Water on manganese doped rutile TiO$_2$ (110) surfaces

Master’s Thesis

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Abstract

Photocatalytic water splitting has been studied as a potential method for solving the energy supply and environmental issues related to the use of fossil fuels since it was first shown to be possible by Fujishima and Honda in 1972 using titanium dioxide as a catalyst. Titanium dioxide is still considered one of the best catalyst candidates due to its low cost, non-toxicity, and chemical stability. Unfortunately, titanium dioxide some issues limiting its usefulness in the photocatalytic water splitting process. One of the ways used to make it a more efficient catalyst is doping it with transition metals, which has been shown to allow titanium dioxide nanoparticles to absorb visible light and increase the photocatalytic activity on its surfaces.

The aim of this work is to use density functional theory based calculations with the projector augmented wave method to study the adsorption behavior of water on clean and manganese doped rutile titanium dioxide (110) surfaces. The activation barriers for the transitions from molecularly adsorbed to decomposed water are computed using the climbing image nudged elastic band method. Additionally, the rates of the transitions were estimated using harmonic transition state theory. It was found that doping the surface with manganese makes the adsorption energies larger in magnitude and decreases the energy difference between molecularly adsorbed and decomposed water. The activation barriers are lowered by roughly a third, and in the case of a sixfold coordinated manganese dopant, the transition becomes slightly endoergic. The transition rates are also increased by the doping. These results suggest that doping with manganese increases the ability of the rutile (110) surface to split water.
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1 Introduction

Due to population growth and increasing expectations for lifestyle standards, the global power consumption has been forecast to almost double by 2050[1]. Most people would likely agree that issues like greenhouse gas emissions, eventual depletion of supplies, and market instabilities make the current degree of reliance on fossil fuels unsustainable, even with the present level of energy consumption. Each of the alternative sources of energy comes with their own set of benefits and limitations; sunlight, for example, is practically unlimited and is capable of irradiating Earth’s surface enough to provide energy to fulfill an entire year’s global demand in less than an hour[2]. It is unfortunate, especially considering the limitations of energy storage technologies, that the availability of sunlight is not constant, but is dependent on geographical location, time of day and year, and even the weather. It would be convenient if solar energy, when and where available, could be somehow converted into a chemical form, for example, hydrogen, a pollutant free fuel with a high energy yield relative to the volume stored. In 1972, Fujishima and Honda published an article showing that such a thing is indeed possible through photoelectrochemical water splitting on titanium dioxide electrodes under ultraviolet irradiation[3]. This discovery sparked an interest among researchers that has resulted in numerous studies on photoelectrochemical water splitting and various semiconductor materials potentially useful as photocatalysts. Indeed, articles related to the phenomenon keep being published to this day.

During the past few decades a diverse array of methods have been developed for the purpose of studying surfaces and the chemical reactions occurring on them. On the experimental side, since ultrahigh vacuum technology allowed the precise control of experimental conditions in which surfaces could be experimented upon, studies of, for example, the adsorption of water on well characterized TiO$_2$ surfaces have been possible. Today, surfaces can be seen in high detail through low-energy electron diffraction (LEED), high-resolution electron energy loss spectroscopy, or any number of other fancy methods. Additionally, the advent of the scanning tunneling microscope (STM) brought with it the ability to directly manipulate atoms or molecules in order to drop them on specific sites on surfaces.

This level of detail not only allows the theoreticians to directly compare their computational results to experiment, but also helps in the process of developing theoretical methods and fine tuning them to better model realistic systems. Parallel to the development of the experimental methods, significant advancements were made in the description of electronic structures from first principles. These ab initio methods are nowadays routinely applied to a
wide variety of chemistry, materials science, and condensed matter physics problems.

However, both experiment and theoretical work are hampered by the so-called "structure gap", a discrepancy between the clean, low-index surfaces that tend to be the focus of research, and the many ways things in reality can be defective and imperfect. For example, a powder of nanoscale particles used as a catalyst will have all sorts of stepped surfaces, facet edges, and quite often multiple polymorphs of the same substance. Furthermore, the catalytic activity of the powder may be largely due to them. While studies increasingly take into account the effects of the diverse forms of defects and impurities, it is impossible to account for all the deviations from idealized systems present in the real world and still learn how they work.

In this work, using the first principles method of density functional theory (DFT) as implemented in the Vienna Ab initio simulation Package (VASP), the effects of introducing a manganese dopant to an otherwise perfect rutile (110) surface are studied, focusing on the changes in the adsorption behavior of water and the reaction barriers involved in the decomposition of water. In Section 2, the basics of water splitting are discussed followed by a look into TiO$_2$ in general and the rutile (110) surface in particular. Section 3 is devoted to the theoretical background of density functional theory. Some aspects of the way the output of a density functional theory calculation can be put to use are discussed in Section 4. In Section 5 we explain how the methods are applied alongside the results of those applications. Section 6 discusses some of the phenomena not addressed in the calculations of the previous section that are involved in the overall process of water splitting, and how those phenomena can be studied.

2 Background

For more than a century now, the formation of white, powdery substance has been observed on exterior walls painted with TiO$_2$ containing paints. It was quite soon realized that this is due to organic compounds in the paint being decomposed under strong solar irradiation. This realization effectively begun the long history of photocatalysis as a topic of study. In addition to its application in photocatalysis, uses for TiO$_2$ have been found in corrosion-protective coatings, water and air purification, anti-fogging, and self cleaning surfaces to name just a few. It is also chemically stable in water, non-photo corrosive, non-toxic and perhaps most importantly, it is easy to produce and, therefore, affordable enough to smear all over walls in paints and people in cosmetics.
2.1 Water splitting on semiconductors

The electronic structure of a semiconductor plays a critical role in photocatalysis; in the ground state, all the relatively easily excitable electrons in a semiconductor fully occupy the valence band, basically making the movement of charge carriers in the semiconductor impossible. Above the valence band, in terms of energy, lies the conduction band. The difference of the highest energy of the valence band and the lowest energy of the conduction band is called the band gap. When the semiconductor absorbs a photon with, by necessity, energy larger than the band gap, an electron occupying the valence band is excited into the conduction band, leaving a hole, an absence of an electron, into the valence band. It is not only the size of the band gap that matters; band gaps can be classified as direct or indirect depending on whether a transition from the top of the valence band to the lowest state of the conduction band requires a change in the momentum of the electron. In the case of an indirect band gap, the transfer requires the creation or annihilation of lattice phonons, lowering the probability of such transitions occurring. The transitions do not necessarily have to happen from the edges of the bands, of course, if the energy of the photon is large enough, and any energy in excess of the band gap will be quickly dissipated through phonon coupling and interactions between charge carriers.

Once created through the absorption of a photon, the electron-hole pair, having opposite charges, will feel a Coulomb attraction. If the attraction is strong enough relative to the other potentials acting on it, the pair can effectively behave like a single particle called an exciton. In the cases relevant to photocatalytic water splitting, there tends to be present an interface between the semiconductor and water. A space charge layer is formed over the interface, separating the charges and allowing the migration of charge carriers. The lifetimes of the excitations are not infinite, however, and the energy will be released in some form or another. The mobility of the charge carriers and the rate of electron-hole recombination depend on the crystalline structure and particle size of the photocatalyst. Any defects in the crystal tend to trap the charge carriers, preventing them from reaching the surface active sites, whereas a smaller particle size means a shorter distance to travel.

If the charge carrier manages to reach the surface, it may take part in the water splitting reaction

\[ \text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2}\text{O}_2. \]

For systems where the water is oxidized on a semiconductor photoanode and the hydrogen reduced on a metal cathode in a liquid water environment, i.e. in photoelectrochemical cells, a more detailed picture of the oxidation half
reaction was put forward by Valdés et al.[4]:

\[2 \text{H}_2\text{O}_\text{(l)} \rightarrow ^\ast \text{OH} + \text{H}^\text{+} + e^-;\]

\[^\ast \text{OH} \rightarrow ^\ast \text{O} + \text{H}^\text{+} + e^-;\]

\[^\ast \text{O} + \text{H}_2\text{O}_\text{(l)} \rightarrow +^\ast \text{OOH} + \text{H}^\text{+} + e^-;\]

\[^\ast \text{OOH} \rightarrow +\text{O}_2\text{(g)} + \text{H}^\text{+} + e^-;\]

where * refers to the surface active site. The total change in free energy in this kind of a reaction has been determined to be 4.92 eV, implying that each of the four electrons involved needs to bring 1.23 eV with it. In non-electrochemical cases, such as when the reaction occurs on a single nanoparticle, the oxidation and reduction half reactions may occur far more independently. This author is unaware of any proposals as to how such a reaction would be likely to proceed beyond the separation of the hydrogen from the oxygen.

In summary, some of the criteria for good photocatalyst for use in water splitting are: band gap larger than 1.23 eV and preferably below 3.0 eV to allow absorption of visible light, high enough charge carrier mobility and a photoexcitation lifetime long enough to allow the charge carriers to reach the surface active sites. Moreover, the material must be stable in an aqueous environment and under solar irradiation.

2.2 Titanium dioxide

In nature, TiO_2 appears in three crystalline forms: rutile, anatase, and brookite. Since only the first two play a significant role in industry, brookite and any of the more exotic synthesizable polymorphs, have not been studied in nearly as great detail as rutile and anatase[5]. The structures of the two most common polymorphs are often described in terms of titanium centered octahedra with oxygen atoms at each of the vertices. Rutile, with the space group \(P4_2/mnm - D_{4h}^{1}\), has its octahedra, elongated in one direction, sharing one corner along the \(\langle 110 \rangle\) directions with the ends of the long axes attached to the ends of short axes, and sharing edges along the \([001]\) direction. In anatase, with the space group \(I4_1/amd - D_{4h}^{10}\), the octahedra share vertices along the \((001)\) planes, and edges with the octahedra in the adjacent planes. To make this description even less intuitive, in the octahedra of both polymorphs, there are three different Ti-O bond angles. In both cases titanium atoms are sixfold coordinated and oxygen threefold coordinated. The bulk structure of rutile is shown in Figure 1.
Figure 1: The rutile Bravais lattice unit cell and the titanium centered octahedra. The edges of the unit cell are marked with the parameters $a$ and $c$. The internal parameter $x$, which is used to define the positions of the oxygen atoms within the unit cell, is also shown.
Rutile has three commonly occurring crystal faces. Of these, the (110) surface is the most stable, and therefore most studied. The (100) surface might also be of interest when studying polycrystalline systems or powders of nanoparticles. The main focus of this work, the rutile (110) surface, is depicted in Figure 2. There are two different kinds of titanium atoms on the surface, alternating in rows along the [001] direction. The atoms in one of the rows retain their sixfold bulk coordination, while the atoms in the other are fivefold coordinated. These will be denoted as Ti$_{6c}$ and Ti$_{5c}$. There are also two kinds of oxygen on the surface. There are threefold coordinated oxygen atoms sharing a plane with the titanium, and above that plane are the so-called bridging oxygen atoms. Because of the coordinative undersaturation of the bridging oxygen atoms, they tend to be removed quite easily. The atoms on the surface of course differ from bulk in their positions. Since the structure is symmetric, the atoms are mainly moved perpendicular to the surface. The only ones moving along the surface are the oxygen atoms sharing a plane with the titanium, which are relaxed toward the coordinatively
undersaturated Ti$_{5c}$ atoms, which relax downwards. The bridging oxygen atoms relax downwards, and the Ti$_{6c}$ atoms upwards.[7] The addition of absorbates or dopants to the surface will, of course, change the structure yet again.

Since many of the applications of TiO$_2$, including water splitting, are in aqueous environments, it is useful to understand how water behaves on its surfaces. For this reason, a surfeit of experimental and theoretical studies have been performed on the adsorption behaviour of water on the surfaces over the last thirty or so years.[8] The theoretical studies often focused on whether the water dissociates upon adsorption. If the water were to dissociate, it would introduce -H and -OH surface functional groups, the latter of which is of central importance in many photocatalytic reactions. Most experimental studies show the likelihood of dissociation on non-defective surfaces to be vanishing at all coverages up to temperatures of 600K[9]. In contrast, a fair number of the computational work predicted the dissociative adsorption to be energetically preferred over molecular adsorption on the rutile (110) surface. In most of the theoretical studies the difference in the energies of the dissociated and molecularly adsorbed water is quite small, making the system sensitive to the choice of computational details, such as the exchange-correlation functional, number of layers in the model slab, surface supercell size, and the coverage.

It is generally agreed that the band gaps of rutile and anatase are direct and indirect, respectively, and in both cases definitely larger than the required minimum of 1.23 eV. The optical band gaps have been experimentally found to be 3.0 eV for rutile[10, 11] and 3.2 eV anatase[12, 13]. These gaps unfortunately limit the ability of the photocatalysts to utilize sunlight to the UV region, which accounts for roughly 5% of solar energy. Some of the methods of extending the absorption spectrum of TiO$_2$ into the visible region include dye sensitization[14], metal or semiconductor heterojunctions[15, 16], and doping with transition metals[17].

Since it is the primary focus of this thesis, it makes sense to discuss manganese doped rutile in a bit more detail. The manganese doped nanoparticle powder photocatalyst Inturi et al. studied in Ref. [17], had its band gap narrowed to 2.86 eV, which is not much below the optical gap of undoped rutile but still allows the absorption of some visible light. Band structure calculations suggest that doping with manganese adds impurity states within the band gap[18, 19], which would allow the absorption of some longer wavelength radiation. It should be noted that both of the cited studies use GGA exchange-correlation functionals, which are known to underestimate the rutile band gap by roughly a third. To the knowledge of this author, no calculations of the band structures of transition metal doped TiO$_2$ using more
accurate methods have been reported.

3 Theory

Within the Born-Oppenheimer approximation, all ground state properties of a system of \( N \) electrons can be in principle obtained by solving the time-independent Schrödinger equation for the many-body wave function \( \Psi(r_1, r_2, ..., r_N) \),

\[
E|\Psi\rangle = \hat{H}|\Psi\rangle = (\hat{T} + \hat{V} + \hat{V}_{\text{ext}})|\Psi\rangle,  
\]

(1)

where the Hamiltonian \( \hat{H} \) consists of the operators for kinetic energy \( \hat{T} \), the electron-electron interaction potential \( \hat{V} \), and the external potential \( \hat{V}_{\text{ext}} \), which includes the Coulombic interaction of the electrons with the nuclei. In practise, however, analytical solutions to the Schrödinger equation do not exist, and the resources required for the numerical computation using approximate methods, such as the Hartree-Fock approximation, increase exponentially with the size of the system. While waiting for the development of ever faster computers with larger capacities for short term storage, one can instead use a method which does not rely on wave functions being the core variational variable, such as the density functional theory (DFT), some elements of which will be described in the following sections.

3.1 Kohn-Sham equations

In 1964, Hohenberg and Kohn proved the existence of two bijective maps, one between the ground state electron electron density \( n \), and the ground state wave function,

\[
n(r) \mapsto |\Psi(r)\rangle,  
\]

(2)

and the other between the density and the external potential

\[
n(r) \mapsto V_{\text{ext}}(r).  
\]

(3)

Since the external potential uniquely determines the ground state wave function, and the ground state electron density can be evaluated from it, the Rayleigh-Ritz variational method, usually used to find the ground state solution to the Schrödinger equation by minimizing the energy with respect to some trial wave function can, by applying the Hohenberg-Kohn theorem, be equivalently minimized with respect to a trial electron density

\[
E_0 = \min_{\Psi} \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \min_{n(r)} E[n(r)].  
\]

(4)
Here, the energy functional

\[ E[n] = T[n] + V_{\text{ext}}[n] + V_H[n] + E_{\text{xc}}[n] \]  

is split into the kinetic energy functional for non-interacting electrons \( T[n] \), the functional of the external potential \( V_{\text{ext}}[n] \), the Hartree energy functional, i.e. the Coulomb interaction between electrons given by

\[ V_H[n] = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{e^2 n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \]

and the exchange-correlation functional \( E_{\text{xc}}[n] \). All the purely quantum mechanical contributions to the energy, such as the exchange interaction, are hidden in the exchange-correlation functional, the exact form of which is unknown, and thus needs to be approximated.

In order to minimize the total energy functional, one expands the electron density into a sum of some basis functions \( \phi_i(\mathbf{r}) \):

\[ n(\mathbf{r}) = \sum_{i=1}^{N} |\langle \phi_i | \phi_i \rangle|^2 \]  

which, plugged into Equation (4) with the expanded energy functional Equation (5), and minimized with the constraint that \( \phi_i \) are all orthonormal, results in the Kohn-Sham[20] equations

\[ \left[ -\frac{\hbar^2}{2m} \nabla^2 + V_{\text{eff}}(\mathbf{r}) \right] |\phi_i(\mathbf{r})\rangle = \epsilon_i |\phi_i(\mathbf{r})\rangle, \]

where the effective potential

\[ V_{\text{eff}}(\mathbf{r}) = V_H(\mathbf{r}) + V_{\text{xc}}(\mathbf{r}) + V_{\text{ext}}(\mathbf{r}) \]  

with

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

being the functional derivative of the exchange-correlation functional. At the first glance one may mistake the Kohn-Sham equations to what results from the Hartree approximation, where the full wave function is written as a direct product of single electron wave functions. It might seem that the only difference is the addition of the exchange-correlation potential \( V_{\text{xc}} \), but it should be noted that the kinetic energy part of the Kohn-Sham equations is not the true kinetic energy of the system, and that the eigenfunctions \( \phi_i \) and the corresponding eigen energies \( \epsilon_i \) have no clear physical meaning. The method
for solving the Kohn-Sham equations is similar to that for the Hartree-Fock equations in that they are solved self-consistently: Starting with some trial density \( n \), one solves the eigenfunctions \( \phi_i \) from the Kohn-Sham equations, where the potentials are computed using the trial. Then, using the resulting eigenfunctions, a new electron density is calculated as in Equation (7). The new density is usually mixed with the old one using e.g. the Pulay mixing scheme[21] to accelerate convergence before it is used to calculate new potentials for the Kohn-Sham equations, whence the eigenfunctions, are calculated again. This self-consistency cycle is repeated until the density no longer changes significantly. The final density can then be used to compute the ground state properties, such as the ground state energy as

\[
E[n] = \sum_{i=1}^{N} \epsilon_i - \frac{1}{2} \int d\mathbf{r} V_H(\mathbf{r}) n(\mathbf{r}) - \int d\mathbf{r} V_{xc}(\mathbf{r}) n(\mathbf{r}) + E_{xc}[n].
\]

The Pulay mixing scheme works by including information from several previous iterations

\[
n_i^{in}_{i+1} = \sum_i \alpha_i (n_i^{out} + \beta R_i),
\]

where the residual, defined as

\[
R_i[n_i^{in}] = n_i^{out}[n_i^{in}] - n_i^{in},
\]

is assumed to be linearly dependent on the old densities:

\[
R_{i+1} = \sum_i \alpha_i R_i.
\]

The optimum set of parameters \( \alpha_i \) is found by minimizing the norm of the residual \( (R_{i+1} | R_{i+1}) \).

### 3.2 Exchange correlation functionals

In density functional theory all quantum mechanical many-body effects reside within the exchange-correlation functional. The functional is not known in a closed analytic form, so an approximation has to be used.

The simplest approximate form is given by the local density approximation (LDA):

\[
E_{xc}[n] \approx \int d\mathbf{r} n(\mathbf{r}) \epsilon_{xc}(n(\mathbf{r})),
\]

where \( \epsilon_{xc} \) is the exchange-correlation energy per particle in a homogeneous electron gas with the density \( n \). The exchange-correlation potential is then
a local function depending only on the position \( \mathbf{r} \):

\[
V_{xc}^{LDA}(\mathbf{r}) = \left. \frac{\partial}{\partial n} n \epsilon_{xc}(n) \right|_{n=n(\mathbf{r})} .
\]  

(16)

The exchange part of \( \epsilon_{xc} \) can be obtained analytically, while the correlation part is fitted into the results of an accurate quantum Monte Carlo calculation, usually one by Ceperley and Alder[22]. Despite its simplicity, LDA gives reasonably good results for metal Fermi surfaces, work functions, and lattice parameters.

For non-metal systems, where the electron structure is more inhomogeneous, the accuracy of the functional can be improved by making it dependent on the local gradient of the density:

\[
E_{xc}^{GGA}[n] \approx \int d\mathbf{r} n(\mathbf{r}) \epsilon_{xc}(n(\mathbf{r}, \nabla n(\mathbf{r}))).
\]  

(17)

This is called the generalized gradient approximation (GGA). GGA functionals come in many forms, but are typically divided into separate exchange and correlation parts, similarly to the LDA. This allows the construction of hybrid functionals, where the exchange energy is mixed with the exact exchange energy taken from Hartree-Fock calculations.

The most often used GGA functional is by Perdew, Burke, and Ernzerhof (PBE). The spin-polarized PBE correlation energy functional is defined by

\[
E_{c}^{PBE}[n_{\uparrow}, n_{\downarrow}] = \int d\mathbf{r} n \left[ \epsilon_{c}^{LSDA}(r_{s}, \zeta) + H(r_{s}, \zeta, t) \right],
\]  

(18)

where \( \epsilon_{c}^{LSDA} \) is the local spin density approximation (LSDA), i.e. a spin-polarized LDA, correlation energy, \( r_{s} \) is the Wigner-Seitz radius,

\[
r_{s} = \left( \frac{3}{4\pi n} \right)^{\frac{1}{3}},
\]  

(19)

\( \zeta \) is the relative spin density, and \( t \) is a dimensionless density gradient

\[
t = \frac{\left| \nabla n \right|}{2\phi k_{s} n},
\]  

(20)

where \( \phi \) is a spin scaling factor

\[
\phi = \frac{1}{2} \left[ (1 + \zeta)^{\frac{5}{3}} + (1 - \zeta)^{\frac{5}{3}} \right],
\]  

(21)
and \( k_s \) is the Thomas-Fermi screening wave number
\[
k_s = \sqrt{\frac{4k_F}{\pi a_0}}; a_0 = \frac{\hbar^2}{me^2}.
\] (22)

Here \( H \) is defined in such a way that in the slowly varying limit \( t \rightarrow 0 \), it is given by its second-order gradient expansion
\[
H \rightarrow \frac{e^2}{a_0} \beta \phi^3 t^2.
\] (23)

In the rapidly varying limit \( t \rightarrow \infty \), \( H \rightarrow -\epsilon_c^{LSDA} \), so that correlation vanishes. Under uniform scaling to the high-density limit \( n(r) \rightarrow \lambda^3 n(\lambda r) \), \( \lambda \rightarrow \infty \), the correlation energy must scale to a constant to cancel out the logarithmic singularity in \( \epsilon_c^{LSDA} \),
\[
H \rightarrow \frac{e^2}{a_0} \gamma \phi^2 \ln t^2.
\] (24)

In the above \( \beta \) and \( \gamma \) are constants. All the above conditions are fulfilled by
\[
H = \frac{e^2}{a_0} \gamma \phi^3 \ln \left[ 1 + \frac{\beta}{\gamma} t^2 \left( \frac{1 + At^2}{1 + A^2 t^2 + A^2 t^2} \right) \right],
\] (25)

where
\[
A = \frac{\beta}{\gamma} \left[ \exp \left( \frac{\epsilon_c}{\gamma \phi^3} \right) \right]^{-1}.
\] (26)

The exchange energy is defined by
\[
E_x^{PBE}[n_{\uparrow}, n_{\downarrow}] = \int d\mathbf{r} \epsilon_x^{LSDA}(n) F_x(s),
\] (27)

where \( s \) is another dimensionless density gradient
\[
s = \frac{|\nabla n|}{2k_F n}.
\] (28)

\( F \) is defined so that it recovers the correct uniform gas limit \( s \rightarrow 0 \), \( F_x \rightarrow 1 + \mu s^2 \), obeys the Lieb-Oxford bound[23]
\[
E_x[n_{\uparrow}, n_{\downarrow}] \leq E_{xc}[n_{\uparrow}, n_{\downarrow}] \leq -1.679e^2 \int d\mathbf{r} n^4,
\] (29)

and the spin-scaling relationship
\[
E_x[n_{\uparrow}, n_{\downarrow}] = \frac{E_x[2n_{\uparrow}] + E_x[2n_{\downarrow}]}{2}.
\] (30)
A simple form of \( F_x \) for which all the above conditions hold is

\[
F_x(s) = 1 + \kappa - \frac{\kappa}{1 + \frac{\mu}{s^2}},
\]

(31)

where \( \mu \) and \( \kappa \) are constants.

In general, compared to LDA, GGA functionals tend to produce more accurate total energies, atomization energies, energy barriers, and structural energy differences. GGA functionals infamously underestimate the band gaps of semiconductors by a significant factor. Since the electron-electron interactions for each basis function are calculated using the whole electron density, each basis function effectively interacts with itself as well as all the others. It is not, however, known how and to what degree this affects the properties of solids and their surfaces. The adsorption energies, for example, are calculated as the difference between the energy of the surface with an adsorbate and the energy of the surface and an isolated adsorbate molecule, which might cancel some of the effects of the self-interaction. Self-interaction corrected functionals do exist\cite{24}, but have been shown to perform worse than their non-corrected counterparts for GGA and hybrid functionals\cite{25}. The self-interaction errors are smaller in hybrid functionals, but that is unlikely to be the main reason to the higher accuracy in many cases. Additionally, hybrid functionals may result in poorer descriptions of extended systems, such as surfaces with adsorbates\cite{26}.

### 3.3 Plane wave basis

In the Kohn-Sham equations (8), the electron density was written as a sum of a basis set of fictitious single partice states. These states can be chosen to be e.g. Gaussian orbitals which work well for molecules, but for periodic systems the natural choice is to use Bloch’s theorem to express the electron density as a linear combination of plane waves,

\[
\phi_{i,k}(r) = \sum_G c_{i,k+G} e^{i(k+G) \cdot r}.
\]

(32)

Here the band index is denoted by \( i \), and the reciprocal lattice points by \( G \) and \( k \), the latter of which lie within the first Brillouin zone. Since performing an infinite number of computations would take quite a while, the numbers of both \( G \) and \( k \) need to be limited. At each \( k \)-point the expansion is truncated at some maximum kinetic energy

\[
E_{\text{cutoff}} = \frac{k^2}{2m}|k + G|^2,
\]

(33)
which is usually chosen to be as small as it can be without significantly affecting the accuracy of the results. The number of $k$-points needs to be limited as well. Of the many schemes developed for the purpose, the one most commonly used is the Monkhorst-Pack\cite{27} scheme, where the first Brillouin zone is sampled on a uniformly spaced grid. The number of $k$-points needed can be further reduced by taking into account the symmetries of the reciprocal cell. The selected sampling can then be used to compute expectation values

$$
\langle X \rangle = \frac{1}{V} \sum_n \int_V d\mathbf{k} X_n(\mathbf{k}) f(\epsilon_n(\mathbf{k})),
$$

(34)

where the integration over the volume $V$ of the first Brillouin zone is replaced with a weighted sum over the selected grid:

$$
\langle X \rangle = \sum_{n,k} w_{nk} X_n(\mathbf{k}) f(\epsilon_n(\mathbf{k}))
$$

(35)

The approximation may be improved by interpolating using the linear tetrahedron method with Blöchl corrections\cite{28}, which is used in the bulk calculations presented in this text. The linear tetrahedron method requires multiple $k$-points in each direction, and thus cannot be used for surface calculations, where no periodicity, and therefore no band dispersion, is assumed in the direction normal to the surface. Gaussian smearing,

$$
f = \frac{1}{2} \left[ 1 - \text{erf} \left( \frac{\epsilon_{n,k}-\mu}{\sigma} \right) \right],
$$

(36)

is used for the surface calculations. In the above $\sigma = k_B T$ is a fictitious electronic temperature that controls the width of the smearing, and $\mu$ is the chemical potential. Using Gaussian smearing results in the total energy no longer being strictly variational, thus making it necessary to replace the total energy in force calculations by some generalized free energy

$$
F = E - \sum_{n,k} w_{nk} - \sigma S(f_{nk}),
$$

(37)

where $S$ is the contribution of entropy to the free energy. The proper total energy can be obtained through an accurate extrapolation for $\sigma \to 0$ as

$$
E(\sigma \to 0) = E_0 = \frac{1}{2} (F + E).
$$

(38)

Using the plane wave basis, the Kohn-Sham equations are turned into a matrix equation

$$
\sum_{G'} H_{G,G'}(\mathbf{k}) c_{i,k}(G') = \epsilon_{i,k} c_{i,k}(G),
$$

(39)
where
\[ \frac{\hbar^2}{2m} |\mathbf{k} + \mathbf{G}|^2 \delta_{\mathbf{GG}'} + V_{\text{eff}}(\mathbf{G} - \mathbf{G}') \]  

(40)

The eigenvalues \( \epsilon_i \) are obtained by diagonalizing the Hamiltonian. Note that the kinetic energy is already diagonal in the reciprocal space. The effective potential is computed first in real space and subsequently Fourier transformed using a Fast Fourier transform (FFT) algorithm.

### 3.4 Slabs

The surfaces of solids are periodic in two spatial dimensions. Using Bloch’s theorem to expand the fictitious states into plane waves, however, requires the system to be periodic in all three. In order to study surfaces while retaining the periodicity along the direction perpendicular to the surface, one uses the slab approach, where a slab with a finite number of layers is placed in the supercell. In the direction perpendicular to the surface one adds a region of vacuum thick enough to avoid interactions between the slab and its repeated images. The number of layers has to be large enough to model bulk states within the slab, and to prevent interactions between the two surfaces of the slab. For low index surfaces, the number of layers required is not very high, and may be reduced by fixing some of the layers to their bulk positions. When the system of interest includes adsorbates, the coverage is adjusted by changing the size of the supercell along the surface. The concentrations of dopants are controlled similarly. An example of supercell containing a slab is presented in Figure 3.

If the slab is relaxed asymmetrically, or molecules are adsorbed only on one side of the slab, as will be the case in the calculations presented below, a dipole moment will build up on the relaxed surface with the adsorbate. Due to the periodicity of the supercell, the dipole moment will be compensated on the other side of the slab, thus creating an implied electrostatic field through the vacuum region. To avoid this kind of field being generated, a correction, where a dipole layer is added into the vacuum in order to negate the dipole moment, is used. This should prevent the surfaces of the slab from interacting with each other through the vacuum. The implementation of the dipole corrections in VASP is a version of the scheme by Neugebauer and Scheffler[29] modified to be more general and to include some corrections.

### 3.5 Hellmann-Feynman theorem

When computing the ground state properties of a system, one usually starts by calculating its equilibrium geometry, since the geometry is influenced by...
computational details, such as the choice of the exchange-correlation functional. In order to relax the structure, one needs to be able to calculate forces between the atoms. The means to do that are provided by the Hellmann-Feynman theorem, which is briefly presented here.

Let the Hamiltonian $H_{\lambda}$ of the system depend on some continuous parameter $\lambda$. For any normalized variational solution $\psi_{\lambda}$, including any eigenstate of $H_{\lambda}$, the energy is given by

$$E_{\lambda} = \langle \psi_{\lambda} | H_{\lambda} | \psi_{\lambda} \rangle.$$  \hfill (41)

Then

$$\frac{dE_{\lambda}}{d\lambda} = \langle \psi_{\lambda} | \frac{\partial H_{\lambda}}{\partial \lambda} | \psi_{\lambda} \rangle + \frac{d}{d\lambda} \langle \psi_{\lambda} | H_{\lambda} | \psi_{\lambda} \rangle \bigg|_{\lambda'=\lambda},$$  \hfill (42)

where the latter term vanishes when $\psi_{\lambda}$ are orthonormal. By associating the parameter $\lambda$ with the nuclear positions $\mathbf{R}_l$, the forces acting on the atoms can be calculated as

$$\mathbf{F}_l = -\frac{dE}{d\mathbf{R}_l} = -\frac{\partial E}{\partial \mathbf{R}_l} = -\int d\mathbf{r} \frac{\partial V_{\text{ext}}(\mathbf{R}_l)}{\partial \mathbf{R}_l} n(\mathbf{r}).$$  \hfill (43)

It should be noted that in many cases $\langle \psi_{\lambda} | \psi_{\lambda} \rangle$ does not exactly vanish, resulting in the so called Pulay forces.
3.6 Projector augmented wave method

In a periodic system, Bloch’s theorem guarantees that the wave functions can be accurately described using plane waves. However, in the vicinity of an atomic nucleus, the Coulombic potential acting on the electrons is steep, resulting in wildly oscillating wave functions. Describing these oscillations requires a computationally expensive number of plane waves, i.e. a large cutoff energy $E_{\text{cutoff}}$. This problem can be dealt with in multiple ways, many of which involve the frozen core approximation, in which one assumes the core electrons of atoms to be largely unaffected by the formation of molecules or solids, and only handles the valence electrons during the self consistency cycle. This kind of separation is justified by noting that most properties of solids are significantly more affected by the valence electrons than the tightly bound core electrons.

In the pseudopotential approach the core electrons are included as sort of a screening effect in the external potential. Pseudopotentials are constructed in such a way that inside some region near a nucleus, the steep Coulombic potential is replaced by a potential that results in valence wave functions with no radial nodes. Outside the core region the pseudopotential, and therefore the pseudo wave functions, are identical to the true all-electron potential and wave functions.

A different approach, which avoids the loss of information on the full wave function near the nuclei, is the linearized augmented plane wave method (LAPW). In LAPW, one uses different basis sets for the core and interstitial regions: spherical harmonics and solutions to the radial Schrödinger equation within the core regions, and plane waves in the interstitial space between the augmentation spheres.

The projector augmented wave (PAW)\cite{30} method can be considered as a generalization of both of the above, as it offers LAPW as a special case\cite{31}, and at least the ultrasoft Vanderbilt\cite{32} pseudopotentials as a well defined approximation\cite{33}. In the PAW method a linear transformation $\mathcal{T}$ is made from the pseudo wave function $|\hat{\psi}\rangle$ to the true all-electron wave function $|\psi\rangle$. Since the wave functions are already smooth beyond some core radius, the transformation should only differ from identity by a sum of atom centered contributions that act only within the augmentation regions around each atom $a$:

$$\mathcal{T} = 1 + \sum_a T^a. \tag{44}$$

Inside the augmentation regions the true wave functions are expanded into partial waves $|\phi^a\rangle$, which are chosen to be the solutions to the radial scalar relativistic non-spin-polarized Schrödinger equation. For each partial wave,
a corresponding smooth auxiliary wave $|\tilde{\phi}_i^a\rangle$ is defined so that
\begin{equation}
|\phi_i^a\rangle = (1 + T^a)|\tilde{\phi}_i^a\rangle. \tag{45}
\end{equation}
If the smooth auxiliary waves form a complete set inside the augmentation region, the pseudo wave functions can be expanded as
\begin{equation}
|\tilde{\psi}_n\rangle = \sum_i c_{ni}^a |\tilde{\phi}_i^a\rangle. \tag{46}
\end{equation}
Similarly, since $|\phi_i^a\rangle = T|\tilde{\phi}_i^a\rangle$,
\begin{equation}
|\psi_n\rangle = \sum_i c_{ni}^a |\phi_i^a\rangle. \tag{47}
\end{equation}
Since the transformation is linear, the coefficients $c_{ni}^a$ must be linear functionals of the pseudo wave functions $|\tilde{\psi}_n\rangle$,
\begin{equation}
c_{ni}^a = \langle \tilde{p}_i^a | \tilde{\psi}_n \rangle, \tag{48}
\end{equation}
where the projector functions $|\tilde{p}_i^a\rangle$ satisfy the condition
\begin{equation}
\sum_i |\tilde{p}_i^a\rangle \langle \tilde{p}_i^a | = 1 \tag{49}
\end{equation}
inside each augmentation region. Using the partial wave and the projector functions, the transformation can be written as
\begin{equation}
T = 1 + \sum_{i,a} \langle |\phi_i^a\rangle - |\tilde{\phi}_i^a\rangle \rangle |\tilde{p}_i^a\rangle, \tag{50}
\end{equation}
using which the true all-electron wave function
\begin{equation}
|\psi_n\rangle = |\tilde{\psi}_n\rangle + \sum_{i,a} \langle |\phi_i^a\rangle - |\tilde{\phi}_i^a\rangle \rangle |\tilde{p}_i^a\rangle |\tilde{\psi}_n\rangle. \tag{51}
\end{equation}

The all-electron wave function is split into three parts, as shown in Figure 4. All quantities that can be calculated using the wave functions can similarly be decomposed into parts. For example, the charge density
\begin{equation}
n(r) = \tilde{n}(r) + n^1(r) - \tilde{n}^1(r), \tag{52}
\end{equation}
where
\begin{equation}
\tilde{n}(r) = \sum_n f_n \langle \tilde{\psi}_n | r \rangle \langle r | \tilde{\psi}_n \rangle, \tag{53}
\end{equation}
Figure 4: A schematic illustration of the separation of the wave function into parts. The augmentation spheres are shown as circles, and the supercell as a box. The gray parts depict the all-electron partial waves.

\[ n^1(r) = \sum_{n,i,j} f_n \langle \tilde{\psi}_n | \tilde{p}_i | \phi_i \rangle \langle \phi_i | r | \phi_j \rangle \langle \phi_j | \tilde{\psi}_n \rangle, \quad (54) \]

and

\[ \tilde{n}^1(r) = \sum_{n,i,j} f_n \langle \tilde{\psi}_n | \tilde{p}_i | \tilde{\phi}_i \rangle \langle \tilde{\phi}_i | r | \tilde{\phi}_j \rangle \langle \phi_j | \tilde{\psi}_n \rangle. \quad (55) \]

Additionally, the projector functions \(|\tilde{p}_i\rangle\), the partial waves \(|\phi_i\rangle\), and the smooth auxiliary waves \(|\tilde{\phi}_i\rangle\) can all be computed beforehand for every atomic species that appears in the system, leaving only the pseudo wave functions \(|\tilde{\psi}_n\rangle\) to be calculated from the transformed Kohn-Sham equations

\[ T^\dagger H T |\tilde{\psi}_n\rangle = \tilde{H} |\tilde{\psi}_n\rangle = \epsilon_n T^\dagger T |\tilde{\psi}_n\rangle, \quad (56) \]

where the transformed Hamiltonian is

\[ \tilde{H} = -\frac{1}{2} \nabla^2 + \tilde{v} + \sum_{i,j} |\tilde{p}_i| \left( \langle \phi_i | -\frac{1}{2} \nabla^2 + v^1 | \phi_j \rangle - \langle \tilde{\phi}_i | -\frac{1}{2} \nabla^2 + \tilde{v}^1 | \tilde{\phi}_j \rangle \right). \quad (57) \]

The expressions of the parts of the potential \(v(r) = \tilde{v}(r) + v^1(r) - \tilde{v}^1(r) = |r| \frac{\partial E}{\partial n} (r)\) can be found in the original PAW paper[30].

Since the total energy is given as a functional of the final electron density

\[ E[n] = \sum_n f_n \langle \psi_n | -\frac{1}{2} \nabla^2 | \psi \rangle \]

\[ + \frac{1}{2} \int dr \int dr' \frac{(n + n^Z)(n + n^Z)}{|r - r'|} \]

\[ + \int dr n \epsilon_{xc}(n), \quad (58) \]
it can be divided into three parts as \( E = \tilde{E} + E^1 - \tilde{E}^1 \). In the above \( n^Z \) is the point charge density of the nuclei. The Hartree atomic units (\( \hbar = e = m_e = 1 \)) are used here for convenience. The smooth part \( \tilde{E} \), which is evaluated on regular grids in real or reciprocal space, is

\[
\tilde{E} = \sum_n f_n (\tilde{\psi}_n) - \frac{1}{2} \nabla^2 (\tilde{\psi}_n) \\
+ \frac{1}{2} \int dr \int dr' \frac{(\tilde{n} + \tilde{n})(\tilde{n} + \tilde{n})}{|r - r'|} \\
+ \int dr \tilde{n} \tilde{v} + \int dr \tilde{n} \tilde{\epsilon}_{xc}(\tilde{n}).
\]

(59)

The one-center contributions, evaluated on atom centered radial grids, are

\[
E^1 = \sum_{n,i,j} f_n (\tilde{\psi}_n | \tilde{\phi}_i) (\tilde{\phi}_j | \tilde{\psi}_n) - \frac{1}{2} \nabla^2 (\tilde{\phi}_j) (\tilde{\phi}_j | \tilde{\psi}_n) \\
+ \frac{1}{2} \int dr \int dr' \frac{(n^1 + n^Z)(n^1 + n^Z)}{|r - r'|} \\
+ \int dr n^1 \tilde{\epsilon}_{xc}(n^1),
\]

(60)

and

\[
\tilde{E}^1 = \sum_n f_n (\tilde{\psi}_n | \tilde{\phi}_i) (\tilde{\phi}_j | \tilde{\psi}_n) - \frac{1}{2} \nabla^2 (\tilde{\phi}_j) (\tilde{\phi}_j | \tilde{\psi}_n) \\
+ \frac{1}{2} \int dr \int dr' \frac{(\tilde{n}^1 + \tilde{n})(\tilde{n}^1 + \tilde{n})}{|r - r'|} \\
+ \int dr \tilde{n}^1 \tilde{v} + \int dr \tilde{n}^1 \tilde{\epsilon}_{xc}(\tilde{n}^1).
\]

(61)

Here \( \tilde{v} \) is an arbitrary potential within the augmentation spheres the contribution of which to the total energy vanishes since \( \tilde{n} = \tilde{n}^1 \) within the augmentation spheres. The potential is used to minimize truncation errors in case the partial wave expansion is not complete. Additionally, the compensation charge density \( \tilde{n} \) was introduced into the expressions. Due to this addition the electrostatic multipole moments caused by the differences in the all-electron and pseudo contributions to the one-center density \( (n^1 + n^Z) - (\tilde{n}^1 + \tilde{n}) \) vanish. The energy due to multipole moments caused by localized charge distribution is transferred into \( \tilde{E} \), using the fact that it depends only on the multipole moments, and not the shape of the charge distribution.
The compensated charge density \( \hat{n} = \sum_r \hat{n}_R \), where
\[
\hat{n}_R(r) = \sum_L g_{RL}(r)Q_{RL}
\]
are sums of generalized Gaussians
\[
g_{RL} = C_l |r - R|^l Y_L(r - R)e^{-(|r - R|/r_c)^2}.
\]
Here \( C_l \) is a normalization constant such that the multipole moment of the generalized Gaussian is unity, \( Y_L \) are spherical harmonics, and \( r_c \) is a decay factor that is chosen so that the compensation charge density vanishes outside the augmentation spheres. The multipole moments are given as
\[
Q_{RL} = \int dr |r - R|^l [n_R^1(r) + n_R^Z(r) - \hat{n}_R^1 Y_L^*(r - R)].
\]
Because the Gaussians need to decay within the augmentation spheres, they tend to have high Fourier components, leading to a large plane wave cut-off in the pseudo charge density. Therefore, another primed compensation charge density \( \hat{n}' \) having the same multipole moments, but using generalized Gaussians with larger decay radii, must be introduced. Using the new compensation charge density, the electrostatic energy in \( \tilde{E} \) can be rewritten as
\[
\frac{1}{2} \int dr \int dr' \frac{(\hat{n} + \hat{n})(\hat{n} + \hat{n}')}{|r - r'|} = \frac{1}{2} \int dr \int dr' \frac{(\hat{n} + \hat{n}') (\hat{n} + \hat{n}')}{|r - r'|} + \int dr \hat{n}(r) \hat{v}(r) + \sum_{R,R'} U_{R,R'}.
\]
The first term of the modified electrostatic energy contains only smooth functions and is easily evaluated in reciprocal space. The second has high Fourier components, but does not contribute to the total energy because they are multiplied with high Fourier components of the pseudo charge density, which are exactly zero when imposing a cutoff energy. The third term is a short range pair potential between atoms, that can be evaluated analytically.

In addition to the charge densities and total energies, the Hellmann-Feynman forces acting in the system will be used to evaluate some quantities of interest. The total force acting on a nucleus is, again, given in three parts \( F_R = F^{(1)}_R + F^{(2)}_R + F^{(3)}_R \), where the first is due to the smooth part of the energy \( \tilde{E} \):
\[
F^{(1)}_R = \int dr \nabla \hat{n}'_R \int dr' \frac{\hat{n} + \hat{n}'}{|r - r'|} + \int dr \hat{n} (\nabla \hat{v}_R + \nabla \hat{v}_R) \\
- \int dr \hat{n} v \nabla \hat{v} - \sum_{R'} \nabla_{R|Q} U_{R,R'},
\]

21
where the first three terms are computed in reciprocal space, the last is related to the derivative of the pair potential for fixed multipole moments and is evaluated analytically. \( \tilde{n}^c \) refers to the density due to the core states. The second term of the total force is due to the change in the shape of the one-center densities in a small displacement of a nucleus,

\[
F_R^{(2)} = -\sum_{i,j} \nabla_R \Theta_{ij} \left( |\phi_i| - \frac{1}{2} \nabla^2 + v^1 |\phi_j| - |\tilde{\phi}_i| - \frac{1}{2} \nabla^2 + \tilde{v}^1 |\tilde{\phi}_j| \right), \quad (67)
\]

where

\[
\Theta_{ij} = \sum_n f_n \langle \tilde{\psi}_n | \tilde{p}_i \rangle \langle \tilde{p}_j | \tilde{\psi}_n \rangle \quad (68)
\]
is a density matrix for the one-center expansions in terms of partial waves. Since the one-center partial waves are displaced along with the nuclei, there is a change in the orthogonality of the all-electron wave functions, leading to the Pulay force

\[
F_R^{(3)} = \sum_{n,m} \frac{f_n + f_m}{2} \langle \tilde{\psi}_n | \hat{H} | \tilde{\psi}_m \rangle \langle \tilde{\psi}_m | \nabla_R \tilde{O} | \tilde{\psi}_n \rangle - , \quad (69)
\]

where

\[
\tilde{O} = 1 + \sum_{i,j} |\tilde{p}_i \rangle [\langle \phi_i | \phi_j \rangle - \langle \tilde{\phi}_i | \tilde{\phi}_j \rangle] |\tilde{p}_j \rangle \quad (70)
\]
is an overlap operator.

4 Calculable physical properties

In the end of a DFT self-consistency cycle one has obtained the equilibrium electron density, the basis functions used to construct it, and the total energy of the system. Out of these three, only the electron density is a experimentally observable quantity. In this section we briefly explain some quantities that can be evaluated using the output of the DFT calculation.

4.1 Surface energy

The surface energy, or the work required to create a surface, is defined as

\[
E_{surf} = \frac{E_{slab} - nE_{bulk}}{2A}, \quad (71)
\]

where \( E_{slab} \) is the total energy of the slab supercell, \( E_{bulk} \) is the total energy of the bulk unit cell, \( n \) is the number of unit cells in the slab, and \( A \) is the
surface area of one of the faces on the slab. The main use of the surface energy is to compare the relative stabilities of the possible surfaces of a solid. Only the rutile (110) surface is considered in this text, but the surface energies of slabs are calculated in order to see the effect the number of layers in the slab has on the surface.

4.2 Adsorption energy

The adsorption energy is defined as

$$E_{ads} = E_{slab + H_2O} - E_{slab} - E_{H_2O},$$

(72)

where $E_{slab}$ is the total energy of the slab without an adsorbate, $E_{H_2O}$ is the total energy of an isolated water molecule, and $E_{slab + H_2O}$ is the total energy of the same slab with a molecule adsorbed on it. It should be noted that the adsorption energy is sometimes defined as the inverse of how it is defined here. This way around, the lower the adsorption energy, the stronger the attractive interaction is between the surface and the adsorbed molecule.

4.3 Density of states

Some aspects of the interaction of an adsorbate and the surface can be elucidated by analyzing the density of states (DOS), which is readily accessible from the results of a DFT calculation as

$$D(E) = \sum_i \delta(E - \epsilon_i),$$

(73)

where the summation is over all the eigenstates of the Kohn-Sham Hamiltonian. Since a finite number of eigenstates are produced in a calculation the distribution is smeared using e.g. the Gaussian smearing scheme in order to get a continuous distribution. The total density of states as defined above does not, however, show a clear picture of how the states of the atoms directly involved in the adsorption process, for example, are affected by the event. To clarify the situation, the DOS can be projected on to the atomic valence orbitals to get the local density of states (LDOS):

$$D_\alpha(E) = \sum_i |\langle \phi_\alpha | \phi_i \rangle|^2 \delta(E - \epsilon_i),$$

(74)

where $\phi_\alpha$ is some localization function. Since the plane wave basis is delocalized and contains no information on atomic orbitals or even the locations of atoms, the projection function truncates the basis to a sphere around a
selected atom, setting the wave function zero outside the sphere. Inside the sphere the basis functions are projected onto spherical harmonics in order to get an angular momentum resolved expansion.

### 4.4 Bader charge density analysis

In some cases it is useful to partition the equilibrium electron density obtained from the DFT calculation into separate contributions by individual atoms. Since the wave functions are expanded into plane wave basis set, any orbital based methods, such as the Mulliken analysis, are not applicable. Therefore, a method which uses only the charge density has to be used. One such method is Bader’s "atoms in molecule” theory, where space is divided into regions based on surfaces that run through points where the gradient of the electron density has no component normal to the surface: \( \nabla n(r) \cdot \hat{e} = 0 \), where \( \hat{e} \) is the unit vector perpendicular to the surface. Each of these Bader volumes \( \Omega_n \) is defined as the set of points whence following a trajectory of maximizing the density reaches a single maximum, usually centered by an atom. The total charge "belonging" to the atom can then be calculated as an integral over the volume \( \Omega_n \). The Henkelman group provides a code for the calculation of Bader charges from VASP output densities[34–37].

### 4.5 Transition state theory

An important problem in theoretical and condensed matter physics and chemistry is the calculation of rates of transitions, such as the rate of transition from a molecularly adsorbed water molecule to a dissociated one on the surface of a solid. Usually the motions of atoms can be described using classical mechanics. Transitions, however, might happen in timescales orders of magnitude larger than the vibrations of atoms, making the direct simulations of transitions unfeasible. For this reason, one uses the transition state theory (TST)[38, 39], a statistical approach for the estimation of transition rates.

In TST one defines a transition state that separates the initial and final states of the transition. The reaction rate is calculated as the probability of finding the system in the transition state relative to the initial state multiplied with the rate of crossing from the initial to the final state, evaluated at the transition state. TST relies on two approximations besides the Born-Oppenheimer approximation. These are: first, the rate is slow enough that a Boltzmann distribution is established at the transition state in addition to the initial and final states, and second, there exists a surface with dimensionality one lower than the number of degrees of freedom in the system,
such that the trajectory from the initial to the final state crosses the dividing surface exactly once. This dividing surface represents a bottleneck for the transition, and is found at a saddle point of the potential energy surface along the trajectory. The dividing surface can be defined as the hyperplane normal to the unstable direction at the saddle point.

Since the atoms in solids tend to be quite tightly bound to their lattice points, the harmonic approximation of TST (HTST) can usually be used to study reactions on the surfaces of solids. In HTST the potential energy surfaces are assumed to be locally harmonic around the initial state and the saddle point, allowing for a second order Taylor expansion of the potential energy surface. This makes the rate constant $k$ for transitions through the saddle point

$$k_{HTST} = \frac{3N}{3N-1} \prod_i \nu_i \exp\left(-\frac{(E^s-E^{init})}{k_B T}\right).$$

In the above expression $E^s$ and $E^{init}$ are the energies of the saddle point and the initial state, respectively, and $\nu_i$ are the corresponding normal mode frequencies. All of the quantities required for the estimation of the HTST transition rate can be evaluated from the potential energy surface at zero temperature, but entropic effects are introduced through the harmonic approximation.

The functional form of the HTST reaction rate is analogous to the empirically derived Arrhenius rate law

$$k_{Arrhenius} = Ae^{-E_a/k_BT},$$

where $A$ is the rate constant and $E_a$ is the activation energy defined as the difference between the saddle point and the minimum in HTST. The exponential term is the Boltzmann probability that a vibration along the trajectory will overcome the activation barrier. This gives an interpretation to the HTST reaction rate as a product of the frequency of attempts and the probability of those attempts to be successful.

### 4.6 Nudged elastic bands

The trajectory connecting the initial and final states with the highest statistical weight is the minimum energy path (MEP). The potential energy maximum along the MEP is the saddle point energy that gives the activation energy barrier. The MEP is found by constructing a set of images
of the system between the initial and final states. A spring interaction is added between adjacent images to ensure the continuity of the band. Minimizing the forces acting on each image brings the band to the MEP. In the nudged elastic band (NEB)[40] method, an elastic band with \(N + 1\) images, \(\{R_0, R_1, ..., R_N\}\), where the endpoints \(R_0\) and \(R_N\) are fixed to predetermined initial and final states of the transition. The other \(N - 1\) images are adjusted by an optimization algorithm. The total force acting on an image is the sum of the spring force along the local tangent and the true force perpendicular to the local tangent

\[
F_i = F_i^s = \frac{\nabla E(R_i)}{\|\nabla E(R_i)\|},
\]

where the true force is given by

\[
\nabla E(R_i) = \nabla E(R_i) - \nabla E(R_i) \cdot \hat{\tau}_i,
\]

where in turn \(E(R_i)\) is the energy of the system and \(\hat{\tau}_i\) is the normalized local tangent at the image \(i\). The spring force is defined by

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

where \(k\) is the spring constant. In some systems when many images are included in the elastic band the force along the MEP can be significantly larger than the restoring perpendicular force. This can introduce kinks into the band, preventing the proper convergence of the band into the MEP. The formation of kinks can be avoided by taking only the adjacent image with the highest energy in the definition of the local tangent[41]:

\[
\tau_i = \begin{cases} 
\tau_i^+ & \text{if } E_{i+1} > E_i > E_{i-1} \\
\tau_i^- & \text{if } E_{i+1} < E_i < E_{i-1}
\end{cases},
\]

where \(\tau_i^+ = R_{i+1} - R_i\), \(\tau_i^- = R_i - R_{i-1}\), and \(E_i = E(R_i)\). If both adjacent images have either higher or lower energies than image \(i\), the tangent is taken to be the weighted average of the vectors to the two adjacent images

\[
\tau_i = \begin{cases} 
\tau_i^+ \Delta E_i^{\max} + \tau_i^- \Delta E_i^{\min} & \text{if } E_{i+1} > E_i > E_{i-1} \\
\tau_i^+ \Delta E_i^{\min} + \tau_i^- \Delta E_i^{\max} & \text{if } E_{i+1} < E_i < E_{i-1}
\end{cases},
\]

where

\[
\Delta E_i^{\max} = \max |E_{i+1} - E_i|, |E_{i-1} - E_i|,
\]

and

\[
\Delta E_i^{\min} = \min |E_{i+1} - E_i|, |E_{i-1} - E_i|.
\]

In any case, the tangent \(\tau_i\) needs to be normalized.
Typically in a band converged using forces as defined in Eq.(77), none of the images have landed at the saddle point, or even near it, and the saddle point energy would have to be estimated by interpolation. However, rigorous convergence of one of the images to the saddle point can be ensured by making the image nearest to the saddle point a climbing image[42]. After a few iterations have been calculated as above, the image with the highest energy $i_{\text{max}}$ is identified, and the force acting on this image is replaced by

$$F_i^{\text{max}} = -\nabla E(R_{i_{\text{max}}}) + 2\nabla E(R_{i_{\text{max}}}) \cdot \hat{r}_{i_{\text{max}}} \hat{r}_{i_{\text{max}}}.$$  \hspace{1cm} (84)

The component of the full force along the elastic band is inverted, and the image is not affected by the spring forces at all, causing the image to move up the potential energy surface along the band, and down perpendicular to the band. The other images define the one degree of freedom for which a maximization of energy is carried out. Since the images in the band eventually converge to the MEP, they give a good approximation to the reaction coordinate around the saddle point. Turning one of the images into a climbing one incurs no additional computational cost, as all the images are minimized simultaneously. Since the climbing image is not affected by the spring forces, the spacing of the images in the band gets uneven around it. This can be remedied by making the spring forces dependent on the energy of the image, which, in addition to evening the spacing around the climbing image, serves to increase the resolution of the band around the saddle point.

### 4.7 Dynamical matrices

As mentioned when discussing the harmonic TST, the potential energy surfaces around the minima of the transition are approximately harmonic. Clearly, in a minimum, the first derivatives of the potential, i.e. forces, vanish, and the second derivatives are positive definite. Therefore, up to second order in its Taylor expansion, the potentials around the minima are

$$V(r_1, r_2, ..., r_{3N}) \approx V_0 + \frac{1}{2} \sum_{ij} \frac{\partial^2 V}{\partial r_i \partial r_j} u_i u_j,$$  \hspace{1cm} (85)

where $r_i$ are the cartesian coordinates of the nuclei, in the $i$ and $j$ refer to the $3N$ degrees of freedom, and $u_i$ are the displacements of the nuclei from their equilibrium positions. Let us define the dynamical matrix as

$$D_{ij} = \frac{1}{\sqrt{m_i m_j}} \frac{\partial^2 V}{\partial r_i \partial r_j} = -\frac{1}{\sqrt{m_i m_j}} \frac{\partial F_j}{\partial r_i}.$$  \hspace{1cm} (86)
The partial derivatives of the forces are evaluated using the finite difference approximation through the introduction of small displacements of the nuclei into the system. Using the definition of the dynamical matrix $\mathbf{D}$ and the mass-weighted generalized coordinates $q_i = \sqrt{m_i}u_i$, the Lagrangian of the vibrational motion in the harmonic approximation is

$$L = \frac{1}{2} \sum_i q_i^2 - \frac{1}{2} \sum_{ij} D_{ij} q_i q_j.$$  \hspace{1cm} (87)

The normal mode frequencies are obtained through the diagonalization of the dynamical matrix, which is done using a transformation to a set of normal mode coordinates

$$q_i = \sum_{\lambda} C_{i\lambda} \xi_{\lambda},$$ \hspace{1cm} (88)

where $\mathbf{C}$ is an orthogonal transformation matrix that comprises the column eigenvectors of $\mathbf{D}$. The Lagrangian is then

$$L = \frac{1}{2} \sum_{\lambda} (\dot{\xi}_{\lambda}^2 - \nu_{\lambda}^2 \xi_{\lambda}^2),$$ \hspace{1cm} (89)

which is exactly the Lagrangian of $3N$ harmonic oscillators in the generalized coordinate $\xi_{\lambda}$ with the frequencies $\nu_{\lambda}$.

The normal mode frequencies obtained using the dynamical matrix have several uses, including the evaluation of the transition rate prefactors and zero-point energy corrections to the barriers\cite{43, 44} as

$$\delta E_{ZP} = \frac{\hbar}{2} \left( \sum_i \nu_i^s - \sum_i \nu_i^{init} \right),$$ \hspace{1cm} (90)

in the low temperature limit. Using the partition function of the quantum mechanical harmonic oscillator, a temperature dependent correction to the classical transition rate can be obtained as

$$k_{qm}^{HTST} = e^{-\delta E/k_B T} k_{^{HTST}},$$ \hspace{1cm} (91)

where the Wigner correction is

$$\delta E = -k_B T \left[ \prod_i \frac{\sinh(x_i^{init})/x_i^{init}}{\sinh(x_i^s)/x_i^s} \right].$$ \hspace{1cm} (92)
\[ x_i = \frac{h \nu_i}{2k_B T} \]

is the ratio of zero-point energy to the thermal energy at each vibrational mode.

Additionally, dynamical matrices can be used to check the validity of the saddle points of the minimum energy paths, as they have a negative second derivative of the potential energy along the path. Thus, exactly one eigenvalue of a dynamical matrix at a saddle point should be negative.

5 Computational details and results

All the calculations presented in this text were done using the Vienna Ab initio Simulation Package (VASP)[45–47] with the spin-polarized Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional described in Section 3.2. PAW potentials generated with PBE are provided with VASP for all elements of the periodic table, some of them in multiple variants which differ in the numbers of semicore electrons that are treated as valence electrons during the self consistency cycle. The atomic species present in the calculations, hydrogen, oxygen, titanium, and manganese, are described using 1, 6, 12 (3s^23p^64s^23d^2), and 13 (3p^64s^23d^5) valence electrons, respectively. All the files defining the positions of the atoms were constructed using the Atomic Simulation Environment (ASE)[48]. The positions of the atoms were relaxed using conjugate-gradient minimization except when stated otherwise.

5.1 Bulk rutile

To construct reliable surface slabs one needs to know the equilibrium geometry of the bulk material from which the slab is cleaved. Initially the atomic positions and the unit cell were both allowed to relax using an energy cutoff of 800 eV, and a $8 \times 8 \times 12$ Monkhorst-Pack $k$-point grid, using the linear tetrahedron method with Blöchl corrections for interpolation.

The parameter that mostly determines the accuracy of the calculations is the plane wave cutoff energy shown in Eq. (33), which determines the number of plane waves used to represent the all-electron wave function at each $k$-point. The larger the number of plane waves, the better the true all-electron wave function, and therefore the electron density, can be approximated as their linear combination. Of course, increasing the number of things needing to be computed increases the amount of memory and processor time required to complete the computation. The optimal cutoff energy
required for the accurate description of any given system depends on the atomic species present and the PAW used to describe the core electrons. In the calculations presented in this text, the four species of atom appear in various combinations, though oxygen and titanium are present in each calculation. The VASP manual, and the PAW potential files themselves, give recommendations for the cutoff energies for each species. The highest of the recommended cutoff energies is for oxygen at 400 eV. While the recommended value should be sufficient in most cases, it is prudent to always check the energy convergence with respect to the cutoff energy.

Since oxygen is obviously present in bulk rutile, the cutoff energy to be used in all subsequent calculations can be, and was, determined using the previously relaxed rutile unit cell, by increasing the cutoff energy in increments of 50 eV from 300 eV to 600 eV. The dependence of the total energy of the bulk unit cell on the cutoff energy is shown in Figure 5. It was found that the recommended cutoff energy of 400 eV is sufficient to converge the total energy to less than 0.1 eV. While it seems a bit high, it should also be noted that the total energy means nothing on its own in most cases, and that relative energy differences tend to converge significantly faster. For example the adsorption energy of molecular water on a six layered slab in a (1×2) supercell was converged to within 5 meV with the kinetic energy cutoff on 400 eV.

The total energy needs to be converged with respect to the density of the k-point grid as well. The number of k-points at which the wave function needs to be computed can be reduced by taking the symmetries present in the cell into account, e.g. the point group of the rutile unit cell is $D_{2h}$, which
reduces a $4 \times 4 \times 6$ grid into 24 $k$-points in the irreducible Brillouin zone. It seems that a $4 \times 4 \times 6$ grid is good enough for the bulk. However, unlike the cutoff energy, which should be kept constant between the calculations, the $k$-point grid needs to be changed. Since the volume of the first Brillouin zone is inversely proportional to the real space size of the supercell, the grids used in the subsequent calculations can have even fewer points. Additionally, only one $k$-point is necessary perpendicular to surfaces in the calculations involving them.

After the converged cutoff energies and $k$-point grids were found, the bulk unit cell was relaxed again. The bulk unit cell parameters were found to be $a = b = 4.5969 \AA$, $c = 2.9525 \AA$, the internal parameter $x = 0.3040$, and $c/a = 0.6423$. These are in excellent agreement with the experimental values of $a = 4.587 \AA$, $c = 2.954$, $x = 0.305$, and $c/a = 0.644$ [49].

5.2 Doped surfaces

Using the unit cell parameters calculated previously, slabs with two (110) surfaces exposed were cut. Since there is only a single $k$-point in the direction perpendicular to the surface, the linear tetrahedron method can no longer be used and is replaced with Gaussian smearing. In the calculations presented here, the two bottom layers were fixed to their bulk equilibrium positions, and the rest were allowed to relax.

The relaxation of the surface changes the positions of the atoms on the topmost layers. The relaxation of the surface decreases the distance between the two differently coordinated titanium atoms, Ti$_5c$ and Ti$_6c$, from 3.570 Å to 3.599 Å. Despite the in-plane oxygen atoms relaxing toward the fivefold coordinated titanium the length of the Ti$_5c$-$O_p$ bond is increased from 1.950 Å to 1.952 Å, due to the vertical displacements. The downward relaxation of the bridging oxygen and the upward displacement of the sixfold coordinated titanium brings the length of the Ti$_6c$-$O_b$ bond from the same 1.950 Å down to 1.827 Å. The interatomic distance differences in the relaxed and unrelaxed surfaces are shown in Figure 6. The change in the surface energy of the rutile (110) with respect to the number of layers is shown in Figure 7. While the surface energy is not necessarily an important quantity here, especially since fixing the two bottom layers makes half of the surface area of the slab unrelaxed, the figure shows clearly the odd-even oscillations that tend to appear in calculations involving (110) slabs of rutile. Two things need to be pointed out in the case of the surface energies: first, the rough value of $60 \text{ meV/Å}^2 = 0.96 \text{ J/m}^2$ is similar to previously reported values [50]. More accurately, it is somewhere between the reported surface energy of a slab that is fully relaxed on both sides and the energy of a completely unrelaxed slab,
Figure 6: The effect of the relaxation of the surface on the various interatomic distances on the surface. The surfaces depicted are (a) the unrelaxed surface, (b) the relaxed clean surface, (c) the surface with the Ti$_5$c site substituted with a manganese atom, and (d) The surface with manganese at the Ti$_6$c site. These were relaxed in a $(2 \times 3)$ supercell with six layers.
Figure 7: The surface energies of clean rutile (110) slabs with a varying number of layers. These were calculated in a (1×2) supercell with a 4×4 Monkhorst-Pack grid. Note the clear oscillation between odd and even numbers of layers, even though one side of the slab is fixed, and therefore the reflection symmetry is broken as the slab relaxes.

which is to be expected. Second, what is not to be expected is the results presented in this text to be accurate at 1 meV precision. The primary reason for the existence of the oscillations is the difference in O2p-Ti3d interlayer hybridization along the slab[51]. Having an odd number of layers the supercell adds a spurious reflection symmetry plane into the middle layer of the slab. Without the symmetry plane, the hybridization causes the formation of TiO2 bilayers that interact weakly with the neighboring bilayers. Due to the symmetry plane, there is no hybridization in the middle layer. This is supported by the fact that removing the Ti3d electrons from consideration removes the oscillation. In reality, even if such a symmetry plane exists, its effect on the surface should be negligible given the sizes of most real samples. Therefore, results obtained using an even number of layers are likely to be more realistic.

When doping rutile with manganese, the dopants are most likely to be substituted at titanium lattice points because of their similar ionic radii[17]. The effects of the dopants on the behavior of water on the surfaces are largest when they are located at the topmost layer of the slab. For that reason, the two unique substitution sites on the top layer were considered for this text. As mentioned in Section 2.2, the atoms are displaced from their bulk positions as the surface relaxes. In the clean surface the fivefold coordinated titanium atoms move down, the sixfold coordinated titanium moves down, the bridging oxygen moves down, and the previously in-plane oxygen move
up and slightly towards the fivefold coordinated titanium.

Substituting one of the fivefold coordinated titanium atoms with manganese causes the following changes relative to the relaxed clean surface: the manganese atom itself is moved up, the sixfold coordinated titanium is pulled closer to the manganese. This is also true for titanium in the [001] direction. The bridging oxygen is displaced upwards and laterally towards the doping site. The in-plane oxygen is displaced down and toward the manganese along the surface.

A manganese atom replacing one of the sixfold coordinated titanium atoms is moved down relative to where the titanium would be. The fivefold coordinated titanium is pulled towards the manganese with little vertical movement. The bridging oxygen moves down with the manganese atom without really changing the bond length. The in-plane oxygen moves down and towards the manganese. In summary, the manganese pulls all its neighboring atoms closer to itself, the fivefold coordinated manganese is pushed slightly outwards, while the sixfold coordinated one is pulled towards the depths of the slab.

Generally, the relative stabilities of solids cannot be determined by just comparing their total energies. Instead, one should compare their formations energies, basically the total energy of the solid versus the energies of the most stable form of the constituent atoms come in. However, since only one kind of dopant atom is under consideration, the total energy is the only contribution to the formation energy where the two possible doped surfaces differ. In a (2×3) supercell with six layers, the doped surface with a sixfold coordinated manganese atom is 0.13 eV lower in energy compared to the alternative. Increasing the size of the supercell into (2×4) surface unit cells changed the energies of the differently doped surfaces by less than 0.01 eV. A single manganese atom in a (2×3) supercell means 1/12 of the titanium on the surface layer is replaced. With six layers, this corresponds to a manganese concentration of 0.5% by number of atoms and 1% by mass. The positions of the dopants on the surface, and their effects on the distances to the surrounding atoms can be seen in Figure 6.

5.3 Water adsorption

In order to study the effects of manganese doping on the behavior of water on the surface of interest, it is first necessary to find out how the computational setup in use (PBE with PAW, energy cutoff of 400 eV, etc.) predicts it to behave on the clean surface. It is especially important in the case of the rutile (110) surface, because of the disagreements between experimental and computational results on the issue. Even among the multitude of theoretical
works there is disagreement on whether molecular or dissociative adsorption is more stable, or some mixture between the two[8]. In contrast, experimental studies show mainly molecular adsorption, and dissociation only on defect sites[52–55]. Dissociation might occur with low coverages of less than an eight of a monolayer, but even that could be due to defects. Most of the theoretical results show the difference in energy between the two cases to be very small, and therefore extremely sensitive to the computational setup.

All that said, the clean surface calculation needs to be done in order to see the changes the doping causes relative to an undoped surface, and to see the convergence of the differences in energy with respect to the number of layers in the slab. Because of the odd-even oscillation discussed before, only even numbers of layers were considered. The adsorption site was chosen to be the same as in most of the literature reviewed by Sun et al.[8]. That is to say, the water molecule is located above the coordinatively undersaturated site, so that the oxygen of the adsorbate effectively brings the coordination of the titanium or manganese atom up to the bulk value of six. One of the hydrogen atoms of the water molecule point towards the nearest bridging oxygen, i.e. to the [110] direction along the surface. The other hydrogen end of the molecule is turned slightly up, away from the surface. The dissociatively adsorbed water is made by simply displacing the hydrogen atom pointing in the [110] direction towards the bridging oxygen. Other possible adsorption sites have been studied in the past[56], finding the conformation described above to be the most stable by quite large a margin due to the formation of a hydrogen bond between the oxygen of the water molecule and the bridging oxygen.

The differences in adsorption energies of molecular and dissociated water were found to be converged to a precision of less than 0.02 eV for the six layer slab, which will have to be enough considering the large surface area of the slabs used in the succeeding calculations. It is assumed in this text that not only are the adsorption energy differences converged, but that the same precision applies to any transition states between the molecular and dissociated states. Using a six layer slab at a half monolayer coverage, i.e. one molecule on a (1×2) slab, and a 4×4×1 Monkhorst-Pack grid, the adsorption energies were found to be -0.61 eV and -0.44 eV for molecular and dissociative adsorption, respectively. This is also similar to previously reported results using roughly the same computational setup[8]. The total energy of the isolated water molecule was calculated in a 15 Å×15 Å×15 Å supercell using a single k-point.

Using a 2×2×1 Monkhorst-Pack grid, the adsorption energies were calculated for molecular and dissociated water on a clean six layer slab in a (2×3) supercell and both kinds of doped surface of the same size. The six
Table 1: The adsorption energies of water in the different surfaces. $E_M$ denotes the energy of molecular adsorption, $E_D$ the energy of dissociative adsorption, and $\Delta E$ their difference.

<table>
<thead>
<tr>
<th>Dopant</th>
<th>$E_M$</th>
<th>$E_D$</th>
<th>$\Delta E$</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>-0.724</td>
<td>-0.655</td>
<td>-0.069</td>
</tr>
<tr>
<td>Mn5c</td>
<td>-0.904</td>
<td>-0.871</td>
<td>-0.033</td>
</tr>
<tr>
<td>Mn6c</td>
<td>-0.781</td>
<td>-0.840</td>
<td>0.059</td>
</tr>
</tbody>
</table>

different configurations are shown in Figures 8, 9, and 10. Since using the dipole corrections slows down the convergence towards the electronic ground state, they were not used in calculations involving supercells this large, noting that the error due to the dipole moment in e.g. adsorption energies should be only a few meV.

Compared to the energies in the higher coverage case discussed above, the one sixth monolayer coverage of water on the clean surface results in higher adsorption energies and brings the energy difference between the cases to less than a half. Doping the surface with manganese increases the adsorption energy, and brings the two configurations even closer together in energy. Based on just the tendency of the manganese dopant to pull all of its neighbors toward itself, the values compared to the undoped case seem intuitive. One might also predict that the energy barrier for the decomposition of water would be increased in the case of the fivefold coordinated manganese dopant, and decreased in the other, based on the same naïve line of thinking.

On a side note, it has been previously shown that doping rutile with transition metals, including manganese, decreases the energy of vacancy formation for bridging oxygen atoms not directly neighboring the dopant[57], which might aid in the decomposition of water. Considerations of the effects of vacancies on the adsorption behavior or the effects of doping on vacancy formation are beyond the scope of this work.

In transition metals in aqueous environments, the charge transfer from water molecules onto the cluster has been shown to be of significant size[58, 59]. Transferring the charge from a water molecule could remove electrons from its bonding orbitals, thus weakening the O-H bonds and making the decomposition easier. In a study by Xu et al.[60], similar magnitude of charge transfer was not found to happen in water adsorption on the clean rutile (110) surface, nor two other metal oxides, namely SnO$_2$ and In$_2$O$_3$. Nevertheless, since calculating Bader charges is relatively effortless, and it would be interesting to know of any simple and computationally inexpensive way of predicting the effects of doping on the water decomposition process, the Bader charges for the water molecule were computed for all the configurations.
Figure 8: The relaxed structures of molecularly adsorbed and decomposed water on the clean (110) surface, and the densities of states of the O2p levels. The shown atomic surfaces are cut out from the (2\times3)-surface. In the surface O2p DOS the contributions from every bridging and in-plane oxygen atom on the top layer are included. The slab O2p DOS contains the densities of states of the oxygen in a relaxed layer within the slab. The DOS marked with black contains only the 2p DOS of the bridging oxygen that captures the hydrogen from the adsorbate. The dotted lines signify the surface without an adsorbate.
Figure 9: The relaxed structures and O2p DOS plots of the fivefold coordinated manganese doped surface.
Figure 10: The relaxed structures and O2p DOS plots of the sixfold coordinated manganese doped surface.
Table 2: The total Bader charges of the atoms of the adsorbate molecule. Here $q_M$ is the charge of the molecularly adsorbed water, and $q_D$ the decomposed water. In parentheses are the charges of the constituent atoms, with the leftmost value belonging to the hydrogen that dissociates from the molecule.

| Dopant | $q_M(|e|)$         | $q_D(|e|)$         |
|--------|--------------------|--------------------|
| None   | 7.97 (0.66 + 0.53 + 6.79) | 7.97 (0.52 + 0.57 + 6.89) |
| Mn$_{5c}$ | 7.90 (0.53 + 0.47 + 6.90) | 8.06 (0.65 + 0.59 + 6.82) |
| Mn$_{6c}$ | 7.99 (0.57 + 0.52 + 6.90) | 8.02 (0.55 + 0.47 + 6.99) |

shown in Figures 8, 9, and 10, and are tabulated in Table 2.

Similarly to the previous results by Xu et al. for the undoped metal oxides, the charge transfers involved in the adsorption process are too small to be indicative of the kind of O-H bond weakening that happens in the transition metals in water. It is worth pointing out, however, that the charge transfer is the largest in the case of the water molecule being adsorbed on top of the manganese dopant.

The same authors concluded that a metal oxide’s capability to split water can be predicted by the position of the 2p levels of the surface oxygen atoms relative to the valence band maximum. According to their results, if the surface oxygen 2p levels are at the top of the valence band, as in indium oxide and tin dioxide (110) surfaces, the metal oxide was found to be very efficient at decomposing water, and conversely, as in the case of rutile TiO$_2$, if the surface oxygen 2p levels lie below the core oxygen 2p levels, the surface is much less reactive. They supported this claim by computing the adsorption energy differences between the molecular and dissociated water, and the minimum energy paths of the transitions using climbing image NEB. In both of the non-TiO$_2$ cases, the barriers to the transition to the decomposed states were either vanishingly small or non-existent.

To check whether the location of the surface oxygen O2p levels could work as a predictor for the catalytic activity of the manganese doped TiO$_2$, the densities of states were calculated for the clean and doped surfaces, and can be seen plotted beside the corresponding surface structures in Figures 8, 9, and 10. In the calculated densities of states the valence band maximum is set to the Fermi level. Clearly, the surface O2p levels are well below the valence band maximum regardless of the existence or the location of a dopant. Additionally, the surface O2p states are concentrated below the equivalent states within the slab. However, in both doped cases without an adsorbate there is a small blip above the slab states, and in the sixfold coordinated manganese case, the blip does not disappear as the water molecule is adsorbed
onto the surface. To see the effect of the dopant on specifically the bridging oxygen involved in the dissociation of the water, their densities of states and those of the manganese dopants are shown in Figure 11. On the sixfold coordinated manganese surface, where the dopant shares a bond with the bridging oxygen, the O2p level involved in the formation of the bond is close in energy to the valence band maximum. As seen in Figure 11 (c), most of the portion of the bridging oxygen DOS around the edge of the valence band moves down quite a bit in energy when forming a bond with the hydrogen. Interestingly, the energy after the decomposition is slightly lower than in the non-doped and fivefold coordinated manganese cases. It seems that the key to the water molecule being more stable in the decomposed state is to have relatively high energy O2p states present in the system, so that they can fall in energy as much as possible, specifically more than breaking the O-H bond in the water molecule increases the energy of the system.

Two points about the computed densities of states are worth noticing: the PBE exchange-correlation functional used in these calculations, like all GGA functionals, seriously underestimates the band gap. This should not matter, since the states of interest are located within the valence band, which the PBE functional should be able to compute accurately enough for the current purpose. Secondly, the resolution at which the densities of states were calculated was not very high, as can be seen in the plots. However, it is high enough to see the positions of the O2p states relative to the valence band maximum.

5.4 Transitions

Using the adsorption energy configurations as endpoints, and with the same setup (2 × 2 × 1 k-point grid, kinetic energy cutoff of 400 eV), the minimum energy paths of the transitions between the molecular and decomposed states were computed using the climbing image NEB method with a version of VASP modified by the Henkelman group. Using scripts provided along the modifications to VASP, an interpolation of three images was generated for each case and then minimized to acquire the minimum energy paths presented in Figures 12, 13, and 14. Due to the constraint on the movements of the images to the hyper-plane perpendicular to the tangent, the conjugate gradient minimization algorithm usually fails to converge. Therefore, the residual minimization method with direct inversion of iterative subspace (RMM-DIIS) was used to relax the transition states.

The various bond lengths and angles in the water molecule in the end points and the saddle point of the minimum energy path are tabulated in Table 3. Regardless of the position of the dopant, the changes in the struc-
Figure 11: The densities of states of the surface (a) without an adsorbate, (b) with molecular water, and (c) with decomposed water. Solid lines show the 2p states of the bridging oxygen that the hydrogen is transferred to. The total DOS of the transferred hydrogen are marked with dashed lines, and the dopants with dotted lines. Positive values are for spin up, negative for down.
The structural parameters of the water molecule during the transition. The columns denoted with $d_{O_w-H}$ are the distances from the oxygen to the hydrogen atoms within the molecule, $d_{O_b-H}$ are the distances from the bridging oxygen to the hydrogen atoms. In both cases the hydrogen closest to the bridging oxygen is given first. $\angle H-O_w-H$ is the bond angle of the water molecule. $d_{Ti/Mn-O}$ is the distance of the adsorbed oxygen to the titanium or manganese. Distances are given in Å and angles in degrees.

<table>
<thead>
<tr>
<th>Dopant</th>
<th>State</th>
<th>$d_{O_w-H}$</th>
<th>$d_{O_b-H}$</th>
<th>$\angle H-O_w-H$</th>
<th>$d_{Ti/Mn-O}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>molecular</td>
<td>0.999 0.973</td>
<td>1.858 3.355</td>
<td>107.5 2.251</td>
<td></td>
</tr>
<tr>
<td></td>
<td>transition</td>
<td>1.567 0.967</td>
<td>1.410 3.524</td>
<td>116.0 2.041</td>
<td></td>
</tr>
<tr>
<td></td>
<td>dissociated</td>
<td>2.140 0.975</td>
<td>0.985 3.696</td>
<td>122.4 1.832</td>
<td></td>
</tr>
<tr>
<td>Mn$_{5c}$</td>
<td>molecular</td>
<td>1.006 0.976</td>
<td>1.834 3.343</td>
<td>108.1 2.077</td>
<td></td>
</tr>
<tr>
<td></td>
<td>transition</td>
<td>1.450 0.968</td>
<td>1.413 3.439</td>
<td>117.5 1.959</td>
<td></td>
</tr>
<tr>
<td></td>
<td>dissociated</td>
<td>1.896 0.978</td>
<td>0.997 3.541</td>
<td>126.0 1.843</td>
<td></td>
</tr>
<tr>
<td>Mn$_{6c}$</td>
<td>molecular</td>
<td>1.003 0.973</td>
<td>1.824 3.336</td>
<td>107.2 2.236</td>
<td></td>
</tr>
<tr>
<td></td>
<td>transition</td>
<td>1.551 0.969</td>
<td>1.396 3.496</td>
<td>113.9 2.037</td>
<td></td>
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<tr>
<td></td>
<td>dissociated</td>
<td>2.102 0.974</td>
<td>0.986 3.658</td>
<td>119.2 1.839</td>
<td></td>
</tr>
</tbody>
</table>

Table 3: The structural parameters of the water molecule during the transition. Initially the bond between the water oxygen and the hydrogen atom closest to the bridging oxygen is stretched slightly from the equilibrium length of 0.973 Å in an isolated water molecule, as relaxed using the setup described in Section 5.3. The other O-H bond in the molecule is shortened slightly during the transition, but relaxes back to almost the same length as in the initial state, while turning away from the hydrogen migrating towards the bridging oxygen. The distance between the adsorbed molecule and the surface adsorption site decreases during the transition. The bond angle of the molecularly adsorbed water is larger compared to the bond angle of the isolated water 104.4°, and grows further during the transition. It seems that the hydrogen dissociating from the water moves in a more or less straight line toward its new resting position on the bridging oxygen, and is roughly halfway through in the saddle point of the minimum energy path.

On rutile with a manganese dopant at the fivefold coordinated site, the hydrogen migrates via the shortest distance during the dissociation, which is to be expected, as the distances between the manganese dopant and its neighboring atoms are decreased compared to the undoped surface. The traveled distance is also shortened by a manganese atom in the sixfold coordinated position, but to a significantly lesser degree.

The minimum energy path of the decomposition of the water molecule on the clean rutile surface is shown in Figure 12. The energies relative to the
Figure 12: The minimum energy path of the dissociation of a water molecule on the clean rutile surface. The energy is given relative to that of the initial state, thus, the energy barrier of the forward transition is simply the energy of the saddle point. The endpoints and the saddle point are marked with dots.

initial state of the saddle point and the final state are $0.297 \text{ eV}$ and $0.069 \text{ eV}$, respectively. Thus, the activation barriers of the forward and backward transitions are $0.297 \text{ eV}$ and $0.228 \text{ eV}$. Substituting the fivefold coordinated titanium with a manganese atom reduces the energy of the saddle point by almost a third to $0.203 \text{ eV}$ as shown in Figure 13. As mentioned before, the difference between the adsorption energies of the molecular and dissociated water, and therefore the energy relative to the initial state, was decreased to $0.033 \text{ eV}$. This means that the barrier for recombination is decreased to $0.170 \text{ eV}$ as well. Having the dopant at the sixfold coordinated site lowers the barrier for decomposition further to $0.178 \text{ eV}$, as can be seen in Figure 14. Additionally, since the adsorbate is more stable in the dissociated state by $-0.059 \text{ eV}$, the probability of recombination is lowered in this case due to the barrier being $0.237 \text{ eV}$.

To check that the minimum energy paths converged correctly and the saddle point was found, dynamical matrices were calculated for the saddle point of each transition. To save time, displacements were performed for only the four atoms that move the most during the transition, which are the atoms of
Figure 13: The minimum energy path of the decomposition of water on the Mn$_{5c}$ doped rutile.

Figure 14: The minimum energy path of the decomposition of water on the Mn$_{6c}$ doped rutile.
the water molecule and the bridging oxygen nearest to it. Once it was confirmed that there was indeed exactly one negative eigenvalue in each case, the same dynamical matrices were computed for the initial states in order to evaluate the zero-point energy and Wigner corrections. The barriers and the temperature dependent Wigner corrections are shown in Figure 15. Of course, the magnitudes of the corrections are affected by the exclusion of the vast majority of the atoms in the slabs from the dynamical matrix calculations. Most of the atoms, being largely unaffected by the decomposition process of the water molecule, would just have their contributions to the initial and transition states cancel each other out. The corrections shown in Figure 15 should not be considered accurate without checking the convergence of their magnitudes with respect to the inclusion of more of the neighboring atoms to the dynamical matrix calculations. This is not done here due to time constraints. Using the frequencies obtained from the same dynamical matrices, the transition prefactors are $3.231 \times 10^{13}$ s$^{-1}$, $4.870 \times 10^{13}$ s$^{-1}$, and $5.011 \times 10^{14}$ s$^{-1}$, for the clean, fivefold coordinated dopant, and the sixfold coordinated dopant cases, respectively. The corresponding transition rates are, at $T = 300$ K, $3.31 \times 10^8$ s$^{-1}$, $1.89 \times 10^{10}$ s$^{-1}$, and $5.19 \times 10^{11}$ s$^{-1}$. The large differences between the rates in different cases might indicate that the constraints imposed on the dynamical matrix calculations were too limiting, but this author is not at this moment familiar enough with neither transition state theory nor the behavior of water on rutile surfaces to state that with any confidence without testing for convergence.

6 Discussion

In this work was presented calculations of the adsorption behavior of water on the manganese doped rutile TiO$_2$ (110) surface. Substitution of the sixfold coordinated titanium atom with manganese in a dry surface was found to be lower in energy by 0.13 eV compared to the fivefold coordinated case. The adsorption energy of water on the fivefold coordinated manganese doped surface, however, was found to be lower than the alternative by 0.12 eV and 0.03 eV for the molecular and decomposed adsorbate, respectively. Notably, the sixfold coordinated dopant makes the decomposition of the water molecule exoergic by 0.06 eV. The dopant in this case makes the formation of an O-H bond at the bridging oxygen energetically preferable to keeping the water molecule intact.

Doping with manganese lowers the barrier for the transition from molecular to decomposed water by roughly a third from 0.30 eV to 0.20 eV and 0.18 eV for the fivefold and sixfold coordinated dopants, respectively, not
Figure 15: The barriers for the clean and doped surfaces. The dotted line is the classical, uncorrected barrier, the dashed line is the zero-point energy corrected barrier, and the solid line the Wigner corrected barrier.
taking into account quantum mechanical corrections. The doping was also found to increase the rate of transition.

While the decomposition is no doubt an important part of the overall water splitting process, it is still only the initial step of a complicated reaction involving at minimum two water molecules, their decomposition, and the desorption of the products. Each of these steps, like the first one, needs some amount of energy to overcome any barriers between the stages.

The idea of photocatalysis is that the energy would come from solar radiation, preferably in the visible region of the spectrum. As discussed before, clean rutile does not absorb visible light, but manganese doped rutile likely does. The lowest amount of energy a semiconductor can absorb is determined by the band gap. As noted before, the exchange-correlation functional used in the calculations presented in this work, being a GGA functional, is not capable of reproducing a passable conduction band on its own, which is to be expected, as there is no theoretical justification to interpreting the DFT eigenvalues to be quasiparticle energies. There are at least two ways of improving the accuracy of the band structures obtained from a DFT calculation: the exchange-correlation functional could be changed to a hybrid one or the exciton energies can be calculated using many-body perturbation theory.

The GW method\cite{61, 62} is widely used to remedy the quasiparticle energy issue, which it can do by including many-body effects in the electron-electron interactions and going beyond the mean-field approximation of independent particles. This can be done through screening the exchange interaction operator with the inverse frequency-dependent dielectric matrix to include many-body interactions between the electrons to replace the effective local exchange-correlation potentials used in DFT. Unfortunately, the GW method requires a relatively large amount of computing power, and is thus usually limited to small systems.

The GW approximation replicates well the band structures of a wide range of systems, but is incapable of describing properly the spectroscopic properties that involve two-particle excitations. An important example related to photocatalysis is the absorption spectrum, as the electron-hole pair created in the absorption process tends to interact quite strongly. In order to calculate accurate absorption spectra, given as the imaginary part of the macroscopic dielectric function, one can use the Bethe-Salpeter equation (BSE)\cite{63, 64}.

The GW and BSE have been used to calculate reasonably accurate band structures and absorption spectra of the rutile, anatase, and brookite phases of TiO$_2$ \cite{65}, but to this author’s knowledge, the same has not been done for doped titanium oxide of any crystalline phase. This is likely due to the computational expenses required to treat systems large enough to make
the dopant concentration reasonable. Both the GW approximation, and the ability to utilize the BSE in order to calculate accurate absorption spectra are implemented in VASP.

Since the absorption of photons does not necessarily occur right where the water molecule happens to be adsorbed, or at the surface at all, another important factor in determining the suitability of a semiconductor as a photocatalyst are its charge carrier transport properties, which are determined by the nonadiabatic coupling of the charge carriers and phonons. The nonadiabatic coupling can be dealt with in several ways, which include methods such as surface-hopping\cite{66}, or the time evolution of the reduced density matrix using multilevel Redfield theory\cite{67}. Both of these have been previously used to study TiO$_2$-water interactions\cite{68,69}.

References


