Chemistry and Physics of Cu and H₂O on ZnO Surfaces

Electron Transfer, Surface Triangles, and Theory

MATTI HELLSTRÖM
Abstract


This thesis discusses the chemistry and physics of Cu and H_2O on ZnO surfaces, based primarily on results from quantum chemical calculations. The underlying context is heterogeneous catalysis, where Cu/ZnO-mixtures are used in the industrial synthesis of methanol and in the water gas shift reaction. Electron transfer between small Cu clusters and ZnO is central to this thesis, as are the design and use of models that can describe realistic and very large-scale ZnO surface structures while still retaining the electronic nature of the system. Method and model enhancements as well as tests and validations constitute a large part of this thesis.

The thesis demonstrates that the charges of small Cu clusters, adsorbed on the non-polar ZnO(1070) surface, depend on whether the Cu clusters contain an even or odd number of atoms, and whether water is present (water can induce electron transfer from Cu to ZnO). On the polar Zn-terminated ZnO(0001) surface, Cu becomes negatively charged, which causes it to attract positively charged subsurface defects and to wet the ZnO(0001) surface at elevated temperatures.

When a Cu cluster on a ZnO surface becomes positively charged, this happens because it donates an electron to the ZnO conduction band. Hence, it is necessary to use a method which describes the ZnO band gap correctly, and we show that a hybrid density functional, which includes a fraction of Hartree-Fock exchange, fulfills this requirement. When the ZnO conduction band becomes populated by electrons from Cu, band-filling occurs, which affects the adsorption energy. The band-filling correction is presented as a means to extrapolate the calculated adsorption energy under periodic boundary conditions to the zero coverage (isolated adsorbate, infinite supercell) limit.

A part of this thesis concerns the parameterization of the computationally very efficient SCC-DFTB method (density functional based tight binding with self-consistent charges), in a multi-scale modeling approach. Our findings suggest that the SCC-DFTB method satisfactorily describes the interaction between ZnO surfaces and water, as well as the stabilities of different surface reconstructions (such as triangularly and hexagonally shaped pits) at the polar ZnO(0001) and ZnO(000T) surfaces.

Keywords: catalysis, density functional theory, SCC-DFTB, band-filling correction

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List of papers

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

I  
**Cu dimer formation mechanism on the ZnO\(\langle 10\bar{1}0\rangle\) surface**  
M. Hellström, D. Spångberg, K. Hermansson, and P. Broqvist  
*Physical Review B* 86, 235302 (2012)

II  
**Small Cu Clusters Adsorbed on ZnO\(\langle 10\bar{1}0\rangle\) Show Even-Odd Alternations in Stability and Charge Transfer**  
M. Hellström, D. Spångberg, K. Hermansson, and P. Broqvist  

III  
**Water-Induced Oxidation and Dissociation of Small Cu Clusters on ZnO\(\langle 10\bar{1}0\rangle\)**  
M. Hellström, D. Spångberg, P. Broqvist, and K. Hermansson  
*The Journal of Physical Chemistry C*. DOI: 10.1021/jp509501z

IV  
**Cu wets the polar ZnO\(\langle 0001\rangle\)-Zn surface because of interaction with subsurface defects**  
I. Beinik, M. Hellström, T. N. Jensen, P. Broqvist, and J. V. Lauritsen  
*Submitted manuscript*

V  
**Band-Filling Correction Method for Accurate Adsorption Energy Calculations: A Cu/ZnO Case Study.**  
M. Hellström, D. Spångberg, K. Hermansson, and P. Broqvist  

VI  
**An SCC-DFTB Repulsive Potential for ZnO and the ZnO-Water System**  
M. Hellström, K. Jorner, M. Bryngelsson, S. E. Huber, J. Kullgren, T. Frauenheim, and P. Broqvist  

VII  
**Large-scale SCC-DFTB calculations of reconstructed polar ZnO surfaces**  
S. E. Huber, M. Hellström, M. Probst, K. Hermansson, and P. Broqvist  
*Surface Science* 628, 50–61 (2014)

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The author’s contributions to the papers

Paper I I contributed to all stages of the work.

Paper II I contributed to all stages of the work.

Paper III I contributed to all stages of the work.

Paper IV I planned, performed, and analyzed the DFT calculations and co-wrote the manuscript.

Paper V I contributed to all stages of the work.

Paper VI I contributed to all stages of the work, except the actual generation of the repulsive potential.

Paper VII I performed the DFT calculations, some of the SCC-DFTB calculations, and co-wrote the manuscript.
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1. Introduction

1.1 Background

Zinc oxide (ZnO) is a material that is used in a wide variety of applications, the most prominent being as an additive to the rubber in car tires. It is also used in creams and ointments because of its anti-inflammatory and bacteriostatic properties, in electronic devices because it is a semiconductor (with a direct band gap of 3.37 eV), and in gas sensors because the surface conductivity changes for different hydrogen and oxygen pressures [1]. However, it is its application in catalysis that is the focus of this thesis.

Catalysts are substances that, without themselves being consumed, speed up chemical reactions by providing an alternative reaction mechanism that somehow involves the catalyst. In heterogeneous catalysis, the catalyst is in a different phase from the reactants. Frequently, the catalyst is a solid material on which molecules from the gasphase adsorb, react, and then desorb [2].

A common form of catalyst consists of metal particles. For example, nickel is used to catalyze the conversion of aldehydes to alcohols, iron is used to synthesize ammonia from nitrogen and hydrogen, and a platinum/rhodium mixture is used to catalyze the reduction of toxic NOx gases in catalytic car converters. The metal particles are often kept separate by a support material, which usually is a metal oxide (e.g. MgO, Al₂O₃, SiO₂, or ZnO). Not only metals can be catalytically active: molybdenum disulfide (MoS₂) can catalyze hydrodesulfurization for the removal of sulfur from fossil fuels, vanadium pentoxide (V₂O₅) is used to produce sulfuric acid, and aluminosilicates (zeolites) are used for the catalytic cracking of crude oil [3]. Sometimes, if two or more materials are combined, a catalyst with greater activity is obtained than what would be expected from the sum of the activities of the individual components; there is a synergy between the different components.

Such a synergy exists between Cu and ZnO in the Cu/ZnO/Al₂O₃ catalyst used for methanol synthesis. Methanol (CH₃OH) is produced on a massive scale of several tens of millions of metric tons each year, because of its widespread industrial usage in the production of paints and plastics, and its application as fuel in fuel cells. It is primarily synthesized from syngas, a mixture of hydrogen (H₂), carbon monoxide (CO), and carbon dioxide (CO₂). The syngas is obtained through steam reforming of natural gas (methane, CH₄):

\[
2\text{CH}_4 + 3\text{H}_2\text{O} \rightarrow \text{CO} + \text{CO}_2 + 7\text{H}_2 \quad (1.1)
\]

Steam reforming of methane is the most convenient, and most widely used, way to industrially obtain H₂. Methanol is then synthesized mostly from the
CO₂ and H₂ in the syngas over the Cu/ZnO/Al₂O₃ catalyst:

\[ \text{CO}_2 + 3\text{H}_2 \xrightarrow{\text{Cu/ZnO/Al}_2\text{O}_3} \text{CH}_3\text{OH} + \text{H}_2\text{O} \] (1.2)

The water (H₂O) formed during methanol synthesis is consumed in the presence of CO (which is present in the syngas) in the water-gas shift reaction (WGSR) over the same Cu/ZnO/Al₂O₃ catalyst:

\[ \text{CO} + \text{H}_2\text{O} \xrightarrow{\text{Cu/ZnO/Al}_2\text{O}_3} \text{CO}_2 + \text{H}_2 \] (1.3)

The resulting CO₂ and H₂ then react to give more methanol (equation (1.2)) [4].

The water-gas shift reaction (1.3), catalyzed by the Cu/ZnO/Al₂O₃ catalyst, does not only occur during methanol synthesis, but is heavily used in industry as a step before the Haber-Bosch process for the synthesis of ammonia (NH₃). In the Haber-Bosch process, ammonia is synthesized from nitrogen (N₂) and hydrogen over an iron (Fe) catalyst. The hydrogen is obtained through steam reforming of methane (equation (1.1)), but before it is used in the Haber-Bosch process, it is important to remove all CO since CO will poison (inactivate) the Fe catalyst. For this purpose, the water-gas shift reaction (1.3) is employed over two different catalysts: the high-temperature Fe₃O₄/ Cr₂O₃ catalyst, and the low-temperature Cu/ZnO/Al₂O₃ catalyst [5].

The Cu/ZnO/Al₂O₃ system can also catalyze steam reforming of methanol, which is essentially the reverse of the methanol synthesis reaction:

\[ \text{CH}_3\text{OH} + \text{H}_2\text{O} \xrightarrow{\text{Cu/ZnO/Al}_2\text{O}_3} \text{CO}_2 + 3\text{H}_2 \] (1.4)

Steam reforming of methanol allows methanol to be used as a portable, easy-to-handle hydrogen source for fuel cell applications [4].

Despite the Cu/ZnO/Al₂O₃ catalyst being heavily utilized in industry (especially for methanol synthesis and the WGSR), the roles of the various catalyst components are not clear. Al₂O₃ most likely simply serves as a “spacer” for the Cu particles, and prevents them from sintering.

The role of ZnO is less clear, for while there is a Cu–ZnO synergy for methanol synthesis, no such synergy necessarily exists for the WGSR. For the WGSR, it is generally agreed that Cu is the active component, and ZnO is used mainly to prevent catalyst deactivation through sulfur poisoning [5, 6, 7], although some recent work [8] questioned this consensus and reported an increased catalytic activity for Cu/ZnO compared to Cu on other supports.

The origin of the Cu–ZnO synergy for methanol synthesis has been under scrutiny for a long time, with explanations ranging from positively charged Cu species on ZnO [9], a Cu–Zn alloy [10, 11, 12], ZnO-induced strain in the Cu particles [13], and most recently Zn\(^{δ+}\) adsorbed on the Cu surface [14].

In the industrial Cu/ZnO/Al₂O₃ catalyst, the different components occur as small nanoparticles, which expose large surface areas, and different crystal...
surfaces demonstrate different catalytic activities. Cu crystallizes in the cubic closed-packed (ccp) crystal structure, with the three primary surfaces (100), (110), and (111) [2]. The (111) surface has the lowest surface energy, and is the surface primarily exposed on Cu particles in vacuum, but the Cu(110) surface is more active for the WGSR [15, 16].

ZnO, on the other hand, crystallizes in the hexagonal wurtzite structure, depicted in Figure 1.1a, where both the Zn and O atoms are four-coordinated with tetrahedral coordination (with one of the four bonds being slightly longer than the other three). ZnO primarily exposes four different surfaces: the non-polar (10\(\bar{1}\)0) and (11\(\bar{2}\)0) surfaces, and the polar Zn-terminated (0001) and O-terminated (000\(\bar{1}\)) surfaces [17]; all are shown in Figure 1.1b–d. The polarity of the (0001) and (000\(\bar{1}\)) surfaces arises because the ZnO structure is composed of double-layers stacked on top of each other (Figure 1.1b), with e.g. Zn\(^{2+}\) in the top half and O\(^{-2}\) in the bottom half of each double-layer. Thus, each double-layer is polar, and stacking such double-layers on top of each other gives even greater polarity in the direction perpendicular to the layers, leading to a divergence in the total energy of the system (which is known as the “polar instability”, or, more dramatically, as the “polar catastrophe”). Therefore, the polar surfaces are not stable unless there is some sort of charge-compensating mechanism, such as the adsorption of charged species or a change in surface stoichiometry [18]. The polar surfaces, being less stable than the non-polar surfaces, are often more reactive and catalytically active. For example, Cu adsorbed on ZnO(0001) is more active than Cu adsorbed on ZnO(10\(\bar{1}\)0) for methanol synthesis [9].

This thesis aims to characterize the interaction between Cu and ZnO, the interaction between ZnO and water, the interaction between Cu and ZnO and water, and the interaction between ZnO and vacuum.

To this end, computations, simulations, and modeling have been used. With the development of faster and more powerful computers, computational approaches are now routinely used either to interpret experimental results, or to predict the chemical properties of materials for which experimental results are lacking.

Although computational chemistry in many cases has been very successful, it is still very difficult to accurately model a multiphase system like the Cu/ZnO/Al\(_2\)O\(_3\) catalyst (which consists of small interdispersed nanoparticles containing many defects and which operates at high pressures and temperatures). Therefore, many simplifying assumptions must be made in the calculations, i.e. model systems must be employed. The model systems, by nature, do not fully resemble the real-life systems, which places a fundamental limit on the quality of the conclusions that can be drawn from the calculations.

Many different types of methods are available to the computational chemist, ranging from the very accurate to the very approximative. In this thesis, most calculations were performed using variations of density functional theory (DFT) (section 2.1), the by far most popular method in the computational
Figure 1.1. (a) The conventional unit cell of wurtzite ZnO (Zn is white and O is red/gray). (b) Side-view of a slab exposing the polar Zn-terminated ZnO(0001) and O-terminated ZnO(000\bar{1}) surfaces. The surface atoms are drawn larger than the other atoms. (c)–(d) Side and top views of the non-polar ZnO(10\bar{1}0) and ZnO(11\bar{2}0) surfaces.
chemistry and computational materials science communities. DFT calculations become prohibitively computationally demanding as larger systems are modeled, and in an effort to enable the modeling of larger and more realistic systems, a part of this thesis concerns the parameterization of the semi-empirical SCC-DFTB method (density functional based tight binding with self-consistent charges, section 2.2) for modeling ZnO.

1.2 Scope of this thesis

Although the aim at the outset of this project was to model the full catalytic cycle for both the methanol synthesis and the water gas shift reactions over the Cu/ZnO/Al₂O₃ catalyst, this did not happen exactly as planned. Indeed, in the end, very little catalysis at all was modeled, and the focus instead became the interaction between Cu and ZnO, between ZnO and water, and between Cu/ZnO/water. The scope was narrowed because we progressively unraveled an increasing number of problems and limitations with standard theoretical methods, which prompted us to try to find ways to approach and to overcome these limitations.

Papers I and II focus on the interaction between small Cu adsorbates and the ZnO(1010) surface, and specifically on the charge of the Cu adsorbates. Paper III has a similar theme, but here the focus is on how the presence of water (which is formed during methanol synthesis and which is a reactant in the water gas shift reaction) affects the charge of the Cu clusters.

Paper IV presents a joint experimental and computational endeavor concerning the charge of Cu and its interaction with subsurface defects on the polar ZnO(0001) surface.

Paper V describes the development and application of a computational method, the band-filling correction, to obtain coverage-independent adsorption energies when an adsorbate on ZnO becomes positively charged in a supercell calculation.

Paper VI describes the generation of a set of parameters for the SCC-DFTB method, so that ZnO and the H₂O/ZnO interface could be modeled in a computationally efficient manner.

Paper VII employs the parameters from Paper VI to study reconstructions at polar ZnO surfaces, in order to explore which kind of reconstructions are stable, as well as the origin of their stabilities.
2. Method

The two primary methods employed in this thesis are density functional theory (DFT, section 2.1) and density functional based tight binding with self consistent charges (SCC-DFTB, section 2.2). The DFT calculations were performed using the Vienna ab initio simulation program (VASP) [19, 20, 21, 22], and the SCC-DFTB calculations were performed using the DFTB+ program [23].

The method development performed in this thesis is summarized in sections 2.1.4 and 4.1–4.2 (the band-filling correction), and section 5.1 (the parameterization scheme for SCC-DFTB repulsive potentials).

2.1 Density functional theory (DFT)

2.1.1 Basics of DFT

Detailed derivations of the various equations used by DFT programs are available in many computational chemistry and physics textbooks (for example Refs. 24 and 25). Here, only a superficial overview of “Kohn-Sham DFT” is given. The total energy $E$ is expressed as a functional of the electron density $n(r)$.

$$E[n(r)] = E_{\text{II}} + E_{\text{kin}}[n(r)] + E_{\text{ext}}[n(r)] + E_{\text{H}}[n(r)] + E_{\text{xc}}[n(r)]$$  \hspace{1cm} (2.1)

where $E_{\text{II}}$ is the repulsive energy from interaction between nuclei (the "ion-ion" repulsion), $E_{\text{kin}}$ is (an approximation to) the kinetic energy of the electrons, $E_{\text{ext}}$ is the energy from the interaction between the electrons and the nuclei, $E_{\text{H}}$ is the Hartree term corresponding to the electron-electron Coulomb repulsion, and $E_{\text{xc}}$ is the exchange-correlation energy together with a correction for the kinetic energy (see below).

The electrons are described by orthonormal non-interacting Kohn-Sham orbitals $\psi_i(r)$. The electron density, $n(r)$, is the sum of the square moduli of these orbitals:

$$n(r) = \sum_{i=1}^{N} |\psi_i(r)|^2$$  \hspace{1cm} (2.2)

The terms $E_{\text{II}}$, $E_{\text{kin}}$, $E_{\text{ext}}$, and $E_{\text{H}}$ can be readily calculated for a given set of atomic positions and orbitals $\psi_i$ (and consequently, a given density $n(r)$), but there is no known expression for the exact exchange-correlation energy functional $E_{\text{xc}}[n(r)]$, which contains not only exchange and correlation contributions but also the difference between the true kinetic energy of the electrons...
and $E_{\text{kin}}[n(r)]$ (which is computed for a set of non-interacting electrons). Thus, $E_{\text{xc}}[n(r)]$ must be approximated in some way and there are several reasonable (and popular) ways to do this. The different exchange-correlation energy functionals have names such as BLYP, PW91, and PBE. The PBE functional \cite{26} was, at least to some extent, used in all Papers in this thesis.

The exchange-correlation potential $V_{\text{xc}}$ is defined as:

$$V_{\text{xc}}(r) = \frac{\delta E_{\text{xc}}[n(r)]}{\delta n(r)}$$

and the one-electron Kohn-Sham equations become:

$$\left\{-\frac{\nabla^2}{2} + V_{\text{ext}} + \int \frac{n(r_2)}{r_{12}} dr_2 + V_{\text{xc}}(r_1)\right\} \psi_i(r_1) = e_i \psi_i(r_1)$$

where $V_{\text{ext}}$ is the external potential from the nuclei, and where $e_i$ is the one-electron energy (or eigenvalue) of the orbital $\psi_i(r)$. The one-electron Kohn-Sham equations (2.4) are solved iteratively. First, they are solved for an initial guess of the density $n(r)$. The resulting orbitals $\psi_i$ give a new density (equation (2.2)), after which the procedure repeats until self-consistency is achieved.

The orbitals $\psi_i$ are expressed as a weighted sum over basis functions, so that when the equations (2.4) are solved, it is really the coefficients of the basis functions that are solved for. The basis functions can take different forms, such as local atom-centered Gaussian functions, or, as in this thesis, delocalized plane-waves.

The core electrons rarely contribute to chemical bonding, and for this reason, the core electrons are (in this thesis) not treated explicitly. Instead, the nuclei and the core electrons are collectively replaced by pseudopotentials, i.e., the valence electrons “see” the pseudopotentials and not the individual nuclei and core electrons. This removes the rapidly oscillating behavior of the valence orbitals near the core regions, and allows the valence orbitals to be described by plane-waves with lower kinetic energy. The core electrons, as part of the pseudopotentials, also enter into the ion-ion repulsion $E_{\text{II}}$ and external potential $V_{\text{ext}}$.

The total energy $E$ may be computed from the eigenvalues $e_i$:

$$E = \sum_{i}^\text{occ} e_i - \frac{1}{2} \int \int \frac{n(r_1)n(r_2)}{r_{12}} dr_1 dr_2 - \int V_{\text{xc}}(r)n(r) dr + E_{\text{xc}}[n(r)] + E_{\text{II}}$$

where the first sum runs over all occupied orbitals $i$, the next three terms are the “double-counting corrections” and the final term is the ion-ion repulsion.

### 2.1.2 Hybrid functionals

Results of DFT calculations can often be improved by using a so-called hybrid density functional, which replace a certain fraction of DFT exchange with
Hartree-Fock exchange. Hartree-Fock (HF) is a wavefunction-based computational method where the calculation of the exchange energy is exact for the calculated orbitals (and not approximate, as in DFT). In hybrid DFT, the HF (exact) exchange is calculated for the Kohn-Sham orbitals. Hybrid functionals have been found to improve, for example, the calculated heat of formation of small molecules [27] and the band gap of semiconductors [28], compared to experimental values.

In the hybrid PBE0 functional [27, 29], which was used in Papers I and V, 25% of PBE exchange is replaced by HF exchange:

\[ E_{\text{PBE0}}^{\text{xc}} = 0.75E_{\text{PBE}}^{\text{x}} + 0.25E_{\text{HF}}^{\text{x}} + E_{\text{c}}^{\text{PBE}} \] (2.6)

The calculation of the HF exchange comes at a significant computational cost when a plane-wave basis set is used. It is possible to speed up the calculation considerably by screening the exact exchange operator at long distances [30]. This is the idea behind the HSE06 functional [28], which uses a screened Coulomb potential to divide the exchange into a short-range (SR) and a long-range (LR) part, and the (screened) exact exchange is used only for the short-range part:

\[ E_{\text{HSE06}}^{\text{xc}} = aE_{\text{x}}^{\text{HF,SR},\omega} + (1 - a)E_{\text{x}}^{\text{PBE,SR},\omega} + E_{\text{x}}^{\text{PBE,LR},\omega} + E_{\text{c}}^{\text{PBE}} \] (2.7)

Here, \( \omega \) is a parameter which controls the extent of the screening, and \( a = 0.25 \) (as in the PBE0 functional). A detailed description of how the screening is accomplished can be found in Refs. 28 and 30. The HSE06 functional was used in Papers II and V.

The calculated ZnO band gap, using the HSE06 functional, is 2.4 eV, which is a considerable underestimation of the experimental value of 3.4 eV. By empirically increasing the fraction of HF exchange, \( a \) in equation (2.7), it is possible to systematically increase the band gap until the experimental value is obtained. A value of \( a = 0.375 \) gives a ZnO band gap of 3.4 eV, and this modified HSE06 functional, which here is denoted HSE06′, was used in Papers II, III, and V. Although HSE06′ improves the description of the ZnO electronic structure (compared to HSE06), there are some downsides: for example, both the calculated ZnO lattice parameters and the Cu cluster ionization energies become (somewhat) too small, compared to experimental values. Nevertheless, we deemed the HSE06′ functional to be the best functional to use in Papers II and III.

### 2.1.3 Periodic boundary conditions

Crystalline materials can be modeled using periodic boundary conditions. In this case, the orbitals \( \psi_i(\mathbf{r}) \) become bands \( \psi_i(\mathbf{k};\mathbf{r}) \) which must obey Bloch’s theorem:

\[ \psi_{i,k}(\mathbf{r} + \mathbf{T}) = e^{i\mathbf{k} \cdot \mathbf{T}} \psi_{i,k}(\mathbf{r}) \] (2.8)
which gives the relation between the band at a point $\mathbf{r}$ and an equivalent point $\mathbf{r} + \mathbf{T}$ elsewhere in the lattice ($\mathbf{T}$ is a lattice vector), and $e^{i\mathbf{k} \cdot \mathbf{T}}$ is a phase factor. To describe the band $\psi_i(\mathbf{k}; \mathbf{r})$, all allowed values of the wavevector $\mathbf{k}$ must be considered. The number of allowed values depends on the number of unit cells in the macroscopic crystal one wants to model, so it is a very large number for an, ideally infinitely large, bulk crystal. In practical calculations, the bands $\psi_i(\mathbf{k}; \mathbf{r})$ are calculated for a finite number of wavevectors $\mathbf{k}$, also known as $k$-points.

The band energy $e_i$ in equation (2.4) will thus depend on the $k$-point $\mathbf{k}$. If $e_{i, \mathbf{k}}$ does not depend much on $\mathbf{k}$, the band is flat, while if $e_{i, \mathbf{k}}$ depends significantly on $\mathbf{k}$, the band is disperse.

A key quantity in the analysis of periodic electronic structure calculations is the density of states (DOS), which describes the number of electronic states (per unit energy) as a function of energy.

Finally, we point out that the term band is used with two different meanings in this thesis. The first meaning is the one explained above, where the band in periodic boundary conditions corresponds to an orbital without periodic boundary conditions, i.e. the band can be occupied by up to 1 electron for each periodically repeated supercell. The second meaning is intended in the terms “valence band” and “conduction band”, which are both collections of “bands”. When “electrons enter the conduction band”, they enter the lowest-energy bands within the conduction band.

### 2.1.4 Band-filling correction

The (lowermost) ZnO conduction band is a very disperse band, meaning that the energy of the band is very $k$-point dependent (and, consequently, that the band is delocalized). In a calculation, an electron which populates the conduction band will consequently span an energy range, if more than one $k$-point is used. This is known as band-filling. Experimentally, the band-filling phenomenon can be seen in the Moss-Burstein shift [31, 32]: for semiconductors that are heavily doped with electron donors, only photons with an energy that is significantly greater than the band gap can excite electrons from the valence band to the conduction band, since many of the conduction band levels are already filled with electrons from the dopants.

The band-filling phenomenon is well-known in the defect physics community, where calculations on shallow donor defects (defects whose bands hybridize with the host conduction band) routinely employ the so-called band-filling correction [33, 34, 35, 36] (in ref. [33] the correction is simply named $E_{\text{corr}}$). The correction is also employed for calculations on shallow acceptors. The purpose of the correction is to calculate the defect formation energy (or, as in this thesis, the adsorption energy) in the dilute limit, i.e., for an isolated de-
fect or adsorbate, and not for a defect or adsorbate that is periodically repeated in space as a consequence of the (unwanted) periodic boundary conditions.

In its simplest form, the band-filling correction ($\Delta E_{bf}$) simply “collapses” the energy range spanned by the conduction band electrons (here, the “conduction band electrons” refer to the electrons which populate bands that are largely derived from the host conduction band) to the conduction band minimum (CBM):

$$\Delta E_{bf} = - \sum_{i, k} \Theta(e_{i, k} - e_{CBM}) w_k \eta_{i, k} (e_{i, k} - e_{CBM})$$  \hspace{1cm} (2.9)

where the sum runs over all k-points and bands, $\Theta$ is the Heaviside step function, $e_{i, k}$ is the eigenvalue of band $i$ at the k-point $k$, $w_k$ is the weight of the k-point $k$, and $\eta_{i, k}$ is the occupation of band $i$ at the k-point $k$. The band-filling correction $\Delta E_{bf}$ is added to the uncorrected total energy to yield the corrected total energy.

In Paper V we showed that, particularly for hybrid DFT functionals, the eigenvalue for the CBM ($e_{CBM}$) shifts to lower energies as the conduction band is populated (the CBM is down-shifted), with the size of the down-shift decreasing as larger supercells are used. Because of the down-shift, we used a slightly modified version of equation (2.9), which takes the energy differences between the unoccupied and occupied CBM eigenvalues into account:

$$\Delta E_{bf} = - \sum_{i, k} \Theta(e_{i, k} - e_{\text{occ}}^{\text{CBM}}) w_k \eta_{i, k} (e_{i, k} - e_{\text{unocc}}^{\text{CBM}})$$  \hspace{1cm} (2.10)

In addition to correcting for the “filling-up” of the conduction band, equation 2.10 also shifts the energy of the occupied CBM ($e_{\text{occ}}^{\text{CBM}}$) to the value of the unoccupied CBM ($e_{\text{unocc}}^{\text{CBM}}$) of the clean slab.

The rationale behind equation (2.10), is that for an infinite crystal, only the very bottom of the conduction band would be populated by an electron originating from an isolated defect (or adsorbate). Thus, in this limit, both the “filling-up” (k-point dependence) and down-shift would disappear.

In Papers I–V, we found that Cu species adsorbed on a ZnO surface can donate electrons to the ZnO conduction band. In Paper V, we showed that it is necessary to employ the band-filling correction in order to obtain the adsorption energy of a Cu atom in the low-coverage limit, and that the eigenvalue of the clean slab CBM ($e_{\text{unocc}}^{\text{CBM}}$) and the eigenvalues in the system with both the slab and adsorbate ($e_{\text{occ}}^{\text{CBM}}$ and $e_{i, k}$) must be aligned with each other. This can be achieved by subtracting the energy of a common reference point in the two cases, and we showed that the electrostatic potential at the center of the slab serves as such a common reference point (provided the adsorption occurs both “above” and “below” the slab, i.e., the adsorption is double-sided).

More background and discussion of the band-filling correction are given in sections 4.1 and 4.2.
Finally, we point out that the band-filling correction, although in this thesis only used with DFT calculations, can equally well be used with other electronic structure methods, such as SCC-DFTB.

2.2 Density functional based tight binding with self-consistent charges (SCC-DFTB)

The SCC-DFTB method is an approximation to Kohn-Sham DFT, and has been described in detail in Refs. 37 and 38. The DFT total energy $E$ from equation (2.5) can be rewritten as:

$$E = \sum_{i}^{occ} \langle \psi_i | -\frac{\nabla^2}{2} + V_{\text{ext}} + \int' \frac{n'}{|r-r'|} + V_{\text{xc}}[n] | \psi_i \rangle$$

(2.11)

where the following short-hand notation has been introduced: $\int dr \rightarrow \int$, $\int dr' \rightarrow \int'$, $n(r) \rightarrow n$, and $n(r') \rightarrow n'$. If this expression is expanded to second order around a reference density $n_0$, it becomes:

$$E = \sum_{i}^{occ} \langle \psi_i | -\frac{\nabla^2}{2} + V_{\text{ext}} + \int' \frac{n'_0}{|r-r'|} + V_{\text{xc}}[n_0] | \psi_i \rangle$$

$$- \frac{1}{2} \int \int' \frac{nn'}{|r-r'|} - \int V_{\text{xc}}[n]n + E_{\text{xc}}[n] + E_{\text{II}}$$

(2.12)

where $\delta n = n - n_0$. Within the SCC-DFTB method, the total energy is written as the sum of three terms:

$$E_{\text{tot}} = E_{\text{bs}} + E_{\text{rep}} + E_{\text{2nd}}$$

(2.13)

where the band-structure energy $E_{\text{bs}}$ corresponds to the first line in equation (2.12), the repulsive energy $E_{\text{rep}}$ corresponds to the second line in equation (2.12), and the second-order energy $E_{\text{2nd}}$ corresponds to the third line in equation (2.12).

The repulsive energy $E_{\text{rep}}$

The repulsive energy is usually approximated by means of a two-body repulsive potential $V_{\text{rep}}(r_{IJ})$ (which is a function of the interatomic distance $r_{IJ}$), summed over all atomic pairs:

$$E_{\text{rep}} = \frac{1}{2} \sum_{I \neq J} V_{\text{rep}}(r_{IJ})$$

(2.14)
The purpose of Paper VI was to optimize such a repulsive potential for ZnO and the H$_2$O/ZnO interface.

The second-order energy $E_{2\text{nd}}$

The second-order energy is approximated by dividing it into atom-centered contributions:

$$E_{2\text{nd}} = \frac{1}{2} \sum_{IJ} \gamma_{IJ}(r_{IJ}) \Delta q_I \Delta q_J$$  \hspace{1cm} (2.15)

where $\Delta q_I$ is the charge of atom $I$, and $\gamma_{IJ}(r_{IJ})$ is a function of the interatomic distance. For long interatomic distances, the second-order energy corresponds to the Coulomb energy between the charges $\Delta q_I$ and $\Delta q_J$, i.e. $\gamma \to 1/r$ as $r \to \infty$. If $I$ and $J$ are the same atom, then $\gamma$ is approximated by the Hubbard $U$, which is twice the chemical hardness of the atom (and which can easily be obtained from a DFT calculation as the second derivative of the total energy of an atom with respect to charge). Thus, $\gamma \to U$ as $r \to 0$. Different examples of functional forms of $\gamma$ can be found in Refs. 37 and 38.

The band-structure energy $E_{bs}$

The orbitals $\psi_i$ (or, in periodic calculations, the bands $\psi_{i,k}$) are expressed as a linear combination of atomic orbitals:

$$\psi_i = \sum_v c_i^v \phi_v(r)$$  \hspace{1cm} (2.16)

In the SCC-DFTB method, the atomic orbitals (the basis functions) $\phi_v$ are obtained from DFT calculations by imposing a confinement radius for the atom in the gas-phase. The orbitals are thus less diffuse than for the free atom, which improves the reference (initial) density $n_0$ for molecules and solids, where neighboring atoms act to decrease the “diffuseness” of the orbitals.

A secular problem is obtained:

$$\sum_v c_i^v (H_{\mu v} - e_i S_{\mu v}) = 0$$  \hspace{1cm} (2.17)

The overlap matrix elements, $S_{\mu v}$, and Hamiltonian matrix elements, $H_{\mu v}$, are:

$$S_{\mu v} = \langle \phi_\mu | \phi_v \rangle$$  \hspace{1cm} (2.18)

$$H_{\mu v} = H_{\mu v}^0 + \frac{1}{2} S_{\mu v} \sum_K (\gamma_{IK} + \gamma_{JK}) \Delta q_K$$  \hspace{1cm} (2.19)

where $\mu \in I$ and $v \in J$, and where the zeroth-order Hamiltonian matrix elements, $H_{\mu v}^0$, are:

$$H_{\mu v}^0 = \langle \phi_\mu | \hat{H}^0 | \phi_v \rangle = \langle \phi_\mu | -\frac{\nabla^2}{2} + V_{\text{ext}} + V_H[n_0] + V_{xc}[n_0] | \phi_v \rangle$$  \hspace{1cm} (2.20)
Although the elements $H^0_{\mu\nu}$ depend on the full reference density $n_0$ (and therefore all atomic positions), it is possible to make good approximations for the matrix elements that depend only on the relative positions of the atoms $I$ and $J$ (where $\mu \in I$ and $\nu \in J$) [37, 38].

One of the primary reasons for the high speed of the SCC-DFTB method, is that no integrals need to be evaluated during the calculation. The matrix elements $S_{\mu\nu}$ and $H^0_{\mu\nu}$ are instead obtained through Slater-Koster transformations of precomputed Slater-Koster integrals for a number of distances $r_{IJ}$ between the centers of the basis functions $\phi_\mu$ and $\phi_\nu$.

Finally, the band-structure energy becomes:

$$E_{bs} = \sum_{i}^{occ.} \langle \psi_i | \hat{H}^0 | \psi_i \rangle = \sum_{i}^{occ.} \sum_{\mu\nu} c^i_\mu c^i_\nu H^0_{\mu\nu}$$ (2.21)

**Self-consistent charges**

The SCC part of the SCC-DFTB method means “self-consistent charges”. The atomic charges $\Delta q_I$ that enter into equations (2.15) and (2.19) are calculated by Mulliken population analysis:

$$\Delta q_I = \frac{1}{2} \sum_{i}^{occ.} f_i \sum_{\mu \in I} \sum_{\nu} (c^i_\mu c^i_\nu S_{\mu\nu} + c^{i*}_\nu c^{i*}_\mu S_{\nu\mu}) - q^0_I$$ (2.22)

where $f_i$ is the occupation number of the orbital, and $q^0_I$ is the number of electrons in the neutral atom.

From an initial guess of the charges $\{\Delta q_I\}$, $H_{\mu\nu}$ can be calculated (equation (2.19)). These matrix elements are then used to solve for the basis function coefficients $c^i_\mu$ (equation (2.17)), which then yield new charges $\{\Delta q_I\}$ (equation (2.22)), and the cycle repeats until self-consistency is achieved.

**Periodic boundary conditions**

The formalism for modeling periodic boundary conditions with SCC-DFTB is similar to the one outlined for DFT in section 2.1.3.
3. The structure and charge of Cu on ZnO

3.1 Motivation

A common theme of Papers I–IV is Cu adsorption on ZnO, and in all of these papers, the charge of the Cu is in focus. The Cu charge depends on the adsorption sites, the number of atoms in and the geometric structure of the Cu cluster or overlayer, whether Cu adsorbs on the ZnO(10\overline{1}0) or ZnO(0001) surface, the geometric structure of the substrate surface, and, specifically in the case of ZnO(0001), whether the surface is reconstructed, and even which kind of reconstruction, and whether other molecules, such as water, are present. To make matters even more complicated (and technical), the calculated charge of the Cu also depends on which computational method is used.

The charge of Cu is interesting not only because a charged Cu species may be more or less catalytically active than a neutral one [9], but also because the charge of the Cu can affect what happens to the ZnO and the Cu-ZnO interaction (as we show in Paper IV).

For theoreticians, another aspect comes into play: it is imperative to identify the charge of Cu simply to know what is being modeled. This is particularly relevant for the modeling of catalysis, where charge transfer is the name of the game. As pointed out in several of the papers in this thesis, the stability of positively charged adsorbates depends on the coverage (supercell size), which might adversely affect any calculated reaction energies unless care is taken to correct for this effect (if an isolated adsorbate is the objective). Not only that, but the charge transfer may arise for the wrong reasons, such as the underestimation of the substrate band gap. This puts pressure on the theoretician to select the “right” method to use. These issues are discussed in more detail in chapter 4.

The present chapter summarizes the results for Cu adsorption on ZnO(10\overline{1}0) (Papers I–III) and on ZnO(0001) (Paper IV). In Paper I, we showed how Cu atoms on ZnO(10\overline{1}0) repeatedly switch between being neutral and positively charged as they diffuse over the surface, and we suggested that this ought to influence the Cu dimer formation mechanism. In Paper II, we showed how the charges of small Cu clusters on ZnO(10\overline{1}0) depend on whether the Cu clusters have an even or odd number of atoms, and in Paper III, we showed that adsorbed \(\text{H}_2\text{O}\) can induce charge transfer between Cu and ZnO, and in some cases even dissociate small Cu clusters. In Paper IV, we showed how negatively charged Cu attracts positively charged subsurface defects, and how this subsequently leads to Cu wetting of the ZnO(0001) surface at elevated temperatures.
3.2 I: Cu dimer formation mechanism on ZnO(10\bar{1}0)

| Purpose: | To investigate the geometric and electronic structures of Cu atoms and dimers adsorbed on ZnO(10\bar{1}0). |
| Methods: | PBE, PBE0. |
| Calculated properties: | Charges of the Cu adsorbates, coverage dependence of adsorption energies, migration barriers. |
| Take-home message: | The charge of the Cu atom depends on the adsorption site. PBE and PBE0 give qualitatively different results. The diffusive motions of two well-separated Cu atoms are correlated because the charges continuously change during diffusion. |

In Paper I, we used the PBE and hybrid PBE0 functionals and found three stable adsorption sites of a Cu atom (sites a, b, and c) and two configurations of a Cu dimer (the lying and standing configurations) on the ZnO(10\bar{1}0) surface. We observed a marked coverage dependence (supercell size dependence) of the calculated adsorption energy for adsorption site b but not for any of the other atomic adsorption sites (nor for any of the dimers), and attributed this effect to the acquired positive charge of the Cu atom at site b and the consequent electrostatic repulsion between the periodically repeated positively charged Cu atoms; the positive charge arose because of electron transfer from the Cu atom to the ZnO conduction band. We calculated the barriers of migration of the adsorbed Cu atoms between the different adsorption sites, and found that migration should occur mainly along the [1\bar{2}10] direction via a hopping mechanism between sites a and b. Finally, based on our computational findings, we proposed a remarkable “dimer formation mechanism”, where the motion of two adatoms (before the formation of the dimer) was correlated already at quite long separations, because of the alternating charges of the atoms as they diffused over the surface.

Geometric and electronic structures for Cu atom adsorption

The structures of the three Cu atom adsorption sites are shown in Figure 3.1a–b. Site a roughly corresponds to the position a Zn atom would have if the surface grew by an additional layer, site b is above and between two surface O atoms, and site c is somewhere between an “ontop O” site and a bridge site.

At site b, the Cu atom transfers an electron to the ZnO conduction band, so that the Cu atom ends up positively charged. In contrast, no such electron transfer occurs for sites a and c. This is indicated in schematically drawn densities of states for sites a and b in Figure 3.1c. At site a, there is a singly occupied state with mainly Cu 4s character (thus localized on the Cu atom), while at site b, the electron enters the ZnO conduction band (and delocalizes over the ZnO substrate).
Figure 3.1. (a)–(b) Top and side views of adsorption sites \( a \), \( b \), and \( c \) for Cu/ZnO(10\(\overline{1}0\)). Zn is white, O is red, and Cu is yellow. In the top view, the surface atoms are larger than the subsurface atoms. In the side views, the top four surface layers are shown. (c) Schematic DOS for Cu atom adsorption on ZnO(10\(\overline{1}0\)) at sites \( a \) and \( b \) (the dots indicate the highest-energy electrons).

Cu dimer formation mechanism on ZnO(10\(\overline{1}0\))

As a Cu atom diffuses across the surface, it will move along the [1\(\overline{2}10\)] crystal direction by hopping between adjacent \( a \) and \( b \) sites (site \( c \) is less stable than both \( a \) and \( b \)), thus repeatedly switching between being neutral and positively charged. We therefore suggested that the minimum energy path for dimer formation was characterized by at least one of two approaching Cu atoms occupying site \( a \). Or, phrased another way, the two approaching Cu atoms would not simultaneously occupy site \( b \), because of the electrostatic repulsion between the positively charged Cu atoms. The end result is shown in Figure 3.2.

Stabilities of different adsorption sites

Our calculations showed that adsorption site \( b \) becomes progressively more stable as the lateral dimensions of the supercell increase (i.e., as the effective coverage of Cu atoms on the surface decreases). In Paper I we attributed this effect to the electrostatic repulsion between neighboring positively charged Cu atoms on site \( b \): a lower coverage of Cu atoms meant lower Coulomb repulsion between the adatoms, and consequently more stable adsorption. We subsequently found that another phenomenon contributed even more to this coverage dependence: the “band-filling” of the ZnO conduction band (this is described in detail in Paper V and section 4.1). No significant coverage dependence of the adsorption energy was obtained at sites \( a \) or \( c \), as the Cu atom remains neutral at those sites, according to our calculations.

We also found qualitative differences between the results obtained with PBE and the PBE0 functionals, because of the different sizes of the computed ZnO band gaps. This point is further discussed in section 4.3. In Paper V (section 4.1), we later outlined some shortcomings of the PBE0 functional and suggested that it is better to use a screened hybrid functional (HSE06′).
Figure 3.2. Minimum energy path of our suggested dimer formation mechanism for Cu on ZnO(10\overline{1}0). The two Cu atoms diffuse along [1\overline{2}10], i.e. horizontally in the figure, by hopping between adjacent $a$ and $b$ sites. At site $a$, the Cu atom is neutral (dark-yellow), while at site $b$ it is positively charged (light-yellow). (a) Two Cu atoms at well-separated $b$ sites. (b) Well-separated $a$ and $b$ sites. The Cu atom at site $b$ hinders the other Cu atom from diffusing towards it because of electrostatic repulsion. Only the Cu atom at site $b$ can diffuse freely. (c) Two Cu atoms at site $a$. (d) Medium-separated $a$ and $b$ sites. Only the Cu atom at site $b$ can diffuse freely. (e) Medium-separated $a$ sites. (f) Nearby $a$ and $b$ sites. (g) The *lying* dimer. (h) The *standing* dimer. More details can be found in Paper I.
3.3 II: Small Cu clusters adsorbed on ZnO(10\overline{1}0) show even-odd alternations in stability and charge transfer

**Purpose:** To find out whether Cu clusters with up to nine atoms, adsorbed on ZnO(10\overline{1}0), donate electrons to the ZnO conduction band, or remain neutral.

**Methods:** PBE, HSE06, HSE06'.

**Calculated properties:** Binding and ionization energies of gas-phase Cu clusters, charges of the adsorbed Cu clusters, adsorption energies.

**The gist:** Odd-numbered Cu clusters on ZnO(10\overline{1}0) can either remain neutral or become positively charged, depending on the structure of the cluster. In contrast, even-numbered clusters are always neutral. The different behavior for odd vs. even can be traced back to the gas-phase behavior of the Cu\textsubscript{n} clusters: odd-numbered Cu clusters have lower ionization energies.

In Paper II, we showed that, similar to the case of Cu atom adsorption in Paper I, Cu clusters with an odd number of atoms can be either neutral or positively charged on ZnO(10\overline{1}0), depending on the structure (and “adsorption site”) of the cluster. In contrast, (reasonably stable) even-numbered clusters are always neutral. We explained this in terms of the ionization energies of gas-phase Cu clusters, which follow an even-odd alternation, being lower for odd-numbered clusters than for neighboring even-numbered clusters (see Figure 3.3).

![Figure 3.3](image)

*Figure 3.3.* Calculated and experimental [39, 40, 41] vertical ionization energies of the most stable Cu clusters of various sizes.

The adsorption energies, calculated using gas-phase Cu atoms and the ZnO slab as references, for the most stable Cu clusters that were either neutral or
positively charged for each Cu cluster size, are shown in Figure 3.4. The most important conclusions that can be drawn from this figure are: (i) there is an even-odd alternation in stability for Cu clusters with size up to 6 atoms, and (ii) adsorbed Cu$_1$ and Cu$_3$ preferentially remain neutral, while Cu$_7$ and Cu$_9$ preferentially become positively charged; for Cu$_5$ both charge states are similarly stable.

Interestingly, the “neutral” data point for Cu$_5$ corresponds to a planar cluster while the “charged” data point corresponds to a polyhedral cluster. Again, we explained this observation by means of the ionization energies of gas-phase clusters, since the ionization energies of polyhedral clusters are smaller than those of planar clusters.

The structures and even-odd alternation of the charges of the most stable adsorbed Cu clusters with 6–9 atoms are shown in Figure 3.5.

Figure 3.4. HSE06'-calculated adsorption energies (normalized with respect to the number of atoms) for the most stable neutral and positively charged Cu clusters on ZnO(1010) as a function of Cu cluster size.
3.4 III: Water-induced oxidation and dissociation of small Cu clusters on ZnO(10\textbar 10)

**Purpose:** To investigate how water adsorption influences the charge transfer between Cu and ZnO for small adsorbed Cu clusters (up to 4 atoms) on ZnO(10\textbar 10).

**Methods:** PBE, HSE06'.

**Calculated properties:** Charges of the adsorbed Cu\textit{n}-(H\textsubscript{2}O)\textit{m} complexes, successive water adsorption energies onto Cu clusters, reaction energies for “water-induced dissociation” of the Cu clusters.

**Highlights:** A water molecule adsorbed onto Cu\textsubscript{1} and Cu\textsubscript{3} clusters on ZnO(10\textbar 10) induces charge transfer from Cu to ZnO. The water adsorption onto Cu\textsubscript{3} also induces dissociation of the cluster into Cu\textsubscript{1} and Cu\textsubscript{2}.

In **Paper III**, we modeled water adsorption onto the most stable Cu clusters with 1–4 atoms adsorbed on ZnO(10\textbar 10) (from **Paper II**).

The odd-numbered (Cu\textsubscript{1}, Cu\textsubscript{3}) and even-numbered (Cu\textsubscript{2}, Cu\textsubscript{4}) clusters in this study behave differently as water molecules move from the ZnO surface to the clusters. When a water molecule adsorbs on an odd-numbered cluster, the cluster becomes positively charged (oxidized) and donates an electron to the ZnO conduction band. In contrast, such oxidation occurs for an even-numbered cluster only if two or more water molecules adsorb, which is always energetically unfavorable. In addition, it is thermodynamically favorable for the Cu trimer to dissociate into an atom and a dimer when the water molecule adsorbs on the cluster (water adsorption-induced dissociation of Cu\textsubscript{3}), see **Figure 3.6**.

**Figure 3.6.** The water-adsorption induced dissociation of Cu\textsubscript{3} on ZnO(10\textbar 10): H\textsubscript{2}O\textsubscript{ad} + [Cu\textsubscript{3}]\textsubscript{ad} \xrightarrow{\Delta E = -20 \text{kJ/mol}} [Cu(OH\textsubscript{2})]^+\textsubscript{ad} + [Cu\textsubscript{2}]\textsubscript{ad} + e^- (ZnO CB). The [Cu(OH\textsubscript{2})]^+\textsubscript{ad} species is in fact H\textsuperscript{+}\textsubscript{ad} + [CuOH]\textsubscript{ad}.  

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3.5 IV: Cu wets the polar ZnO(0001) surface because of interaction with subsurface defects

**Purpose:** To characterize and explain the experimentally observed behavior of Cu/ZnO(0001) as a function of temperature.

**Method:** STM, XPS, DFT (PBE).

**Calculated properties:** Cu atom adsorption energies, total energy changes as defects are moved towards the surface/interface.

**Key results:** Cu forms 3D islands on ZnO(0001) at room temperature, and becomes negatively charged. As the temperature increases, the adsorbed Cu “pulls” positively charged defects towards the interface, which increases the Cu adhesion energy and causes it to completely wet the ZnO(0001) surface.

The deposition of 0.25 ML Cu on a cleaned (by Ar+ ion sputtering) ZnO(0001) surface was followed by cycles of annealing to different temperatures and subsequent analysis by scanning tunneling microscopy (STM) and x-ray photoelectron spectroscopy (XPS). Three distinct temperature ranges were identified: range I (300 K – 435 K), where the Cu particles grew in size with an Ostwald ripening mechanism; range II (435 K – 570 K), where Cu began to wet the ZnO(0001) surface; range III (570 K – 650 K), where much Cu was lost by in-diffusion.

At 450 K many small triangular pits started to form on the ZnO(0001) surface. Both the measured band bending and core-level binding energy shifts suggested that the adsorbed Cu obtained a negative charge.

The DFT calculations suggested that, in the presence of shallow donors (i.e. when the conduction band is populated), both an adsorbed Cu atom on the surface and an adsorbed Cu metal overlayer will become negatively charged, in agreement with the experimental picture. We also showed how the conduction band being populated led to stronger binding of the Cu atom to the surface.

We placed various types of defects beneath the adsorbed Cu metal overlayer: a zinc vacancy ($V_{\text{Zn}}$), a hydrogen interstitial ($H_I$), a hydrogen substituting for an oxygen ($H_O$), and an oxygen vacancy ($V_O$). The resulting charges of the different defects were $V_{\text{Zn}}^{2-}$, $H_I^+$, $H_O^+$ and $V_O^{2+}$. The calculations revealed that the diffusion of positively charged subsurface defects ($H_I^+$, $H_O^+$, $V_O^{2+}$) towards the surface is enhanced in the presence of adsorbed Cu, while the driving force for diffusion of negatively charged defects ($V_{\text{Zn}}^{2-}$) decreases.

Thus, we conclude that the Cu, when deposited on ZnO(0001), becomes negatively charged, and attracts positively charged subsurface defects, such as $H_O^+$. These kinds of defects help to form the triangular pits at 450 K, and as more and more defects are attracted towards the surface region, Cu binds more strongly to the substrate and completely wets the ZnO(0001) surface.
4. Cu/ZnO modeling challenges and developments

There are two “problems” that make modeling Cu/ZnO with DFT particularly challenging: the issue of band-filling (sections 4.1 and 4.2) and the band-gap problem (section 4.3). Another problem is that of the choice of ZnO surface model (section 4.4), where, for example, choices must be made whether to adsorb on only one or both sides of the slab, or if the surface needs to be passivated. This chapter discusses the progress that has been made to solve, mitigate or overcome these problems.

4.1 V: Band-filling correction method for accurate adsorption energy calculations: A Cu/ZnO case study

**Purpose:** To evaluate the band-filling correction method as a way to obtain the adsorption energy for an isolated adsorbate when the structural model is periodic, and when the adsorbate (in this case a Cu atom) donates an electron to the substrate (in this case ZnO) conduction band.

**Methods:** PBE, PBE0, HSE06, HSE06′.

**Calculated properties:** CBM down-shifts, band-filling corrections, the band-filling correction error for bulk ZnO, adsorption energies for different coverages and k-point samplings.

**The bottom line:** The band-filling correction is quite successful in delivering adsorption energies that do not depend on adsorbate coverage (i.e., the size of the substrate surface supercell) in cases where the substrate conduction band has become populated. The correction works only for non-hybrid functionals, such as PBE, and screened hybrid functionals, such as HSE06, provided the supercell is large enough.

The band-filling problem for Cu/ZnO arises when the ZnO conduction band becomes populated through electron donation from adsorbed Cu. Because the conduction band is very disperse, the donated electron will span an energy range. Thus, even for very large supercells, the model does not correspond
to an isolated adsorbate on the surface. The band-filling correction serves to "restore" the isolation of the adsorbate, by removing the adsorption energy dependence on supercell size and k-point sampling.

In Paper V, we first systematically evaluated the band-filling correction (section 2.1.4) for an excess electron in the bulk ZnO conduction band for different functionals, supercell sizes, and k-point samplings. We found that that the correction works well with PBE for both small and large supercells, but with HSE06 and HSE06' only for larger supercells. With PBE0, the band-filling correction did not work very well for any "reasonably" sized supercell. Then, we used the approach outlined in section 2.1.4 to calculate the band-filling correction for a Cu atom adsorbed at site $b$ on the ZnO(1010) surface (see section 3.2) for systematically smaller coverages, and found that that the uncorrected adsorption energy approached the corrected value as the coverage was decreased (this was particularly clear when the PBE functional was employed).

The band-filling phenomenon can easily be illustrated for bulk ZnO. Instead of introducing a shallow donor defect, an extra electron can simply be added to the system (the introduction of a uniformly distributed positively charged background ensures that the system as a whole is charge-neutral). Figure 4.1 shows the calculated electronic density of states (DOS), with and without an excess electron, for a bulk ZnO supercell containing 48 formula units. Two effects are readily visible: (i) when the conduction band is popu-
lated, the CBM is down-shifted by 0.21 eV with the hybrid functional HSE06' (Figure 4.1a), although this effect becomes smaller with PBE (Figure 4.1b-c), and (ii) when more than one k-point is used (Figure 4.1c), the excess electron spans an energy range of 1.15 eV.

Both of these effects become smaller as the size of the supercell increases (i.e. as the “excess electron concentration” decreases). The band-filling correction estimates the total energy error that these two effects give for a finite defect (excess electron) concentration, which is used in the calculation, compared to an infinitesimal defect (excess electron) concentration, which is what one aims to model.

In Paper V, we verified that this correction works well for the PBE functional, as well as for the screened hybrid functionals HSE06 and HSE06' if the supercell was “large”, but not so well for the hybrid PBE0 functional. We drew this conclusion by comparing the total-energy differences obtained upon addition of an excess electron with the eigenvalues of the unoccupied conduction band for various k-point samplings and functionals. The reason the correction does not work as well with the hybrid functionals as with PBE appears to be long-range exact exchange for the delocalized conduction band electron. Because the exact exchange is screened in HSE06 and HSE06', the correction works well for supercells with a size that is at least of the order of the screening length (for these two functionals about 10 Å).

We subsequently applied the band-filling correction to the Cu/ZnO adsorption system. We adsorbed a Cu atom on the ZnO(1010) surface and systematically decreased the coverage. At site b (see section 3.2), the Cu atom donates an electron to the ZnO conduction band. Because the effect of the band-filling becomes smaller as the surface supercell size is increased (as the Cu coverage decreases), the uncorrected adsorption energy at this adsorption site is highly dependent on supercell size (and k-point sampling, see Supporting Information to Paper V). In contrast, for another adsorption site (site a), the Cu atom does not donate an electron to the ZnO and the adsorption energy is practically independent of the coverage and k-point sampling.

Table 4.1 (from Paper V) gives the adsorption energies for sites a and b for various methods and supercell sizes, as well as the “down-shift” \( \Delta e_{\text{CBM}} \) of the CBM when the conduction band is populated, and the band-filling correction \( \Delta E_{\text{bf}}/2 \) (the factor 1/2 is used because one Cu atom is adsorbed on each side of the slab, and the adsorption energy is given per Cu atom).

Clearly, the band-filling correction removes the coverage dependence of the adsorption energy for site b for the PBE method. For the hybrid methods, the corrected adsorption energies are not as nicely converged, although it seems that the correction works reasonably well with HSE06 and HSE06'. The performance for PBE0 is worse.
### Table 4.1.

Calculated adsorption energies (both uncorrected, $E_{ads}$ and $E_{uncorr}^{ads}$, and corrected for band-filling, $E_{corr}^{ads}$), CBM down-shifts $\Delta e_{CBM}$, and band-filling corrections $\frac{1}{2}\Delta E_{bf}$ for various coverages (supercell sizes) of Cu/ZnO(1010) for sites a and b. All energies are given in eV. Because of the large errors connected to the band-filling correction obtained with PBE0, the corrected adsorption energies for site b (marked with an asterisk) may contain considerable errors.

<table>
<thead>
<tr>
<th>Cell</th>
<th>Area (nm²)</th>
<th>Method</th>
<th>$E_{ads}$</th>
<th>$E_{uncorr}^{ads}$</th>
<th>$\Delta e_{CBM}$</th>
<th>$\frac{1}{2}\Delta E_{bf}$</th>
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<tbody>
<tr>
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<td>-1.60</td>
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</tbody>
</table>

4.2 Is the band-filling correction right for you?

The band-filling phenomenon, although well-known in the defect physics community for defects in bulk materials, had previously not been reported for adsorbate/substrate systems. The phenomenon certainly occurs for more systems than just Cu/ZnO, although ZnO is a material where the effect is unusually pernicious, because of the disperse nature of the ZnO conduction band. Another technologically relevant material with a disperse conduction band and where the band-filling may be significant is, for example, graphene.

Is the band-filling correction, then, an indispensable tool that belongs in the repertoire of every computational chemist? No, for there are certainly many adsorbate/substrate systems for which there is no (or very little) need to apply it, also in cases where charge transfer between the adsorbate and substrate occurs. For example, in the field of catalysis, most reactions occur on metal surfaces. Metals, in general, have a fairly high density of states near the Fermi level (as many bands cross the Fermi level), so that an electron transferred from a molecule to the metal will span only a miniscule energy range. Another material relevant for catalysis is ceria, CeO$_2$, which acts as an oxygen buffer in catalytic car converters. It is a “reducible” oxide, meaning that the cerium ions can toggle between charges of Ce$^{4+}$ and Ce$^{3+}$. An electron transferred to ceria will thus localize on a cerium ion (Ce$^{4+}$ + e$^-$ $\rightarrow$ Ce$^{3+}$) instead of entering a delocalized conduction band as is the case for ZnO. Localized states
correspond to flat bands, so the energy of the band will not depend on the k-point, which renders the band-filling correction meaningless.

The band-filling correction aims to remove the coverage (and k-point) dependence of calculated adsorption energies when the ZnO conduction band becomes populated. In Paper V, it was shown that the correction works remarkably well when the PBE functional is used, so that virtually no coverage dependence remains if the correction is applied. Is this reasonable? In Paper I, before we had identified the band-filling phenomenon, we attributed the coverage dependence to the positive charge of the Cu adsorbate. This is certainly not an unreasonable interpretation, and intuitively, it seems that (in addition to the band-filling-derived coverage dependence) there should be some coverage dependence arising from the repulsion between the positive adsorbates. Subsequent (unpublished) calculations, performed by the author of this thesis, for two Cu atoms on ZnO(10\bar{1}0) with varying interatomic distances (keeping the supercell and accordingly the band-filling constant) have shown that there indeed is repulsion between the positively charged Cu atoms. Thus, we conclude that the minimum energy path for dimer formation suggested in Paper I still holds, at least with respect to the fact that two nearby Cu atoms should not simultaneously occupy adsorption sites where they become positively charged.

There is still one unanswered question: Why does the band-filling correction work so well if there is repulsion between adsorbates for which the correction “makes no correction”? Admittedly, the answer to this question probably involves some degree of luck and error cancellation. For example, although the two positively charged adsorbates will repel each other more at shorter distances (i.e., higher coverages), they will also feel a greater attraction to the negatively charged substrate (because the negative charge is less “smeared out” when the supercell is small). Another consideration is that the conduction band is less “pure” when the supercell is small, since the hybridization between the conduction band and Cu-derived states will be larger in small supercells than in large ones.

There are two important points about the band-filling correction that were not explicitly mentioned in Paper V. The first point, just briefly alluded to in the supporting information of Paper V, is that, because the band-filling correction is used as a means to extrapolate to isolated adsorbates, and hence to “remove” the k-point dependence of the energy of the conduction band, it is perhaps more sensible to use just a single k-point in the calculations than to use a full set of k-points and subsequently correct for the k-point dependence of the energies. For reasonably sized supercells, all bands within the valence band will be virtually flat compared to the conduction band, so by using a single k-point, only the description of the conduction band is affected. For the PBE functional, this single k-point could be the \Gamma-point (where the CBM is located) since the down-shift is small. For hybrid functionals, some k-point other than the \Gamma-point (perhaps obtained by trial-and-error), which restores the
ZnO band gap, despite the conduction band down-shift, could be used. This would negate the need for the band-filling correction.

The second point is more subtle, namely that the coverage dependence for the uncorrected adsorption energies is a real effect. This means that in order to model different coverages, it is necessary to use a fully converged k-point sampling even for very large supercells, in order to get the correct adsorption energy.

4.3 Which density functional should be used to model Cu/ZnO?

The experimental ZnO band gap is 3.4 eV, but most DFT calculations on ZnO yield a much smaller band gap (the band-gap problem). For example, the PBE-calculated band gap is only 0.7 eV. It is possible to improve the calculated band gap by using a hybrid density functional, which includes a fraction of exact exchange (section 2.1.2). PBE0 gives a band gap of 3.2 eV, near the experimental value. If the exact exchange interaction is screened, as in HSE06, the band gap decreases to only 2.4 eV. By empirically increasing the fraction of exact exchange from 25% to 37.5%, as done with the HSE06′ functional, the band gap matches the experimental value of 3.4 eV.

The calculated band gap is a crucial quantity when the Cu adsorbate donates an electron into the conduction band (in fact, it is not the band gap as such that is important but the relative positions of Cu-derived electronic states and the conduction band states). We first showed this in Paper I, where we compared the results for Cu atom adsorption on ZnO(1010) obtained with PBE and PBE0. We later evaluated PBE, PBE0, HSE06, and HSE06′ more systematically in Paper V, where we showed that the description of the occupied conduction band was problematic with PBE0. Because of the delocalized nature of the conduction band, the CBM down-shifted in a big way, i.e. the effective band gap decreased, as a result of long-range exact exchange. This down-shift could be counteracted by screening the exact exchange in the HSE06 and HSE06′ functionals. Because HSE06′ gives the experimental band gap, we proposed that the results obtained with HSE06′ are the most reliable. The band-filling correction also worked better with the HSE06′ functional than the PBE0 functional.

The PBE and HSE06′ functionals give qualitatively different results for the relative stabilities of adsorption sites a and b (depicted in Figure 3.1a–b) for a Cu atom on ZnO(1010), see Figure 4.2 (these adsorption energies can also be found in Table 4.1). If the PBE functional is used, the adsorption energy for the neutral Cu atom at site a becomes -1.6 eV. The adsorption for the positive Cu atom at site b (when the Cu donates an electron to the ZnO conduction band) is 0.3 eV more stable, with an adsorption energy of -1.9 eV. Thus, the PBE functional predicts that the positively charged species is more stable, but
Figure 4.2. PBE- and HSE06'-calculated adsorption energies for a Cu atom on ZnO(10¯10) in the low-coverage limit for adsorption sites \( a \) (where Cu is neutral) and \( b \) (where Cu donates an electron to the ZnO conduction band and ends up positively charged).

this is an artefact of the underestimated band gap (or, more precisely, it is an artefact of the erroneous relative positions of energy levels on the Cu and the ZnO), which makes it too easy to populate the conduction band.

In contrast, if the HSE06' functional, which reproduces the experimental band gap, is used, the adsorption energy for the neutral Cu atom at site \( a \) becomes -1.2 eV and the adsorption energy for the positive Cu atom at site \( b \) becomes -0.9 eV, i.e. site \( a \) is 0.3 eV more stable than site \( b \), the exact opposite of what was obtained with the PBE functional.

In some cases, the size of the band gap also influences whether charge transfer from Cu to ZnO occurs at all, as we showed in Paper III where, for example, the Cu trimer became positively charged with PBE but not with HSE06', despite the optimized structures being very similar with the two methods.

Because HSE06' produces such a good ZnO band gap, the results obtained with this functional were in focus in Papers II and III. However, the HSE06' functional is computationally very demanding, and it was not feasible to explore the potential energy landscape (different adsorption configurations) to any significant degree with this functional. Therefore, we used an approach where we first screened a large number of adsorption configurations at the PBE level, and subsequently selected the most promising (stable) configurations for further evaluation at the HSE06' level. This turned out to be a successful approach, as the relative stabilities of any two configurations, with the same charge, at the PBE level, in general were the same as those obtained at the HSE06' level.

In Paper IV, where Cu adsorption on ZnO(0001) was modeled, only the PBE functional was used, and not HSE06'. The reason for this was quite simple: the computational models were simply too large to be modeled with HSE06'. However, we were still able to draw a number of useful conclusions from the PBE calculations, despite the shortcomings of the PBE functional. For example, the adsorbed Cu metal overlayer became negatively charged de-
spite the small band gap — a larger band gap would not cast any doubt on this conclusion.

4.4 What constitutes a good ZnO surface model?

The ZnO(10\text{\overline{1}}0) surface has been modeled (using DFT) in two different ways in this thesis. In Paper I, the surface was modeled as a four double-layer thick slab, with the bottom two layers kept fixed, and the adsorption occurring only on the “top” (relaxed) side. In contrast, in Papers II, III, and V, the same number of double-layers were used but now all of the atoms were allowed to relax and the adsorption occurred on both sides of the slab. What brought forth this change in surface model was the use of the band-filling correction, which requires that there be a region in the slabs with and without adsorbate that are “similar”. If the adsorption occurs only on one side of the slab, and the adsorbate ends up positively charged, there will be an electric field over the slab, which makes the finding of such a region much more difficult than if the adsorption is double-sided.

The Zn-terminated ZnO(0001) surface was also modeled (using DFT) in two different ways. In Paper IV, the ZnO(0001) surface was modeled as a slab where the O-terminated side of the slab was passivated by pseudoatoms, as is customary when modeling this polar surface with DFT [42, 43, 44]. In contrast, in Paper VII (section 5.2) no such passivation was used and the Zn-terminated (0001) and O-terminated (000\text{\overline{1}}) surfaces were modeled simultaneously for some simple reconstructions. Modeling both surfaces simultaneously is, in most ways, inferior to using the pseudoatom passivation approach, because it is difficult to decouple the effects on the Zn-terminated and O-terminated surfaces. However, in Paper VII the DFT calculations were performed only to validate the SCC-DFTB calculations (which modeled both surfaces simultaneously, in exactly the same way as the DFT calculations). The benefit of avoiding the pseudoatoms is that an absolute cleavage energy can be readily calculated (section 5.2).

A more fundamental question relates to how realistic the surfaces models are. In Paper IV, the adsorbed Cu atom on ZnO(0001) could either become positively or negatively charged, depending on the surface reconstruction used in the calculations. If the conduction band was completely depleted before the adsorption, the Cu atom donated an electron into the conduction band, while if the conduction band was already populated before the adsorption, the Cu atom accepted an electron from the conduction band. This statement highlights an important point that was largely neglected in Papers I–III. These papers concerned Cu adsorption on ZnO(10\text{\overline{1}}0), and the ZnO slab was always “perfect”, i.e., without defects. Because of this, the “starting position” in the calculations before Cu adsorption, was a ZnO slab with the valence band occupied and the conduction band empty. Then, for the Cu to donate electrons to the ZnO, the
electrons would have to enter the conduction band. Conversely, for the ZnO to donate electrons to the Cu, the electrons would have to come from the valence band. Real-life ZnO occurs almost exclusively as n-type ZnO, meaning that there are plenty of donor-type defects, which sets the Fermi level around the CBM. Thus, in real life, it may be that the neutral species in Papers I–III should in fact accept electrons from available shallow donors and become negative. A more realistic model of a ZnO surface could perhaps be a slab with some shallow donor defects, e.g. H interstitials, in the center of the slab, which could provide electrons for the Cu to accept (or, as may well be the case, reject). The species that ended up being positively charged in Papers I–III donated electrons to the conduction band, near the real-life Fermi level, and were thus modeled “correctly” in this respect.
5. Multi-scale modeling of ZnO surfaces

One of the drawbacks of DFT, and particularly hybrid DFT, is the significant computational effort required to perform calculations for large systems (and long times). This part of the thesis concerns the parameterization of the semi-empirical SCC-DFTB method, which is much less computationally demanding than DFT, and which allows for the simulations of larger and more realistic systems than what is possible at the DFT level. Results from DFT calculations were used to find good parameters for the SCC-DFTB method in Paper VI. This way of using results from a relatively “accurate” method to parameterize a faster (and hopefully not much less accurate) method is part of the so-called multi-scale modeling approach. The parameters were then used in Paper VII to model large polar surface reconstructions.

5.1 VI: An SCC-DFTB repulsive potential for ZnO and the ZnO-water system

| **Purpose:** | To generate an SCC-DFTB repulsive potential for ZnO and the H2O/ZnO interface. |
| **Methods:** | PBE, SCC-DFTB. |
| **Calculated properties:** | Energy-volume scans, surface energies, electronic band structures, water adsorption energies. |
| **In a nutshell:** | With the znorg-0-1 SCC-DFTB parameter set for ZnO from the literature, the NaCl-type polymorph of ZnO more stable than the (experimentally obtained) wurtzite polymorph. Our newly generated znopt repulsive potential solved this inconsistency, and also improved the description of water adsorption on ZnO surfaces. |

Moreira et al. [45] generated SCC-DFTB parameter sets (electronic parameters stored in Slater-Koster tables, as well as a repulsive potentials $V_{\text{rep}}$), collectively called znorg-0-1, for Zn-X, where X was any of the elements H, C, N, O, S, and Zn. In Paper VI, we identified what we considered to be a serious limitation with the znorg-0-1 parameter set, namely that it makes the NaCl-type polymorph of ZnO (which is experimentally obtainable only at high pressures) more stable than the wurtzite polymorph (which is experimentally obtained at ambient conditions).
Figure 5.1. Energy-volume scans calculated for the NaCl-type and wurtzite polymorphs with the DFT (PBE functional) and SCC-DFTB (new \textit{znopt} and old \textit{znorg-0-1} parameter sets) methods.

In the NaCl-type polymorph, the Zn and O atoms are six-coordinated, with relatively long interatomic distances ($\sim 2.2$ Å), while in the wurtzite polymorph, the atoms are four-coordinated, with relatively short interatomic distances ($\sim 2.0$ Å). Our idea was to generate a new repulsive potential with increased repulsion for the longer interatomic distances, which would decrease the stability of the NaCl-type polymorph and make it less stable than the wurtzite polymorph. In order to keep compatibility with all the other elements in the \textit{znorg-0-1} parameter set, we only modified the repulsive potential between Zn and O, and not any of the electronic parameters. The newly generated repulsive potential, in combination with the “old” electronic parameters, is called \textit{znopt}.

Figure 5.1 shows the energy-volume scans for both the NaCl-type and wurtzite polymorphs, calculated with the \textit{znorg-0-1} and \textit{znopt} parameter sets, and a comparison is made to DFT results at the PBE level. Clearly, the new \textit{znopt} repulsive potential managed to solve the problem with the too stable NaCl-type polymorph. The energy-volume scans (calculated with PBE) for the wurtzite and NaCl-type polymorphs formed the \textit{training set} of the parameterization, i.e., the repulsive potential was changed until good fits between the SCC-DFTB and PBE results were obtained for these two polymorphs. It turned out, that including both of these polymorphs (with different coordination environments) in the training set was crucial for guaranteeing that the correct stability order of the polymorphs was obtained (in contrast to, for example, the \textit{znorg-0-1} parameterization by Moreira et al. [45], where only a single polymorph was included in the training set).

We then verified that the \textit{znopt} parameter set gives reasonable results (relative stabilities and bulk moduli) for other “potential” polymorphs of ZnO: the CsCl-type, graphitic-like, zincblende, body-centered tetragonal (BCT), and cubane polymorphs.
In fact, we found that the \textit{znopt} parameter set outperformed the \textit{znorg-0-1} parameter set for several different types of systems. For example, the ZnO surface energies, surface atom relaxation, and nanowire formation energies were improved. In addition, we found that the adsorption energies for water molecules and water monolayers on ZnO(10\bar{1}0) were greatly improved. We also saw an improvement for the H$_2$O/ZnO(1\bar{1}20) binding energies, but on this surface, there were still some inconsistencies compared to DFT calculations concerning the most stable configuration. We suggested that in order to solve this inconsistency, the electronic parameters for H, O, and Zn, might need to be modified.

5.2 VII: Large-scale SCC-DFTB calculations of reconstructed polar ZnO surfaces

| Purpose: | To evaluate the SCC-DFTB method for calculations of polar surface reconstructions by comparison to experiments from the literature, and to identify which factors govern the formation of stable surface reconstructions. |
| Methods: | PBE, SCC-DFTB. |
| Calculated properties: | Cleavage energies. |
| The abridged version of the results: | Surface vacancies and triangular pits stabilize the ZnO(0001)-Zn surface, while a hexagonal defect pattern with some atoms shifted far from their bulk-terminated positions stabilizes the ZnO(000\bar{1})-O surface. |

The polar Zn-terminated ZnO(0001) and O-terminated ZnO(000\bar{1}) surfaces form different types of \textit{reconstructions} in ultra-high vacuum. Because ZnO is a largely ionic material, the polar surfaces are not stable unless some sort of reconstruction occurs.

The Zn-terminated (0001) surface morphology is, as determined by STM and AFM measurements, characterized by a large number of \textit{triangular pits} of various sizes [46]. Other types of reconstructions, such as aligned rows of Zn vacancies (\textit{stripes}) have also been observed [47].

At the O-terminated (000\bar{1}) surface, hexagonal reconstructions with some surface atoms shifted from the normal wurtzite stacking sequence, have been shown to form [48].

In \textbf{Paper VII} we modeled many different types of reconstructions, such as surface vacancies, stripes, and triangular and hexagonal pits, at both the Zn-terminated and O-terminated surfaces using the SCC-DFTB method with the \textit{znopt} parameter set from \textbf{Paper VI}.  

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We found that the *excess surface vacancy concentration*, $\theta_{\text{vac}}$, was a useful descriptor to characterize the surface reconstructions. For the Zn-terminated (0001) surface, it corresponds to the number of “more” Zn atoms than O atoms (normalized per number of surface unit cells) that are removed from the surface in the creation of the reconstruction. An equivalent way of phrasing it is that it corresponds to the *excess O* at the surface, i.e. how many “more” O atoms than Zn atoms remain (normalized per the number of surface unit cells).

More succinctly:

$$
\theta^{(0001)}_{\text{vac}} = \frac{N^{\text{surface region}}_{\text{missing Zn}} - N^{\text{surface region}}_{\text{missing O}}}{N^{\text{ideal surface}}_{\text{surface sites}}} = \frac{N^{\text{surface region}}_{\text{O}} - N^{\text{surface region}}_{\text{Zn}}}{N^{\text{ideal surface}}_{\text{surface sites}}} 
$$

(5.1)

where the “surface region” extends as far below the surface as the reconstruction reaches. For the O-terminated (000 1) surface, the roles of the Zn and O atoms are interchanged in the above equation.

If the Zn and O atoms are assumed to be completely ionic with charges +2 and -2, then if $\theta_{\text{vac}} = 0.25$ at both surfaces, the excess charge at each of the surfaces would (approximately) vanish. Since the excess charges are what gives rise to the “polar instability”, this ionic model predicts that reconstructions with $\theta_{\text{vac}}$ near 0.25 should be the most stable.

Indeed, we found through our SCC-DFTB calculations that reconstructions with $0.22 \leq \theta_{\text{vac}} \leq 0.25$ were particularly stable, although stability also depended on the actual structures of the reconstructions.

The stability of the reconstructions was characterized through the *cleavage energy*, $E_{\text{cleav}}$:

$$
E_{\text{cleav}} = \frac{E^{\text{slab}} - n \times E^{\text{bulk}}}{A}
$$

(5.2)

where $n$ is the number of ZnO formula units, $E^{\text{bulk}}$ is energy per formula unit in bulk ZnO, and $A$ is the surface area at one side of the slab. In our calculations, we simultaneously modeled reconstructions at the Zn-terminated and O-terminated surfaces (on different sides of the slab) with the same $\theta_{\text{vac}}$. Thus, although the individual surface reconstructions did not retain the Zn$_1$O$_1$ stoichiometry, the overall slab did.

We explored many different types of reconstructions at the two surfaces, e.g. *stacked triangular pits* as depicted in Figure 5.2a, and *Lauritsen-defects* as depicted in Figure 5.2b. The latter kind of defect has been shown to occur in experiment [48] at the O-terminated (000 1) surface, and consists of hexagonal pits and hexagonal islands with alternating wurtzite and zincblende stacking.

Our results are summarized in Figure 5.3, where the cleavage energies for different combinations of defects at the Zn-terminated and O-terminated surfaces are given as a function of the excess surface vacancy concentration $\theta_{\text{vac}}$. 

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Figure 5.2. Examples of reconstructions at polar ZnO surfaces. (a) A triangular pit with side length 2 inside a triangular pit with side length 5 next to another triangular pit with side length 2 at the (0001) surface in a $6 \times 6$ supercell ($\theta_{\text{vac}} = 0.25$). (b) A Lauritsen-defect at the (000$\bar{1}$) surface in a $5 \times 5$ supercell, with hexagonal pits, and hexagonal islands with alternating wurtzite and zincblende stacking ($\theta_{\text{vac}} = 0.16$).

Figure 5.3. Cleavage energies calculated with SCC-DFTB for different combinations of defects at the Zn-terminated and O-terminated polar surfaces as a function of the excess surface vacancy concentration $\theta_{\text{vac}}$. 
We find that at the Zn-terminated surface, surface vacancies and triangular pits of different sizes are particularly stable while Lauritsen-defects are unstable. In contrast, Lauritsen-defects are stable at the O-terminated surface, although other kinds of defects, such as hexagonal and triangular pits, are close in energy. In any case, a condition for a reconstruction to be stable is that the surface stoichiometry, expressed in terms of the excess surface vacancy concentration $\theta_{\text{vac}}$, lies in the range $0.22 \leq \theta_{\text{vac}} \leq 0.25$.

5.3 Scientific impact of our ZnO multi-scale modeling

The goal of our multi-scale modeling endeavor was to explore the properties of more realistic systems than what is possible at the DFT level, with respect to the number of atoms, the timescales involved, temperature and pressure. The SCC-DFTB method is certainly fast enough to allow for this, yet one could say that the calculations presented in the preceding sections (5.1–5.2) did not live up to this ambitious goal, as there were, for example, no dynamical simulations performed.

However, in this author’s opinion, it is, before one applies a new method (like the znopt SCC-DFTB parameters) to complicated systems (like the dynamical simulations of ZnO nanoparticles in e.g. aqueous environment), important to validate the method for much simpler problems to which one already “knows” the answer (like the validations performed in Paper VI and to some extent in Paper VII). This validation serves the purpose of highlighting any flaws or shortcomings with the new method. Only if the shortcomings of the method are known, can intelligent scientific questions be posed that can be answered by the use of the method.

Thus, we conclude that the SCC-DFTB parameterization and validation are only the beginning — time does not end now, and future work will use the new parameters, or perhaps other better suited parameters, to model these kinds of realistic systems with nanoparticles, interfaces, defects and chemical reactions. Hopefully, that will result in new physical insights into the behavior of ZnO, in any of its many applications.
Cu/ZnO/Al₂O₃ catalysts are used industrially for methanol synthesis and the water gas shift reaction. In this thesis, theoretical models and calculations were used to characterize the adsorbate–substrate interplay for Cu and H₂O on ZnO surfaces. The reliability of the computational methods were critically evaluated.

Computational chemistry is a rapidly growing field of research, with great potential for the future. The structural and mechanistic detail available is unprecedented and constitutes an invaluable complement to experiments. At the same time, there are many pitfalls for the unwary practitioner, not least when it comes to modeling ZnO. Some such pitfalls have been highlighted and discussed in this thesis, the two most important being the band-gap problem and the issue pertaining to band-filling. With “normal” density functional theory (DFT), the band gap of ZnO is heavily underestimated (the band-gap problem), and electrons can too easily move from adsorbates into the conduction band. When electrons enter the conduction band, band-filling occurs: the electrons span an energy range, because of the disperse nature of the conduction band. Thus, the adsorption energy depends on the adsorbate coverage, since the extent of the band-filling depends on the size of the supercell used in the calculation. The band-gap problem can be overcome by using a hybrid density functional theory, and if one aims to model an isolated adsorbate on the surface, the band-filling problem can be mitigated by using the band-filling correction.

After taking care to avoid the two above problems, the interaction between Cu and ZnO was modeled and the results were intriguing: the calculations suggested that electronic charge can be transferred from Cu to ZnO, from ZnO to Cu, or not at all, depending on the Cu size and shape, the ZnO surface facet, the presence or absence of adsorbed water, and the presence or absence of defects in the ZnO.

The computationally efficient SCC-DFTB electronic structure method was, via a multi-scale modeling approach, parameterized and then used to model and characterize the various kinds of surface reconstructions that occur at the polar ZnO surfaces (for example, the triangular surface pits and islands that occur at the Zn-terminated ZnO(0001) surface). The SCC-DFTB method is efficient enough to allow for future large-scale simulations of realistic ZnO particles.

This thesis only begins to explore the rich chemistry and physics that occur at ZnO surfaces when they come into contact with Cu or H₂O, which leaves much more to be discovered. For example, some of the open questions, that still remain, are: What, if any, effect do other molecules that adsorb...
on the Cu/ZnO catalyst (e.g. CO, CO$_2$, H$_2$, CH$_3$OH) have on the Cu–ZnO charge transfer? Will experiments confirm that small Cu clusters adsorbed on ZnO(10\,\overline{1}0) really show an even-odd alternation in stability and charge transfer? What happens for adsorbed Cu clusters with more than nine atoms? How do Cu nanoparticles interact with ZnO nanoparticles? What are the reaction mechanisms for the methanol synthesis and water gas shift reactions? What is the origin of the Cu–ZnO synergy for methanol synthesis? Do vacancies, dopants, or surface steps increase the catalytic activity? Are the computationally very demanding hybrid functionals really necessary to model the catalyst, or could less demanding methods, like SCC-DFTB, be used in their stead?

Although all of these open questions remain, substantial progress was still made in a few key areas: (some of) the factors governing Cu–ZnO charge transfer were elucidated, the SCC-DFTB method was parameterized and used to explain the appearance of triangular pits at a ZnO surface, and the band-filling correction was for the first time applied to model an isolated adsorbate on a surface in a supercell calculation.
7. Acknowledgments

I cannot take all the credit for the research conducted as part of this PhD project and presented in this thesis. Prof. Kersti Hermansson’s visionary leadership, extensive scientific know-how, and remarkable knack for literary criticism were all key ingredients to making the research stronger, and many of the papers would not have materialized if not for the ambitious and creative minds of Dr. Daniel Spångberg and Dr. Peter Broqvist.

Some of the papers have other co-authors, who all made useful contributions. I am particularly happy to have collaborated with Dr. Stefan E. Huber from Innsbruck University on the SCC-DFTB project, and Dr. Igor Beinik and Dr. Jeppe Lauritsen from Aarhus University on the Cu/ZnO(0001) project.

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8. Summary in Swedish: Kemi och fysik för Cu och H₂O på ZnO-ytor

Zinkoxid (ZnO) är ett material med många olika tillämpningsområden, där det mest framstående är som tillsats i gummit i bildäck. Det används också i hudkrämer, varistorer, gassensorer, och katalysatorer [1]. Den här avhandlingen fokuserar på den senare tillämpningen.

Katalysatorer påskyndar kemiska reaktioner utan att själva förbrukas. En typ av katalysator som är bekant för många är trevägskatalysatoren i bilar, vilken underlättar reduktionen av giftiga NOx-gaser till kvävgas, och oxidationen av giftiga kolväten och kolmonoxid (CO) till koldioxid (CO₂).

Katalysatorer används också inom industrin för tillverkning av nya kemikalier, till exempel metanol (CH₃OH), som används flitigt som baskemikalie i färg- och plastindustrin, och som även fungerar som bränsle i bränsleceller. Metanol framställs från syntesgas, en blandning av CO, CO₂, och vätgas (H₂), där koldioxiden och vätgasen reagerar över en katalysator bestående av koppar (Cu), zinkoxid, och aluminiumoxid (Al₂O₃):

\[
\text{CO}_2 + 3\text{H}_2 \xrightarrow{\text{Cu/ZnO/Al}_2\text{O}_3} \text{CH}_3\text{OH} + \text{H}_2\text{O} \quad (8.1)
\]

Det bildade vattnet (H₂O) i reaktionen ovan reagerar sedan vidare med kolmonoxidien i syntesgasen, över samma Cu/ZnO/Al₂O₃-katalysator i den så kallade vattengasskiftreaktionen:

\[
\text{CO} + \text{H}_2\text{O} \xrightarrow{\text{Cu/ZnO/Al}_2\text{O}_3} \text{CO}_2 + \text{H}_2 \quad (8.2)
\]

Produkterna CO₂ och H₂ reagerar sedan vidare och bildar mer metanol enligt ekvation (8.1) [4]. Vattengasskiftreaktionen (8.2) är också industriellt viktig i sig själv, då den används för att renna välgas från CO, något som är helt nödvändigt innan välgasen används i framställningen av ammoniak (NH₃). Ammoniak är en av världens mest producerade kemikalier, och används i sin tur bland annat för att framställa salpetersyra och konstgödsel.

Både metanol syndes och vattengasskiftreaktionen sker alltså över en katalysator bestående av koppar, zinkoxid, och aluminiumoxid. Trots att denna typ av katalysator används industriellt i många årtionden är det fortfarande oklart vilka roller de olika komponenterna i katalysatorn spelar. Den här avhandlingen behandlar hur koppar och zinkoxid växelverkar på atomär och subatomär nivå, samt vilket inflytande vatten har över denna växelverkan. Syftet är att få en djupare insikt i hur katalysatorn fungerar för de båda reaktionerna. I
förlängningen kan denna kunskap komma att underlätta utvecklingen av effektivare katalysatorer.

För att karakterisera interaktionen mellan koppar och zinkoxid har teoretiska modeller, simuleringar, och beräkningar använts. Beräkningskemi är ett forskningsämne som utvecklas snabbt, och som ofta används som komplement till experiment för att få en mer detaljerad bild av ett kemiskt ämne eller kemiskt förföll. Med kvantkemiska beräkningsmetoder (vilka tillämpats i den här avhandlingen) är det möjligt att följa varje enskild elektron i varje enskild atom eller molekyl. En sådan metod, täthetsfunktionalteorin (eng. density functional theory, DFT), sticker ut som den i särklass mest populära, då metoden i många fall lyckas väl med att beskriva bindningslängder, vibrationsfrekvenser, reaktionsenergier och -barriärer, och mekaniska och magnetiska egenskaper.

Även om DFT ofta fungerar bra, kräver beräkningarna ansenliga datorresurser, och det är därför inte praktiskt möjligt att tillämpa metoden på lite större och mer komplicerade, eller med andra ord realistiska, system. För att tackla den typ av frågeställningar som kräver modellering av stora system måste därför andra metoder användas. En uppstikkarmetod i det sammanhangen är täthetsfunktionalbaserade linjärkombinationer av atomcentrerade orbitaler med kort räckvidd i kombination med självkonsistenta laddningar (eng. density functional based tight binding with self-consistent charges, SCC-DFTB), som baseras på DFT men som innehåller många förenklande antaganden, vilket gör metoden betydligt snabbare än DFT. SCC-DFTB-metoden innehåller ett antal parametrar, och en del av den här avhandlingen handlade om att ta fram sådana parametrar så att ZnO kunde modelleras på ett riktigt sätt.


I artikel I visade vi hur kopparatomer adsorberade på ZnO(1010), vilket är den mest stabila ZnO-ytan, kontinuerligt ändrar laddning när de rör sig över ytan. Detta påverkar mekanismen för bildandet av en kopparlager (Cu2) på ytan på så sätt att när två kopparatomer närmar sig varandra bör endast en av dem, vid varje givet tillfälle, vara laddad.

I artikel II modellerade vi större kopparpartiklar med upp till nio atomer adsorberade på ZnO(1010), och visade hur en kopparpartikels laddning och stabilitet i stor utsträckning beror på om partikeln har ett udda eller ett jämnt antal atomer.
I artikel III lade vi till vattenmolekyler till några av de mindre kopparpartiklarna på ZnO(10\overline{1}0), och visade hur adsorptionen av vatten kunde medföra elektronöverföring från Cu till ZnO för både kopparatomen och koppartrimener. Ytterligare ett intressant fenomen kunde påvisas, nämligen hur en vattenmolekyl kunde dissociera koppartrimener till en atom och en dimer. 

Artikel IV tillkom som ett resultat av ett samarbete med forskare som experimentellt hade deponerat koppar på den polära ZnO(0001)-ytan. De fann i sina mätningar att koppar vid höga temperaturer vätte ZnO-ytan, och vi kunde med hjälp av beräkningar förklara detta genom att den deponerade kopparen blev negativt laddad och attraherade positivt laddade defekter under ytan. Detta ledde i sin tur till att Cu/ZnO-interaktionen blev starkare — tillräckligt mycket starkare för att Cu skulle väta ZnO-ytan. 

I artikel V beskrev vi bandfyllnadseffekten som uppstår i beräkningarna när Cu ger ifrån sig elektroner till ZnO. Elektronerna hamnar då i ZnO:s ledningsband, vilket indirekt leder till att stabiliteten hos den adsorberade kopparen beror på yttäckningsgraden.Om man vill bestämma stabiliteten för adsorberad Cu vid låg yttäckningsgrad, krävs att man vidtar speciella åtgärder, t.ex. den så kallade bandfyllnadskorrektionen (eng. band-filling correction). Vi beskrev för första gången hur man kan tillämpa korrektionen för specier adsorberade på ytor. Tidigare hade bandfyllnadskorrektionen bara använts för defekter i bulkmaterial. 

I artikel VI utvecklade vi SCC-DFTB-parametrar, för att göra det möjligt att modellera ZnO med denna metod. Genom att först utföra beräkningar med DFT för ZnO i olika kristallstrukturer, fick vi ett ”facit” att jämföra våra SCC-DFTB-beräkningar mot. Vi varierade alltså parametrarna i SCC-DFTB-metoden tills vi fick liknande resultat som med DFT, och fann att de slutgiltiga parametrarna inte bara tillfredsställande kunde beskriva ZnO i olika kristallstrukturer, utan även adsorptionen av enskilda vattenmolekyler och vattenmonolager på ZnO-ytor. 

I artikel VII, slutligen, använde vi SCC-DFTB-metoden för att beskriva stora ytrekonstruktioner av de polära ZnO(0001)- och ZnO(000\overline{1})-ytorna. Vi fann att SCC-DFTB-metoden gav liknande resultat som tidigare DFT-studier, och även i stora drag kunde reproduceras de typer av rekonstruktioner som har setts experimentellt. Även om de resultat som presenteras i den här avhandlingen kanske inte ger konkreta fingervisningar om koppar respektive zinkoxids roller i katalysatorn för metanolsyntes och vattendesskiftreaktionen, så har betydande framsteg ändå gjorts på ett antal områden: vi har visat hur bandfyllnadskorrektionen kan användas för att beräkna adsorptionsenergier när laddningsöverföring sker mellan adsorbat och substrat, vi har visat hur kopparss laddning beror på storleken och formen hos Cu, ZnO-ytan, och närvaron eller frånvaron av vatten, och vi har utvecklat en metod snabbare än traditionell tätheitsfunktionalteori för att kunna modellera stora och realistiska ZnO-system.
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