Computational studies of hybrid interface formation



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Title image: APTES coadsorption by Jan M. Knaup

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Abstract

Hybrid interfaces are interfaces between different classes of materials; among these, the hybrid interface between native metal oxides and polymers is of great interest for the technologies of adhesive joining, polymer coatings and metal/polymer hybrid materials. The properties of these metal oxide/polymer interfaces are performance critical. A deep understanding of the interface properties and the chemical processes from which they emerge is prerequisite for technological advancement.

As experimental observation of processes at buried interfaces at atomic resolution is highly challenging, computer simulations are a valuable tool to understand them. However, preexisting computational methods that are able to describe chemical reactions at solid surfaces with the necessary accuracy, can barely handle the system sizes necessary for a realistic modeling of the interface. Techniques to couple atomically resolved simulation methods of different accuracy in order to limit the computational cost of simulations are widely employed in protein and polymer chemistry. In these approaches, quantum mechanical electronic structure (QM) methods are only applied to those parts of the system, where their accuracy is needed, while treating the rest of the system with less complicated molecular-mechanical (MM) methods. Due to the higher density of bonds, these coupling schemes cannot be directly applied to solids, especially polar ones. Using the density-functional based tight-binding method as the quantum mechanical part, the existing QM/MM coupling schemes have been adapted to polar solids. Suitable methods to treat the QM/MM boundary in directly coupled simulations have been transferred from biophysical applications. New methods to treat cluster charge artifacts, resulting from selecting a QM zone in a polar material, were developed and tested on different classes of solids. These methods are applicable to various oxide surfaces, including metal oxides. The QM/MM approach allows considerable savings in computer time and thus enables simulations of more complex systems, e.g. taking into account effects of the environment.

Aluminum is gaining importance in automotive industry and is the main structural material in aerospace applications. Under ambient conditions, aluminum is covered by a native oxide layer. For corrosion protection as well as for the construction of lighter parts, combining metal and fiber reinforced polymers, the adhesion of polymers on this native oxide layer is extremely important. The formation of the hybrid interface between native alumina and a model epoxide adhesive system was simulated. Fully quantum mechanical simulations were used to calculate the thermodynamics and barrier energies of the chemisorption of the model adhesive's components. The results are in good agreement with experimental observations and offer a good explanation for the effect of silane adhesion promoters: their chemisorption is favorable at more surface sites than that of the other components, leading to an increase in the density of covalent bonds across the interface. The new possibility of QM/MM simulations of this hybrid interface allows to include the effect of the environment on single adsorption reactions. Initial results indicate that water at the surface, which is present natively and formed during the condensation of adhesive components, has a crucial influence on the interface formation.

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Kurzzusammenfassung

Hybridgrenzflächen sind Grenzflächen zwischen Materialien verschiedener Klassen. Unter diesen ist die Hybridgrenzfläche zwischen natürlichen Metalloxyden und Polymeren von großem Interesse für die Technologien von Klebeverbindungen, Polymerbeschichtungen und Metall/Polymer Hybridmaterialien. Die Eigenschaften dieser Metall/Polymer Grenzflächen ist entscheidend für die Leistung entsprechender Bauteile. Ein tiefes Verständnis der Grenzflächeneigenschaften sowie der chemischen Prozesse aus denen diese hervorgehen, ist die Voraussetzung für technologischen Fortschritt auf diesem Gebiet.

Da die experimentelle Beobachtung von Prozessen an verdeckten Grenzflächen mit atomarer Auflösung sehr schwierig ist, stellen Computersimulationen ein wertvolles Mittel für deren Verständnis dar. Allerdings sind existierende Simulationsmethoden, die chemische Reaktionen auf Festkörperoberflächen mit hinreichender Genauigkeit beschreiben können, kaum in der Lage, für die realistische Modellierung dieser Grenzflächen hinreichend großer Systeme zu beschreiben. Techniken, atomar aufgelöste Simulationsmethoden verschiedener Genauigkeiten direkt miteinander zu koppeln sind in den Bereichen der Protein- und Polymerchemie weit verbreitet. Bei diesen Ansätzen werden quantenmechanische Elektronenstrukturmethoden (QM) nur auf diejenigen Teile des Systems angewandt, bei denen diese Genauigkeit erforderlich ist, während der Rest des Systems mit einfacheren molekularmechanischen (MM) Methoden simuliert wird. Wegen der höheren Dichte an Bindungen, können diese Kopplungsschemata nicht direkt auf Festkörpersysteme angewandt werden, insbesondere nicht auf Polare Festkörper. Unter Verwendung von dichtefunktionalbasiertem Tight-Binding als QM Methode, wurden die existierenden QM/MM Kopplungsschemata, von biophysikalischen Anwendungen kommend, auf Festkörpersysteme transferiert. Geeignete Methoden zur Behandlung der QM/MM Grenze wurden transferiert. Gleichzeitig wurden neue, geeignete Methoden zur Behandlung von Ladungsartefakten, die durch die Auswahl einer QM Zone aus einem polaren Festkörper entstehen, entwickelt und an verschiedenen Klassen von Festkörpern getestet. Diese Methoden können auf verschiedene Oxydoberflächen, einschließlich Metalloxyden, angewandt werden. Dieser QM/MM Ansatz erlaubt erhebliche Einsparungen an Rechenzeit, wodurch die Betrachtung komplizierter Systeme, z.B. unter Berücksichtigung von Umgebungseinflüssen, ermöglicht wird.

Aluminium gewinnt an Bedeutung für die Automobilindustrie und ist nach wie vor das vorherrschende Strukturmatieral in der Luft- und Raumfahrt. Unter normalen Umgebungsbedingungen, ist Aluminium stets mit einer natürlichen Oxydschicht bedeckt. Zum Korrosionsschutz wie auch für die Herstellung leichterer Bauelemente, die Metall- und faserverstärkte Kunststoffteile vereinen, ist die Haftung von Polymeren auf dieser natürlichen Oxydschicht von größter Bedeutung. Die Ausbildung der Hybridgrenzfläche zwischen ist dafür von besonderer Bedeutung. Sie wurde für die Grenzfläche zwischen nativem Aluminiumoxyd und einem Modellsystem für Epoxydklebstoffe simuliert. Mittels voll quantenmechanischer Simulationen wurden die Thermodynamik und die Energiebarrieren der Chemisorptionsreaktionen der einzelnen Klebstoffkomponenten berechnet. Die Ergebnisse sind in guter Übereinstimmung mit experimentellen Beobachtungen und bieten eine gute Erklärung für den Wirkmechanismus von Silan-Haftvermittlern: deren Chemisorption ist an mehr Stellen der Oberfläche energetisch günstig, als die anderer Komponenten. Auf diese Weise führt der Haftvermittler zu einer Erhöhung der Dichte an kovalenten Bindungen über die Substrat/Polymer Grenzfläche. Die neue Möglichkeit, QM/MM Simulationen dieser Hybridgrenzfläche durchzuführen, erlaubt die Berücksichtigung von Umgebungseinflüssen auf die einzelnen Adsorptionsreaktionen. Erste Ergebnisse zeigen, dass Wasser an der Oberfläche, welches sowohl von Natur aus dort vorhanden ist, als auch im Laufe der Kondensation von Klebstoffkomponenten dort gebildet wird, entscheidenden Einfluss auf die Grenzflächenausbildung ausübt.

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Chapter 1

Introduction

Two of the most grave challenges faced by humankind today are the global warming and the expiration of fossil fuel supplies. Both are closely related, since a large part of the greenhouse effect is caused by CO_2 emissions from the burning of these fossil fuels [1]. As fossil fuels are currently the most important source of energy for human societies, this will have deep ramifications on the future lifestyle of all humankind, if no solutions are found. One necessary part of any solution will be energy conservation measures: in the short term to slow down CO_2 emissions, in the middle run to facilitate the transition to sustainable energy sources and on the long term to allow the worldwide standard of living to increase sustainably to the level of industrialized countries. At the same time, the rising prices of fossil fuels, especially oil, create a strong economic incentive to reduce consumption of these commodities.

One way to conserve energy is to reduce the use of energy-consuming technologies (e.g. all kinds of electronics). This is in strong conflict with the natural human desire to improve the individual standard of living and the humanitarian aim to reduce poverty. Therefore, fossil fuel conservation by abstinence from technology can only be applied to a limited extent without raising severe social problems. Another possibility is to increase the energy efficiency of current technologies. In this work, I will concentrate on one aspect: the development of more capable adhesive joining technologies, which, among others, enable lighter and thus more energy efficient transportation.

Adhesive joints work from the principle of inserting a layer of a third material between the surfaces of the parts which are to be joined. This intermediate layer must at the same time form a strong bond to the surfaces of both joined parts and have sufficient cohesion to be able to transmit the mechanical forces between them. Additionally, the intermediate layer fills the roughness of the joined part's surfaces, thus filling the gap between the parts and sealing the joint against gases or liquids. Very closely related to adhesives are coatings applied in liquid form, i.e. paints. In principle, a paint is nothing more than a mixture of an adhesive and some type of dye or pigment. In both cases, the adhesion between the polymer phase and the substrate is of paramount importance. In my work, I concentrate on the adhesion at the polymer/substrate interface.

In most cases, the adhesive is applied to the surfaces in liquid form and then cured to form a solid layer. Curing can be achieved in several ways: e.g. by evaporation of a solvent, by means of a phase change upon cooling, or by polymerization of an adhesive mixture. For automotive and aerospace applications, the latter class of adhesives are of great interest, because of their high mechanical and chemical endurance. Therefore I will concentrate on this type of adhesives, especially on a model epoxide resin adhesive. Its chief characteristics are being a thermoset type polymers, i.e. the polymerization is thermally activated, and the fact that a strongly cross-linked network is formed from relatively low molecular weight precursors. Although automotive industry has moved away from the formerly widely employed epoxy paints, for reasons of work safety and expensive waste disposal, these paints still play a very important role in aerospace applications. Results obtained on the interface properties between a substrate surface and an epoxy polymer can be equally applied to joining and coating technologies. I focus my interest on the interface between the natively oxidized aluminum surface and a model epoxide adhesive polymer, especially on the chemical processes from which the properties of this interface arise. This choice of materials is governed by the tradition of using aluminum as a lightweight structural material in aerospace applications and the trend in automotive industry to (partly) replace steel by aluminum to conserve weight. A good understanding of the fundamental mechanisms is critical for being able to improve any technology in a systematic and efficient manner.

When aiming to understand these underlying mechanisms of a chemical process, it is necessary to analyze the behavior of the atoms involved. In many cases experimental observation is very difficult. The direct observation of individual atoms during a reaction is only possible with very large effort and only for a few specific reactions at solid surfaces in (nearly) vacuum. Here, the theoretical modeling of the reaction of interest in a bottom-up approach, i.e. simulating the behavior of the individual atoms from first principles, can give extremely valuable insights. However, since modeling reactions at hybrid interfaces requires the simulation of comparatively large numbers of atoms¹, usual *ab initio* methods for atomistic simulation are too computationally involved. At the same time, simpler methods lack transferability, the ability to describe bond formation or breaking (or both) and they are less accurate. Methods that model parts of an examined system at different resolutions, e.g. taking into account the electronic structure in one part, while using empirical interatomic potentials in another, depending on the accuracy required for each part, have been successfully applied in biophysics and polymer science. However, these approaches are cannot be readily transferred to solids.

In this work, I present my results on porting the approaches to couple the approximate density functional theory method DFTB to classical force-fields from biophysical applications to solid surfaces. I apply both DFTB and DFTB/MM to examine the formation of the interface between a model epoxide adhesive and the native oxide surface on aluminum. I shall demonstrate that DFTB coupled to classical force fields is capable of providing deep insight into the formation processes of hybrid interfaces.

 $^{^{1}}$ Compared to what is generally referred to as "quantum chemistry", where mostly systems of <100 atoms are regarded.

Chapter 2

Quantum Mechanical Treatment of Molecules and Solids

The description of the electronic properties of solids and molecules requires a quantum mechanical treatment. This section shall describe the quantum mechanical methods employed in this work.

My aim is to simulate solid surfaces and interfaces at atomic resolution in a computationally efficient yet accurate manner, in order to model chemical reactions at hybrid interfaces. I will employ a coupling scheme between density-functional based tight-binding (DFTB) and molecular mechanics (MM) force-fields, concentrating on the quantum mechanics side of the coupling. As a foundation for describing the DFTB method and DFTB/MM coupling in solids, I shall first give an introduction into the quantum mechanical description of solids in general and into density functional theory, to which DFTB is an approximation.

In this chapter, I shall give a concise description of the theoretical foundations of my research presented in this thesis. For an in-depth introduction, the reader should consider one of the excellent textbooks available on this matter, e.g. Refs [2-5].

2.1 Notation and units

Since in this work I treat both molecules and solids, I shall use the term *system* unless a statement explicitly refers to either an infinite crystal, or a finite molecule or section of a crystal.

The number of electrons in a system is N and indices i run over the electrons. Likewise, M is the number of atoms, indexed by j. Indices k, l refer to electrons or nuclei, depending on whether they are used in conjunction with i or j.

Vectors \mathbf{r} without an index contain the spacial coordinates of the whole electronic system, while \mathbf{r}_i give the coordinates of a single (quasi-) particle. In contrast, vectors \vec{r} are three-dimensional vectors in real space. Similarly vectors \mathbf{R} and \mathbf{R}_i refer to the nuclei.

 $\Phi(\mathbf{r}, \mathbf{R}, t)$ and $\Psi(\mathbf{r}, t)$ are the wave functions of the whole system and the electronic subsystem, respectively. If present, α and β refer to the two spin components of the electronic system. (Note that the independent variable \vec{r} is omitted by text-book convention, except for some special occasions.) If the time variable t is absent, wave functions give the stationary ground-state. Similarly, $n(\vec{r})$ gives the total electronic charge density of the system, while $n_i(\vec{r})$ is the density contribution of a single quasi-particle.

In the following, equations will be given in atomic units [6, 7], which are defined by assigning unity values to the electron rest mass m, elementary charge e, $\frac{1}{4\pi\epsilon_0}$ and reduced Planck constant \hbar . From this definition

follows, that the Bohr radius $r_B = \frac{\hbar^2}{me^2} \approx 0.5291 \text{ Å}$ and Hartree energy $E_H = \frac{me^4}{\hbar^2} \approx 27.2114 \text{ eV}$ assume unity values as well. Since this makes most constant prefactors vanish from the equations, these units are very often applied in quantum mechanics. Additionally, atomic units also reduce numerical complexity. The units of length and energy are also referred to as Bohr and Hartree. Using them, new dimensionless variables **r** and *E* are defined:

$$\mathbf{r} = \frac{\tilde{\mathbf{r}}}{r_B}, \qquad \qquad E = \frac{\tilde{E}}{E_H}.$$
 (2.1)

Here, \tilde{r} and \tilde{E} denote the corresponding variables with dimension. Using atomic units, e.g. the Schrödinger equation of a single electron in the potential of a nucleus with the charge Z, changes from

$$\left[-\frac{\hbar^2}{2m_e}\tilde{\Delta} - \frac{Ze^2}{4\pi\varepsilon_0|\tilde{\mathbf{r}} - \tilde{\mathbf{R}}|}\right]\Psi_i(\tilde{\mathbf{r}}) = \tilde{E}_i\Psi_i(\tilde{\mathbf{r}})$$

into the dimensionless form

$$\left[-\frac{1}{2}\Delta - \frac{Z}{|\mathbf{r} - \mathbf{R}|}\right]\Psi_i(\mathbf{r}) = E_i\Psi_i(\mathbf{r}).$$

2.2 Condensed matter as a many body problem

The theory behind the description of molecules and solids is in many aspects the same. In practically all aspects, the description of the solid state contains all the necessary elements for the modeling of molecules plus some additional features introduced by the symmetries of the solid state, covered in section 2.4.

In order to examine different geometrical or chemical configurations of a solid or molecule, one needs to know its total energy depending on the geometry as well as the derivatives of the total energy in the systems coordinates.

The quantum mechanical state ground state of a system of N electrons and M nuclei is described by the time independent Schrödinger equation

$$\hat{H}\Phi = \mathcal{E}\Phi \tag{2.2}$$

with the (non-relativistic) Hamiltonian

$$\hat{H} = \underbrace{-\sum_{j=1}^{M} \frac{1}{2M_{j}} \Delta_{\mathbf{R}_{j}}}_{T_{N}} + \underbrace{\frac{1}{2} \sum_{j \neq j'}^{M} \frac{Z_{j} Z_{j'}}{|\mathbf{R}_{j} - \mathbf{R}_{j'}|}_{C_{N}}}_{C_{N}} \underbrace{-\frac{1}{2} \sum_{l=1}^{N} \Delta_{\mathbf{r}_{l}}}_{T_{el}} + \underbrace{\frac{1}{2} \sum_{l \neq l'}^{N} \frac{1}{|\mathbf{r}_{l} - \mathbf{r}_{l'}|}_{C_{el}}}_{C_{el}} - \underbrace{\sum_{j,l}^{M, N} \frac{Z_{j}}{|\mathbf{R}_{j} - \mathbf{r}_{l}|}}_{C_{el,N}}.$$
 (2.3)

The corresponding wave function Φ describes the *M* nuclei and *N* electrons. Since no general analytic solution to this problem is known, approximations must be made, which will be described below.

2.3 The Born-Oppenheimer approximation.

The first approximation generally made in the simulation of solids and molecules is the Born-Oppenheimer approximation, which is based on the mass ratio of nuclei versus electrons of about 10^3 [8]. As the forces acting on nuclei and electrons can be regarded as within the same order, the momenta of both will also be similar. Comparing T_N and T_{el} in equation 2.3 shows that the nuclear kinetic energy will then be only about 10^{-3} of kinetic energy of the electrons. This allows to separate the nuclear and electronic wave functions according to the adiabatic theorem[9]. Therefore, the motion of electrons and atoms may be treated separately, with the atomic coordinates at a given time as a (constant) input parameter to the electronic equation and the time average of the electronic configuration as a constant in the atomic

2.4. MODELING THE SOLID STATE

equations of motion. This separation is exact if the potential acting on the nuclei is strictly harmonic in the vicinity of its local minima¹.

In the context of chemical reactions, the system of nuclei is usually treated classically, i.e. by solving the Newton's equations of motion for the nuclei. The electron problem remains to be treated quantum mechanically with the electron Schrödinger equation

$$\hat{H}_{\rm el}\left(\mathbf{R}_{j}\right)\Psi = \mathcal{E}_{\rm el}\Psi\tag{2.4}$$

and its Hamiltonian

$$\hat{H}_{\rm el} = -\sum_{i=1}^{N} \Delta_{r_i} + \frac{1}{2} \sum_{i \neq i'}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_{i'}|} - \sum_{j,i}^{M,N} \frac{Z_j}{|\mathbf{R}_j - \mathbf{r}_i|}.$$
(2.5)

Here Ψ is the electronic wave function. In the following, \hat{H} will be used as a shorthand to denote the *electronic* Hamiltonian, where not specified otherwise. Still, even the electron many-body-wave function cannot be solved analytically. This makes further approximations necessary to be able to solve the problem numerically. Before describing one possible approaches to achieve this in section 2.5, it is necessary to discuss some general concepts for the description of solids and the electronic wave functions.

2.4 Modeling the Solid State

When dealing with the defective solid, one cannot handle every atom of a system of technologically relevant size explicitly. Therefore a model of adequate size is required. In the case of the perfect crystal, the translational symmetry can be utilized, but that is broken by the introduction of a defect. In the following section, starting from the treatment of the perfect crystal, I shall describe possibilities to handle the defective solid.

2.4.1 The perfect crystal

The perfect crystal is by definition invariant under translation by the lattice vectors

$$\mathbf{R}_l = \sum_{i=1}^3 l_i \mathbf{a}_i \tag{2.6}$$

with the primitive unit cell vectors \mathbf{a}_i and arbitrary integers l_i . As a consequence, a reciprocal lattice in momentum space can be constructed with the reciprocal lattice vectors

$$\mathbf{G}_g = \sum_{j=1}^3 g_j \mathbf{b}_j \tag{2.7}$$

with arbitrary integers g_j and the primitive reciprocal lattice vectors \mathbf{b}_j

$$\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi \delta_{ij}.\tag{2.8}$$

The symmetric unit cell of the reciprocal lattice is defined as the set of points closer to one lattice point than to all others and is called the Brillouin zone (BZ), i.e. the Wigner-Seitz cell of the reciprocal lattice.

¹Which, is often not the case, especially for point defects in solids. Still the harmonic approximation must be made, because the full Schrödinger equation is computationally too involved to solve for systems large enough to allow the modeling of the relaxations around such point defects.

Bloch's theorem states that, due to the translational symmetry, the electronic wave functions of the solid (called Bloch-electrons) can be expressed by the Bloch-wave functions

$$\varphi_{nk}(\vec{r}) = u_{nk}(\vec{r})e^{i\mathbf{k}\cdot\vec{r}}.$$
(2.9)

With the wave-vector **k** restricted to the BZ and the function $u_{nk}(\vec{r})$ being periodic on the lattice, the Bloch-wave functions satisfy Bloch's periodicity condition

$$\varphi_{nk}(\vec{r} + \mathbf{R}_l) = \varphi_{nk}(\vec{r}) \cdot e^{(i\mathbf{k}\mathbf{R}_l)}$$
(2.10)

Since the translational invariance along arbitrary lattice vectors implies an infinite crystal, while the real solid is finite (N_i unit cells along the lattice vector a_i ,) the perfect translational symmetry must be ensured by imposing artificial macroscopic periodicity, i.e. applying the cyclic boundary conditions of Born and von Kármán:

$$\varphi_{nk}(\vec{r} + N_i \mathbf{a}_i) = \varphi_{nk}(\vec{r}) \tag{2.11}$$

which makes the number of k-vectors in the BZ equal to $N = N_1 N_2 N_3$ and their density equal to $V/8\pi^3$ with the volume of the solid V.

Due to this construction, an identical set of **k**-dependent equations applies for all unit cells. In principle, these equations should be solved for all k-points in the BZ, since they contain an average over all k. Instead, the so-called *special* **k**-*point theorem* [10] is often applied to reduce the number of equations to be solved. It states, that the average of the function $f(\mathbf{k})$

$$\overline{f} = \frac{1}{V_{\rm BZ}} \int_{V_{\rm BZ}} f(\mathbf{k}) d^3 \mathbf{k}$$
(2.12)

can be approximated by a weighted sum over special k-points

$$\tilde{f} = \sum_{q} \omega_q f(\mathbf{k}_q). \tag{2.13}$$

If f(k) is invariant under translation by the reciprocal lattice vectors G_g and to the symmetry operation $\hat{\alpha}$ of the point group G of the lattice, then the Fourier expansion of f(k) can be split at a term M:

$$f(\mathbf{k}) = f_0 + \sum_{m=1}^{M} f_m A_m(\mathbf{k}) + \sum_{m=M+1}^{\infty} f_m A_m(\mathbf{k})$$
(2.14)

with

$$A_m(\mathbf{k}) = \frac{1}{N_G} \sum_{\hat{\alpha} \in G} e^{ik(\alpha \hat{R_m})}, \qquad (2.15)$$

where N_G is the number of elements in the point group. Since for any m, the BZ-integral of $A_m(\mathbf{k})$ vanishes, \overline{f} equals f_0 . Substituting equation 2.14 into equation 2.13 then yields

$$\tilde{f} = \sum_{q} \omega_{q} f_{0} + \sum_{m=1}^{M} f_{m} A_{m}(\mathbf{k}) + \sum_{m=M+1}^{\infty} f_{m} A_{m}(\mathbf{k}).$$
(2.16)

For sufficiently high M, the Fourier coefficients f_m , m > M become negligible, so that the last term can be neglected. Provided, that the sum of the weighting factors ω_q is unity, the error of the approximation is determined by

$$\tilde{f} - \overline{f} \approx \sum_{m=1}^{M} f_m \sum_{q} \omega_q A_m(\mathbf{k}_q).$$
(2.17)

Therefore, the special k-point set and the corresponding weighting factors should be chosen so that $\sum_{q} \omega_q A_m(\mathbf{k}_q)$ vanishes for m < M. The error of this approximation diminishes almost exponentially with M.

2.4. MODELING THE SOLID STATE

Generally, the procedure proposed by Monkhorst and Pack [11] is used to generate special **k**-point sets with M as high as possible. For a given number Q, the special **k**-point set is generated from the primitive reciprocal lattice vectors with the coefficients

$$q_i = \frac{2p_i - Q - 1}{2Q} + q_{0,i}p_i, \ i = 1, 2, 3; \ p_i = 1 \dots Q$$
(2.18)

with the weighting factors $\omega_q = 1/Q^3$ and global shifts $q_{0,i} \in [0..1]$, generally chosen as either 0 or 0.5 to specifically include or exclude $\mathbf{k} = \vec{0}$. The set obtained from this procedure is called a QxQxQ MP set. For lattices with lower than cubic symmetry, Q may be different in the three directions of the reciprocal lattice vectors. Under the symmetry operations of the group, some of the resulting **k**-points may be equivalent, in such cases, only one **k**-point has to be evaluated with the respective weighting factor multiplied by the degeneracy of the **k**-point. In this case, non-scalar properties are automatically symmetrized.

2.4.2 Defective crystals

A single point defect introduced into a crystal destroys the translational symmetry completely. Thus, in principle, equations for all atoms in the solid have to be solved. One could, in principle, treat a smaller piece but in order to model the behavior of a defect in an otherwise undisturbed crystal, the model has to be large enough, that a sufficient amount of atoms remain undisturbed by the defect to preserve the crystalline properties of the solid. This means that at the edges of the model,

- 1. the amplitude of the localized wave functions,
- 2. the deviations of charge density and
- 3. the deviations of the host atom positions with respect to the perfect crystal

must vanish at least approximately. Since the perturbations from point defects can have ranges of $10 - 50\text{\AA}$, $\sim 2500 - 25000$ atoms would be necessary to achieve this. Such numbers of atoms are orders of magnitude larger than what can be handled routinely with *ab initio* methods on computers of the present and the foreseeable future. Therefore, simplified models become necessary, which basically means, that the fulfillment of the conditions mentioned above is assumed for a smaller group of atoms around the defect usually referred to as the *cluster*. When constraining the calculations to manageable cluster sizes, these criteria usually cannot be met, therefore some allowance for deviations must be made and some kind of convergence test for all three of them becomes necessary in order to assess the deviations.

The first approach is to handle only the atoms of the cluster explicitly and embed them into an unperturbed crystalline background.

The simplest way to achieve this is the so-called molecular cluster model (MCM), which is based on the assumption, that the electronic states of some solids are well described by localized bonds. This is mostly the case with semiconductors. Ideally, the quantum mechanical interaction of the cluster with the background is completely described by a set of localized bonds crossing the interface between the two regions. If these bonds could be kept unchanged when cutting off the atoms of the background, the embedding would still be perfect, except for long range Coulomb interactions. Since the dangling bonds at the interface can never be saturated in a way that keeps them perfectly unchanged, in most cases hydrogen atoms are used to saturate them. The hydrogen saturated cluster is a molecule in the chemical sense, hence the name molecular cluster model. The MCM also forms the basis for quantum mechanics to molecular mechanics (QM/MM) coupling schemes, which will be described in detail in section 2.8.

More complicated are the perturbed crystal and perturbed cluster approaches. In the case of the perturbed crystal approach, the Hamiltonian is separated into the Hamiltonian of the perfect crystal and a perturbation \hat{U} relative to that:

$$H = H + \dot{U} \tag{2.19}$$

which can be solved using a Green's-function approach [12–14]. In the perturbed cluster approach, relying on a localized basis, the Hamiltonian is partitioned in direct space according to basis functions in the cluster (C) and the background (B)[15]

$$H = \begin{bmatrix} H_{CC} & H_{CB} \\ H_{BC} & H_{BB} \end{bmatrix}.$$
 (2.20)

Another possibility is called the supercell model (SCM). In this approach, the translational symmetry is restored artificially by constructing a periodic superlattice with the cluster as unit cell [16, 17]. This requires that the cluster is shaped in a way that allows periodic repetition without gaps or overlaps. Clusters of this kind are generally referred to as *supercells*. In the supercell model, the momentum space description of the perfect crystal outlined above can be applied directly without modification. One must consider however, that the supercell usually contains a multitude of primitive unit cells in terms of the perfect lattice. Therefore, the BZ of the supercell is reduced relative to the primitive Brillouin zone (PBZ) and is consequently called the reduced BZ (RBZ). In a perfect supercell, i.e. one without any defect, the vectors K of the RBZ each represent a set of primitive k-vectors, so that, if the superlattice has the same point group as the primitive one, the set $\{k\}_0$ corresponding to the center of the RBZ (K = 0) forms a special k-point set [18]. Therefore, with a properly chosen SCM, a calculation limited to the Γ -point (K = 0) of the RBZ may give a good description of the extend crystalline states.

If, however, the supercell contains a defect, the Γ -point is definitely no special k-point for the superlattice of defects and, unless the supercell is sufficiently large, that K = 0 approximation might not be adequate. The neutral vacancy in Si is a good test case for convergence. It has been shown [19] that the formation energy computed in the Γ -point approximation and with a 2x2x2 MP set in 32, 64, 128 and 216 atom supercells differs by 3.05, 0.56, 0.30 and 0.04eV respectively. This shows the importance of testing the K-point set used in supercell calculations, especially in relatively small supercells.

In practice, the atoms at the boundary of the supercell are sometimes fixed during calculations. This assumes, that the third criterion from page 7 is met. (For deep levels, the defect wave function is only considerably influenced by the relaxation in the first 1–2 neighbor shells of the defect.) This artificial restriction of the host atom relaxation is desired in order to limit the effect of defect-defect interactions introduced by long range relaxation beyond the SCM boundary.

Criterion 2 is usually met by SCM-s in the size range of 50–100 atoms in metallic or purely covalent solids, but may require considerably larger cell sized for strongly ionic materials. Due to the long range of the Coulomb interaction, the defect may cause far reaching polarization effects which have to be accounted for in a self-consistent manner.

It should be noted, that the periodic boundary conditions can lead to severe problems in the coulomb energy terms. If the SCM has a total charge, the interaction between this charge and its infinite number of periodic images will lead to an infinite coulomb energy. Therefore a total charge of the supercell must be neutralized, which is generally done by applying a uniform compensating charge density over the whole volume of the supercell: $\rho_{\rm comp} = \frac{-Q_{\rm tot}}{V_{\rm cell}}$. However, this approach can lead to severe artifacts which depend, among others, on the supercell size. Therefore, the convergence of the calculation results with supercell size should be checked. Similarly, an overall dipole moment of a supercell will also lead to divergent coulomb energy. This is generally compensated by a shift of the charge density with respect to the nuclei. This effect leads to an artificial energetic destabilization of defect configurations with dipole moments. In covalent solids, this is generally not a serious problem, while in polar materials, the error can become severe. Again, convergence checks with supercell size are necessary to check for this problem, however, increasing the supercell size is often impractical.

2.5 Density Functional Theory

2.5.1 Exact DFT

In materials science, the most frequently employed method to tackle the electronic problem is the density functional theory (DFT). An in-depth treatment of this method can be found in the original articles by Hohenberg and Kohn [20], Kohn and Sham [21] and the more mathematical treatment by Lieb [22]. DFT is based on the theorem by Hohenberg and Kohn [20] that the non-degenerate ground state of an electronic system and its ground state energy are unique functionals of its particle density $n(\mathbf{r})$

$$\mathcal{E}_0 = \mathcal{E}[n(\vec{r})]. \tag{2.21}$$

This allows to replace the wave function $\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ with the particle density $n(\mathbf{r})$ as the central variable. The particle density² is an observable of the quantum mechanical system given by

$$n(\vec{r}) = \langle \Psi | \sum_{i=1}^{N} \delta(\vec{r} - \mathbf{r}_i) | \Psi \rangle.$$
(2.22)

The total energy from equation 2.21 is given by the Kohn-Sham energy functional H[n]:

$$H[n] = [-T[n(\vec{r})] + v_{\text{eff}}[n(\vec{r})]], \qquad (2.23)$$

where the first term is the kinetic energy $T[n(\vec{r})]$ and $v_{eff}[n(\vec{r})]$ is the effective potential, which comprises the terms

$$v_{\rm eff}[n(\vec{r})] = v_{\rm ext}(r) + \int \frac{2n(\vec{r'})}{|\vec{r} - \vec{r'}|} d\vec{r'} + V_{\rm XC}[n(\vec{r})].$$
(2.24)

Here v_{ext} describes the external potential (the potential of the nuclei and external electromagnetic field), the middle term is the Coulomb potential, v_c , and $V_{XC}[n(r)]$ is the exchange-correlation potential, which describes all many-particle effects.

With an expansion of the particle density into effective single particle wave functions $\Psi_i(\vec{r})$, the so-called Kohn-Sham orbitals

$$n(r) = \sum_{i=1}^{N} |\Psi_i(\vec{r})|^2, \qquad (2.25)$$

the N-electron equation can be converted into a system of N coupled effective-single-electron equations, the Kohn-Sham equations [21]

$$\left[-\frac{1}{2}\Delta + v_{\text{eff}}[n(\vec{r})] - \mathcal{E}_i\right]\Psi_i(\vec{r}) = 0.$$
(2.26)

Both v_c and V_{XC} are functionals of the particle density n(r) and therefore all other Kohn-Sham orbitals $\Psi_j(r)$ with $j \neq i$. Thus the effective potential couples all effective single particle equations – the Ψ_i are only formally independent.

Like the potential, the total energy can be split up into its known components:

$$E_{\rm tot}[n(\vec{r})] = T[n(\vec{r})] + \iint \frac{n(\vec{r}) n(\vec{r'})}{|\vec{r} - \vec{r'}|} d\vec{r} d\vec{r'} + \int v_{\rm ext}(\vec{r}) n(\vec{r}) d\vec{r} + E_{\rm XC}[n(\vec{r})].$$
(2.27)

In equations. (2.24) and (2.27), all terms but the last, follow directly from regarding the system as the composition of N independent, non-interacting particles. Thereby all many-body effects, except the

 $^{^{2}}$ The particle density of the electronic system is also referred to as the charge density. Both terms are used synonymously here, as in atomic units the electron charge, e, is unity.

coulomb repulsion, have been combined in the V_{XC} and E_{XC} terms. The exchange-correlation potential and the exchange-correlation energy are connected by the functional derivative

$$V_{\rm XC} = \frac{\partial E_{\rm XC}[n(\vec{r})]}{\partial n(\vec{r})}.$$
(2.28)

Up to this point, DFT is a reformulation of the Schrödinger equation without neglect of any part, as long as the ground state can be expressed as a sum of single-determinant wave functions. However, neither the exact form of $E_{\rm XC}$ nor that of $V_{\rm XC}$ is known. Therefore, the computational advantage of transforming the total energy expression from being dependent on a 3N dimensional function in space to just one, has been bought with the need to introduce an approximation for $E_{\rm XC}$ or $V_{\rm XC}$.

2.5.2 The local density approximation (LDA)

The first approximation to the exchange-correlation functional in DFT to be presented here is the local density approximation. It is based on the assumption that $V_{\rm XC}$ is only locally dependent on n(r). Thus, it can be expressed in an integral form with an integrand $\epsilon_{XC}[n(r)]$, that only locally depends on the density

$$E_{\rm XC}[n(\vec{r})] \approx \int n(\vec{r}) \epsilon_{\rm XC}[(n(\vec{r})]d\vec{r}$$
(2.29)

for the exchange-correlation potential, this leads to:

$$v_{\rm XC} = \frac{\partial E_{XC}[n(\vec{r})]}{\partial n(\vec{r})} \approx \frac{\partial}{\partial n(\vec{r})} \int n(\vec{r}) \epsilon_{\rm XC}[n(\vec{r})] d\vec{r}$$
(2.30)

$$= \epsilon_{\rm XC}[n(\vec{r})] + n(\vec{r}) \frac{\partial \epsilon_{\rm XC}[n(\vec{r})]}{\partial n(\vec{r})}$$
(2.31)

which then gives the Kohn-Sham equations in this local approximation

$$\left[-\frac{1}{2}\Delta + v_{\text{eff}} - E_i\right]\Psi_i(\vec{r}) = 0$$
(2.32)

with $v_{\text{eff}}(\vec{r}) = v_{\text{c}}(\vec{r}) + v_{\text{xxc}}(\vec{r}) + v_{\text{XC}}(\vec{r})$. The equations are still coupled via the effective potential v_{eff} , the Kohn-Sham equations must be solved self-consistently.

It should be noted at this point, that all standard implementations of local exchange-correlation functionals suffer from the problem, that the gap energies of solids are underestimated by 30-50%. This will be discussed further in section 2.5.6. In some pathological cases, narrow gap semiconductors even appear to be metallic.

2.5.3 Treating electron spin (LSDA)

For non closed-shell systems, it is necessary to include spin-polarization effects into the calculations. The easiest way to describe a spin polarized system is, to split the charge density n(r) into two components for the two possible spin orientations

$$n(\vec{r}) = n^{\uparrow}(\vec{r}) + n^{\downarrow}(\vec{r}) \tag{2.33}$$

in this case the DFT becomes spin density functional theory (SDFT). The two components are then treated in exactly the same way, as the particle density in the case of neglected spin effects, including any approximations. (I.e. the local density approximation becomes the local spin density approximation — LSDA.) With this, the one can define the spin- or magnetization density

$$m(\vec{r}) = n^{\uparrow}(\vec{r}) - n^{\downarrow}(\vec{r}) \tag{2.34}$$

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and the corresponding spin-polarization

$$\xi = \frac{m(\vec{r})}{n(\vec{r})} = \frac{n^{\uparrow}(\vec{r}) - n^{\downarrow}(\vec{r})}{n^{\uparrow}(\vec{r}) + n^{\downarrow}(\vec{r})}.$$
(2.35)

This allows to treat spin-polarization effects of the system and perform open-shell calculations.³

2.5.4 Beyond LDA

Although LDA-DFT performs well for most applications, in some cases the purely local exchangecorrelation functionals do not produce sufficiently accurate results. To improve on the local functionals, without having to apply a fully non-local formulation, which would be computationally far more expensive, the generalized gradient approximation (GGA) was developed. It works by extending the LDA $E_{\rm XC}$ with a term dependent on the local gradient of the charge density

$$E_{\rm XC}^{\rm GGA}[n(\vec{r})] = E_{\rm XC}^{\rm LDA}[n(\vec{r})] + E_{\rm XC}[\nabla n(\vec{r})].$$

$$(2.36)$$

As they take into account the surrounding density around each point r without being fully non-local, these functionals are also called *semi local*. For molecular systems, functionals combining the exchange functional by Becke [23] with a correlation term proposed by Lee, Yang and Parr [24], called BLYP[25] is very popular, in solid state physics, the exchange-correlation functional by Perdew, Burke and Ernzerhof [26] (PBE) is widely used. One must, however, be mindful that the GGA does not always improve on LDA, one prominent example being metals.

2.5.5 The DFT gap error

As mentioned earlier, the HF method, using exact exchange, is rather costly (~ N^4) even without considering correlation corrections, the calculation of which scales > N^4 . On the other hand, the very effective local density or gradient corrected approximations of DFT fail to describe the excited electronic states of most systems.

The LDA, commonly used in defect physics, is a very good approximation for systems where the electrons are rather delocalized [27]. However, when the static electron-electron interaction becomes strong enough that electrons get localized on atomic sites in a solid, the LDA, as well as GGA, fail to describe the correct ground states. One of the most prominent examples are the 3d transition metal oxides like NiO (and probably also TiO₂) which are Mott insulators characterized by localized *d*-electrons [28]. The LSDA in contrast predicts somewhat too small magnetic moments and vanishing or at least *very small gaps*, also observed in case of semiconductors [29]. Unfortunately, this error also influences the accuracy of calculating spectroscopic properties of defects therein. Wrong excited states and underestimated transition levels between the different charge states are the consequence.

An important insight on the central origin of these problems can be obtained by the observation that localized orbitals in the LDA give rise to an error due to a spurious self-interaction contained in the effective potential

$$E_{\rm SI}^{\rm LDA}[n_i] = \int \frac{n_i(\vec{r})n_i(\vec{r'})}{|\vec{r} - \vec{r'}|} d\vec{r} d\vec{r'} + \int n_i(\vec{r})\epsilon_{\rm XC}^{\rm LDA}(n_i(\vec{r})) d\vec{r} \neq 0.$$
(2.37)

This error increases the more localized the orbitals become. For rather delocalized electrons, however, the self-interaction is negligible or zero. In HF theory, where the exact exchange is calculated, the self-interaction vanishes.

 $^{^{3}}$ In order not to overload the formalism, the spin indices will be neglected in the following. The approach for spin polarized systems is completely analogous.

2.5.6 Hybrid exchange functionals

Since the exchange energies are typically an order of magnitude higher than the correlation energies, it could be shown [30], that using exact exchange within DFT can largely eliminate the gap error. Still, at present, no implementation of exact exchange DFT exists, which could be used efficiently on large systems [31].

For the description of exited states a hybrid functional, e.g. the B3-LYP functional [25], is often used. This is constructed by mixing exact exchange to the DFT exchange.

It has been shown [32] that with the mixing in the form of

$$E_{\rm XC} = E_{\rm XC}^{\rm LSDA} + \lambda (E_{\rm X}^{\rm exact} - E_{\rm X}^{\rm LSDA}), \qquad (2.38)$$

where λ denotes the empirical mixing factor, the gap error can be effectively eliminated.

Previous work [25, 33] has shown, that a 20% admixture of exact exchange can reproduce the experimental band gaps of 3C- (2.4 eV) and 4H-SiC (3.3 eV) as well as the positions of known defect levels very well. However the empirical mixing factors, fitted to the fundamental gap, are not well transferable. The same mixing factor only yields a band gap of 8.1 eV for α -quartz, as opposed to the experimental value of 9 eV, while a mixing weight of 28% proves optimal for this material.

Still, within one material, consistently good results can be obtained for all properties. E.g., for silicon, a mixing factor of 12% optimizes not only the gap, but the whole electronic structure (e.g. the valence band width and all observed direct transitions between the VB and the CB,) as well as the elastic properties. (The mixing has no significant effect on the binding energies and the lattice constant[34].)

The price for the improved precision is the need to evaluate four-center integrals, which entails a significantly larger computational cost and larger memory requirements compared to pure DFT methods, which make geometry optimizations of surface or interface models using hybrid exchange (HE) impractical. However, tests have shown, that an additional geometry optimization is only necessary, when the system contains a shallow defect[34]. Therefore, it is possible to obtain an improvement of the electronic structure derived from LDA calculations, by making a single HE calculation on LDA-optimized geometry.

2.6 The pseudopotential method

The bonding behavior of atoms in solids is mainly determined by their valence shell electrons. The inner shell electrons basically act the same way as in an isolated, i.e. unbonded, atom and also screen the valence electrons from the nuclear charge. It seems to be a promising approach to neglect the core electrons in the self-consistent calculation of the charge density and instead include them into a new external potential, called a pseudopotential v^{ps} , which now combines the potential of the nuclear charge with the core electron potential [35–38]. This pseudopotential converts the wave function into a pseudo-wave-function which is smooth and node-less close to the core but fits the all electron wave function accurately in the outer region of the atom, and which yields the same valence energy eigenvalues as the all electron wave function

$$\mathcal{E}_v^{\rm ps} = \mathcal{E}_v^{\rm AE}.\tag{2.39}$$

Forming the pseudopotential entails the substitution of the charge density $n(\vec{r})$ by the valence charge density $n^v(\vec{r})$ that now only contains the valence shell electrons. The effective potential then takes the form

$$v_{\rm eff}[n^{v}(\vec{r})] = v^{\rm ps}(\vec{r}) + v_{\rm c}(\vec{r}) + v_{\rm XC}[n(\vec{r})]$$
(2.40)

or in the local density approximation

$$v_{\rm eff}(\vec{r}) = v^{\rm ps}(\vec{r}) + v_{\rm c}(\vec{r}) + v_{\rm XC}(\vec{r})$$
(2.41)

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here $v^{\rm ps}(\vec{r})$ is given by the superposition of the single core ion pseudo-potentials

$$v^{\rm ps} = \sum_{j=1}^{M} v_j^{\rm ps}(\vec{r} - \mathbf{R}_j)$$
(2.42)

where R_j are the positions of the respective nuclei.

The pseudopotential v^{ps} can be obtained by calculating the effective potential of a single, isolated atom and then subtracting the valence electron contributions

$$v_j^{\rm ps}(\vec{r}) = v_{\rm eff}(\vec{r}) - \int \frac{n_j^v(\vec{r'})}{|\vec{r} - \vec{r'}|} d\vec{r} - v_{\rm XC}[n_j(\vec{r})].$$
(2.43)

As long as a *frozen core* is assumed, the same pseudopotential can be used for any spatial distribution of ionic cores.

In practice, several different forms of pseudopotentials are used:

norm-conserving pseudopotentials [38, 39] meet the conditions that the normalized radial electronic pseudo-wave-function at the angular momentum l is equal to the corresponding all-electron radial wave function beyond a chosen cutoff radius r_{cl}

$$R_l^{\rm ps}(r) = R_l^{\rm AE} \text{ for } r > r_{cl}$$

$$\tag{2.44}$$

or converges rapidly to that value, and that the charge enclosed within r_{cl} for the two wave functions is equal:

$$\int_{0}^{r_{cl}} |R_l^{\rm ps}(r)|^2 r^2 dr = \int_{0}^{r_{cl}} |R_l^{\rm AE}(r)|^2 r^2 dr$$

- **soft or ultrasoft pseudopotentials** [40–42] here the restraint of norm-conservation is dropped in order to be able to create smoother pseudo-wave-functions and thus enable the use of smaller plane-wave basis sets.
- the projector augmented-wave method [43] indirectly uses pseudopotentials. It divides the wave functions into an atom-centered sphere in which the wave function is represented by partial waves and an outer (bond-) region, where it is represented by an envelope function, which in turn can be expanded into an arbitrary basis, usually plane waves.

Here the pseudopotential approach is applied to the construction of the partial-wave basis for the core region.

Beside the striking advantage of reducing the number of electrons to be considered quantum-mechanically, and thus greatly reducing the computational cost, the pseudopotential method has another, not so obvious point in its favor — When total energies are compared, the differences are relatively small compared to the energy values; therefore small errors, that occur in the treatment of each single electron can sum up to significant values, in total energy differences. By using pseudo-potentials, the number of treated electrons, and therefore the number of possible sources of error is reduced. In addition to this, the numerical value of the total energy is reduced, thus decreasing the effect of possible errors on total energy differences.

As long as only total energies and electronic properties of the valence shell are of interest, as is the case in this work, the impact of neglecting the interaction of inner shell electrons on the valence shell is very small. However, the ability to calculate some experimentally observable properties, such as electron spin resonance (ESR) and nuclear magnetic resonance (NMR) is lost.

2.7 Density Functional based Tight Binding

2.7.1 Tight Binding schemes

Tight-binding (TB) approaches work on the principle of treating the electronic wave function of a system as a superposition of atom-like wave functions. The electrons are tightly bound to the cores in the sense that the electrons are not allowed to delocalize beyond the confines of a minimal LCAO basis.

In the popular semi empirical tight-binding (SETB) schemes, the Hamilton matrix elements are approximated by analytical functions, the parameters of which are optimized to reproduce experimental data, as are the atomic basis functions. This allows a much faster calculation of the total energy than DFT or other *ab initio* methods, while retaining an ability to account some for quantum mechanical effects. In such an approach, total energy can, e.g. be expressed as

$$E_{\rm TB} = \sum_{i}^{N} \epsilon_i + \frac{1}{2} \sum_{j \neq k}^{M} v^{j,k} (|R_j - R_k|).$$
(2.45)

Here $v^{j,k}(r)$ is an interatomic potential depending on the distance. The ϵ_i are taken to be eigenvalues of a non self-consistent Schrödinger-like equation

$$\epsilon_i \Psi_i(\vec{r}) = \left[-\frac{1}{2} \Delta + V(\vec{r}) \right] \Psi_i(\vec{r}), \qquad (2.46)$$

which is solved variationally using the atom-like basis set leading to a secular equation

$$|\underline{H} - \epsilon \underline{S}| = 0 \tag{2.47}$$

with the Hamilton and overlap matrices \underline{H} and \underline{S} . In the most stringent application of the tight binding principle, only the diagonal matrix elements would be regarded, however, this would exclude any interatomic interactions, so that they are instead assumed to vanish beyond the first or second shell of neighbor atoms [44]⁴.

2.7.2 DFTB

In contrast to SETB, the Density Functional based Tight Binding (DFTB) derives its parametrization from *ab initio* DFT calculations. In the following I shall sketch the formalism and the approximations therein. A more detailed description of the method and its derivation can be obtained from the original works of Seifert, Porezag *et. al.* [45–47], later reviews [48] and [49]. Ref [50] extends the original method to include spin polarization effects.

Basic Formalism

Based on the DFT total energy expression after the introduction of the effective single particle wave functions (equation 2.27),

$$\mathcal{E}[n(\vec{r})] = \sum_{i}^{\text{occ}} n_{i}(\vec{r}) \int \Psi_{i}^{*}(\vec{r}) \left[\underbrace{-\frac{\nabla^{2}}{2} + \frac{1}{2} \int \frac{n(\vec{r'})}{|\vec{r} - \vec{r'}|} d\vec{r'} + v_{\text{nuc}}(\vec{r})}_{H_{0}[n_{0}(\vec{r})]} \right] \Psi_{i}(\vec{r}) d\vec{r} + E_{\text{XC}}[n(\vec{r})],$$
(2.48)

⁴Often, the basis functions are assumed to be orthonormal, so that \underline{S} becomes the unit matrix.

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with the normalized occupation numbers n_i following Janak

$$n(\vec{r}) = \sum_{i}^{\text{occ}} n_i |\Psi_i(\vec{r})|^2; \ N = \sum_{i}^{\text{occ}} n_i,$$
(2.49)

the first step is to approximate equation (2.48) by Taylor-expanding it in a norm-conserving density fluctuation $\Delta n(\vec{r})$, around a reference density $n_0(\vec{r})$. This expansion is then truncated after the second order. With $\Delta n(\vec{r}) = n(\vec{r}) - n_0(\vec{r})$, $\hat{H}[n(\vec{r})]$ as defined in (2.23) and the internuclear energy $E_{\rm NN}$ the Taylor-expansion leads to

$$\mathcal{E}[n(\vec{r})] = \underbrace{\sum_{i}^{occ} n_{i} \int \Psi_{i}^{*}(\vec{r}) \hat{H}_{0}[n_{0}(\vec{r})] \Psi_{i}(\vec{r}) d\vec{r}}_{E_{BS}}}_{\substack{+\frac{1}{2} \int \int \frac{n_{0}(\vec{r}) n_{0}(\vec{r'})}{|r - r'|} d\vec{r'} d\vec{r} + E_{XC}[n_{0}(\vec{r})] - \int v_{XC}[n_{0}(\vec{r})] n_{o}(\vec{r}) d\vec{r} + E_{NN}}_{E_{rep}}}_{\substack{+\frac{1}{2} \int \int \left[\frac{1}{|\vec{r} - \vec{r'}|} + \frac{\partial^{2} E_{XC}[n(\vec{r})]}{\partial n(\vec{r'})^{2}}\right]_{n_{0}} \Delta n(\vec{r}) \Delta n(\vec{r'}) d\vec{r'} d\vec{r} + \mathcal{O}(\Delta n(\vec{r})^{3}). \quad (2.50)$$

Here the terms in the first two lines only dependent on n_0 and the third line contains the second order contributions and truncation error. (Note that the first order terms cancel out.) More concisely, the total energy is expressed as

$$\mathcal{E}[n] \approx \mathcal{E}_{\text{DFTB}} = E_{\text{BS}} + E_{\text{rep}}(\mathbf{R}) + E_{\text{2nd}}.$$
(2.51)

In systems in which interatomic charge transfer and long range Coulomb interactions play no significant role, E_{2nd} can be neglected. The energy expression then only depends on the reference density $n_0(\vec{r})$, leading to the non self-consistent version of DFTB. Otherwise, E_{2nd} can be calculated self-consistently[48]. This addition to the original DFTB method is called self-consistent charge DFTB (SCC-DFTB).

Following the tight-binding philosophy, all interactions are assumed to be short-ranged and pairwise, no three- or more center interactions are regarded.

Hamilton matrix elements

The elements of the zeroth order Hamilton matrix \underline{H}_0 depend on the basis functions used to expand the Ψ_i . DFTB uses a minimal localized valence basis set

$$\left|\Psi_{i}(\vec{r})\right\rangle = \sum_{\nu} c_{\nu i} \left|\phi_{\nu}^{j}(\vec{r} - \mathbf{R}_{j})\right\rangle,\tag{2.52}$$

where the ϕ_{ν}^{j} are taken to be linear combinations of Slater orbitals obtained from a self-consistent DFTB reference calculation using a neutral, spherical symmetric pseudo atom. The reference density then becomes the superposition of atomic reference densities

$$n_0(\vec{r}) = \sum_j^M \sum_{\nu}^{\nu \in j} \left\langle \phi_{\nu}^j(\vec{r}) \right| \phi_{\nu}^j(\vec{r}) \right\rangle = \sum_j^M n_0^j(\vec{r}).$$
(2.53)

Within the two-center approximation and neglecting the crystal-field terms, the Hamilton matrix elements thus become

$$h_{\mu,\nu}^{0} = \begin{cases} \epsilon_{\nu}^{\text{tree atom}} & \mu = \nu \\ \left\langle \phi_{\mu} | \, \hat{t} + \hat{V} [n_{0}^{j(\mu)} + n_{0}^{k(\nu)} \right\rangle & \mu \neq \nu, j(\mu) \neq k(\nu) \\ 0 & \mu \neq \nu, j(\mu) = k(\nu) \end{cases}$$

with $j(\mu)$ and $k(\nu)$ the corresponding atoms to the atomic orbitals μ and ν . The diagonal elements of this matrix would be the respective eigenvalues of the DFT reference calculation. However, in order to obtain the correct dissociation limit, the eigenvalue of the free atom is used. The non-zero matrix elements are calculated element-pairwise and tabulated over a range of interatomic distances. At the same time, also the overlap matrix elements are calculated and tabulated. In practice, the wave function and charge density of free atoms (or dimers) are not well suited to describe the more localized electrons of condensed matter. Therefore, during the DFT reference calculations, the wave functions and densities are artificially compressed to resemble the circumstances in the target system.

 $E_{\rm rep}(\mathbf{R})$

In the same two-center approach as for the Hamilton matrix elements, the repulsive energy term is expressed as a sum of pairwise, radial symmetric atomic contributions

$$E_{\rm rep}(\mathbf{R}) = \frac{1}{2} \sum_{j \neq k} v_{\rm rep}^{j,k}(|\mathbf{R}_j - \mathbf{R}_k|).$$
(2.54)

After the Hamilton matrix elements have been calculated, the repulsive potentials $v_{\rm rep}^{j,k}(r)$ correct the difference between the DFTB band structure energy $E_{\rm BS}$ and the total energy from the reference DFT method. They can be calculated from the energy differences over a range of interatomic separations

$$v_{\rm rep}^{j,k}(r_{j,k}) = E_{\rm DFT}^{tot}(r_{j,k}) - E_{\rm BS}(r_{j,k}) - E_{\rm 2nd}(r_{j,k}).$$
(2.55)

 $(E_{2nd} \equiv 0 \text{ if second order terms are neglected.})$

In practice, the repulsive potentials thus obtained often do not yield satisfactory accuracy. Therefore the repulsive potentials are rather constructed by fitting a predefined function to the atom-atom distance dependent energy differences in more extended systems, e.g. the C–C distances in $HC\equiv CH$, $H_2C=CH_2$ and H_3C-CH_3 . By this approach, the error from neglecting multicenter and crystal-field terms is partly corrected in the repulsive potentials

$$v_{\rm rep}^{j,k}(r) \approx \left\langle E_{\rm DFT}^{tot}(r) - E_{\rm BS}(r) - E_{\rm 2nd}(r) \right\rangle_{\rm fit\, systems}$$

Evolutionary algorithms can help to fit $v_{\text{rep}}^{j,k}(r)$ give an accurate reproduction of different reference DFT methods [51].

Second order corrections

In systems which show significant charge transfer or long-range Coulomb interactions, the densityfluctuation dependent terms summarized in E_{2nd} must be taken into account. To this end, Δn is decomposed into atomic contributions, as it is done for n_0 in equation 2.53

$$\Delta n(\vec{r}) = \sum_{j}^{M} \sum_{l,m} c_{lm}^{j} \mathcal{F}_{lm}^{j} \gamma_{lm}^{j} \approx \sum_{j}^{M} \mathcal{F}_{00}^{j} \gamma_{00}^{j} \Delta q^{j}, \qquad (2.56)$$

where truncation after the monopole term accounts for the most important contributions and the coefficients c_{lm}^{j} are set to fluctuations of the atomic Mulliken charges defined as

$$\Delta q^j = q^j - q_0^j \tag{2.57}$$

with

$$\Delta q^{j} = \sum_{i}^{N} n_{i} \sum_{\mu,\nu \in j} c_{\mu,i} c_{\nu,i} S_{\mu,\nu}.$$
(2.58)

Here, q_o^j represents the number of valence electrons of the neutral atom j. Substituting this into the expression for E_{2nd} given in Equation 2.50 leads to

$$E_{2nd} = \frac{1}{2} \sum_{j,k}^{M} \gamma_{jk} (|\mathbf{R}_j - \mathbf{R}_k|) \Delta q^j \Delta q^k$$

where $\gamma_{jk} = \iint \left[\frac{1}{|\mathbf{r} - \mathbf{r}'|} + \frac{\partial V_{\text{XC}}[n]}{\partial n(\mathbf{r}')} \right] \mathbf{F}_{00}^j(\mathbf{r}_j) \mathbf{F}_{00}^k(\mathbf{r}'_k) \frac{1}{4\pi} d\vec{r} d\vec{r'}.$

Here, the $F_{00}(\vec{r})$ are fixed and radial orbital relaxation functions, thus the γ_{jk} depend only on the interatomic distances. This assumes, that the electrostatics of the system can be described by atomcentered monopoles. The second-order corrections to DFTB are discussed in detail in Refs [48].

Total energy and secular equation

With the approximations and contributions discussed so far, the DFTB total energy expression from equation 2.48 becomes

$$E_{\rm tot} = \sum_{i}^{occ} \sum_{\mu\nu} c_{\mu i}^* c_{\nu i} h_{\mu\nu}^0 + \frac{1}{2} \sum_{j}^{M} \sum_{k}^{M} \gamma_{jk}(\mathbf{R}_{jk}) \Delta q_j \Delta q_k + E_{\rm rep}(\mathbf{R}).$$
(2.59)

The total energy is minimized by variation of the LCAO coefficients c. This leads to a eigenvalue problem with the secular equation

$$\sum_{\nu} c_{\nu i} \left(h_{\mu\nu} - \epsilon_{\nu} S_{\mu\nu} \right) = 0 \,\forall i, \mu.$$
(2.60)

As the $c_{\nu i}$ and the atomic Mulliken charges depend on each other, this equation must be solved selfconsistently.

2.7.3 Extensions to SCC-DFTB

As a prerequisite to the development of the QM/MM embedding schemes laid out in detail in chapter 4, further extensions must be added to the SCC-DFTB method: the influence of an external electrostatic field and the possibility to constrain atomic charges during the SCC iterations.

External electric field

Similar to the SCC-DFTB QM/MM coupling approach introduced in Ref [52] for biological molecules, the DFTB Hamiltonian was extended by an additive term describing the coulomb interaction of the DFTB treated atoms with external monopoles. The energetic contribution U^X of external point charges in a Coulomb energy of the form

$$U^{\mathbf{x}} = \sum_{I}^{\text{ext atoms}} \sum_{A}^{\text{atoms}} \frac{1}{r_{IA}} q_A \cdot q_I.$$
(2.61)

Starting from the derivative of the Mulliken populations with respect to the $c_{i\lambda}$

$$\frac{\partial q_A}{\partial c_{i\lambda}} = \frac{1}{2} n_i \left[\sum_{\nu} \delta_{B(\lambda)A} c_{i\nu} S_{\lambda\nu} + \sum_{\mu(A)} c_{i\mu} S_{\lambda\mu} \right]$$
(2.62)

we can formulate the derivative of $U^{\mathbf{X}}$

$$\frac{\partial U^{\mathrm{X}}}{\partial c_{i\lambda}} = \frac{\partial}{\partial c_{i\lambda}} \left[\sum_{I} \sum_{A} \frac{1}{r_{IA}} q_A \cdot q_I \right] = \left[\sum_{I} \sum_{A} \frac{1}{r_{IA}} q_I \frac{\partial q_A}{\partial c_{i\lambda}} \right]$$
(2.63)

$$= \sum_{I} \sum_{A} \frac{1}{r_{IA}} q_{I} \cdot \left\{ \sum_{\nu} \delta_{B(\lambda)A} c_{i\nu} S_{\lambda\nu} + \sum_{\mu(A)} c_{i\mu} S_{\lambda\mu} \right\}$$
(2.64)

$$= \frac{1}{2} \sum_{I} q_{I} \left\{ \sum_{A} \sum_{\nu} \frac{1}{r_{IA}} \delta_{B(\lambda)A} c_{i\nu} S_{\lambda\nu} + \sum_{A} \sum_{\mu(A)} \frac{1}{r_{IA}} c_{i\mu} S_{\lambda\mu} \right\}$$
(2.65)

$$= \sum_{\nu} \left\{ \sum_{I} q_{I} \cdot \frac{1}{2} S_{\lambda\nu} \left[\frac{1}{r_{IA(\nu)}} + \frac{1}{r_{IB(\lambda)}} \right] \cdot c_{i\nu} \right\},$$
(2.66)

which leads to the expression for the matrix element contribution of the external point charges:

$$U_{\mu\nu}^{\rm X} = \sum_{I} q_I \frac{1}{2} S_{\mu\nu} \left[\frac{1}{r_{IA(\mu)}} + \frac{1}{r_{IB(\nu)}} \right].$$
(2.67)

The external point charges can be replaced by Gaussian charge distributions of variance σ^2 to better represent charged atoms in the surroundings, which are not point-like but spatially extended. In that case, the coulomb energy transforms to

$$U_{\rm gauss}^{\rm x} = \frac{q_A q_I}{r_{IA}} \cdot \operatorname{erf}\left(\frac{r_{IA}}{\sigma}\right) \tag{2.68}$$

and the respective matrix element contributions become

$$U_{\mu\nu}^{\rm X} = \sum_{I} q_I \frac{1}{2} S_{\mu\nu} \left[\operatorname{erf}\left(\frac{r_{IA(\mu)}}{\sigma}\right) \cdot \frac{1}{r_{IA(\mu)}} + \operatorname{erf}\left(\frac{r_{IB(\nu)}}{\sigma}\right) \cdot \frac{1}{r_{IB(\nu)}} \right].$$
(2.69)

Effectively, this scales the influence of external charges on close QM atoms down. The choice of a single Gaussian to represent the spatial extent of the external charge distribution is arbitrary and based on mathematical convenience.

Charge constraints

To achieve a bulk-like electronic structure of an embedded cluster, it can be helpful to constrain the electronic structure of certain atoms of such a cluster, usually that of the boundary atoms. Since the varied quantity in DFTB is the Mulliken population, this is where the electronic constraint must be applied. This is done by adding a penalty potential U^{constr} to the total energy expression of the form [53]

$$U^{\text{constr}} = \sum_{A} U_A (\underbrace{q_A - q_A^0}_{\Delta q_A})^2.$$
(2.70)

Here, U_A is an atom-wise potential strength, q_A is the Mulliken population of atom A, q_A^0 its target population and Δq_A its charge deviation. The quadratic form ensures a symmetric penalty for positive and negative deviations. As the penalty potential affects the atomic charges, it leads to a perturbation of the Hamiltonian which can be calculated by variation of U^{constr} in the LCAO coefficients $c_{\lambda k}$ of the basis orbital λ in eigenvector k:

$$\frac{\partial U^{\text{constr}}}{\partial c_{\lambda k}^*}.$$
(2.71)

2.7. DENSITY FUNCTIONAL BASED TIGHT BINDING

Starting from the derivative of the Mulliken population q_A

$$\frac{\partial q_A}{\partial c_{\lambda k}^*} = \frac{1}{2} \frac{\partial}{\partial c_{\lambda k}^*} \sum_{i}^{\text{occ.}} n_i \left[\sum_{\mu(A)} \sum_{\nu} c_{\mu i}^* c_{\nu i} S_{\mu \nu} + \sum_{\mu(A)} \sum_{\nu} c_{\mu i} c_{\nu i}^* S_{\nu \mu} \right]$$
(2.72)

in its symmetric form that ensures real population values at all k-points:

$$\frac{\partial q_A}{\partial c_{\lambda k}^*} = \frac{1}{2} \sum_{i}^{\text{occ.}} n_i \left[\delta \sum_{\nu} \delta_{ki} \delta_{\lambda \mu} c_{\mu i}^* c_{\nu i} S_{\mu \nu} + \sum_{\mu (A)} \sum_{\nu} c_{\mu i} c_{\nu i}^* S_{\nu \mu} \right]$$
(2.73)

$$=\frac{1}{2}n_k \left[\sum_{\nu} \delta_{B(\lambda)A} c_{k\nu} S_{\lambda\nu} + \sum_{\mu(A)} c_{k\mu} S_{\lambda\mu} \right]$$
(2.74)

the derivation in equation 2.71 can now be executed:

$$\frac{\partial U^{\text{constr}}}{\partial c_{\lambda k}^*} = \sum_A U_A 2\delta q_A \frac{\partial q_A}{\partial c_{\lambda k}^*} = \sum_A \Omega_A \frac{\partial q_A}{\partial c_{\lambda k}^*}$$
(2.75)

$$=\frac{1}{2}n_k\sum_A\Omega_A\left[\sum_{\nu}\delta_{B(\lambda)A}c_{k\nu}S_{\lambda\nu} + \sum_{\mu(A)}c_{k\mu}S_{\lambda\mu}\right]$$
(2.76)

$$=\frac{1}{2}n_{k}\left[\sum_{\nu}\sum_{A}\Omega_{A}\delta_{B(\lambda)A}c_{k\nu}S_{\lambda\nu}+\sum_{A}\sum_{\mu(A)}\Omega_{A}c_{k\mu}S_{\lambda\mu}\right]$$
(2.77)

$$=\frac{1}{2}n_k \left[\sum_{\nu} \Omega_{B(\lambda)} c_{k\nu} S_{\lambda\nu} + \sum_{\nu} \Omega_{A(\nu)} c_{k\mu} S_{\lambda\mu}\right]$$
(2.78)

$$=\frac{1}{2}n_k\sum_{\nu}c_{k\nu}S_{\lambda\nu}\left[\Omega_{B(\lambda)}+\Omega_{A(\nu)}\right]$$
(2.79)

Thus, the perturbation becomes

$$\Delta H_{\mu\nu}^{\text{constr}} = S_{\mu\nu} \left[U_{A(\mu)} \Delta q_{A(\mu)} + U_{B(\nu)} \Delta q_{B(\nu)} \right].$$
(2.80)

In addition to this, the constraint potential can also lead to a perturbation in the forces, which can be derived in a similar manner to the Hamiltonian perturbation:

$$\Delta F_c = -\frac{\partial U^{\text{constr}}}{R_c} = -\sum_A U_A 2\Delta q_A \cdot \frac{\partial q_A}{\partial R_C} \quad \text{with Eq 2.72}$$
(2.81)

$$= -\sum_{A} U_{A} 2\Delta q_{A} \left[\frac{1}{2} \sum_{i} n_{i} \sum_{\mu(A)} \sum_{\nu} c_{\mu i}^{*} c_{\nu i} \frac{\partial S_{\mu\nu}}{\partial R_{c}} + c_{\mu i} c_{\nu i}^{*} \frac{\partial S_{\nu\mu}}{\partial R_{c}} \right]$$
(2.82)

$$= -\sum_{i} n_{i} \sum_{\mu} \sum_{\nu} \left[\sum_{\nu} c_{\mu i}^{*} c_{\nu i} \frac{\partial S_{\mu\nu}}{\partial R_{c}} + c_{\mu i} c_{\nu i}^{*} \frac{\partial S_{\nu\mu}}{\partial R_{c}} \right] U_{A(\mu)} q_{A(\mu)}$$
(2.83)

$$= -\sum_{i} n_{i} \left\{ \sum_{\mu} \sum_{\nu} c_{\mu i}^{*} c_{\nu i} \frac{\partial S_{\mu \nu}}{\partial R_{c}} U_{A(\mu)} \Delta q_{A(\mu)} \right.$$
(2.84)

$$+\sum_{\nu}\sum_{\mu}c_{\nu i}c_{\mu i}^{*}\frac{\partial S_{\mu\nu}}{\partial R_{c}}U_{A(\nu)}\Delta q_{A(\nu)}\bigg\}$$
$$=\sum_{i}n_{i}\sum_{\mu}\sum_{\nu}c_{\mu i}^{*}c_{\nu i}\frac{\partial S_{\mu\nu}}{\partial R_{c}}\left[U_{A(\mu)}\Delta q_{A(\mu)}+U_{A(\nu)}\Delta q_{A(\nu)}\right].$$
(2.85)

Equations 2.80, 2.85 show that both the energy and force perturbation from the electronic constraint potential vanish, if the constraints are well fulfilled after electronic convergence.

2.8 Methods of QM/MM coupling

My primary interest rests on the description of reactive events at hybrid interfaces, which imposes the necessity to model such interfaces with sufficient realism. The size of the models needed to properly describe a surface or interface leads to extreme computational cost. However, at solid/liquid or solid/polymer hybrid interfaces, the large difference in rigidity between the solid and liquid or polymer sides causes large parts of the solid surface to be subject to only small mechanical distortions by a single reactive event. Therefore, this part of the surface can be regarded as an external bath for the QM calculation. Classical force fields are in most cases sufficiently accurate to model this bath. In many cases, even fixing the external bath, thus avoiding to model its internal interactions at all, can give satisfactory results.

To couple theoretical modeling at different levels of detail within a single system, two different approaches are currently in use: *additive* and *subtractive* schemes. Important implementations of the latter are the ONIOM[54] method and its predecessor IMOMO[55]. Here, in the first step, energy and gradients for the whole system are calculated using the less complex *low-level method*. Subsequently, energy and gradients of the part of the system to be treated with the more detailed *high-level method*, the high-level or QM cluster, are calculated with both the low-level and high-level methods. Finally the low-level contributions of the high-level cluster are subtracted from the full system result and the high-level energy and gradients are added:

$$E_{\text{full}}^{\text{ONIOM}} = E_{\text{full}}^{\text{low}} - E_{\text{hlc}}^{\text{low}} + E_{\text{hlc}}^{\text{high}}$$
 (2.86)

$$\vec{F}_{\text{full}}^{\text{ONIOM}} = \vec{F}_{\text{full}}^{\text{low}} - \vec{F}_{\text{hlc}}^{\text{low}} + \vec{F}_{\text{hlc}}^{\text{high}}$$
(2.87)

where the superscripts denote the low-level, high-level and ONIOM methods, the subscripts denote the full system and the high-level cluster (HLC). A major drawback of this method is, that both parts of the system must be described using the low-level method. This makes the subtractive scheme unsuitable for the QM/MM examination of reactive events, unless a reactive force field is available. However, such force fields are rather difficult to handle and their development is not as far advanced as for the non-reactive case. Based on these considerations, I choose to focus on the additive coupling scheme:

In contrast to the subtractive scheme, the additive scheme directly couples the low- and high-level zones, by partitioning the Hamiltonian:

$$\hat{H} = \hat{H}^{\text{high}} + \hat{H}^{\text{low}} + \hat{H}^{\text{high/low}}$$
(2.88)

which avoids low-level calculations on the high-level zone, but on the other hand imposes the problem of formulating a suitable high-/low-level coupling Hamiltonian.

The popular hybrid quantum mechanical/molecular mechanical (QM/MM) [56–63] approach combines the advantages of quantum mechanical methods in describing chemically active regions with a description of the remaining system by interatomic potential functions as force fields [64] or by ion-pair potential functions [65].

Since the introduction of the QM/MM idea around the mid-1970s [56], numerous studies have been conducted examining both performance of different schemes as well as interesting applications to various solution and catalytic systems [61, 62, 66–80]. These previous studies have clearly demonstrated that carefully applied QM/MM methods can provide useful insights into chemical mechanisms in complex systems that are difficult to obtain otherwise.

In commonly used QM/MM schemes, the Hamiltonian operator of the entire system, \hat{H} , is written as the sum of those for the QM partition, \hat{H}_{QM} , the MM partition, \hat{H}_{MM} and the interaction between

the two, $\hat{H}_{\rm QM/MM}$, The precise expression of $\hat{H}_{\rm QM/MM}$ varies but generally has contributions from electrostatic, van der Waals, bonded interactions, and possibly additional constraints [57],

$$\hat{H}_{\rm QM/MM} = \hat{H}_{\rm QM/MM}^{\rm elec} + \hat{H}_{\rm QM/MM}^{\rm vdW} + \hat{H}_{\rm QM/MM}^{\rm bonded} + \hat{H}_{\rm QM/MM}^{\rm cons}$$
(2.89)

The bonded terms and constraints (e.g., fixed bond distance between boundary QM and MM atoms) are used for keeping the proper connectivities and geometries when cutting through covalent bonds at the QM/MM interface. The QM/MM van der Waals terms can be optimized to improve properties such as distribution of MM groups around the QM group [81]. The electrostatic component, which is missing in some early implementations for organometallic systems [60], is crucial for the investigation of reactions in polar surroundings like water or many solids.

2.8.1 The QM/MM boundary

An issue that has been repeatedly raised, concerns the treatment of the QM/MM boundary. The interaction between MM atoms and nearby QM atoms should be carefully treated to reliably describe the effect of the environment on chemical properties of the QM region. Complications in the calculation of equation 2.88 arise in particular if the QM/MM partition involves dividing the system across covalent bonds.

The large number of proposed hybrid methods differ in the way this problem is dealt with and which contributions of equation 2.89 are calculated quantum mechanically. The most straightforward approach involves saturating dangling bonds by link atoms, which are typically chosen as hydrogen atoms between the QM host atom (QMH, see Fig. 2.1) and the MM host atom (MMH) [57]. The link atom (QML) is treated at the QM level, and may be subject to an angular and distance constraint to lie along the bond between QMH and MMH at a fixed bond distance. The link atom typically interacts with MM atoms through electrostatic terms but not through van der Waals terms.

Instead of regular hydrogen atoms, hydrogen-like atoms or



Figure 2.1: Illustration of a covalent bond crossing the QM/MM boundary, showing the MM host atom (MMH), QM host atom (QMH) and QM link atom (QML).

pseudo halogens have been used to terminate the QM region [82, 83]. In those approaches, the link atom coincides with the MMH. The electronic nature of this atom is modified to mimic the behavior of the MM host atom or MM host group (MMHG). Instead of using pseudo-atoms as QML, the bond QMH–QML distance is often scaled so smaller values than their equilibrium bond length. This approach is taken from the general practice of constructing 2D-slab models of solid state interfaces, where hydrogen atoms are often used to terminate the dangling bonds on the backsides of the adjoined layers. As the symmetric-antisymmetric splitting of two molecular orbitals is proportional to the overlap S of the underlying atomic orbitals, which in turn varies inversely with the bond distance, reducing the QMH–QML distances can often shift spurious gap states originating from the QMH–QML bonds out of the band gap.

Other approaches to the QM capping problem include the use of hybrid orbitals [56] such as the localized self consistent field (LSCF) [84–87] and the generalized hybrid orbital method (GHO) [88, 89].

Here, I write the potential energy of the QM/MM system as (see equation 2.88):

$$U^{tot} = \left\langle \Psi \left| \hat{H}_{QM} + H_{QM/MM}^{ele\hat{c}} \right| \Psi \right\rangle +$$

$$U^{vdW}_{QM/MM} + U^{bonded}_{QM/MM} + U_{MM}$$
(2.90)

where Ψ is the electronic wave function of the QM region using the SCC-DFTB method. The operator describing QM/MM electrostatic interactions, $H_{QM/MM}^{elec}$, has the form of Coulomb interaction between the MM point charge Q_A and the Mulliken charge Δq_B on the QM atom [52]

$$H_{QM/MM}^{elec,pointcharges} = \sum_{A \in MM} \sum_{B \in QM} \frac{Q_A \Delta q_B}{|\mathbf{r}_A - \mathbf{r}_B|}$$
(2.91)

(cf. equation 2.67).

In practice, the QML often fall very close to the MMH, which can cause severe problems in the quantum mechanical description. Many different approaches have been developed to overcome this difficulty in biochemical applications [61, 90], however, most of these are not applicable to the solid state systems, which are the primary interest of my work. One example is the charge deletion approach, relies on the (formal) neutrality of groups within the examined amino acids or monomers. The charge of the MMH atom is simply deleted and the neutrality of the group is restored by applying compensating charges to the other atoms in the group.

In contrast, the approach to apply a Gaussian broadening to the point-charge distribution of the MM atoms, however, can be transferred without difficulties. The idea of this approach is to reduce the short-range influence of an atomic charge, while retaining the point-charge character at long distances. This is achieved by applying a Gaussian broadening of standard deviation σ to the point charge. This is justified by the fact that atomic point charges actually represent a point-like nuclear charge which is surrounded and (partly) shielded by a spatially extended electron distribution. The mathematical formulation by means of a Gaussian function is chosen for the sake of mathematical simplicity: the coulomb interaction is simply scaled by a an error-function prefactor, so that the coupling Hamiltonian becomes:

$$H_{QM/MM}^{elec,gaussharges} = \sum_{A \in MM} \sum_{B \in QM} \frac{Q_A \Delta q_B}{|\mathbf{r}_A - \mathbf{r}_B|} \cdot \operatorname{erf}\left(\frac{|\mathbf{r}_A - \mathbf{r}_B|}{\sigma}\right).$$
(2.92)

(cf. equation 2.69) The property of the error-function to vanish at $x \to 0$ and quickly converge to unity at $x > \sigma$, scales down the influence of a close-by point-charge while maintaining the influence of the further parts of the charge distribution. Since the error-function term converges to unity for $\sigma \to 0$, equation 2.91 can be regarded as the limit of equation 2.92 for vanishing size of the charge-distribution. σ should be chosen appropriately, to alleviate the quantum mechanical problems between QML and MMH, while keeping the coulomb interaction between QMH and MMH intact.

Chapter 3

Modeling Chemical Reactions

3.1 Reaction energetics at 0 K

At zero temperature, the transition between two stable states of a system follows a *minimum energy* path (MEP) on the system's potential energy hypersurface (PES). It is defined as the path connecting the minima in a manner that the potential energy gradients vanish in all directions orthogonal to the path. The MEP is the transition route which requires the least energy to follow. At finite temperatures the system can deviate from the MEP with the extent of the deviations governed by the relation between the depth of the MEP valley and the thermal energy. Maxima along the MEP and their associated geometries are termed transition states¹ and are saddle points of first order on the PES. For a single step reaction, the energy difference between the reactant and the transition state is called the barrier energy

$$E_{\rm b} = E_{\rm tot}^{\rm max} - \sum_{k}^{reactants} E_{\rm tot}^{k}.$$
(3.1)

(Note that by definition $E_{\rm b} \ge 0$.)

The energy difference between two local minima defines the reaction energy ΔE of the corresponding reaction. By convention, it is defined as

$$\Delta E = \sum_{k}^{products} E_{\text{tot}}^{k} - \sum_{k}^{reactants} E_{\text{tot}}^{k}.$$
(3.2)

A reaction with negative reaction energy is called exothermic, as energy is released by the system. Analogously, a reaction with positive energy is called endothermic. The terms exothermicity and endothermicity are synonyms for the energies of exothermic and endothermic reactions, respectively. The calculation of ΔE of any reaction is straightforward, it only requires the calculation of product and reactant energies by means of geometry optimization of the respective compounds.

3.1.1 Finding barrier energies

Over the years, a large number of methods to find the saddle point(s) of a given transition on a specific PES have been developed. The conventional approach is to search for a system configuration in which

¹Some authors distinguish between the transition *state* and the transition *structure* [2], in which the former refers to a free energy path and only the latter to an MEP. I choose not to follow this convention, as it is not followed consistently throughout the literature and prone to confusion. Therefore I prefer to clarify in each case, whether I am referring to free or potential energies.



Figure 3.1: Illustration of two adiabatic mapping path-searches in a Müller-Brown Potential [91] using differently defined reaction coordinates. The parallel solid lines mark the lines of minimization perpendicular to the chosen reaction coordinate. After [92].

its matrix of energy second derivatives with respect to the atomic degrees of freedom $r_i, j \in 1...3M$

$$\begin{pmatrix} \frac{\partial^2 E_{\text{tot}}}{\partial r_1 \partial r_1} & \frac{\partial^2 E_{\text{tot}}}{\partial r_1 \partial r_2} & \cdots & \frac{\partial^2 E_{\text{tot}}}{\partial r_1 \partial r_{3M}} \\ \frac{\partial^2 E_{\text{tot}}}{\partial r_2 \partial r_1} & \ddots & \vdots \\ \vdots & & \ddots & \vdots \\ \frac{\partial^2 E_{\text{tot}}}{\partial r_{2M} \partial r_1} & \cdots & \cdots & \frac{\partial^2 E_{\text{tot}}}{\partial r_{3M} \partial r_{3M}} \end{pmatrix},$$
(3.3)

called the Hessian matrix, has exactly one negative eigenvalue. This so-called surface walking is performed by following the Hessian's eigenvectors, which can be very computationally demanding if analytical second derivatives are not available. Since the numerical evaluation of the Hessian demands $2(3M)^2$ total energy calculations, such algorithms are impractical for systems with a large number of degrees of freedom. Interface reactions are such problems, since a realistic description of the surfaces generally demands a large number of movable atoms.

One class of methods developed to reduce the computational costs are path sampling or chain-of-states methods. They explore reaction paths and do not aim at locating the exact minima and maxima along a reaction pathway, but rather on sampling the total energies along the path. The simplest of these methods is the adiabatic mapping approach, but other methods have been developed to overcome the limitations of this rather simplistic approach. These methods work on the principle of iteratively refining an initial reaction coordinate guess, either during the construction of the reaction path, as in the growing string method [93], or by refining an initial guess of the whole path, as in the nudged elastic band approach, outlined in section 3.1.2 below.

Adiabatic mapping [94, 95], also referred to as the drag method, scans the PES along one or more predetermined reaction coordinates, while minimizing the total energy in all orthogonal degrees of freedom. This reduces the problem of finding the MEP to a number of constrained geometry optimizations equal to the desired number of samples along the path, completely avoiding the calculation of second derivatives for the path search. However, the necessity to define a suitable reaction coordinate in advance is a serious drawback, as it can be very challenging to do so without excluding large portions of the PES *a priori*. This problem is illustrated in Fig 3.1. Note that, although the choice seems obvious in this simple, two-dimensional case, in practical systems with a large number of degrees of freedom, this can be very different. Additionally, the saddle point is not obtained directly but only approximated by the samples closest to it, so that the barrier energy and structure must be interpolated. This limitation is,
however, offset by the robustness of these methods in terms of convergence [94] and their inherent ability to describe more complicated concerted reactions, which exhibit several saddle points along along the MEP.

More sophisticated techniques of surface walking [96–101] rely on the educated guess that the eigenmode of the smallest force constant leads to a saddle-point. Therefore they rely on optimizing the geometry to a saddle point, starting from the reactant configuration, climbing uphill along the smallest frequency eigenmode. But still, these methods require the costly calculation of the full Hessian.

To overcome this problem, a large number of approaches have been developed. They comprise, among others, the method by Dewar, Healy and Steward[102], the ridge method by Ionova and Carter[103] or the dimer method[104] by Henkelman and Jónsson, but also the conjugate peak refinement algorithm (CPR) by Fischer[105]. The first three methods use a pair of images which is advanced towards the saddle point, in an attempt to place the images close to each other on both sides of the transition state. The idea behind these methods is to perform surface walking without the calculation of the whole Hessian. Instead, the second derivative is only calculated in the direction of smallest curvature, using a finite-difference approximation. An improved version of the dimer method by Heyden and Keil [106] uses a modified representation of the dimer to avoid two total energy calculations per geometry iteration.

The CPR method relies upon line minimizations along linearly interpolated reaction path segments. Hence it is able to describe reaction paths with several local minima and maxima, yielding the exact transition state(s) and intermediary configurations. It can be regarded as a hybrid method between surface walking and the chain-of-states methods described below.

3.1.2 Nudged elastic band

Within the category of the chain-of-states methods, the nudged elastic band[107] (NEB) approach is one of the most prominent. As it is the main path-search method used in this work, I shall describe it in detail. In NEB, the intermediate states are called images. They are are connected by virtual springs to distribute the images evenly along the MEP. NEB differs from other chain-of-states methods[94] in that along the path direction, only spring forces are regarded, the tangential components of the calculated atomic forces are neglected. The chain of images is then optimized to minimize the NEB force for all intermediate images along the path, usually under the constraint of fixed start- and end-geometries. The even spacing of images along the sampled MEP helps to avoid the so-called valley-hopping problem: for many MEP search methods it is not assured, that the path segments on the product and reactant sides belong to the same PES valley. In that case, the maximum along the calculated MEP does not refer to the reaction barrier, but to the (higher) barrier of changing between the two reaction mechanisms (cf. figure 3.1, which illustrates the problem for adiabatic mapping).

As stated in section 3.1.1, the barrier energy must be interpolated when using a path-sampling method. This interpolation is frequently performed by a cubic spline fit of the image energies, with the gradients at the start- and end-images set to zero. Another approach is to fit a cubic polynomial to each segment connecting two images, using the tangential *real force* (i.e. calculated force) components to determine the energy gradient at each image[108].

A more elaborate version of NEB is the ANEB method[109], which uses adaptive spring forces proportional to the image energy, in order to achieve an aggregation of the images around the transition state. This improves the quality of the MEP estimate in the vicinity of the transition state, without imposing the greater computational cost of using a larger number of images, by locally raising the sampling resolution.

The Climbing Image NEB method (CI-NEB)[110] uses the image closest to the transition state (identified by its total energy), as a starting geometry for a saddle point refinement, using the rest of the MEP estimate to obtain a local reaction coordinate at the image being moved to the transition state and inverting the gradient component, parallel to this coordinate. In this context, it can be understood as a synthesis of standard NEB and a surface walking method. Similarly, it is a frequently employed approach, to use the highest energy NEB image as the input configuration for a surface walking algorithm.



Figure 3.2: Illustration of an NEB path optimization in a Müller-Brown Potential [91]. a) initial guess b) intermediate path estimate, c) final path estimate, d) path interpolation between images.

3.2 Beyond the minimum energy picture

For many applications, the reaction energies and MEPs provide sufficient information. Naturally, the quasi-static picture, neglecting temperature effects, is most suitable to situations in which reaction energonicities and barriers are large, when compared to the thermal energies. If, however, that is not the case, e.g. when solvent effects or van-der-Waals bonding are important, entropic effects must be taken into account and therefore free energy differences and paths must be calculated.

The Gibbs free energy G, in the following just free energy, is defined as

$$G = U - TS + PV, \tag{3.4}$$

where the internal energy $U = E_{\text{tot}} + E_{\text{kin}}$ is the sum of potential and kinetic energies, T the absolute temperature, S the entropy and PV the volume work needed to "make room" for the system at constant pressure P. Note, that the last term is only meaningful, if the simulated system interacts with an outside system via an identifiable wall. The free energy difference ΔG of a reaction gives the outside work that can be extracted from or must be invested into a reaction, the free energy barrier of a reaction describes the amount of outside work necessary activate it. Via the entropy term, the free energy can differ significantly from the (non-free) reaction energy and barrier.

Thermodynamic simulation Macroscopic thermodynamic properties, are always averages of their microscopic constituents. Therefore, either a time- or ensemble average must be performed to calculate them. The latter approach is the basis of Monte-Carlo (MC) methods, first employed by Metropolis et. al. [111] in which a statistical sampling of configurations according to a Boltzmann distribution is performed. I shall not go into any more detail here, as I do not use atomistic Monte-Carlo methods in this work.

The other possibility to obtain a thermodynamic average is by time-averaging over the trajectory of the examined system. To obtain these, the equations of motion of the pertinent system must be solved. In the case of a chemical reaction, these are the EOMs of the atomic nuclei. Most frequently, the atoms are treated classically, using Newton's EOM

$$\dot{\mathbf{R}}(t) = \frac{1}{\mathbf{M}} \left. \frac{dE_{\text{tot}}}{d\mathbf{R}} \right|_{t},\tag{3.5}$$

regardless whether the interatomic forces are calculated quantum-mechanically or by means of classical (empirical) force-fields. Thus a time-resolved trajectory of the molecular dynamics (MD) is obtained.

The EOM are generally solved by integrating them under the starting conditions of some initial atomic positions, which are often chosen as a minimum energy configuration, and a set of Boltzmann-distributed, random atomic velocities. The correct dynamics of the system can only be captured, if the integration time-step is less than $\frac{1}{2}$ of the shortest atomic vibration period in the system², which leads to time steps of ~ 10^{-15} sec, if hydrogen is present in the system. This severely limits the time-scales accessible by molecular dynamics. Approaches to overcome this limitation are based on the assumption that certain internal vibrations of a molecule are irrelevant to the dynamics on the timescale of interest. In this case, they can be neglected, either by constraining the relative positions of the respective atoms [2], or by coarse-graining approaches, in which whole groups of atoms are mapped to bead-like superatoms [115–117]. Nevertheless, explicitly following the time evolution of a system severely limits the accessible time scales, typically to a maximum of a few ps with *ab initio* energies and forces and < 1 μ s with classical force fields.

3.3 Modeling rare events

 $^{^{2}}$ This can be understood in the context of Nyquist-Shannon-Whittaker sampling theorem [112–114].



Figure 3.3: Illustration of a rare reactive event. The system performs a large number of vibrations, attempting to cross the barrier. After [118].

longer time scales.

When faced with rare reactive events, i.e. transitions between minima separated by barriers high in energy with respect to thermal energies at temperatures of interest, the methods described in section 3.2 generally fail to describe the timeevolution of the system from state to state³. Figure 3.3 illustrates the problem: The system undergoes a large number of vibrations, while most of these attempts to cross the barrier remain unsuccessful. It is not only uneconomical to simulate each of these, but in many cases the computational cost is prohibitive. At the same time, the sampling of the PES in the vicinity of the transition state is coarse, so that the quality of the thermodynamical averaging in this crucial region is relatively low. The latter problem can be solved by biased MD techniques, like umbrella sampling [2], however, they do not give access to

A very successful ansatz to model the time development of such rare events is the Kinetic Monte Carlo (KMC) method [118, 119], which as been applied to a wide range of topics, such as radiation damage annealing [120], surface adsorption, diffusion and growth [121–123], or semiconductor processing [124]. The basis of this method is to solve the time-scale problem, by operating on a dynamic time step. In contrast to the MD technique, where the system is developed along the time axis by integrating the EOMs over a pre-determined time step, here the time the system stays in its current state *i* before making a transition, is determined. To this end, the rate constants k_{ij} for the transitions from state *i* to each adjacent state *j* are calculated. The probability $p_{ij}(t)$ that a system has not undergone the transition to state *j* is assumed to be

$$p_{ij}(t) = k_{ij}e^{-k_{ij}t}. (3.6)$$

This assumption is true, as long as the system stays in each state i long enough to "forget" from which state it arrived, i.e. subsequent transitions are uncorrelated. This is true for rare events, as defined above. If all rate constants for all transitions are known, the residence time of a system in state i and the final state of the transition can be determined randomly. This way, a trajectory of the system trough the minima of its PES can be determined. The great advantage of this method is, that not every *potential* transition must be simulated, as in MD, but only *actual* transitions. The crucial point of this method, however, is that all possible transitions with their associated rate constants must be known in advance.

The difference between KMC and the MC methods, mentioned in section 3.2, is that the latter aim at sampling the PES of a system with thermodynamic weighting to calculate the free energies of certain points of the PES. KMC, in contrast, aims at sampling the kinetics of the system between them. Therefore, KMC does not only work on a (usually) larger time-scale than MD, but also on a larger length scale — the degrees of freedom along the pathway(s) are only sampled at the minima and saddle points while the degrees of freedom normal to the path are neglected.

The rate constants for each pathway can be calculated from the potential energy surface, using the transition state theory⁴ [125, 126] (TST). The rate constant k_{ij} is taken to be the equilibrium flux through a dividing surface, separating states *i* and *j* in phase space [118]. As an equilibrium property, the TST k_{ij} can be determined without examining dynamical trajectories, it is simply proportional to the Boltzmann probability of the system being at the dividing surface, relative to the probability of being in state *i*. Often, the harmonic transition state theory (HTST) is used. Here it is assumed, that the PES is

³Here, a state is defined as a local minimum of the PES, separated by barriers from other local minima.

 $^{^{4}}$ Or, more accurately, chemical transition state theory, which should not be confused with Slater transition state theory. The latter describes the transition of electrons between electronic eigenstates of a system.

3.3. MODELING RARE EVENTS

harmonic in the vicinity of the local minima i and j, as well as in all directions normal to the transition at the transition state between them. In this case, the rate constant becomes

$$k_{ij}^{\text{HTST}} = \frac{\prod_{i}^{3N} \nu_{i}^{\text{min}}}{\prod_{i}^{3N-1} \nu_{i}^{\text{sd}}} e^{-\frac{E_{b}^{\text{static}}}{b} \mathbf{B}^{T}},$$
(3.7)

where $E_{\rm b}^{\rm static}$ is the static barrier height of the transition, and ν_i are the non-imaginary mode frequencies at the PES minimum and saddle points. As can be seen in equation 3.7, the temperature dependence is strictly exponential. Experience shows, that the prefactors are frequently within the range of $10^{12} \dots 10^{13} \sec^{-1}$, wherefore it is often arbitrarily set to a value from that range, to save the effort of calculating all vibrational modes at the minima and saddle points[118].

Recent developments aim at coupling KMC simulations to continuum descriptions, e.g. using phase-field models [127]. On the one hand, this enables the simulation of even larger length scales, as with KMC alone, on the other hand, it allows to include processes like diffusion within the bulk phases on both sides of an interface, without having to model these in the KMC framework, the computational cost of which is often prohibitive.

Chapter 4

QM/MM Embedding of DFTB clusters at solid surfaces

The appeal of QM/MM embedding schemes lies in their capacity to describe an extended system with nearly quantum-mechanical accuracy at much lower computational cost than a fully quantum mechanical calculation. Figure 4.1 shows the mechanical and electronic changes of a γ -Al₂O₃ surface along the MEP of the adsorption of a small organic molecule. It demonstrates the local character of the mechanical and electronic changes during the examined reactions and so proves that it is indeed justified to treat different parts of this system at different resolutions. These representative results were obtained from fully quantum mechanical calculations using SCC-DFTB (cf. chapter 5). The surface atoms are only displaced significantly within a very short range around the adsorption site (cf. figure 4.1(a)). The movement further away from the adsorbate is limited to re-orientations of polar OH groups, which are driven by the Coulomb interaction and can be well described using molecular mechanics. At the same time, significant charge transfer virtually only occurs within the adsorbate and up to its second-nearest neighbors on the surface (cf. Figure 4.1(b)). They suggest, that full quantum mechanical precision is only required within a limited range around the adsorption site, while the influence of the largest part of the surface is electrostatic. These parts of the surface undergo only small movements and electronic changes and can therefore be treated by classical force-fields or even kept fixed.

By determining, which part of the system requires which level of detail in its description, and only applying methods of the required level to each part, QM/MM coupling allows to obtain the desired



Figure 4.1: RMS displacement and maximum atomic charge difference during the adsorption of $AMEO^{(hyd)}$ on γ -Al₂O₃ (cf. chapter 5).

results economically. The techniques to calculate total energies and forces in a QM/MM coupling scheme have already been described in section 2.8. In this chapter, I shall focus on the treatment of the QM/MM boundary on the QM side of such an additive coupling scheme. The MM part of the calculation is modeled as a distribution of fixed charges, and the mechanical coupling by fixing the positions of the QMH and QML atoms.

4.1 Challenges of QM/MM embedding in solids



Figure 4.2: Illustration of the bonding situation of a fictitious QM cluster, cut from a surface slab model of γ -Al₂O₃ around the adsorption site of a small organic molecule.

QM/MM embedding approaches have been applied very successfully to biochemical and polymer systems for several years (cf. section 2.8). Characteristically, the primary structure of these systems is a one dimensional chain¹. Additionally, polypeptides and polymers comprise only a limited number of monomer types, many of which contain $-H_2C-CH_2-$ motives. The, nearly unpolar central C-C bond of these is a natural choice for a QM/MM boundary. All of this lets the number of covalent QM/MM bonds be comparatively limited and the bonds easily be described with good precision.

In solids, however, the situation is different. One of the characteristics of solids is the high coordination of each heavy atom by other heavy atoms. In the systems of interest for this work, i.e. SiO_2 and Al_2O_3 , (aside from interfaces or defects) each atom has at least as many nearest neighbors, as it has natural valences. Additionally, every single bond in these systems is polar. This has important consequences for the coupling between QM and MM zones within a single calculation.

While in biochemical systems, most problems can be avoided by appropriate choice of the QM cluster, i.e. problematic QM–MM links can be avoided by extending the cluster to include them in the QM zone

 $^{^1}$ with some side chains

and place the boundary at a more favorable site, such possibilities are very limited in a solid. First of all, polar bonds cannot be avoided in a polar material. Secondly, extending the QM cluster also increases the number of QM–MM links and is therefore likely to cause more problems² than it solves. And lastly, a QM cluster containing an interface in a polar solid is usually charged, if it does not have the bulk stoichiometry and symmetry and no manipulation of the charges is applied. In a bulk polar solid, where the polarity is caused by charge transfer between atoms of different elements, any cluster of the correct stoichiometry and symmetry should be neutral. As the trials show, this can lead to serious distortion of the electronic structure of the QM cluster compared to the fully QM treated system.

4.2 Embedding approaches for solid state materials

4.2.1 Representation of the external field

The first issue to be addressed in a QM/MM coupling scheme is, how to implement the coupling terms in the QM zone Hamiltonian. The quantum mechanical issues in this, have already been discussed in chapter 2.8, in the following I describe the tested approaches in their practical implementation.

Simple point charge embedding

The simplest scheme to implement is the representation of the electric field of the MM zone as a distribution of point charges corresponding to the MM partial charges at the respective atomic positions. To take into account the effect of the external point charges on the QM calculation, a coupling term is added to the total Hamiltonian, as described in equations 2.67, 2.91 (cf. chapter 2.8 on page 20). The point charges can either be obtained from the force-field or, as it is done here, from a QM reference calculation on a small periodic unit cell. In this work, the DFTB Mulliken populations obtained from these reference calculations.

One of the problems that can arise from using point charges, are unphysical populations or even convergence failure, in case QML atoms are too close ($< \sim 0.4$ Å) to the point charge of their respective MMH atom. This can lead to severe problems in the calculations, as discussed in chapter 2.8.1 on page 21.

Uniformly Gaussian blurred point charges

To eliminate such problems at the QM/MM frontier, the charge of the MMH atom is often removed and distributed among the remaining atoms of its neutrality group, e.g. a single amino acid. This approach [61], which is successful for biochemical applications, it cannot be transferred to the solid state, as no general definition of a neutrality group is possible there³.

In a more elaborate approach, the point charges are replaced by Gaussian-shaped charge distributions of variance σ . This effectively reduces the close-range intensity of the electric field, while maintaining the overall charge of the full charge distribution, introducing only a small perturbation of the long-range field (cf. equations 2.69,2.92 in section 2.8.1). Physically, replacing the point charge by a spatially extended charge distribution is justified, since atoms are not points but formed by the combination of nuclear charge and the charge distribution of its electrons. The choice of a Gaussian charge distribution is arbitrary and motivated by mathematical convenience. σ should be chosen so that the embedded QM cluster reproduces the properties of a fully QM calculation as closely as possible.

For a heteronuclear material element-specific, i.e. non-uniform, Gaussian blurring of the atomic partial charges would be possible. I choose not to do this, as it would increase the number of parameters in the embedding too much.

 $^{^{2}}$ In the treatment of the QM–MM boundary. Of course, the primary criterion for the cluster size is determined by the extent of the effects which have to be treated quantum mechanically.

³Charge neutrality groups are often defined for ionic crystals, but in the case of disordered systems, such as γ -alumina, or interfaces between solid phases, the description of which is the goal of this work, these approaches cannot be applied.

4.2.2 Treatment of the dangling QM–MM bonds

The second issue of QM/MM coupling is the treatment of the dangling bonds which occur on the QM cluster surface. The following approaches can be combined in any manner with the electrostatic coupling methods described above.

Simple link atoms embedding (SLA)

In the simplest and most popular approach, the dangling QM–MM bonds are completely ignored on the MM side and the QMH–MMH bond distance is constrained to a fixed value. The bond on the QM side is then saturated by adding a hydrogen atom at its equilibrium bond distance to to the QMH.

Link-atom distance scaling

However, additional gap states are often induced by the QMH–QML bonds. If these states are unoccupied, they can be shifted out of the gap, by increasing the overlap between QMH and QML orbitals involved in the bond. This is achieved by shortening the QMH–QML distance below the equilibrium bond distance. Additionally, sometimes erroneously high charge transfer into the QMH–QML bonding state(s) can be alleviated by modulating the bond distance. When scaling the QMH-QML distance to higher values, it should be kept in mind, that the QML should not come too close to the MMH point charge, since convergence problems and other difficulties may arise (cf. section 4.2.1).

The link atom distance scaling was implemented by multiplying the QMH–QML equilibrium distance, determined from their tabulated covalent radii, with a link-atom distance factor (LADF).

Charge constraints

In addition to placing hydrogen saturators at the QM/MM boundary, it is also possible to constrain the Mulliken populations of the QMH atoms to the charges they (or their symmetry equivalents in a smaller cell) show in a full DFTB single-point reference calculation. The charge constraints are implemented as described in section 2.7.3.

4.2.3 Neutralization of the spurious cluster charge

The last, important issue is the neutralization of the artificial cluster charge, to avoid erroneous filling or emptying of the band edges. The schemes developed here aim at removing this artificial total charge of a cluster that arises as a result of cutting the cluster from the polar bulk (cf. figure 4.3). Desired charges, e.g. when examining the interaction of a charged amino acid with a surface, must not be neutralized by any of these methods. The cluster neutralization is independent on the electrostatic embedding, yet the approaches discussed here are tailored to link-atom termination of the dangling bonds.

Homogeneous Charge Subtraction (HCS) embedding scheme

As discussed in section 4.1, in polar systems, only special QM clusters are neutral. To cure this problem I artificially enforce the neutrality of the QM and MM zones by shifting part of the MMH's partial charge



Figure 4.3: Illustration of the QM zone neutralization. In a neutral polar material, each neighbor of an atom compensates a portion of its partial charge. (In most cases, this is formally achieved by the nearest neighbors only, and I will adhere to this convention.) The QM/MM boundary leads to the effect that the partial charges of the QMH atoms are not fully compensated within the QM zone(left). Overall neutrality of the QM cluster is restored by moving the missing compensating charge from the MMH atom onto the QML atom and thus into the QM zone (right).

to its associated QM link atom⁴ (cf. figure 4.3):

$$Q'_{i} = Q_{i} - \frac{Q_{\text{QM}}^{\text{tot}}}{N_{\text{QML}}} \forall i \in \text{QML}, \ j \in \text{MMH}, \ i \text{ terminates bond to } j$$
(4.1)

$$Q'_{j} = Q_{j} + \frac{Q_{\rm QM}^{\rm tot}}{N_{\rm QML}}$$

$$\tag{4.2}$$

where Q'_i , Q'_j are the modified QML and MMH charges; Q_i , Q_j are the respective original charges, $Q_{\rm QM}^{\rm tot}$ is the total QM cluster charge and $N_{\rm QML}$ is the number of QM–MM links (\equiv number of QML atoms, assuming that no higher-order or aromatic bonds cross the QM/MM boundary). After this rearrangement, both the QM cluster and MM zone are neutral, provided the whole system was neutral before. This eliminates the imperfect filling of valence or conduction band in the charged clusters. However, a spurious dipole moments at the QM/MM border is introduced:

$$\vec{d}_{\rm err} = \frac{Q_{\rm QM}^{\rm tot}}{N_{\rm QML}} (\vec{r}_{\rm MMHA} - \vec{r}_{\rm QML}).$$

$$\tag{4.3}$$

Since the MMH–QML distance is often very small (<0.1 Å) and the dipoles are normal to the QM/MM boundary, their influence is comparatively small. The error caused by these dipoles is smaller than the error resulting from the charged-cluster problem, as the results presented in section 4.3.3 show.

It should be noted, that this scheme depends on the QM cluster to be constructed in a way which ensures that all QMH-s and all MMH-s are of the same type, respectively.

Bond Charge Transfer Compensation (BCTC) embedding

The HCS scheme introduced above relies on the ability to construct a cluster where only one type of bonds cross the QM/MM boundary. This imparts severe limitations not only on the choice of QM clusters, but

⁴The charges of the QM zone atoms are not necessarily constrained during the embedded calculations, in fact the atomic charges of the QM zone core atoms must be free to be able to describe chemical reactions. Here the atomic partial charges are only used to determine the cluster total charge by summing them up.

also on the choice of examined systems. In compound materials, where a portion of the cluster surface corresponds to a non-polar crystal surface, the need for only one certain bond type crossing the border, will lead to a very rough cluster surface and an increased number of interrupted bonds which have to be saturated (cf. figure 4.2 on page 32). Additionally, this situation will tend to enforce increasing sizes, with unfavorable consequences on the computational cost. Furthermore, solid interfaces like SiC/SiO₂ cannot be treated in the QM zone, as the two phases make it impossible to limit the QM–MM links to just one bond type.

To overcome this limitation, I extended the HCS scheme to a more general formulation: The assumption of a homogeneous charge transfer for a specific combination of bond partners is retained. However, a matrix of per bond-type charge transfer parameters $dq_{a,b}$ is constructed. For a system with N elements, the $N \times N$ matrix Q has the form:

$$\mathbf{Q} = \begin{pmatrix} dq_{1,1} & dq_{1,2} & \cdots & dq_{1,N} \\ dq_{2,1} & dq_{2,2} & \cdots & dq_{2,N} \\ \vdots & \vdots & \ddots & \vdots \\ dq_{N,1} & dq_{N,2} & \cdots & dq_{N,N} \end{pmatrix} = \begin{pmatrix} 0 & dq_{1,2} & \cdots & dq_{1,N} \\ -dq_{1,2} & 0 & \cdots & dq_{2,N} \\ \vdots & \vdots & \ddots & \vdots \\ -dq_{1,N} & -dq_{2,N} & \cdots & 0 \end{pmatrix}$$
(4.4)

where the physical assumption that the charge transfer is caused by differences between the chemical elements leads to the zero diagonal matrix elements and the preservation of charges leads to the $dq_{a,b} = -dq_{b,a}$ antisymmetry. This approach is inspired by the charge increments formalism used in many force fields to set the atomic partial charges. To determine the $dq_{a,b}$ for a specific system, a set of linear equations, expressing the Mulliken charge Q_i of each atom of element *a* in terms of charge transfers with its bond partners was constructed:

$$Q_i = \sum_{b=1}^N \left\{ \begin{array}{cc} n_{a,b} \cdot dq_{a,b} & a < b\\ -n_{a,b} \cdot dq_{a,b} & a \ge b \end{array} \right\},\tag{4.5}$$

where $n_{a,b}$ is the number of bond partners of element *b*. In a model with *M* atoms, this procedure yields a set of *M* equations for the upper triangle of **Q** from (equation 4.4), *including* the diagonal elements. The diagonal elements are included for two reasons: first, it implementation is easier and secondly, the deviations of the diagonal elements from zero allow to assess the quality of the solution found for equations 4.5.

The equations are constructed from the results on the fully QM treated system. To solve equation. 4.5, I use the linear least squares method, since it is well known to be an efficient and precise method to solve an overdetermined system of linear equations[128]. It is robust against degeneracy introduced by periodic expansion of the underlying molecular model and scales favorably with the number of equations.

The modification of the formal atomic charges of MMH and QML is performed equivalently to the HCS method. Equations 4.1, 4.2 become:

$$Q'_{i} = Q_{i} - dq_{\mathrm{el}(i),\mathrm{el}(j)} - q_{\mathrm{hom}} \,\forall i \in \mathrm{QML}, \, j \in \mathrm{MMH}, i \text{ terminates bond to } j$$
(4.6)

$$Q'_{j} = Q_{j} + dq_{\mathrm{el}(i),\mathrm{el}(j)} + q_{\mathrm{hom}}$$

$$\tag{4.7}$$

where el(i) is the element of the QMH atom saturated by the QML atom i, el(j) is the element of MMH j and q_{hom} is a small homogeneous compensating charge. It becomes clear that HCS is a special case of the BCTC approach where $dq_{a,b}$ is approximated by $\frac{Q_{\text{QM}}^{\text{tot}}}{N_{\text{QML}}}$. The compensating charge q_{hom} is necessary since, unlike with HCS, the sum of $dq_{a,b}$ -s applied to the cluster will only neutralize it within the variance of the $dq_{a,b}$. q_{hom} compensates for this residual charge error by an additional homogeneous charge transfer between QM and MM zone, calculated as:

$$q_{\text{hom}} = \frac{1}{N_{\text{QML}}} \left(Q_{\text{QM}}^{\text{tot}} - \sum_{i}^{QML} \sum_{j}^{MMHA} dq_{\text{el}(i),\text{el}(j)} \right).$$
(4.8)

4.3 Validation of the QM/MM embedding in different materials

4.3.1 Evaluation Criteria

Electronic properties

In the framework of SCC-DFTB the atomic Mulliken population of the valence shell is varied selfconsistently. Therefore, the converged Mulliken charge of each atom should be the principal property for the evaluation of a QM/MM embedding scheme. From this follows, that the first evaluation criterion should be the sum of Mulliken charge differences on the atoms of the QM cluster between full SCC-DFTB and the QM/MM embedding scheme. This indicates an erroneous charge transfer between QMH and QML atoms:

$$\Delta Q^{\text{tot}} = \sum_{i \in \text{QM}} Q_i^{\text{QM/MM}} - Q_i^{\text{DFTB}}$$
(4.9)

where QM is the set of atoms in the QM cluster. It should, however, be considered, that the bond-termination might induce a tolerable amount of disturbance on the QM border atoms.

Besides erroneous charge transfer to or from the QML-s, charge oscillations within the cluster can be induced by the QM zone termination. Additionally, the choice of a suitable QM cluster, regarding its size, stoichiometry and the minimization of cross-zone bonds, can influence on the achievable quality of the QM/MM coupling. To detect intra-cluster charge oscillations and to facilitate comparison at different cluster sizes, the root of mean squares of QM atom charge deviations will be the second criterion:

$$RMSQ = \sqrt{\sum_{i \in QM} \frac{\left(Q_i^{QM/MM} - Q_i^{DFTB}\right)^2}{N^{QM}}}$$
(4.10)

The second, equally important property of the embedded QM cluster, is the reproduction of the density of states (DOS) and the Fermi energy $E_{\rm f}$. Ideally, the QM cluster should exhibit no additional gap states, although some very shallow ones might be acceptable, as long as their nature is similar to those of the band edges of the reference. Any other gap states would lead to severe distortion of the chemical behavior of the cluster, rendering the examination of chemical reactions impossible. Deviations in the Fermi level can be accounted for in reaction energetics but should, obviously, be avoided. However, comparison of the Fermi level between periodic and cluster calculations is difficult, since the periodic boundary conditions may introduce a global shift of the band structure, which does not influence energy differences between structures. Since my primary focus rests on molecules and clusters, I only regard the DOS at the γ -point, calculated in the conventional way by convolution of the eigenspectrum with a Lorentz function (which is simplified by the discrete eigenspectrum obtained from DFT(B)):

$$DOS(E) = \sum_{i=1}^{N} \frac{1}{\pi} \frac{s}{s^2 + (E - \epsilon_i)^2}$$
(4.11)

where N is the number of effective single-particle eigenstates, ϵ_i the *i*-th eigenvalue and s is the (arbitrarily chosen) half-width at half-maximum (HWHM) of the Lorentzians. I then examine the DOS of each cluster to check for spurious states within the gap of the periodic reference system. I write E_f with reference to the highest occupied molecular orbital HOMO energy of the respective reference system.

I check the DOS replication by two criteria: first I determine the overall shift of the DOS by finding the maximum in the cross correlation between reference DOS and the DOS of the examined embedded cluster:

$$R(\Delta E) = \int_{E} DOS(E - \Delta E) \cdot DOS_{ref}(E) dE.$$
(4.12)

As long as the densities of states are of reasonably similar shape, the cross-correlation is a good means to find the overall shift of the band-structure. Secondly, I integrate the number of states within the shifted energy range, corresponding to the gap of the reference DOS

$$G = \int_{E_V^{\text{ref}} + \Delta E}^{E_C^{\text{ref}} + \Delta E} \text{DOS}(E) dE, \qquad (4.13)$$

where E_V^{ref} and E_C^{ref} correspond to the valence and conduction band edges of the reference DOS.



Figure 4.4: The cross correlation between a reference density of states and the DOS of an embedded cluster (a) and sum of states within that shifted range (b). Here, the full model of the 2x1 reconstructed Si surface and a cluster of 29 Si atoms and 28 saturator atoms, embedded in 5.0 a.u. Gaussian-broadened charges are shown.

Figure 4.4(a) illustrates, how the band shift can be determined using the cross-correlation function. The cross correlation (blue line) has a distinct absolute maximum at +0.16 eV. This means that the cluster DOS must be shifted up by 0.16 eV to coincide best with the reference DOS. The two side maxima around ± 6.5 eV correspond to the superposition of the reference CB with the cluster VB and vice-versa. Figure 4.4(b) illustrates, how the number of gap states varies with the parameters of embedding. The Gaussian blur width has very little effect on the number of gap states in contrast to the link-atom distance scale. Here, downscaling the link-atom distance obviously introduces a large number of new states within the gap (cf. section 4.2.2).

Due to the product in the cross-correlation function (cf. equation 4.12), higher features of the DOS (i.e. the bulk bands) have a greater weight in determining the shift than, e.g. single gap states. Care must be taken in examining the cross correlation, if one of the densities of states has a high peak not present in the other, in this case the cross-correlation maximum can coincide with the superposition of this singular peak with one of the bulk bands.

Geometry reproduction

To check the quality of geometry reproduction, the geometry of the embedded cluster is optimized, keeping the QML and QMH atoms fixed and employing the conjugate gradients method. The root of mean squares displacement (RMSD) of the QM zone atoms, excluding the QML atoms is then calculated as the criterion for geometry reproduction:

$$\text{RMSD} = \sqrt{\frac{\sum_{i=1}^{N_{\text{QM} \notin \text{QML}}} |\mathbf{r}'_i - \mathbf{r}_i|^2}{N_{\text{QM} \notin \text{QML}}}},$$

where \mathbf{r}' are the optimized and \mathbf{r} the original atomic coordinates.

In addition to the RMSD, I also visually check the optimized geometries for qualitative changes, e.g. bond-breaking or -formation.

Since the geometry optimization is computationally highly involved, I only perform this check for the embedding parameters chosen from the electronic evaluation results.

Reaction Energies

Since reactions are the focus of this work, the ability of an embedding scheme to reproduce reaction energetics is the ultimate requirement: The enthalpy of a simple interface reaction is calculated, if an embedding scheme appears promising for a specific substrate, and compared to the results from a fully SCC-DFTB treated, periodic interface model.

4.3.2 The fully QM treated surface

The gain in computational speed, achieved by employing a QM/MM coupling scheme can only be utilized to gain efficiency, when the error imparted by this simplification remains within the bounds of tolerance imposed by the application. To asses the error introduced by partitioning a surface or interface model into parts which are treated classically or quantum mechanically, respectively, I start from the assumption, that any deviation from a fully quantum mechanical treatment, exhibited by a QM/MM coupled simulation, is erroneous⁵. The first step towards evaluating different QM/MM coupling schemes therefore lies in the examination of the fully quantum mechanically described surface to obtain references for the criteria introduced in section 4.3.1.

Computational details

All reference and test calculations are performed using SCC-DFTB, using the pbc-1 set of Slater-Koster files for Si-containing systems and the alo-1 set for the two alumina examples (cf. Chapter 5). I iterate the SCC calculation, until the total charge difference between two subsequent cycles falls below 10^{-5} a.u. Unless stated otherwise, I perform geometry optimization using a CG algorithm until the maximum force component is below 10^{-4} a.u. To avoid possible convergence problems due to nearly degenerate states around the gap, I apply a Fermi-Dirac distribution function with a temperature of 300 K to the occupation of the eigenstates. For the calculation of the DOS, I employ a half-width of 0.1 eV.

Classes of materials

Based on the intended application of the QM/MM coupling scheme, i.e. reactions at the γ -alumina surface, which has rather complicated properties, I will test the different embedding approaches on materials from different classes. I will start with a simple, ideally coordinated, homonuclear material – silicon. From there I shall advance to silicon oxides, which introduce polar, heteronuclear bonding but remain ideally coordinated. The third class of materials will be different phases of alumina, i.e. α -Al₂O₃ which is over-coordinated⁶ but still crystalline, and native or γ -Al₂O₃, which is over-coordinated and amorphous.

 $^{^{5}}$ The underlying assumption, that the fully periodic quantum mechanical simulation is free of errors, is somewhat problematic: It beats the idea that QM/MM coupling should make larger and hence more realistic models accessible. However, within the set of test-systems presented here, which are mostly undisturbed surfaces and interfaces, it can be assumed to hold.

⁶More precisely: each atom has more direct neighbors than formal valences.

Example surfaces

Since this work aims at surface and interface studies, all test- and reference systems chosen for the evaluation of QM/MM embedding schemes, contain some kind of surface. I perform the SCC-DFTB reference calculation for a small periodic model of each test system. In the following paragraphs, I describe the characteristics of of each test system as found in the reference calculations.

Si (Si-2x1)



Figure 4.5: SCC-DFTB total densities of states around the band gaps of the Si (2x1) (0001) surface (a) and bulk Si (b). For the bulk, the Γ -point DOS and a DOS from an 8x8x8 MP calculation are given, for comparison.



Figure 4.6: Structure and charge distribution (a) and atomic charge histogram (b) of the 2x1 Si(001) surface, determined using SCC-DFTB.

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The first reference surface is the 2x1 reconstructed Si (001) surface. I model the surface as a 2D slab showing the 2x1 reconstruction on one side and hydrogen termination of the dangling bonds at the opposite face. To accommodate a QM zone later on, the model is periodically expanded to include 2x2 reconstruction units, as it is shown in figure 4.6 (a)). The surface model is characterized by a non-polar bulk (a small perturbation in the form of a $\sim +0.1$ e charge of the lowermost Si layer is introduced by the H termination of dangling bonds) and charges of $\sim \pm 0.2$ e on the reconstructed atoms. In this homonuclear system (the saturator hydrogens are not part of the system being modeled), the calculation of BCT coefficients makes no sense, although the system shows a distinct charge transfer between neighboring silicon atoms in the reconstruction dimers. The BCTC approach, however, only uses the core charge to identify an atom type, so that it cannot describe this particular situation. Since the bulk is apolar, it makes much more sense to just avoid cutting through a reconstructed dimer than to further extend the cluster neutralization formalism.



Figure 4.7: Isosurface (in arbitrary units) of the localized density of states in a 8x8 Ålateral cutout of the Si (001) 2x1 reconstructed surface. Energy range -5.26 - -3.96 eV.

Figure 4.5(b) shows the DOS of bulk Si at the

gamma-point and using a 8x8x8 Monkhorst-Pack k-point sampling [11]. The DOS shows the typical behavior of SCC-DFTB, which gives a good reproduction of the direct band gap, but (due to the omission of d-orbitals) fails to reproduce the indirect gap of Si. The SCC-DFTB direct HOMO-LUMO gap of the surface model is ~0.89 eV. The DOS plot in Fig 4.5 (a) shows a narrowing of the HOMO-LUMO gap compared to bulk Si, which is caused by a peak of unoccupied states around mid-gap. In comparison to the bulk data, (taking into account an overall shift of the surface eigenspectrum towards lower energies), it appears that the VB–CB gap actually widens from ~1.4 eV to nearly 2 eV, while a peak of unoccupied states is introduced by the surface around mid-gap. Figure 4.7 shows the localized density of states, defined as the sum of the density contributions of the effective single particle eigenstates within a certain energy range:

$$LDOS = \frac{\sum_{i, E_{lo} < \epsilon_i < E_{hi}} |\Psi|^2}{E_{hi} - E_{lo}}$$

$$(4.14)$$

where $E_{\rm lo}$ and $E_{\rm hi}$ represent the high and low boundaries of the energy interval in question. It shows clearly, that the eigenstates corresponding to the DOS peak just below -4 eV are strongly localized to the reconstructed surface dimers. These results are in good agreement with earlier theoretical work, using DFT to examine Si surface reconstructions (cf. e.g. [129]).



Figure 4.8: Densities of states around the band gaps of the α -SiO₂ (a) and SSZ60 (b) reference structures.

α -Quartz



Figure 4.9: Structure of the 1x1 reconstructed α -SiO₂ surface model (a) and atomic charge histograms (b) from the SCC-DFTB reference calculation

The next evaluation system is one of the (0001) surfaces of α -quartz. It shows a 1x1 surface reconstruction by re-arrangement of siloxane bridges, which eliminates all dangling bonds. As in the Si surface model, one face of the 2D slab model is reconstructed, while on the other face dangling bonds are saturated by H atoms. The silica class materials are characterized by stronger polarity of the bulk, while the reconstructed surface shows no significant difference in polarity, compared to the underlying bulk (figure 4.9). The heteroatomic BCT coefficients in this model, listed in table 4.1, conform to the expectations from

Elements	H–H	H–O	H–Si	0–0	O–Si	Si–Si
$\mathrm{dq}_{a,b}$	0.000	0.000	-0.159	0.000	-0.262	0.000

Table 4.1: Bond charge transfer coefficients of the α -quartz surface model. The error is $\sigma = 0.019$.

experience. The homonuclear coefficients are $< 10^{-8}$ and their variance is reasonable, showing that the coefficients are of suitable quality.

The reference direct band gap of this surface is \sim 7.94 eV. As can be seen in Fig 4.8(a), the surface does not cause any deep gap states in this case, however, small DOS peaks close to the band edges appear, leading to a narrowing of the gap of \sim 1 eV.

SSZ60-zeolite



Figure 4.10: Geometry and Mulliken charge distribution (a) and atomic charge histogram (b) of SSZ60 Zeolite, calculated using SCC-DFTB.

The second silica class test system is a model bulk SSZ60 zeolite. It stands out from other references examined here, by not having an outer surface, but inner surfaces on the walls of its pores. In its electronic properties, it differs only slightly from the α -quartz phase, it is included to be able to assess the transferability of coupling schemes within a class of materials. Figure 4.10 shows a 2x2x2 periodically expanded version of the basic model for clarity. As can be seen from the charge histograms, the partial charges are very similar to the α -quartz phase. The O–Si BCT coefficient is equal to that in the α -quartz (cf. tables 4.1, 4.2) with a very reasonable error.

Elements	0-0	O–Si	Si–Si
$\mathrm{dq}_{a,b}$	0.000	-0.261	0.000

Table 4.2: Bond charge transfer coefficients of the bulk SSZ60 model. The error is $\sigma = 0.015$.

The HOMO-LUMO gap found in the reference calculation is ~ 9.33 eV. In this system, the DOS, plotted in Fig 4.8(b), does not show any striking features, which is to be expected, as a perfect bulk system is examined here.

α -Al₂O₃ (corundum)



Figure 4.11: SCC-DFTB densities of states around the band gaps of the α - (a) and γ - (b) Al₂O₃ reference structures, calculated using SCC-DFTB.



Figure 4.12: Geometry and Mulliken charges (a) and atomic mulliken charge histograms (b) of the α -Al₂O₃ (0001) surface from the SCC-DFTB reference calculation.

The last class of test materials are different phases of alumina. The first example is the highly ordered α -Al₂O₃ phase, also known as corundum or sapphire⁷. It has high symmetry and evenly distributed polarity of the bonds. The high degree of coordination (all atoms are over-coordinated) hints, that the bonding is much less covalent in nature than in the preceding examples. Yet, the polarity is comparable to silica and by no means ionic. As shown in table 4.3, the O–Al bond charge transfer is much smaller

Elements	H–H	H–O	H–Al	0–0	O–Al	Al–Al
$\mathrm{dq}_{a,b}$	0.000	0.278	0.000	0.000	-0.100	0.000

Table 4.3: Bond charge transfer coefficients of the bulk α -Al₂O₂ model. The error is $\sigma = 0.049$.

than the O–Si value in the silica systems, with a large relative error. This hints that the BCT model does not describe the bonding situation perfectly.

I employ a 2D slab model, with the surface in (0001) direction. The Al terminated surface is 2x2 reconstructed, while on the O terminated side, the dangling bonds are terminated using hydrogen atoms. Figure 4.12 shows, that the distribution of partial charges is uniform throughout the bulk, with only a small distortion introduced by the hydrogen termination of the $(000\bar{1})$ surface. The surface Al-Atoms however differ by having much smaller partial charges than in the bulk. Curiously, this is the opposite behavior from the Si (001) surface (cf. figure 4.6). The comparison of the surface model DOS and bulk DOS in figure 4.11 shows that the surface leads to a downwards shift of the whole eigenspectrum by about 2 eV and to the introduction of a whole spectrum of, mostly empty, gap states.

Hydroxylated γ -Al₂O₃



Figure 4.13: Results of the SCC-DFTB reference calculation on the hydroxylated γ -Al₂O₃ surface model used for the adhesion studies in chapter 5 (a): structure and charge distribution, (b): atomic charge histograms

⁷In geology, sapphire denotes all natural corundum precious stones, except the red varieties, which are generally known as ruby. The colors of these materials are caused by (usually metal ion) impurities, e.g. Cr^{3+} ions in rubies.

The last, and definitively most complicated evaluation system is a model of native alumina. Its most striking difference to corundum is its pseudo-amorphous structure, a more in-depth discussion of which is given in chapter 5^8 . I employ the surface model described in chapter 5 as a reference for the desired application scenario. The results for the stoichiometric unit cell are illustrated in figure 4.13. The difficulties in the description of this material, in addition to those described above for corundum, stem from the amorphous structure: Al appears in tetrahedral and octahedral configurations imposed by the spinel structure and the defects (i.e. Al vacancies) lead to fluctuating coordinations for each atom leading to distinctly fluctuating atomic partial charges, as can be clearly seen when comparing the atomic Mulliken charge histograms (cf. figures 4.6, 4.9, 4.10, 4.12, and 4.13). The average BCT coefficients (cf.

Elements	H–H	H–O	H–Al	0–0	O–Al	Al–Al
$\mathrm{dq}_{a,b}$	0.000	0.285	0.000	0.000	-0.119	0.000

Table 4.4: Bond charge transfer coefficients of the γ -Al₂O₃ surface model. The error of σ =0.14733 hints, that the definition of $dq_{a,b}$ has difficulties in describing this system.

table 4.4) match those found for corundum, but with a relative error > 1 (for O–Al), considerable doubt is cast on the BCT model. However it should be considered, that the –OH groups attached to the surface Al atoms will disturb the BCT coefficient calculation.

The HOMO–LUMO gap of this surface model is only ~ 0.019 eV, but as can be seen in figure 4.11(b), this is not the band gap of the bulk material but caused by surface states.

4.3.3 Evaluation of coupling schemes

When chemical reactions are examined, the major contributions⁹ originate from changes in the chemical bonding, while changes within the more distant environment are small (cf. figure 4.1). Therefore, the first step in testing a QM/MM coupling scheme is to ensure that the description of the embedded QM zone meets the requirements of the intended application. This means that the representation of the QM zone should match fully QM calculated references as closely as possible with respect to the criteria defined in section 4.3.1. The internal dynamics of the MM zone should be neglected during these tests, since a molecular-mechanical description of the MM zone may inherently introduce systematic deviations from the QM description, e.g. by slightly shifting the positions of the external charges. The effects of such changes could not be easily distinguished from errors introduced by the transition from a fully QM to an embedded modeling. Additionally, a force-field description of the MM zone adds to the overall complexity of the system and therefore introduces further potential errors. I therefore use the atomic equilibrium positions and partial charges as a fixed model of the MM part in my evaluation of the different embedding schemes.

Since the QM calculations are limited to small periodic supercells, or even the unit cell, I periodically expand the distribution of "MM atoms" in order to obtain a sufficiently large MM zone¹⁰ (cf. figure 4.14). In addition to the computational details described in Section 4.3.2, I keep the link-atoms and QM border atoms fixed during geometry optimization, unless stated otherwise. I keep the whole QM cluster geometry fixed while searching for embedding parameters, in order to limit the computational cost. After that, I select a set of embedding parameters and relax the geometry using these parameters.

The complete set of plotted evaluation results, can be found in appendix A.

⁸Suffice to say here, that the native Al_2O_3 phase, labeled γ - Al_2O_3 , is best described as a defective spinel structure, with the oxygen part forming a perfect fcc lattice and the Al part on tetrahedral and octahedral positions. To ensure stoichiometry, Al atoms must be randomly removed from the perfect spinel structure. Additionally, the native oxide surface is generally hydroxylated.

⁹energetic and otherwise

¹⁰The original, periodic supercell is split into the QM- and MM zones. The external charges are then the atomic Mulliken charges of the MM zone. Additionally, one or more shells of charge distributions of the full supercell (containing the charges of QM- and MM zone atoms) may be added around the original cell.



Figure 4.14: Illustration of the embedding of a QM zone (green) within the charge distribution of the MM zone, which comprises the MM atoms of the original supercell (red) and further replicas of the whole original charge distribution (blue).

Simple link atoms (SLA)

The simple link atoms approach (cf. section 4.2.2) with point charges performs well for the (2x1) reconstructed Si surface. Due to the nearly vanishing point charges, the cluster charge is very small (0.081 e), so that only small errors are expected to arise from this; the Fermi level will be shifted to the VB edge but the difference in occupation of <1 e will not influence reaction energetics significantly.



Figure 4.15: Charge distribution (a) and atomic charge histogram (b) of the Si_{13} 2x1 Si(001) surface using point-charge modeling of the MM zone.

Using a QM core of 29+28 (29 QM + 28 QML) atoms in a 3x3 expanded surface supercell to accommodate the larger cluster, the charge distribution of the inner QM atoms matches that of the reference quite closely, as can be seen from figures 4.15(a) and 4.6. The calculated HOMO-LUMO gap of 0.97 eV is slightly larger than the reference of 0.84 eV, as would be expected as a result of the electronic confinement.



Figure 4.16: QMH atom total and RMS charge errors of the 29+28 atom cluster embedded into Gaussian blurred charges, dependent on the Gaussian blur width. Crosses mark calculated values, lines serve to guide the eye.

From figure 4.15(b), it can be seen that simple hydrogen termination causes some charge distortions on the QMH atoms (cf. the histogram peaks around +0.02 e in the reference and -0.1 e in the embedded calculation). To investigate chemical reactions at one of the reconstructed dimers, a larger QM cluster which contains at least three of these dimers would be necessary, to isolate the central dimer from termination-induced polarization effects by at least one shell of non-border neighbor atoms. Gaussian broadening has a detectable effect on the QM atom charge deviations with distinct minima, however, as can be seen from figure 4.16, this effect is very small. (The maximal difference is~ 0.01 e in dQ and RMSQ.) This is to be expected, since the point charges themselves are very small.

Changing the link-atom distance has no beneficial effect on this embedded cluster, as can be seen in figure 4.17. Outside an unfavorable region of short QMH–QML distances at small charge broadening, the RMSQ is virtually independent on the distance scale. The band shift has its minimum for a QML distance factor of 1.0, independent of the Gaussian broadening. Figure 4.4(b) on page 38 shows a very similar picture for the number of gap states as for the band shifts.

Overall, it appears that using an SLA cluster combined with a Gaussian broadening of the external charges by 5.0 Bohr radii and no link-atom distance scaling gives a very good representation of the 2x1 reconstructed Si surface. When simulating chemical reactions, the cluster size must me checked, to ensure that the QMH atoms are not the nearest neighbors of atoms involved in the reaction.

The picture changes, however, when applying the SLA embedding approach to silicon and aluminum oxide systems. First of all a considerable number of gap states appear (cf. figure 4.18(a)) in SiO₂, when placing the QML atoms at their equilibrium bond distance to the QMH atoms. Depending on the cluster size and QMH atom type, the range of useful link-atom distances and Gaussian blur widths can be very limited (cf. figures A.2–A.6 or figure 4.18 as an example for α -quartz). E.g. for the Si₇O₈ α -quartz cluster, the LADF range is ~ 0.8–0.9 and gaussian blur widths should be >~ 3.75 a.u. (cf. figure 4.18(a)).Within these constraints, the choice of embedding parameters is then governed by the minimization of the RMSQ.

System	CC	$N_{\rm QM}$	$N_{\rm QML}$	$N_{\rm MM}$	$Q_{\rm clst}^{\rm tot}$	$N_{\rm SCC}$	RMSQ	RMSD	$\Delta E_{\rm b}[{\rm eV}]$	$\sigma_{ m gb}$	LADF	QMH	$\mathrm{Q}_{\mathrm{QMH}}$	Figure
Si 2x1	Si_{29}	29	28	4371	+0.08	17	0.18	0.01	-0.16	5.0	1.0	Si	free	A.1
α -quartz	$\mathrm{Si}_7\mathrm{O}_8$	15	12	885	+3.11	1001^{*}	0.10	0.27	-1.11	4.0	0.85	Si	free	A.2
	$\mathrm{Si}_7\mathrm{O}_{20}$	27	12	873	-3.15	89	0.20	1.71▲	+0.74	1.8	0.85	0	free	A.3
SSZ60	$\mathrm{Si}_3\mathrm{O}_{10}$	13	8	10739	-2.07	121	0.16	0.41	-1.65	2.8	1.0	0	free	A.4
	$\mathrm{Si}_{11}\mathrm{O}_{10}$	21	24	10731	6.26	102	0.11	0.15▲	-2.80	4.0	0.80	Si	free	A.5
	$\mathrm{Si}_{11}\mathrm{O}_{34}$	45	24	10707	-6.21	55	0.28	0.08	-0.09	4.0	0.95	0	free	A.6
α -Al ₂ O ₃	$Al_{20}O_{30}$	50	60	1138	-1.63	$\begin{array}{c} 24 \\ 40 \end{array}$	$\begin{array}{c} 0.18\\ 0.06\end{array}$	$\begin{array}{c} 0.11 \\ 0.06 \end{array}$	-0.67 -0.30	$1.6 \\ 1.7$	$1.075 \\ 1.175$	N/A	free constr	A.7 A.8
	$Al_{20}O_{51}$	71	102	1117	-9.71	27 38	$0.21 \\ 0.11$	0.68▲ 0.46▲	-1.35 -2.10	$\begin{array}{c} 1.7\\ 1.0 \end{array}$	$1.0 \\ 1.05$	0	free constr	A.9 A.10

Table 4.5: Summary of the test results for SLA embedding. The column CC gives the cluster composition without hydrogen link atoms; $N_{\rm QM}$, $N_{\rm QML}$ and $N_{\rm MM}$ give the numbers of QM atoms, saturators and and external charge centers, respectively. $Q_{\rm clst}^{\rm tot}$ is cluster total charge in e, $N_{\rm SCC}$, RMSQ, RMSD and $\Delta E_{\rm b}$ are the number of SCC cycles until convergence, RMS charge deviation of the QM atoms in e, RMS movement of the core QM atoms and band shift at the selected embedding parameters $\sigma_{\rm gb}$, the Gaussian blur width in a.u. , and LADF, the link-atom distance factor. QMH gives the element of the QMH atoms of the cluster, if all QMH are of the same element. * SCC did not converge for this calculation. The geometry underwent qualitative reconfiguration during the optimization run.



Figure 4.17: RMS charge deviations of the QM atoms (excluding QML)(a) and overall band structure shift(b) of 29+28 atom the 2x1 Si(001) surface cluster, dependent on QML distance scale and gaussian broadening of the external charges.



Figure 4.18: States in the shifted gaps of the 15+12 atom (a) and 27+12 atom (b) α -quartz clusters dependent on gaussian blur width and QML distance factor.

Table 4.5 summarizes the evaluation results obtained with the SLA scheme. It turned out that any cluster of reasonable shape¹¹ cut from polar materials was severely charged, even if it had the correct stoichiometry, like the $Al_{20}O_{30}(+H_{60})$. Additionally, in all cases, the number of SCC cycles until convergence was high in the regions of good charge and band-structure reproduction. This is understandable, since in the bulk, the band edges are generally degenerate at the Γ -point, which makes convergence of charged bulk structures extremely difficult. More series however, are the large geometry distortions present in all SLA embedded systems, except Si and the 45-atom SSZ60 cluster, when relaxing the non-host QM atoms. The large RMSD values for these structures (table 4.5) indicate severe problems. At visual inspection, it turns out that in all cases with RMSD > 0.2 bonds inside the QM cluster were broken.

 $^{^{11}}$ defined as a mostly convex surface with only one QM–MM link per MMH atom. The latter cannot be fully achieved for alumina materials, because of the high atomic coordination numbers.

In the Al_2O_3 test cases, the stoichiometric $Al_{20}O_{30}$ cluster showed reasonable geometry (RMSD 0.11). In this cluster, the bond breaking occurred in the vicinity of the QMH atoms. This suggests that this problem could be caused by erroneous charge transfers to or from these atoms. Therefore, test calculations with the charges of the QMH atoms constrained to their reference values were performed for the two Al_2O_3 clusters. The results show that, although the charge constraints lead to an overall improvement in all benchmark values (e.g. RMSD $0.11 \rightarrow 0.06$ and $0.68 \rightarrow 0.48$ for $Al_{20}O_{30}$ and $Al_{20}O_{51}$, respectively), the qualitative failure in geometry representation in the $Al_{20}O_{51}$ cluster could not be cured. Additionally, the charge constraints make the SCC convergence more difficult, resulting in a increase of about 50% in the needed SCC iterations and therefore the calculation time.

Still, the Fermi level was pinned to the VB or CB edge in each polar cluster, which would lead to severe errors in the description of chemical reactions. Therefore, embedding schemes which leave a residual cluster charge are unsuitable for the simulation of polar materials.

Neutralized cluster schemes

To solve the problems arising from the cluster charge introduced by the SLA embedding scheme in polar materials, HCS and BCTC embedding (see section 4.2.3f.) were employed. The comparison between the results from SLA calculations in table 4.5 and the neutralized cluster schemes (table 4.6) shows that they are successful in this. Except for the very small clusters¹², the RMSQ is significantly smaller for the HCS and BCTC schemes, and in each case, the number of SCC cycles until convergence is much smaller.

The biggest improvement, however, is found in the atomic RMSD of the test clusters. Bond reconfiguration only occurred in the case of the oxygen terminated $Al_{20}O_{51}$ cluster.

A detail of note is the fact that the band offsets are somewhat larger than with SLA embedding. This is mostly caused by the additional dipole moments introduced by the charge relocation, as discussed in sections 4.2.3 f.. However, as this external field acts uniformly on all eigenstates, it should only result in a small global shift of total energies, while not significantly influencing relative energetics, i.e. reaction energies, -barriers etc.

For the very small quartz and SSZ60 clusters, some rotation of most Si–O–Si bridges around the O–O axes is observed and causes the slightly above average RMSD values.

The results for Al_2O_3 indicate, that oxygen QMH clusters do not provide adequate results, with or without charge neutralization (cf. tables 4.5 and 4.6). Increasing the MM zone size does not cure these problems. An Al-QMH cluster provides reasonable results with charge constraints, however, the neutralized stoichiometric clusters clearly give the best reproduction of the results from a fully periodic model. In all cases, charge constraints lead to an improvement of the RMSQ by about 50% at the cost of an increase in calculation time by > 50% (cf. tables 4.5 and 4.6). Embedding parameters in the γ -alumina clusters are quite close to each other and comparable to those in the stoichiometric $Al_{20}O_{30}$ α - Al_2O_3 cluster. This observed transferability between clusters as well as different phases of one material shows, that the embedding approach is stable and not over-parametrized. Therefore it can be assumed with reasonable conviction that the clusters can also be used to examine chemical reactions at the surface.

Based on the α -alumina results, the hydroxylated γ -Al₂O₃ surface is modeled using neutralized, stoichiometric clusters (i.e. keeping the Al₂O₃ stoichiometry of the alumina phase — the surface hydroxyl groups distort the overall stoichiometry). The Al₂₄O₄₀H₆ (+saturators) cluster is centered around the -OH group called site 1 in the surface adsorption studies (cf. chapter 5). It contains three binary and three ternary OH groups, formed from the dissociation of three water molecules. The stoichiometry of the Al₂O₃ part is not ideal — it has one excess oxygen, which cannot be avoided with reasonable effort in this pseudoamorphous phase. The results show, that the embedding is quite successful in reproducing a fully periodic model. One surface Al atom, which forms an O-Al-O bridge between two QMH oxygens, rotates around the O–O axis during relaxation. Since this case is somewhat pathological and the Al is located at the edge of the QMZ, I extend the QMH geometry constraints to include this atom.

 $^{^{12}}$ Which are anyway problematic for the description of chemical processes (cf. section 4.3.3).

System		CC	$N_{\rm QM}$	$N_{\rm QML}$	$N_{\rm MM}$	$N_{\rm SCC}$	RMSQ	RMSD	$\Delta E_{\rm b}[{\rm eV}]$	$\sigma_{ m gb}$	LADF	QMH	$\mathrm{Q}_{\mathrm{QMH}}$	Figure
α -quartz	HCS	$\rm Si_7O_8$	15	12	885	13	0.15	0.12	0.82	2.2	0.80	Si	free	A.11
		$\mathrm{Si}_7\mathrm{O}_{20}$	27	12	873	4	0.05	0.08	-2.06	2.0	0.80	0	free	A.12
SSZ60	HCS	$\mathrm{Si}_{11}\mathrm{O}_{10}$	21	24	10731	13	0.32	0.10	-0.01	1.6	0.80	Si	free	A.13
		$\mathrm{Si}_{11}\mathrm{O}_{34}$	45	24	10707	12	0.04	0.07	-3.77	1.4	0.65	0	free	A.14
α -Al ₃ O ₃	BCTC	$Al_{20}O_{51}$	71	102	1117 10621	23 39 22	$0.19 \\ 0.22 \\ 0.15$	0.33▲ 0.48▲ 0.34▲	0.85 7.04 -21.80	$1.5 \\ 1.0 \\ 3.0$	1.0 1.0 1.0	0	free constr free	A.15 A.16 -
	BCTC	$Al_{20}O_{30}$	50	60	1138	23 38	$\begin{array}{c} 0.11 \\ 0.05 \end{array}$	$\begin{array}{c} 0.07 \\ 0.07 \end{array}$	$0.25 \\ 0.05$	$1.5 \\ 1.5$	$1.2 \\ 1.2$	N/A	free constr	A.17 A.18
	BCTC	$Al_{32}O_{18}$	50	81	1138	33 68	$\begin{array}{c} 0.23 \\ 0.04 \end{array}$	$\begin{array}{c} 0.10\\ 0.08 \end{array}$	-1.60 -1.20	$2.5 \\ 3.0$	$0.75 \\ 0.75$	Al	free constr	A.19 A.20
γ -Al ₃ O ₃	BCTC	$\mathrm{Al}_{24}\mathrm{O}_{40}\mathrm{H}_{6}$	70	52	13955	37 63	$\begin{array}{c} 0.17\\ 0.03 \end{array}$	$\begin{array}{c} 0.14 \\ 0.13 \end{array}$	-2.625 -2.85	$1.5 \\ 2.2$	1.0 1.0	N/A	free constr	A.21 A.22
	BCTC	$Al_{36}O_{56}H_{12}$	104	67	13921	32 57 69	0.11 0.02 0.03	0.18 0.22 0.19	-2.425 -0.275 -1.625	2.0 2.0 2.0	$1.05 \\ 0.80 \\ 1.0$	N/A	free constr constr	A.23 - A.24

Table 4.6: Summary of the test results for neutralized cluster embedding. The column CC gives the cluster composition without hydrogen link atoms; N_{QM} , N_{QML} , N_{MM} and give the numbers of QM atoms, saturators and external charge centers, respectively; N_{SCC} , RMSQ, RMSD and ΔE_{b} are the number of SCC cycles until convergence, RMS charge deviation of the QM atoms in e, the RMS displacement of the core QM atoms in Åand band shift in eV at the selected embedding parameters σ_{gb} , the Gaussian blur width, and LADF, the link-atom distance factor in a.u. QMH gives the element of the QMH atoms of the cluster. The geometry underwent qualitative reconfiguration during the optimization run.



Figure 4.19: The tested γ -Al₂O₃ clusters. The cluster containing both sites is an extension of the site 1 cluster.

For the calculations in shown in table 4.6, the γ -alumina clusters are surrounded with a distribution of external charges containing 5x5 original supercells (a total of 13955 external charge centers for the site 1 cluster). To check for convergence with the size of the external charge distribution, I repeat the geometry check of the non charge-constrained BCTC embedded Al₂₄O₄₀H₆ cluster with external charge distribution sizes ranging from 1x1 to 11x11 original supercells. The results are listed in table 4.7¹³. They

cells	ext. charges	$E_{\rm tot}$ [H]	$dE_{\rm tot}$ [H]	RMSQ $[e]$	RMSD $[Å]$
1x1	491	-176.951781	-0.0602	0.14024	0.157802
3x3	4979	-176.913209	-0.0572	0.14050	0.157484
5x5	13955	-176.910081	-0.0567	0.14053	0.156064
7x7	27419	-176.908993	-0.0565	0.14056	0.155394
9x9	45371	-176.908452	-0.0564	0.14058	0.155023
11x11	67811	-176.908130	-0.0563	0.14060	0.154787

Table 4.7: Charge distribution convergence check results for the $Al_{24}O_{40}H_6 \gamma$ -alumina cluster. RMSQ here is *after* geometry optimization and therefore not directly comparable to table 4.6. $dE_{\rm tot}$ gives the energy gain by geometry optimization (see footnote 13 on p 53).

show, that the originally chosen 5x5 point charge distribution is reasonably sized, however, a 7x7 charge distribution would provide somewhat better results. In all examined criteria, the results can be regarded as converged at the 7x7 external charge distribution. Note that the RMSQ differs only within the same order of magnitude as the SCC convergence criterion $(10^{-5} \text{ electrons})$.

The second γ -alumina cluster examined here is an extended version of the site 1 cluster, constructed so as to also include the surroundings of site 2 (cf. chapter 5). The results show, that the larger γ -alumina cluster exhibits a slightly better behavior than the site 1 cluster, in terms of SCC convergence and charge deviation. This can be expected from the smaller ratio of QM core to QMH and QML atoms, leading to more bulk-like behavior of the cluster. (Note that the RMSD value entails a sight rotation of the O-Al-O bridge, which was kept fixed in the site 1 cluster. This accounts for 0.2 in the RMSQ in each case.)

¹³It should be noted, that the final geometric configuration of the surface –OH groups strongly depends on the initial geometry and the resulting charge distribution — starting a new calculation from the final geometry of a previous one, without reading the charges, leads to relaxation to a different (albeit very shallow) local minimum with visible displacement of the hydroxyl groups. This behavior can also be observed in fully QM calculations and is not inherent to the embedding.

Differences between SiO_2 and Al_2O_3

The embedding evaluations so far show one interesting and unexpected result: Although SiO₂ and Al₂O₃ appear to be quite similar materials at first glance: both materials are insulators with direct band gaps of $\sim 9 \text{ eV}$ for SiO₂ and $\sim 6 \text{ eV}$ for alumina. As can be seen in section 4.3.2, their polarities, in terms of atomic charges quite comparable and the electronegativity differences between oxygen and the heavy atom are similar, as are those between the material's atoms and the hydrogen saturators. All these similarities lead to the expectation that both materials should behave similarly in a QM/MM framework.

Yet the cluster compositions which work very well for the SiO₂ systems, i.e. clusters with homogeneous QMH elements, fail for alumina. Instead, in this system the correct cluster stoichiometry plays a central role. The reason for this difference is not clear, but the observed bond-breaking in the non-stoichiometric Al_2O_3 clusters suggests a connection to the structure of the valence band. Figure 4.20 shows the wave function coefficients of the HOMOs and LUMOs of one unit cell of bulk quartz and sapphire. Comparing the HOMOs of both materials, one finds that the VB edge of quartz is almost exclusively composed of oxygen orbitals, as it is common text-book knowledge (note that in the SK parametrization employed, the Si-d orbitals act as diffuse functions for the oxygens[130]). In comparison, the contribution of Al orbitals to the VB edge in α -Al₂O is much larger than that of Si in quartz (the ratio of oxygen to aluminum contributions is considerably smaller in α -Al₂O). This may explain, why the valence band of alumina is much more sensitive to deviations from stoichiometry, which disturb the composition of the VBE states, than that of silica.



Figure 4.20: Atomic orbital coefficients of the HOMO and LUMO of bulk α -quartz and α -Al₂O₃, ordered by Atom and, shell *n* and magnetic quantum number *m*. Each consecutive line represents one atom.

Reaction energies

After having established suitable embedding parameters for surface and interface clusters in the test systems, the final test of the developed embedding scheme will be the reproduction of reaction energies. In order to limit the computational cost, I concentrate on the α -quartz surface and the γ -alumina surface, examining the reactions:

$$\alpha - \text{quartz} + \text{H}_2\text{O} \longrightarrow [\alpha - \text{quartz} + \text{H} + \text{OH}], \qquad (4.15)$$

$$\gamma - Al_2O_3 - OH + AMEO \longrightarrow [\gamma - Al_2O_3 + AMEO] + H_2O.$$
 (4.16)

Reaction 4.15 is the dissociative water adsorption on α -quartz. Reaction 4.16 describes the condensation of a 1,3-trihydroxiaminopropylsilane at a surface hydroxyl group on native alumina, as described in chapter 5.

I examine each reaction using BCTC embedding with the cluster which has shown the best results and the appropriate parameters determined in the previous section. The last parameter that remains to be studied in a systematic manner, is the size of the external charge distributions.

 $\alpha - quartz + H_2O \longrightarrow [\alpha - quartz + H + OH]$



Figure 4.21: Si-(OH)-Si bridges formed by adsorption of an H₂O molecule on α -quartz. Atoms from the dissociatively adsorbed water molecule are marked blue.

I use the Si₇O₂₀ α -quartz HCS neutralized surface cluster with the embedding parameters from table 4.6. The geometry of the dissociatively adsorbed water molecule is shown in figure 4.21. To obtain optimal transferability, I treat the reactants in isolated calculations, i.e. the water is not in vicinity of the surface before the adsorption. As a reference, I calculate the reaction energy in the full periodic 6x6 surface cell (cf. figure 4.9).

The reaction is endothermic by 1.02 eV in the periodic reference calculation, while the endothermicity converges to 0.87 eV in the (non-periodic) embedded calculations with up to 42x42 lateral cells in the external charge distribution (figure 4.22). It can be seen, that the reaction energy converges to a value about 0.2 eV less endothermic than in the fully periodic reference.



Figure 4.22: Calculated reaction energies for the dissociative H_2O adsorption on α -quartz plotted over the charge distribution surface area. Text labels give the number of lateral surface cells.

 $\gamma - \mathrm{Al_2O_3} - \mathrm{OH} + \mathrm{AMEO} \longrightarrow [\gamma - \mathrm{Al_2O_3} + \mathrm{AMEO}] + \mathrm{H_2O}$



Figure 4.23: Calculated reaction energies for the condensation of AMEO on γ -alumina plotted over the charge distribution surface area. Text labels give the number of lateral surface cells.

(1,3)-trimethoxyaminopropylsilane, also known as APTES or AMEO, plays an important in the alumina/adhesive interface formation examined in chapter 5. Reaction 4.16 is the acid-base condensation of hydroxylated AMEO with the -OH group at site 1 of the Al₃₆O₅₆H₁₂ cluster containing both adsorption sites used in chapter 5. Using BCTC embedding with free charges and the parameters listed in table 4.6, I calculate the condensation energy of AMEO, following the same procedure as for reaction 4.15. As shown in figure 4.23, the reaction energies calculated with QM/MM converge to -2.10 eV, while the periodic full-DFTB calculation gives a reaction energy of -1.84 eV (cf. table 5.2), i.e. the QM/MM calculation finds the adsorbate to be ~0.25 eV more stable.

General considerations

In all examined reactions, the adsorbate appears $\sim 0.2-0.3$ eV more stable in the non-periodic embedded calculations than in the periodic full-DFTB calculation. This raises the question, whether this deviation indicates a systematic error introduced by the QM/MM embedding. It must be noted here, that the embedded calculations and the full DFTB calculations differ in one very important respect: to avoid the problems of bond termination, the full DFTB calculations employ periodic boundary conditions. This

means, that the full DFTB calculations model infinite surfaces with an infinite number of defects, one per supercell. In contrast, the embedded calculations model one single defect on a finite crystallite.

All examined reactions lead to changes in the dipole moments of the surfaces, especially the added hydroxyl groups and the AMEO molecule introduce additional dipole moments. The self-interaction of these dipoles across the periodic boundary may explain the observed reaction energy differences. To test this hypothesis directly, it would be necessary to re-calculate the reaction energy in a series of supercells of different sizes, to check whether the reaction energy difference scales with $\frac{1}{r^3}$, like the dipoledipole interaction does. At the current state of the art this is impossible, since the employed supercells are already at the boundary of what can be handled with reasonable computational effort. Shrinking the supercells is not a sensible option, as this incurs the danger of introducing further self-interaction problems, beyond the electrostatic self-interaction. Since the number of atoms N scales as a^2 with the lateral length of the supercell and the computational cost scales proportional to N^3 , doubling the supercell size leads to four times the memory requirements and (at least) 64 times the CPU requirements. Due to these constraints, a systematic study of this problem is impractical.

4.4 Summary

The evaluation of the tested embedding schemes leads to two results. Firstly, it could be shown that QM/MM embedding with DFTB as the QM method can give reliable results, so that the method is suitable to simulate solid surfaces and interfaces which would would be inaccessible to pure QM calculations, due to their size. Secondly, the tests show that the necessary embedding scheme strongly depends on the material system at hand. While in SiO₂, non-stoichiometric QM clusters with homogeneous QMH atoms can be successfully employed, this cluster construction leads to severe problems in Al₂O₃. It becomes also clear, that in polar materials, the clusters must be carefully neutralized; here the BCTC method, developed in the course of this work proves well suited for solid surfaces.

CHAPTER 4. DFTB QM/MM EMBEDDING

Chapter 5

Epoxy adhesives on native Al_2O_3

During the past two decades aluminum has constantly gained importance in technical applications, with its use spreading from aerospace to automotive applications and now covering nearly every area of industrial and consumer appliances. Parallel to this development, adhesive technology has achieved advances which enable adhesive bonding of metal parts to supplement or even replace traditional metal joining technologies such as welding, bolting or riveting. Related to this is the development of metal-resin or metal-resin-fiber compound materials, which have recently advanced to the point of technical application. The demands for lighter and at the same time stronger materials, in order to build more fuel-efficient, i.e. lighter, vehicles and aircraft without sacrificing structural strength leads to a strong interest in the development and improvement of fiber reinforced aluminum-polymer hybrid materials and adhesive bonding technology for aluminum. For both of these technologies, the aluminum-polymer adhesion is of crucial importance.

Since, outside high vacuum environments, aluminum instantly develops a surface oxide layer[131, 132], the problem of adhesion on aluminum translates into the problem of adhesion on native aluminum oxide. The improvement of adhesion technology requires an understanding of the underlying chemical processes of the bonding of organic adhesives to the alumina surface. In this study I aim at finding a suitable methodology for gaining insight into the initial bonding of adhesive component molecules as well as the bonding competition between different organic species at the native Al₂O₃-surface. To achieve this, I concentrate on a model adhesive system, comprising diglycidylesterbisphenol-A (DGEBA) as the resin, diethyltriamine (DETA) as the curing agent and 3-aminopropyltrimethoxysilane (sold as: Dynasilan AMEO, here referred to as AMEO, also known as APTES) as an adhesion promoter component. Although our results are focused on an adhesive, some of the examined components are also used in compound materials or paints, and the method is sufficiently general, to be transferable to the adsorption of any organic molecule of similar size on inorganic surfaces.

5.1 The native Al_2O_3 surface

Native alumina, created by corrosion of Al in air, is usually described as γ -Al₂O₃, which is formed by a pseudo-amorphous defective spinel structure in which Al atoms and vacancies are randomly distributed among the tetrahedral and octahedral sites within a perfect fcc sub-lattice of oxygen atoms[133–138]. However there is still controversy in the literature concerning the crystallography of γ -alumina. An extensive study, combining experimental and theoretical approaches, suggests, that the description of γ -alumina requires a significant number of Al atoms on non-spinel positions to be accurate[139]. Extensive review of the literature concerned with the bulk structure of γ -alumina is given in Refs. [140, 141]. As the underlying bulk structure is amorphous, the surface does not exhibit any regular reconstruction. The main characteristics of the surface are the distribution statistics and density of surface Al on tetrahedral

and octahedral sites as well as on the distribution of hydroxyl groups at the surface. A mesoscopic model of the (100) surface of spinel-like γ -alumina and its hydroxylation has already been presented in Ref. [142].

It is well known that in a moist environment, such as air, the Al_2O_3 surface quickly absorbs water, both molecularly and dissociatively [142–145]. It is therefore essential to include the hydroxylation of the surface in any study of its chemistry. Since alumina in general and especially γ -alumina is of high interest as a catalyst for the chemical industry, a large number of studies on the surface reactivity have been performed, most of which are concerned with the surface acidity. An extensive overview can be found in [138, 146] and references therein.

5.2 A model adhesive system

Investigations on the adsorption of methanol at the hydroxylated surface show that these react with hydroxyl groups attached to surface aluminum atoms by condensation.[147, 148]. A study of the adsorption of maleic acid anhydride[149], and theoretical investigations[150] on the adsorption of adhesive components on amorphous SiO₂ and hydroxylated α -Al₂O₃ also find condensation reactions on the alumina surface, except for DGEBA, which is found to react with the surface by additive ring-opening. I therefore assume that similar reactions will occur in the system studied here, however, we assume the ring-opening of DGEBA to occur in the liquid phase of the adhesive mixture, independent of the surface. Therefore we examine the ring-opening of DGEBA by water and the condensation reaction of the opened DGEBA separately.



Figure 5.1: The molecules of the model adhesive system: (a) DGEBA, (b) t-DGEBA, (c) t-DGEBA^(open), (d) DETA, (e) AMEO, (f) AMEO^(hyd). From [151].

In a recent study of the DETA absorption energetics [152] reaction energies of ~ 35 kcal mol⁻¹ have been observed for a chemisorption at an octahedral surface aluminum site. In this study, I concentrate on the interaction of the adhesive components with surface hydroxyl groups, which results in a condensation reaction for the adsorption of DETA.

As DGEBA has a mirror plane, I consider a truncated molecule which only contains one phenol-ring and one epoxy group, referred to as t-DGEBA (c.f. Fig. 5.1(a),(b)). Since AMEO can be expected to rapidly lose its ethyl groups and hydrolyze in an aqueous solution, I only study the interaction of the hydrolyzed form of AMEO which I refer to as $AMEO^{(hyd)}$ (c.f. Fig. 5.1(e),(f)). In my model, the adsorption of DGEBA depends on the prior opening and hydroxylation of at least one oxirane ring. This catalyzed
5.3. SURFACE MODEL PREPARATION

reaction is not limited to the alumina surface but must happen throughout the adhesive mixture, the ringopened, truncated DGEBA molecule will henceforth be referred to as t-DGEBA^(open) (c.f. Fig. 5.1(c)). After these considerations, I examine the following reactions at the surface:

$$t-DGEBA^{(open)} + surf. \xrightarrow{\Delta E} (t-DGEBA + surf.) + H_2O$$
 (5.1)

DETA + surf.
$$\xrightarrow{\Delta E}$$
 (DETA + surf.) + H₂O (5.2)

$$AMEO^{(hyd)} + surf. \xrightarrow{\Delta E} \left(AMEO^{(hyd)} + surf. \right) + H_2O$$
(5.3)

where *surf.* denotes the hydroxylated surface model and (*species*+surf.) denotes the structure of the organic *species* adsorbed at the surface. Additionally, I also consider the reaction

$$t-DGEBA + 2H_2O \xrightarrow{\Delta E} t-DGEBA^{(open)} + H_2O.$$
(5.4)

Here, the second water molecule stabilizes the ring-opening.

5.3 Surface model preparation

5.3.1 Bulk γ -Al₂O₃

The results presented in this subsection were published in a joint publication with Blumenau and Amkreutz [151]. They are presented here, as the foundation of the hydroxylated model construction described below. As stated in section 5.1, the structure of γ -alumina is still under discussion in the literature. The consensus is however, that it resembles a close packed oxygen (fcc-) lattice with Al atoms and vacancies statistically distributed among the tetrahedral and octahedral sites. It can be generated either from a strained hausmannite or a spinel structure, by removing Al atoms to achieve Al₂O₃ stoichiometry. Due to the statistical distribution of vacancies, the structure can be regarded as *pseudo-amorphous*.

structure	$N_{\rm cell}$	$E_{\rm tot}^{\rm DFTB} [eV/Al_2O_3]$	$E_{\rm tot}^{\rm LDA} \left[{\rm eV} / {\rm Al}_2 {\rm O}_3 \right]$	$\varrho^{\rm DFTB} [{\rm g \ cm^{-3}}]$	Al– O^{DFTB} [Å]
hausmannite	80	-334.98	-1425.70	3.65	1.88(0.07)
spinel cub. 1	160	-335.35	-1426.30	3.66	1.88(0.07)
spinel cub. 2	160	-335.41	-1426.36	3.66	1.88(0.07)
spinel cub. 3	160	-335.39	-1426.37	3.64	1.88(0.06)
spinel rhomb.	80	-335.05	-1425.74	3.66	1.88(0.06)

Table 5.1: SCC-DFTB and LDA results on γ -Al₂O₃. N_{cell} is the number of atoms per unit cell, Al-O is the mean Al-O bond length and its statistical error. From [151].

Five different models of γ -Al₂O₃ were constructed, one based on a hausmannite cell, one based on a rhombohedral representation of spinel and three based on a cubic representation of the spinel structure. For the cubic spinel case, three different starting structures in which different Al atoms have been randomly removed were examined. The atomic positions were relaxed in all cells, optimizing the cell volume. Table 5.1 lists the characteristic data of the relaxed cells. We find that the differences in terms of density of the optimized unit cell and Al-O bond lengths are negligible and that the densities correspond well to the experimentally reported value of 3.67 g cm⁻³[153]. The energy differences between the three different basic structures (i.e. hausmannite, cubic spinel and rhombohedral spinel) deviate slightly, indicating that the cubic representation is slightly favorable. Notably, the differences between the three different cubic spinel based models are negligible in all respects.



Figure 5.2: Views along the $(00\overline{1})$ (left) and (010) (right) directions of the hydroxylated γ -Al₂O₃ surface model. The selected adsorption site 1 is marked blue, site 2 is marked green. (Note that, due to the periodic repetition, each adsorption site appears twice.)

5.3.2 The hydroxylated γ -Al₂O₃ surface

To generate a model of the γ -Al₂O₃ surface, the first of our 4 oxygen-layer thick, 160-atom cubic-spinel based models was chosen (second line in table 5.1). The bulk alumina was cut by increasing the length of the cell vector along the (001) direction to 60 Åwithout changing any of the atomic positions. The resulting slab model was then relaxed using conjugate gradients (CG).

To hydroxylate the surface, a 10 Åthick layer of H_2O molecules, cut from a larger, geometry-optimized supercell of liquid water, was placed on top of the surface model and then performing a 1 ps SCC-DFTB MD run at 300 K, followed by a second 1 ps MD run at 600 K to remove the non-adsorbed water molecules. This procedure does not lead to chemisorption of water molecules at the surface, but since sufficiently long MD runs to achieve this are computationally far too expensive, I then manually split the physisorbed water molecules, forming an OH-group at the adsorption site and using the split-off hydrogens to protonate nearby Al-O-Al bridges. After this procedure, I relax the geometry again using CG. During the whole procedure, the lowermost oxygen and aluminum layers were held fixed.

The surface supercell generated this way has a surface area of ~ 24 Å x 8 Å, which is too small in (0, 1, 0) direction, wherefore it was duplicated model along this axis. The resulting model contains 374 atoms in a 23.7 x 15.8 x 60 Å³ periodic supercell (figure 5.2). To limit the computational cost of the study, the two sites marked in in the figure were chosen out of the 13 inequivalent –OH groups for the studies of adsorption reactions, based on the different distribution of neighboring hydroxyl groups and tetrahedrally coordinated aluminum atoms.

5.4 The H₂O-assisted ring-opening of DGEBA

In order to gain an understanding of the chemical reactions from which the alumina/adhesive interface arises, I calculate the reaction enthalpies and MEPs of the condensation reactions between the model adhesive system's components and the surface hydroxyl groups at the two selected reaction sites.

As described in section 5.2, the nucleophilic ring-opening of the oxirane rings in DGEBA by water molecules occurs throughout the adhesive mixture and is independent of the surface. Therefore this reaction is modeled independently of the surface adsorption reactions. To conserve calculation time,



Figure 5.3: Minimum Energy path of the ring-opening of t-DGEBA by H_2O . Atoms of the phenyl group are rendered transparent for clarity, circles mark energies of the configurations shown above.

I regard only one of the oxirane rings in the molecule and therefore simulate a t-DGEBA, instead of DGEBA (cf. figures 5.1, 5.3). In the mixture, the DGEBA molecules are surrounded by other components with polar groups as well as some water molecules. As a simple model of the stabilizing effect of such surrounding polar groups, a water molecule is included in the ring-opening path-search calculations[154].

I use the SCC-DFTB method, applying the alo-1 Slater-Koster data sets. The SCC is iterated until the energy difference between two subsequent iterations falls below 10^{-6} H and determine the minimum energy configurations of reactants and products by CG optimization until the forces fall below 10^{-3} a.u. The MEP is then searched using NEB, where the path optimization was started by an adaptive displacement steepest-descent algorithm for the first few hundred iterations, then switching to a projected velocity-Verlet scheme, which is iterated until the maximum forces at the images fall below 10^{-3} a.u. I construct the initial path by linear interpolation of the Cartesian coordinates between the reactant, a guessed transition state and product configurations. The transition sate guess is necessary, since the reaction coordinate has dihedral rotation components, which cannot be reproduced by linear interpolation in Cartesian coordinates. A reaction coordinate is segment-wise as the linear displacement between images:¹

$$c_i = \frac{\left|\vec{R} - \vec{R_i}\right|}{l_i}$$

with

$$l_i = \left| \vec{R_{i+1}} - \vec{R_i} \right|$$

¹Note that this differs from the reaction coordinate used in Ref [151].

for a position \vec{R} along the path in the segment between images i and i + 1, leading to the normalized position along the reaction path

$$x = \frac{\sum_{j=1}^{i} l_j + c_i}{\sum_j l_j}.$$

The total energies are interpolated along this reaction coordinate, following the interpolation procedure described in Ref $[108]^2$:

$$E(x_{i}) = -E_{i} + x_{i} \cdot -F_{i}^{t}$$

$$+ x_{i}^{2} \left(\frac{3(E_{i+1} - E_{i})}{l_{i}^{2}} + \frac{-2(F_{i}^{t} - F_{i+1}^{t})}{l_{i}} \right)$$

$$+ x_{i}^{3} \left(\frac{-2(E_{i+1} - E_{i})}{l_{i}^{3}} - \frac{F_{i}^{t} - F_{i+1}^{t}}{l_{i}^{2}} \right).$$
(5.5)

The climbing image NEB method is not employed in this study for two reasons. First, the interest rests not only on finding the barrier energy, but on obtaining an overview of the whole reaction mechanism. Second, not all reaction paths examined here have well defined barrier, e.g. the AMEO adsorption reactions (cf. section 5.5.3).

Fig 5.3 shows the calculated image energies and structures (crosses), as well as the cubic interpolation of the total energy (red line). I find a barrier energy of ~ 1.91 eV and an exothermicity of ~ 1.88 eV. No direct comparison data is available, however for the similar reaction

$$\underbrace{C_{2}H_{4}O}_{oxirane} + H_{2}O \longrightarrow \underbrace{H_{2}HOC - CH_{2}OH}_{1.2 \text{ Ethanediol}}$$

reference data using PBE and an 6-31G basis [155] gives a reaction enthalpy of -1.31 eV, which is in good agreement with my calculation results, taking into account the formation of a hydrogen bond between one of the formed OH-groups and the catalyzing H₂O. Before the formation of this bond, the reaction energy is ~ -1.2 eV (cf. figure 5.3).

5.5 Adsorption of single adhesive component molecules in vacuum

To examine the energetics of reactions 5.1–5.3, I follow the procedure verified above for the t-DGEBA ring-opening. Each of these reactions is simulated at both adsorption sites described in section 5.3.2. The results of these calculations are summarized in table 5.2. Two reaction energies for the condensation of each species are given: $E_{\rm ads}^{\rm comb}$ and $E_{\rm ads}^{\rm sep}$. The former is extracted from the adsorption paths, as the difference between final and first image. It includes an additional contribution from the physisorption of the water molecules generated during the reaction. The latter was calculated from separate simulation of reactants and products and is therefore free of such influences. It can be seen, that the water adsorption results in an exothermic shift of the reaction energies of $\sim 0.5-\sim 2$ eV. These shifts are unrealistic under real conditions, since the oxide surface is known to be covered by at least one monolayer of water molecules [142–145] — a site at which water may be adsorbed with an energy gain of 2 eV will surely be already occupied. On the other hand, $E_{\rm ads}^{\rm sep}$ is unrealistically low, as the solvation of the condensated water molecule will always release some energy. However, as table 5.2 shows, these uncertainties do not change the relative energetics qualitatively. In the following I shall give a detailed description of the reaction mechanisms found for each compound. (Figures showing the adsorption MEPs are given on pages 67–72.)

 $^{^{2}}$ Note, that the equations given in reference [108] do not match the derivation described in the text, due to several errors. Here, I present the corrected energy interpolation formula.

component	site	$E_{\rm ads}^{\rm comb.}$ [eV]	$E_{\rm ads}^{\rm sep.}$ [eV]	$E_{\rm barr} [{\rm eV}]$
t-DGEBA	ringopen	-1.8780	-	1.9081
t -DGEBA $^{(open)}$	$\frac{1}{2}$	-0.42741 -2.5298	-0.11970 -1.6108	$2.0726 \\ 0.1282$
$AMEO^{(hyd)}$	$\frac{1}{2}$	-4.0815 -4.4355	-2.1364 -2.0329	0.0^{*} ~ 0.35^{*}
DETA	$\begin{array}{c} 1\\ 2\end{array}$	0.20411 -0.47487	$2.3602 \\ 2.0022$	$1.1583 \\ \sim 0.8^{*}$

Table 5.2: Calculated reaction energies and barriers of the adsorption and ring-opening reactions of the model adhesive system on Al₂O₃. $E_{\rm ads}^{\rm comb.}$ gives the adsorption energy with physisorption of the condensed H₂O, $E_{\rm ads}^{\rm sep.}$ with the condensed water isolated in vacuum. *Cf. sections 5.5.2 and 5.5.3 for a discussion of these values.

5.5.1 DETA

Table 5.2 clearly shows, that the condensation of the curing agent DETA is very unfavorable. The reaction energies without the contribution of the physisorption of the condensed water molecule $E_{\text{ads}}^{\text{sep.}}$ are endothermic by more than 2 eV. At site 2 the adsorption path has a local minimum before the actual condensation, (cf. figure 5.6) which is in agreement with findings, that DETA can bond to the surface non-covalently via hydrogen bonding [152]. The Barrier given for this reaction is calculated between the local minimum and the following maximum.

5.5.2 t-DGEBA^(open)

The picture for t-DGEBA^(open) shows significant differences between both adsorption sites. While at site 2 a second, ternary hydroxyl bond to the surface is formed, between the second hydroxyl group of the opened epoxy ring and a clean Al atom at the surface(cf. figure 5.8), at site 1 only the C-O-Al bridge from the condensation reaction appears (cf. Fig 5.7). This leads to large differences in the reaction energetics at both sites — at site 1 the adsorption is only slightly exothermic, while being hindered by a 2 eV barrier³; at site 2 only a negligible barrier is found, while the condensation reaction is highly favorable. At both sites, the transition state is characterized by a strong repulsion between the surface-and molecules OH groups — the Al-O-C bridge can only form after one of the hydroxyl groups has been release by proton transfer from the other. At site 2 this transition state is stabilized by the formation of a the ternary OH group with the free surface Al atom.

5.5.3 AMEO^(hyd)

I only examine the adsorption of the silanol function of AMEO, since its amine group will behave very similar to the amine groups of DETA. Their interaction with the surface is so unfavorable, that a qualitatively different behavior of the amine function in AMEO cannot be expected.

For the condensation of AMEO, no barriers appear between the starting configurations ~ 5 Aabove the surface. The barrier given for site 2 is most likely caused by a local valley of the electrostatic potential, which the AMEO molecule slides into during the approach to the surface, but has to leave before the condensation reaction. At both sites, the AMEO molecule forms two covalent Si-O-Al bridges to the surfaces, by reacting with a second, unhydroxylated Al atom nearby (cf. figures 5.9, 5.10). Also, at

 $^{^{3}}$ which is large in comparison with thermal energies at ambient temperatures



Figure 5.4: Comparison of the calculated adsorption MEPs on the Al₂O₃ surface.

both sites the adsorption of the condensated water molecule is very exothermic. Fig 5.10 shows, that at site 2 the transition state is marked by a five-fold coordination of the Si atom by four hydroxlys (three binary and one ternary) and one carbon. Subsequently one of these binary OH groups is released by a short-range proton transfer from the ternary hydroxyl bridge. Neither the OH group formation, nor the proton transfer show significant barriers.

5.5.4 Comparison of adsorption mechanisms

Figure 5.4 illustrates the energetic differences between the adsorption mechanisms of the model adhesive system. It shows very clearly, that AMEO is the most favorable adsorbate at both surface sites (green lines). It is also the the only adsorbate, which shows no significant adsorption barriers at both sites. In contrast, the chemisorption of DETA (blue lines) is unfavorable. It can rather form a hydrogen bond, which is, however, much weaker than the favorable covalent bonds possible in this system. The resin component, DGEBA (red lines) shows diverse behaviors in the sense, that it can compete with the AMEO adsorption at site 2, while its chemisorption at site 1 is thermodynamically on par with the physisorption of DETA, while being hindered by a high barrier.

The differences between DGEBA and AMEO can be understood, when scrutinizing the transition states. The silicon atom of AMEO allows for a five-fold coordinated configuration, which makes it possible to form the Al-O-Si bridge, before the proton transfer and H_2O condensation. In contrast to this, the carbons of the opened oxirane rings in DGEBA do not have this possibility. In addition to this, DGEBA with its bulky phenyl ring exhibits a much higher steric hindering, so that it is not always possible to form additional, ternary OH-group links to surface Al atoms. The much more linear and smaller $AMEO^{(hyd)}$, in contrast, can adapt much easier to the local conditions at the adsorption site.

These findings allow an explanation of the working mechanism AMEO as an adhesion promoter. In an adhesive mixture without adhesion promoter, only the resin component can form strong, covalent bonds to the native alumina surface. However, only a part of the available surface hydroxyl groups is available for adsorption. At other sites, the formation of covalent bonds between DGEBA and surface is not distinctly favorable and must compete with the physisorption of curing agent molecules. The silane-based adhesion promoter AMEO can improve the linkage between surface and polymer, mostly because its adsorption is favorable at more surface sites, especially such sites, where the formation of a covalent bond between DGEBA and the surface is not. Therefore, it can be concluded, that the chief effect of the adhesion promoter is to increase the number and density of covalent links between polymer and surface.

Since the favorable effect of AMEO is closely related to the chemistry of its Si atom, it can be concluded that similar silanes should show a similar effect, as long as no too strong steric hindering from its backbone or other functional groups occurs.

Adsorption path figures



Figure 5.5: Minimum Energy path of the condensation of DETA at site 1. Insets show a cutout of the surface model in the vicinity of the adsorption site.



Figure 5.6: Minimum Energy path of the condensation of DETA at site 2. Insets show a cutout of the surface model in the vicinity of the adsorption site.



Figure 5.7: Minimum Energy path of the condensation of t-DGEBA at site 1. Insets show a cutout of the surface model in the vicinity of the adsorption site.



Figure 5.8: Minimum Energy path of the condensation of t-DGEBA at site 2. Insets show a cutout of the surface model in the vicinity of the adsorption site.



Figure 5.9: Minimum Energy path of the condensation of $AMEO^{(hyd)}$ at site 1. Insets show a cutout of the surface model in the vicinity of the adsorption site.



Figure 5.10: Minimum Energy path of the condensation of $AMEO^{(hyd)}$ at site 2. Insets show a cutout of the surface model in the vicinity of the adsorption site.



Figure 5.11: Minimum Energy path of the coadsorption of AMEO at site 1 in the vicinity of AMEO at site 2.



Figure 5.12: Minimum Energy path of the coadsorption of DGEBA at site 1 in the vicinity of AMEO at site 2.

Site 1	Site 2	$\mathbf{E}_{\mathrm{ads}}^{\mathrm{tot}}$	ΔE_{ads}
AMEO	AMEO	-4.38	-0,50
	DGEBA	-3.22	0,23
	DETA	0.26	0,08
DGEBA	AMEO	-2.17	-0,01
	DGEBA	-1.89	-0,17
	DETA	1.90	-0,01
DETA	AMEO	0.25	-0,06
	DGEBA	-7.01	-7,76
	DETA	4.40	0,03

Table 5.3: Influence of nearest neighbor adsorbates on adsorption energies. Energies in eV, both adsorbates in the same half of the surface model (cf. section 5.3). $\Delta E = E_{ads}^{tot} - (E_{ads}^1 + E_{ads}^2)$.

Ads. 1	Ads. 2	Site	$\mathbf{E}_{\mathrm{ads}}^{\mathrm{tot}}$	ΔE_{ads}
AMEO	AMEO	1	-3,84	-0,16
		2	-4,09	$0,\!00$
	DGEBA	1	-2,27	-0,32
		2	-3,66	-0,01
	DETA	1	$0,\!49$	-0,02
		2	$2,\!62$	$2,\!64$
DGEBA	DGEBA	1	-0,22	0,00
		2	-3,20	0,01
	DETA	1	$2,\!24$	$0,\!00$
		2	$0,\!42$	0,00
DETA	DETA	1	4,71	0,00
		2	$4,\!05$	$0,\!01$

Table 5.4: Influence of second neighbor adsorbates on adsorption energies. Energies in eV, both adsorbates at the same site in different halves of the surface model (cf. section 5.3). $\Delta E = E_{ads}^{tot} - (E_{ads}^1 + E_{ads}^2)$.

5.6 The effect of neighboring adsorbates

Beyond the adsorption of isolated adhesive components, the influence of neighboring adsorbates on the condensation reactions can be used to gain further insight into the alumina–adhesive interface formation.

5.6.1 Adsorption energies

To examine, how the presence of an adsorbate influences the condensation reaction of a second molecule from the adhesive mixture, I calculate the reaction energies for these reaction in the presence of a second adsorbate in first or second nearest neighbor position. Tables 5.3 and 5.4 list the results of these calculations.

For the interaction between nearest-neighbor adsorbates, the adsorption of two AMEO^(hyd) molecules in close vicinity is very favorable, while putting a t-DGEBA^(open) beside the AMEO is unfavorable. A slight advantage of condensating two t-DGEBA molecules in close vicinity can be inferred from the data. The co-adsorption of DETA at site 1 and DGEBA at site 2 appears to be extremely favorable. As can be



Figure 5.13: Co-adsorbed structure of t-DGEBA^(open) at site 2 and DETA at site 1. Dashed lines indicate hydrogen bonds.

seen in figure 5.13, the molecules are oriented nearly parallel in this case, leading to several hydrogen bonds and a strong electrostatic interaction between both molecules. It should be kept in mind, that here the simplified model of the adhesive components and surface can lead to unrealistically high adsorption energy estimates. In this case, it is to be expected that in a liquid polymer mixture, the bond sites interacting here, will already be occupied by hydrogen bond partners before the adsorption reactions. In all other cases, the adsorption energy differences are < 0.1 eV, which is insignificant, taking into account general limitations of the employed model (cf. 5.3.2).

As expected, table 5.4 shows that the presence adsorbates on the second dearest neighbor sites has much smaller influence on the condensation reaction energetics. In comparison to the nearest neighbors' influences, it can be seen that co-adsorption of AMEO is still favorable at longer distances, at least at site 1. Interestingly, the co-adsorption of AMEO and DGEBA is significantly more favorable at second nearest neighbor sites, indicating that the pronounced shift towards endothermicity in the nearest neighbor site case is caused by steric hindering. Similarly, steric hindering is culpable for the clear unfavorability of co-adsorbing AMEO and DETA. A different orientation of the DETA, which adsorbs nearly parallel to the surface at this site (cf. figure 5.6) may alleviate this, however it should be kept in mind that the adsorption of DETA is highly unfavorable in any case. In the vast majority of examined reactions, the presence of a second neighbor adsorbate did not influence the adsorption energetics significantly.

5.6.2 Adsorption paths

The computational effort needed to calculate the adsorption paths presented in section 5.5 makes a systematic study of the influence of the surroundings on the adsorption reactions impractical. Therefore I switch to the DFTB based QM/MM scheme presented in chapter 4. The $Al_{36}O_{56}H_{12}$ QM Zone containing both adsorption sites verified in that chapter is employed. Here I will only examine two coadsorption reactions, to demonstrate the suitability of my QM/MM approach to simulate complex reactions at hybrid interfaces. The adsorptions of an AMEO^(hyd) molecule at site 1 in the presence of a second AMEO at site 2 (with the water molecule created during the condensation of AMEO at site 2 still physisorbed at the surface), and the adsorption of a t-DGEBA^(open), also at site 1 in the same surroundings were simulated.



Figure 5.14: Comparison of site 1 adsorption energy profiles for isolated adsorption and in the vicinity of a second adsorbed AMEO.

AMEO + AMEO Figure 5.14(a) shows the energy profiles for the condensation of AMEO at site 1 with and without a neighboring adsorbed AMEO. The first notable difference lies in the total energy of the reaction. This difference is caused by the fact, that the water molecule created during the course of the condensation reactions at both sites physisorbs at the same surface Al atom. Therefore, another place had to be chosen for the second water molecule in the coadsorption case. As can be seen, the adsorption of the water molecule is very favorable at the original surface atom. The second, stark difference is in the existence of a significant secondary barrier of ~0.95 eV for the physisorption of the second water molecule. This difference is also related to the choice of a different site for the second water molecule (cf. figure 5.11). However, the barrier is still small enough that it can be overcome by the energy gained from the condensation reaction itself.

Besides the differences stemming from the different disposition of the water molecule, the adsorption reactions occur in a very similar manner (cf. figures 5.9 and 5.11). It can be concluded, that the condensation reaction of AMEO is not strongly influenced by the presence of neighboring AMEO adsorbates. This is in good agreement with the results on the thermodynamics, presented in the preceding section.

AMEO+DGEBA In contrast to AMEO, t-DGEBA^(open) reacts sensitively to the presence of a neighboring AMEO adsorbate or, more precisely, to the presence of the water molecule formed during the condensation of the latter. The presence of a neighboring AMEO does not significantly influence the adsorption enthalpy. However, the deep intermediate minimum in the path shows that another reaction that does not lead to condensation of the DGEBA^(open) is actually much more favorable. When the geometry is optimized, starting from one of the intermediate geometries between reaction coordinates 0.3-0.4 of the coadsorption path (cf. figure 5.12(c)), the resulting minimum energy configuration is very different from the result of the condensation reaction (figure 5.15^{-4}). The physisorbed water molecule from the preceding AMEO condensation is split up to form a surface hydroxyl group. The proton released by this reaction then attacks the the opened oxirane ring and passivates one of it's -OH groups. Finally, the dangling carbon bond resulting from the preceding step is passivated by another proton transferred from a nearby Al–(OH)–Al bridge at the surface.

Even taking into account the inevitable error of this calculation due to the too small surface cluster, this result is gives extremely interesting insight into the interface formation process at hand. It clearly shows

 $^{^{4}}$ Note that the final geometry from this calculation exhibits the problem, that the free products of the reaction, i.e. the passivated DGEBA and the water molecule marked orange, have moved beyond the surface cluster. Therefore this equilibrium geometry is not realistic and its energy is useless. Nevertheless it shows the main features of the alternate reaction path found here.



Figure 5.15: DGEBA^(open) passivated by a physisorbed water molecule stemming from the nearby condensation of AMEO. The formerly physisorbed water forms an –OH group (marked blue), transferring one of its protons to one of the –OH groups of the opened oxirane ring which then forms a water molecule (orange). The dangling C- bond is then saturated by a hydrogen atom taken from a formerly protonated Al–O–Al surface bridge (green).

that water at the surface plays a very important role. Further, systematic studies are necessary, which take into account the presence of a physisorbed water layer between the surface hydroxyl groups. This singular result also points at a mechanism of the effect of water at the surface that is likely to be highly important. Depending on the pH value and surface hydroxylation density⁵, surface water can strongly react with the surfactants by proton transfer processes. These can lead to the passivation of functional groups of the adhesive components, which may lead to a degradation of the adhesion between polymer and substrate.

Comparison of these first results on AMEO and DGEBA suggests, that the epoxy resin component is more susceptible to this passivation process than the silane adhesion promoter. This is in good agreement with the experimental observation that silane components improve the adhesion significantly. It is also consistent with the conclusion from section 5.5.4, that the effect of the adhesion promoter appears to be based on an increase of the density of covalent polymer–substrate bonds.

5.7 Summary

The results presented in this chapter, demonstrate, that minimum energy paths, obtained from NEB calculations and the DFTB method can provide very useful insight into the basic mechanisms of adhesive molecule adsorption on inorganic surfaces. The different components of the adhesive mixture show qualitatively different adsorption energetics, so that, consistent with experimental observation, a clear preference for the adsorption of the silane adhesion promoter could be established. At the same time, it could be demonstrated that condensation of the amine curing agent is unfavorable. Furthermore, the calculated MEPs also provide insight into the mechanisms leading to these differences. The condensation of amine functionalities is unfavorable, because necessary the removal of the surface hydroxyl group is extremely unfavorable. The silane adhesion promoter has more possibilities to form bidentate links to the surface, which is more difficult for the DGEBA resin, chiefly because of steric hindering at part of the available adsorption sites.

 $^{^{5}}$ Which had to be neglected so far, due to of the prohibitive computational cost of modeling them.

5.8. OUTLOOK

The thermodynamics of the adsorption reaction show some influence from the presence of neighboring adsorbates, however these differences are small compared to the adsorption energies. First results on the adsorption paths in the presence of neighboring adsorbates give two important results. Firstly, the adsorption of AMEO is only weakly influenced by the presence of adsorbates on neighbor sites, which supports the conclusion that AMEO can serve to increase the number of covalent links between substrate and polymer. Secondly, the presence of water has a much larger influence on the behavior of DGEBA at the interface, that neighboring adsorbates do. The results propose that, depending on the pH value, physisorbed water can react with the ring-opened DGEBA in a manner which partly passivates the –OH groups of the opened oxirane ring and leads to further hydroxylation of the surface.

Finally, it must be stated that the results obtained so far are not fully satisfactory in three respects: first, only a small fraction of the adsorption sites present in the surface model could be examined, better statistics would be highly desirable. Secondly, the influence of neighboring adsorbates could only be analyzed in the reaction energies but not the barriers. The third and most severe limitation lies in the examined model itself. The influence of physisorbed surface water and the surrounding polymer mixture had to be neglected completely. All of these limitations are based on the prohibitive computational cost that would otherwise arise. QM/MM coupling promises to alleviate these problems, and first results on the coadsorption of different components support this expectation. They show that QM/MM is indeed capable to give further insight into interface chemistry at greatly reduced computational cost, compared to pure QM simulations. It has become clear, that further studies of the interface formation reactions are needed, especially concerning the influence of water, and that these studies can now be conducted in practice.

5.8 Outlook — Kinetics simulation of the adhesive-alumina interface formation

Even considering the possibilities (and sometimes necessity) for improving on the findings so far obtained on the mechanisms of polymer/solid interface formation on an atomic scale, the limits of the atomistic perspective become apparent. Even with big improvements in computational efficiency, the accessible length and time scales cannot be extended qualitatively. In so far, simulating the whole process of interface formation on an atomic scale appears unrealistic. However, qualitative and quantitative insight into the chemistry of interface formation at the high level of detail attained in this study, can serve as the basis for examining larger time and length scales. One very promising way to achieve this lies in using the available results as input data to kinetic Monte Carlo simulation of the the interface formation. Reaction energies and barriers, which are the basic input data for this approach (cf. section 3.3) are available, even allowing to (partly) take into account the influence of neighboring sites. Studies to employ the data presented here as input to the KMC part of a coupled KMC/continuum model [127] are underway in cooperation with the developers of this scheme. Valuable insights into the larger scale mechanism of interface formation and resulting interface properties, e.g. the distribution of different adsorbates along the surface, are expected from this ongoing research. CHAPTER 5. EPOXY ADHESIVES ON NATIVE AL_2O_3

Chapter 6

Conclusion

During the work presented here, advancements in both computational methodology and the understanding of the alumina/epoxy polymer interface were achieved.

Concerning methodology, the applicability of the DFTB/MM coupling method was extended from biomolecules to solid state systems and especially solid surfaces. To this end, a bond-termination scheme employing ordinary hydrogen atoms at fixed non-equilibrium distances to their QM host atoms is used. The bond distances are optimized to remove bonding states between saturators and host atoms from the band gap of the solid model. The electrostatic embedding of the QM zone into the MM zone is implemented by a Hamiltonian which allows to apply spherical Gaussian smearing to the point charges of the MM zone. This allows to circumvent problems originating from the unphysical proximity of the saturator atoms to the first layer of MM point charges. The two free parameters of this embedding scheme, i.e. the link-atom distance scaling and the Gaussian smearing width, must be optimized for each materials system to minimize charge distribution errors in the QM zone. The results show, however, that the optimized parameters are, within their error bars, independent on the chosen QM zone. They are also very similar between closely related materials, e.g. different phases of SiO₂ or Al₂O₃, clearly indicating that the embedding scheme is not over-parametrized.

The choice of a proper QM cluster depends on the individual materials system. In silica systems, characterized by ideal nearest neighbor coordination, a cluster in which all QM host atoms are oxygens, regardless of the cluster stoichiometry, is favorable. In contrast, alumina systems, characterized by an overcoordinated bonding situation, only small deviations from Al_2O_3 stoichiometry in the solid part of the surface are tolerable. Under this constraint it is not possible to construct a cluster with only one element type as QM host atoms and a reasonable surface to volume ratio. Constraints on individual atom's Mulliken populations, especially those of the QM host atoms, can help to reduce charge oscillations introduced by the QM/MM boundary, but they do not solve the problems introduced by non-stoichiometric alumina cluster composition.

Regarding formation between natively oxidized aluminum and an epoxy-type adhesive system, an insight into the working mechanism of silane-based adhesion promoters could be achieved from examining the minimum energy paths of the condensation reactions of the model adhesive's components in vacuum. One important effect of the adhesion promoter is an increase in the number of covalent substrate–polymer links, due to the fact that condensation of such adhesion promoters is favorable at more surface sites than for the other components.

Furthermore, first results on the influence of neighboring adsorbates during the interface formation, indicate that the direct influence of other adhesive components in the vicinity of the adsorption site is small, both in absolute terms and in comparison to the effect of water. Even most of the effect of the neighboring adsorbates is caused by the addition of water molecules formed during the condensation reactions leading to covalent surface–polymer bonds. These initial results, which only take into account the influence of water formed during the interface formation suggest, that proton-transfer processes at the

surface, during the adsorption of adhesive components can strongly influence the surface hydroxylation and may lead to the passivation of functional groups of epoxy resins.

From this, the course for further work to understand the formation of the alumina–adhesive interface becomes clear. The influence of water is of paramount importance and must be studied in a systematic manner. The extensive calculations necessary for this have been enabled by the development of a computationally efficient QM/MM coupling scheme applicable the surfaces of polar solids. Parallel to this, the knowledge about interface reaction energetics obtained during these studies at atomic resolution can serve as input parameters for Kinetic Monte-Carlo simulations aimed at understanding the interface formation process on larger length- and time scales.

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Appendix A

QM/MM Evaluation Data

A.1 Simple Link Atoms



Figure A.1: SLA evalution data for the 29+28 Si cluster.



Figure A.2: SLA evalution data for the 15+12 α -quartz cluster. The circle marks the selected embedding parameters for this system.



Figure A.3: SLA evalution data for the 27+12 α -quartz cluster. The circle marks the selected embedding parameters for this system.



Figure A.4: SLA evalution data for the 13+8 SSZ60 cluster. The circle marks the selected embedding parameters for this system.


Figure A.5: SLA evalution data for the 21+24 SSZ60 cluster. The circle marks the selected embedding parameters for this system.



Figure A.6: SLA evalution data for the 45+24 SSZ60 cluster. The circle marks the selected embedding parameters for this system.



Figure A.7: SLA evalution data for the 50+60 atom α -Al₂O₃ cluster. The circle marks the selected embedding parameters for this system.



Figure A.8: SLA with charge constraints evalution data for the 50+60 atom α -Al₂O₃ cluster. The circle marks the selected embedding parameters for this system.



Figure A.9: SLA evalution data for the 71+102 atom α -Al₂O₃ cluster. The circle marks the selected embedding parameters for this system.



Figure A.10: SLA with charge constraints evalution data for the 71+102 atom α -Al₂O₃ cluster. The circle marks the selected embedding parameters for this system.



A.2 Neutralized Clusters

Figure A.11: HCS evalution data for the 15+12 α -quartz cluster. The circle marks the selected embedding parameters for this system.



Figure A.12: HCS evalution data for the 27+12 $\alpha\text{-quartz}$ cluster.



Figure A.13: HCS evalution data for the 21+24 SSZ60 cluster. The circle marks the selected embedding parameters for this system.



Figure A.14: HCS evalution data for the 45+24 SSZ60 cluster. The circle marks the selected embedding parameters for this system.



Figure A.15: BCTC evalution data for the $Al_{20}O_{51}+H_{102}$ α - Al_2O_3 cluster. The circle marks the selected embedding parameters for this system.



Figure A.16: BCTC with charge constraints evalution data for the $Al_{20}O_{51}+H_{102}$ α - Al_2O_3 cluster. The circle marks the selected embedding parameters for this system.



Figure A.17: BCTC evalution data for the $Al_{20}O_{30}+H_{60} \alpha$ - Al_2O_3 cluster. The circle marks the selected embedding parameters for this system.



Figure A.18: BCTC with charge constraints evalution data for the $Al_{20}O_{30}+H_{60} \alpha$ - Al_2O_3 cluster. The circle marks the selected embedding parameters for this system.



Figure A.19: BCTC with data for the $Al_{32}O_{18}+H_{81} \alpha$ - Al_2O_3 cluster. The circle marks the selected embedding parameters for this system.



Figure A.20: BCTC with charge constraints evalution data for the $Al_{32}O_{18}+H_{81} \alpha$ - Al_2O_3 cluster. The circle marks the selected embedding parameters for this system.



Figure A.21: BCTC evalution data for the $Al_{24}O_{40}H_6+H_{52}$ (site 1) γ -Al₂O₃ cluster. The circle marks the selected embedding parameters for this system.



Figure A.22: BCTC with charge constraints evalution data for the $Al_{24}O_{40}H_6+H_{52}$ (site 1) γ -Al₂O₃ cluster. The circle marks the selected embedding parameters for this system.



Figure A.23: BCTC evaluation data for the $Al_{36}O_{56}H_12+H_{67}$ (both sites) γ -Al₂O₃ cluster. The circle marks the selected embedding parameters for this system.



Figure A.24: BCTC with charge constraints evalution data for the $Al_{36}O_{56}H_12+H_{67}$ (both sites) γ -Al₂O₃ cluster. The circle marks the selected embedding parameters for this system.

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Colophon

Most graphical representations of molecular and crystal structures were created using VMD [156]. DFTB calculations were performed using DFTB⁺ [157] version 1.0.1 and development versions.

COLOPHON

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