Metallic nanostructures offer the possibility of controlling and optimizing catalytic activity and selectivity towards specific chemical reactions by very subtle changes in size and geometry. To utilize this high degree of control in chemistry, the relationship between catalytic performance and atomic as well as electronic factors, must be understood.

In this thesis a quantum mechanical approach within density functional theory is employed to obtain an atomic level understanding of CO dissociation on iron nanostructures. This important reaction controls the reactivity and selectivity in, e.g., Fischer-Tropsch synthesis for hydrocarbons and synthesis of carbon nanotubes.

The results of this thesis indicate the structural requirements for efficient CO dissociation, reveal the possibility of controlling iron-based chemistry by magnetism and also present an efficient method for improving transition state searches in computational nanoparticle.
Reactivity of Iron Nanostructures from Density Functional Theory

Marko Melander
Abstract

Most chemical processes rely on heterogeneous catalysis. The role of a catalyst is to provide an environment for more facile breaking and making of chemical bonds without being consumed itself. Catalytic performance is determined by the electronic structure, which can be modified by changing the atomic structure and composition. Conventional heterogeneous catalysis takes place on large crystal surfaces where the catalytic activity is determined mostly by the surface structure. However, catalyst particles smaller than 10 nm exhibit finite-size effects and the catalytic properties become very dependent on the size and geometry of the particle.

The size- and geometry-dependent properties allow the modification of nanostructures towards specific catalytic applications. To reach this goal the relationships between catalytic performance and atomic and electronic factors must be understood. In this thesis a quantum mechanical approach within density functional theory is employed to obtain an atomic level understanding of CO dissociation on iron nanostructures. This is an important initial step for the total efficiency and selectivity in, e.g., Fischer-Tropsch synthesis for hydrocarbons and synthesis of carbon nanotubes.

Results on 0.5-1.5 nm icosahedral, BCC, and amorphous iron nanoparticles show that the larger particles are more reactive towards CO dissociation. The presence of particle edges is essential for facile CO dissociation and on BCC particles very low dissociation barriers are observed even without atomic steps, which are the active sites on crystal surfaces. The reactivity of particle edges is explained by favorable orbital interactions between the metal surface and CO's LUMO orbital stabilizing the transition state. An optimal site for facile CO dissociation needs to fulfil several requirements: 1) CO is adsorbed at a BCC(100) like four-fold hollow site in the initial state, 2) CO breaks over an atomic step, and 3) C is adsorbed in a fourfold site and O in a three-fold site in the final state.

All properties of magnetic materials depend on their magnetic state but the effect of different magnetic states on catalytic activity has been largely ignored. In this thesis it is shown that the electron donation and reactivity of FCC(111) iron surface can be modified by changing the magnetic state. This gives a justification for magnetically controlled catalysis.

Besides studies on reactivity of nanostructures, a general algorithm for improving transition state methods used in computational nanocatalysis was developed. The method removes external degrees of freedom using quaternion algebra and the new NEB-TR and DIMER-TR methods were shown to use fewer iterations to converge to a saddle point and describe minimum energy pathways more accurately in the case of NEB-TR.

Keywords Nanoparticle, Catalysis, Reactivity, Density Functional Theory, Iron

Tässä väitöskirjassa on hyödynnetty kvanttimekaniikan pohjautuvaa aallon ymmärrystä hiilimonoksidin hajoamisesta erilaisten rautananorakenteiden pinnalla. Tämän reaktioaskeleen on esitetty olevan keskeinen sekä selektiivisyyden että aktiivisuuden kannalta mm. pitkin hiilivetyjen Fischer Tropsch -synteesissä sekä hiilitappien synteesissä.

Tutkimalla hiilimonoksidin hajoamista 0.5-1.5 nm rautananopartikkelien pinnalla havaittiin, että suuremmat partikkelit ovat reaktiivisempia ja että partikkelien reunat ovat keskeisiä reaktiivisuuden kannalta. Etenkin FCC-rakenteen partikkelien reunat ovat hyvin reaktiivisia, mikä osoittaa, että katalyyti voi olla hyvin aktiivinen ilman atomikokoelmaa. Partikkelien reunojen reaktiivisuus johtuu matalaenergisista siirtymätilasta, mikä voidaan osoittaa orbitaaliteorian avulla. Hiilimonoksidin hajottamiseen vaadittavan aktiivisen kohdan tulee täyttää seuraavien vaatimusten mukaisesti: 1) CO on sitoutunut FCC(111)-tyyppiseen kuoppapaikkaan, 2) CO hajoaa atomikokoisen askelman yli ja 3) hiili ja happi ovat vastaavasti neljän tai kolmen atomikuoppapaikkaa.

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I also wish to thank Professor Hannes Jónsson for taking an interest in my work, our fruitful collaboration, and helpful discussions. I also want to thank Professor Kyösti Kontturi for encouraging my aspirations towards a career in science. As you said, the road towards becoming a doctor has been a unique chance for professional and personal growth.

Work would have been far less enjoyable without the encouraging and relaxed atmosphere at the Physical Chemistry Lab. Especially our solid group of computationalists has been a source of both comfort and inspiration.

This thesis would have never been completed if it weren't for my family: Marika, Emil, Nea, and Rudy. Marika, your constant love, support, and care mean more than I can ever express. Thank you for standing by me no matter what!

What lies behind us and what lies ahead of us
are tiny matters to compared what lives within us.

H.D. Thoreau

Espoo, August 2015

Marko Melander
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<th>Description</th>
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<tbody>
<tr>
<td>BCC</td>
<td>Body-Centered Cubic</td>
</tr>
<tr>
<td>CI-NEB</td>
<td>Climbing Image Nudged Elastic Band</td>
</tr>
<tr>
<td>CNT</td>
<td>Carbon Nanotube</td>
</tr>
<tr>
<td>DDI</td>
<td>Density Difference Integration</td>
</tr>
<tr>
<td>DFA</td>
<td>Density Functional Approximation</td>
</tr>
<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
</tr>
<tr>
<td>DOS</td>
<td>Density of States</td>
</tr>
<tr>
<td>FCC</td>
<td>Face-Centered Cubic</td>
</tr>
<tr>
<td>FIRE</td>
<td>Fast Inertial Relaxation Engine</td>
</tr>
<tr>
<td>FTS</td>
<td>Fischer-Tropsch Synthesis</td>
</tr>
<tr>
<td>HEG</td>
<td>Homogenous Electron Gas</td>
</tr>
<tr>
<td>HK</td>
<td>Hohenberg-Kohn</td>
</tr>
<tr>
<td>HTST</td>
<td>Harmonic Transition State Theory</td>
</tr>
<tr>
<td>KS</td>
<td>Kohn-Sham</td>
</tr>
<tr>
<td>LCAO</td>
<td>Linear Combination of Atomic Orbitals</td>
</tr>
<tr>
<td>LDA</td>
<td>Local Density Approximation</td>
</tr>
<tr>
<td>LDOS</td>
<td>Local Density of States</td>
</tr>
<tr>
<td>MD</td>
<td>Molecular Dynamics</td>
</tr>
<tr>
<td>MEP</td>
<td>Minimum Energy Path</td>
</tr>
<tr>
<td>NEB</td>
<td>Nudged Elastic Band</td>
</tr>
<tr>
<td>N-P</td>
<td>Nilsson-Pettersson model</td>
</tr>
<tr>
<td>PAW</td>
<td>Projector Augmented-Wave method</td>
</tr>
<tr>
<td>PBE</td>
<td>Perdew-Burke-Erzenhoff</td>
</tr>
<tr>
<td>PDOS</td>
<td>Projected Density of States</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>------------------------------------------------</td>
</tr>
<tr>
<td>PW</td>
<td>Plane wave</td>
</tr>
<tr>
<td>revTPSS</td>
<td>Revised Tao-Perdew-Staroverov-Scuseria</td>
</tr>
<tr>
<td>TPD</td>
<td>Temperature Programmed Desorption</td>
</tr>
<tr>
<td>$\hat{H}$</td>
<td>Hamiltonian operator</td>
</tr>
<tr>
<td>$Z$</td>
<td>Nuclear charge</td>
</tr>
<tr>
<td>$r_i$</td>
<td>Electron position</td>
</tr>
<tr>
<td>$R_i$</td>
<td>Nuclear position</td>
</tr>
<tr>
<td>$N$</td>
<td>Number of electrons</td>
</tr>
<tr>
<td>$\Psi$</td>
<td>Wave function</td>
</tr>
<tr>
<td>$n(r)/\rho(r)$</td>
<td>Electron density</td>
</tr>
<tr>
<td>$\phi(r)/\varphi(r)$</td>
<td>Molecular/atomic orbital</td>
</tr>
<tr>
<td>$v$</td>
<td>Potential</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Spin</td>
</tr>
<tr>
<td>$E^\dagger$</td>
<td>Transition state energy</td>
</tr>
<tr>
<td>$k_B$</td>
<td>Boltzmann coefficient</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
</tr>
<tr>
<td>$F$</td>
<td>Force</td>
</tr>
<tr>
<td>$\varepsilon_d$</td>
<td>d-band energy</td>
</tr>
<tr>
<td>$V_{ad}$</td>
<td>Coupling term between d-orbitals and adsorbate orbital</td>
</tr>
</tbody>
</table>
List of Publications

This doctoral dissertation consists of a summary and of the following publications which are referred to in the text by their numerals

I. **Melander, Marko; Latsa, Ville; Laasonen, Kari** 2013, *CO dissociation on iron nanoparticles: Size and geometry effects*, Journal of Chemical Physics, 139, 164320, DOI 10.1063/1.4827078


Author’s Contribution

**Publication 1:** *CO dissociation on iron nanoparticles: Size and geometry effects.*

The author planned all and performed most of the DFT calculations, interpreted the data, and wrote the manuscript with the co-authors.

**Publication 2:** *Effect of Magnetic States on the Reactivity of an FCC(111) Iron Surface.*

The author planned and executed all the DFT calculations, modelled the temperature dependent desorption spectra, interpreted the results, and wrote the manuscript with the co-authors.

**Publication 3:** *Identifying the Active Sites for CO Dissociation on Fe-BCC Nanoclusters*

The author planned and executed all the DFT calculations, interpreted the results, and wrote the manuscript with the co-author.

**Publication 4:** *Removing External Degrees of Freedom from Transition State Search Methods using Quaternions.*

The author formulated the approach for removing the external degrees of freedom, wrote the Python script used in the transition state searches, conducted the simulations, and wrote the manuscript with the co-authors.
1. Introduction

Catalysis has a profound impact on modern society enabling the efficient pro-duction of industrial and domestic chemicals as well as materials we use daily. The range of products produced using heterogenous catalysts varies from plastics, food, and cosmetics to petrochemistry, energy production, automotives, and beyond. [1] [2] From a very broad social perspective, “a world without catalysis would be hungry, immobile, dirty, and unable to combat pests and diseases” as stated by Adams [2].

Efficiency and importance of catalysis should also be viewed from economic and environmental perspectives. Due to the wide-spread use of catalytic pro cesses, the catalysis industry is of enormous economic importance; the overall impact is estimated to be $15 trillion per year. [2] Catalysis also plays a key role in eliminating, or at least reducing, environmental pollution and energy consumption due to chemical processes. [1]

To meet the social, economic and environmental demands, development of more efficient and selective catalysts from abundant elements is required. Due to the inherent complexity of a catalytic cycle spanning several time and length scales [3], this is a formidable task. The ultimate goal is the ability to control and modify reactivity and selectivity of catalysts in an atom-by-atom fashion. Here we restrain to heterogeneous catalysis where reactants and the catalyst are in different phases.

Properties of a catalyst are ultimately determined by its electronic structure, which can be modified by changing the atomic structure and composition. The role of a catalyst is to provide an environment for more facile breaking and making of chemical bonds without being consumed itself. The atomic and electronic structure of the catalyst defines the active site where chemical transformations take place. On conventional crystal surfaces, the catalytic performance is determined mostly by surface structure whereas catalysis on nanoparticles is highly dependent on size and geometry of the particle.

Experimentally, the relationships between catalytic performance and atomic and electronic factors, that is the nature of the active site, can be studied using the tools of modern surface science [4]. The increase in computer power and
development of theoretical methods has enabled the use of quantum mechanical simulations on heterogenous catalyst materials. Especially, the development of density functional theory [5] [6] has proven to provide good accuracy and speed for studying the basic reaction steps on heterogenous catalysts.

The main advantage of DFT is the ability to provide detailed atomic level understanding of the basic processes taking place on the surface of a heterogeneous catalyst. Especially, the kinetics and thermodynamics of various adsorption, desorption, diffusion, and reaction steps on a well defined catalytic system can be studied. Using DFT an accurate mapping between the electronic structure, catalyst structure, nature of the active site, and catalytic behaviour can be obtained. Apart from basic atomic understanding of catalysis and catalytic trends, data from DFT calculations provide a solid background for simulating chemical processes [7] and designing new catalysts [8] even at the industrial level [9].

The articles included in the thesis are mainly focused on using DFT for obtaining a fundamental view of CO dissociation on iron nanostructures. This is an important initial step for the total efficiency and selectivity in Fischer-Tropsch synthesis for hydrocarbons as well as synthesis of carbon nanotubes. The main goal here is to understand and explain the particle size and geometry effects in CO dissociation on iron nanoparticles and to identify the active sites. We also investigate how magnetism of iron thin films can be used for modifying the catalytic properties and develop theoretical methods for investigating the reactivity on nanoparticles.

This intro focuses on presenting the theoretical framework used in the publications. First, I review the computational methods, including a general scheme for computational heterogeneous catalysis and basics of DFT as well as methods for finding reaction mechanisms and analysis of DFT calculations. A discussion of heterogeneous catalysis with a special focus on nanocatalysis and CO dissociation is provided next. After this, the most important properties of iron nanoparticles and surfaces for CO dissociation are reviewed. Finally, a summary of the results is provided.
In this thesis a molecular and computational approach to heterogenous catalysis is applied. Since the interest is on understanding the very fundamental concepts and interactions between a surface and atoms or molecules, a quantum mechanical description is required.

In quantum mechanics the system is described by the Schrödinger equation. However, this is a very difficult problem to solve due to the many-body nature of the wave function and approximations are needed to solve it. In this thesis I have used density functional theory which is in principle exact and offers a good balance between accuracy and efficiency.

This chapter provides a brief introduction to the Schrödinger equation and DFT along with the main assumptions used in the publications. Also an overview of a computational approach to heterogenous catalysis is provided along with methods for finding minimum energy pathways and analysing the results of DFT calculations.

2.1 Computational Approach to Heterogeneous Catalysis

On the most fundamental level, performance of a catalyst is determined by its electronic structure and can be understood using quantum mechanical methods. While quantum approaches can provide an atomistic description of a chemical transformation, a realistic catalytic process spans several time and lengths scales making the complete process too complex for a fully quantum mechanical description. For modelling an entire chemical reactor based on a quantum mechanical description, a multiscale model and some coarse grainning is mandatory. A systematic way to approach a reactor scale from an atomistic perspective has been reviewed in [10] and the main features are presented in Figure 1. Original references for each method are provided in the cited article.

On the shortest time and length scales, the catalytic process is described by the atomic presentation of adsorption, bond breaking and making, and desorption dictated by quantum mechanics. Based on the reaction mechanisms and related energetics, the reaction energies and kinetics, derived from transition state theory, are obtained. Longer time and lengths scales may be studied using either \textit{ab initio} or semiemprical molecular dynamics. The information
obtained at the atomic level can then be used for finding and parametrizing reactivity descriptions, usually in the form of BEP linear free energy relationships.

![Figure 1. Various time and length scales in computational catalysis design. Acronyms from top to bottom: TST, transition state theory; QM, quantum mechanics; BEP, Brønsted-Evans-Polanyi linear free energy relations; MD, molecular dynamics; AIT, Ab Initio thermodynamics, KMFM, kinetic mean-field modelling, also known as Microkinetic modelling; KMC, kinetic Monte-Carlo, CE, cluster expansion; CFD, computational fluid dynamics. The figure is adapted from [10].]

While the atomistic description is applied mainly on rather ideal and simple systems, it provides the basic understanding of the atomic processes. To reach more realistic systems in terms of time, length and complexity, the interactions from QM can be used for parametrizing coarse grained models. The thermodynamics of rather large systems may be obtained from either ab initio thermodynamics or cluster expansion combined with statistical mechanics. Kinetic information and, e.g., product distribution as a function of control variables, such as pressure and temperature, can be computed with kinetic Monte-Carlo or kinetic mean field modelling.

The local temperature and pressure inside a reactor can be coupled with KMC and KMFM by using computational fluid dynamics or some simpler reactor models. This describes the coupling of heat and mass transport on the catalyst surface. The reactor models can further be inserted in process and plant simulations to include unit operations and cost indicators, for example. This also completes the multiscale modelling of heterogeneous catalysis. The goal of this thesis is to apply quantum mechanical methods to help understanding and explaining the atomic interactions and their catalytic implications on a larger scale.
2.2 The Schrödinger Equation

A quantum mechanical system is described by the Schrödinger equation and all the information of the physical state of a system is contained in the wave function \( |\Psi \rangle \). The interactions present in the system are described by the many-body Hamiltonian \( \hat{H} \). Here we focus only on the time-independent and non-relativistic Hamiltonian and within this frame the Schrödinger equation takes the form

\[
\hat{H} |\Psi \rangle = E |\Psi \rangle \tag{1}
\]

As a solution of this eigenvalue problem, energy and wave function of the system are obtained. When considering a system of nuclei and electrons, the Born-Oppenheimer approximation is usually invoked and the total wave function can be separated to nuclear and electronic wave functions. The electronic wave function depends parametrically on the positions of the nuclei and the electronic Hamiltonian for a Coulomb system in atomic units is written as

\[
\hat{H} = \hat{T} + \hat{V}_{\text{ext}} + \hat{W}
\]

\[
= -\frac{1}{2} \sum_{i=1}^{N} \nabla_i^2 - \sum_{i=1}^{N} \sum_{A=1}^{M} \frac{Z_A}{|\mathbf{r}_i - \mathbf{R}_A|} + \sum_{i \neq j}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \tag{2}
\]

Here \( \hat{T} \) is the kinetic energy operator for electrons, \( \hat{V}_{\text{ext}} \) is the operator for an external potential, in this case an electron interacting with a nucleus of \( Z_A \) charge, and \( \hat{W} \) is the electron-electron operator.

Solving equation (1) with the Hamiltonian in equation (2) is a formidable task due to the many-body nature of the Hamiltonian. For solving the problem some approximations must be made for all but the simplest systems. The difficulty comes from treating the correlated behaviour of electrons. In quantum chemistry, electron correlation can be taken into account using well-defined and hierarchical approaches [11], such the Möller-Plesset perturbation theory and coupled-cluster methods. However, such methods soon become untraceable when the system size is increased and systems relevant for heterogenous catalysis are rarely modelled using these approaches.

2.3 Density Functional Theory

Instead of working directly with the complicated wave function, Hohenberg and Kohn [12] have proven that the ground state of properties of a many-body quantum system can be fully characterized by the ground state electron density, \( n_0(\mathbf{r}) \). As a result of HK theorem, the simple three-dimensional electron density contains the same information as the wave function since the mapping between these is bijective as shown below. Here DFT is presented as in [5].
The relationship between the ground state wave function and ground state density can be written using the density operator $\hat{n}(r)$ and integrating over the spin variable, $\sigma$,

$$n_0(r) = \langle \Psi_0 | \hat{n}(r) | \Psi_0 \rangle$$

$$= N \sum_{\sigma_1 ... \sigma_N} \int dr_2 ... dr_N |(r_1 \sigma_1 ... r_N \sigma_N | \Psi_0)|^2$$

(3)

The proof of HK theorems is based on *reductio ad absurdum* by first showing the two different external potentials cannot produce the ground state wave function. The second HK theorem shows that two different ground state wave functions do not produce the same electron density. Thus, there is a unique and bijective mapping of the form

$$\vec{U}_{ext} \leftrightarrow |\Psi_0 \rangle \leftrightarrow n_0(r) \leftrightarrow \langle \Psi_0 | \hat{n}(r) | \Psi_0 \rangle$$

(4)

Mapping in equation (4) means that the ground state wave function is unique functional of the density: $|\Psi_0 \rangle = |\rho(n_0)\rangle$. This shows that the ground state wave function contains the same information as the ground state electron density. Consequently, observables of the ground state can be written as

$$O[n] := \langle \Psi[n] | \vec{O} | \Psi[n] \rangle$$

(5)

The most important observable is the energy which takes the form

$$E[n] := \langle \Psi[n] | \vec{H} | \Psi[n] \rangle$$

$$= F_{HK}[n] + \int dr \nu_{ext}(r)$$

(6)

Here $F_{HK}$ is the Hohenberg-Kohn functional which is written as

$$F_{HK}[n] := \langle \Psi[n] | \vec{T} + \vec{W} | \Psi[n] \rangle$$

(7)

Furthermore there is a variational principle which allows determination of the ground state energy as well as the ground state density

$$E_0 = \min_{n \rightarrow n_0} \left\{ F_{HK}[n] + \int dr \nu_{ext}(r) \right\}$$

(8)

The HK theorem applies only to non-degenerate ground states, which are $\nu$-presentable. These constraints can, however, be lifted using the Levy constrained search method [13].

While HK theorem and Levy constrained search show that density can be used as the basic variable for studying the ground state properties of an electronic system, the many-body complications are still present in the functional $F_{HK}$. Unfortunately, the form of this functional is unknown. To make the problem more tractable, Kohn and Sham [14] proposed mapping the interacting $N$-particle problem in the form of a non-interacting particles. In this case
the Hamiltonian is simply a sum of one-particle operators and the wave function is presented by a single Slater determinant. The electron density can now be presented with one-particle wave functions, $\psi_i(r)$, which are recognized as KS molecular orbitals

$$n_o(r) = n_{KS}^o(r) = \sum_{i=1}^{N} |\psi_i(r)|^2$$  \hspace{1cm} (9)

Furthermore, the kinetic energy term takes a particularly simple form

$$T_{KS}[n] = -\frac{1}{2} \sum_{i} \langle \phi_i | (\nabla^2) \phi_i \rangle$$  \hspace{1cm} (10)

The HK functional can now be defined using the non-interacting kinetic energy

$$F_{HK}[n] = T_{KS}[n] + E_H[n] + E_{xc}[n]$$  \hspace{1cm} (11)

Here $E_H[n]$ is the classical Hartree (Coulomb) term and $E_{xc}[n]$ is the exchange-correlation energy. All terms in Equation (11) except $E_{xc}$ are known and this equation defines $E_{xc}[n]$; it contains all the difficult many-body effects. Using equations (6)-(11) the energy can now be written as

$$E_0 = \min_{\phi_i, \phi_j} \left\{ \frac{1}{2} \sum \langle \phi_i | (\nabla^2) \phi_i \rangle + \langle \phi_i | v_{KS}[n] | \phi_j \rangle \mid \langle \phi_i | \phi_j \rangle = \delta_{ij} \right\}$$  \hspace{1cm} (12)

The $v_{KS}$ potential is defined as

$$v_{KS}[n](r) = v_{\text{ext}}[n](r) + v_{H}[n](r) + v_{XC}[n](r)$$  \hspace{1cm} (13)

where $v_H$ is the Hartree (Coulomb) potential

$$v_H[n](r) = \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$  \hspace{1cm} (14)

and the exchange-correlation potential is

$$v_{XC}[n](r) = \frac{\delta E_{XC}[n]}{\delta n(r)}$$  \hspace{1cm} (15)

The minimization of equation (12) is carried out using Lagrange multipliers under the indicated constraint and yields an eigenvalue problem from which the molecular orbitals and their energies can be solved; this is called the Kohn-Sham equation.

$$\left\{ -\frac{1}{2} \nabla^2 + v_{KS}[n] (r) \right\} \phi_i(r) = \varepsilon_i \phi_i(r)$$  \hspace{1cm} (16)

This equation must be solved iteratively since $v_{KS}$ depends on the molecular orbitals. Energy of the system can now be obtained using, e.g., Equation (6).

DFT can also be extended to treat spin-polarized systems, which is necessary in this thesis since the research is focused on describing iron systems. In the
case of collinear spin (non-collinearity was omitted in studies of this thesis), extension of DFT to spin-polarized systems is straightforward and the direction for spin projection is arbitrary in absence of spin-orbit coupling. It can be shown [5] that there is a direct unique correspondence between \( |\Psi_0\rangle \) and total density \( n_0 \) and z-component of the magnetization density, \( m_{z,0} \). This can be expressed as

\[
|\Psi_0\rangle \leftrightarrow (n_{0,0}, m_{z,0}) \rightarrow |\Psi_0\rangle = |\Psi_0[n_{0,0}, m_{z,0}]\rangle
\]

(17)

In the case of spin-polarization, one-particle wave functions are labelled using both the spatial and spin variables, \( \phi_i(r \sigma) \), and are called spin-orbitals. Also the potentials are spin-dependent and the KS equation becomes

\[
\left\{ -\frac{1}{2} \nabla^2 + v_{KS}^\sigma[n, n_{\sigma}](r) \right\} \phi_i(r \sigma) = \varepsilon_i \phi_i(r \sigma)
\]

(18)

where the spin-polarized KS potential takes the form

\[
v_{KS}^\sigma[n, n_{\sigma}](r) = v_{ex}[n](r) + v_H[n](r) + v_{xc}^\sigma[n, n_{\sigma}](r)
\]

(19)

and the spin-polarized exchange-correlation potential is written in terms of the spin-density \( n_{\sigma} \)

\[
v_{xc}^\sigma[n, n_{\sigma}](r) = \frac{\delta E_{xc}[n, n_{\sigma}]}{\delta n_{\sigma}(r)}
\]

(20)

The extension to spin-polarized systems allows the potential and energy depend not only on electron density but also on the distribution of spin in the system.

### 2.3.1 Exchange-Correlation Functionals

As discussed above, KS-DFT is an exact formulation for ground state properties of a many-body quantum system. However, the form of \( E_{xc} \) remains unknown and various density functional approximations have been developed to model the exchange-correlation effects. This term includes all the complicated many-body terms such anti-symmetrizity of the wave function, electron-electron correlation as well as kinetic energy contributions between the non-interacting electrons and real interacting electrons. Consequently, the form of \( E_{xc} \) must be very complicated.

Estimating the exchange-correlation term is therefore a central problem in DFT and the quality of this term determines quality of the results. In theory there should exist a universal functional to describe all systems but in reality a suitable functional for the problem at hand must be chosen from a very large variety of functionals. Even though general guidelines for choosing a functional exist [15] [16], the choice should be made with care and several problematic situations still exist [17] [18]. Next, the functionals used in the articles are introduced.
An important interacting many-body system, for which $E_{xc}$ is known very accurately, is the homogeneous electron gas. In DFT the functional form is known as the Local Density Approximation. The general equation for LDA reads

$$E_{xc}^{\text{LDA}}[n] = \int dr \, n(r) \epsilon_{xc}^{\text{HEG}}(n(r))$$  \hspace{1cm} (21)

The exchange part is known analytically [14] [19]

$$E_x^{\text{LDA}}[n] = -\frac{3}{4} \left(\frac{3}{\pi}\right)^{1/3} \int dr \, n(r)^{4/3}$$  \hspace{1cm} (22)

Analytical form for the correlation term is not known, instead several parametrizations exist [20] [21] based on accurate quantum Monte-Carlo simulations [22] of the HEG. Despite its simplicity, LDA performs surprisingly well for systems where local density variations are small, such as simple metals. However, it fails to produce correct magnetism for iron, overbinds molecules on surfaces and underestimates the bond lengths, which are essential quantities for application of DFT on catalysis.

Following the hierarchy of Perdew’s ladders for constructing density functional approximations [23], all improvements on LDA should retain its exact features and conditions [6]. Accuracy of DFAs can be increased by introducing, e.g., gradient and Laplacian of the electron density, dependence on occupied and unoccupied orbitals or other nonlocal quantities. The first improvement upon LDA is the introduction of the electron density gradient dependence. Such functionals are called Generalized Gradient Approximations which adopt the following general form

$$E_{xc}^{\text{GGA}}[n] = \int dr \, \epsilon_{xc}^{\text{HEG}}(n(r)) F_{xc}(n(r),\nabla n(r))$$  \hspace{1cm} (23)

where $F_{xc}$ is known as the enhancement factor. A popular variant of GGA, known as PBE [24], was used in publications I and III of this thesis. The exchange part of PBE is

$$F_x^{\text{PBE}}(s) = 1 + \kappa - \frac{\kappa}{1 + \mu s^2/\kappa}$$  \hspace{1cm} (24)

where $\kappa = 0.804$ and $\mu \equiv 0.21951$ as derived from conditions of Lieb-Oxford bound and LDA linear response. $s = |\nabla n(r)|/2k_F n(r)$ is a dimensionless density gradient and $k_F = [3\pi^2 n(r)]^{1/3}$ is the Fermi wave vector. The correlation part of PBE is

$$F_c^{\text{PBE}}(r_s, \zeta, t) = 1 + \frac{H(r_s, \zeta, t)}{e_{xc}^{\text{HEG}}(r_s, \zeta)}$$  \hspace{1cm} (25)

where $r_s = [4\pi/3 \, n(r)]^{1/3}$ is the Seitz radius, $\zeta = (n_1 - n_2)/n$ is the relative spin polarization and $t = |\nabla n(r)|/(2gk_F n(r))$ is another dimensionless density
gradient. $g = \left[ (1 + c)^{2/3} + (1 - c)^{2/3} \right]/2$ is the a spin-scaling factor and $k_x = (4k_F/n)^{1/2}$. $H$ takes the following form

$$H = g^3 \frac{\beta^2}{\alpha} \ln \left[ 1 + \frac{t^2 + At^4}{1 + At^2 + A^2t^4} \right]$$

(26)

with parameters $A = 2a/\left( \beta \exp(2a e_c^{HEG}/g^3 \beta^2) \right) - 1$, $\alpha = 0.09$ and $\beta \approx 0.066725$. Finally the PBE enhancement factor can be written as

$$F_{xc}^{\text{PBE}} = F_{xc}^{\text{PBE}}(s) + \frac{e_x^{\text{HEG}}(t_s, \zeta)}{e_x^{\text{HEG}}(n)} F_{xc}^{\text{PBE}}(t_s, \zeta, t)$$

(27)

PBE can be characterized as a good overall functional for studying heterogeneous catalysis. PBE outperforms LDA on all aspects and is well suited for molecular properties, adsorption energies, barrier heights as well as bond lengths. Usually PBE gives qualitatively correct results and trends are well produced but absolute adsorption energies are overestimated while reaction barriers are underestimated. Other variations of PBE have been introduced by altering the exact conditions met by the PBE functional and, thus, modifying $F_x$. Such functionals include RPBE [25] and PBEsol [26], which improve upon adsorption energies and lattice constants, respectively. However, RPBE produces worse structural properties than PBE while PBEsol yields poor adsorption energies.

[27]

The need to compensate in either structural properties, adsorption energies or to obtain generally decent behavior is a consequence of the restricted form of GGAs. By introducing a more flexible functional form more exact conditions can be met and the overall performance is improved. Building on LDA and GGAs, a Laplacian of the electron density or kinetic energy density can be introduced to obtain metaGGA functionals. The mGGA functionals have the form

$$E_{xc}^{\text{mGGA}} = \int d\mathbf{r} \ e_x^{\text{HEG}}(n(\mathbf{r})) F_{xc}(n(\mathbf{r}), \nabla n(\mathbf{r}), \mathbf{r})$$

(28)

where $\tau = \frac{1}{2} \sum_i^\text{occ} |\nabla \phi_i|^2$ is the kinetic energy density. In article II the revTPSS functional [28] was used. Compared to PBE and other GGAs, revTPSS yields good adsorption energies without structural compromises [27] and is an excellent overall functional for studying heterogeneous catalysis.

Neither LDA, GGA or mGGA can describe van der Waals dispersion forces which are especially important for weakly bound systems such as formation of a physisorption bond. Several approaches of varying complexity have been developed (for reviews see [29] [30]) the most common being the $C/r^6$ –type functionals and non-local vdW-DF correlations approximations to an integral kernel $\phi(\mathbf{r}, \mathbf{r}')$ in the $\int \int \rho(\mathbf{r}) \phi(\mathbf{r}, \mathbf{r}') \rho(\mathbf{r}')$ functional. Both type of dispersion corrections statistically improve upon LDA, GGA, and mGGA functionals for
adsorption energies and barrier heights. [31] [32] Surprisingly, the dispersion corrections also mend deficiencies in DFT description of strong chemical bonding; inclusion of vdW-DF corrections can predict the correct CO binding site and improve adsorption energies on late 4d and 5d transition metal surfaces where LDA, GGA, and mGGA fail. [33]

Even though inclusion of dispersion usually improves energetics related to adsorption and reactions, the performance is highly method-dependent and depends on the underlying GGA functional. The vdW-DF scheme is also very time-consuming. Furthermore, neither of the above methods includes electronic screening effects which are important in surface chemistry. Because of these uncertainties and the ability of GGAs to reproduce qualitatively correct CO binding properties on iron, the dispersion effects were neglected in the articles.

2.3.2 Projector Augmented Wave –Method

The difficulty of solving the KS equation depends on the external potential, usually set up the nuclei. For example, the electron-nucleus potential diverges at short distances and kinetic energy of electrons is high leading to oscillations in the wave function and hampers numerical solutions. This high kinetic energy also means that the region near nuclei is quite insensitive to the environment whereas the outer, valence wave functions depend strongly on the environment. Thus, the valence electrons largely determine the chemistry and inner electrons may be replaced by a numerically manageable, smoother potential. The smoother wave functions can be described using fewer basis functions and fewer explicitly considered electrons significantly speeds up the solution of the KS equations.

The inner electrons may be eliminated using pseudopotentials or effective core potentials. In the articles included in the thesis the Projector Augmented-Wave method [34] [35] was applied. The PAW method is closely related [36] to commonly used ultrasoft pseudopotentials [37]. PAW is the most general form of pseudopotentials and even the frozen core all-electron wave function may be retrieved if necessary. PAW is based on a transform between the real one-electron wave function with complicated nodal structure, |ψn⟩, and a smooth auxiliary wave function, |ψ̃n⟩,

\[ |ψ_n⟩ = T|ψ̃_n⟩ \]  

(29)

Using this transformation, the auxiliary wave function can be expanded using a convenient set of basis functions making the numerical solution easy. All physical properties can then be obtained either from the true or auxiliary wave function. To preserve correct nodal structure, the transformation operator is written as a sum over all atomic sites, δ̃R.
\[ T = 1 + \sum_{\mathcal{R}} S_\mathcal{R} \] (30)

\( S_\mathcal{R} \) are determined by solutions \((\phi_i)\) of the Schrödinger equation for isolated atoms. The set \(\{\phi_i\}\) of partial wavefunctions is used for constructing the valence wave functions near the corresponding nucleus within some cut-off distance

\[ \langle r | \psi \rangle = \psi(r) = \sum_{i \in \mathcal{R}} c_i \phi_i(r) \quad \text{for} \quad |r - R_\mathcal{R}| < r_{\text{cutoff}} \] (31)

where \(i\) contains the site and angular momentum components. Inner electrons are usually kept frozen so that the density and energy of inner electrons correspond to those of the isolated atoms. Both the transformation operator and \(\{\phi_i\}\) are orthogonal with respect to the inner electrons. Now, the partial wave functions are constructed from a chosen set of partial auxiliary wave functions \(\{\tilde{\phi}_i\}\)

\[ |\phi_i\rangle = (1 + S_\mathcal{R})|\tilde{\phi}_i\rangle \]
\[ S_\mathcal{R}|\tilde{\phi}_i\rangle = |\phi_i\rangle - |\tilde{\phi}_i\rangle \] (32)

which defines the transformation operator. \((1 + S_\mathcal{R})\) modifies the wave function locally and after a certain cutoff \(|\phi_i\rangle\) and \(|\tilde{\phi}_i\rangle\) are identical. Within the cutoff radius, the auxiliary wave function is expanded in terms of the partial auxiliary waves

\[ \tilde{\psi}_n(r) = \sum_{i \in \mathcal{R}} \tilde{\phi}_i(r) \langle \bar{p}_i | \tilde{\psi} \rangle \] (33)
\[ \langle \bar{p}_i | \tilde{\psi} \rangle = \delta_{ij} \]

which defines the projector operator \(\bar{p}_i\). Now the transformation operator takes the form

\[ T = 1 + \sum_{i} (|\phi_i\rangle - |\tilde{\phi}_i\rangle) \langle \bar{p}_i | \tilde{\phi}_i\rangle \] (34)

where the sum runs over all partial waves of all atoms. The true wave function becomes

\[ |\psi_n\rangle = |\tilde{\psi}_n\rangle + \sum_{i} (|\phi_i\rangle - |\tilde{\phi}_i\rangle) \langle \bar{p}_i | \tilde{\psi}_n \rangle \]
\[ = |\tilde{\psi}_n\rangle + \sum_{\mathcal{R}} (|\psi^2_\mathcal{R}\rangle - |\tilde{\psi}^2_\mathcal{R}\rangle) \] (35)

The color-coding corresponds to Figure 2 where the PAW decomposition of a wave function is shown. From this figure it can be seen that the oscillating wave function is replaced by a smoother one. As a result of the PAW decomposition, expectation values can be computed either from the true or auxiliary wave function
\[
\langle \mathcal{O} \rangle = \sum_{n \in \text{valence}} f_n(\psi_n) \hat{\mathcal{O}} |\psi_n\rangle + \sum_{n \in \text{core}} f_n(\hat{\psi}_n) |\hat{\mathcal{O}}|\psi_n\rangle = \sum_{n \in \text{valence}} f_n(\psi_n) \hat{\mathcal{T}}^+ \hat{\mathcal{T}} |\psi_n\rangle + \sum_{n \in \text{core}} f_n(\hat{\psi}_n) |\hat{\mathcal{O}}|\psi_n\rangle
\]

(36)

The explicit forms for, e.g., energy and density may be found in [34] and [35].

Figure 2. PAW presentation for the p-\(\sigma\) orbital in Cl\(_2\). The colours and symbols refer to equation 35. |\psi\rangle, |\tilde{\psi}\rangle, |\psi^{1}\rangle, and |\tilde{\psi}^{1}\rangle are the true, auxiliary, real partial and auxiliary partial wave functions, respectively. [35]

2.3.3 Basis Sets

To solve the molecular orbitals or KS states from Equation (16), the orbitals need to be represented using a basis set. The most commonly used basis set in quantum chemistry is the linear combination of atomic orbitals, where a fixed set of atomic orbitals \(\{\varphi_{\mu}\}\) is used

\[
\phi_{\text{LCAO}}(r) = \sum_{\mu} c_{\mu} \varphi_{\mu}(r)
\]

(37)

Performance of the LCAO basis set depends dramatically on the chosen atomic orbitals. The accuracy and cost are increased by introducing more atomic orbitals but there is no single parameter for controlling accuracy since the \(\varphi_{\mu}\)s are not usually orthogonal. Also different systems require different LCAO basis functions; diffuse functions need to be added when modelling metals and charged systems whereas neutral molecules utilize more compact functions. In this thesis the numerical atomic orbitals [38] included in GPAW
were used for initial structure optimization due to increased speed comparing to the grid basis described below.

In computational solid state chemistry and physics the molecular orbitals are often expanded using the plane wave basis

$$\phi_{iK}(r) = \sum_G c_{iG} e^{i(K+G)r}$$  \hspace{1cm} (38)

where $G$ is the reciprocal lattice vector and $K$ is a wave vector. Advantages of PWs are their completeness and orthogonality and single-parameter control of accuracy (kinetic energy cutoff). PWs are also inherently periodic which makes them ideal for solid state systems where translational symmetry occurs. However, nanoparticles and surfaces require large simulation cells to avoid unphysical periodic interactions.

Most computations in this thesis take advantage of presenting the KS state numerically on a real-space grid as implemented in GPAW [39] [40]. Here the integrals are replaced by sums over the grid points. GPAW uses a double-grid to obtain high accuracy without compromising for efficiency. Grid calculations are easily parallelized and, thus, suitable for modern supercomputers. Also the accuracy can be controlled by using a single parameter, the grid spacing.

2.4 Finding Minimum Energy Pathways

Chemical reactions, diffusion and configurational changes can be described as transitions from some initial atomic structure to another. The optimal path between initial and final state is called the minimum energy path, which defines the reaction mechanism. From the energies of the initial and final states reaction energies can be obtained while highest energy along the MEP gives the activation energy, $E^\dagger$, of the transition. The rate constant of a thermally activated reaction can be estimated using harmonic transition state theory

$$k_{\text{HST}} = k_0 \exp \left[ \frac{-(E^\dagger - E_{\text{init}})}{k_b T} \right]$$  \hspace{1cm} (39)

Here, $E^\dagger$ is the energy of the (highest) saddle point on the MEP between the initial and final state and $E_{\text{init}}$ is the energy of the initial state. The pre-exponential factor, $k_0$, accounts for entropic effects and is computed from normal mode frequencies at the initial state minimum and at the saddle point, $k_b$ is the Boltzmann factor and $T$ the temperature of the heat bath.

Finding the MEPs or activation energies is generally a very difficult task. In the articles included in this thesis the Nudged Elastic Band [41] [42], Climbing Image Nudged Elastic Band [43], and DIMER [44] methods were used. NEB and CI-NEB methods are used for finding the MEP between fixed initial and final states. The MEP is presented with a set of images $[R_0, R_1, R_2, ... R_N]$ and the structures of the $N-1$ images are optimized until they lie on the MEP.
the articles of the thesis the FIRE algorithm [45], based on modified Newton’s equations, was used for optimizing the (CI-)NEB path.

The total NEB force, \( F_i \), on an image is the sum of a spring force along the local tangent, \( F_i^t \), and the perpendicular, \( F_i^\perp \), component of the real force. \( F_i^t \) holds the images properly spaced along the MEP and prevents them from sliding down to the minima while \( F_i^\perp \) pushes the images to the MEP

\[
F_i = F_i^t - F_i^\perp
\]

\[
F_i^t = \nabla E(R_i) - \nabla E(R_i) \cdot \hat{t}_i \hat{t}_i
\]

\[
F_i^\perp = k(|R_{i+1} - R_i| - |R_i - R_{i-1}|) \hat{t}_i
\]

where the local unit tangent is \( \hat{t}_i = \tau_i / |\tau_i| \) and a simple estimate for the tangent is

\[
\tau_i = \frac{R_i - R_{i-1}}{|R_i - R_{i-1}|} + \frac{R_{i+1} - R_i}{|R_{i+1} - R_i|}
\]

While NEB finds the MEP between fixed initial and final states, DIMER is used for finding a transition state from a given initial structure. No information of the possible final state is assumed. DIMER can be characterized as a minimum normal mode following algorithm where only first derivatives are used, which makes it suitable also for large systems. The DIMER method uses two images, \( R_1 \) and \( R_2 \), which are separated by a fixed distance, \( 2\Delta R \). The dimer is directed along a unit vector \( \vec{N} \)

\[
R_1 = R_0 + \Delta R \vec{N} \quad \text{and} \quad R_2 = R_0 - \Delta R \vec{N}
\]

Search for the transition state comprises of two steps: rotation of the dimer along a minimum mode and translation along minimum mode direction. First, a rotational force, \( F_R \), is used for rotating the dimer along a normal mode corresponding to the lowest eigenvalue. Once this direction has been found, a translational force, \( F_T \), is applied to move the dimer along this direction

\[
F_R = (\nabla E_1 - \nabla E_2) + [(-\nabla E_1 + \nabla E_2) \cdot \vec{N}] \vec{N}
\]

\[
F_T = \nabla E_0 - 2(\nabla E_0 \cdot \vec{N}) \vec{N}
\]

with \( \vec{N} = (R_1 - R_2) / 2 \).

NEB and DIMER are most often used for studying chemical reactions or diffusion on surfaces or in bulk. Such systems are free of overall translations and rotations during the optimization of NEB or DIMER. However, non-periodic systems, such as molecules and nanoparticles, are free to rotate along the MEP. This significantly hampers transition state searches using conventional NEB and DIMER resulting in slow convergence and bad presentation of the
MEP. In publication IV a method for removing overall translations and rotations is presented.

2.5 Methods for Explaining and Analysing Reactivity in Computational Heterogenous Catalysis

Heterogeneous catalysis is based on the ability of surfaces to make and break chemical bonds. A catalytic cycle is presented in detail in Section 3, and here it suffices to introduce the four most important, interlinked roles of the surface: adsorption, diffusion, rearrangement of atoms due to changes in bonding, and desorption. Understanding how these four steps determine the catalytic activity forms the basis for analyzing, explaining and even predicting performance of catalysts. The maximum catalytic rate is obtained when these interactions are optimal. All four qualities are ultimately determined by orbital interactions and are, thus, suitable for analysis by DFT methods.

The chemical bond between an adsorbate and surface is often described in terms of electron bands of the surface and (molecular) orbitals of the adsorbate. This is schematically presented in Figure 3. Here an orbital is first coupled to the sp-band of the metal causing broadening of the initially sharp orbital. Then, this broad orbital couples with the d-states to form bonding and antibonding orbitals at low and high energies, respectively. Depending on position of the Fermi-level, these resulting orbitals are either filled or empty.

![Figure 3. Interaction of an orbital (left) with electron bands of the surface (right). DOS is the density of state and $\epsilon_F$ is the Fermi-level. Adapted from [1].](image)

The density of states describes the amount of monoelectronic states in an energy interval. Once the KS orbitals have obtained as described earlier, the DOS is easily computed

$$\rho(\epsilon) = \sum_n \langle \Psi_n | \Psi_n \rangle \delta(\epsilon - \epsilon_n)$$  \hspace{1cm} (44)

24
While the DOS presents the total density partitioning of the system as a function of energy, a local, atomic DOS is obtained by inserting the identity $\int d\mathbf{r} |\psi(r)|^2 = 1$ in Equation (44). LDOS can be used for, e.g., understanding differences in orbital energies in various environments

$$\rho(\varepsilon, \mathbf{r}) = \sum_n |\langle \psi_n | \mathbf{r} \rangle|^2 \delta(\varepsilon - \varepsilon_n)$$

(45)

Another partitioning of the DOS is based on the completeness of atomic or molecular orbitals, $\sum_i |\phi_i \rangle \langle \phi_i | = 1$. This yields the PDOS, which is useful for investigating properties of, e.g., d-states of a particular atom and their coupling with a molecular orbital of an adsorbate. The PDOS takes the form

$$\rho_1(\varepsilon) = \sum_n |\langle \psi_n | \phi_i \rangle|^2 \delta(\varepsilon - \varepsilon_n)$$

(46)

A particularly good analysis for understanding of the adsorption and dissociation of molecules on a surface is obtained by integrating over the PDOS. By assuming the molecular orbitals, $\phi_i$, are well presented by KS states of the surface, $\psi_n$, the identity $\sum_i |\psi_n \rangle \langle \psi_n | = 1$ can be introduced in Equation (46) and the integral over the PDOS becomes

$$\int d\varepsilon \rho_1(\varepsilon) = 1$$

(47)

Equation (47) is a measure of the overlap between the surface and adsorbate; larger the integral, stronger the interaction. Integral from $-\infty$ to $\varepsilon_F$ describes the filling of the molecular states due to adsorption while integrating from $\varepsilon_F$ to $\infty$ is a measure for the interaction between the empty molecular orbitals with the surface which are available for bond breaking. Such analysis was used in articles I and III.

The very popular d-band model [46] [47] for describing and predicting adsorption energies describes a situation similar to Figure 3. The d-band model assumes that differences in adsorption energy result from only differences in the d-band and that the d-contributions can be estimated with non-consistent one-electron energies. As shown below, the d-band characteristics, namely the center and width, are obtained from PDOS integration and, thus, depend on the (surface) structure. These assumptions are then introduced in the Newns-Anderson [48] model to yield a simple function for the location of the up- and down-shift of the bonding ($\omega_-\varepsilon$) and antibonding states ($\omega_+\varepsilon$), respectively

$$\delta E_{d\text{-hyb}} = -2(1 - f)\Delta\omega$$

$$\omega_{\pm} = \frac{|\varepsilon_d - \varepsilon_a|}{2} \mp \sqrt{\frac{V_{ad}^2}{4} + \left(\frac{\varepsilon_d - \varepsilon_a}{2}\right)^2}$$

$$\Delta\omega = \omega_+ - \omega_- \approx \frac{V_{ad}^2}{|\varepsilon_d - \varepsilon_a|} \quad \text{if} \quad |V_{ad}| \ll |\varepsilon_d - \varepsilon_a|$$

(48)
where $\Delta \omega_i$ is the change in the energy of bonding and antibonding states, $f$ is the filling factor of the d-states, $V_{ad} = \sum_k \langle a | f | k \rangle$ is the interaction between a valence orbital of the adsorbate and d-states, $\epsilon_d$ is the d-band energy center with respect to the Fermi-level, and $\epsilon_a$ is the energy of the adsorbate valence orbital. The d-band center and width are the first and second moments of the d-projected PDOS, respectively, and are used throughout this thesis. The PDOS naturally depends on the studied system and all metals and surface structures yield their characteristic d-band properties.

\[
M_r = \frac{\int_{-\infty}^{\infty} d\epsilon \, \epsilon n_d(\epsilon)}{\int_{-\infty}^{\infty} d\epsilon \, n_d(\epsilon)}
\]

with $M_1 = \epsilon_d$ and $M_2 = W_d$ and the d-projected PDOS takes the form

\[
n_d(\epsilon) = \sum_k |\langle k|d\rangle|^2 \delta(\epsilon - \epsilon_k)
\]

The last form Equation (48) is the usual perturbation theory results showing that splitting of bonding and antibonding states depends on the position of the d-band with respect to the atomic orbital; when the d-band energy is high, the antibonding orbital is pushed above the Fermi-level and remains empty. Thus, the adsorption is strong when the d-band center lies close to the Fermi-level.

The d-band model can also be extended to predict dissociation energies directly from the surface’s electron structure. [49] The transition state energy is estimated from interaction of the adsorbate’s HOMO and LUMO orbitals with the d-states of the metal.

\[
\delta E_{TS} = -2f \frac{V_{LUMO,d}^2}{|\epsilon_d - \epsilon_{LUMO}|} - 2(1 - f) \frac{V_{HOMO,d}^2}{|\epsilon_d - \epsilon_{HOMO}|} + \alpha V^2
\]

where the last term accounts for the (Pauli) repulsion. Another common application of the d-band model for predicting transition state energy is to use it in conjunction with the Brønsted-Evans-Polanyi linear free energy model [50]. Here the d-model is a descriptor for, e.g., adsorption energy and it is assumed that a linear correlation between adsorption or reaction energy and transition state energies exists

\[
\delta E^{\mp} = \alpha \delta E^{ads/react} + \xi \quad (0 < \alpha < 1)
\]

While the d-band model assumes that energetic changes during adsorption are caused mainly by hybridization between the d-band and adsorbate orbital and that charger-transfer during adsorption is minimal, several adsorbates do cause significant charge reorganization. The charge-transfer effects can be quantified, e.g., by computing the atomic Bader charges [51] for the adsorbate, surface, and the adsorption complex. Changes in spin-density can be analyzed similarly. Charge-transfer effects, such as bonding and back-bonding (see
Chapter 3.2.), can also be quantified using density difference integration. In DDI, the density difference is defined as

$$\Delta \rho(x, y, z) = \rho_{\text{surf} + \text{ads}} - \rho_{\text{surf}} - \rho_{\text{ads}}$$ \hspace{1cm} (53)$$

which accounts for density reorganization during adsorption. The density difference can now be integrated perpendicular to the surface

$$\Delta q(z) = \int_{-\infty}^{z} dz' \int_{-\infty}^{\infty} dx' \int_{-\infty}^{\infty} dxdy \Delta \rho(x, y, z')$$ \hspace{1cm} (54)$$

As bonding contributions are characterized by positive and back-bonding by negative $\Delta q(z)$ values [52], charge displacement analysis given by Eq.54 can be used to analyse bonding/back-bonding effects as in Article II.
3. Heterogeneous Catalysis

At the heart of all of catalysis lies the catalytic cycle describing the elementary steps from reactants to products. In heterogeneous catalysis four elementary steps can take place: adsorption, breaking and making of chemical bonds, diffusion, and finally desorption. In all steps the bond formed between the surface and atomic and molecular species determines the chemistry and functionality of the catalyst. In this chapter, the catalytic cycle is first introduced after which bonding and dissociation, especially for CO, on crystal surfaces and nanoparticles is discussed.

3.1 The Catalytic Cycle

The energetic changes along the catalytic cycle are often depicted using a reaction energy diagram, schematically presented in Figure 4 using a Langmuir-Hinselwood type mechanism as an example. Reaction (Gibbs) energies can be computed from energy differences of two stable states to yield a microscopic thermodynamic description of the reaction. Kinetic information based on the transition state theory (see Section 2.4) is obtained from energy barriers between two stable minima. According to Sabatier principle [1], the optimal combination of all energies during all steps of the catalytic cycle yields the best possible catalyst.

Figure 4. Schematic reaction energy diagram for CO dissociation yielding gaseous oxygen and surface-bound carbon. The elementary steps include adsorption, diffusion, C-O bond dissociation, recombination of the adsorbed atomic oxygens, and desorption of oxygen. Carbon stays on the surface for further reactions, e.g., FTS or CNT. A green bar denotes an energy minimum while a red bar denotes a transition state (first order saddle point).
3.2 Crystal Surfaces as Heterogeneous Catalysts

Crystal surfaces are obtained by cleaving a bulk material in a certain direction. The surface feels an entirely different environment than the bulk due to the scission of chemical bonds leading to changes in the geometric and electronic structure. The surface structure may be labelled using Miller indices derived from cutting of the unit cell (see Figure 5) and stability of the surface depends on its surface energy. Depending on direction of the cut, the surface exposes different atomic structures and coordinatively unsaturated, ‘dangling’ bonds. Thus, the surface atoms with unsaturated valence exhibit different reactivity than atoms in the bulk. This undersaturation forms the basis for various surface phenomena, such as chemisorption, surface relaxation and reconstruction.

![Figure 5. Three simple BCC surfaces. From left to right the (100), (110), and (111) surfaces are presented from above and from the side. The colour coding describes the layer in which an atom is located.](image)

Apart from van der Waals forces leading to weak physisorption binding, atoms and molecules can form chemical bonds with surfaces in the process of chemisorption. During chemisorption the electronic structure of the adsorbate and the surface are changed. Like chemical bonding in general, also chemisorption is highly directional and depends on specific orbital interactions between the surface and the adsorbate. The geometric and electronic structures of surfaces are determined by the surface orientation as shown in Figure 6. On more complex surfaces the electronic structure, and consequently bonding, varies along structurally different sites of the surface.
Figure 6. Spin-dependent density of states for iron BCC(100) and BCC(110) surfaces. The red dashed line denotes the Fermi-level. $\epsilon_d$ and $W_d$ are the d-band energy center and width, respectively.

Formation of a chemisorption bond is often depicted as in Figure 3 of Section 2.5. First the narrow gas-phase orbitals interact with the broad sp-bands of the surface to stabilize and broaden the adsorbate’s orbitals and energy levels in the DOS diagrams. Next, the broad band interacts with the d-orbitals and is split to bonding and antibonding states. Splitting depends on the orbital interactions between the adsorbate and surface while the Fermi-level determines filling of the formed hybrid orbitals; orbitals below the Fermi-level are populated and states above it remain empty. A more complete picture due to Hoffmann [53] shown in Figure 7 identifies five different contributions to chemisorption. These interactions determine the strength of the chemisorption bond at a given surface site, called the adsorption energy. Hoffmann’s view of chemisorption retains the molecular orbital picture of chemical bonding and the main difference between molecular bonding and chemisorption is the presence of a Fermi-level. The special case important for this thesis, the CO chemisorption, is discussed in detail in Section 3.2.1.

Figure 7. Five different orbital interactions in chemisorption: 1) Donation from adsorbate HOMO to empty surface states, 2) back-donation from the surface to adsorbate’s LUMO, 3) repulsion between filled states, 4) hybridization of two empty orbitals which may lead to occupied bands below the Fermi-level, and 5) electronic excitations of the surface and adsorbate leading to population/depletion of the bonding/antibonding interactions.
Besides chemisorption, surfaces also catalyse the formation and breaking of chemical bonds. Propensity towards a given chemical reaction is again determined by the geometric and electronic properties of the surface. More specifically, depending on the type of chemical bond to be activated, different arrangements of surface atoms significantly alter the energy needed to induce a chemical reaction. Such behaviour can be coined in the term ‘active site’; “A surface may be regarded as composed of atoms in varied degrees of saturation by neighbouring metal atoms. The varying degree of saturation of the catalyst atoms also involves a varying in catalytic capacity of the surface atoms. There will be all extremes between the cases in which all the atoms in the surface are and that in which relatively few are so active.” [54]

The nature of the active site with the lowest activation energy depends on the type of chemical bond that needs to be activated. For example, breaking of a $\sigma$-type C-H bond is most facile on a single metal atom. Breaking the $\pi$-bonds in CO on the other hand requires contact with multiple metal atoms. Thus, $\sigma$-bonds are usually broken at top-sites while $\pi$-bonds tend to break at high-coordinated hollow-sites. [55] The active sites exhibit the most favourable orbital interactions which can be quantified as in Equation (51); the adsorbate’s filled HOMO and LUMO interact with metal states resulting in weakening of the adsorbates bonds. The presence or absence of certain type of sites may have significant implications on both catalyst activity and selectivity. Again, the special case of CO dissociation is treated in Section 3.2.1.

### 3.2.1 CO Adsorption and Dissociation on Surfaces

Cleavage of the C-O bond in carbon monoxide is a highly structure sensitive reaction. Facile CO dissociation requires contact with several metals atoms at atomic step or edge sites. Interaction between CO and metal surfaces is often explained using the Blyholder model [56] [57] based on symmetry considerations of the frontier orbitals. This model consists of two dominating orbital interactions: donation from the CO's occupied $5\sigma$ orbital to empty $d_{xz/yz}$-states of the metal and back-donation from filled $d_{xz/yz}$ orbitals to the degenerate, empty $2\pi^*$-orbitals of CO. A competing picture of CO adsorption is provided by the Nilsson-Pettersson [58] model. As presented in Figure 8, this model is based on allylic bonding within the $\pi$-system and repulsive interaction between $5\sigma$ and the filled metal states. The allylic bond formation requires the hybridization of the $1\pi$ with $2\pi^*$, which partially weakens the $\pi$-bonding (denoted as radical formation in Figure 8). This hybrid orbital together with the ‘pure’ $\pi$-orbitals then forms bonding contributions with the metal $d$-states.
Both CO chemisorption models predict bonding from carbon to the metal, which indeed is the case on most transition metal surfaces. Furthermore, both models predict competition between $\sigma$ and $\pi$ bonding contributions albeit the interactions are different. According to the Blyholder picture, $\sigma$-bonding contributions are more dominating for low-coordinated adsorption site (top-sites) while $\pi$-bonding becomes more important in highly coordinated (hollow) sites. The N-P model suggests that both allylic bonding and repulsion are stronger in high coordination sites and the most favorable adsorption site is determined by competition between repulsive and bonding interactions.

Of the two CO chemisorption models, the N-P model is physically sounder; first, the $d_{xz}$ orbitals are rarely empty in transition metals as required by the Blyholder model and, second, N-P succeeds in explaining trends with respect to the d-band model. Furthermore, the N-P model is strongly supported by XPS experiments. [58] The good correspondence between the N-P and d-band model can be attributed to smaller $\sigma$-repulsion and larger $\pi$-bonding for higher energy $d$-orbitals, which lead to stronger chemisorption on metals with high-energy d-orbitals.

While the N-P model is physically more sound, both bonding models predict the formation of $\bar{\sigma}$ and $\bar{\pi}$ hybrid orbitals. Furthermore, bonding and antibonding states are formed, which is shown in Figure 9 for $5\sigma$ and $2\pi^*$ orbitals interacting with different d-orbitals of the metal. From Figure 9, it can be seen that HOMO of CO, the $5\sigma$, is mainly coupled to the $d_{xz}$ orbital, which is in line with the Blyholder model. Both bonding (around -9.8eV) and antibonding (-8 to -6 eV) parts of $5\sigma$ lie almost completely below the Fermi-level. Interactions between the surface and the two LUMO orbitals of CO can be mainly attributed to $2\pi^* - d_{xz+yz}$ contributions. The bonding contribution is around -3 to -1.5 eV and antibonding region is pushed above the Fermi-level. The hybridization can also depend on the electron spin as in Figure 9. Population of the bonding hybrid orbitals leads to formation of a stable chemisorption bond while the empty, antibonding states are important for dissociation of the C-O bond.
In addition to orbital hybridization, also significant charge redistribution can take place during formation of the CO chemisorption bond. An example of charge reorganization is shown in Figure 10. Electrons are transferred to oxygen, carbon, and, most importantly, to region between iron and carbon to form the chemisorption bond.

![Figure 9](image)

**Figure 9.** Density of states for CO’s $5\sigma$ and $2\pi^*$ orbitals interacting with different d-orbitals of ferromagnetic (FM) FCC(111) iron surface.¹

The same orbital interactions present in chemisorption are also responsible dissociation of CO. In the Blyholder model, both donation and back-donation weaken the C-O bond. However, the N-P model repulsive $\sigma$-bonding leads to strengthening of the C-O bond while $\pi$-bonding weakens it. Then according to the N-P model, facile CO dissociation requires a delicate balance between repulsion and filling of the $\pi$-system. As discussed earlier, adsorption at top-site
minimizes the repulsion while adsorption at hollow-sites leads to increased population of the $\pi$-orbitals due to better overlap with the metal orbitals. It is important to notice that this does not necessarily result in stronger chemisorption; increased overlap with the empty antibonding $\pi$-orbitals is paramount since these orbitals become populated during rupture of the C-O bond. [50] [58]

Figure 10. Electron reorganization during CO adsorption on ferromagnetic Fe-FCC(111) surface. The yellow denotes electron depletion and violet electron accumulation. The red, blue, and pink spheres present oxygen, carbon, and iron atoms, respectively.

The $d - 2\pi^*$ overlap is largest at atomic steps and cluster edges. Furthermore, carbon and oxygen do not bind to the same atoms which reduces repulsive interactions. Steps and edges are also geometrically favourable since less CO bending is required to reach a transition state. At smooth surfaces the C-O has to bend perpendicular to the surfaces. [50] These three arguments explain the structure sensitivity of CO dissociation and the need of atomic steps or edge sites for facile CO dissociation.

At the transition state, the C-O bond is highly elongated to 1.85-2.05 Å compared to gas-phase bond length of 1.14Å and CO dissociation is said to have a late transition state. In terms of BEP linear free-energy relations, the activation energy has the form of Equation (52) and for a late transition state slope, $\alpha$, is close to unity. Usually, the BEP relationship applies only when CO dissociation takes place on topologically similar surfaces and universally valid, simple BEP, covering smooth surfaces, steps and edges, has not been found [55]. However, several diatomic molecules exhibit two distinct BEP relationships for stepped and smooth surfaces. [59] [60] Yet, the activation energy of CO dissociation, at least on iron surfaces, seems to correlate much better with adsorption energies of individual oxygen and carbon [61] or CO (publication III) adsorption energy at the transition state geometry.
3.3 Nanocatalysis

Most heterogeneous metal catalysts are dispersed as small particles. When the particle size is reduced below some threshold, usually about 10 nm [55], chemical and physical properties become size-dependent. From a catalytic point of view, the most important size-dependent quantities are electronic structure and particle geometry, which also depend on each other. The size- and geometry-dependent catalytic properties of small particles enable vast possibilities for tuning the reactivity as well as selectivity of catalysts. Here general features of nanocatalysis are presented while an in-depth discussion of iron nanoparticles is provided in Chapter 4.

The special properties of nanoparticles originate mainly from their high surface-to-volume ratio. This is depicted in Table 1. Due to the high percentage of surface atoms, the surface energy is a major contribution to the total energy of nanoparticles. To minimize their surface energy and area, particles in the size range 1 to 2-3 nm often adopted densely-packed, polygonal shapes of cuboctahedron, dodecahedron or even icosahedron, for example. Such nanoparticles present low-coordinated and active sites not present in the bulk or large clusters. Nanoparticles in the size range 2-3 to 10 nm usually adopt the bulk geometry and the particle shape is determined by competition between surface and cohesive energy of the inner parts. Minimization of surface area is also presented in shortened bond lengths compared to the bulk phase. [55] [62] [63]

Changes in particle size, geometry, and bond lengths have non-trivial effects on the electronic structure and consequently catalytic properties of the particle.

A useful concept in nanocatalysis is scalability [64]; properties of a particle larger than some threshold size can be scaled to the bulk limit. Often the scaling adopts $N^{-3}$ dependency on the number of atoms, $N$. Properties of particles in the scalable regime can be extrapolated from larger or smaller particles having the same geometry. An example of such behaviour has been presented for gold nanoparticles where adsorption energies of CO and oxygen smoothly approach the bulk adsorption energies for 147-923 atomic particles. [65] Properties of particles smaller than the threshold for scalability can exhibit oscillatory behaviour and in the smallest, atomic clusters each atom can dramatically affect catalysis [63], as demonstrated for CO adsorption on Pt nanoparticles [66].

However, it is necessary to realize that not all properties of a particle scale similarly. For example, different chemical reactions have different active sites which might have low concentration or might not even be present in a particle of a given size and geometry. This leads to the concept of size- and geometry sensitivity which is schematically presented in Figure 11. Reactions taking place at particle facets, such as $\pi$-bond formation, occur more frequently on larger particles and exhibit negative size-sensitivity due to the increased exposure of facet sites at larger particle sizes. Also $\pi$-bond breaking exhibits nega-
tive size-sensitivity since this reaction is most active at stepped surfaces, which become geometrically possible only in particles larger than 3nm. When π-bond breaking takes place at particle edges, mixed size-sensitivity is observed since smallest particles do not have suitable edge sites while their concentration is small on large particles. Increase in reactivity or positive size-sensitivity is typically observed for reactions taking place over a single atom, such as σ-bond breaking in C-H cleavage. Reactions in this class usually take place at low-coordinated atoms, such as corner atoms with localized and high energy d-orbitals, which have high concentration in small particles. Some reactions, e.g., C-H bond formation, are rather independent of particle size due to the mild dependence between activation energy and reaction site. [55] [63] The term size-sensitivity is obviously related to the nature of the active site and whether such sites are present in the given particle geometry.

<table>
<thead>
<tr>
<th>Shells</th>
<th>Total number of atoms</th>
<th>Number of surface atoms</th>
<th>% surface atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>13</td>
<td>12</td>
<td>92</td>
</tr>
<tr>
<td>2</td>
<td>55</td>
<td>42</td>
<td>76</td>
</tr>
<tr>
<td>3</td>
<td>147</td>
<td>92</td>
<td>63</td>
</tr>
<tr>
<td>4</td>
<td>309</td>
<td>162</td>
<td>52</td>
</tr>
<tr>
<td>5</td>
<td>561</td>
<td>252</td>
<td>45</td>
</tr>
<tr>
<td>6</td>
<td>923</td>
<td>362</td>
<td>39</td>
</tr>
<tr>
<td>7</td>
<td>1415</td>
<td>492</td>
<td>35</td>
</tr>
<tr>
<td>8</td>
<td>2057</td>
<td>642</td>
<td>31</td>
</tr>
<tr>
<td>9</td>
<td>2869</td>
<td>812</td>
<td>28</td>
</tr>
<tr>
<td>10</td>
<td>3871</td>
<td>1002</td>
<td>26</td>
</tr>
</tbody>
</table>

In addition to unique geometries and various possible active sites, nanoparticles also differ from bulk in terms of their electronic structure. The smallest nanoparticles with under ~100 atoms (<1.5 nm) even display discrete electronic structure [63]. Above this size range particles exhibit a continuous electronic structure, which may differ significantly from larger particles or the bulk. Also local electronic structures (LDOS) of atoms in similar geometric environments depend largely on particle size.

Nanoparticles are often immobilized on a solid support, usually an oxide. Catalytic activity of nanoparticles can also be tuned by modifying the support material. The support has an effect on electronic as well as geometric properties of the particle through, e.g., charge-transfer process, differences in interfacial energies and strain effects. Also region at the interface and diffusion of reactants between the catalyst and support, namely the spillover region, can affect total activity of a catalyst. Overall, catalyst supports greatly affect the total activity and selectivity of a catalyst via several mechanisms. [63] In this thesis, however, only free, unsupported particles were studied.
Figure 11. Above: Size-sensitivity in nanocatalysis after [55]. TOF is turn-over frequency which denotes the catalytic activity scaled by the number of surface atoms. Below: The percentage of different surface sites in icosahedral particles as a function of number of atoms.
4. Structure, Magnetism, and Catalytic Properties of Iron Nanostructures

Iron is the most abundant transition metal in the Earth’s crust making it a cheap and accessible material. Especially noteworthy property of bulk iron is its large magnetic moment combined with a high Curie temperature. Already the bulk magnetism warrants iron as a highly potential material but when dispersed as nanoparticles or grown as thin layers, magnetism can be greatly modified. For example, small and super-paramagnetic nanoparticles have vanishing coercivity making them ideal for transformer applications while particles with high coercivity are required in storage applications. [67] As will be discussed below, the magnetism in iron nanostructures depends strongly on the size, shape and geometry of the nanostructure.

Besides interesting magnetic properties, iron is (in)famous for its high reactivity especially with oxygen and water leading to facile oxidation and formation of iron oxides. But under highly reducing conditions iron surfaces and nanoparticles display excellent catalytic properties especially for the formation and cleavage of carbon-carbon and carbon-oxygen bonds. Traditionally, heterogeneous iron catalysis is used in Fischer-Tropsch synthesis (FTS) for production of long hydrocarbons from synthesis gas [68] allowing production of fuels derived from biomass. Recently iron nanoparticles have gained popularity in the production of high quality carbon nanotubes (CNT) from, e.g., carbon monoxide [69] [70]. The overall reaction schemes for these reactions are

\[
\text{FTS: } n\text{CO} + (n+1)\text{H}_2 \leftrightarrow n\text{H}_2\text{O} + \text{C}_n\text{H}_{n+2}
\]

\[
\text{CNT: } n\text{CO} \leftrightarrow \text{C}_n + \frac{n}{2} \text{O}_2
\]

(55)

In all the reactions, carbon monoxide is used as the carbon source. Even though the actual growth mechanism of both reactions is heavily debated on (H-assisted CO dissociation [71]and the presence of iron carbides as the active phase [72] [73]), CO dissociation is usually consired as the first and often rate-limiting step in FTS, and CNT syntheses. As discussed in Section4.4.1., CO dissociation rate greatly affects both selectivity and yield in both syntheses. Studying and understanding how CO dissociation depends on the size, geometry and structure of iron nanostructures form the core of this thesis. In this Chapter the properties of bulk iron and its crystal surfaces are first reviewed. Then geometry and magnetism of iron nanoparticles and thin films is dis-
Structure, Magnetism, and Catalytic Properties of Iron Nanostructures

cussed. Finally, CO dissociation on different heterogeneous iron systems is discussed before a brief summary.

4.1 Structures of Bulk Iron and Crystal Surfaces

In the bulk, iron can adopt either BCC, FCC, or HCP structures. BCC is the most commonly encountered form which is stable at 'low' pressures (<13 GPa) and temperatures under 1150 K and between 1700-1850 K. FCC structured iron is met at all pressures in temperatures between 1050 and 2200 K. HCP iron is stable only in pressures higher than 12 GPa and temperatures below 1000-1500 K. Melting occurs between 1850 and 2500K depending on the pressure. [74] Most studies on catalytic properties of iron are focused on BCC iron which is present in usual catalytic conditions. However, FCC iron may be encountered in FTS reaction and CNT synthesis in which high temperatures of ~1000 K are used or in thin film catalysts.

BCC iron is always ferromagnetic with an atomic magnetic moment of 2.23 $\mu_B$ at zero K and equilibrium lattice constant of 2.87Å. The moment starts declining rapidly around 1000 K. The Curie temperature is rather close to the BCC-FCC transition state at 1043 K. [75] FCC iron exhibits a rich magnetic phase diagram with different magnetic orderings and moments at different lattice constants. In Cu precipitates FCC iron takes a double-layered antiferromagnetic form with an atomic magnetic moment of 1.90 $\mu_B$ at the lattice constant of 3.54 Å. [76] [77] [78] At shorter lattice constants the most stable magnetic structure is a noncollinear spin-spiral state [77]. The transformation from BCC to FCC phase follows the tetragonal Bain pathway and is accompanied by a change from a ferromagnetic to the double-layered antiferromagnetic spin structure [79] [80] probably via a noncollinear spin state.

Practically all studies on heterogenous iron catalysis have focused on BCC surfaces. Even different BCC surface structures give rise to rich chemistry and form the basis for understanding structure and reactivity of nanostructured systems. The most stable Fe-BCC surfaces are illustrated in Figure 12 along the corresponding surface energies in Table 2. It is noteworthy that there are several stable stepped surfaces which are often the most catalytically active surfaces. In the densely-packed (100) and (110) surfaces only small, 1-3%, inward relaxations take place while the more open surfaces relax by 10-25 %. The high surface energies correlate very well with increasing roughness and large inward relaxation. [81]

<table>
<thead>
<tr>
<th>Surface</th>
<th>110</th>
<th>100</th>
<th>111</th>
<th>211</th>
<th>710</th>
<th>310</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma$ [mJ m$^{-2}$]</td>
<td>2.37 [81]</td>
<td>2.47 [81]</td>
<td>2.66 [81]</td>
<td>2.50 [81]</td>
<td>2.50 [61]</td>
<td>2.53 [81]</td>
</tr>
<tr>
<td>$\gamma^{a(1)} / \gamma^{10}$</td>
<td>1.00</td>
<td>1.04</td>
<td>1.09</td>
<td>1.05</td>
<td>1.05</td>
<td>1.07</td>
</tr>
</tbody>
</table>

Table 2. Surface energies ($\gamma$) of most stable BCC iron surfaces.
4.2 Nanoparticles

4.2.1 Structure and Energy of Nanoparticles

Geometry and structure of nanoparticles depend strongly on the size of the particle and physicochemical properties of the surroundings. In nanoparticle synthesis the resulting particle structure and size are determined by competitive kinetic and thermodynamic factors [82]. The final structure may deviate significantly from structures found in bulk phases. Here we focus only on the thermodynamic stability of different structures and their size-dependent stability of iron nanoparticles.

The total (Gibbs) energy of nanoparticles contains contributions from bulk and surface of the particle as well as particle edges and vertices. The total energy of a particle can then be written as a sum of the different terms including stress energy [83] [84]

\[
E(N) = E_{\text{bulk}} + E_{\text{surface}} + E_{\text{edge}} + E_{\text{vertex}} + E_{\text{strain}} = \Delta_f E + \sum_{(hkl)} A_{(hkl)} \gamma_{(hkl)} + \sum_i L_i \lambda_i + \sum_i W_i \kappa_i + \int dV \sum_{ij} s_{ij} \sigma_{ij} \tag{56}
\]

where \( \Delta_f E \) is the bulk formation energy, \( A_{(hkl)} \) and \( \gamma_{(hkl)} \) are the area and surface energy of a surface defined by its Miller indices, \( L_i \) and \( \lambda_i \) are the total length and energy per unit length of an edge, \( W_i \) and \( \kappa_i \) are the number and energy of an vertex while the strain term contains both the surface and bulk terms and can be written in terms of the strain tensor \( s_{ij} \) specifying the direc-
tion of deformation and $\sigma_{ij}$ is the stress tensor. Often the energy is approximated using a simple polynomial [85]

$$E \approx aN + bN^{2/3} + cN^{1/3} + d$$  \hspace{1cm} (57)

where $N$ is the number of atoms and the first term corresponds to volume contribution, while the others present surface, edge, and vertex terms. In this expression strain has been adsorbed in the volume contribution. It is clear that the nanoparticle structure is determined by competition between several energy terms and the minimization of the total energy gives rise to several possible structures; energy of small particles is primarily determined by contributions from low-coordinated atoms at edges and vertices while large particles are very well described in terms of bulk and surface energies.

To minimize their surface energy, small metallic nanoparticles often adopt some layered, shell-like and highly geometric polyhedral shape. Common shapes are various cuboctahedral, decahedral, or icosahedral shapes. While cubocta- and decahedral particles are crystalline, icosahedra are noncrystalline and are not found in bulk size clusters. Particularly stable structures are referred to as magic clusters, which complete either a geometric or electronic shell structure. For example, stable icosahedral particles are formed when an atomic shell is completed at atomic numbers

$$N_{ico} = (10n^3 + 15n^2 + 11n + 3)/3$$  \hspace{1cm} (58)

Often small (<100 atoms) particles take icosahedral structures to obtain low-energy FCC(111)-like, densely-packed surfaces. However, the icosahedral particles are highly strained and, thus, unstable at large sizes. Decahedral clusters also have low surface-to-volume ratio but they contain more open surfaces than icosahedra. They are also less strained than icosahedra making the decahedral clusters appear in large sizes than the icosahedral. Still larger particles are observed to take an octahedral shape which are less strained but expose more open surfaces. [85]

Geometry of nanoparticles larger than ~10 nm can be predicted from macroscopic surfaces energies by using the Wulff construction [86] which minimizes the (free) energy of the particle.

$$E_{Wulff} = \min_{V=constant} \left\{ \sum_{hkl} A_{hkl} \gamma_{hkl} \right\}$$  \hspace{1cm} (59)

where $hkl$ are the Miller indices considered in the construction, $\gamma_{hkl}$ is the corresponding surface energy and $d_{hkl}$ is the distance from the origin: $d_{hkl} = d_{111} \gamma_{hkl}/\gamma_{111}$. Following this construction the particle structure is simply determined from surface energy ratios. The Wulff construction is a macroscopic
description and does not contain surface energy of edges of corners or the effect strain. An example of iron Wulff construction is given in Figure 13.

4.2.2 Structure and Magnetism of Iron Nanoparticles

Already the phase diagram of bulk iron shows that iron can exist in different forms and also in the nanoscale a competition between several structures is observed. DFT studies [87] [88] have shown that 13-atom (0.5 nm) iron particles adopt a (Jahn-Teller distorted [89]) icosahedral structure. In 55-atom (1.0 nm) clusters a clear competition between icosahedral, BCC and FCC structures is observed and Mackay transformed icosahedra have lower energy than perfect icosahedra. [87] The Mackay transformation is a gradual transformation from icosahedral to BCC geometry analogous to Bain transformation between FCC-BCC bulk symmetries. In iron nanoparticles the Mackay transformation retains the icosahedral five-fold symmetry but the central atoms have a local FCC coordination while surface atoms already have BCC –type coordination. [87] [90] The Mackay icosahedra are more stable than perfect icosahedra in all sizes beyond 13 atoms. However, according to DFT calculations, clusters larger than 140 atoms (1.5 nm) always adopt the BCC geometry. [87]

While DFT calculations are done at zero Kelvins, molecular dynamics (MD) provide access to finite temperatures at the cost of switching DFT to empirical potentials. In MD simulations using the EAM potential fit to bulk BCC iron [91], only icosahedral and FCC particles are observed in the size and temperature range of 100-432 atoms and 300-1000 K, respectively. The smallest clusters are mainly icosahedral while increases in size and temperature make the FCC structures more stable than the icosahedra. At 1024 atoms (~2.5 nm) only BCC geometry is observed below 1000 K. Unfortunately, the crossover sizes and temperatures have not been obtained in these simulations. MD simulations predict the change from icosahedra and FCC to BCC occurs at larger sizes than in DFT studies. Unlike DFT studies, the empirical models do not describe magnetism explicitly, which might explain the differences between MD and DFT. The transformation pathway in MD simulations is, however, similar to DFT results going from icosahedra to FCC (Mackay transformation) to BCC as the size increases. Again, a density functional tight-binding study [92] has shown that an initially icosahedral structure can become seriously deformed in high temperatures or presence of adsorbates, in conditions relevant for CNT growth.

Experimentally iron particles larger than 6 nm are observed to have BCC geometry and the structure is well described by the Wulff construction derived from surface energies of crystal BCC-Fe surfaces. [93] This structure is shown in Figure 13 and it can be seen that macroscopic iron clusters consist mainly of smooth BCC(100) and BCC(110) surfaces and the concentration of stepped surfaces is small. While BCC appears to be the thermodynamically most stable phase in particles larger than 2.5 nm, dynamically trapped icosahedra can be
synthesized in even 5-13 nm sizes. [94] In CNT synthesis conditions BCC [95] [96], FCC [70] [97], and amorphous [98] iron clusters have been observed.

Figure 13. Wulff construction of a macroscopic (“infinite size”) iron nanoparticle using the surface energies of Table 2.

DFT studies have shown that magnetism and structure of iron nanoparticles are intimately coupled and that magnetism plays a definite role in determining stability. [88] As a general trend, Fe nanoparticles have larger atomic magnetic moments than bulk BCC iron as summarized in Figure 14. The enhanced magnetic moment is mainly due to undercoordination at the particle surface which explains the very high moments in the smallest clusters. It is also typical that a shell-wise magnetic structure is observed. As the cluster size is increased, magnetic moments approach the bulk value of 2.23 $\mu_B$ non-monotonically.

Depending on the geometry, Fe nanoparticles can obtain antiferromagnetic, ferromagnetic, or even noncollinear magnetic structures. Noncollinearity is observed in Fe$_5$ and icosahedral Fe$_{13}$ clusters in which the collinear state is retained if lowering of symmetry is allowed [89]. The icosahedral Fe$_{13}$ takes a ferromagnetic ground state while large icosahedral Fe$_{55}$ and Fe$_{147}$ have an antiferromagnetic spin-structure. [88] Fe-FCC particles can take either a ferromagnetic [88] or antiferromagnetic [99] structure depending on the particle size; small, under 1.5 nm are predicted to be antiferromagnetic while larger particles have a competition between the two states. BCC particles are always ferromagnetic independent of the size. [100] [101]

Comparison of experimentally obtained [102] [103] and DFT computed magnetic moments in Figure 14 show that computed values for icosahedral Fe$_{13}$ particles are in good agreement with the observed magnetic moments. Around 55 atoms the normal and the Mackay transformed icosahedron capture the drop magnetic moment seen in the experiments. In larger clusters the moments computed for the BCC particles show best agreement with the experiments.
4.3 Thin Films

Depending on the underlying substrate, iron thin films can adopt either BCC or FCC geometry with strong variations in their magnetic structure. The substrate provides a stencil for epitaxial growth and the lattice constant mismatch significantly affects the magnetic properties. Also the nature of chemical bonding between the thin film and substrate affect the magnetism of the film. For example, a two monolayer BCC iron grown on W(110) has a magnetic moment of $2.84 \mu_B$ compared to bulk iron ($2.23 \mu_B$) or crystal Fe-BCC(110) surface ($2.57 \mu_B$). On the other hand BCC-Fe on InAs(001) surface has a vanishing magnetic moment. [104]

Even more interesting are iron films grown on FCC materials offering a natural way for accessing FCC iron which is unstable in the bulk and rarely observed in nanoparticles. Depending on the substrate and thickness, Fe-FCC films can be found in ferromagnetic, antiferromagnetic, or noncollinear spin states. The small energy differences between various spin structures allow facile excitation between the states by, e.g., external magnetic fields. As discussed in Section 4.1, magnetism in FCC iron is very sensitive to the lattice constant; by subtle changes in the substrate, large changes in the electron structure and magnetism can be achieved. [104] For example, in Fe(100)/Cu$_{1-x}$Au$_x$ the lattice constant of the substrate varies between 3.61 and 3.70 Å with corresponding magnetic moments of 0.3 and 2.0 $\mu_B$ in the iron layer. [105]
By far the most studied substrate for iron thin films is copper. This systems bears a small lattice mismatch (-0.6%) making the thin films particularly stable. Depending on the number of iron layers, either a ferromagnetic or double-layered antiferromagnetic spin structures is observed on the Cu(001) surface. However, on the Cu(111) surface both the ferromagnetic and double-layer antiferromagnetic structures are equally stable.

4.4 Heterogenous Iron Catalysts for CO Dissociation

4.4.1 On the Importance of CO Dissociation

CO adsorption and dissociation are key steps in several industrially relevant systems and also common probes for understanding surface properties of heterogeneous systems due to its apparent simplicity and yet rich chemical interactions. Industrially the most important and traditional use of heterogeneous iron catalysts is the Fischer-Tropsch synthesis of hydrocarbons from CO and H₂. A more modern application relying on CO dissociation on iron nanoparticles is the growth of carbon nanotubes.

Kinetic studies of van Santen et al. have shown how the relative rates of CO dissociation and chain growth affect the growth and activity in FTS. [108] [109] [110] It appears that maximum CO consumption (and FTS activity) is achieved when chain growth is the limiting step and fast CO dissociation provides a constant carbon feedstock. To achieve high activity and selectivity in production of long hydrocarbon chains, CO dissociation should have a low dissociation barrier without poisoning the active site. As CO dissociation is a highly structure sensitive reaction proceeding much faster on step edges than smooth surfaces, the chain propagation must take place at different sites than CO dissociation preventing poisoning of the surface by carbon. [110] [111] This dual site model exemplifies that an efficient catalyst must provide sites for all steps of the catalytic cycle. Furthermore, rate of CO dissociation is closely related to both activity and selectivity of the over-all FTS cycle.

Besides FTS, the growth of carbon nanotubes (CNT) by chemical vapor deposition has attracted much attention in recent years. A common way for producing high-quality CNTs is the use of iron nanoparticles and CO as the carbon source. While the growth mechanism of CNTs is still debated on, four basic steps and roles of the catalyst particle have been identified [98] [112]: 1) dissociation of the carbon source, 2) diffusion and reaction of carbon intermediates, 3) provide a template for nucleation, and 4) maintenance of a reactive nanotube rim for growing the tube. Recently the importance of dynamic particle reconstruction has been shown experimentally. [113] It is evident that size and geometry of the catalyst particle control all the four steps and, thus, the structure and properties of the CNT. Most computational studies on CNT growth have focused on aspects of 2-4. [98] [112] Only few studies have addressed dissociation of the carbon sources on iron nanoparticles beyond > 1.0nm [114]
which are relevant for CNT growth. As discussed what regards to FTS synthesis, dissociation of the carbon source can be important for selectivity and activity of the whole CNT synthesis. In this context the proposal by Fiawoo et al. is particularly interesting; CNT chirality can be controlled under mild conditions near thermodynamic equilibrium. This suggests that either step 3 or 4 should be rate-limiting while constant carbon feed is provided by faster steps 1 and 2.

The above discussion reveals several important points in CO-based chemistry. First, the adsorption of CO should be sufficiently strong to populate the sites where facile CO dissociation takes place. Usually this imposes no problems because reactions are carried at rather high temperatures and CO diffusion is fast compared to dissociation. However, strong CO adsorption might stabilize the complex too much leading to slower dissociation and poisoning of catalytic sites by carbon since C and CO adsorption energies are positively correlated in the BEP sense. Secondly, to reach high reactivity and selectivity of the entire catalytic cycle, the CO dissociation should not be the rate-limiting step. Rather, CO dissociation should provide a constant feed of carbon. Fast CO dissociation also enables the use of more benign reaction conditions improving the energy efficiency and minimizing entropic contributions which usually hamper selectivity. Third, CO based chemistries on iron should be carried out at reductive environments to prevent oxygenation and carburization of the surface. Finally, the catalytic particles should provide sites for CO dissociation as well as other steps of the catalytic cycle, e.g., formation of carbon-carbon bonds.

4.4.2 Crystal Surfaces

The importance of CO adsorption and dissociation on iron has led to an extensive amount of experimental and computational surface science studies. Here we focus on the computational results in [61] and [117] while overviews of the experimental results can be found in the same references. The chosen computational studies cover all the most important BCC iron surfaces in Figure 12, and the results can be compared without the uncertainty rising from the choice computational methods. A comprehensive overview on the effect of different computational methods on the CO adsorption energies, dissociation barriers and reaction energies can be found in [117] and Appendix of [118].

CO adsorption energies on different Fe-BCC surfaces at low coverage (0.25 ML) are presented in Table 3. The adsorption process is highly exothermic on all surfaces. CO adsorbs strongest on the hollow sites and the four-fold hollow site on Fe(100) has the largest CO adsorption energy. The stepped surfaces have slightly smaller adsorption energies than smooth surfaces. During adsorption, the C-O bond is elongated to 1.17-1.21 Å from the gas-phase value of 1.14 Å. The bond is more elongated at high-coordinated hollow sites as a result of more favourable back-bonding from iron to CO’s 2π*-orbitals. Overall, the CO adsorption is rather independent of the surface crystal structure with ad-
sorption CO adsorption energies varying only by 0.36 eV between the different surfaces.

Dissociation barriers on the other hand differ by up to 0.87 eV depending on the surface expressing the site sensitivity observed in CO chemistry. Dissociation is most facile on stepped surfaces where CO is adsorbed in four-fold coordination sites and repulsion between C-and O-fragments is minimized at the transition and final states. At the transition state, carbon is located in the initial (hollow) site and oxygen has migrated to the bridge-site connecting the adjacent hollow-sites. CO dissociation has a very late transition state where the C-O bond is highly elongated to 1.89-2.01 Å.

**Table 3.** CO adsorption energies ($E_{ads}$), dissociation barriers ($E'$), reaction energies ($\Delta E$), CO vibrational frequencies (Freq. [cm$^{-1}$]) for CO dissociation on various Fe-BCC crystal surfaces. The CO adsorption and dissociation sites {H} and {T} correspond to hollow and top sites, respectively. All the values are from Ref. [61] and given in eV. The gas-phase CO vibrational frequency is 2143 cm$^{-1}$

<table>
<thead>
<tr>
<th>Surface</th>
<th>$E_{ads}$ (eV)</th>
<th>$E'$ (eV)</th>
<th>$\Delta E$ (eV)</th>
<th>Freq. (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(100){H}</td>
<td>-2.12</td>
<td>1.07</td>
<td>-0.45</td>
<td>1189</td>
</tr>
<tr>
<td>Fe(110){T}</td>
<td>-1.92</td>
<td>1.54</td>
<td>0.50</td>
<td>1928</td>
</tr>
<tr>
<td>Fe(111){H}</td>
<td>-2.09</td>
<td>0.91</td>
<td>-1.14</td>
<td>1815</td>
</tr>
<tr>
<td>Fe(211){H}</td>
<td>-1.96</td>
<td>1.02</td>
<td>-0.24</td>
<td>1634</td>
</tr>
<tr>
<td>Fe(710){H}</td>
<td>-1.80</td>
<td>0.67</td>
<td>-1.20</td>
<td>1147</td>
</tr>
<tr>
<td>Fe(310){H}</td>
<td>-1.76</td>
<td>0.72</td>
<td>-1.14</td>
<td>1134</td>
</tr>
</tbody>
</table>

CO dissociation is an exothermic reaction on all but the Fe(110) surface. Carbon and oxygen favour adsorption in four- and three-fold hollow sites, respectively, which largely determines the reaction energy; when both carbon and oxygen are the preferred sites the reaction is thermodynamically very favourable.

In realistic synthesis conditions of FTS, and CNT growth iron surfaces are hardly empty or have low coverage. At low temperatures and pressures the surfaces are covered only with CO while high temperatures and pressures lead to only dissociatively adsorbed CO. The reactions are usually carried in temperatures $>500$ K and pressures 0.05-2.0 MPa [63] [69] and in these conditions all iron surfaces are covered with a mixture of CO as well as atomic carbon and oxygen [117]. Increasing coverage leads to lower adsorption energies and less exothermic reactions. In relevant reaction conditions and surface coverages, smooth surfaces become even less reactive and the dissociation barriers can grow by over an eV. However, stepped surfaces, such as Fe(310), retain their activity even at high coverages and the barriers vary only by ±0.2 eV compared to empty surfaces. [117]

It is common [8] that reaction barriers are predicted using simple descriptors such as the d-band energy center or adsorption and reaction energies to form linear, BEP free-energy relations described in Section 2.5. In papers I and III it was noted that neither CO adsorption nor dissociation on iron obey the simple d-band model when the $V_{ad}$ couplings are assumed to remain unchanged for different surfaces and nanoparticles. The failure of the d-band...
model in predicting CO adsorption energies on transition metal surfaces seems to be quite universal [57] eventhough CO adsorption on some (noble) metal surfaces can be predicted from the d-band model [119]. Also, from Table 3 it is visible that CO dissociation barriers are not linearly correlated with adsorption or reaction energies. Also the CO vibrational frequencies have been shown to scale rather linearly with the d-band center; higher d-band energies result in larger filling of the $\pi^*$-orbital and lower CO vibrational fruencies. [57] Instead of using d-band energies or the simple BEP, it has been shown [61] that CO dissociation barriers on iron can be predicted from adsorption energies of individual carbon and oxygen atoms bound in the final state and from the number of iron atoms bridging C and O at the transition state. In the Results section the use of PDOS integration (Eq. 47) is proposed as a useful predictor for CO dissociation barriers.

4.4.3 Nanoparticles

Compared to the vast literature available for catalysis on crystal iron surfaces, reactivity of iron nanoparticles has received little attention. The earliest [120] experimental of CO adsorption on Fe nanoparticles study showed that 1.0-12.8 nm nanoparticles have only one C-O IR absorption peak around 1890-1950 cm$^{-1}$ which presumably corresponds to top-site adsorption [121] on Fe-BCC(110) (see Table 3). Also iron clusters with 18-27 atoms (<1.0 nm) also adsorb CO on top-sites. [121]

While experimental studies clearly propose top-sites as the most favourable adsorption sites, computational studies have given contradictory results. A study on icosahedral Fe$_{55}$, predicted that adsorption is favoured on top-sites with adsorption energy of -1.83 eV. [122] In a more comprehensive study, CO is found to adsorb stronger on hollow than top sites in all cluster sizes and morphologies in Fe$_{3-65}$ clusters. In clusters smaller than 25 atoms, the adsorption energy oscillates between 1.43 and 2.10 eV while converging to ~1.8 eV in larger clusters. Furthermore, CO dissociation is predicted to be exothermic in clusters larger than 11 atoms. [123] CO adsorption on BCC and icosahedral particles studied in this thesis is discussed in the Results section.

Previously CO dissociation on iron nanoparticles has been considered only for the icosahedral Fe$_{13}$ and Fe$_{55}$. On Fe$_{13}$ the dissociation barrier from a hollow site is 1.80 eV. [124] On Fe$_{55}$ the most facile dissociation pathway starts from vertex top-site and has activation energy of 0.66 eV when CO breaks over the particle edge. [122] However, this value is incorrect, since it actually corresponds to CO diffusion barrier for top-to-hollow process as proven in the Supporting Information of publication I. A large part of the Results section is devoted to size- and geometry-dependence of CO dissociation on iron nanoparticles.
4.5 Summary

Iron exists in a diversity of geometric and magnetic structures depending on particle size and conditions. The magnetism varies from the antiferromagnetic FCC iron and ferromagnetic BCC to highly size- and geometry-dependent magnetism found in Fe nanoparticles. Several crystal surfaces of iron have similar surface energies enabling several different facets to appear in large BCC nanoparticles. Small iron nanoparticles adopt either icosahedral or BCC geometries depending on the particle size while thin films often adopt an FCC configuration.

Since CO dissociation is a very structure sensitive reaction, the dissociation barriers vary significantly among the possible iron systems. To optimize yield and selectivity facile CO dissociation is required to provide a reservoir carbon for further reaction steps such as chain growth. Dissociation studies on crystal surfaces have shown that stepped surfaces or similar particle edges are essential for meeting this criterion of low CO dissociation barriers in both UHV and reactor conditions. However, the concentration of stepped surfaces is very small as seen from the Wulff construction in Figure 13 and in nanoparticles stepped surfaces become geometrically possible only in particles larger than 3nm. Yet, particle edges are often modelled using step as presentative models as will be discussed below.

While reactivity of BCC crystal surface towards CO dissociation is well understood and studied, the reactivity of iron nanoparticles is scarce. Here the essential questions are how particle size and geometry affect the reactivity. Since nanoparticles provide reaction sites not found on crystal surfaces, the nature of active site is of high importance and can guide rational catalyst design. Furthermore, to my knowledge, there have not been any studies on reactivity of FCC iron even though such structures are realized in thin films and at high temperatures in bulk iron. Also the effect of magnetism and different magnetic states, a fundamental property of iron, on heterogeneous reactions is largely unexplored.
5. Results

5.1 Size- and Geometry-Dependence of CO Dissociation on Iron Nanoparticles

The central research questions in this thesis are how geometry and size affect the propensity of iron nanoparticles for CO dissociation. Another important aspect is the nature of the active site; CO dissociation usually takes place at stepped surfaces which are absent in clusters smaller than 3 nm and scarce even in large particles. Yet, even small, 1-2 nm iron nanoparticles are very good catalysts for CNT growth. Particle edges are often modelled using steps as presentative models for edges but in this thesis the actual edges or other similar models are used. In publications I and III the reactivity of small Fe nanoparticles and use of different simplified models have been addressed.

To answer these questions three of the smallest icosahedral particles (Fe\textsubscript{13,55,147}), an amorphous Fe\textsubscript{78}, BCC-structured Fe\textsubscript{145} shown in Figure 15 were studied. The icosahedral particles are the most stable geometries for iron in clusters smaller than 140 atoms whereas larger clusters adopted the BCC structure. However, high temperatures and presence of adsorbates may deform the smooth and symmetric icosahedral and BCC structures; the amorphous Fe\textsubscript{78} presents a particle in conditions relevant for CNT synthesis.

![Figure 15. Iron nanoparticles and their adsorption sites modelled in this work.](image)
First, CO adsorption was studied on all the non-equivalent sites presented in Figure 15. The corresponding adsorption energies are given in Table 4. It can be seen that CO adsorption is very exothermic in all cases and the adsorption energy is 2.0 ± 0.2 eV for all but the smallest, Fe$_{13}$ nanoparticle. CO adsorption is strongest in hollow-sites despite changes in particle geometry and even though Fe$_{55}$ and Fe$_{78}$ have identical adsorption energies for hollow- and top-sites. Also the computed adsorption energies, apart from Fe$_{13}$, are similar as found for several bulk BCC surfaces in Table 3.

Table 4. CO adsorption energies [eV] on the most stable sites in the studied iron nanoparticles.

<table>
<thead>
<tr>
<th>Site</th>
<th>Energy</th>
<th>Site</th>
<th>Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_{13}$</td>
<td>-1.54</td>
<td>2</td>
<td>-1.69</td>
</tr>
<tr>
<td>Fe$_{55}$</td>
<td>-2.13</td>
<td>4</td>
<td>-2.14</td>
</tr>
<tr>
<td>Fe$_{147}$</td>
<td>-2.12</td>
<td>4</td>
<td>-2.21</td>
</tr>
<tr>
<td>Fe$_{78}$</td>
<td>-1.95</td>
<td>8</td>
<td>-1.94</td>
</tr>
<tr>
<td>Fe$_{145}$</td>
<td>-1.82</td>
<td>4</td>
<td>-1.93</td>
</tr>
</tbody>
</table>

CO dissociation barriers starting from various adsorption sites with different final structures were determined for all the particles. The most favourable pathways along dissociation barriers and energies are presented in Table 5. Comparison among the icosahedral particles shows that activity increases as particles size increases. The reaction also becomes thermodynamically feasible on the larger icosahedral particles. In Fe$_{13}$ and Fe$_{55}$ the most favourable pathways start from low-coordinated top-sites at the particle vertex whereas the most reactive site of Fe$_{147}$ is a three-fold hollow-site at the cluster edge. This shows that the nature of the active site changes as particle size is changed. In publication I the increasing reactivity and change in the active site were attributed to the larger elongation of Fe-Fe bonds in larger particles. This elongation leads to a better overlap between the particle and empty $2\pi^*$-orbitals of CO as deduced from analysis of equation (47) and comparison of icosahedral particles with crystal Fe-FCC(111) at different bond lengths.

Table 5. Activation ($E^\ddagger$) and reaction energies ($\Delta E$) [eV] for the most favourable CO dissociation pathways on the studied clusters. The nomenclature for the paths as follows: Fe$_{13}$-CO1C2O2 denotes CO dissociation on Fe$_{13}$ with CO adsorbed in site 1 in the initial state and C and O in sites 2 and 2 in the final states.

<table>
<thead>
<tr>
<th>Path</th>
<th>$E^\ddagger$</th>
<th>$\Delta E$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_{13}$-CO1C2O2</td>
<td>1.90$^\ddagger$</td>
<td>0.54</td>
</tr>
<tr>
<td>Fe$_{55}$-CO1C4O4</td>
<td>1.63</td>
<td>-0.36</td>
</tr>
<tr>
<td>Fe$_{147}$-CO4C4O4</td>
<td>1.1</td>
<td>-0.4</td>
</tr>
<tr>
<td>Fe$_{145}$-CO6C8O7</td>
<td>1.12</td>
<td>0.03</td>
</tr>
<tr>
<td>Fe$_{145}$-CO4C4O1</td>
<td>0.89</td>
<td>-0.21</td>
</tr>
</tbody>
</table>

Around 140 atoms a change from icosahedral to BCC geometries takes place and in publication III the changes in reactivity due to this phase change was studied using the BCC-structure Fe$_{145}$ particle. This particle contains both 100 and 110 facets and is closely related to the Wulff geometry of very large iron nanoparticles. The vertices of Fe$_{145}$ bear close resemblance with the BCC (310) surface, which is particularly active for CO dissociation. Fe$_{145}$ exhibits lowest
CO barriers of all the studied clusters and is more reactive than smooth BCC surfaces of iron.

Stepped surfaces prove to be slightly more reactive than similar sites on Fe$_{145}$ and the 110_100-saw-tooth models of Figure 16. On Fe$_{145}$ the most favourable pathway starts from a four-coordinated hollow site and CO breaks over a particle edge with carbon and oxygen ending in four- and three-fold hollow sites, respectively; this pathway contains optimal binding sites for both the initial and final states. Comparison of Fe$_{145}$ with different periodic structures and application of PDOS integration (Eq. 47) shows that the presence of a particle edge with optimal adsorption sites forms the ideal active site for CO dissociation on iron nanoparticles.

The amorphous Fe$_{78}$ is a minimum energy structure for an empirical Finnis-Sinclair potential presenting iron. [125] This structure is very rugged and contains various adsorption sites ranging from deep, four-fold hollow-sites to very low-coordinated top-sites. As a result of its structural diversity, CO dissociation barriers on Fe$_{78}$ vary between 1.12 and 1.88 eV depending on the reaction site. For this cluster similar dissociation barriers for both top- and hollow-site reactions are observed; the very low-coordinated atoms are crucial for reactivity.

The observed reactivity can be analysed in several ways. The commonly applied d-band theory of equations (48)-(50) and BEP-relationships based on either reaction or adsorption energies fail in explaining the observed trends. The failure of these two commonly applied models can be explained after realizing that both assume that bonding interactions and the reaction mechanism stay similar at different sites; this is to say that the $V_{ad}$-term is independent of the reaction. For the systems studied in this thesis, CO bonding and dissociation mechanism are sensitive to the particle size and geometry and $V_{ad}$ cannot be assumed to be a constant. Instead, PDOS integration of equation (47) captures the essential ingredient for facile CO dissociation; the metal surface must have a large overlap with CO’s empty 2π*-orbitals. Larger overlap leads to an increased stability of the transition state and the stability of the transition state is a very good indicator of the observed dissociation barrier [61], III.

The results presented above show that the reactivity of iron nanoparticles towards CO dissociation depends significantly on particle size and geometry. In general, activity increases as particle size is increased. The icosahedral particles are less reactive than amorphous or BCC particles. In the smallest clusters top-site reactivity is observed whereas high-coordinated hollow-sites are more reactive in larger particles; especially the presence of particle edges is essential for CO dissociation.

It is clear that the nature of the active site changes along with the particle. Small icosahedral particles favour CO dissociation from top-sites at particle
Results

edges while larger icosahedra break CO from hollow-sites at particle edges. A combination of edge-sites with optimal sites for CO, C, and O shows that facile CO dissociation can be obtained without stepped surfaces on Fe\textsubscript{145} or similar BCC nanoparticles; the optimal active site seems to have CO adsorbed at a BCC(100)-like four-fold hollow site in the initial state, CO breaking over an atomic step, and C in a four-fold site and O in a three-fold site in the final state. Similar active sites can also be found from (710) and (310) BCC stepped surfaces which have the lowest activation energies for CO dissociation. Also periodic “saw-tooth” 110\_100A and 110\_100A structures in Figure 16 have similar local geometries. The energetics of these reactions is recapped in Table 6.

![Figure 16](image)

Table 6. Activation energies, reaction energies and C-O bond lengths at the transition state for surfaces and particles with similar local geometries.

<table>
<thead>
<tr>
<th>Surface</th>
<th>(E) [eV]</th>
<th>(\Delta E) [eV]</th>
<th>C-O [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe\textsubscript{145}</td>
<td>0.89</td>
<td>-0.21</td>
<td>1.89</td>
</tr>
<tr>
<td>Fe\textsubscript{110_100A}</td>
<td>0.85</td>
<td>-0.59</td>
<td>1.86</td>
</tr>
<tr>
<td>Fe\textsubscript{110_100B}</td>
<td>0.87</td>
<td>-0.51</td>
<td>1.88</td>
</tr>
<tr>
<td>Fe\textsubscript{(310)}</td>
<td>0.72</td>
<td>-0.89</td>
<td>~1.8</td>
</tr>
<tr>
<td>Fe\textsubscript{(710)}</td>
<td>0.67</td>
<td>-1.19</td>
<td>1.78</td>
</tr>
</tbody>
</table>

From Table 6 it may be seen that the finite-size Fe\textsubscript{145} cluster and the saw-tooth models have very similar activation energies and C-O bond lengths at the transition state. However, the reaction energies and PDOS profiles for these models are very different. Even though the stepped surfaces (310) and (710) have very similar active sites and CO bonding geometries as Fe\textsubscript{145} and the saw-tooth models, they exhibit 0.15-0.25 eV smaller CO dissociation barriers, have earlier transition states than the finite-size models, and are more exothermic. Thus, the stepped surface cannot be considered as good models for finite-size particles or structures similar to the saw-tooth models.
It can be concluded that an active site for facile CO dissociation must meet several requirements: 1) CO adsorbed at a BCC(100)-like four-fold hollow site in the initial state, 2) CO breaks over an atomic step, and 3) C in a four-fold site and O in a three-fold site in the final state. Yet, the different models containing such an active site give rise to quite different barriers, reaction energies and transition states and the exact, global structure cannot be neglected; finite-size effects are still prevailing and contribute to the reactivity of the clusters and saw-tooth models.

The presence of such edge-sites very probably explains the reactivity of small iron nanoparticles where stepped micro-surfaces are geometrically impossible. Yet, it is plausible that particle reconstruction enables the formation of small step facets and increasing reactivity. [126] Knowing the above requirements for facile CO should provide helpful guidelines for better control on reactivity and selectivity in CO-iron chemistry in CNT synthesis, for example.

5.2 Magnetic State Effects on the Reactivity of Fe-FCC(111) Surfaces

Magnetism is an essential property of iron and is related to practically all of its properties. Still, effect of magnetism in heterogeneous catalysis has largely been neglected. To study the interplay of magnetism and catalysis, H\textsubscript{2} and CO dissociation on FCC iron in different magnetic states was studied in publication II.

FCC iron surfaces can be realized as thin-films on various FCC metals and depending on the lattice constant of the underlying substrate, several magnetic structures can be formed. In publication II, only the collinear ferromagnetic and antiferromagnetic structures were included and their relative bulk stability at different lattice constant is presented in Figure 17. At very short lattice constants all the studied structures are equally stable and have vanishing magnetic moments. The double-layered AFM\textsubscript{2} phase is the ground-state structure and has an equilibrium lattice constant of 3.55 Å. The FM has a transition from low-spin to high-spin state at the lattice constant 3.575 Å.

To obtain the largest possible change in magnetic moment, reactivity was studied for AFM\textsubscript{2} and FM at the lattice constant 3.575 Å. H\textsubscript{2} adsorbs on topsites on the FM surface but is spontaneously dissociated on AFM\textsubscript{2}, as shown in Figure 18. On FM, a barrier of 0.35 eV separates the adsorbed and dissociated states. Studies on charge reorganization during H\textsubscript{2} dissociation show that both spin-states have similar total charge-transfer from the surface to the adatoms. However, analysis of DDI (equation 54) presented in Figure 19 shows the increased build-up of electrons between the surface and H on AFM\textsubscript{2} compared to FM. Thus, the AFM\textsubscript{2} spin-state donates more charge to the newly formed Fe-H bond more efficiently than FM which explains the observed molecular and dissociative adsorption.
Results

To study magnetic state effects on CO chemistry, CO adsorption energies were first computed. As shown in Table 7, AFM$_2$ adsorbs CO slightly stronger than the FM surface which is due to more potent electron transfer from the AFM$_2$ as analysed from DDIs shown in Figure 19. Barriers for CO dissociation from the top-site are 1.40 and 1.67 eV for reactions on FM and AFM$_2$, respectively. Even though, AFM$_2$ donates electrons more easily in the adsorption complex, the transition state is more stable on the FM surface; FM has more overlap with the empty $2n^*-\text{orbitals}$ of CO enabling stronger bonding as the C-O bond becomes elongated.

Figure 17. Left: Different collinear magnetic structures of FCC iron. Right: Energies and magnetic moments as a function of lattice constant. FM, AFM$_1$, and AFM$_2$ correspond to ferromagnetic, antiferromagnetic, and double-layered antiferromagnetic structures, respectively.

Figure 18. Minimum energy pathways for H$_2$ dissociation on FM and AFM$_2$ Fe-FCC(111) surfaces.
Table 7. CO adsorption energies on AFM2 and FM surfaces of FCC(111) Iron

<table>
<thead>
<tr>
<th></th>
<th>Top</th>
<th>HCP</th>
<th>FCC</th>
</tr>
</thead>
<tbody>
<tr>
<td>FM</td>
<td>-2.15</td>
<td>-1.72</td>
<td>-1.73</td>
</tr>
<tr>
<td>AFM2</td>
<td>-2.31</td>
<td>-1.90</td>
<td>-1.61</td>
</tr>
</tbody>
</table>

To demonstrate the effect of different magnetic states in terms of experimentally obtainable quantities, temperature programmed desorption spectra were computed for H\(_2\) in the two magnetic states. The TPD analysis predicts that H\(_2\) is desorbed around 380 K from the FM surface and around 790 K from the AFM2 surface, a very clear difference.

As a conclusion, the results show that spin-structure can strongly affect orbital occupation of the surface and especially charge-transfer between the catalyst surface and the adsorbate; H\(_2\) and CO adsorption and dissociation are modified by changes in spin-structure. In both cases, charge transfer on AFM2 is greater than that on FM. Interestingly, H\(_2\) dissociation occurs more readily on AFM2, whereas CO dissociation is more facile on the FM surface, which is explained by the larger overlap between the metal surface and 2\(\pi^*\)states. These findings suggest that several important reactions utilizing H\(_2\) and CO as reactants, including Fischer-Tropsch synthesis and the water-gas shift reaction on magnetic iron catalysts, may be sensitive to the spin-state of the catalyst. As the magnetic state can be changed by applying external perturbations, such as magnetic fields, these considerations point to ways of modifying the thermodynamics and kinetics of heterogeneously catalyzed reactions.
5.3 Improving Transition-State Searches in Computational Nanocatalysis

Finding MEPs and/or transition states is a central problem in computational chemistry. Once an MEP is known, mechanistic as well as kinetic and thermodynamic aspects of a reaction have been characterized. NEB and DIMER methods introduced in section 2.4. are commonly applied tools for finding the MEPs and/or transition states for reactions on surfaces or in the bulk. However, non-periodic systems without constraints are free to rotate and translate during NEB and DIMER calculations leading to severe convergence problems, artificial elongation of the reaction pathways and eventually poor description of the MEP. In publication IV a method based on quaternion algebra was introduced for removing these external degrees of freedom from NEB and DIMER calculations. The performance of the quaternion approach is demon-
strated below and the modified methods are labelled by “TR” suffix to distinguish them from the original methods.

First, the reorganization of a Lennard-Jones tetramer cluster was studied with NEB and NEB-TR methods. The Lennard-Jones potential is empirical potential having the form

\[
V_{lj} = 4\epsilon \sum_{i<j} \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^{6} \right]
\]  

(60)

where \(r_{ij}\) is the distance between two particles and \(\epsilon = \sigma = 1\), in the present case. The two possible MEPs are presented in Figure 20 and the comparison of NEB-TR and NEB is presented in Table 8.

![Figure 20. A) Triangular (left) and rhombohedral (right) transition states for reorganization of LJ\(_4\) and B) MEP for LJ\(_4\) reorganization using NEB-TR and NEB at force tolerance 10\(^{-3}\).](image)

From Table 8 it can be seen that NEB-TR convergences with significantly fewer iterations than the uncorrected NEB. When the tolerance for the maximum atomic force is reduced below 10\(^{-3}\) \(\epsilon/\sigma\), the regular NEB does not converge. Furthermore, NEB-TR in all the calculations converges to the lower energy, rhombohedral transition state. The regular NEB converges to the MEP with triangular, high-energy saddle point when the tolerance is large. MEPs found using NEB-TR also have shorter path lengths defined as

\[
l_{path} = \sum_{i=0}^{N-1} \sqrt{(R_{i+1} - R_i)^2}
\]

(61)

The regular NEB artificially overestimates the length of MEPs because translation and rotation are allowed. The effect of translation and rotation can also be seen in Figure 20 where several NEB images have the same energy as the initial and final structures; the images with equal energy correspond to the
translated or rotated images as a result of force minimization. In NEB-TR all adjacent images have different energies and the MEP is better described.

Table 8. Transition state energies ($E^\ddagger$), number of iterations and NEB pathlengths found for LJ$_4$ reorganization using NEB-TR and NEB with different force tolerances $f_{\text{max}}$.\textsuperscript{N}

<table>
<thead>
<tr>
<th>$f_{\text{max}}$ [e/\textit{\AA}]</th>
<th>$E^\ddagger$ [eV]</th>
<th>Iterations</th>
<th>Path length [\textit{\AA}]</th>
<th>$E^\ddagger$ [eV]</th>
<th>Iterations</th>
<th>Path length [\textit{\AA}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>1.516</td>
<td>52</td>
<td>5.633</td>
<td>2.766</td>
<td>79</td>
<td>7.55</td>
</tr>
<tr>
<td>0.1</td>
<td>0.931</td>
<td>68</td>
<td>5.628</td>
<td>0.935</td>
<td>321</td>
<td>20.984</td>
</tr>
<tr>
<td>0.01</td>
<td>0.926</td>
<td>88</td>
<td>5.622</td>
<td>0.926</td>
<td>895</td>
<td>10.719</td>
</tr>
<tr>
<td>0.001</td>
<td>0.926</td>
<td>421</td>
<td>5.622</td>
<td>0.926</td>
<td>2397</td>
<td>10.034</td>
</tr>
<tr>
<td>0.0001</td>
<td>0.926</td>
<td>773</td>
<td>5.622</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

NEB-TR was also applied for studying CO dissociation on an Fe$_{13}$ nanoparticle at the DFT-level which was identified as a difficult system to converge using regular NEB in publication I. As shown in publication IV, NEB-TR converges faster than the regular NEB. Furthermore, NEB-TR can be used with fewer images. Figure 21 shows that NEB-TR with eight images has found a saddle point (flat tangent) with an energy of 1.90 eV in 50 iterations. However, the normal NEB struggles to find the saddle point and the highest energy image keeps drifting around with an energy of around 2.3 eV. Also the path length of an NEB-TR calculation is shorter than found using NEB which illustrates that NEB-TR describes the MEP more accurately.

Figure 21. Minimum energy pathways of CO dissociation on Fe$_{13}$ computed with NEB-TR and NEB. The green lines denote the tangents along the MEP.\textsuperscript{IV}
The DIMER-TR was applied for studying transitions of an Au trimer on a cuboctahedral Pt$_{55}$ nanoparticle. The interactions were modelled using the EMT potential. The initial minimum energy state and some transition states are presented in Figure 22. From this figure it can also be seen that DIMER-TR consistently requires fewer iterations than DIMER to converge to a saddle point. DIMER-TR seems to find slightly more low-energy saddle points. However, using the same atomic displacements as an initial guess, both methods usually converge to the same saddle point with DIMER-TR using fewer iterations.

![Figure 22. A) Initial and several transition states and B) number of iterations in DIMER-TR and DIMER calculations for reorganization of the Fe55-Au3 system.](image)

To conclude, the removal of external rotational and translational degrees of freedom from NEB and DIMER leads to significant improvements in convergence compared to the uncorrected methods. Furthermore, NEB-TR describes the MEPs more accurately and can be used with fewer images than the regular NEB. The NEB-TR and DIMER-TR are expected to prove particularly useful for finding MEPs and/or transition states of non-periodic systems such as nanocatalysts and gas-phase reaction. The methods are available through the Atomic Simulation Environment for several quantum chemical, DFT, and empirical models.
6. Summary and Outlook

This thesis addresses the reactivity of iron nanostructures towards CO dissociation. An atomistic perspective based on quantum chemistry is adopted to determine and explain the interactions responsible for the observed reactivity. Particular emphasis is put on understanding how size and geometry of iron nanoparticles affect their ability to dissociate CO. Also the utilization of magnetism in controlling catalysis has been explored. The results identify structural requirements for enhancing CO dissociation rates which is determining step for overall rate and selectivity in Fischer-Tropsch synthesis of high alkanes, and carbon nanotube synthesis, for example.

CO dissociation is a highly structure sensitive reaction usually taking place at atomic steps. However, only particles larger than 3 nm can sustain such stepped surfaces and, yet Fe particles smaller than 2 nm are excellent catalysts for growing high-quality CNTs. To explain the catalytic activity of small iron nanoparticles, density-functional theory was used to investigate CO dissociation on 0.5-1.5 nm (13-147 atoms) Fe nanoparticles in icosahedral, BCC, and amorphous structures. The results show that larger iron particles are in general more active in CO dissociation. Also depending on particle size and geometry the nature of the active site changes dramatically but particle edges are essential for facile CO dissociation independent of particle size and geometry. Edges of BCC iron nanoparticles exhibit lowest CO dissociation barriers and such sites are almost as reactive as stepped surfaces which can account for the catalytic activity of >3 nm iron nanoparticles. From an atomic and quantum chemical viewpoint, lowered CO dissociation barriers are related to the increased stability of the transition state; the stability is closely linked with orbital overlap between the metal surface and empty $2\pi^*$-orbitals of CO. An active site for facile CO dissociation needs to fulfil several requirements: 1) CO is adsorbed at a BCC(100)-like four-fold hollow site in the initial state, 2) CO breaks over an atomic step, and 3) C is adsorbed in a four-fold site and O in a three-fold site in the final state. Such sites can be found at edges between BCC(110) and BCC(100) facets as well as stepped BCC(310) and BCC(710) surfaces. The real particle edges have 0.15-0.25 eV higher dissociation barriers and are thus, less reactive than the stepped surfaces despite similar geometries of the active site.

In highly magnetic systems, such as iron nanostructures, orbital energies and interactions depend significantly on the magnetic structure. Yet, studies
on magnetic state effects in heterogeneous catalysis are scarce. Studies on double-layered antiferromagnetic and ferromagnetic spin structures of FCC(111) iron thin films strongly affect the orbital occupations and interactions. Especially charge-transfer between the catalysts surface and the adsorbate are highly sensitive to the spin-structure; the AFM2 surface is a more efficient electron donator. In the case of H₂ dissociation AFM2 is more reactive whereas CO dissociation is more facile on the FM surface, which is explained by more favourable orbital overlap between the FM surface and CO’s 2π*-orbital.

The ability of different iron nanostructures to dissociate CO can largely be rationalized by the orbital interactions between the surface and the antibonding 2π*-orbital of CO. Based on the studies in this thesis, CO dissociation barriers appear to be highly sensitive to the overlap between an iron surface and empty 2π*-states which become occupied when the C-O breaks; understanding how size, geometry and magnetic structure affect this overlap enables the rational development of heterogeneous iron catalysts for systems where CO dissociation is a key reaction step. The identified and required structural properties of active edge sites should also prove to be useful when rationalizing, predicting, or designing iron nanoparticle catalysts.

Besides studies on specific heterogeneous catalyst systems, a general algorithm for improving transition state methods used in computational nanocatalysis was developed. The modification removes the troubling translational and rotational degrees of freedom hampering convergence and description of reaction mechanisms of regular NEB and DIMER methods. The new NEB-TR and DIMER-TR methods were shown to use fewer iterations to converge to a saddle point and describe minimum energy pathways more accurately in the case of NEB-TR. The modified methods have been implemented as a part of the Atomic Simulation Environment open source software to enable their application with several empirical and first-principles potentials. The NEB-TR and DIMER-TR methods are expected to prove particularly useful in calculations of paths and saddle points in systems representing nanocatalysts and gas-phase chemical reactions.

In summary, this thesis shows that even a seemingly simple reaction such as CO dissociation can exhibit very complex catalytic behavior at the nanoscale. Since changes in size and geometry of nanoparticles directly affect orbital interactions, simple models based on crystal surfaces and scaling laws may not be directly applicable when predicting and explaining reactivity of nanoparticles. The inadequacy of crystal surface models for nanoparticles is also demonstrated in the absence of certain active sites, e.g., cluster edges which are crucial for CO dissociation on particles smaller than 3 nm or the noncrystalline character of icosahedral clusters. The computational approach for nanocatalysis is thus necessarily more complex than traditional heterogeneous catalysis on macroscopic surfaces.
The presented computational work has provided several new viewpoints into CO dissociation also from an experimental perspective. First, the predicted structural requirements for facile CO dissociation on small iron nanoparticles should provide useful when explaining reactivity or designing new catalysts. Another experimentally very interesting concept is the use of magnetism and magnetic fields in modifying reactivity and catalysis.

6.1 Suggestions for Further Work

In this thesis the reactivity of iron nanostructures towards CO dissociation is shown to depend on the overlap between the orbitals of the metal surface and 2\pi'-'orbital of CO. It would be very interesting if the PDOS integration used for measuring the overlap could be used as a descriptor for CO dissociation. This would be very useful since common methods such as the simple d-band model and BEP relations fail to predict CO dissociation barriers. The justification of PDOS integration as a descriptor can be based on a simple perturbation theory result [127] and equation (51) similar to the d-band model:

\[ E^d \propto \int \frac{V_{2\pi',d}^2}{\epsilon_d - \epsilon_{2\pi'}} \frac{S_{2\pi',d}^2}{\epsilon_d - \epsilon_{2\pi'}} \]

\[ V_{2\pi',d} = \sum_{k \in d\text{-states}} \langle 2\pi'|\bar{f}|k \rangle \]

\[ S_{2\pi',d} = \sum_{k \in d\text{-states}} \langle 2\pi'|k \rangle = \sum_{k \in d\text{-states}} S_{2\pi'k} \]

The \( S_{2\pi',d} \)-term is directly related to the PDOS integral via Equations (46) and (44): \( \int_{E_F}^{\infty} d\epsilon \left[ S_{2\pi',d} \right]^2 \delta(\epsilon - \epsilon_d) \). Thus, using PDOS integration could provide a simple way for obtaining a correlation between the adsorbed CO and the stability of the transition state which controls the CO dissociation barrier.

Another very interesting and important field to study is the role of magnetism in catalysis. Especially the prospect of controlling or modifying heterogeneous reactions by magnetic fields should be explored. For this purpose, we have established collaboration with an experimental group for studying reactivity of FeNi (nano)alloys in the presence of magnetic fields. The synergy between computational chemistry and experiments provides a theoretical understanding of the atomistic basis for magnetic fields effects as well as their realization in actual catalytic conditions.

We are also working on predicting finite-temperature phase diagrams of FeNi nanoparticles. This work combines the structures obtained from cluster expansion Hamiltonian parametrized using DFT with their reactivity towards CO dissociation. Such a multiscale approach is a general way to approach reactivity of nanoalloys in realistic conditions and as a function of atomic concentration for, e.g., CNT synthesis.
References

Summary and Outlook


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Summary and Outlook


Metallic nanostructures offer the possibility of controlling and optimizing catalytic activity and selectivity towards specific chemical reactions by very subtle changes in size and geometry. To utilize this high degree of control in chemistry, the relationship between catalytic performance and atomic as well as electronic factors, must be understood.

In this thesis a quantum mechanical approach within density functional theory is employed to obtain an atomic level understanding of CO dissociation on iron nanostructures. This important reaction controls the reactivity and selectivity in, e.g., Fischer-Tropsch synthesis for hydrocarbons and synthesis of carbon nanotubes.

The results of this thesis indicate the structural requirements for efficient CO dissociation, reveal the possibility of controlling iron-based chemistry by magnetism and also present an efficient method for improving transition state searches in computational nanoparticle