.3: A plot of the full electron wave function vs the pseudo wave function.

CHAPTER

FOUR

Methodology, Simulations and Results

4.1 Introduction

We have done several simulations to better understand what will happen on the Germanium surface when a water molecule interacts with it. But first of all, we need to know more about the different types of surfaces. We need to consider the choice of the cell structure, a proper basis set, pseudo potentials and more.

4.2 Choosing the Model

If we choose our model too big, it will take a longer time for the super computer to calculate any results. We have to find some sort of balance between the expensive computer time and the size of our model by choosing an approximate structure. We can work with two types of models, clusters or super-cells. In most cases the computational cost is higher for super-cells than clusters with similar size.

4.2.1 Cluster

Clusters are small groups of atoms or molecules. The cluster model can be seen as a big molecule cut out from a crystal. The cutting process results in free dangling bonds at the boundary. To avoid boundary effects that is physically unlikely, we saturate the boundary with hydrogen. This tricks

the the inner atoms into thinking that it's a constraint crystal. The crystal model is not periodic, hence localized basis must be used i.e. plane waves doesn't work in this model. This results in a real Hamiltonian which becomes much faster to calculate because it takes a shorter time for the computer to calculate real numbers than complex numbers.

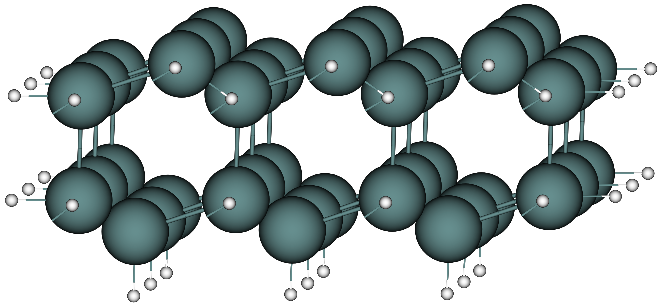

Figure 4.1: Hydrogen saturated cluster

4.2.2 Super-Cells

Just like the cluster model, we cut a part of the crystal. But instead of saturating the boundary with hydrogen atoms, we periodically repeat the super-cell to form a continuous crystal. The result is a periodic boundary condition and a simulation of an infinite big crystal. We can choose the top of the crystal to be in vacuum so that we get an empty space. But we have to remember to choose the empty space big enough so that when we periodically repeat the super-cell the surface and the bottom of the super-cell don't interact.

4.3 Simulations

4.3.1 SIESTA - Spanish Initiative for Electronic Simulations with Thousands of Atoms

We started first using the *ab initio* software SIESTA[1] to perform our electronic structure calculations. It has many nice futures like molecular dynamics simulations and the memory is allocated dynamically thanks to *Fortran 90*. It uses Kohn-Sham density functional method in the local or generalized gradient (GGA) approximations and norm-conserving pseudo potentials in its fully nonlocal form. SIESTA uses numerically defined basis functions and all the calculations are also done numerically. The source code is free and available for anyone to fiddle with. You can compile the code yourself so

[1] http://www.uam.es/departamentos/ciencias/fismateriac/siesta/

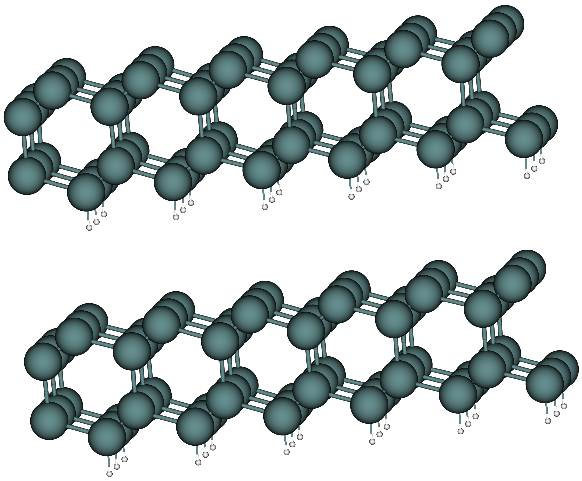

Figure 4.2: Supercell

that the executable file can be run for serial or parallel execution and of course optimize it for speed for your own computer and processor. Most important for the beginners, it has a very nice user's guide to get started with. The SIESTA source code comes a nice software called ATOM[2] to generate a pseudo potential file that can been used for input in SIESTA.

4.3.2 AIMPro - Ab Initio Modeling Program

We changed from SIESTA to AIMPro very early in our work. So we didn't get the chance to explore SIESTA any further. AIMPro is easier to understand and work with. It's written in *Fortran 95* and the source code and documentation is not available to public. Calculations are done analytically and it uses a local basis set of Gaussian type functions. The structure optimization are found by an efficient conjugate gradient method incorporating analytical evaluation of the forces. The latest version has been implemented with improvements $O(n^2)$ and $O(n)$ scaling which gives an efficient method to solve larger atomic systems and most important it has been optimized for surface calculations.

[2]Originally written by Sverre Froyen

4.4 Results

4.4.1 The Water Molecule (H_2O)

As a simple test of our Pseudopotentials, we simulated a water molecule, and compared the angle between the bonds, and the length of the bonds, with the results that experiments gives.

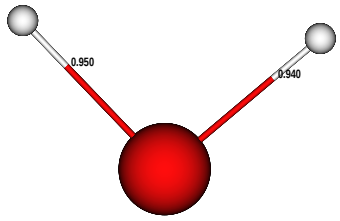

Figure 4.3: The angel of this water molecule is $\sim 93^o$ degrees

From the coordinates in table 4.1 , we can see that the angle is $\sim 93^o$, see fig 4.3

Table 4.1: Coordinates of the disturbed water molecule

Element	x-coordinate	y-coordinate	z-coordinate
O	0.0000000000	-0.3880000000	0.0000000000
H	0.7510000000	0.1940000000	0.0000000000
H	-0.6146650000	0.3235080000	0.0000000000

The first simulation with the LDA[3] gave us the coordinates shown in table 4.2 i.e a water molecule with a bonding angle of 103.80, see fig 4.4

Table 4.2: Coordinates of the water molecule after the first simulation using LDA

Element	x-coordinate	y-coordinate	z-coordinate
O	0.00668325	-0.35635707	0.00000000
H	0.82348418	0.16716256	0.0000000000
H	-0.69479820	0.31790573	0.0000000000

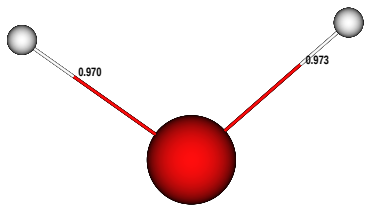

Figure 4.4: The angel of this water molecule is 103.80 degrees

[3]Local density approximation

After a simulation with the GGA[4], we got the coordinates given in table 4.3, i.e a bonding angle of 103.88, see fig 4.5, compare this with experiment[5], that gives that the angle is 104.45, and the length of the bond is 0.9584Å

Table 4.3: Coordinates of the water molecule after the second simulation using GGA

Element	x-coordinate	y-coordinate	z-coordinate
O	0.00486509	-0.35166876	0.00000000
H	0.82067553	0.16521388	0.0000000000
H	-0.69078482	0.31440809	0.0000000000

The final structure of the water moluecul, after simulation using GGA. (See figure 4.5)

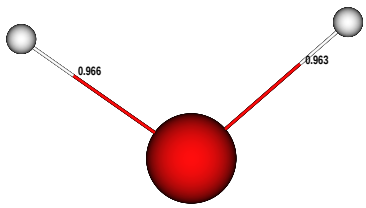

Figure 4.5: The angel of this water molecule is 103.88 degrees

The conclusion is that the pseudopotential for Hydrogen and Oxygen work very well.

[4]Gradient corrected approximation
[5]wikipedia

4.5 Simulation of a Germanium surface using the Supercell model

4.5.1 Relaxation

We started with a supercell containing 36 Germanium atoms, saturated with 9 Hydrogen atom seen in figure 4.6

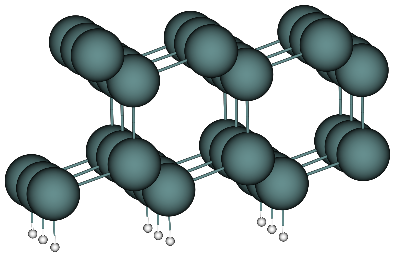

Figure 4.6: Ground supercell Ge36H9

after relaxation, we got the structure shown in fig 4.7. We can see that there has not been any big changes in the structure. The energy of the system has been lowered 0.0163824 eV.

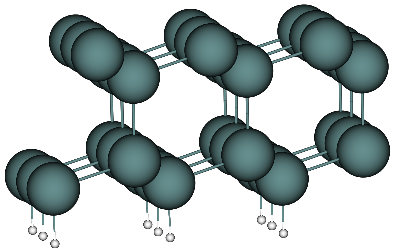

Figure 4.7: Relaxed ground supercell Ge36H9

4.6 Adding water molecule to the surface

After the relaxation of the staring surface, we used a matlab to add a water molecule to the system, see fig 4.8.

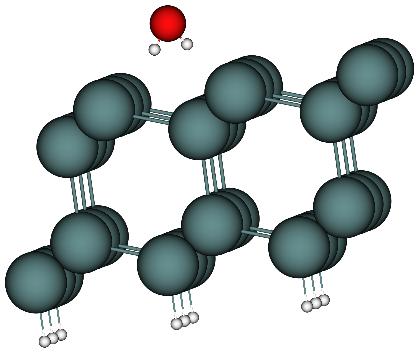

Figure 4.8: Surface with a water molecule

The water molecule interacted with surface as a molecule see figure 4.9.

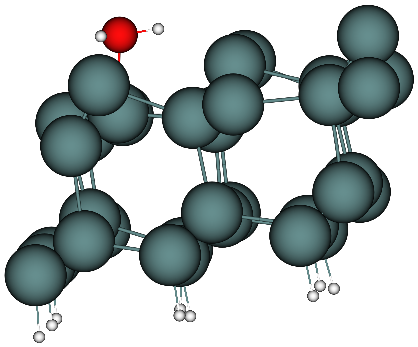

Figure 4.9: Resulting surface with a water molecule

The resulting final energy

Table 4.4: Final energy of the water molecule, interacting with the surface

	Data of Figure 4.9
Final energy	-165.70481631

To investigate if the result was a global or local minimum, we also added a separated water molecule (figure 4.10), because, in reality, we have thermal energy in the system. And that energy could be used to separate one of the

Hydrogen atoms from the water molecule, if it would result in a lower energy of the system.

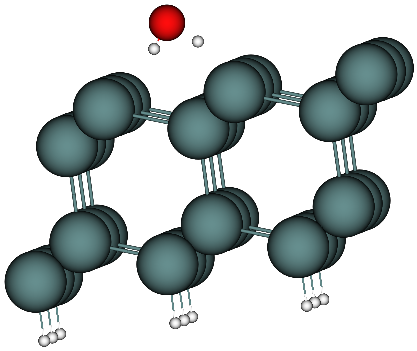

Figure 4.10: Separation case I. Surface with a water molecule (hydrogen moved approximately 0.5Å from its orignal position)

As shown i figure 4.11 we can see that the small changes (approximate 0.5Å) that we made, only resulted in the hydrogen atom binding back to the Oxygen-Hydrogen-ion, and ending up in a structure (see Figure 4.11) similar to the orignal case in Figure 4.9.

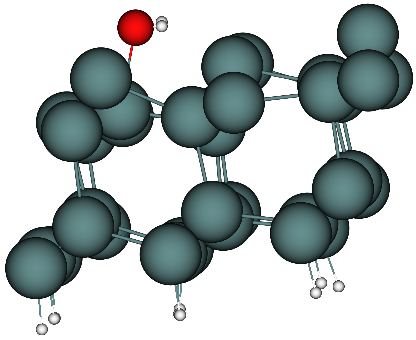

Figure 4.11: Resulting surface of Figure 4.10

We only got a small change in final energy between separation case I and our original case.

Table 4.5: Final energy of water molecule interacting with the surface in Figure 4.11

	Data of Figure 4.11
Final energy	-165.70441560

To further investigate the interaction we did a second separation case (Separation case II) where we separated the hydrogen atom approximately 1.5Å as shown in Figure 4.12.

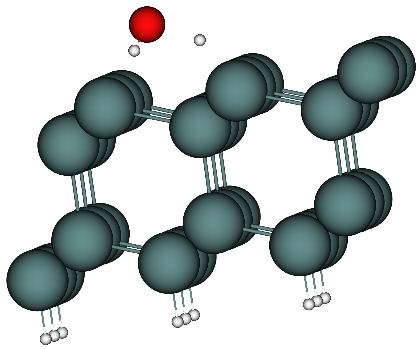

Figure 4.12: Separation case II. Surface with water molecule.

One can see in figure 4.13 that the Hydrogen atom and the Oxygen-Hydrogen-ion have bonded to the surface separately. This is likely to happened in a real system since the final energy is the lowest.

Table 4.6: Final energy of the water molecule, interacting with the surface in separation case II.

	Data of Figure 4.13
Final energy	-165.72735292

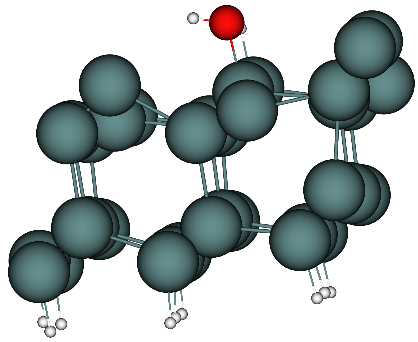

Figure 4.13: Resulting surface with a water molecule of Separation case II.

4.7 Summary and conclusions

To sum up all the results, we can see in table 4.7 that the energy between the Original case and Separation case I are very close, but Separation case II has a much lower energy, and is more likely to happen in a real system. It is likely that the Orignal case and Separation case I results correspond to a local minimum and the Separation case II corresponds to a global minimum.

However, if we had used a larger model, then it is likely that the change of the original structure of the cell had been smaller.

We tried to do the simulations with a larger cell, but we had some trouble, and did not get any results by the time of this report.

Density Functional Theory, as a tool works very well, one are able to get results with high accuracy, with relatively small computer effort. The negative part of DFT, is that, we can only calculate the groundstate energy, but must of the times, that information is all one need.

Table 4.7: The final energy of the different simulations

	Original case	Separation case I	Separation case II
Final energy	-165.70481631	-165.70441560	-165.72735292

BIBLIOGRAPHY

[1] D. Bransden and J. Brussels. *Quantum Mechanics*. Pearson, 2 edition, 2000.

[2] K. Capelle. A bird's-eye view of density-functional theory. *arXiv.org*, 4, 2005. http://arXiv.org/archive/cond-mat.

[3] A. Gross. *Theoretical Surface Science*. Springer, 1 edition, 2003.

[4] P. Hellström. *Ab Initio Modeling of Xanthate Adsorption on ZnS Surface*. Licentiate thesis, Luleå University of Technology, 2005.

[5] C. Kittel. *Introduction to Solid State Physics*. John Wiley and Sons, 8 edition, 2005.

[6] W. Kohn and L. J. Sham. Self-consistent equations including exchange and correlation effects. *Physical Review*, 140(4A):1133–1138, June 1965.

[7] E. Kreyszig. *Introductory Functionl Analysis with Applications*. John Wiley and Sons, 1 edition, 1989.

[8] D. Logan. *Applied Mathematics*. John Wiley and Sons, 2 edition, 1997.

[9] F. Nogueira and M. Marques. A tutorial on density functional theory. *Springer-Verlag*, 1, 2003.

[10] L. Råde and B. Westergren. *Mathematics Handbook for Science and Engineering*. Studentlitteratur, 4 edition, 2004.

[11] G. Sparr and A. Sparr. *Kontinuerliga System*. Studentlitteratur, 2 edition, 1999.