First-principles study of the electric field effect on the water-adsorbed rutile titanium dioxide surface

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First-Principles Study of the Electric Field Effect on the Water-Adsorbed Rutile Titanium Dioxide Surface

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by

Abraham L. Hmiel

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Abstract

TiO\textsubscript{2} is a semiconducting material that has been used extensively in many industrial applications, and recently has become a candidate for photocatalytic water splitting, fuel cell anode support materials, sensors, and other novel nanodevices. The interface of TiO\textsubscript{2} with water, historically well-studied but still poorly understood, presents a ubiquitous environmental challenge towards the ultimate practical usefulness of these technologies. Ground-state density functional theory (DFT) calculations studying the characteristics of molecular adsorption on model surfaces have been studied for decades, showing constant improvement in the description of the energetics and electronic structure at interfaces. These simulations are invaluable in the materials science innovation pipeline because they can interpret the results of experiments and investigate properties at the nanoscale that traditional methods cannot reach.

In this work, spin-polarized DFT calculations within the generalized gradient approximation and with the recent self-consistent opt-B88 van der Waals functional have been applied to investigate the problem of molecularly adsorbed water on the rutile (110) TiO\textsubscript{2} surface under the influence of an applied electric field. The effective screening medium theory is used to break the symmetry of the simulation in the slab normal direction and implement a metal-like boundary condition at the edges of the simulation cell to model the charged capacitor in a real electrochemical device. This study begins with an investigation of bulk and surface properties of TiO\textsubscript{2} to obtain a sound theoretical baseline. Following that, an attempt to obtain simple and meaningful structure-property relationships of rectangular TiO\textsubscript{2} nanowires with (110) facets resulting from quantum confinement. Finally, a systematic study of energetics, geometrical configuration, charge partitioning, and electronic structure of water in monomer coverage up to monolayer coverage provides insight into the usefulness of the inclusion of self-consistent van der Waals correlation effects and the effect of an external electric field in this model of adsorption on a prototypical metal oxide surface. Nontrivial differences between the two functionals’ description of adsorption of water, electrostatic characteristics, and electronic structure of the model surface are reported in the zero-field limit as well as with an applied field.
To all my teachers, to my parents, Drew and Karen, to my brother Benjamin, and
to the memory of Marta Grzegorek

Shapes in space display their grace
The mind entwines all sound in time
All creeping things and those that sleep
A cosmic carcass of pregnant eyes

A line extends to intersect
As points disperse to imply a plane
Shapes arranged in the shape of space
So that we may harvest the name from the named

The name gives shape to shapeless states
This name was created that it may create
Your skull is a tunnel, a passage-way
Through which a world must emanate

The name takes shape in signals and signs
The form and the structure of creation align
The name gathers shapes to its nameless breast
Enthroned, embodied, blaspheming, and blessed

Lungfish, Shapes in Space
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It is commonly said that the acknowledgments section is the only part that everyone who picks up a dissertation will actually read. I’m so excited that another human being has actually picked this document up or otherwise has its contents entering one’s eyeballs from a screen that I must first thank you, dear reader! It is my earnest hope that you are reading this from somewhere interesting, you learn something within, and you’re planning to eat a delicious vegan meal later this evening while listening to challenging post-punk on vinyl (or at least WCDB Albany 90.9FM).

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### Glossary

<table>
<thead>
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<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>$\chi$</td>
<td>Energy density</td>
</tr>
<tr>
<td>$E$</td>
<td>Electric field</td>
</tr>
<tr>
<td>$\Psi_n$</td>
<td>Wavefunction at band index $n$</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Density of states</td>
</tr>
<tr>
<td>$\rho_n$</td>
<td>Projected density of states (onto basis vectors)</td>
</tr>
<tr>
<td>$E$</td>
<td>Energy</td>
</tr>
<tr>
<td>$n$</td>
<td>Electron density</td>
</tr>
<tr>
<td>$V$</td>
<td>Potential</td>
</tr>
<tr>
<td>BC1</td>
<td>ESM Boundary condition one (vacuum–slab–vacuum)</td>
</tr>
<tr>
<td>BC2</td>
<td>ESM Boundary condition two (metal–slab–metal)</td>
</tr>
<tr>
<td>BE</td>
<td>Binding energy</td>
</tr>
<tr>
<td>BSSE</td>
<td>Basis set superposition error</td>
</tr>
<tr>
<td>COOP</td>
<td>Crystal orbital overlap population</td>
</tr>
<tr>
<td>CP</td>
<td>Counterpoise correction</td>
</tr>
<tr>
<td>DFT</td>
<td>Density functional theory</td>
</tr>
<tr>
<td>DOS</td>
<td>Density of states</td>
</tr>
<tr>
<td>DZP</td>
<td>Double-zeta plus polarization</td>
</tr>
<tr>
<td>ESM</td>
<td>Effective screening medium</td>
</tr>
<tr>
<td>GGA</td>
<td>Generalized gradient approximation</td>
</tr>
<tr>
<td>IBZ</td>
<td>Irreducible Brillouin zone</td>
</tr>
<tr>
<td>LAPW</td>
<td>Linearized augmented plane wave</td>
</tr>
<tr>
<td>LCAO</td>
<td>Linear combination of atomic orbitals</td>
</tr>
<tr>
<td>LDA</td>
<td>Local density approximation</td>
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<tr>
<td>LDOS</td>
<td>Local density of states</td>
</tr>
<tr>
<td>LSDA</td>
<td>Local spin density approximation</td>
</tr>
<tr>
<td>MO</td>
<td>Molecular orbital</td>
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<tr>
<td><strong>opt-b88</strong></td>
<td>Optimized van der Waals Density Functional with Becke-88 exchange [5]</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
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<tr>
<td>PAW</td>
<td>Projector-augmented wave</td>
</tr>
<tr>
<td>PBC</td>
<td>Periodic boundary condition</td>
</tr>
<tr>
<td>PBE</td>
<td>Perdew-Burke-Ernzerhof (exchange-correlation functional)</td>
</tr>
<tr>
<td>PDOS</td>
<td>Projected density of states</td>
</tr>
<tr>
<td>PES</td>
<td>Potential energy surface</td>
</tr>
<tr>
<td>PW</td>
<td>Plane-wave</td>
</tr>
<tr>
<td>SCF</td>
<td>Self-consistent field</td>
</tr>
<tr>
<td>SIESTA</td>
<td>Spanish initiative for electronic simulations with thousands of atoms</td>
</tr>
<tr>
<td>SZ</td>
<td>Single-Zeta</td>
</tr>
<tr>
<td>TL</td>
<td>Trilayer</td>
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<tr>
<td>TM2</td>
<td>Improved Troullier-Martins</td>
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<tr>
<td>UHV</td>
<td>Ultra high vacuum</td>
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<tr>
<td>vdW</td>
<td>van der Waals</td>
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<td>van der Waals density functional</td>
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<tr>
<td>xc</td>
<td>Exchange-correlation</td>
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1

Introduction

1.1 Motivation

For more than two decades, the avenue of simulating real physical systems with *ab initio* (from the beginning) quantum mechanics has been explored with resounding successes across many branches of the natural sciences. In particular, a prominent calculation method called density functional theory (DFT) has been able to do what was once long thought impossible: to gain targeted knowledge about every aspect of the behavior of chemicals, bulk materials, and nanosstructures in a timely and efficient manner. It is estimated that the number of published works on DFT that appear every year is approaching 10,000 according to the Web of Science [6]. DFT has been of particular interest to the materials science community for its ability to make potentially cost-saving predictions on the viability of compounds for various purposes. The relatively unconstrained simulation design of theoretical techniques can allow investigators to manipulate matter at the nanoscale in a such a manner that is completely outside the reach of laboratory techniques, while simultaneously having typically far smaller expenses of research equipment and materials costs and mitigating dangers that may be present in real compounds like toxins or highly reactive materials. Calculations using DFT are often used to corroborate the results of experiments with energetic, geometrical, electronic and electrostatic insight into relevant mechanisms, to search for brand-new physics and chemistry, and to spur the further development of DFT through benchmarks of its own accuracy. Walter Kohn shared the 1998 Nobel prize in chemistry with John Pople for the development of the theory and for developing facile computational methods, respectively. Since then, many new developments to DFT have been researched to rectify the shortfalls of the approach. Due to the rapid increase in speed of
computer processors and expansion of memory available to calculations in recent years, simulations of nanomaterials may now be performed with typical consumer desktops. In addition, owing to the advancement of codes and supercomputer clusters, automated systematic comparisons of various materials is now being performed to find good candidates for Li-air batteries [7], catalysts [8], and photovoltaics [9]. The applications of DFT to clean energy are clear: using first-principles methods, materials can be screened for desirable properties and their physical composition while for promising candidates, the mechanisms of their surface reactions and specific electronic structure can be studied in great detail. Our research casts eyes toward a common-earth material, Titanium dioxide (TiO$_2$) in order to enrich our theoretical knowledge of how it operates in a real electrochemical device. Titanium dioxide, also known as titania, is an invaluable material for myriad consumer and infrastructural products, having a global sales revenue of over $4.5 billion annually [10]. About 60% of the global supply chain of titania is used in the pigment industry, where its bright whiteness and other characteristics are valued for aesthetics and durability in paint and food dye and its ability to shield the skin from UV-B rays in sunscreen due to its high refractive index. The high dielectric constant of TiO$_2$ is useful to the semiconductor industry, as well as its ability to seed crystals. In nanoscience, TiO$_2$ is an important material for heterogeneous catalysis and photo-catalysis, and has been widely used as a model system for the study of fundamental surface science processes in oxide materials. [11, 12, 13] Recently, TiO$_2$ nanostructures including thin films, nanotubes, nanowires, and nanoparticles have shown promise in a great array of applications including dye-sensitized solar cells, environmental purification, proton-exchange-membrane fuel cells, photocatalytic water splitting, ReRAM, and gas sensors. [14, 15, 16, 17, 18, 19, 20] In real environments, devices encounter molecules adsorbed on their surfaces which modify their surface chemistry in a manner that is sensitive to the specific 3D arrangement of those molecules. Additionally, the devices may also be under electrical bias which further complicates their surface chemistry. Understanding the role that surface structure plays in the surface chemistry of metal oxides is a problem of paramount importance that may direct the function and synthesis of these novel devices. The economic and societal implications of functional devices made from TiO$_2$ may be staggering.

The rutile allotrope of TiO$_2$ is among the most widely-used and well-studied oxide materials and its interface with water is similarly well-studied, for many reasons. The rutile TiO$_2$ (110) surface is generally considered to be the prototypical, best-characterized, metal oxide surface.
Under ambient conditions most surfaces are wetted by a thin film of water or low surface coverage of water, which is also a major component of residual gases in UHV chambers, likely to interact with surfaces even in tightly-controlled experiments, and most photocatalytic reactions occur in an aqueous environment. [11] The ubiquitousness of water on earth makes it an excellent candidate for study across the natural sciences, especially surface science. Previous *ab-initio* studies [21, 22, 23, 24, 25, 26, 27, 28] have reported geometrical configurations and adsorption energies for water on TiO$_2$ with coverages ranging from the monomer limit to monolayer and multilayer coverage. However, neither a consistent theoretical picture of how this surface/adsorbate system behaves in the presence of an applied electric field yet exists, nor an understanding of how the recent self-consistent van der Waals density functional [29] affects its description. Previously, certain van der Waals density functionals have been applied to solids [30] including TiO$_2$, [31] but only in the bulk limit. A recent work by Otani and Sugino, the effective screening medium (ESM) theory, [32] has enabled a realistic and flexible description of electric field effects inside electrochemical systems. To date, it has not been shown whether or not the inclusion of vdW-DFT or ESM grants an enhanced description of the TiO$_2$-H$_2$O interface. Since it has been previously reported that only a small number of surface trilayers of TiO$_2$ are required to obtain a reliable description of adsorption and surface properties, many timely problems in surface chemistry on TiO$_2$ nanostructures may be studied with a relatively simple theoretical model of the surface. [33]

1.2 Goals

The main drive for this work is to understand the adsorption of water on the rutile TiO$_2$ (110) surface through the the modulation of the structural arrangement and energetics of the adsorbate arising from a strong applied electric field and evaluate the choice of exchange-correlation functional in the GGA or vdW-DFT schemes in the description of the system’s electronic structure and material properties. A systematic first-principles-based study making use of the Green’s function approach to solving the Poisson equation may help to explain experimental results with a flexibility that traditional DFT calculations cannot offer. Since the underlying mechanisms responsible for the surface chemistry at this interface are still largely unexplored, a carefully-constructed DFT model can provide a rich and robust look into its surface processes.
This work marks the first time that vdW-DFT and the ESM theory have been used in tandem with each other using the SIESTA code.

A secondary goal for this work involves understanding the quantum confinement properties of one-dimensional rutile TiO$_2$ nanowires, which have been utilized extensively in real applications of gas sensors, fuel cells, and dye-sensitized solar cells. In the regime of nanowire diameter larger than $\sim 10$ nm, the individual facets can be accurately modeled as infinite slabs, but nanostructures with smaller diameters experience quantum-confinement effects of electronic states that are strongly modulated by the shape of the nanostructures and their surface functionalization. In this respect, ground-state DFT models can elucidate trends in the electronic and structural properties of TiO$_2$ nanowires that will be amenable to band-gap engineering and surface functionalization in real devices.

The goals of this thesis can be summarized succinctly as follows:

- Create a model of the rutile TiO$_2$ bulk and (110) TiO$_2$ surface with vdW-DFT and compare the geometry relaxation and electronic structure to traditional GGA functionals
- Present a clear analysis of the structure-property relationships of rutile [001] TiO$_2$ nanowires with (110) facets
- Develop a consistent theoretical picture of how both the TiO$_2$ surface and the TiO$_2$-H$_2$O interface behave in response to an external electric field in term of its structural, energetic, electrostatic, and electronic-structural characteristics.
- Assess whether the inclusion of the self-consistent vdW-DFT functional enhances the description of the TiO$_2$-H$_2$O interface in the unbiased and biased regimes.

1.3 Outline

This thesis will be organized in the following manner: in chapter 2 the methods used in all the calculations involved in this thesis will be developed, starting from the fundamentals of DFT. Two new theories which are extensions to the traditional DFT will be discussed, as with the implementation of the theory in the SIESTA code.

Chapter 3 revolves around the simulation of bulk rutile TiO$_2$ and the surface slab models that will be used in chapters 4 and 5 to create other models. The simulation parameters will be discussed in detail, both to support the idea that they are well-converged, and to
allow the facile duplication of the results of this thesis if the reader is interested. Both GGA and vdw-DFT exchange-correlation functionals will be used to study the energetics, geometry, and electronic structure of the bulk solid, and differences between the two functionals will be expressed quantitatively. Then, a model of the (110) surface will be created and converged with respect to slab thickness and other geometrical constraints. A similar exploration of the different descriptions of the model surface through the properties obtained with the different xc-functionals will be given. Finally, a short section will obtain a reliable description of the water molecule and dimer in vacuum.

In chapter 4 the effect of shape modulation on quantum confinement for rutile TiO$_2$ nanowires with (110) facets will be analyzed in detail using the PBE (GGA) functional. It will comment on the electronic and structural properties of the nanowire which arise from the interplay between quantum confinement and surface relaxation. The trends in the structure-property relationships of these nanowires can be summarized in regards to the symmetries present along each confinement direction, which may be tuned separately.

Chapter 5 will focus on the goal of ab-initio simulation of the water-TiO$_2$ interface under electrical bias. The first order of business is to determine the effect of the electric field using the PBE (GGA) and opt-B88 (vdW) exchange-correlation functionals on the bare surface’s electronic and geometric structure. Then, the examination of the electric field effect on water monolayers (including dissociative adsorption) and sub-monolayers on TiO$_2$ using will be accomplished. The energetics, charge rearrangement, and geometry of the interface will be studied in detail with respect to its surface coverage, exchange-correlation functional, and electrical bias. Particular attention will be paid to the electronic structure of the interface as it relates to the hydrogen bond network near the TiO$_2$ surface, which is a key element in studying the solvent environment of the surface of real catalysts.

To close, chapter 6 will present a short recitation of the main results of this thesis and conclude with a discussion of the meaning of these results and outlooks to the future.
Methodology

The objective of this chapter is to familiarize the reader with the 'first-principles’ theory and simulation methods that will be used in the rest of the thesis in a manner that is not exhaustive, yet thorough enough to facilitate understanding of the material without being an expert. First-principles, or \textit{ab initio} methods are a class of tools in computational chemistry that are built upon a rigorous quantum-mechanical formalism rather than hard-sphere, force-field, or continuum approaches. Density functional theory (DFT) is one of these tools that has been a major success for over two decades and is the one on which we will focus. The nanoscale nature of these simulations allows an investigator to explore nuanced atomic configurations that may be outside the experimentalist’s reach. Fundamentally, the desired knowledge imparted by DFT arises from the configuration of atoms and electrons in materials, which gives rise to all subsequent physical phenomena, including energetics, vibrational states, optical and electronic structure, and other properties. In turn, the analysis of first-principles simulations can advance the fundamental state of knowledge about a particular system by offering sound interpretations of experiments, mechanisms of the underlying physics, and much more, especially when post-DFT methods are applied.

This section will begin with an introduction to the principles of how DFT is implemented in 2.1 and two major extensions to the basic theory which are employed in the rest of this thesis in 2.2–2.3. A brief rundown of how the DFT scheme, with our modifications, proceeds in the SIESTA code is presented in 2.4 and a summary is given in 2.5.
2.1 Foundations of Density Functional Theory

In the early twentieth century, the arrival of quantum mechanics as a mathematically sound, reliable, testable physical theory heralded a new era in science. As computing power has increased throughout the twentieth century through today, it has become ever easier to overcome computational hurdles that once stood in the way of studying chemistry and physics from the bottom-up. Of the mainstream quantum chemical methods to study materials, DFT has enjoyed a litany of remarkable achievements, while having good accuracy and moderate computational cost even for “large” systems with critical dimensions around a few nanometers.

DFT has been used extensively in a wide range of physical sciences due to the quality of predictions it can make from a relatively small set of parameters and knowledge about a system. In the fields of semiconductor physics and materials science, biology, chemistry, geoscience, atmospheric science and more, DFT has been advancing the current state of knowledge by extracting meaningful, qualitatively and quantitatively correct information out of the electronic structure of a material’s ground state electronic and atomic configuration. These nanoscale simulations are constructed from fundamental equations of quantum mechanics and not empirically-fitted terms like in force-field based methods, but one must still make some approximations and choices as to how the calculations proceed. This section aims to instill in the reader a working understanding of the theory and general practical methods for computation so that they will recognize how to gauge the quality and intent of a first-principles simulation themselves.

2.1.1 The many-body Schrödinger equation

The general form for the Schrödinger equation, which describes the behavior of a set of arbitrary quantum particles, in time-independent form, is:

\[ \hat{H}(\mathbf{r}, \mathbf{R})\Psi(\mathbf{r}, \mathbf{R}) = E\Psi(\mathbf{r}, \mathbf{R}) \] (2.1)

where \( \mathbf{r} \) and \( \mathbf{R} \) represent the three-dimensional coordinates of the \( N_e \) electrons and \( N_i \) ion cores, respectively. The set of solutions \([E_n, \Psi_n]\) describe the stationary states of the system from which fundamental properties can be deduced. The complete Hamiltonian \( \hat{H}(\mathbf{r}, \mathbf{R}) \) for a system of interacting atoms may be expressed as:

\[
\hat{H} = -\sum_i^{N_e} \frac{1}{2} \nabla_i^2 + \frac{1}{2M_{\alpha}} \nabla_{\alpha}^2 - \sum_i^{N_e} \sum_{\alpha}^{N_i} \frac{Z_{\alpha}}{|\mathbf{R}_\alpha - \mathbf{r}_i|} + \sum_{i \neq j}^{N_e} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{\alpha \neq \beta}^{N_i} \frac{Z_{\alpha}Z_{\beta}}{|\mathbf{R}_\alpha - \mathbf{R}_\beta|} \] (2.2)
where $M_\alpha$ is the atomic mass and $Z_\alpha$ is the atomic number, Latin indices correspond to electronic degrees of freedom and Greek indices correspond to ionic ones, and atomic units are used where $\hbar = m_e = e = \frac{1}{4\pi\epsilon_0} = 1$. Equation 2.2 may be simplified as:

$$\hat{H} = \hat{T}_e(\mathbf{r}) + \hat{T}_i(\mathbf{R}) + \hat{V}_{ie}(\mathbf{r}, \mathbf{R}) + \hat{V}_{ee}(\mathbf{r}) + \hat{V}_{ii}(\mathbf{R})$$

(2.3)

where the first two terms are the electronic and ionic kinetic energy operators, the third term is the attractive electronic-ionic Coulomb potential, and the last two terms are the electronic-electronic and ionic-ionic Coulomb repulsion potentials.

In practice, it is extremely cumbersome, if not downright impossible, to solve eq. 2.1 directly for any systems of interest, owing to two main reasons. One is that the Hamiltonian in eq. 2.2 is not separable into an ionic and electronic part. If this were so, the wavefunction solutions could be written as the product of an electronic contribution and an ionic contribution. The $\hat{V}_{ie}(\mathbf{r}, \mathbf{R})$ cross-term in eq. 2.3, which couples the electronic and ionic potentials, prevents this. Meanwhile, the $\hat{V}_{ee}(\mathbf{r}, \mathbf{R})$ term creates a tangled mess of $O(N_e^2)$ integrals to solve as the number of electrons in a system increases. As such, the many-body Schrödinger equation is the theoretical foundation by which typical quantum chemistry calculations are realized, but is itself not tractable without a cabal of approximations and additional theoretical techniques, except for systems of $O(1)$ first or second-row atoms.

### 2.1.2 The Born-Oppenheimer approximation

The first order of business to simplify the many-body Schrödinger equation involves decoupling the electronic and ionic degrees of freedom to the extent that we are able. Since the ion cores are at least on the order of 1,000 times more massive than the electrons, the $\hat{T}_i(\mathbf{R})$ term in eq. 2.3 becomes small compared to $\hat{T}_e(\mathbf{r})$. This supports the assertion that the nuclei may be treated classically, and the $\hat{T}_i(\mathbf{R})$ term may be neglected outright. [34] Therefore, any dynamical evolution of the nuclei is not allowed and the electronic configuration should instantaneously “snap” to the prevailing ionic configuration. Furthermore, the contribution to the Hamiltonian from the $\hat{V}_{ii}(\mathbf{R})$ potential term with fixed $\mathbf{R}$ becomes a constant, which does not affect the eigenspectrum of $\Psi$. With that observation, the $\hat{V}_{ii}(\mathbf{R})$ term may also be removed from eq. 2.3, where the remainder of the terms form the electronic Hamiltonian:

$$\hat{H}_e = \hat{T}_e(\mathbf{r}) + \hat{V}_{ie}(\mathbf{r}, \mathbf{R}) + \hat{V}_{ee}(\mathbf{r})$$

(2.4)
and the expression for the total energy is the sum of the electronic total energy and the ionic repulsion energy:

$$E_{\text{tot}} = E_e + \sum_{\alpha \neq \beta}^N \frac{Z_\alpha Z_\beta}{|\mathbf{R}_\alpha - \mathbf{R}_\beta|}. \quad (2.5)$$

This treatment is called the Born-Oppenheimer approximation. In the form of eq.2.4, the $N_e$ interacting electrons can be construed as moving in an effective external field created by the nuclei. The electronic solutions to the Schrödinger-like equation using the Hamiltonian of 2.5 are thus valid only at fixed ionic positions, and by changing those positions one may develop a potential energy surface (PES) for the total energy as a function of nuclear coordinates. More will be discussed on this matter in section 2.1.9.

### 2.1.3 The Hohenberg-Kohn theorems

There exist several methods to solving the Schrödinger equation with wavefunction-based methods, expanding the wavefunction using Slater determinants as the basis [35]. The Hartree-Fock method [36, 37] is the earliest example of this, and is still employed as a useful theoretical construction to improve quantum chemical theories. More sophisticated “Post-Hartree-Fock” methods exist as well, but wavefunction-based approaches suffer from the massive computational effort required to simulate systems larger than a few atoms. Thus, facile solutions to the Schrödinger equation must require a different approach than using wavefunctions as the prime operating variable. We consider the fact that the ground-state electron density can be represented as a sum over all occupied electron orbitals of a system:

$$n(r) = \sum_{i}^{N_{\text{occ}}} |\psi_i(r)|^2. \quad (2.6)$$

In 1964, Pierre Hohenberg and Walter Kohn published a derivation containing two theorems predicated upon the use of the electron density as a fundamental variable which provides the theoretical groundwork for DFT [38]:

**Theorem 1.** For a system of interacting particles in some volume under the influence of an external potential $V_{\text{ext}}(r)$, the ground state particle density $n(r)$ in a certain volume uniquely determines the value of $V_{\text{ext}}(r)$, up to a constant.

**Theorem 2.** $E[n(r)]$ is a universal functional of the electron density $n(r)$ for any given external potential $V_{\text{ext}}(r)$. The exact electronic ground state density $n_0(r)$ is determined from the electron density at the global minimum of $E[n(r)]$, which is the ground state energy.
As a corollary to the first Hohenberg-Kohn theorem, the electronic density uniquely determines any and all properties of the system, including its many-body wavefunctions and any information about the system that can be reconstructed from them. Furthermore, the Hohenberg-Kohn functional:

\[ F[n] = T[n] + U[n] \]  

(2.7)
is a universal functional of the electron density, in that it does not depend on the external potential. Accordingly, a new expression for the total energy as a functional of the electronic density may be written as:

\[ E[n] = F[n] + \int V_{\text{ext}}(r)n(r) \, d^3r. \]  

(2.8)

\( V_{\text{ext}} \) is the potential of the electrons moving in the external field of the nuclei or any other additional electric fields in space, and is equivalent to \( V_{\text{ie}} \) that appears earlier in the absence of any of additional electric fields in space. The existence of the H-K functional in eq. 2.7 is guaranteed, but the exact analytical form is not known, therefore approximations are required for its practical use, as will be detailed in the next section. In practice, the total energy in eq. 2.8 may be minimized through the use of Lagrange multipliers, finding the ground state electronic density and ground state energy concurrently. Under the constraint that particle number is conserved,

\[ N_e = \int n(r) \, d^3r \]  

(2.9)

and the ground state electron density which minimizes the total energy obeys the expression:

\[ \frac{\delta F[n]}{\delta n(r)} + V_{\text{ext}}[n] = \mu \]  

(2.10)

where \( \mu \), the system’s chemical potential, is varied until the constraint (eq. 2.9) is satisfied.

### 2.1.4 The Kohn-Sham equations

The year after Hohenberg and Kohn’s paper was published, Kohn and Lu Jeu Sham developed a method [39] to create a meaningful expression for the total energy functional, based on substituting an auxiliary, \textit{effective} electronic problem for the true many-body problem. In practice, this involves using an analytical approximation for the effect of Pauli exclusion and the electron-electron many-body correlation on the electronic energy and separating that effect from the electron-electron two-body total energy (called the Hartree energy):

\[ E_H[n] = \frac{1}{2} \iint \frac{n(r)n(r')}{|r - r'|} \, d^3r \, d^3r' \]  

(2.11)
Figure 2.1: Schematic cartoon illustrating the difference between interacting electrons in many-body theory (left) and non-interacting, fictitious particles which are immersed in an effective potential (right).

with the factor of $\frac{1}{2}$ included to avoid double-counting. Similarly, the Hartree potential $V_h(r)$ can be expressed as above without the second integral over $r$. The Kohn-Sham scheme has the immediate effect of creating an additional effective potential that the electrons see, $V_{xc}$, whereby they can then be treated as non-interacting charged point particles. The central idea of this theory is expressed in cartoon form in figure 2.1. The independent-electron system has a modified kinetic energy, $T_H$, which makes a contribution to the correlation energy, and we account for this difference in the non-interacting system. The exchange-correlation energy functional is defined as:

$$E_{xc}[n] = T[n] - T_H[n] + U[n] - E_H[n].$$  \hspace{1cm} (2.12)

We substitute eq. 2.12 into eq. 2.8 and rearrange the terms to form a new expression of the universal total energy functional:

$$E[n] = T_H[n] + E_{xc}[n] + E_H[n] + \int V_{ext}(r)n(r) \, d^3r$$ \hspace{1cm} (2.13)

whose ground state energy and density, in principle, is considered to be the same as the original, fully-interacting system. This gives rise to the Kohn-Sham equations used in DFT, which are cast in terms of orthonormal single-particle basis orbitals $\psi_i$ subject to an orthonormality constraint:

$$\delta_{ij} = \langle \psi_i | \psi_j \rangle$$ \hspace{1cm} (2.14)
preserving the idea that the single-particle states are fermions. The previously-mentioned $V_{xc}$ is a functional derivative of the exchange-correlation energy with respect to the electronic density:

$$ V_{xc} = \frac{\delta E_{xc}[n]}{\delta n(r)} \quad (2.15) $$

and the $N$ resultant single particle equations (over index $i$) using the Kohn-Sham Hamiltonian $\hat{H}_{KS}$ are:

$$ \left[ \frac{1}{2} \nabla^2 + V_{ext}(r) + V_H(r) + V_{xc}(r) \right] \psi_i = \epsilon_i \psi_i \quad (2.16) $$

with $\epsilon_i$ denoting the effective single-particle energies, which are Lagrange multipliers. The three potential terms in the above sum are commonly abbreviated as $V_{eff}$:

$$ V_{eff} = V_{ext}(r) + V_H(r) + V_{xc}(r). \quad (2.17) $$

Equations 2.16 and 2.17 are known as the Kohn-Sham equations. The ground state energy and density may be determined completely self-consistently with known ionic positions, an approximation for $V_{xc}$, a primary guess at the single-particle wavefunctions, and a tolerance for convergence according to the scheme:

$$ \psi_i(r) \to n(r) \to V_{eff} \to \hat{H}_{KS} \to \psi_i(r) \to \ldots \quad (2.18) $$

Finally, the total energy at each step of this iteration may be expressed as the following:

$$ E_{tot} = \sum_i N \epsilon_i + \int V_H(r) d(r) + E_{xc}[n] - \int V_{xc}(r) d^3r \quad (2.19) $$

where the ground-state total energy is subject to the variational calculus of eqs. 2.9-2.10. These equations are normally solved for a simulation box with periodicity in all three dimensions. Full derivations of the Kohn-Sham formulas are present in the original literature [39] as well as electronic structure textbooks [40].

### 2.1.5 Form of the exchange-correlation functional

Despite the useful formalism outlined in the previous section, we are still left with the issue of what form $V_{xc}$ should take. Fortunately, since the size of this term is relatively small compared to the other contributions to $\hat{H}_{KS}$, it is possible to recover mostly correct behavior of the electron density even using relatively simple approximations for $V_{xc}$ like the homogeneous electron gas. Two basic modes of generating $V_{xc}$ exist: the local density approximation (LDA) and the
generalized gradient approximation (GGA). Another, which is used extensively in this thesis, shall be discussed in section 2.2.

In the LDA, the exchange-correlation energy takes the form of an integral over the space of the entire system with the exchange-correlation energy density at each point, $\chi_{xc}(n(r))$, presumed to be identical to that of a homogeneous electron gas with density equal to the density at that point. Therefore, by separating the energy density into separate exchange and correlation parts (which is a simpler form while discussing specific functionals in use):

$$
E_{xc}^{LDA}[n] = \int n(r)\chi_{xc}^{HEG}(n(r))d^3r \\
E_{xc}^{LDA}[n] = \int n(r)[\chi_{xc}^{HEG}(n(r)) + \chi_{xc}^{HEG}(n(r))] d^3r
$$

(2.20)

where $\chi_{xc}^{HEG}$ is the energy density of a homogeneous electron gas. More generally, though, the electronic charge density is a function of spin ($\uparrow$, $\downarrow$) in addition to space, and the LDA can be generalized to the local spin density approximation. In the rest of this thesis, we will use LDA and LSDA interchangeably with the understanding that all of our work is done in the spin-polarized case, even though this may amount to a negligible effect on the electronic structure.

The exchange energy density as a function of spin density of an electron gas is known [40]:

$$
\chi_{xc}^{HEG}[n^{\uparrow}, n^{\downarrow}] = -\frac{3}{4} \left( \frac{6}{\pi n^\sigma} \right)^{\frac{1}{3}}
$$

(2.21)

and in the common Perdew-Zunger form, the correlation energy density is:

$$
\chi_{xc}^{PZ}(r_s) = -0.0480 + 0.0311\ln(r_s) - 0.0116r_s + 0.0020r_s\ln(r_s), \quad r_s < 1 \\
\chi_{xc}^{PZ}(r_s) = -\frac{0.1423}{1 + 1.9529\sqrt{r_s} + 0.3334r_s}, \quad r_s > 1
$$

(2.22)

where $r_s$ is a parameter that defines the radius of a sphere which contains one electron on average. $V_{xc}$ can then be reconstructed from $E_{xc}$ by eq. 2.15 and the Kohn-Sham equations solved to one’s satisfaction. On the whole, LDA performs generally quite well for materials where the electron density is similar to that of a uniform electron gas like metals, while it performs worse for isolated molecules and poorer still for strongly-correlated materials.

The GGA functionals, often referred to as semilocal functionals, represent improvements over the LDA for many systems which afford quantum chemistry the accuracy and versatility to be useful to a wide range of scientific fields. In general, the GGA exchange-correlation density
built by using the magnitude of the gradient of the electron density in addition to the electron density itself:

\[
E_{xc}^{GGA}[n^\uparrow, n^\downarrow] = \int n(r) \chi_{xc}^{GGA}(n^\uparrow, n^\downarrow, |\nabla n^\uparrow|, |\nabla n^\downarrow|) \, d^3r \tag{2.23}
\]

\[
E_{xc}^{GGA}[n^\uparrow, n^\downarrow] = \int n(r) \chi_{xc}^{HEG} F_{xc}(n^\uparrow, n^\downarrow, |\nabla n^\uparrow|, |\nabla n^\downarrow|) \, d^3r
\]

where \( F_{xc} \) is a dimensionless quantity called the exchange and correlation enhancement factor that satisfies a set of conditions based on the formalism of the exchange-correlation hole and may be also separated into exchange and correlation parts similar to eq. 2.20. Myriad formulas for \( F_{xc} \) have been expounded in the literature, here will discuss the Perdew-Burke-Ernzerhof (PBE) functional [41] which will be employed at length in this work. PBE is a very strong general purpose functional that is generated without being fitted to empirical data. It is based upon the PW91 [42] functional which contains much of the known physics of the exchange and correlation interactions, however PBE ignores some of these features, namely the correct second-order gradient expansion coefficients of \( \chi_{x}^{PBE} \) in different limits: the parameters chosen for the PBE functional satisfy local limits for the size of the exchange energy density but ignore global limits (the Lieb-Oxford bound [43]). More recent revisions to the PBE functional called RPBE and revPBE adjust the mathematical form of \( \chi_{x}^{PBE} \). The exchange part of the revPBE functional in particular was chosen to be the underlying basis for the Dion van der Waals functional (see section 2.2.1). The form of \( F_{x}^{PBE} \) for PBE and other GGA functionals is:

\[
F_{x}^{PBE}(s) = 1 + \frac{\kappa - \kappa \frac{\mu s^2}{\kappa}}{1 + \frac{s^2}{\kappa}} \tag{2.24}
\]

where \( s \) is a dimensionless quantity based on the density gradient [44]:

\[
s = \frac{|\nabla n(r)|}{2k_F n} \tag{2.25}
\]

and for PBE, \( \kappa = 0.804 \) and \( \mu = 0.21951 \). A more in-depth discussion of \( E_{xc} \) of PBE and other GGA functionals can be found in [41, 44, 45] or Appendix B of [40].

### 2.1.6 Bloch’s theorem and k-point sampling

So far, the quantum-mechanical approaches to solving the Schrödinger equation have ignored the infinity of electrons in solid-state or extended systems. In practice, this is easy to surmount by an application of Bloch’s theorem, which reduces the number of electrons that must be taken into account to ones that reside inside the unit cell. Mathematically, Bloch’s theorem states
that the eigenstates of any perfectly periodic operator (the Hamiltonian in our case) may be chosen with definite values of $k$ which label an excitation inside a periodic crystal:

$$\psi_k(r) = e^{ik \cdot r} u_k(r)$$  \hspace{1cm} (2.26)$$

where $u_k(r)$ is periodic, $u_k(r + T_n) = u_k(r)$, and $T_n$ is a lattice translation vector. [40] Also, $k$ is a reciprocal lattice vector in the first Brillouin zone, which is the Wigner-Seitz cell of the reciprocal lattice.

The effectively infinite number of electrons in a solid thus give rise to an infinite number of $k$-points that must be taken into account, which may seem like replacing one infinity with another, but there are definite advantages to using this method. First, at each $k$-point, only a finite number of electron energy levels will be occupied which makes the eigenspectrum solvable, leading to bands of eigenvalues $\varepsilon_{i,k}$ with band index $i$ and wavevector $k$ (and regions of energy where no allowed eigenstates can exist for any $k$, the energy gaps). Second, since the electron wavefunctions will be essentially identical for different, yet nearby $k$-points, only a single $k$-point needs to be taken into account for a particular region of $k$-space while still allowing for a neat representation of $k$-points in the crystal.

A $k$-point grid must be chosen to adequately sample the reciprocal lattice of the solid. In practice, the choosing of the $k$-point mesh for a solid tends to take the form of the Monkhorst-Pack grid. [46] The $k$-points are thus distributed in a uniform manner over the space as:

$$k = x_{1j} b_1 + x_{2j} b_2 + x_{3j} b_3$$  \hspace{1cm} (2.27)$$

$$x_{ij} = \frac{j}{m_i}, j = 0, \ldots, m_i - 1$$  \hspace{1cm} (2.28)$$

where $m_i$ is a specified index corresponding to the desired number of $k$-points in the set along a particular lattice translation direction $i$. Any integrated function over the entire reciprocal space may be transformed via a Fourier series to be written as a sum over $k$-points in a symmetry-reduced wedge of the Brillouin zone (IBZ):

$$f(r) = \frac{\Omega}{(2\pi)^3} \int_{BZ} F(k) dk = \sum_j^{IBZ} w_j F(k_j)$$  \hspace{1cm} (2.29)$$

where $\Omega$ is the volume of the unit cell, $F(k)$ is the Fourier transform of $f(r)$, and $w_j$ are weighting factors corresponding to the number of $k$-points with equivalent $k$ in the IBZ from the zone-folding scheme.
When a continuous line of k-points is needed, for example, in a band structure calculation, they are interpolated from the k-point mesh that was used in the ground-state calculation. On the other hand, if a calculation requires a very large unit cell, for single-molecule adsorptions on a surface or single-molecule calculations in vacuum, only one k-point is needed: the Γ-point at \( \mathbf{k} = (0, 0, 0) \), and there is no k-point dispersion in any direction. As a general rule for extended systems, increasing the density of the k-point mesh increases the accuracy to a degree, but also the computational effort. Some systems like metals or graphene require very dense k-point grids to obtain converged results, but other systems like insulators tend to be more forgiving of sparser k-point grids. It is highly important to converge calculations with respect to k-point grid for these reasons.

### 2.1.7 Pseudopotential theory

In the spirit of replacing difficult problems with simpler, more tractable ones, we revisit the notion that every electron must be explicitly accounted for in our \( \textit{ab initio} \) model. It is known that core electrons are typically chemically inert and screen the Coulombic potential experienced by the valence electrons from the ion cores. The wavefunctions of valence electrons at radii inside the nucleus must vary rapidly due to the orthonormality constraint and thus require more basis functions and larger arrays to represent them numerically. Each additional electron in the system increases the size of the ultimate problem that is attempted to be solved. Therefore, the replacement of the ionic cores and core electrons with an effective \textit{pseudopotential} to mimic the underlying physics seems like an attractive option as long as we carefully mind the details as to how they are constructed.

The prime concern in pseudopotential construction is to ensure that the wavefunctions and potential profile as a function of distance from the ion cores is comparable between the pseudopotential case and the all-electron (AE) case outside a certain cutoff radius. The values and the logarithmic derivatives of \( \psi_l \) and \( V_l \) (at a particular angular momentum channel \( l \)) should be continuous across the cutoff boundary and the values of these radii at different angular momentum quantum numbers should be chosen with care to ensure this and the eigenvalue differences between the two cases are small (\( \sim 1 \text{ mRyd} \)). Pseudopotentials must be rigorously tested in known situations before use. The pseudopotentials used in this work are of the improved Troullier-Martins type (TM2) \[47\] and have been thoroughly tested to perform well in the chemical environments examined. The norm-conserving constraint demands that the norm
of the pseudo and AE wavefunctions be identical within the defined core region \( r \leq r_c \). In general, different pseudopotentials may have different transferability, which is related to accuracy in different environments, and hardware requirements for proper computation (hardness). TM2 pseudopotentials are constructed to allow for smoothly-varying charge densities on a uniform spatial grid.

The \( V_{\text{ext}} \) term in the Kohn-Sham Hamiltonian 2.16 which represents the electron-ion-core interactions is modified in the following manner, with the introduction of local (which are the same for all angular momentum quantum numbers) and non-local parts formed by summing Kleinman-Bylander projectors [48] acting on single-electron states to form the pseudopotential \( V_{\text{pp}} \) [49]:

\[
\hat{V}_{\text{pp}} = V_{\text{local}}(\mathbf{r}) + \hat{V}_{KB}
\]

\[
\hat{V}_{KB} = \sum_{l=0}^{l_{\text{max}}} \sum_{m=-l}^{l} \sum_{n=1}^{N_l} |\varphi_{lmn}\rangle V_l \langle \varphi_{lmn}|.
\]

(2.30)

The local part of \( V_{\text{pp}} \) must obey a Coulombic potential profile as \( r \to \infty \) and but is otherwise arbitrary and here is optimized for smoothness. \( \varphi_{lmn} \) are orthogonalized according to the Blöchl scheme [50] for single-electron eigenstates of the semilocal potentials \( V_l \).

### 2.1.8 Numerical orbital basis set

To solve the Kohn-Sham equations, the wavefunctions that create \( n(\mathbf{r}) \) must be expanded using a finite number of weighted basis functions in Hilbert space:

\[
\psi_i = \sum_m c_m \varphi_m
\]

(2.31)

where the \( c_m \) are expansion coefficients and \( \varphi_m \) are orthogonal basis states. In principle, a basis set may be chosen from one of two major types: plane-waves and numerical orbitals. Plane waves are convenient due to their Fourier decomposition and clean interface with Bloch’s theorem to solve the KS equations in a crystal, their neat description of electron bands in the nearly-free electron model, and the fact that the representation of the kinetic energy operator is diagonal in momentum space, but suffer from large computational times required at chemical accuracy. In a numerical orbital basis set the molecular orbitals are generated from linear combinations of pseudoatomic orbitals which are eigenstates of the radial Schrödinger equation for the single-ion pseudopotentials for each angular momentum channel. The basis orbitals
are confined to a hard well potential to ensure that the basis stays localized, that is, the basis orbitals are strictly zero past a certain cutoff radius \( r_c \) to save computational effort while keeping the basis wavefunction and its first derivative continuous at \( r_c \). This reduction in computational complexity is especially handy when a simulation cell contains a large amount of vacuum since plane waves will fill the entire cell (and waste effort) and LCAO basis functions will fill only the parts close to atom cores. The LCAO basis may be written as:

\[
\varphi_i(r) = \frac{u_i(r)}{r} Y_{lm}(\theta \phi)
\]

where the \( Y_{lm} \) are spherical harmonics and the form of \( u_i \) is numerically-tabulated and flexible to suit the experiment.

The numerical orbitals in this work follow the 'multiple-\( \zeta \)' approach to their construction, [51] where each \( \zeta \) for a particular quantum number \( l, m, n \) in the valence shell has the same angular dependence, but different radial dependence. In this work, the DZP, or double-\( \zeta \) plus polarization basis is generally used, as it provides a reasonable balance between good accuracy while having a small computational cost. Double-\( \zeta \) basis sets are created by splitting the calculated numerical atomic orbitals in two: a smooth, short range part and a longer range part, that are treated as independent basis orbitals. This procedure can be repeated to generate multiple-\( \zeta \) bases for each valence orbital. Polarization orbitals are applied by applying a small perturbing electric field to an orbital to correct for the deformation of charge associated with bond formation. This results in a more robust basis set by adding an additional single-\( \zeta \) orbital (SZ) with \( l \) one higher than in the highest-occupied valence state. More details about basis set generation in the multiple-\( \zeta \) LCAO basis are given in the original SIESTA paper [49]. It is also possible to create basis orbitals for core and so-called semicore states, filled core shells just underneath the valence orbitals in energy that improve the description of the atoms by increasing the size of the basis set. These states are frequently useful in treating transition metals in oxide compounds and heavy \( p \)-block elements and generally require modified pseudopotentials. Additionally, additional basis orbitals called diffuse functions of SZ character, typically with \( l = 0 \) and principal quantum number one higher than the highest filled s-shell, are important in increasing the performance of DFT during structural relaxations and energy calculations involving surface-adsorbate chemistry by completing the basis set in a sparse region of space.

The main disadvantage of the LCAO method is the lack of systematic methods for optimal convergence of the parameters of the basis set; optimization is typically handled on a case-
by-case basis. In this work, basis sets were optimized according to the simplex method [52]. Hypertetrahedra were generated with coordinates equal to the radial cutoffs and Sankey soft-confinement parameters of each $\zeta$ of each basis orbital in bulk rutile TiO$_2$ with a fixed geometry corresponding to that of a preliminary relaxation done with a DZP basis, then settling on vertices of this hypertetrahedron that minimizes the $E_{tot}$ of the arrangement.

**Basis set superposition error and counterpoise correction**

One consequence of using the LCAO method is that since the basis set is localized, the energetic description of a system will depend upon the geometric arrangement of its component atoms. When additional atoms are added to a system, that system will enjoy an enhanced description from the increased size of its basis. This effect comes about especially during adsorption energy calculations, when dissimilar system components are brought near each other and the volume of space corresponding to their interaction has an increased basis set size compared to each component on their own. When the system’s total energy is minimized as a function of the whole system’s geometry, the short-range energies from the mixed basis sets must be compared with the long-range energies from the unmixed sets. An error is introduced from this mismatch called the basis set superposition error (BSSE) which may be fixed by applying the counterpoise correction (CP): [53]

$$E_{ads}^{CP} = E_{surf} + E_{molec} - E_{surf+molec} + \left( E_{surf}^{\dagger} + E_{molec}^{\dagger} - E_{surf}^{*} - E_{molec}^{*} \right)$$

(2.33)

where the term in the parenthesis is the BSSE correction. Daggers indicate the use of unoccupied basis functions but no pseudopotential (“ghost atoms”) on the absent object in the equilibrium geometry and stars completely ignore the other object in the equilibrium geometry. $E_{surf}$ and $E_{molec}$ are calculated by relaxing the system’s geometry without the presence of the other object. Single-point calculations, rather than geometry relaxations, are used to obtain these energies.

**2.1.9 The Hellman-Feynman force theorem and stress minimization**

Fully equipped with the tools to solve the KS equations, we are able to find the electronic ground state of a given system given some set of initial parameters: the nuclear coordinates of the system, the xc-functional desired, the character of the basis set and pseudopotentials, and some stopping criteria for the self consistent field (SCF) iterations (typically, when the maximum difference between density matrix elements falls below a certain tolerance). At the
end of each SCF cycle, the forces are calculated on each atom by direct differentiation of the total energy from the Hellman-Feynman force theorem [36]:

\[ F_{x_{i}}^{\alpha} = -\frac{\partial E_{tot}}{\partial x_{i}^{\alpha}} = \langle \Psi | \frac{\partial H}{\partial x_{i}^{\alpha}} | \Psi \rangle \] (2.34)

where \( \alpha \) is a Cartesian coordinate direction and the position of each atom \( i \) is updated according to the force on it, in the aim to find the global minimum of the ground-state energy with respect to atomic positions. The details of this procedure are outlined in the next section. When the magnitude of the maximum force vector falls below a tolerance, the geometric relaxation step is completed and the simulation is finished.

In bulk simulations, the lattice vectors may undergo a relaxation as well, by minimizing the uniaxial stress through the derivative of the Energy with respect to the strain tensor:

\[ \sigma_{\alpha\beta} = -\frac{1}{\tau_{cell}} \frac{\partial E_{KS}}{\partial \epsilon_{\alpha\beta}} \] (2.35)

where \( \alpha, \beta \) are Cartesian coordinate indices and the stress is translated to standard units of pressure through dividing by the unit cell-volume \( \tau_{cell} \) and changing sign [49]. Although not done in this work, a nonzero target stress may be achieved to probe the properties of materials at pressure.

2.1.10 Global energy minimization techniques

Many methods exist to find the global minimum of a multivariate function. In our case we are primarily concerned with finding the ground state energy and geometry of a system, where the minimization constraint is the lowest maximum absolute value of the force on the atoms. Even in cases where the energy landscape is highly complex, a good approximation to the global minimum may be found.

The most mathematically simple choice for function minimization is the steepest descents method. For a functional \( F(x) \), the direction of steepest descent, \( g(x) \) is simply \( -\nabla_{x_{1}} F \), where \( x_{1} \) is the point where \( F \) is evaluated. Consequently, one then proceeds with a line minimization to obtain another guess at the minimum, \( x_{2} \), and evaluate the gradient and repeat the procedure until a minimum is reached (to a numerical tolerance). This method is not particularly well-suited to electronic structure applications because first, it is not guaranteed to converge, and second, only takes into account information at the current sampling point, possibly dooming it to run in circles around a minimum or diverging.
The conjugate-gradient (CG) search, is an efficient and stable solution to global minimization problems that is often used in electronic structure codes. [54] The immediate advantage to the CG method is that it uses a whole history of function sampling points to ensure that each search direction is linearly independent of all the previous steps. Considering the minimization problem to live in an \( n \)-dimensional vector space, each step of the CG algorithm reduces the dimension of the space by one, and thus convergence is guaranteed after \( n \) steps. Beginning from the steepest descent direction \( \mathbf{g}_m(\mathbf{x}) \) described previously (at a particular step \( m \)), the conjugate gradient vector \( \mathbf{d}_m(\mathbf{x}) \) is:

\[
\mathbf{d}_m(\mathbf{x}) = \mathbf{g}_m(\mathbf{x}) + \gamma_m \mathbf{d}_{m-1}(\mathbf{x}); \quad \gamma_m = \frac{\mathbf{g}_m \cdot \mathbf{g}_m}{\mathbf{g}_{m-1} \cdot \mathbf{g}_{m-1}}
\]  

(2.36)

and \( \gamma_1 = 0 \).

In the context of this work, the CG algorithm is used only for the force minimization, since the minimum of the total energy functional is reached through direct diagonalization. Furthermore, the convergence of the forces to a global minimum is not strictly guaranteed to arbitrary precision in a certain number of steps due to the transformation between energy and forces, and the fact stems from how the Kohn-Sham manipulations on the total energy functional must be performed between subsequent CG steps. Even considering this, however, there still remains the issue of the force minimization settling into a local, rather than a global, minimum. The solution is to take care in making sure that the SCF steps are highly converged and to approach geometric convergence in a stepwise manner, that is, to begin with a small number of CG steps using a coarse force tolerance and large allowed atomic displacements between steps to scan the potential energy landscape, and then move to finer adjustments of the atomic positions and stricter force tolerances as the number of CG steps can expand to search the space for the global minimum. Such an analysis requires experience, finesse, and the ability to hone in on minor details of the geometry to judge the appropriateness of the current minimization trajectory. Sometimes, a series of simulations needs to be performed with varying initial atomic coordinates and configurational energy of each relaxed system is compared to find the lowest value and thus an approximation to the global minimum.

### 2.2 The van der Waals density functional

DFT falls short of a realistic description of compounds and interactions between complexes with strong van der Waals (vdW) character [5, 29]. These vdW interactions may take the form of:
forces between two permanent dipoles (Keesom force)
• forces between a permanent dipole and an induced dipole (Debye force)
• forces between two instantaneously induced dipoles (London dispersion force). [55]

Of these, the dispersion force is generally the strongest, and represents a long-range electronic interaction which traditional LDA and GGA functionals cannot reproduce because instantaneous interactions are ignored. Dispersion is a net attractive interaction which is generated from the response of electrons in one volume to instantaneous charge density fluctuations in a different volume. The leading term of such an interaction is well-known as the $1/r^6$ decay of the interaction energy with respect to interatomic distance $r$ which appears in the Lennard-Jones potential.

The essential problem of dispersive effects with traditional functionals is that LDA and GGA functionals exhibit incorrect asymptotic behavior of the interaction energy between dispersion-bound systems. [5, 29, 56, 57] Examples of strongly dispersion-bound systems are DNA, proteins and biomolecules, molecular crystals, and vdW complexes. The energetic minimum of two vdW-bound monomers with respect to separation distance is described erratically by typical functionals: LDA is strongly overbinding while some GGA functionals lead to a repulsive interaction potential and others describe an attractive one with various depths.

The field of vdW-DFT has been robust in the past several years, owing to the tremendous amount of effort put into developing new methods and functionals to treat systems with strong vdW character in a manner that is amenable to the real physics of these systems. Various schemes to semiempirically correct the DFT energies for the vdW dispersion interactions exist as inexpensive a posteriori corrections like the Grimme [57] and Tkatchenko-Scheffler [58] corrections, but the method of handling the vdW interactions explicitly in the exchange-correlation functional will be discussed in this section and used in the rest of this thesis.

2.2.1 The Dion functional

The first fully self-consistent van der Waals DFT functional was published in 2004 by Dion and his co-workers [29], applicable to layered materials. The exchange part of this functional was identical to the form of revPBE because this parameterization was similar to exact-exchange Hartree Fock, while the correlation part was split into a local term (equal to LDA) and a nonlocal
term that accounted properly for the nonlocal instantaneous electron density dispersion effects. Thus, \( E_{xc}^{\text{vdW}} \) could be written as:

\[
E_{xc}^{\text{vdW}} = E_x^{\text{GGA}} + E_c^{\text{LDA}} + E_c^{nl}
\]

(2.37)

where the form of \( E_c^{nl} \) is expressed as a double integral of interacting electron densities over real space:

\[
E_c^{nl} = \frac{1}{2} \iint n(r)n'(r')\phi(q_1, q_2, r_{12}) \, d^3r \, d^3r'
\]

(2.38)

The kernel \( \phi(q_1, q_2, r_1) \) is a given, general function which has arguments of \( r_{12} = |r_2 - r_1| \) and the universal functional \( q_m(n(r), |\nabla n(r)|) \) in the neighborhood of \( r_1 \) and \( r_2 \). This vdW-DF reduces to the LDA correlation functional in the limit of constant electron density and recovers the correct \( 1/r^6 \) decay of the interaction energy between two dispersion-bound molecules at large \( r \), provided that \( \phi \) is carefully chosen. More details about vdW-DF can be found in [59].

2.2.2 The Roman-Perez scheme

For systems of interest to vdW-DFT like molecular dimers, surface-adsorbate interactions, and biomolecular complexes, large unit cells must be used which makes the practical implementation of eq. 2.38 cumbersome, owing to the computationally expensive nature of the double real-space integral. In 2009, G. Román Pérez et al. derived an efficient implementation of vdW-DF that allowed mainstream DFT codes to feasibly use vdW-DF by reducing the amount of time required to calculate the vdW xc-potential in a large unit cell by a factor of \( \sim 1000 \) [60]. This represents only about a \( \sim 10 \)-fold increase in the time required to set up the xc-potential for a GGA calculation.

The critical step for the efficient implementation of the vdW-DF is to expand the kernel \( \phi \) as:

\[
\phi(q_1, q_2, r_{12}) \approx \sum_{\alpha\beta} \phi(q_\alpha, q_\beta, r_{12}) p_\alpha(q_1)p_\beta(q_2)
\]

(2.39)

where \( q_\alpha \) are fixed values chosen to ensure a satisfactory interpolation of \( \phi \). The \( p_\alpha(x_\alpha) \) are series of cubic polynomials which in every interval \([x_\alpha, x_{\alpha+1}]\) match the value and the first two derivatives at every point \( x_\alpha \). While the \( p_\alpha \) are sensitive to the scheme of interpolation and the fixed points \( x_\alpha \), they do not depend on the interpolated function. Hence, eq. 2.39 can be
readily substituted into eq. 2.38:

\[
E_{n_l}^c = \frac{1}{2} \sum_{\alpha \beta} \int \int \phi_{\alpha \beta}(\mathbf{r}_{12}) \, d^3r \, d^3r' \\
E_{n_l}^c = \frac{1}{2} \sum_{\alpha \beta} \int \theta_{\alpha}(\mathbf{k}) \theta_{\beta}(\mathbf{k}) \phi_{\alpha \beta}(k) \, d^3k
\]

where \( \theta_{\alpha}(\mathbf{r}) = n(\mathbf{r}) p_{\alpha}[q_0(n(\mathbf{r}), \nabla n(\mathbf{r}))] \) and \( \theta_{\alpha}(\mathbf{k}) \) is its Fourier transform, while \( \phi_{\alpha \beta}(k) \) is the Fourier Transform of \( \phi_{\alpha \beta}(r) \equiv \phi_{\alpha \beta}(q_\alpha, q_\beta, r) \). This kernel need only be calculated once and stored as a file in spherical coordinates in \( k \) for interpolation, while the computationally heavy part of the calculation of \( E_{n_l}^c \) becomes the calculation of the \( N_\alpha \) fast Fourier transforms of \( \theta_{\alpha}(\mathbf{r}) \).

### 2.2.3 Recent advancements in vdW-DFT functionals

Since the advent of the original vdW-DF, several new self-consistent functionals that account for nonlocal electron correlation have been researched and applied to various systems. The original vdW-DF, although it represented a great theoretical advancement in DFT, was too repulsive. A common testbed for checking the nature of new vdW-DF functionals involves using the S22 dataset, which consists of small to relatively large (30 atoms) complexes of common molecules containing only C, N, O and H, and single, double and triple bonds [61]. Most typical noncovalent interactions, including hydrogen bonds, dispersion interactions (stacked parallel and T-shaped), and mixed electrostatic-dispersion interactions are represented. The interaction distances and energies for the S22 dataset are calculated with a large basis set and compared with the very accurate (but extremely computationally demanding) coupled-cluster (CC) post Hartree-Fock methods in the single and double-excitation (CCSD) perturbation theories.

One main characteristic of the extensions to vdW-DF theory are that they all consider dispersion to be pairwise-additive, and differences between the functionals represent different choices of the functional for the exchange energy and how many gradient terms in \( n \) to include in the kernel function for the nonlocal correlation energy. The vdW-DF2 [56] functional uses the PW91 exchange functional instead of revPBE and the use of a large-N asymptote gradient correction in determining the vdW kernel which improves the binding around energy accurate semilocal exchange functional and is used in a wide array of applications. [62, 63, 64] Meanwhile, other vdW-DF functionals have been proposed to remedy some of the shortfalls of Dion’s vdW-DF including too large intermolecular binding distances and inaccurate binding energies due to the repulsive revPBE exchange. The “opt-B88” and “opt-PBE” exchange
functionals have been shown to offer very good performance for a wide variety of materials, complexes and interfaces. [5, 30]

The opt-B88 functional

A major focal point of this work is the description of molecule–adsorbate systems with the opt-B88 functional, which will be summarized here. The exchange enhancement factor $F_x$ (eq. 2.23) of the B88 exchange functional [65], analogous to eq. 2.24, is:

$$F_{x,B88}(s) = 1 + \frac{\mu s^2}{1 + \beta s \arcsinh(2\pi(3\pi^2)^{1/3} s)}.$$  \hspace{1cm} (2.41)

In the opt-B88 functional, the ratio $\mu/\beta$ is chosen to optimize the binding energies of the dimers in the S22 dataset [61] to be as closely aligned with calculations performed with the CCSD method. A spectacular $\sim 10$ meV mean absolute deviation in S22 dimer binding energies is achieved with the choice $\mu/\beta = 1.2$ and $\beta = 0.22$. Hydrogen-bound complexes and networks are described very well by this functional both in the original work and elsewhere [66, 67].

2.3 Effective screening medium theory

First-principles calculations lend themselves particularly well to the study of surfaces and interfaces using a slab model in which a region of atoms is sandwiched by enough vacuum ($\sim 15$ Å) so that image atoms from neighboring cells do not interact. Properties like the work function and surface reconstructions can be deduced from the atomic and electronic ground state of the two-surfaced slab. However, in a 3D-periodic cell, artifacts are created from the unphysical behavior of the electrostatic potential across the slab boundaries. One scheme to remove unphysical behavior is the slab dipole correction, [68] which introduces a sheet of charge in the vacuum region to cancel this artificial field while still maintaining a correct form of the electronic contribution to the total energy. The slab dipole correction has been used to a great extent and is implemented in many mainstream DFT codes. This correction makes explicit use of stacked unit cells in the slab normal direction and as the name implies, removes spurious dipole moment in a symmetric slab calculation with the downside of introducing a different electrostatic potential on each side of the slab. A discontinuity of the electrostatic potential in the vacuum region has a consequence for work function calculations, which require the potential inside the material and at infinite distance (in practice, far enough away from the slab).
A recent 2006 paper by Otani and Sugino [32] described a procedure for modeling complex electrochemical systems with DFT using a nonrepeated slab approach dubbed the effective screening medium (ESM) theory. In this spirit, the 3D periodicity of the unit cell is broken in the slab normal direction and the dielectric permittivity $\epsilon(r)$ is introduced as a function of position. This allows a more flexible and physically correct DFT model using control over the image charge placement and sensible boundary conditions at infinity. The modified Poisson equation is:

$$\nabla \cdot [\epsilon(r) \nabla V(r)] = -4\pi n_{tot}(r)$$  \hspace{1cm} (2.42)

where the value of $\epsilon$ determines the character of a semi-infinite media: if $\epsilon$ is one, that particular region becomes akin to an ultrahigh vacuum; if $\epsilon$ is infinity, that region is a perfect conductor. The total charge $n_{tot}$ refers to not only electrons and nuclei but also external charges added to or removed from the simulation cell. A cartoon of the ESM model is shown in figure 2.2. The modified Poisson equation is recast with Green’s functions:

$$\nabla \cdot [\epsilon(r) \nabla G(r - r')] = -4\pi \delta(r - r')$$  \hspace{1cm} (2.43)

and solved with the relation:

$$V(r) = \int G(r - r') n_{tot}(r') \, d^3r.$$  \hspace{1cm} (2.44)

The Kohn-Sham equation is solved just like normal, since the size of the vacuum region is assumed large enough to create no spurious image effects and the electrons are bound close to the surface. The total energy of the system, reflecting the separation of the Poisson equation from the Kohn-Sham equation is:

$$E[n_e, V] = \hat{T}[n_e] + E_{xc}[n_e] - \int \frac{\epsilon(r)}{8\pi} |\nabla V(r)|^2 + \int [n_e(r) + n_i(r)] V(r) \, d^3r$$  \hspace{1cm} (2.45)
which can be recast in terms of the Green’s function Poisson equation (eq. 2.43):

\[
E[n_e, V] = \hat{T}[n_e] + E_{xc}[n_e] + \frac{1}{2} \int \int n_e G(\mathbf{r}, \mathbf{r'}) n_e \ d^3 \mathbf{r} \ d^3 \mathbf{r'} + \frac{1}{2} \int \int n_i G(\mathbf{r}, \mathbf{r'}) n_i \ d^3 \mathbf{r} \ d^3 \mathbf{r'} + \int \int n_e G(\mathbf{r}, \mathbf{r'}) n_i \ d^3 \mathbf{r} \ d^3 \mathbf{r'}
\]

(2.46)

where the last term may be further simplified in the pseudopotential scheme (see appendix C of [32]) and the densities \( n_e \) and \( n_i \) arise from electronic and nuclear charge, respectively. Since pseudopotentials are calculated by considering an atom in vacuum, the pseudopotentials used in the ESM model must be placed within a region of \( \epsilon = 1 \) to remain transferable.

The Green’s function can be determined analytically for several pertinent boundary conditions, two of which will be discussed in sections 2.3.1 and 2.3.2 which will form a theoretical basis for understanding the effect of adding a bias voltage across a surface slab. The dielectric permittivity \( \epsilon(\mathbf{r}) \) is considered to only depend on the slab normal direction \( \hat{x} \). Then, in the reciprocal space (Laue) representation which is facile for computer solvers, the Poisson equation 2.43 becomes:

\[
[\partial_x [\epsilon(x) \partial_x] - \epsilon(x) g_{\parallel}^2] G(g_{\parallel}, x, x') = -4\pi \delta(x - x')
\]

(2.47)

where \( g_{\parallel} \) is a wave-vector parallel to the surface and \( g_{\parallel} = |g_{\parallel}| \).

### 2.3.1 Isolated slab model

The first case is the simplest, where regions I and III of fig. 2.2 are vacuum (\( \epsilon = 1 \) everywhere). In this case, no screening exists in the ESM model and the boundary condition for the potential can be written as:

\[
\partial_x V(g_{\parallel}, x) \bigg|_{x=\pm\infty} = 0, \quad \epsilon(x) = 1
\]

(2.48)

The Green’s function can be solved easily from eq. 2.47 to be:

\[
G^{IS}(g_{\parallel}, x, x') = \frac{4\pi}{2g_{\parallel}} e^{-g_{\parallel}|x-x'|}
\]

(2.49)

One advantage of using the ESM isolated slab model is that the electrostatic potential always refers to the vacuum level, which is not true in general for repeated 3D slab simulations and allows facile calculation of work functions for complex surfaces and interfaces. Another is that no slab dipole correction is needed to rectify the behavior of the potential in the vacuum, even in cases where the slab has a net dipole moment and \( V(z \to \pm\infty) \) has a long tail. The isolated slab model requires that the entire system is charge-neutral, otherwise the potential has a linear increase or decrease with increasing \( x \) and the electrostatic energy will diverge.
2.3.2 Charged capacitor model

In the charged capacitor ESM model, here regions I and III of fig. 2.2 are made of an ideal conducting material ($\epsilon = \infty$) and region II is vacuum ($\epsilon = 1$). Here the system approximates an STM experiment where the tip-to-surface distance is large enough so that any orbital overlap between the metal and surface can be dismissed. Then, the boundary condition for the electrostatic potential becomes:

$$V(g_{\parallel}, \pm x_1) = 0, \quad \epsilon(x) = \begin{cases} 1 & \text{if } |x| < x_1 \\ \infty & \text{if } |x| \geq x_1 \end{cases}$$ (2.50)

where $x_1$ refers to the position of the (optional) spacer region in fig. 2.2 between the DFT simulation cell and the semi-infinite media. The Green’s function can then be solved as:

$$G^{CC}(g_{\parallel}, x, x') = \frac{4\pi}{2g_{\parallel}} e^{-g_{\parallel}|x-x'|} + \frac{4\pi}{2g_{\parallel}} \times \left( e^{-2g_{\parallel}x_1} - 1 \right) \frac{\cosh[g_{\parallel}(x-x')]}{\sinh(2g_{\parallel}x_1)}$$ (2.51)

where the first term is the same as eq. 2.49, the bare Coulomb Fourier component, and the second term may re-written as a series over mirror-image Coulomb charges:

$$\frac{4\pi}{2g_{\parallel}} \sum_{m=0}^{\infty} \left( \exp[-g_{\parallel}(x-x'+4m+4)x_1] + \exp[g_{\parallel}(x-x'-4m+4)x_1] \\ - \exp[-g_{\parallel}(x+x'+4m+2)x_1] - \exp[g_{\parallel}(x+x'-4m+2)x_1] \right)$$ (2.52)

and $x, x'$ both lie inside the domain $|x| < x_1$.

The Green’s function technique is able to accurately calculate the contribution of the Hartree interaction with the image charges on the pseudo-electrodes, but the corresponding exchange-correlation interaction is ignored. This is done with the rationale that nonlocal electron correlation effects are presumed to be much weaker than that of the Hartree interaction at typical surface-to-STM-tip distances ($\sim 10$ Å).

The charged-capacitor ESM model is amenable to simulation of charged unit cells and external electric fields alike. In each case, it is possible to unambiguously determine a bias voltage $\Delta V$ across an uncharged slab through the geometry of the system and the electric field $E$ which points in the slab normal direction $\hat{x}$ and is provided as an input to the calculation:

$$\Delta V = -2E_{ext}x_1$$ (2.53)

At the beginning of each SCF cycle in the calculation, the input electric field is orthogonalized so that the field in all bulk-directions is zero (in case of an invalid input), then the electric field potential is calculated at each mesh point, then summed onto the total potential.
2.4 Implementation of vdW-DFT+ESM in SIESTA

In this work, we use the SIESTA code [49, 69] (Spanish Initiative for Electronic Structure using Thousands of Atoms), which is free under academic license. SIESTA is an LCAO code with TM2 pseudopotentials that has the capability to solve large systems in $O(n)$ time using a special functional, and is employed extensively throughout the literature for both ground-state DFT and also \textit{ab initio} molecular dynamics (AIMD). At the time of publication, the most recent release of SIESTA is 3.2 but this version does not include vdW-DFT functionality. Therefore, we use development snapshot 'trunk-364' and make small modifications to it: the rectification of an issue of the external electric field not being applied to all processing nodes in a parallel computation, and the inclusion of the ESM theory of section 2.3 using a modified patch to the release version which changes the Poisson solver, fast Fourier transform in 1D, and the SCF routine step. This version of the code includes vdW-DF functionality in the SiestaXC package, which includes the original vdW-DF [29], vdW-DF2 [56], and opt-B88 [5] functionals implemented in the Roman-Perez scheme.

The series of steps involved in a SIESTA calculation, at a bird’s eye view, may be summarized as follows:

- Read values of parameters (tolerances, xc-functional, basis, numerical grids, atomic species and positions, etc.) from an input file
- Create the real-space mesh, and allocate memory for variables that depend on it
- Initialize atomic orbitals, density and potential
- Find SCF electron density at mesh points from single-particle wavefunctions (beginning of the SCF loop)
- Find Hartree Potential and Hartree Energy
- Add potential arising from an external electric field (if present)
- Find exchange-correlation energy
- Find SCF contribution to Hamiltonian matrix elements
• Check if the maximum absolute value of the difference in the density matrix elements between this step and the previous one is beneath the specified tolerance (if not, return to the start of the SCF loop)

• Find forces and stress and move atoms to search for a minimum in the total energy

• Check if the maximum absolute value of all forces on atoms (and the stress) is beneath the specified tolerance (if not, restart the SCF loop using the most recent wavefunction coefficients)

• Print volumetric data, eigenvalues, energy decomposition, forces, etc. for analysis and end the program.

2.5 Conclusions

In this section a methodical introduction to the fundamentals of DFT was presented, along with a description of extensions to the theory to study systems with a strong dispersion component and inside electrochemically-relevant boundary conditions and how they are implemented inside the SIESTA code. It is not possible to estimate the error in a particular DFT calculation without first comparing it to other calculations using the same functional and basis set. Therefore, to study a particular system and create calculations which hold value with a new functional or approach, values of key parameters should be compared to similar systems previously computed. This is the focus of chapter 3, where a the bulk rutile TiO$_2$ and model slab systems are scrutinized in detail with respect to experimental setup.

It should be noted here that some aspects of a DFT calculation are unreliable. The most well-known shortfall of DFT in general is its inability to correctly estimate the band gap of insulators. DFT theory is a ground-state theory, and the energetic placement of the conduction bands above the Fermi level $E_F$, along with optical calculations that rely heavily on excited states, are not to be trusted on their own without additional extensions to the theory. However, it is the trends in these parameters that can be meaningfully extracted from a series of similar calculations. Furthermore, the overall accuracy of the DFT calculation is very sensitive to the density of the numerical real-space and reciprocal space grids. Errors can accumulate if the grids are too small, but calculation time increases as the grid becomes more tight. An investigator
using DFT and quantum chemistry methods in general must be able to balance these extremes with finesse.
3

Bulk rutile TiO$_2$, its (110) surface, and water in the zero-field limit

The following three chapters of this work are devoted to the study of the rutile (110) surface of TiO$_2$. This chapter begins with a short summary on the current state of knowledge of the surface science of TiO$_2$ in the experimental and theoretical regimes. Then, DFT will be utilized to set up a consistent theoretical model of the surface starting from the bulk geometry and analyzing its converged atomic structure, energetics and electronic structure in the light of previously-reported results in the literature. Then, the model of the surface is created by cleaving the bulk crystal so that the experimentally-observed (110) surface is obtained, and the model is further refined by considering the slab geometry and thickness. Again, the geometrical structure, energetics, and electronic structure of the surface are studied with respect to parameters of the model and compared to previous results in the literature. Finally, the last section of this chapter briefly deals with the DFT model of the water molecule and water dimer insofar as it relates to the eventual goal of simulating the TiO$_2$-H$_2$O interface under electrical bias.

3.1 Introduction

Many research groups over the past several decades have studied the surface science of crystalline titanium dioxide in order to gain physical insight at the most fundamental level which would inevitably lead to better device performance across a range of different fields. Thin films of TiO$_2$ are currently being investigated in semiconductor devices, as coatings for materials to keep them clean or to serve as a high-$k$ dielectric, for photocatalytic water splitting, as sensors and many other applications, and materials vendors are able to stock polished samples of high quality for
study. Its phase stability and also the fact that it is a very widely-studied and well-characterized material makes it an excellent substrate for experimentalists and metrologists because of the wide variety of experimental techniques that allow access to its properties. In fact, the nonpolar, (110) surface of rutile TiO$_2$ may be considered the model system in the surface science of metal oxides in general. DFT is just one of the techniques that allow for a clearer picture of the physics and chemistry at the nanoscale which make TiO$_2$ such a remarkable material, and is a promising tool for deep investigation into materials properties because it attempts to answer the questions of why rather than just how. In this light, the laser-focused nature of theoretical techniques can study the atomic-size events and configurations in a way that the traditional experimental methods cannot.

The crystal structure of rutile TiO$_2$ is shown in figure 3.1 for one unit cell. The crystal system is tetragonal with a space group of $P4_2/mnm$. In this symmetry group, one Ti atom is located at the origin (0, 0, 0) and repeated at the body center and an Oxygen atom is located at a certain point in scaled coordinates ($u$, $u$, 0) which is repeated three times in an octahedral pattern around the Ti atom in the cell. The $c$ direction is the short direction of the rutile unit cell, and the $a$ and $b$ directions are equal in length.

### 3.2 Convergence of properties of bulk TiO$_2$

In order to model systems more complicated systems like nanowires, surfaces or clusters, the bulk crystal structure must be relaxed to its atomic and electronic ground state first and tested for convergence with respect to the spacing of the real-space and k-point grids. This ensures
that properties of the crystalline solid are well-converged and extensible to a reliable model of bulk-truncated surfaces or other structures. Then, a systematic study of the atomic and electronic structure may be performed, either comparing the results to previously-published data for posterity or, in the case of the vdW-DF functionals, reporting new findings.

Once a reliable bulk crystal unit cell has been created, it is a trivial matter to create supercells of the bulk lattice and 'carve' them in different ways to produce structures like nanowires and surfaces, preserving information about their lattice constants so that those extended systems may be simulated cleanly. The remainder of this section details the process of converging the bulk TiO$_2$ structure, sparing no details in the computational setup and taking an accordingly detailed look at what the DFT simulations yield.

3.2.1 Computational methods: bulk TiO$_2$

The bulk TiO$_2$ structure was created by using the experimental lattice constants ($a = b = 4.594$ Å, $c = 2.959$ Å) and atomic positions obtained from [70]. The pseudopotentials used in this calculation were generated using the ATOM program [71] with the corresponding DFT functionals. In the pseudopotential generation procedure, the valence electron configuration was chosen to be an ionic $3s^23p^63d^2$ for Ti and $2s^22p^4$ for O, while the cutoff radii for the $[s,p,d,f]$ angular momentum channels were 1.30, 1.30, 1.30, 1.98 Bohr and 1.14, 1.14, 1.14, 1.14 Bohr for Ti and O respectively. All calculations are spin-polarized using the optimized double-zeta DZP basis set and a real-space mesh cutoff of 570 Ry. The cutoff radii and soft-confinement parameters for the numeric orbital basis functions of Ti and O were obtained by minimizing the Harris energy in the bulk rutile TiO$_2$ crystal in a multi-step approach using the simplex method [52] as implemented within the SIESTA code. [49, 51]. Tests indicated that the inclusion of Ti 3s and 3p semicore states were necessary to obtain good agreement with experimental and previously-published computational studies of structure, energetics and electronic structure in TiO$_2$. [21, 31, 72, 73] No relativistic or partial core corrections were used in the pseudopotential generation. The electronic relaxation was performed by a blocked Davidson diagonalization algorithm and the structural relaxation utilized the conjugate gradient (CG) method to find the global minimum in the total energy with respect to atomic positions. The electronic step of the SCF cycle terminated when the maximum absolute value of the difference in the density matrix elements between a step and the previous step was less than 0.0001 which yielded convergence in the total energy to less than 0.0001 eV. The structural relaxation was considered complete.
Figure 3.2: Progress of a structural relaxation of bulk TiO$_2$ with the PBE functional. The black line denotes the total energy convergence with respect to the minima and the blue lines denotes the maximum Hellman-Feynman force (solid) and its convergence criteria (dash-dotted).

when the maximum absolute value of the Hellman-Feynman forces on all atoms was less than 0.005 eV/Å, while the absolute maximum element of the stress tensor was less than 0.0008 eV/Å$^3$ (0.128 GPa) so that the lattice vectors could relax in addition to the atomic positions. Convergence of the total energy was checked with respect to the maximum equivalent plane-wave energy cutoff and found to be satisfactory for a cutoff of 570 Ry, guaranteeing a total energy divergence of less than 0.01 eV/atom between the converged estimate and its asymptotic value. This value of the energy cutoff guaranteed that any artifacts resulting from positional energy dependence (egg-box effect) had an amplitude of less than 0.0001 eV. Likewise, an $8 \times 8 \times 12$ Γ-centered Monkhorst-Pack k-point grid [46] was found to be a well-converged value with respect to total energy for sampling the reciprocal space. The relaxations are performed for the LDA, PBE, vdW-DF, vdW-DF2, and opt-B88 functionals to gauge their performance.

Figures 3.2 and 3.3 show the progress of a sample relaxation with regards to the maximum absolute value of forces and total energies and maximum absolute value of the stress tensor matrix elements and lattice constants, respectively. The forces and energies are the main objects of concern when structural relaxations are performed.
Figure 3.3: Progress of a structural relaxation of bulk TiO$_2$ with the PBE functional. The black line denotes the length of the $a$ lattice constant and the blue lines denotes the maximum absolute value of the stress tensor (solid) and its convergence criteria (dash-dotted).

3.2.2 Structure

The results of the structural relaxations for different xc-functionals is shown in table 3.1, along with a comparison to reported values from the literature. PBE, which is a GGA functional that yields fairly across-the-board good results for most condensed matter systems, is used throughout this thesis, while LDA appears to check certain results. At the time of writing, the development trunk of SIESTA has three vdW-xc functionals available [5, 29, 56], and all of them were tested in this regard. The lattice parameters $a$ and $c$ are shown for each functional tested, along with structure parameter $u$, where $u$ is the location of the O atom in the rutile crystal using the space group $P4_2/mnm$ and scaled coordinates: Ti is at (0, 0, 0) and O is at $(u, u, 0)$.

The comparison shows that our computed results for the PBE and LDA structures is in excellent agreement with previously-reported computational studies, even considering that the LCAO method was used here rather than the PW method of basis orbital construction. The average equilibrium Ti-O bond distances in rutile for PBE (opt-B88) were 1.986 (1.981) Å, and there was slightly more variation in the Ti-O bond distances in the opt-B88 crystal than for
Table 3.1: Benchmark comparison of lattice parameters $a$ and $c$ and structural parameter $u$ for bulk rutile crystal of $\text{TiO}_2$ between our linear-combination-of-atomic-orbital (LCAO) calculation and selected theoretical and experimental studies.

<table>
<thead>
<tr>
<th>Method</th>
<th>$a$ (Å)</th>
<th>$c$ (Å)</th>
<th>$u$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LCAO-PBE (This work)</td>
<td>4.657</td>
<td>2.989</td>
<td>0.304</td>
</tr>
<tr>
<td>LCAO-LDA (This work)</td>
<td>4.551</td>
<td>2.953</td>
<td>0.304</td>
</tr>
<tr>
<td>LCAO-vdW-DF (This work)</td>
<td>4.741</td>
<td>3.037</td>
<td>0.288</td>
</tr>
<tr>
<td>LCAO-vdW-DF2 (This work)</td>
<td>4.749</td>
<td>3.048</td>
<td>0.290</td>
</tr>
<tr>
<td>LCAO-opt-B88 (This work)</td>
<td>4.653</td>
<td>2.980</td>
<td>0.303</td>
</tr>
<tr>
<td>PW-PW91 [72]</td>
<td>4.658</td>
<td>2.977</td>
<td>0.305</td>
</tr>
<tr>
<td>PW-PW91 [74]</td>
<td>4.639</td>
<td>2.976</td>
<td>0.305</td>
</tr>
<tr>
<td>PAW-PBE [74]</td>
<td>4.594</td>
<td>2.959</td>
<td>0.306</td>
</tr>
<tr>
<td>PAW-PBE [75]</td>
<td>4.647</td>
<td>2.974</td>
<td>0.305</td>
</tr>
<tr>
<td>PAW-LDA [75]</td>
<td>4.557</td>
<td>2.928</td>
<td>0.304</td>
</tr>
<tr>
<td>LAPW-PBE [76]</td>
<td>4.622</td>
<td>2.958</td>
<td>0.305</td>
</tr>
<tr>
<td>LAPW-LDA [76]</td>
<td>4.563</td>
<td>2.939</td>
<td>0.304</td>
</tr>
<tr>
<td>PW-PBE [24]</td>
<td>4.649</td>
<td>2.966</td>
<td>0.305</td>
</tr>
<tr>
<td>Experiment 1 [70]</td>
<td>4.594</td>
<td>2.958</td>
<td>0.305</td>
</tr>
<tr>
<td>Experiment 2 [77, 78]</td>
<td>4.587</td>
<td>2.954</td>
<td>0.305</td>
</tr>
</tbody>
</table>

PBE (1.940-2.060 Å vs. 1.958-2.028 Å). The bond distances are consistent with experiments and theory [11, 79] that suggest that there are two types of Ti-O bonds in rutile: short ($\sim 1.95$ Å) 'in-plane' bonds and long ($\sim 1.98$ Å) 'out-of-plane' bonds.

Since no data was available at the time for self-consistent van der Waals rutile crystal structure parameters, we made the judgment, based on table 3.1, that the vdW-DF and vdW-DF2 functionals were too underbinding, increasing the lattice constants by almost 5% over PBE and opt-B88, and should not be used for the rest of the computations in this thesis. The opt-B88 functional had performance very similar to in obtaining correct structure parameters, and was thus chosen as the self-consistent van der Waals functional. This choice is rationalized further in light of the fact that the original vdW-DF functional and the vdW-DF2 functional perform worse, in general, for molecular complexes in the S22 dataset than opt-B88 [5] in addition to having underbinding character in the atomic positions and lattice constant and being “too-soft” (weaker bulk moduli) for different solid-state metals and ionic compounds [30].
3.2.3 Energetics

One typical and facile method of measuring the energetics of bulk materials through first principles is the calculation of the cohesive energy, $E_{coh}$. This is equivalent to the difference between the total energy of the crystal and the sum of the total energies of its constituent isolated atoms, divided by the number of formula units in the unit cell:

$$E_{coh} = \frac{1}{2}(E_{bulk} - 2E_{Ti,atom} - 4E_{O,atom}) \quad (3.1)$$

For our PBE (opt-B88) rutile TiO$_2$ model, the cohesive energy was found to be 23.61 (24.01) eV, compared with the PBE result of 21.44 eV [80] and the experimental value of 19.9 eV [81]. Although agreement in the energetics is worse (∼9% error with other DFT results, ∼15% error with respect to experiment) than the agreement in the structure data, some of the difference may be due to the fact that a PW basis was used in the calculation, and the error with respect to experiment may be an unavoidable aspect of the DFT simulation, as indicated by the further data presented in [80].

Another standard check to ensure that the chosen simulation parameters yield reasonable energetic properties is the calculation of the bulk modulus, which is the ratio of an infinitesimal uniform pressure subjected on a body to its volume deformation. Here, the bulk modulus of the bulk rutile TiO$_2$ crystal is found by a fit to the Murnaghan equation of state: [82]

$$E(V) = E_0 + K_0 V_0 \left[ \frac{1}{K'_0(K'_0 - 1)} \left( \frac{V}{V_0} \right)^{1-K'_0} + \frac{1}{K'_0 V_0} - \frac{1}{K'_0 - 1} \right] \quad (3.2)$$

where the main assumption is that the bulk modulus $K$ is a linear function of the pressure, $K = K_0 + PK'_0$, and that our interest lies in the equilibrium value of $K = K_0$. The derivative of the bulk modulus with respect to pressure, $K'_0$, changes little with pressure and thus is treated as a constant. By scaling the volume of the TiO$_2$ unit cell while keeping the fractional positions of the atoms the same, a single-point energy calculation is performed for each volume deformation and the results are fitted first to a second-order polynomial as an initial guess and then refined to 3.2 for the PBE and opt-B88 functional. Experimental values of the bulk modulus of TiO$_2$ range from 211 GPa [83] to 230 GPa [84] by X-ray diffraction. A plot of the fit of total energy and volume parameters to the equation of state is shown in 3.4 for the PBE (a) and opt-B88 (b) functionals. The computed result for the bulk modulus was found to be 216 GPa for PBE and 222 GPa for opt-B88, which represent improvements over previous results (∼240
Figure 3.4: Fit of energy and volume parameters to the Murnaghan equation of state (3.2 to find the bulk modulus with PBE (a) and opt-B88 (b). The markers show the results of the single-point DFT simulations and the curves are the numerical fit.

GPa and higher) performed with the LDA and Hartree-Fock methods of exchange-correlation treatment. [85]

3.2.4 Electronic Structure

The typical tools to analyze the electronic structure of solids include calculating the electronic band structure (BS), the (projected) density of states (DOS/PDOS) and the crystal orbital overlap populations (COOP). Here we present the electronic band structure for bulk rutile TiO$_2$ near the fundamental gap (fig. 3.5) and inside the highest-lying valence bands (fig. 3.6). The positions of the high-symmetry points in k-vector notation are printed in table 3.2. [86, 87] The band structure plot illustrates the dispersion of the discrete energy levels of the rutile crystal along the marked path in k-space. In both figures the band structure has overall good agreement between the two functionals and with previous ab initio results. [75, 88] Some notable differences include the presence of an indirect electronic bandgap (1.78 eV) for the PBE functional and a direct bandgap (1.74 eV) for opt-B88 whereas only direct bandgaps could be found in the literature. The direct bandgap at the Γ-point for the PBE functional was 1.82 eV. The...
Table 3.2: The k-vector coefficients for the high-symmetry points of the reciprocal lattice of the $P4_2/mnm$ space group corresponding to rutile. k-vector coefficients are in terms of the reciprocal lattice vectors $b_1$, $b_2$, $b_3$ for figs. 3.5 and 3.6.

<table>
<thead>
<tr>
<th>Label</th>
<th>k-vector</th>
</tr>
</thead>
<tbody>
<tr>
<td>Γ</td>
<td>(0,0,0)</td>
</tr>
<tr>
<td>X</td>
<td>(0, $\frac{1}{2}$, 0)</td>
</tr>
<tr>
<td>R</td>
<td>(0, $\frac{1}{2}$, $\frac{1}{2}$)</td>
</tr>
<tr>
<td>Z</td>
<td>(0,0, $\frac{1}{2}$)</td>
</tr>
<tr>
<td>M</td>
<td>( $\frac{1}{2}$, $\frac{1}{2}$, 0)</td>
</tr>
<tr>
<td>A</td>
<td>( $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$)</td>
</tr>
</tbody>
</table>

Placement of the electronic bands relative to each other was very similar in the valence band, with corresponding PBE and opt-B88 bands separated by at most 0.3 eV from each other, which usually occurred at extrema at high-symmetry points. The agreement between the descriptions of the lowest-lying conduction bands was on average worse than in the valence bands. However, since DFT is a ground state theory, it is not expected that the conduction band structure from a calculation is perfect; rather, it is the trends in the band energies that are important. No discernible differences in electronic structure between majority and minority-spin electrons presented themselves, even though the calculation was spin-polarized.

Although the bandgaps are smaller than their accepted experimental values by $\sim$ 1.2 eV, they compare well with DFT results from the literature, as shown in table 3.3. Overall variance in the theoretical magnitude of the bandgap among xc-functionals is small, excepting the original vdW-DF result in this study, about 1 eV larger in magnitude than the rest.

Figure 3.7 shows the total and projected density of states for the bulk rutile crystal. The PDOS $\rho_n$ requires the projection of the Kohn-Sham eigenstates $|\varphi_n\rangle$ onto a set of orthonormal states $|\psi_n\rangle$, in this case, the basis orbitals of O and Ti atoms:

$$\rho_n(E) = \sum_n |\langle \varphi_n | \varphi_n \rangle|^2 \delta(E - E_n)$$  \hspace{1cm} (3.3)

Where in practice, the delta function above is replaced by a Gaussian broadening factor (here, 0.070 eV) and the sum takes place over a specified weighted set of k-points in the reciprocal lattice. The blue and red lines show the density of states projected onto the 2$p$ orbitals of oxygen and the 3$d$ orbitals of titanium, respectively. From the plot, it is clear that the conduction band is composed of states arising from the 3$d$ orbitals of Ti and the highest-lying valence band is
Figure 3.5: Electronic band structure of the bulk rutile TiO$_2$ crystal along high-symmetry lines in the irreducible Brillouin zone for the PBE (black) and opt-B88 (blue) functionals near the fundamental gap.

Table 3.3: Benchmark comparison of fundamental electronic bandgap between our LCAO calculation and selected theoretical and experimental studies. Values denote the direct bandgap at Γ, the quantity in parenthesis is the value of the indirect bandgap.

<table>
<thead>
<tr>
<th>Method</th>
<th>Gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LCAO-PBE (This work)</td>
<td>1.82 (1.78)</td>
</tr>
<tr>
<td>LCAO-LDA (This work)</td>
<td>1.76</td>
</tr>
<tr>
<td>LCAO-vdW-DF (This work)</td>
<td>2.83</td>
</tr>
<tr>
<td>LCAO-vdW-DF2 (This work)</td>
<td>1.68</td>
</tr>
<tr>
<td>LCAO-opt-B88 (This work)</td>
<td>1.74</td>
</tr>
<tr>
<td>PW-PW91 [72]</td>
<td>1.75</td>
</tr>
<tr>
<td>PAW-PBE [75]</td>
<td>1.69</td>
</tr>
<tr>
<td>LAPW-PBE [76]</td>
<td>2</td>
</tr>
<tr>
<td>LAPW-LDA [76]</td>
<td>2</td>
</tr>
<tr>
<td>PW-PBE [24]</td>
<td>1.86</td>
</tr>
<tr>
<td>Experiment [77, 78]</td>
<td>3.05 (2.95)</td>
</tr>
</tbody>
</table>
Figure 3.6: Electronic band structure of the bulk rutile TiO$_2$ crystal along high-symmetry lines in the irreducible Brillouin zone for the PBE (black) and opt-B88 (blue) functionals in the highest-lying valence bands.

composed of O2$p$ states. The feature in the deep valence band is composed of mostly O2$s$ and Ti3$p$ (not shown) core and semicore states. Agreement in the PDOS is rather good between the two functionals, reproducing the bandwidths and peak structure well.

Satisfied that the PBE and opt-B88 functionals reproduce the bulk properties of rutile TiO$_2$, we move to model its (110) surface. Many more material properties can be ascertained by ground state DFT, but we stop here because they likely do not fundamentally alter the judgment that our computational setup is good enough to proceed in the study.

3.3 Convergence of properties of the rutile TiO$_2$ (110) surface

The previous section outlined the process of obtaining a well-converged bulk rutile crystal with the PBE and opt-B88 functionals singled out for their excellent performance at reproducing geometric and electronic results from the literature. From there, a model surface may be created by “cleaving” a bulk supercell to the desired size. The stoichiometric TiO$_2$ surface is composed of alternating rows of fivefold-coordinated Ti$^+$ sites and twofold-coordinated O$^-$ sites that occur in equal proportions, and so the surface is nonpolar. Using a slab model composed
of 3–7 TiO$_2$ layers with zero or two bottom layers fixed at the corresponding bulk positions, we were able to reproduce the well-known even-odd oscillation in surface energy and band gap with respect to the number of TiO$_2$ layers, with the relaxed bond lengths in the surface and sub-surface layers and inter-layer distances being in good agreement with those documented in literature. [3, 24, 72, 74, 89] This section describes how the (110) surface slab model is tested for convergence with respect to size in the normal direction using structural, electronic and energetic parameters as principal figures of merit, and how the ultimate choice for the slab model used in the rest of this thesis (four trilayers) is decided upon.

### 3.3.1 Computational methods: model TiO$_2$ surface

The pseudopotentials used for studying the rutile (110) TiO$_2$ surface were identical to those given in section 3.2.1 and the basis set was similarly utilized, except the top two atomic layers of TiO2 on the model surface, where an additional SZ s-like diffuse function was included in the 3s shell of O and the 5s shell of Ti of radii 7.00 bohr and 8.00 bohr, respectively. This is to eventually provide a more complete basis set for adsorption, but the calculations for the clean surface must include the same basis to not introduce spurious errors into the energetic
calculations, since basis orbitals without diffuse functions contributes slightly less toward the total energy.

The supercell size was chosen to give a vacuum region of 14 Angstrom in the normal direction between the rows of bridging oxygens on the image slabs in the x-direction. This spacing between the images ensured a DFT energy convergence of less than 0.1 meV per atom. We employ the effective screening medium Green’s function technique [32] which solves the Poisson equation exactly in the surface normal direction. This allowed us to (eventually) explicitly specify a bias voltage across the model TiO$_2$ slab with the correct physical behavior of the electrostatic potential in the vacuum region without introducing additional (or deficit) electrons into the simulation. Accordingly, no slab dipole correction [68] was needed to modify the electrostatic potential inside the vacuum region in the ESM model. A spacer region $(x_1 - x_0)$ measuring 3 Å was inserted between the periodic cell boundary and the metal boundary so that the distance between the bridging oxygen atoms of the surfaces and the metal electrodes were $\sim$ 1 Å. The total size of the model cell $(2x_1)$ was 33 Å and a schematic of the unit cell is shown in Fig. 3.5.

The metal-slab-metal boundary condition, performed using the Green’s function technique as detailed in section 2.3.2, has the physical effect of modeling the STM experiment, where the STM tip is located above the reconstructed surface and the back-gate is behind the other side of the slab model. Some simulations were performed without the ESM boundary condition and in the vacuum-slab-vacuum ESM boundary condition to test the reliability and proper convergence of the computational setup. The slab dipole correction was used in the first of these special cases.

Three main slab supercells are utilized in the surface calculations that follow here and in chapter 5: a $1 \times 1$ supercell, a $2 \times 1$ supercell and a $4 \times 2$ supercell, with the intention that the large supercell will be used to study the monomer adsorption case (low partial pressure) and the $2 \times 1$ supercell will be used to study the $\frac{1}{2}$ ML and 1 ML adsorption cases. The $1 \times 1$ supercell is reserved for studying structure-property relationships as a function of slab layers and is only used to determine the ideal thickness for the slab model. Previous studies [24, 90, 91] indicate that the $2 \times 1$ and $4 \times 2$ supercell geometries are sufficient to avoid spurious interactions between an adsorbate molecule and its image across unit cells, which is supported by inspecting the relevant cutoff radii of the basis set. The geometrical parameters $\sqrt{2}a$ and $c$ which form the dimensions of the $1 \times 1$ (110) surface unit cell were 6.586 (6.580) Å and 2.989 (2.980) Å for
the PBE (opt-B88) functional, where $a$ and $c$ are the translation vectors for the bulk rutile unit cell.

The 2D Brillouin zone of the model slab was sampled using a $1 \times 1 \times 1$ Monkhorst-Pack k-point mesh\cite{46} for the $4 \times 2$ surface unit cell, a $1 \times 6 \times 6$ mesh for the $2 \times 1$ surface unit cell and a $1 \times 12 \times 6$ mesh for the $1 \times 1$ unit cell. The real-space energy grid cutoff was again, 570 Ry. The total energy convergence threshold was set at $1 \times 10^{-4}$ eV and the conjugate gradient (CG) method was used to relax the structures. The maximum Hellman-Feynman force on each atom to converge the simulations was 0.02 eV/Å in the zero-field limit. The number of surface trilayers in the (110) rutile model varied from three to seven. Using any slab larger than 7 trilayers is prohibited because in the $4 \times 2$ rutile surface cell, our model to study water monomer adsorption, the simulation runs out of memory (\sim 64 GB) for the opt-B88 functional case on the NNIN supercomputer cluster. Furthermore, other studies have shown that any additional trilayers beyond seven affect the geometry relaxation in a trivial manner.

Many of the surface slab models we use in these calculations (and all of those in section 5) have their bottom two trilayers fixed to the bulk positions for the PBE and opt-B88 bulk geometries. This is done following refs. [3, 24] who have found that fixing the bottom two layers for large-scale TiO$_2$ surface slab calculations makes the surface properties converge much faster as a function of the number of layers than they would otherwise. In those studies, well-converged results are seen with only four trilayers, so here we check if this is a worthwhile shortcut to structure-property convergence. This approach has benefits and detriments: since the two (110) surfaces are dissimilar (one is relaxed while the other is not), adsorbates only need to be placed above one surface, the configurational space for geometry optimization is smaller, and the model slab approaches the conceptualized bulk TiO$_2$ quickly. On the other hand, care needs to be taken to include these effects in calculating work functions and surface energies, and be aware of other complications: the electronic convergence of surface states may be affected by the dangling bonds on the bottom side. Since the system is out of true equilibrium due to the frozen atoms, a vibrational analysis is impossible. The forced top-bottom asymmetry of the fixed slab model is overall physically appropriate for simulations involving an applied electric field, which is inherently asymmetric in the geometries that are investigated. If a symmetric surface slab with an odd number of layers was used instead, fixing the central layer to the bulk positions (or fixing no layers), an applied field would subject one side of the slab to field $+F$ and the other side $-F$ with respect to the slab normal. Thus, the two bottom layers of the slab are frozen to
Figure 3.8: Surface slab model of the relaxed 4(2) $1 \times 1$ (110) rutile TiO$_2$ surface. The solid black box denotes one trilayer of the structure while the dashed box denotes the atoms that are held fixed to the bulk positions in the simulations performed. Atoms in the two topmost surface trilayers are labeled in black and the bonds between them (repeated in table 3.4 for clarity) are labeled in blue numerals to facilitate discussion of the relaxation. Atoms marked with one or multiple apostrophes are related by symmetry to the ones without, belonging to the subsurface trilayers.

prevent this confusing situation, becoming even more of a concern when adsorbates are added and exaggerating small asymmetries in atomic positions that may be present. Nonetheless, it is critical to compare the fully-relaxed slab model to those with two trilayers fixed in order to ascertain any salient differences in their description of the energetics and electronic structure of the slab.

3.3.2 Structure of the model TiO$_2$ surface

The first objective is to optimize the geometry of surface slabs of (110)-oriented TiO$_2$ consisting of 3–7 trilayers in the zero-field situation and observe how the relaxation of the topmost surface atoms compares to the unrelaxed slab. The stacking sequence of atoms in a single trilayer along [110] follow: O–Ti$_2$O$_2$–O. Figure 3.8 shows the nomenclature used to describe the topmost slab layer atoms and bonds, which are also indicated in tabular form for clarity (table 3.4). The atoms are marked with primes (') denote atoms in trilayers beneath the first and are labeled
Table 3.4: Nomenclature used to describe the bonds indicated by the blue labels in 3.8

<table>
<thead>
<tr>
<th>Label in 3.8</th>
<th>Atoms in bond</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ti₆c–Obr</td>
</tr>
<tr>
<td>2</td>
<td>Ti₆c–Ou</td>
</tr>
<tr>
<td>3</td>
<td>Ti₆c–Os₁/₂</td>
</tr>
<tr>
<td>4</td>
<td>Ti₅c–Os₁/₂</td>
</tr>
<tr>
<td>5</td>
<td>Ti₅c–Obr'</td>
</tr>
<tr>
<td>6</td>
<td>Ti₅c’–Ou</td>
</tr>
<tr>
<td>7</td>
<td>Ti₆c’–Obr'</td>
</tr>
<tr>
<td>8</td>
<td>Ti₆c’–Ou'</td>
</tr>
<tr>
<td>9</td>
<td>Ti₆c’–Os₁/₂'</td>
</tr>
<tr>
<td>10</td>
<td>Ti₅c’–Os₁/₂'</td>
</tr>
<tr>
<td>11</td>
<td>Ti₅c’–Ou’</td>
</tr>
</tbody>
</table>

according to their coordinations: Obr is the 'bridging oxygen' atom furthest from the bulk, Ti₅c and Ti₆c are the fivefold and sixfold-coordinated titanium atoms, respectively, Os1 and Os2 are the (symmetrically equivalent) oxygen atoms in the middle atomic plane of a particular trilayer, and Ou is the oxygen atom that lies underneath the Ti₂O₂ layer in the x-direction. Even though the Ti₅c’ atom is sixfold-coordinated in trilayers under the first, the name is kept similar to “Ti₅c” to denote the underlying symmetries in structure to the fivefold-coordinated Ti atom on the surface.

Tables 3.5 (PBE) and 3.6 (opt-B88) show the relaxed atom positions for rutile TiO₂ (110) surface slabs of 3–7 trilayers with different ESM boundary condition, expressed in terms of the Ti–O bond lengths, which are a robust measure of the physical properties of the surface [3]. A fewer number of surface trilayers is required to converge the bond lengths in the surface relaxation as opposed to δdₓ values, the difference in the surface normal direction compared to the unrelaxed slab. The deviation in bond lengths between ESM boundary conditions for a given slab thickness is very small, always less than 0.01 Å, and on the order of 0.001 Å for atoms in the top surface trilayer. Similar to the results for bulk TiO₂, agreement between the bond lengths of the surface slab models the for PBE and opt-B88 functionals is very good, on the order of 0.01 Å. There exists a small oscillatory effect in some bond lengths (and other properties) between even and odd numbers of trilayers, which will be discussed further in the context of the TiO₂ nanowires in chapter 4. The bonds with the highest degree of oscillation with increasing slab size are the bottom-most O–Ti bonds that lie parallel to the surface normal.
Table 3.5: Bond lengths (in Angstrom) for the bare (110) rutile TiO₂ slab with two bottom layers fixed to the bulk positions and the PBE functional, as a function of the number of TiO₂ trilayers in the model and the ESM boundary condition. Daggers indicate the bond lengths of the bulk TiO₂ crystal. Bond label numbers in the table header are referenced in figure 3.8 and table 3.4.

<table>
<thead>
<tr>
<th>Model</th>
<th>PBE, bond lengths in Angstrom</th>
</tr>
</thead>
<tbody>
<tr>
<td>3(2) PBC</td>
<td>1.857 2.107 2.083 1.950 1.878 1.966 1.958† 2.028† 1.958† 1.982†</td>
</tr>
<tr>
<td>3(2) BC1</td>
<td>1.857 2.106 2.083 1.951 1.878 1.966 1.958† 2.028† 1.958† 1.982†</td>
</tr>
<tr>
<td>3(2) BC2</td>
<td>1.857 2.106 2.083 1.951 1.878 1.966 1.958† 2.028† 1.958† 1.982†</td>
</tr>
<tr>
<td>4(2) PBC</td>
<td>1.837 2.130 2.059 1.969 1.812 1.855 1.895 1.998 1.984 2.217</td>
</tr>
<tr>
<td>4(2) BC1</td>
<td>1.837 2.131 2.059 1.969 1.812 1.855 1.895 1.999 1.986 2.224</td>
</tr>
<tr>
<td>4(2) BC2</td>
<td>1.836 2.131 2.059 1.969 1.812 1.855 1.895 1.999 1.986 2.224</td>
</tr>
<tr>
<td>5(2) PBC</td>
<td>1.834 2.127 2.062 1.970 1.814 1.850 1.902 1.997 1.990 2.179</td>
</tr>
<tr>
<td>5(2) BC1</td>
<td>1.838 2.126 2.061 1.970 1.814 1.848 2.056 1.903 1.996 1.990 2.177</td>
</tr>
<tr>
<td>5(2) BC2</td>
<td>1.838 2.126 2.062 1.970 1.814 1.850 2.058 1.903 1.997 1.990 2.178</td>
</tr>
<tr>
<td>6(2) PBC</td>
<td>1.835 2.131 2.057 1.974 1.804 1.835 2.073 1.884 2.007 1.987 2.260</td>
</tr>
<tr>
<td>6(2) BC1</td>
<td>1.835 2.130 2.058 1.973 1.804 1.833 2.074 1.883 2.008 1.987 2.265</td>
</tr>
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</tr>
<tr>
<td>7(2) PBC</td>
<td>1.836 2.131 2.058 1.974 1.806 1.833 2.076 1.886 2.008 1.987 2.265</td>
</tr>
<tr>
<td>7(2) BC1</td>
<td>1.835 2.128 2.058 1.974 1.805 1.833 2.075 1.886 2.009 1.988 2.255</td>
</tr>
<tr>
<td>7(2) BC2</td>
<td>1.835 2.130 2.059 1.974 1.804 1.832 2.075 1.886 2.008 1.988 2.256</td>
</tr>
</tbody>
</table>

in the second-highest trilayer.

The three-trilayer model is the only surface slab with significant deviations from the thicker slabs, and this supports the assertion that four surface trilayers (with the bottom two trilayers fixed to their bulk positions) produce a satisfactory model, especially when considering issues that may arise from additional computational effort in simulating thicker slabs.

The distance between successive Ti₂O₂ planes, which are additional structural parameters used to characterize the surface while being less rigidly tied to bond lengths, was also calculated for model slabs of 3–7 trilayers. This was accomplished by averaging the atomic positions along the x-direction for the four nearly planar Ti₂O₂ atoms belonging to the family Ti5c-Ti6c-Os1-Os2. Because of the large overall agreement in geometries between the PBC, BC1 and BC2 boundary conditions, only the BC2 condition is investigated here. The results are shown in table 3.7 for the PBE and opt-B88 functionals.

Agreement between the PBE and opt-B88 functionals is again very good, noting that the largest differences between them stem from the inter-layer distances between the bulk end of
Table 3.6: Bond lengths (in Angstrom) for the bare (110) rutile TiO$_2$ slab with two bottom layers fixed to the bulk positions and the opt-B88 functional, as a function of the number of TiO$_2$ trilayers in the model and the ESM boundary condition. Daggers indicate the bond lengths of the bulk TiO$_2$ crystal. Bond label numbers in the table header are referenced in figure 3.8 and table 3.4.

<table>
<thead>
<tr>
<th>Model</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
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</tr>
</thead>
<tbody>
<tr>
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<td>1.851</td>
<td>2.090</td>
<td>2.069</td>
<td>1.950</td>
<td>1.873</td>
<td>1.951</td>
<td>1.940</td>
<td>1.998</td>
<td>2.002</td>
<td>1.970</td>
<td>2.060</td>
</tr>
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<td>3(2) BC1</td>
<td>1.852</td>
<td>2.086</td>
<td>2.069</td>
<td>1.951</td>
<td>1.871</td>
<td>1.949</td>
<td>1.940</td>
<td>1.998</td>
<td>2.002</td>
<td>1.970</td>
<td>2.060</td>
</tr>
<tr>
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<td>2.087</td>
<td>2.069</td>
<td>1.951</td>
<td>1.871</td>
<td>1.951</td>
<td>1.940</td>
<td>1.998</td>
<td>2.002</td>
<td>1.970</td>
<td>2.060</td>
</tr>
<tr>
<td>4(2) PBC</td>
<td>1.841</td>
<td>2.120</td>
<td>2.054</td>
<td>1.965</td>
<td>1.818</td>
<td>1.865</td>
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<td>1.899</td>
<td>1.984</td>
<td>1.988</td>
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<td>2.120</td>
<td>2.054</td>
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<td>1.900</td>
<td>1.983</td>
<td>1.988</td>
<td>2.197</td>
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<td>4(2) BC2</td>
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<td>2.123</td>
<td>2.053</td>
<td>1.965</td>
<td>1.818</td>
<td>1.861</td>
<td>2.043</td>
<td>1.899</td>
<td>1.983</td>
<td>1.988</td>
<td>2.198</td>
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<tr>
<td>5(2) PBC</td>
<td>1.841</td>
<td>2.115</td>
<td>2.055</td>
<td>1.966</td>
<td>1.817</td>
<td>1.856</td>
<td>2.049</td>
<td>1.898</td>
<td>1.987</td>
<td>1.988</td>
<td>2.179</td>
</tr>
<tr>
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<td>1.841</td>
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<td>2.055</td>
<td>1.967</td>
<td>1.818</td>
<td>1.857</td>
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<td>1.985</td>
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<td>1.967</td>
<td>1.818</td>
<td>1.857</td>
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<td>1.901</td>
<td>1.985</td>
<td>1.990</td>
<td>2.175</td>
</tr>
<tr>
<td>6(2) PBC</td>
<td>1.840</td>
<td>2.125</td>
<td>2.052</td>
<td>1.970</td>
<td>1.811</td>
<td>1.845</td>
<td>2.064</td>
<td>1.887</td>
<td>1.993</td>
<td>1.987</td>
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<td>1.840</td>
<td>2.124</td>
<td>2.053</td>
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<td>1.811</td>
<td>1.843</td>
<td>2.064</td>
<td>1.888</td>
<td>1.993</td>
<td>1.988</td>
<td>2.235</td>
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<td>6(2) BC2</td>
<td>1.839</td>
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<td>2.053</td>
<td>1.969</td>
<td>1.814</td>
<td>1.842</td>
<td>2.062</td>
<td>1.888</td>
<td>1.993</td>
<td>1.988</td>
<td>2.236</td>
</tr>
<tr>
<td>7(2) PBC</td>
<td>1.841</td>
<td>2.123</td>
<td>2.053</td>
<td>1.969</td>
<td>1.811</td>
<td>1.843</td>
<td>2.061</td>
<td>1.887</td>
<td>1.993</td>
<td>1.989</td>
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<tr>
<td>7(2) BC1</td>
<td>1.840</td>
<td>2.122</td>
<td>2.053</td>
<td>1.970</td>
<td>1.811</td>
<td>1.840</td>
<td>2.062</td>
<td>1.889</td>
<td>1.987</td>
<td>1.989</td>
<td>2.213</td>
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<tr>
<td>7(2) BC2</td>
<td>1.839</td>
<td>2.123</td>
<td>2.052</td>
<td>1.970</td>
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<td>1.838</td>
<td>2.061</td>
<td>1.889</td>
<td>1.987</td>
<td>1.989</td>
<td>2.217</td>
</tr>
</tbody>
</table>

Table 3.7: Inter-layer distances (Å) in the surface normal direction for the TiO$_2$ model slab for the PBE and opt-B88 functionals starting from the relaxed surface (left) and proceeding into the bulk-like region.

<table>
<thead>
<tr>
<th>PBE</th>
<th>Inter-layer Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3TL</td>
<td>3.373</td>
</tr>
<tr>
<td>4TL</td>
<td>3.380</td>
</tr>
<tr>
<td>5TL</td>
<td>3.360</td>
</tr>
<tr>
<td>6TL</td>
<td>3.367</td>
</tr>
<tr>
<td>7TL</td>
<td>3.361</td>
</tr>
<tr>
<td>opt-B88</td>
<td>Inter-layer Distance (Å)</td>
</tr>
<tr>
<td>3TL</td>
<td>3.365</td>
</tr>
<tr>
<td>4TL</td>
<td>3.378</td>
</tr>
<tr>
<td>5TL</td>
<td>3.359</td>
</tr>
<tr>
<td>6TL</td>
<td>3.370</td>
</tr>
<tr>
<td>7TL</td>
<td>3.363</td>
</tr>
</tbody>
</table>
the slabs are dissimilar by about 0.043 Å. Even though the lattice parameters were very similar (to less than 0.01 Å) between the PBE and opt-B88 bulk crystals, this difference is precipitated by small adjustments in the geometric coordinates of the atoms in the crystal which in turn affect the averaged coordinates in the plane of the surface.

Meanwhile, we note that there is an oscillatory effect on the inter-layer distances measurements as additional rows are added. The oscillatory effect is strongest for the topmost surface trilayers. It seems that the distances between these top two relaxed surface layers are converging towards a value of ~ 3.365 Å for both functionals, and that the trilayers approach the bulk value as subsequent inter-layer distances are considered for the thicker slabs. It should be noted that in all cases, the Ti5c atom was shifted in the $-x$ direction by ~ 0.3 Å and the Ti6c atom shifted in the $+x$ direction by less than 0.1 Å relative to the oxygen atoms that lie in the atomic plane. This data suggests that the oscillatory inter-layer distances and the large surface-subsurface inter-layer distance for the four-trilayer slab may weigh into our choice of model slab and we shall revisit this later in chapters 4 and 5.

### 3.3.3 Energetics and electronic structure of the model TiO$_2$ surface

To understand energetic and electronic consequences arising from finite quantum size effects in the rutile slab model, while continuing to determine the validity of a few-layer slab model, the surface energies, band edge characteristics, projected density of states (PDOS), and crystal orbital overlap populations (COOP) are calculated for the model slabs and discussed in this section.

Although difficult to measure experimentally, the surface energy is a good benchmark for size convergence of surface slab models. The surface energy per unit cell $\sigma$ may be readily calculated from the total energy of the model surface slab, and is conceptualized as the energy required to create a new surface along a particular Miller plane. The typical definition for $\sigma$ for an $N$-atom slab using computational chemistry is: [92]

$$\sigma_N = \frac{1}{2N} (E_{N,slab} - NE_{bulk})$$

(3.4)

where $E_{N,slab}$ is the total energy of an $N$-atom surface slab, $E_{bulk}$ is the total energy of the bulk crystal divided by the number of atoms in the bulk unit cell, and the factor of $\frac{1}{2}$ represents the fact that there are two surfaces in the unit cell. However, this formula suffers from poor convergence with respect to the number of surface layers as it is highly sensitive to variations
in the determination of $E_{\text{bulk}}$, as previously shown in [93]. Instead, we use a different approach first proposed in [94] and applied to the quantum size effect of metal slabs [95, 96] and later used with success for modeling surface energies of TiO$_2$ slabs. [74] Here, the surface energies are calculated by a rearrangement of 3.4 into:

$$E_{N,\text{slab}} = 2\sigma + NE_{\text{bulk}}$$

(3.5)

whereby the bulk energy is extracted from a series of total energy calculations for increasing numbers of surface trilayers with non-equilibrium bulk geometries, creating a linear fit for the slope $E_{\text{bulk}}$ and the y-asymptote $2\sigma$. Since the top and bottom slab surfaces are different in the case of the surface models with atoms frozen to their bulk positions, one further refinement is necessary: the subtraction of the energy difference between the unrelaxed and relaxed surfaces, $\Delta E_{N,\text{slab}}$, resulting in the surface energy per unit cell of only the relaxed, top surface. Finally, by dividing by the area per unit cell, the formula for the surface energy of the slab per unit area $\sigma_A$, may be written as:

$$\sigma_A = \frac{\sigma_N - \Delta E_{N,\text{slab}}}{A}.$$ 

(3.6)

Surface energies were calculated for rutile TiO$_2$ (110) slabs with 3-7 surface trilayers with the PBE and opt-B88 functionals, using 4-11 unrelaxed surface trilayers to perform the fitting for $E_{\text{bulk}}$. These results are shown in figure 3.9, following the usual even-odd oscillation in calculated surface properties observed elsewhere [3, 74, 89] for PBE. No difference in this trend was observed when the ESM boundary condition was varied, whereas quantitative differences in the surface energies corresponded to < 0.01 eV/atom. As such, only the data for the periodic boundary condition are shown in figure 3.9. The relative range of energies for both the unrelaxed and relaxed slabs is similar to previous plane-wave calculations as well, but some notable differences can be discerned. First, the unrelaxed and relaxed slabs with the PBE functional displays stronger oscillations (for $N > 3$) than previously reported, 0.2 J/m$^2$ compared to $\sim 0.03 - 0.08$ J/m$^2$. [24] This is probably a consequence of the atomic orbital basis set, as the surface energy difference between the unrelaxed and relaxed slabs converges to a common value as $N$ increases. Second, the surface energy for the opt-B88 slab tends to be about double the PBE value. Most likely, this is due to the construction of the opt-B88 pseudopotentials. Since the only methods to arrive at surface energy are theoretical rather than experimental for TiO$_{2}$, this calculation is meaningful only when comparing the energies of different surface orientations and observing the effect of different simulation setups on recovered properties. Finally, the extent of even-odd
Figure 3.9: Plot of the surface energies of the unrelaxed (dashed lines), fully-relaxed (dash-dotted lines), and bottom-two-trilayers-fixed TiO$_2$ slabs as a function of slab thickness, with the PBE (black) and opt-B88 (blue) functionals.

oscillations in the opt-B88 slabs is muted with increasing number of trilayers, achieving a nearly converged value of 0.75 J/m$^2$ at 7 trilayers.

Another quality of the surface, the work function, defined as the minimum energy required to promote an electron from the surface to the vacuum, has important consequences for surface reactivity. The work function is typically defined as the energy difference between the vacuum level and the Fermi level. However, for semiconducting materials (wherein no electronic states exist in the gap region near the Fermi level) the inverse position of the valence band maximum, referenced to the vacuum level, is used in the work function calculation instead because the position of the Fermi level is arbitrary within the gap [97, 98]. The ESM boundary condition allowed for an unambiguous determination of the vacuum level because the electrostatic potential always refers to the vacuum level (unlike the PBC simulations) in the vacuum-slab-vacuum (BC1) condition and becomes identically equal to zero (on both sides) for the metal-slab-metal condition (BC2). [32] Both the valence band maximum and conduction band minimum occur at the Γ-point for each model slab studied, confirmed by inspecting band diagrams plotted in k-space.

Figure 3.10 shows the absolute position of the valence (full markers) and conduction (empty markers) energy levels as a function of slab thickness for the fully-relaxed model slab (black)
Figure 3.10: Plot of the absolute valence (filled squares) and conduction band (open squares) energies for the PBE (a) and opt-B88 (b) relaxed TiO$_2$ slabs using the BC1 (red) and BC2 (blue) boundary conditions, with the bottom two trilayers fixed. The absolute energy scale is on the left side (for solid lines). The band gap energies are plotted as half-full squares with a scale on the right side (for dotted lines).
and model slab with the bottom two trilayers fixed (red and blue for BC1 and BC2, respectively). The bandgap for the two ESM boundary conditions is essentially identical everywhere, converging to a value near 1.15 eV for PBE and a low value of about 0.4 for opt-B88, where for the full, symmetric relaxation those values are closer and higher, at about 1.80 for PBE and 1.75 eV for opt-B88, where there is about 0.2 eV of variance between even odd and layers. The valence and conduction band levels and their trends are very close to ref. [72] for the fully-relaxed slab. The opt-B88 shows slightly less of the typical odd-even oscillation in work function and bandgap as the number of TiO$_2$ trilayers is increased for the fixed slab, especially with attention to the BC2 condition, with a noticeably smaller bandgap than in PBE by about $\sim 0.7$ eV. Also, the BC1 and BC2 results for the electronic gap are different by about 0.04 eV for all model slabs, with the BC2 bandgap being larger. The BC1 and BC2 results for the placement of the band edges are in very good agreement to within $\sim 0.03$ eV.

The variance between the bottom-fixed and free bandgaps is about 0.65 eV and 1.35 eV for PBE and opt-B88, respectively, signifying that the electronic structure of the model slab has been significantly modulated by fixing the bottom two layers of the slab. This is the first indication of a significant theoretical result which will be revisited often in this work.

The converged BC1 and BC2 results for the work function are 6.8 eV for PBE and 6.65 eV for opt-B88, respectively, which agrees with previously-published first principles results of 6.90 eV (VASP, 5TL partially-relaxed slab) [99] and $\sim 7.0$ eV [74] with the PBE functional. A small underestimation of work function is consistent with the recent study in Ref. [51] on the accuracy of strictly localized atomic orbital bases in describing surface properties, considering the fact that the work function is sensitive to the long range tails of wavefunction decay in the vacuum region. Published LDA results for the work function are also generally close to what was obtained here. Using the fully linearized augmented plane-wave method (FLAPW) and 3TL relaxed slabs, values of 6.79 eV [100], 7.09 eV [101], and 7.16 eV [102] have been reported by Vogtenhuber et al. The results for the PBE and opt-B88 work functions also comes close to some experimental work (6.83 eV) using scanning tunneling microscopy (STM) on a clean, stoichiometric TiO$_2$ surface which is cited in [100]. Some other reported experimental values of the work function fall into the range of 5.1-5.6 eV [103, 104, 105], but it has been noted that changing the stoichiometry of the surface layer from Ti$_4$O$_8$ to Ti$_4$O$_7$ (an oxygen vacancy) results in a reduction of the work function by $\sim 2.0$ eV using both theoretical [102] and experimental methods including local barrier-height imaging. [103, 106] These results give us confidence in
the BC2 ESM condition as a worthy scheme of simulation, recovering true surface properties from \textit{ab-initio} simulations as well as being very close to other published results with similar methods.

The dependence of the electronic structure of the TiO$_2$ model slabs with respect to the number of surface trilayers is probed using two analyses: the projected density of states (PDOS) and the crystal orbital overlap population (COOP). Using equation 3.4 and summing over each of the orbitals of interest, the total DOS, O$_2$p PDOS and Ti3$d$ PDOS are plotted, concentrating on the differences between the electronic structure of PBE and opt-B88. The number of trilayers is varied in figures 3.12-3.11 for the simulation slabs with the two bottom trilayers fixed and those allowed to fully relax, respectively, and the ESM boundary condition is varied in figure 3.13. The Monkhorst-Pack k-point mesh used to calculate the PDOS was $(1 \times 24 \times 12)$, at least double the density used in the DFT simulation to offer a better sampling of the reciprocal lattice.

It is obvious from comparing figures 3.12-3.11 that the addition of trilayers between the surface and the frozen layers influences the PDOS in a small, but detectable manner. Specifically, there is a small “shoulder” that appears in the valence band maximum DOS for even numbers of trilayers and appears in the conduction band minimum for odd numbers of trilayers in the fully-relaxed slabs. The small amount of variance between the features of the DOS/PDOS as a function of the number of trilayers in the slab gives even further credence to the assertion that four trilayers again seems to be thick enough of a model surface to show converged behavior in the description of electronic states. In figure 3.11, where the slab is allowed to fully relax, the energy gap between the valence and conduction bands is almost equal in PBE and opt-B88 and the features of the PDOS are very similar. Comparing to the case of holding the bottom two trilayers fixed (figure 3.12), a downshift of electronic levels of the opt-B88 functional becomes very clear. Furthermore, a spike at the valence band maximum DOS appears for the fixed half-slab that is absent in the fully-relaxed slab.

It is clear from figure 3.13 that the variation of ESM boundary conditions does not influence the PDOS significantly. The unrelaxed slab has a similar electronic structure to the rest of the relaxed PBE model slabs in the different boundary conditions than the relaxed slabs discounting a strengthening of the O$_2$p peak at the valence band edge, but the opt-B88 unrelaxed slab could be considered metallic due to the removal of the fundamental electronic gap in 2a. Therefore,
Figure 3.11: Total (black) and projected (blue: Ti3d, red: O2p) density of states for the (110) TiO\textsubscript{2} surface for the PBE (1a-1d) and opt-B88 (2a-2d) functionals with increasing numbers of trilayers (TL) in the model surface allowed to fully relax.
Figure 3.12: Total (black) and projected (blue: Ti3d, red: O2p) density of states for the (110) TiO$_2$ surface for the PBE (1a-1d) and opt-B88 (2a-2d) functionals with increasing numbers of trilayers (TL) in the model surface with the bottom two trilayers fixed to their bulk positions.
Figure 3.13: Total (black) and projected (blue: Ti3d, red: O2p) density of states for the four-trilayer (110) TiO$_2$ surface for the PBE (1a-1d) and opt-B88 (2a-2d) functionals in the unrelaxed case (a), the periodic boundary conditions without ESM (b), and with the ESM BC1 (c) and BC2 (d) boundary conditions. The bottom two rows of atoms are fixed.
the geometry relaxation effect on the electronic structure is much more important for opt-B88 than it is for PBE.

For a closer inspection into the details of the electronic structure, we examine the PDOS of the O2p and Ti3d orbitals decomposed into their trilayer position, starting from the top surface and going down into the bulk-like region. This plot is shown in figure 3.14 for the PBE (1) and opt-B88 (2) functional with the 4-trilayer model slab. Here, we obtain evidence that for both PBE and opt-B88, the only significant contribution to the electronic states at the valence band edge come from the O2p orbitals on the bottom, bulk-like, portion of the model slab (figure 3.141,2d). The profile of the DOS appears similar for that trilayer in both PBE and opt-B88 for both the valence and conduction bands. The remainder of the PDOS plots in 3.14 show clearly that the energy levels of the non-symmetric slab with the opt-B88 functional are depressed in energy compared to the non-symmetric PBE model slab, and that the greatest energy shift is observed for the top two trilayers (2a,b). Since this downshift in energy was not present in the bulk simulations as evidenced by figure 3.7, nor the symmetrically-relaxed slabs, it must be a specific artifact introduced by the fixing of the bottom two trilayers to their bulk positions. This analysis shows that two possible weaknesses in the opt-B88 functional are the increased sensitivity to atomic relaxation and the large (∼0.7 eV) reduction in the electronic gap due to a downshift of the electronic levels of the entire conduction band and the states contributing to the valence band from the relaxed trilayers.

For insight into the chemical bonds of the TiO₂ surface, we employ the COOP method briefly mentioned in section 3.2.4. The COOP is essentially a weighted DOS curve (also as a function of energy) between two specific orbitals of different atoms (which may be included as a sum over many orbitals that could participate in a chemical bond). Mathematically, it is defined as:

\[
COOP_{x,y}(E) = \sum_{m \in X, n \in Y, i, k} \frac{2}{m} \langle \phi_m | \phi_i \rangle \delta(E - \epsilon_{ik})
\]  

(3.7)

where \(x\) and \(y\) are atomic labels (although these could be omitted for a single bond rather than a whole-crystal analysis), the indices \(i, k, l, m\) refer to the eigenvalue (eigenvector) indices and atomic orbital indices, respectively, and the overlap matrix elements \(S_{mi} = \langle \phi_m | \phi_l \rangle\). Physically, this an extension of the Mulliken population analysis formalism to (semi)infinite crystalline systems.[107, 108] Energy ranges where the COOP is positive reflect an overall bonding interaction and where it is negative, the interaction is anti-bonding. Similar to the PDOS analysis
Figure 3.14: Total (black) and projected (blue: Ti3d, red: O2p) density of states for the four-trilayer (110) TiO$_2$ surface for the PBE (1a-1d) and opt-B88 (2a-2d) functionals, with varying x-position in the model slab, starting from the topmost surface trilayer (a) progressing into the layers at the bottom of the slab fixed to the bulk positions (c,d).
Figure 3.15: Plot of the COOP between the 3d orbitals of the Ti atom and the 2p orbitals of the O atom delineated by the bond pairs designated graphically in model on the right-hand side for the PBE (1a-1d) and opt-B88 (2a-2d) functionals with increasing number of trilayers (TL). The bottom two rows of atoms are fixed in each model slab.
presented earlier, the $\delta(E - \epsilon_{ik})$ term in practice is a Gaussian with half-width 0.07 eV. Analogous to figure 3.12, COOP plots for the O2p and Ti3d overlap are presented in figure 3.15 as a function of the number of trilayers. The selected bonds are chosen to describe the inter-trilayer binding, since it was already determined that for the energy ranges that interest us in the valence and conduction band near the Fermi energy, the dominant electronic orbitals are O2p and Ti3d.

The COOP plots show that the inter-trilayer binding tends to be bonding in the valence band rather than antibonding, and the degree of bonding between the 1st-2nd trilayers (black and red) is much greater than the bonding between the 2nd-3rd trilayers. The dependence of the COOP on the number of total trilayers in the surface model is not significant in these selected bonding arrangements by comparing figure 3.15-1 to 3.15-2, while there is likewise no dependence of the COOP on the ESM boundary condition (not shown). Furthermore, the Ti-O bond that occurs between the Ti5d and Obr' site (bond number 5) is downshifted in energy compared to the bond between the Ti5d' and Ou atoms (bond number 6), which lies closer to the valence band edge. One major difference between the COOP for the PBE and opt-B88 functionals is, again, the net downshift in energy of the opt-B88 functional’s valence and conduction band, and since the three top trilayers of the 4TL model are scrutinized here, this plays directly into the observation from figure 3.14 that the uppermost (non-fixed) trilayers experience a large downshift in energy for the opt-B88 functional. Meanwhile, it is clear from the small peak at the conduction band edge that the Ti5d-Obr’ bond has a stronger binding character for opt-B88 than it does for PBE, while for the conduction band further than $\sim 1$ eV above the conduction band edge, bonds 5 and 6 retain a pronounced anti-bonding character. Since the Ti5d atom has an incomplete electron shell, it is plausible that any molecule with unpaired electrons will gravitate toward that site, while the COOP for the Ti5d-Obr’ bond at the conduction band edge has a bonding character of higher degree with opt-B88 than for PBE and hence a greater probability that more states will contribute to the binding of a new species to the Ti5d site. Therefore, we expect that the adsorption energy for a water molecule to be larger for the opt-B88 functional than for PBE and also the Ti5d-Obr’ bond to weaken slightly as a result of adsorption in both cases.

Finally, we again reach the conclusion that the four-trilayer slab with the two bottom layers fixed is a computationally simple model which shows sufficiently converged behavior of relevant
electronic and energetic properties of the surface. It is this model that will continue to be used in chapter 5 to examine adsorption of water and the effect of the applied electric field.

3.4 Convergence of properties of H$_2$O

There has been considerable interest in the simulation of water in its vapor, liquid, and solid forms due to its ubiquity on earth and its fundamental role in the world’s oceans, biology, atmospheric science, and other physical processes. Because of this, a great wealth of results of experiments and simulations of water molecules exists.

This short section lays the theoretical groundwork for simulating single and multiple H$_2$O molecules which will be further used in chapter 5. Again, the objective is to establish firm structural, energetic, and electrostatic parameters for water in the monomer and dimer limit (in vapor phase). Fortunately, PBE and opt-B88 results for water geometries and energies is plainly accessible, and in addition to that, higher-level, post-DFT calculations like CCSD are available because of the small system sizes involved.

3.4.1 Computational methods: H$_2$O

The monomer and dimer of H$_2$O were simulated with SIESTA by using initial geometries freely available from the NIST Computational Chemistry Comparison and Benchmark Database (CC-CBD) [109]. The unit cell of the simulation was chosen to be 11 Å × 11 Å × 11 Å to minimize the effect of images from neighboring cells. A DZP basis plus diffuse s orbitals of SZ-character with radii of 7.000 (O) and 3.000 (H) Bohrs was utilized for all water molecule calculations. The simulations were performed with an energy mesh cutoff of 550 Ry and a single k-point. The counterpoise correction [53] was used in all calculations of dissociation energy for the water dimers. No ESM boundary conditions were used; the simulations in this section are performed with the usual periodic boundary conditions. Convergence in the electronic step of the SCF cycle terminated when the maximum absolute value of the difference in the density matrix elements between a step and the previous step was less than 0.0001 and the force convergence criteria for structural relaxation was 0.008 eV/Å. Only the PBE and opt-B88 functionals are utilized in the water molecule simulations.
3.4.2 Results: structure, energetics, and electronic structure of H$_2$O

Like the bulk materials already discussed, the simplest molecular parameters to compute and analyze for the water molecule and dimer are its geometrical parameters. A survey of those geometric parameters along with energetic levels and electrostatic characterizations are given in tables 3.8-3.9 for our calculations and a selection of previous calculations with PBE and opt-B88 functionals (with a PW basis), [66], CCSD(T) simulations in the complete basis set limit, [109] and experiments. A schematic of bond and angle labels is shown in figure 3.16.

The calculated bond lengths and angles for the isolated H$_2$O molecule are close to each other and also previously reported DFT results for PBE and opt-B88 with a PW basis. The bond lengths are about 0.02 Å longer than fully ab initio simulations in the complete basis set limit and experimental results. The calculated bond angles agree to almost 1% as well, but are smaller than both other PBE and opt-B88 results and also the CCSD(T) results and experiment. The dipole moment difference between our PBE and opt-B88 results was about 5% but were nevertheless close to the other DFT results and experiment. Energy eigenvalues for the HOMO and LUMO states and the three occupied states beneath it were calculated and agree with each other to $\sim$ 0.1 eV, but do not agree with experiment or the CCSD(T) results. This is a fairly common shortfall of DFT not reproducing the correct ionization energies and HOMO-LUMO gap.

In principle, one could choose from a number of charge partitionings to estimate partial atomic charges: Mulliken population analyses, the Bader charge partitioning scheme, Hirschfield charge analysis, and others. This variance of methods introduces a great amount of variability.
Table 3.8: Properties of the gas-phase water monomer, calculated by PBE and opt-B88, with comparisons to prior calculations and experiment. \( \text{O}_d - \text{H}_f \) is the distance between the oxygen atom and a hydrogen atom (the two are essentially equivalent) in Angstroms. \( \Theta_{\text{H}_2\text{O}} \) is the H-O-H bond angle in degrees. \( p \) is the magnitude of the dipole moment in Debye. \( E_{2a_1} \) is the lowest-occupied electron energy eigenvalue in eV (excluding the 1s core state), with respect to the Fermi energy. \( E_{1b_2}, E_{3a_1}, E_{1b_1} \) (HOMO) are the three occupied levels above it, and \( E_{4a_1} \) is the LUMO level. \( q_O \) and \( q_H \) are the partial charges on the Oxygen and Hydrogen atoms calculated by a Mulliken population analysis, in terms of the elementary positive charge \( e \). Labels for the distances and angles are given in figure 3.16.

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<tbody>
<tr>
<td>( \text{O} - \text{H} ) (Å)</td>
<td>0.975</td>
<td>0.977</td>
<td>0.972</td>
<td>0.973</td>
<td>0.956</td>
<td>0.957 [110]</td>
</tr>
<tr>
<td>( \Theta_{\text{H}_2\text{O}} ) (°)</td>
<td>103.1</td>
<td>103.5</td>
<td>104.3</td>
<td>104.4</td>
<td>104.6</td>
<td>104.5 [110]</td>
</tr>
<tr>
<td>( p ) (D)</td>
<td>1.90</td>
<td>1.80</td>
<td>1.811</td>
<td>1.813</td>
<td>1.98</td>
<td>1.855 [111]</td>
</tr>
<tr>
<td>( E_{2a_1} ) (eV)</td>
<td>-23.890</td>
<td>-23.863</td>
<td></td>
<td></td>
<td></td>
<td>-32.4 [112]</td>
</tr>
<tr>
<td>( E_{1b_2} )</td>
<td>-11.714</td>
<td>-11.776</td>
<td></td>
<td></td>
<td></td>
<td>-18.7 [112]</td>
</tr>
<tr>
<td>( E_{3a_1} )</td>
<td>-7.963</td>
<td>-8.009</td>
<td></td>
<td></td>
<td></td>
<td>-14.8 [112]</td>
</tr>
<tr>
<td>( E_{1b_1} )</td>
<td>-5.751</td>
<td>-5.889</td>
<td></td>
<td>-13.863</td>
<td>-12.6</td>
<td>[112]</td>
</tr>
<tr>
<td>( E_{4a_1} )</td>
<td>1.570</td>
<td>1.463</td>
<td></td>
<td>0.795</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( q_O ) (e)</td>
<td>-0.836</td>
<td>-0.854</td>
<td></td>
<td>-0.274</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( q_H ) (e)</td>
<td>0.418</td>
<td>0.427</td>
<td></td>
<td>0.137</td>
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In results according to the chosen Hamiltonian (level of theory) and basis sets used in the calculation. [113] Here we use the simplest approximation for atomic charges, the Mulliken population analysis, [114] where the partial charges on each atom \( A \) are constructed from the basis functions through the overlap matrix:

\[
\mathbf{Q}_A = \mathbf{Z}_A - \sum_{\mu\nu} \mathbf{D}_{\mu\nu} \mathbf{S}_{\mu\nu}
\]  

(3.8)

where \( \mathbf{Z}_A \) is the number of (valence) electrons in the isolated free atom, \( \mu \) and \( \nu \) are basis functions and atomic orbitals, respectively, and \( \mathbf{D} \) and \( \mathbf{S} \) are the density and overlap matrices. Generally, the Mulliken analysis is the most computationally inexpensive method to partition charges and it can give chemically intuitive charge sign on atoms and generally acceptable magnitudes, but it has the greatest variability in terms of basis set and calculation method of all the charge partitioning schemes. Furthermore, this method always equally distributes shared electrons between atoms due to how the off-diagonal components of the overlap and density matrices are given equal weight on any given atom pair. This variability is illustrated in the \( q_O, q_H \) rows of table 3.8: the CCSD(T) and DFT partial charges are far from each other.
Table 3.9: Properties of the gas-phase water dimer in the donor–acceptor position, calculated by PBE and opt-B88 in the fully optimized geometry, with comparisons to prior calculations and experiment. Labels for the distances and angles are given in figure 3.16. Subscripts $d$ and $a$ refer to the donor and acceptor $H_2O$ molecule and subscripts $f$ and $b$ denote the free and bound H atoms of the donor. The dihedral angle $\delta$ is the angle in the first quadrant between each water molecule’s plane, $E_d$ is the binding energy (or alternatively, the hydrogen bond dissociation energy), and $p_{\text{net}}$ is the net dipole moment of the arrangement. The experimental value for the water dimer dissociation energy is deduced from the reference by neglecting vibrational nuclear quantum effects. [2]

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<tbody>
<tr>
<td>$O_d - H_f$ (Å)</td>
<td>0.975</td>
<td>0.976</td>
<td></td>
<td></td>
<td></td>
<td>0.957</td>
</tr>
<tr>
<td>$O_d - H_b$ (Å)</td>
<td>0.987</td>
<td>0.986</td>
<td>0.982</td>
<td>0.982</td>
<td></td>
<td>0.964</td>
</tr>
<tr>
<td>$O_a - H_a$ (Å)</td>
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<td>0.978</td>
<td></td>
<td></td>
<td></td>
<td>0.959</td>
</tr>
<tr>
<td>$H_b - O_a$ (Å)</td>
<td>1.904</td>
<td>1.917</td>
<td></td>
<td></td>
<td></td>
<td>1.951</td>
</tr>
<tr>
<td>$O_b - O_a$ (Å)</td>
<td>2.884</td>
<td>2.891</td>
<td>2.895</td>
<td>2.909</td>
<td></td>
<td>2.909 ± 0.03 [115]</td>
</tr>
<tr>
<td>$\Theta_{H_2O,d}$ (°)</td>
<td>103.2</td>
<td>103.7</td>
<td></td>
<td></td>
<td></td>
<td>104.4</td>
</tr>
<tr>
<td>$\Theta_{H_2O,a}$ (°)</td>
<td>103.3</td>
<td>103.6</td>
<td></td>
<td></td>
<td></td>
<td>104.5</td>
</tr>
<tr>
<td>$\Theta_{O_bH_bO_a}$ (°)</td>
<td>171.5</td>
<td>168.4</td>
<td>173.8</td>
<td>174.2</td>
<td></td>
<td>172.7 ± 20 [115]</td>
</tr>
<tr>
<td>$\delta$ (°)</td>
<td>56.1</td>
<td>55.1</td>
<td></td>
<td></td>
<td></td>
<td>56.0 ± 10 [115]</td>
</tr>
<tr>
<td>$E_d$ (eV)</td>
<td>0.234</td>
<td>0.232</td>
<td>0.219</td>
<td>0.209</td>
<td></td>
<td>0.218</td>
</tr>
<tr>
<td>$p_{\text{net}}$ (D)</td>
<td>2.401</td>
<td>2.310</td>
<td></td>
<td></td>
<td></td>
<td>2.638</td>
</tr>
</tbody>
</table>

and barely merit a comparison at all.

For the water dimer in vacuum, our PBE and opt-B88 results again come very close to each other. Values of geometric parameters, the dissociation energy $E_d$, and the net dipole moment $p_{\text{net}}$ are displayed in table 3.9. The $H_b - O_a$ hydrogen bond length and $O_b - O_a$ distance is slightly longer (0.007 Å) with opt-B88 than PBE, a trend that occurs elsewhere in the literature. [66] This O–O distance, about 2.89 Å, is coincidentally close to the distance between adjacent Ti5c sites on the rutile (110) TiO$_2$ surface, ~2.98 Å and also the distance characterized by peaks in the $R_{OO}$ distribution function in ensemble simulations. [25] The angle $\Theta_{O_bH_bO_a}$ is less shallow for our opt-B88 results than our PBE results or for other first-principles simulations. Good agreement was also found in the dihedral angle $\delta$, the angle in the first quadrant between each water molecule’s plane. The dissociation energies of the PBE and opt-B88 water dimer are also much closer to each other than for other DFT results, which indicate a slightly deeper potential energy well for our results, but very close to experiment (neglecting nuclear quantum effects). The net dipole moments are also close to each other, having a difference between PBE and opt-B88 nearly equal to that which is observed for the water monomer.

A further electrostatic analysis employed here and later in this work is the electrostatic
charge transfer between a system and its composite parts. The induced charge or charge transfer is simply defined as a difference in charge densities between a composite system in its relaxed geometry and its components at those fixed geometries. Therefore, the induced charge for a water dimer, \( n_\delta \), is:

\[
 n_\delta = n_{2\text{H}_2\text{O}} - n_{\text{H}_2\text{O},1} - n_{\text{H}_2\text{O},2}
\]

(3.9)

and a similar expression may be concocted for an adsorbate on a surface. A plot of \( n_\delta \) is shown in figure 3.17 for PBE (a) and opt-B88 (b) water dimers in their relaxed geometries with yellow regions signifying electron accumulation and blue regions signifying electron depletion. The agreement between the two functionals is superb and corroborates previous calculations. [117]

It is clear from this picture that most of the charge rearrangement in the water dimer occurs in the direction of the H\(_b\) – O\(_a\) hydrogen bond. The donor and acceptor molecules display nearly opposite charge rearrangement about their central O atoms which identifies polarization in both molecules to be a result of the formed hydrogen bond. Finally, the donor H atom which participates in the hydrogen bond shows pronounced electron depletion compared to the isolated molecule.

3.5 Conclusion

The purpose of the simulations performed in this chapter for the bulk rutile TiO\(_2\) crystal and its (110) surface were to establish a firm theoretical base for the more complicated systems performed in later chapters of this work. The PBE and opt-B88 functionals had very good agreement in overall structure, energetics, and electronic structure of the bulk crystal. The variance in atomic bond lengths between PBE and opt-B88, between ESM boundary conditions, and also between the 4-trilayer model slab with those having up to 7 trilayers, was overall very small, on the order of 0.01 Å at most.

PBE and opt-B88 displayed different behavior of the convergence of the surface energy with increasing number of trilayers in the model slab, with opt-B88 predicting a much greater converged value. The two functionals predicted similar behavior of the work function to \( \sim 0.15 \) eV. The projected density of states of the model surface was qualitatively similar between PBE and opt-B88 in that the valence band was mostly made of O2\( p\) states and the conduction band made of Ti3\( d\) states, the PDOS showed an indifference to ESM boundary condition, and similar convergence behavior as the number of trilayers increased. However, the bandgap of
Figure 3.17: Plot of the charge density difference between the H$_2$O dimer and two individual H$_2$O molecules in the relaxed geometry of the dimer. Yellow and blue regions correspond to an accumulation and depletion of electrons, respectively. The isosurface level is at 0.0005e/bohr$^3$. 

a) PBE

a) opt-B88
the (non-fully-relaxed) opt-B88 surface was reduced by $\sim 0.7$ eV in comparison to PBE where their difference in bandgap for the fully-relaxed surfaces was much smaller, about 0.1 eV. The origin of the reduction of bandgap for both PBE and opt-B88 seems to stem from fixing the two bottom trilayers of the slab, inducing a downshift in energy of all electronic states projected on the topmost (relaxed) trilayers of the model slab, where the states that arise from the bulk-like fixed layer do not downshift in energy, pinning the states at the valence band edge in energy while the downshift occurs for nearly all other electronic states. A COOP analysis for Ti–O bonds parallel to the surface normal showed that interlayer binding between the first two trilayers is much stronger than the interlayer binding between the second and third trilayer, which is not significantly modified as additional trilayers are added to the model surface. It was determined that the four-trilayer slab showed sufficient convergence to the bulk limit while being small enough to make large unit cell calculations facile.

Finally, water molecule properties were calculated in the gas-phase monomer and dimer configurations and compared to previous calculations at similar levels of theory, in the complete basis set limit, and to experiments. PBE and opt-B88 recovered similar properties for the water molecule geometries in most cases, which in turn showed good agreement with previously published \textit{ab initio} and experimental results.
Quantum Confinement and Shape Tunability in TiO$_2$ Nanowires

4.1 Introduction

Recently, TiO$_2$ nanowires in different crystalline order have been exploited in a wide range of applications including dye-sensitized solar cells, proton-exchange-membrane fuel cells and gas sensors. [118, 119] Many of these applications have focused on nanowires with diameters of tens of nanometers. The recent developments in synthesis of TiO$_2$ nanowires with diameters on the atomic-scale [120, 121] have opened up new grounds for studying structure-property relationships in the regime where quantum confinement effects are important. In the sub-nanometer range, the properties of nanowires can be sensitive to atomic-level control of surface morphology, functionalization, and nanowire stoichiometry during the growth and fabrication processes, thereby opening the way for new applications.

Relatively few theoretical studies on atomic-scale TiO$_2$ nanowires in either rutile or anatase structures have been published. [90, 122, 123, 124, 125, 126, 127, 128] In particular, two recent studies [127, 128] have shown that the stability and electronic properties of TiO$_2$ nanowires are sensitive to the nanowire orientation, the presence of screw symmetry and the size of the nanowires. Both works have focused on nanowires with square cross section. In this chapter, we attempt to shed light on the structure-property relationship in these novel one-dimensional (1D) nanomaterials by presenting a systematic density functional theory (DFT) study on the size- and shape-dependent atomic and electronic properties of rutile TiO$_2$ nanowires with rectangular cross section of different size and aspect ratio.

The TiO$_2$ nanowires studied correspond to those with a cross section in the 001 plane of the...
bulk rutile crystal and enclosed by the \{110\} facets, which are the most stable facets for [001]-oriented rutile nanowires. [125, 127]. We use the notation m×n to classify these stoichiometric nanowires of rectangular cross section, where the two indices m and n characterize the number of TiO$_2$ layers parallel to the facets along each lateral dimension. The examples of 6×8, 5×8, and 3×7 nanowires are shown in Fig. 4.1. We note that the TiO$_2$ layer is composed of a mixed Ti-O plane with equal number of Ti and O atoms sandwiched between two layers of O atoms. At the (110) surface, rows of six-fold coordinated Ti atoms (Ti-6c) alternate with rows of five-fold coordinated Ti atoms (Ti-5c) along the [001] direction. The bridging O atoms in the outermost layer are two-fold coordinated (O-2c), while all other O atoms are three-fold coordinated (O-3c) as in the bulk (Fig. 4.1).

For square m×m rutile nanowires oriented along the [001] direction, we can identify two rotational axes parallel to the nanowire axis: [128] one 4-fold screw axis going through the interstitial region in the middle of the concentric squares of Ti atoms for even number of m and one 2-fold axis going through the Ti atoms for odd number of m. Recent studies [127, 128] have shown that the presence or absence of the screw axis in the square nanowires is coupled to the indirect or direct character of the band structure, with the m×m nanowire with odd (even) m having direct (indirect) band gap. In addition, square wires with screw symmetry have been found to possess consistently lower formation energy and higher band gap than square wires without it. [127, 128]

However, for general m×n nanowires, this simple classification no longer applies, as the nanowires possess different reduced symmetry depending on the even-odd parity of m and n. We show instead that the key element determining the difference in electronic properties of rectangular nanowires is the presence (when m or n is odd) or absence (when m or n is even) of a mirror Ti-O plane in either confinement direction, with the square nanowires being a special case of the general classification. In addition, if both m and n are odd and m≠n, two different ways of constructing nanowires exist that are not related to symmetry but depends on whether the mirror Ti-O plane terminates on the 6-fold (Ti-6c) or 5-fold (Ti-5c) coordinated Ti atoms at the facet surfaces along each confinement direction. The example of 3×7 nanowire is shown in Fig. 4.1(B). We find that the differences in the electronic properties of these rectangular nanowires are a direct consequence of the different surface relaxations occurring along each lateral confinement direction as a function of the corresponding number (m or n) of TiO$_2$ layers.
Figure 4.1: Atomic structures of the 6×8 (left figure in A), 5×8 (right figure in A), 3×7₁ (left figure in B) and 3×7₂ (right figure in B) rutile TiO₂ nanowires oriented along the [001] direction. For the type-1 3×7₁ nanowire, the mirror Ti-O plane along the first confinement direction terminates on the Ti-5c atoms at the corresponding facet surfaces. For the type-2 3×7₂ nanowire, the mirror Ti-O plane instead terminates on the surface Ti-6c atoms which are bound to the 2-fold coordinated bridging O atoms (O-2c). For each nanowire, both the axial view (upper figure) and side view (lower figure) are shown.
The importance of the even-odd parity of the number of TiO$_2$ layers in determining the electronic properties of ultrathin rutile TiO$_2$(110) films was first recognized by Bredow et al. [72] and used in section 3.3 of this work. It has also been extensively studied in the context of slab model calculations of the rutile TiO$_2$(110) surface, mainly to determine the number of layers that are needed to obtain a reliable description of surface and adsorption properties. [3, 24, 74, 89, 129, 130, 131] In this paper we show that the ability to tune separately the number of TiO$_2$ layers along two confinement directions leads to additional subtle and interesting effects arising from the interplay between surface relaxation and quantum confinement in rutile TiO$_2$ nanowires.

4.2 Computational methods

Our first-principles density functional theory (DFT) calculations are performed using version 3.0 of the SIESTA code [49] with norm-conserving TM2 pseudopotentials. [47] Either the Perdew-Burke-Ernzerhof parameterization [41] within the generalized gradient approximation (GGA) or the Perdew-Zunger parameterization [132] within the local density approximation (LDA) of the exchange-correlation functional have been employed. The basis set and pseudopotentials were chosen in a manner identical to that of section 3.2.1, which, as discussed in sections 3.2-3.3, compare well with both the experimental values [70, 77, 78] and results from previous DFT calculations [24, 72, 75, 76, 129, 131] using plane wave (PW) basis set and the projector augmented wave (PAW) or linearized augmented plane wave (LAPW) methods. The bulk indirect and direct band gaps are found to be 1.78 and 1.82 eV respectively, in good agreement with previous DFT calculations but being significantly smaller than the experimental values. [77, 133, 134] We note that this well known under-estimation of band gap in the current DFT-GGA functionals [135] can be corrected within the quasi-particle approach using the the self-consistent GW approximation, [136] as shown in a recent study on bulk rutile TiO$_2$. [137] However, due to its large computational cost, similar studies on TiO$_2$ nanowires have not been reported in literature. The present investigation may serve as a useful qualitative guide to the more rigorous (and more expensive) quasi-particle calculations.

With the validity of our computational setup verified, we performed a systematic study on the atomic and electronic properties of a series of rectangular [001]-oriented rutile TiO$_2$ nanowires with cross sectional areas between 0.2 and 4.8 nm$^2$ (defined through the four bridging
O atoms at the corner, see Fig. 4.1), corresponding to the number of TiO$_2$ layers $m$ and $n$ ranging from 3 to 8. The nanowire structure is considered fully relaxed if the force on any atom is reduced below 0.016 eV/Å. The lattice constant along the nanowire axis (chosen as the $z$-axis) is optimized by minimizing the uniaxial stress. The supercell sizes were chosen to give a vacuum region of at least 1.3 nm in the lateral directions between the image nanowires. This spacing between the nanowire images ensures an energy convergence of less than 0.1 meV per atom. The 1D Brillioun zone was sampled using a $1 \times 1 \times 16$ Monkhorst-Pack k-point mesh. The total energy convergence threshold is set at $1 \times 10^{-4}$ eV.

4.3 Results and discussion

4.3.1 Structure and Energetics

We report in this section trends in the dependence of nanowire structural and energetic properties on the number of TiO$_2$ layers in each confinement direction. Due to their small size, the nanowires undergo significant relaxation in both the surface and interior layers. Along each confinement direction, the deviation from the bulk-like termination follows a general pattern depending on the even-odd parity of the number of TiO$_2$ layers ($m$ or $n$), similar to that observed in the TiO$_2$(110) thin films. [72] This is illustrated in Tables 4.1-4.4, where we show the inter-layer distances along both confinement directions for the four nanowire series. The inter-layer distances are defined through the average distance between the Ti atoms facing each other on neighboring TiO$_2$ layers. [72]

For all the nanowires studied except for the smallest $2 \times n$ and $3 \times n$ nanowires, the first and second TiO$_2$ layers are separated by a distance ranging from 3.28 to 3.31 Å, slightly longer than the bulk value of 3.27 Å. If the number of layers ($m$ or $n$) along any confinement direction are even, the distance between the second and third layers becomes considerably larger by at least 0.08 Å and up to 0.14 Å. This oscillation in inter-layer distance persists into the interior of the larger nanowires, albeit with reduced magnitude. As a result, the nanowire can be considered as composed of a series of dual trilayers with the first two surface layers weakly bound to the rest along the corresponding confinement direction. In contrast, when $m$ or $n$ are odd, no oscillation in the inter-layer distance is observed. Although the distance between the second and third layers is still larger than that between the first and second layers, the difference is
**Table 4.1:** Inter-layer distances (Å) along both confinement directions for \(m \times n\) TiO\(_2\) nanowires where both \(m\) and \(n\) are even

<table>
<thead>
<tr>
<th>(m \times n)</th>
<th>Interlayer Distance (Å)</th>
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<tbody>
<tr>
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<td>3.31 3.45 3.31</td>
</tr>
<tr>
<td>4 \times 6</td>
<td>3.31 3.47 3.30</td>
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<tr>
<td></td>
<td>3.32 3.40 3.29 3.40 3.30</td>
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<tr>
<td>4 \times 8</td>
<td>3.31 3.48 3.31</td>
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<tr>
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<td></td>
<td>3.30 3.39 3.28 3.36 3.28 3.39 3.30</td>
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</table>

**Table 4.2:** Inter-layer distances (Å) along both confinement directions for \(3 \times n\) TiO\(_2\) nanowires

<table>
<thead>
<tr>
<th>(m \times n)</th>
<th>Interlayer Distance (Å)</th>
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<tbody>
<tr>
<td>3 \times 2</td>
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<tr>
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<td>3.31 3.31</td>
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<tr>
<td>3 \times 5(_2)</td>
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<td>3.27 3.33 3.32 3.27</td>
</tr>
<tr>
<td>3 \times 6</td>
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<tr>
<td></td>
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<tr>
<td>3 \times 7(_1)</td>
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<td></td>
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<tr>
<td>3 \times 7(_2)</td>
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<td></td>
<td>3.34 3.38 3.31 3.31 3.38 3.34</td>
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Table 4.3: Inter-layer distances (Å) along both confinement directions for 5×n TiO$_2$ nanowires

<table>
<thead>
<tr>
<th>$m \times n$</th>
<th>Interlayer Distance (Å)</th>
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<tbody>
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<tr>
<td>5 × 6</td>
<td>3.30 3.32 3.33 3.30</td>
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<tr>
<td></td>
<td>3.29 3.44 3.30 3.43 3.33</td>
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<tr>
<td>5 × 7$_1$</td>
<td>3.29 3.33 3.33 3.28</td>
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<td></td>
<td>3.32 3.36 3.30 3.30 3.36 3.32</td>
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<tr>
<td>5 × 7$_2$</td>
<td>3.31 3.35 3.35 3.31</td>
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<td></td>
<td>3.28 3.36 3.28 3.28 3.37 3.28</td>
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<tr>
<td>5 × 8</td>
<td>3.29 3.33 3.33 3.29</td>
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<td>3.30 3.42 3.29 3.38 3.29 3.42 3.32</td>
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Table 4.4: Inter-layer distances (Å) along both confinement directions for 7×n TiO$_2$ Note that the 7 × 5$_{1,2}$ nanowires are rotationally equivalent to the 5 × 7$_{1,2}$ nanowires.

<table>
<thead>
<tr>
<th>$m \times n$</th>
<th>Interlayer Distance (Å)</th>
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<tr>
<td>7 × 4</td>
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<td></td>
<td>3.34 3.48 3.29</td>
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<tr>
<td>7 × 5$_1$</td>
<td>3.32 3.36 3.30 3.30</td>
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<tr>
<td></td>
<td>3.36 3.36 3.32</td>
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<tr>
<td>7 × 5$_2$</td>
<td>3.28 3.36 3.28 3.28</td>
</tr>
<tr>
<td></td>
<td>3.37 3.28 3.31</td>
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<td>7 × 6</td>
<td>3.30 3.35 3.29 3.35</td>
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<td>3.29 3.36 3.29 3.29</td>
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<td></td>
<td>3.36 3.29 3.31</td>
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</table>
reduced compared to that of even \( m \) or \( n \). This trend is consistent with previous studies on rutile TiO\(_2\)(110) thin films. [72]

The key element distinguishing the nanowires with odd number of TiO\(_2\) layers from the even ones is the presence of a mirror Ti-O plane, which ensures the center TiO\(_2\) layer not being skewed as shown in Fig. 4.1. If either \( m \) or \( n \) is odd, pairs of surface Ti-5c or Ti-6c atoms exist that face each other on the opposite facets along the corresponding confinement direction. Since the Ti-5c (Ti-6c) atoms on the rutile (110) surface tends to relax inward (outward), surface relaxations on opposite facets tend to interfere with each other. This is not the case when \( m \) or \( n \) is even, where we find pairs of Ti-5c and Ti-6c atoms facing each other on the opposite facets.

The changes in the energetic and electronic properties of the rectangular nanowires are a direct consequence of the different structural rearrangements occurring in the nanowires as a function of the number of TiO\(_2\) layers \( m \) and \( n \) along each confinement direction. The trends in the formation energies are shown in Fig. 4.2, where we show also the optimized lattice constant \( c \) along the nanowire axis. The formation energies determine the relative stability of the nanowires compared to the bulk rutile phase of TiO\(_2\) and are computed from

\[
E_{\text{form}} = (E_{\text{NW}} - \mu_{\text{TiO}_2} n_{\text{TiO}_2})/n_{\text{TiO}_2},
\]

where \( E_{\text{NW}} \) and \( n_{\text{TiO}_2} \) are the total energy and number of TiO\(_2\) units in the nanowires respectively. \( \mu_{\text{TiO}_2} \) is the chemical potential of a TiO\(_2\) unit in the bulk rutile crystal. Note that we have neglected the vibrational contributions to the formation energy, because their effects were found to be small from a previous study on square nanowires. [128]

If both \( m \) and \( n \) are even, the formation energy of the \( m \times n \) nanowires decreases monotonically with increasing perimeter and cross sectional area. The other nanowires corresponding to \( m=3,5,7 \) show even-odd oscillation with respect to the number of TiO\(_2\) layers \( n \) along the other confinement direction, with the formation energy of the \( 3 \times n \) series of nanowires being significantly larger. This is consistent with previous study of rutile TiO\(_2\)(110) thin films, [72] where the surface energy of a 3-layer film is found to be significantly larger than that of other thin films. If we specialize to the square \( m \times m \) nanowires, we observe strong even-odd oscillation in formation energy with respect to \( m \) with the nanowires with screw symmetry (even \( m \)) being consistently more stable, in agreement with previous studies. [127, 128] In contrast, the axial lattice constant \( c \) increases toward the bulk value with similar functional dependence on the perimeter and cross sectional area for all nanowires studied, although the \( 3 \times n \) nanowires have
Figure 4.2: The upper figures show the dependence of the axial lattice constant on the perimeter (left) and cross sectional area (right) with the PBE functional. The horizontal line denotes the corresponding bulk value. The lower figures show the formation energy per TiO$_2$ unit as a function of the perimeter (left) and cross sectional area (right). In all figures, the filled markers denote a direct band gap at the Γ-point and empty markers denote an indirect gap.
4.3.2 Electronic Band Structure

We report in this section trends in the dependence of nanowire band structures on the number of TiO$_2$ layers in each confinement direction. The computed band gaps and conduction/valence band edges using PBE-GGA functional are shown in Fig. 4.3 as a function of both the nanowire perimeter [138] and cross sectional area. The band edges are aligned by lining up the Fermi levels of all the nanowires studied, which are chosen as the energy reference. Three distinct trends can be identified. First, if both $m$ and $n$ are even, the corresponding nanowires have $C_{2h}$
Figure 4.4: Dependence of the band gap (upper figures) and the conduction and valence band edges (lower figures) of the rectangular rutile TiO$_2$ nanowires on the perimeter (left figures) and cross sectional area (right figures) computed at the PBE relaxed geometries using the LDA exchange-correlation functional and corresponding pseudopotentials, similar to those shown in Fig. 4.3.
symmetry and possess an indirect band structure with the band gap decreasing monotonically toward the bulk value with increasing cross sectional area (perimeter). The reduction in band gap is accomplished by both decrease in conduction band edge and increase in valence band edge as expected from simple quantum confinement consideration. From the computed band structure, we find that the valence band maximum (VBM) is located at the Γ-point, while the conduction band minimum (CBM) shifts gradually from nearly (0,0,0.5) for the smallest 2×2 nanowire to nearly (0,0,0.4) for the largest 6×8 nanowire along the Γ–X direction in the 1D Brillioun zone. In comparison, the conduction band minimum in the bulk rutile crystal is located at the M points with a k-vector of \( \left( \frac{1}{2}, \frac{1}{2}, 0 \right) \) and equivalent.

Second, for 3×n nanowires with the smallest odd number of TiO₂ layers along the first confinement direction, both indirect and direct band structures are observed. Note that for odd \( n \) and \( n \neq 3 \), there are two ways to construct stoichiometric rutile 3×n (in general, also for odd \( m \times n \) nanowires with \( m \neq n \)) nanowires that are not related to symmetry. The example of the 3×7 nanowire has been shown in Fig. 4.1(B). For the type-1 3×7₁ nanowire, the mirror Ti-O plane along the first confinement direction terminates on the Ti-5c atoms at the corresponding facet surfaces. For the type-2 3×7₂ nanowire, the mirror Ti-O plane instead terminates on the surface Ti-6c atoms which are bound to the 2-fold coordinated bridging O atoms (O-2c). This seemingly trivial difference in structure can lead to significant change in the electronic structure, as we find that the type-2 3×n nanowires possess direct band structure, with both CBM and VBM located at the Γ point. In contrast, all other 3×n nanowires possess indirect band structure, with the CBM located at the Γ point and the VBM shifted toward the X point.

Finally, the 5×n and 7×n nanowires possess a direct band structure with both CBM and VBM located at the Γ point, for both even and odd \( n \) and for both types of surface termination schemes when \( n \) is odd. Overall an even-odd oscillation can still be observed in the computed band gap for the 3×n, 5×n and 7×n nanowires depending on the number of TiO₂ layers \( n \) along the second confinement direction. However, the changes in the conduction band and valence band edges are similar with increasing perimeter and cross sectional area (Fig. 4.3).

If we consider again only the cases of square \( m \times m \) nanowires, the computed band gaps show strong even-odd oscillations with respect to \( m \), with the nanowires with screw symmetry (even \( m \)) being indirect and having consistently larger band gap, which are also observed in previous studies. [127, 128] The convergence of the computed band gap towards bulk value with increasing number of layers is rather slow and far from being completed for the nanowires studied here.
which is consistent with previous studies on rutile TiO$_2$(110) thin films and surfaces [3, 24, 72, 74, 89] but differs from that in Ref. [127] where the convergence toward bulk value is already achieved around $m=8$. We note that a significantly smaller real space mesh cutoff (150 Ry) is used in Ref. [127] than that used here (570 Ry), probably to the detriment of their study.

Since the computed band structures may be sensitive to the choice of exchange-correlation functionals, a spin-polarized LDA calculation with the corresponding pseudopotentials has also been performed for all the nanowires studied at the PBE relaxed geometries. We note that such LDA band structures often form the basis for the more rigorous quasi-particle calculation. [136, 137]. The results are shown in Fig. 4.4. We find that the absolute difference in the band gap between the PBE and LDA calculations typically ranges from 0.01 to 0.07 eV. And for the nanowires studied, the choice of PBE or LDA functionals does not affect the trends in band structure character as a function of either nanowire perimeter or cross sectional area (Fig. 4.4).

4.3.3 Density of States and Orbital Interaction Analysis

To provide a deeper understanding into the electronic origin of the structural changes with the number of layers and its effect on the direct and indirect character of the nanowires, We analyze the band structure through the density of states projected onto the 3d and 2p orbitals of the surface Ti and O atoms (PDOS) in Fig. 4.5, the nature of the wavefunctions at the conduction and valence band edges through the spatial distribution of the local density of states (LDOS) in Figs. 4.6-4.7, and the orbital interaction within the nanowire through the crystal orbital overlap population (COOP) [108] in Fig. 4.8 for selected nanowires along both confinement directions.

The plot of the PDOS is shown in Fig. 4.5 for the 6×8 TiO$_2$ nanowire, where we find the conduction band states are contributed predominantly by the 3d orbitals of Ti atoms, while the valence states arise primarily from the 2p orbitals of O atoms with some mixing from the 3d orbitals of Ti atoms. For the even 6×8 nanowire, the surface PDOS plots along both confinement directions are qualitatively similar to that obtained from slab model calculation of rutile TiO$_2$(110) surface with an even number of (unfixed) layers. [24]

From the LDOS plots of the 6×8 nanowire in Fig. 4.6A, we find clearly the signature of the formation of dual trilayers within the nanowire along both confinement directions. The spatial distribution of the wavefunctions at both conduction and valence band edges are nearly identical moving along each confinement direction. The state at the conduction band edge is mainly contributed by the 3d orbitals of the surface Ti-5c atoms and the neighbor subsurface
Figure 4.5: Density of states projected onto the 3d orbitals of Ti and the 2p orbitals of O atoms on both the first and second TiO$_2$ layers along the horizontal (a) and vertical (b) confinement directions for 6×8 nanowire. The zero of the DOS energy scale is the vacuum level. We have also shown the total DOS of the nanowire as a common reference in both figures.

Ti-6c atoms, the tails of which penetrate into the interior of the nanowire. The state at the valence band edge is contributed mainly by the 2p orbitals of the 3-fold coordinated O atoms (O-3c) and is delocalized throughout the nanowire. Due to the small size of the nanowire, both surface and interior atoms contributes to the total DOS as shown in the LDOS plot of Fig. 4.6A.

The mixed-parity 5×8 nanowire exhibits an interesting spatial separation between the electron and hole states due to the lack of mirror symmetry along the vertical confinement direction, as demonstrated in Fig. 4.6B (similar patterns are also observed in other mixed-parity nanowires). The wavefunction at the valence band edge is localized at the top half of the nanowire. Along each confinement direction, the spatial distribution of the wavefunction is qualitatively similar to that of the 6×8 nanowire, with additional contributions from the O-2c atoms at the outermost layers and corners of the nanowire. In contrast, the wavefunction at the conduction band edge is localized primarily at the second layer from the bottom facet. Along the horizontal confinement direction, the wavefunction remains mainly contributed by the 3d orbitals of the surface Ti-5c and the subsurface Ti-6c atoms, with significant mixing with the 2p orbitals of the intermediate O atoms.

The 3×n nanowires are rather special due to the absence of a surface dual trilayer when
Figure 4.6: Isosurface plots of the local density of states (LDOS) at the valence band maximum (left figure) and the conduction band minimum (right figure) for the $6 \times 8$ (A) and $5 \times 8$ (B) rutile TiO$_2$ nanowires. The large gray and small red spheres represent Ti and O atoms respectively. For each nanowire, both the top view (upper figure) and side view (lower figure) of the LDOS are shown.

Figure 4.7: Cross-sectional view of the type-1 $3 \times 7_1$ (A) and type-2 $3 \times 7_2$ (B) nanowires. For each nanowire, we have shown the isosurface plots of the LDOS at the valence band edge (left figure) and the conduction band edge (right figure). The type-1 $3 \times 7_1$ nanowire has an indirect gap due to a shift in the valence band maximum away from the Γ-point (empty marker in Fig. 4.3), while the type-2 $3 \times 7_2$ nanowire has a direct gap at Γ-point (filled marker in Fig. 4.3).
there are only three TiO$_2$ layers along the first (horizontal) confinement direction (Fig. 4.7). We find that the opposite tendency for surface Ti-5c and Ti-6c atoms to relax inward and outward is significantly enhanced along the first confinement direction, with the relative displacement between the two types of Ti atoms along the surface normal increased to around 0.25 Å compared to 0.1-0.15 Å in other nanowires. Consequently the nanowire property becomes sensitive to whether the mirror Ti-O layer terminates on the Ti-5c or Ti-6c atoms along the horizontal confinement direction. From the LDOS plots in Fig. 4.7, we find that the wavefunctions at the conduction band edge for both $3 \times 7_1$ and $3 \times 7_2$ nanowires are centered around the Ti-6c atoms on the mirror Ti-O plane, which bridge the two Ti-5c atoms on opposite facets along the horizontal confinement direction with significant mixing with the 2p orbitals of the intermediate O atoms. In contrast, the wavefunctions at the valence band edge are contributed by both the surface O-2c atoms and the subsurface O-3c atoms that bridge the Ti-6c atoms on both the mirror Ti-O layer and the opposite facets along the horizontal confinement direction.

Further insights into the nature of bonding within the TiO$_2$ nanowires are provided by the COOP plots (Fig. 4.8). Close to the conduction band edge of the $6 \times 8$ nanowire, we find the overlap between the 3d orbitals of the surface Ti-5c and subsurface Ti-6c atoms possess strong anti-bonding character along both confinement directions. Consequently the conduction band edge decreases in energy with increasing cross sectional area as the quantum confinement effect is reduced (Fig. 4.3). Close to the valence band edge, we find the overlaps between the 3d orbitals of the subsurface Ti atoms and the 2p orbitals of the O atoms above (underneath) possess strong bonding (nearly non-bonding) character. This explains the strong coupling between the first and second layers, which in turn are weakly bound to the interior of the nanowires, corroborated by the tables of inter-trilayer distances in Tables 4.1-4.4.

For the mixed-parity $5 \times 8$ nanowire, we find that the overlap between the 3d orbitals of surface Ti-5c and subsurface Ti-6c atoms remains strongly anti-bonding from the COOP plot in Fig. 4.8. Due to the localized nature of the wavefunction at the conduction band edge, the quantum confinement effect is effectively reduced. This lowers the conduction band energy at the Γ point and gives rise to a direct band gap. We note that the anti-bonding character between the surface Ti and O orbitals in the conduction band appears at much lower energy in the horizontal direction than that in the vertical direction, showing that the change in band structure arises from quantum confinement effect along the horizontal direction. Between the
Figure 4.8: COOP plot for the 6×8, 5×8, 3×7₁ and 3 × 7₂ TiO₂ nanowires. For each nanowire, a and b show the COOP between the 3d orbitals of the surface Ti-5c and subsurface Ti-6c atoms (“5c-6c”) and the COOP between the 3d orbitals of the surface and subsurface Ti-6c atoms (“6c-6c”) along both horizontal (a) and vertical (b) confinement directions. c and d show the COOP between the 3d orbitals of the second layer Ti atoms and the 2p orbitals of the O atoms above (“Ti 3d - O 2p 2:1”) and the COOP between the 3d orbitals of the second layer Ti atoms and the 2p orbitals of the O atoms underneath (“Ti 3d - O 2p 2:3”) along both horizontal (c) and vertical (d) confinement directions. For the two 3×7 nanowires, (e) shows the COOP plots between the 2p orbitals of the neighbor O layers along both the horizontal (“O 2p-O2p m”) and vertical (“O 2p-O2p n”) confinement directions. The zero of each energy scale is set to the vacuum level.
5\times n and 7\times n nanowires, we find instead overall similar characteristics in both the LDOS and COOP plots, leading to qualitatively similar trend in their band structures.

From the COOP plot between the surface Ti and O atoms in Fig. 4.8, we find the corresponding orbital overlap changes from non-bonding in the indirect-band $3 \times 7_1$ nanowire to strong anti-bonding character in the direct-band $3 \times 7_2$ nanowire close to the conduction band edge along the second (vertical) confinement direction. Close to the valence band edge, the corresponding orbital overlap changes from anti-bonding in the indirect-band $3 \times 7_1$ nanowire to non-bonding character in the direct-band $3 \times 7_2$ nanowire (curve d in the corresponding COOP plots of Fig. 4.8). As the indirect band character of $3 \times 7_1$ nanowire is caused by the shift in the VBM away from the $\Gamma$ point, we analyze in addition the COOP between the 2p orbitals of the surface and subsurface O atoms (curve e in the corresponding COOP plots of Fig. 4.8). We find that close to valence band edge, the anti-bonding character between the neighbor O layers is significantly more enhanced in the indirect-band $3 \times 7_1$ nanowire than that in the direct-band $3 \times 7_2$ nanowire along the horizontal confinement direction. Since the indirect and direct gaps differ by less than 0.03 eV in the $3 \times 7_1$ nanowire, the different effects arising from quantum confinement along both directions are sufficient to change the band characters between the two types of $3 \times 7$ nanowires.

4.4 Conclusion

In this chapter an analysis was presented on the atomic and electronic properties of rectangular rutile TiO$_2$ nanowires oriented along the [001] direction and enclosed by \{110\} facets. We find that the dependence of the nanowire properties on the number of TiO$_2$ layers are largely connected to the presence or absence of a mirror Ti-O plane along each confinement direction. Although this dependence on the even-odd parity of the number of TiO$_2$ layers has been discussed in previous studies on rutile TiO$_2$(110) thin films and surfaces, we find that the ability to tune separately the number of layers in each confinement direction leads to novel size- and shape- dependent electronic properties in rutile TiO$_2$ nanowires, which arise from the interplay between surface relaxation and quantum confinement effects. Nanowires with even m,n tend to have the lowest formation energies. The general rule for creating a direct bandgap in rectangular rutile TiO$_2$ [001]-oriented nanowires is to ensure that they do not possess $C_{2h}$ symmetry. In other words, at least one of the indices $m\times n$ must be odd, which in turn tends to increase the
formation energy. For all nanowires, the localization of the HOMO and LUMO wavefunctions follow definite shape-dependent rules related to the position of fivefold-coordinated Ti sites and O bridging atoms.

We note that functionals in the LDA and GGA both carry the same predictions for the trends in the electronic states, which carries the expectation that the inclusion of vdW-DF will not affect these trends as well since the contributions to the energy from geometric rearrangement are much larger than the contributions from electron correlation.
Electric field Effect on TiO$_2$ (110) + H$_2$O

5.1 Introduction

In this chapter, spin-polarized density functional theory calculations within the generalized gradient approximation and with the vdW-opt-B88 functional have been applied to investigate the problem of molecularly adsorbed water on the rutile (110) TiO$_2$ surface under the influence of an applied electric field. The effective screening medium theory is used to break the symmetry of the simulation in the slab normal direction and implement a metal-like boundary condition at the edges of the simulation cell to model the charged capacitor in a real electrochemical device. A systematic study of energetics, geometrical configuration, charge partitioning, and electronic structure of water in monomer coverage up to monolayer coverage provides insight into the usefulness of the inclusion of self-consistent van der Waals correlation effects and the effect of an external electric field in this model of adsorption on a prototypical metal oxide surface. Nontrivial differences between the two functionals’ description of adsorption and electronic structure of the model surface are reported in the zero-field limit as well as with an applied field.

Rutile is an incipient ferroelectric material and a high-k dielectric, making it an attractive choice for many possible technological devices, many of which, notably novel ReRAM devices, rely on large electric fields across a TiO$_2$ thin film. The decision to implement a simulation of TiO$_2$ at electrical bias begs the question: what magnitude shall the electrical bias be? The degree to which we apply a simulated electric field should have some relationship to what kind of electric fields it will be exposed to in various applications. It is not enough to simply choose
an electric field of particular magnitude (alternatively, bias voltage in the ESM model) because it is simulated easily within DFT. A recent study by McPherson et al. concluded that the theoretical dielectric breakdown strength $E_{bd}$ for rutile TiO$_2$ is 4.1 MeV/cm, or 0.04 V/Å [139], while Strukov et al. concluded that it is possible to have year-scale retention in device integrity even at continuous field of up to 15 MeV/cm (0.15 V/Å) for materials with high activation energy of charged oxygen vacancies, of which rutile TiO$_2$ is a member. [140] Fields as high as 30 MeV/cm may be pulsed for short periods of time $\sim$10 ns, which is simultaneously relevant for the switching mechanism of ReRAM and the development of conductive fuel cell supports, while having a characteristic time-scale that is within reach of molecular dynamics simulations. Therefore, it is fair to set a maximum upper limit near the 30 MeV/cm mark and step the field in regular increments in the positive and reverse bias situations. Having electric fields that are too close to zero will likely effect little to no changes in the DFT-derived geometries and their physical properties. These electric fields are similar in magnitude than other previous ab initio calculations for semiconductors [141, 142].

5.2 Computational Methods

The calculations in this chapter were performed with nearly identical parameters to those given in section 3.3: PBE and opt-B88 functionals were used with TM2 pseudopotentials in the SIESTA code. A DZP basis was used on all atoms, except the top two atomic layers of TiO$_2$ on the model surface and the water molecules, where an additional unoccupied s-like diffuse functional with SZ character was used with radii 8.000 (Ti), 7.000 (O) and 3.000 (H) Bohrs. This was done to provide a slightly more complete basis set in the geometrical range that could correspond to adsorption situations. Binding energies for all water configurations were calculated using the Boys-Bernardi counterpoise correction for the localized atomic orbital basis set. [53]

Like in section 3.3, The supercell size was chosen to give a vacuum region of 14 Angstroms in the normal direction between the rows of bridging oxygens on the image slabs in the x-direction. The ESM method is employed with the metal-slab-metal boundary conditions which allowed us to explicitly specify a bias voltage across the model TiO$_2$ slab with the correct physical behavior of the electrostatic potential in the vacuum region without introducing additional (or deficit) electrons into the simulation. No slab dipole correction [68] was needed to modify the
electrostatic potential inside the vacuum region. The electric field (and hence the bias voltage across the slab) ranged from $-0.257$ to $+0.257$ V/Å ($-8.48$ to $+8.48$ V) in steps of $0.0642$ V/Å ($2.121$ V), except near the zero-field limit ($\left| E_{\text{ext}} \right| < 0.0642$ eV), where the step size was reduced by one-half to try to capture more detailed information around the zero of the electric field.

A spacer region ($x_1 - x_0$) measuring 3 Å was inserted between the periodic cell boundary and the metal boundary so that the distance between the adsorbate and the metal electrode was nearly 1 Å. The total size of the model cell in the x-direction ($2x_1$) was 33 Å and a schematic of the unit cell is shown in Fig. 5.1. Four trilayers of TiO$_2$ were utilized in the surface slab model, as per the prescription given in section 3.3, coinciding with recommendations from the literature. [24, 72, 143] The area of the $2 \times 1$ unit cell is $\sim 39.2$ Å$^2$ for PBE and $\sim 39.5$ Å$^2$ for opt-B88.

The maximum Hellman-Feynman force on each atom to converge the simulations was 0.02 eV/Å, for electric fields $E_{\text{ext}} < 0.100$ V/Å and 0.04 for $E_{\text{ext}} > 0.100$ V/Å. This is done because for electric fields far from the zero-field-limit, force convergence is extraordinarily hard to reach, and the small compromise in this threshold was necessary to achieve satisfactory results without waiting a long amount of time for the convergence trajectory to fall deeper into a low-energy basin for our series of simulations at various field strengths and surface coverages.

5.3 Results: TiO$_2$ slab

The next set of theoretical calculations in this chapter involve the application of a bias voltage across the TiO$_2$ model slab with no adsorbed H$_2$O. This is accomplished to set a reliable baseline for the adsorbate calculations as far as surface relaxations and electrostatics are concerned.
with respect to both the electric field and also the choice of xc-functional. All calculations in this section are performed with the metal-slab-metal (BC2) ESM boundary condition which approximates an STM experiment. Here, a $2 \times 1$ surface unit cell is used instead of the $1 \times 1$ cell in section 3.3 because the lowest-energy state for water monolayer adsorption is known also be a $2 \times 1$ surface unit cell (used in 5.4) and this method establishes total energy references for those adsorption situations at each electric field strength.

### 5.3.1 Electrostatics

Intuitively, the application of an external electric field should induce some polarization of electrons within a surface, with electrons fleeing from the direction of the field lines. This section will investigate whether the ESM approach provides a physically realistic model of the electrostatic potential and electric field within the simulation cell for the 4-trilayer model surface. Figure 5.2 shows a diagram of the electrostatic potential inside the ESM BC2 (metal-slab-metal) simulation scheme. The electrostatic potential in-between the metal ESM regions in fig. 5.2a is determined unambiguously, and only from the external electric field strength defined in the SIESTA input file. For metallic slabs, the electric field should be completely quenched within the slab region and for semiconductors, a small field will remain, but there will be local field enhancement on the two sides of the slab regardless of the slab material (fig. 5.2b).

Figures 5.3-5.4 show the difference in the $yz$-planar-averaged electrostatic potential plotted as a function of $x$ in a four-trilayer simulation cell in the ESM BC2 condition at a particular bias (in its relaxed geometry) minus the electrostatic potential of the zero-field case in its own relaxed geometry, called $\Delta V_{elec}$. This subtraction is performed to minimize the impact of the pseudopotential, which imparts a large negative potential well to the electrostatic potential. It is plain to see that there is some oscillation in $\Delta V_{elec}$ from around $x = 0$ Å to $x = 6.5$ Å, especially as the field reaches its higher magnitudes. This is probably due to atomic displacements out of the plane of the TiO$_2$ trilayer and will be investigated further in section 5.3.2. For comparison, observe that the region of the surface slab between about $-6.5$ Å and 0 Å is the bulk-like, fixed-atom region, which displays a very smooth transition in $\Delta V_{elec}$. The local field enhancement in the vacuum region indeed occurs as predicted for both the $2 \times 1$ and the $4 \times 2$ unit cells. The placement of the voltage at each metal ESM region is different between the two surface unit cells as can be inferred from comparing fig. 5.3a to fig. 5.4 (or the like). Furthermore, the degree of oscillatory action of $\Delta V_{elec}$ is on average much lower for the $4 \times 2$ cell. This is due to
Figure 5.2: Schematic of the electrostatic potentials for ESM BC2 (metal-slab-metal) simulations. Lines denote electrostatic potential in the simulation region. Figure a) shows the potential in the cell and the associated field (slope of the potential) from biased metal leads with no constituent atoms. Figure b) shows the electrostatic potentials when a slab comprised of atoms is inserted into the calculation region. The solid black line denotes a metallic surface, the solid red line denotes a semiconductor surface, and the diagonal dotted black line is the electrostatic potential from an empty cell. Horizontal lines denote the placement of the electrostatic potential inside the ESM (metal) regions, indicating electrical bias. Image credit: Yoshinari Takimoto of The Institute for Solid State Physics of the University of Tokyo

the enhanced degrees of freedom for surface atoms to relax in the larger surface cell; they are not forced to adopt positions of small repeat distance that may be subject to a small degree of buckling. Also as expected, the $\Delta V_{\text{elec}}$ is largely quenched inside the slab region, and increases somewhat when the field strength increases.

The levels of the electrostatic potential at the endpoints of the DFT cell were extrapolated by a linear fit to the ESM boundary and were checked for each simulation in these series against a numerical calculation of the electrostatic potential due to the field by multiplying the external field input from the user by the ESM cell length. Errors between the two methods were less than 0.01%, verifying that the ESM method’s modifications to the SIESTA code produced the results it claimed.

To qualitatively measure the electric field enhancement we calculate the averaged electric field in the three regions corresponding to the vacuum underneath the slab, the slab itself, and the vacuum region above the slab. The calculation is accomplished by dividing the simulation slab into three regions of size 10 Å, 13 Å (the slab), and 10 Å, then finding the average slope of $\Delta V_{\text{elec}}$ in each region with respect to distance to obtain $E_{\text{eff}}$. $V_{\text{elec}}$ in the zero-field case is verified to quickly approach its asymptotic value of 0 V on both ends of the slab. The data for $E_{\text{eff}}$ is shown in table 5.1. The enhanced field in the vacuum region corresponds to about
Figure 5.3: Plot of the difference in total electrostatic potential $\Delta V_{\text{elec}}$ as a function of position between biased TiO$_2$ slabs that has undergone geometry relaxation and the relaxed slab in the zero-field limit. The unit cell is a $2 \times 1$ supercell of the clean (110) surface. (a) and (b) show results for the PBE functional, while (c) and (d) show results for the opt-B88 functional.
Figure 5.4: Plot of the difference in total electrostatic potential $\Delta V_{\text{elec}}$ as a function of position between biased TiO$_2$ slabs that has undergone geometry relaxation and the relaxed slab in the zero-field limit. The unit cell is a $4 \times 2$ supercell of the clean (110) surface. (a) and (b) show results for the PBE functional, while (c) and (d) show results for the opt-B88 functional.
Table 5.1: Effective electric field at the fixed and free ends of the surface slab, and inside the surface slab due to local field enhancement in the vacuum region.

<table>
<thead>
<tr>
<th>Locally-modified effective Electric field $E_{eff}$ (V/Å)</th>
<th>PBE</th>
<th>opt-B88</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{ext}$ (V/Å)</td>
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<td></td>
</tr>
<tr>
<td>Fixed Slab Free</td>
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<tr>
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<td>0.201</td>
<td>0.016</td>
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<td>0.101</td>
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<tr>
<td>-0.257</td>
<td>-0.401</td>
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</table>

0.100 V/Å for each 0.064 V/Å of applied external field $E_{ext}$ which enters into the SCF portion of the DFT simulation, and is roughly the same for both PBE and opt-B88. However, the local electric field inside the opt-B88 slab is quenched to a greater degree than in the PBE slab, and shows a stronger degree of anisotropy about the zero-field value.

### 5.3.2 Atomic Structure

Measuring bond lengths between the atoms which constitute the rutile (110) TiO$_2$ surface have been shown to be a well-converged measure of surface geometry from section 3.3.2. Those bond lengths are shown in tables 5.2 (PBE) and 5.3 (opt-B88) for the four-trilayer slab with the bottom two trilayers fixed to their bulk positions, using the same terminology as in figure 3.8. Since the surface unit cell is doubled, the values printed in the tables are averaged over all equivalent pairs of atoms in the cell, of which there may be two, four or eight by symmetry.

The geometry relaxation data presented in tables 5.2-5.3 indicate that there is overall a low propensity for structural rearrangement in rutile TiO$_2$ (110) in response to an applied field. For bridge-type bonds 1, 2, 7, and 8 there is about a 0.01 Å increase in bond length between the maximal negatively-biased and positively biased cases for both PBE and opt-B88. The in-plane bonds 3, 4, 9 and 10 show even less of a change, about 0.006 Å at most, as the electric field changes for both PBE and opt-B88. However, the bonds in the direction of the surface normal tend to have their lengths changed by a larger degree. Bond 5 between the Ti5d and O6 sites
Table 5.2: Bond lengths (in Angstrom) for the bare (110) rutile TiO$_2$ four-trilayer slab with two bottom layers fixed, as a function of increasing applied electric field $E$ in the $+x$ direction using the PBE functional. Bond labels are the same as used in figure 3.8 and table 3.4. Results from a recent similar theoretical study [3] and experiment [4] are shown as well (in the zero-field limit).

<table>
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<tr>
<th>$E_{ext}$ (V/Å)</th>
<th>1</th>
<th>2</th>
<th>3</th>
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<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
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<th>11</th>
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<tbody>
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<td>1.829 2.138 2.060 1.968 1.819 1.840 2.055 1.901 1.998 1.989 2.255</td>
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<tr>
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<tr>
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Ref. [3] | 1.84 2.11 2.04 1.92 1.82 1.87 2.04 1.90 1.97 1.97 2.19
Exp. [4] | 1.85 2.08 2.15 1.90 1.79 1.90 2.01 1.89 1.92 2.00 2.11

Increases in length by 0.013 Å (PBE) and 0.010 Å (opt-B88) as the electric field increases from $-0.257$ to $+0.257$ V/Å while bonds 6 decreases increase in length by 0.032 Å (PBE) and 0.022 Å (opt-B88) and bond 11 increases in length by 0.041 Å (PBE) and 0.022 Å (opt-B88) over the same field interval. Although these structural rearrangements are small overall, they could introduce significant effects in the binding of adsorbates, which will be examined later in this chapter. Abrupt changes in bond lengths as the electric field increases also occur, for example the change in bond 11 for the PBE functional around $E = +0.193$. The reason for this seems to be correlated with the strong oscillatory effect on the electric potential difference between the zero and nonzero field strength as indicated in figure 5.3. Since one of the dominant contributions to the total electrostatic potential in the slab region arises from the pseudopotential, displacements in that potential well have a destabilizing effect on the local electrostatic potential. It is also possible that strong polarizations across the unit cell may induce strong shifts in the PES of the system and thus favor certain local atomic rearrangements that reduce the total energy.

Analogous to table 3.7, inter-layer distances for the four-trilayer slab have been calculated and are shown in table 5.4. The small variance between the inter-layer distances in the zero-field limit here and in table 3.7 (≈ 0.005 Å) are likely due to the symmetry-breaking involved...
Table 5.3: Bond lengths (in Angstrom) for the bare (110) rutile TiO$_2$ four-trilayer slab with two bottom layers fixed, as a function of increasing applied electric field $E$ in the +$x$ direction using the opt-B88 functional. Bond labels are the same as used in figure 3.8 and table 3.4.

<table>
<thead>
<tr>
<th>$E_{ext}$ (V/Å)</th>
<th>1</th>
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<td>1.987</td>
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Table 5.4: Inter-layer distances (Å) in the surface normal direction for the four-trilayer TiO$_2$ (110) model slab for the PBE and opt-B88 functionals as a function of applied electric field $E$ in the +$x$ direction. The left inter-layer distance column is the distance between the top two trilayers of the relaxed surface and the right column is the distance between the first sub-surface layer and the first fixed bulk layer. The bulk trilayer distances are omitted, as they are identical to those in table 3.7.

<table>
<thead>
<tr>
<th>$E_{ext}$ (V/Å)</th>
<th>Inter-layer Distance (Å)</th>
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<tr>
<td>PBE</td>
<td>opt-B88</td>
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<tr>
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<td>3.377 3.360</td>
</tr>
<tr>
<td>+0.193</td>
<td>3.377 3.359</td>
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<tr>
<td>+0.129</td>
<td>3.376 3.354</td>
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<tr>
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<td>3.381 3.336</td>
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</tr>
<tr>
<td>-0.032</td>
<td>3.380 3.333</td>
</tr>
<tr>
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<td>3.375 3.331</td>
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<tr>
<td>-0.257</td>
<td>3.376 3.334</td>
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in the doubled unit cell. The major inter-layer distance trends to report are that the 1–2 layer
distance decreases for the opt-B88 functional as a function of increasing \( E \) in the \(+x\)-direction,
and the 2–3 layer distance increases for the PBE functional as a function of increasing \( E \) in
the same direction, but this increase is nonlinear. The 2–3 inter-layer distance for PBE in
particular seems to make a large jump between the \(+0.064 \text{ V/Å}\) and \(+0.129 \text{ V/Å}\) applied fields,
The 1–2 inter-layer distance for PBE changes abruptly at \( \pm 0.129 \) as well, but the magnitude
is about four times smaller at \( 0.005 \text{ Å} \). The dependence on the \( E \)-field on the other distance
measurements is small or otherwise dominated by numerical noise. The lateral displacement of
atoms within a trilayer, although not recorded in these tables, is more pronounced for opt-B88
slabs than PBE as a function of electric field.

5.4 Results: \( \text{TiO}_2 \) slab \( + \) \( \text{H}_2\text{O} \)

The last series of calculations in this work revolve around the adsorption of \( \text{H}_2\text{O} \) on the rutile
\( \text{TiO}_2 \) \((110)\) surface while under an applied external electric field. The system is allowed to be re-
leraxed to its electronic ground state, and from there its atomic structure, energetics, electrostatic
characteristics, and electronic structure can be analyzed. From there, general trends in the de-
scription of adsorption and effects arising from the external electric field can be determined as
they relate to the choice of exchange-correlation functional.

The size of the surface unit cells for water adsorption are chosen carefully. If a water
molecule is placed at any point in the large \( 4 \times 2 \) cell, the closest distance from this molecule
to an image molecule in the nearest cell is \( \sim 12 \text{ Å} \). This distance is much larger than the basis
functions that describe the electrons in the molecule and even larger than the O–H bond. It
is simple to Verify that no electronic interaction exists between two water molecules that are
separated by such a distance. For the smaller unit cells, the relevant dimension is \( \sim 6 \text{ Å} \), still
larger than the basis functions on H and O but by much less, making it conceivable that not
only image water molecules in adjacent cells interact, but also a certainty that the structural
rearrangement on the surface will have a small repeat distance which in turn, could exaggerate
certain characteristics of the equilibrium geometry.
Figure 5.5: Top-view of the monomer (a), half-monolayer (b) and monolayer (c) H$_2$O coverages (in ball-and-stick representation) studied on the TiO$_2$ model surface (shown in vdW spheres representation) in the zero-field limit.

5.4.1 Atomic Structure

The relaxed geometries of the TiO$_2$+H$_2$O system were calculated in the associative water monomer ($\frac{1}{8}$ ML), half-monolayer ($\frac{1}{2}$ ML), and monolayer (ML) coverages in an initial configuration close to their previously-reported lowest-energy configurations [24] and in the zero-field limit as shown in Fig. 5.5a-c for the PBE and opt-B88 functionals. Using the relaxed geometry of the zero-field limit configuration for each adsorbate as an initial configuration, an electric field in the ±$x$ direction was applied to the simulation cell modeling the TiO$_2$+H$_2$O interface inside a charged capacitor and each system was further relaxed. Selected geometrical parameters of those relaxed geometries are shown in tables 5.5 and 5.6 for monomer and monolayer adsorption, respectively for the PBE and opt-B88 functionals.

Water is adsorbed associatively on TiO$_2$ atop the Ti5c site on the surface, which moves closer to the water oxygen atom from its depressed position on the clean surface. Hydrogen bonding tilts the Oxygen bridge atoms and H$_2$O toward one another. The geometric properties of water monomer adsorption can be ascertained from table 5.5. The tilt angle between the plane of the H$_2$O molecule and the $yz$-plane, $\Theta_{H_2O}$, increases for both PBE and opt-B88 as $E_{ext}$ is swept from its largest negative value to its most positive. The total change in $\Theta_{H_2O}$ is about the same for the two functionals, although opt-B88 the inclination angle is about 6° higher for all samples. The monomer adsorption geometry has one H atom hydrogen-bound to a bridging O atom on the TiO$_2$ surface, so the free atom is moving progressively farther away from the surface as the electric field becomes stronger in the +$x$ direction. This is consistent with the local charge on the atoms of the top surface having a net deficit of electrons, as intuition suggests.
Table 5.5: Configuration details for single water monomer associative adsorption on the rutile (110) TiO$_2$ four-trilayer slab with the PBE and opt-B88 functionals as shown in Fig. 5.3a, as a function of increasing applied electric field $\varepsilon$ in the $+x$ direction. $\Theta_{\text{H}_2\text{O}}$ is the tilt angle of the plane constituted by the three atoms in the H$_2$O molecule above the $yz$ plane. $d_{\text{O}-\text{Ti}}$ is the distance between the water oxygen and the Ti surface atom beneath it. $d_{\text{O}-\text{H}}$ is the hydrogen bond distance between a bridge oxygen atom and the water hydrogen closest to it. $\Delta p$ is the change to the dipole moment of the simulation cell after H$_2$O adsorption. The applied electric field and dipole moment are in the direction of the slab normal, with the positive $x$ direction indicated as in Fig. 5.1.

<table>
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<tr>
<th>$\frac{1}{8}$ ML</th>
<th>E$_{\text{ext}}$ (V/Å)</th>
<th>$\Theta_{\text{H}_2\text{O}}$ ($^\circ$)</th>
<th>$d_{\text{O}-\text{Ti}}$ (Å)</th>
<th>$d_{\text{O}-\text{H}}$ (Å)</th>
<th>$\Delta p$ (D)</th>
<th>PBE</th>
<th>opt-B88</th>
</tr>
</thead>
<tbody>
<tr>
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<td></td>
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<td></td>
<td></td>
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<td>2.484</td>
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</table>
The Ti5c–O\textsubscript{H\textsubscript{2}O} distance in the next column of the table (O-Ti) also has a clear decrease as a function of applied field. For PBE, the decrease is mostly linear in the $E_{\text{ext}} = 0 \rightarrow +0.257$ (V/Å) regime and reaches a saturation around +0.193 (V/Å). For opt-B88, the decrease is nearly linear across the whole range of $E_{\text{ext}}$. A recent scanned-energy mode photoelectron diffraction experiment places the length of the bond between the surface Ti5c site and the nearest adsorbed water molecule to be 2.21 ± 0.02 Å. [144]. This is in good agreement with our results of 2.20-2.29 Å for the water in the monomer limit and much longer than the Ti–O bond in the bulk crystal. Meanwhile, the hydrogen bond distance $d_{\text{O-H}}$ attains its maximum at the zero-field limit and decreases with increasing $E_{\text{ext}}$ magnitude in either field direction. The hydrogen bond is shortened by a maximum of ∼17% with PBE and ∼7% with PBE, which occur in opposite directions of the electric field. The net change in dipole moment due to adsorption, $\Delta p$, is calculated by subtracting the net out-of-plane components between the water-adsorbed and clean slabs. The magnitude of the dipole moment of a single water molecule from the calculations in 3.4.2 is 1.80 eV (1.90 eV) for PBE (opt-B88), and in the adsorption geometry is tilted into a much more flat arrangement with respect to the slab normal. Since $\Delta p \sin(\Theta_{\text{H\textsubscript{2}O}})$, the approximate out-of-plane contribution to $Deltap$ from the water molecule is 1.0 D (1.2 D) for PBE (opt-B88) in the zero-field limit, this suggests some large degree of local charge rearrangement all over the the surface. $Deltap$ has a linearly-changing character in $E_{\text{ext}}$ in the positive direction for opt-B88, while having a more abrupt change for PBE and is nearly linear while $E_{\text{ext}} < 0$. The magnitude of $\Delta p$ is about 0.5 D larger for opt-b88 than PBE, suggesting that the xc-functional plays a major role in charge rearrangement.

Moving on to the associatively adsorbed monolayer on the 2×1 cell, we note that many of the same geometric parameters can be used here to describe the adsorption as well. Noticing that the two water molecules adsorbed on top of the TiO\textsubscript{2} slab are not identical, that they respond differently to the applied electric field, we refer to the H\textsubscript{2}O molecule that forms hydrogen bonds “1” and “2” in fig. 5.5c as H\textsubscript{2}O-1 and the molecule that forms hydrogen bonds “3” and “4” in fig. 5.5c as H\textsubscript{2}O-2.

The angular tilt parameters, $\Theta_{\text{H\textsubscript{2}O,1}}$ and $\Theta_{\text{H\textsubscript{2}O,2}}$, are smaller than for the monomer case. $\Theta_{\text{H\textsubscript{2}O,2}}$ in particular obeys a similar response to $E_{\text{ext}}$ in the tilt angle geometry for PBE and opt-B88, where the opt-B88 case has a larger tilt at the extremes of the electric field window. $\Theta_{\text{H\textsubscript{2}O,1}}$ on the other hand displays slightly different behavior: for the PBE it attains a maximum tilt angle of ∼21° at the extremes of the $E_{\text{ext}}$ window but a minimum near the zero-field limit.
Table 5.6: Configuration details for water monolayer associative adsorption on the rutile (110) TiO$_2$ four-trilayer slab with the PBE functional as shown in Fig. 5.5c. Subscripts on the $d_{O-H}$ distances refer to the labels there.

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<th>$\Theta_{H_2O,1}$</th>
<th>$\Theta_{H_2O,2}$</th>
<th>$d_{O-Ti,1}$</th>
<th>$d_{O-Ti,2}$</th>
<th>$d_{O-H,1}$</th>
<th>$d_{O-H,2}$</th>
<th>$d_{O-H,3}$</th>
<th>$d_{O-H,4}$</th>
<th>$R_{O-O}$</th>
<th>$\Delta p$</th>
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<th>$\Theta_{H_2O,2}$</th>
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<th>$d_{O-Ti,2}$</th>
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<tr>
<td>-0.193</td>
<td>20.14</td>
<td>14.69</td>
<td>2.344</td>
<td>2.325</td>
<td>2.300</td>
<td>1.838</td>
<td>2.055</td>
<td>1.999</td>
<td>3.004</td>
<td>1.561</td>
</tr>
<tr>
<td>-0.257</td>
<td>19.69</td>
<td>13.85</td>
<td>2.351</td>
<td>2.331</td>
<td>2.314</td>
<td>1.827</td>
<td>2.042</td>
<td>1.992</td>
<td>2.998</td>
<td>1.309</td>
</tr>
</tbody>
</table>
but for opt-B88 the maximum tilt angle is obtained at the zero-field limit and a minimum at the extremes. The difference between the maximum tilt angle $\Theta_{H_2O,1}$ is $\sim 2.5^\circ$ for PBE and $\sim 4.0^\circ$ for opt-B88. The presence of the hydrogen bond network is a likely factor that more solidly “locks” the adsorbates into place in a near-planar configuration than in the monomer limit. The distance between the oxygen of each water molecule and the Ti atom below it followed similar trends for PBE and opt-B88, almost 0.1 Å further away from the surface than in the monomer limit, possibly again due to the increased total coordination of each water molecule complex on the surface; instead of binding to one Ti atom and one bridging oxygen atom, the formerly free hydrogen is now hydrogen-bonded to the next water molecule in the chain.

The hydrogen bond lengths $d_{O-H,1}$, $d_{O-H,2}$, $d_{O-H,3}$ and $d_{O-H,4}$ are highly anisotropic with regard to adsorption site for both PBE and opt-B88. For PBE, $d_{O-H,1}$ decreases by $\sim 0.1$ Å as $E_{ext}$ increases from - to $+0.257$ V/Å while $d_{O-H,1}$ decreases by a larger $\sim 0.3$ Å over that interval. $d_{O-H,2}$ attains its maximum value for PBE at zero electric field while it attains a maximum for opt-B88 at $E_{ext}$. On the whole, the variation of the hydrogen bond lengths over the entire range of $E_{ext}$ field strengths and directions is greater for PBE. The increased response of the water molecules to the external field may corroborate suggestions of the over-structure of hydrogen bond networks with GGA functionals. Hydrogen bond distances $d_{O-H,3}$ and $d_{O-H,4}$ display entirely different behavior than the previous two. $d_{O-H,3}$ increases nearly linearly with increasing applied field for both functionals while $d_{O-H,4}$ attains a maximum near the zero field limit for opt-B88 while decreasing as $E_{ext} \rightarrow +0.257$. We notice that for opt-B88 simulations with negative $E_{ext}$, the hydrogen bond distances do not change quite as much as they do in response to a positive applied field, while the reverse is true for the PBE functional; at positive external fields the change is small approaching the zero-field limit. The lesson from the inspection of the hydrogen bond lengths is that the bond network is highly sensitive to the applied field but also displays behavior specific to the exchange-correlation functional.

The water–water oxygen–oxygen distances $R_{O-O}$ are larger here than that of the isolated dimer by at least 0.1 Å. It is clear from the schematic in fig. 5.5c that they are nearly centered on the Ti5c atop site, and since the PBE lattice constant is larger by about 0.01, it is reasonable that the PBE O–O distances are larger, which they are except for large negative values of $E_{ext}$. $R_{O-O}$ tends to take a maximum near the zero-field limit. Finally, the net dipole moment change upon adsorption $\Delta \mu$ displays similar character and magnitude to what was recorded in the monomer case, but slightly smaller for most values of the external electric field. Although

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there are two water molecules here, it appears that their nearly-flat configuration helps to reduce
the net polarization of the surface slab by a small amount. Although not mentioned in these
tables, neither the H–O–H angles internal to each water molecule nor do the water O–H bonds
change appreciably as a result of the electric field. The internal degrees of freedom for the water
molecules are thus essentially fixed.

5.4.2 Energetics

Much of the prior work on the TiO$_2$–H$_2$O interface concentrates on the relative energy ordering
between the amount of surface coverage on adsorption sites and the associative or dissociative
nature of the water adsorption. Here, the dependence of the adsorption energy on the electric
field and the van der Waals exchange correlation functional will be discussed as well. In the
past, there was considerable controversy about the energetic favorability of water dissociation on
the clean TiO$_2$ surface, which was observed by some experiments in low coverages while others
observed dissociation of water only at defects, some at very low coverages, and associative
adsorption otherwise. [11, 145, 146, 147] Some early DFT calculations predicted dissociation
was favored, while others predicted the opposite, until better experiment design, larger unit
cells, more robust xc-functionals, and improved electronic structure codes settled on molecular
adsorption being the energetically favorable mode, with dissociation favored at defects.

The adsorption energy is calculated as in equation 2.33. For adsorption scenarios that
contain more than one water monomer, a preliminary analysis was performed to see if the BSSE
error was affected by considering the two water molecules individually rather than together in
the BSSE term. It was discovered that the difference in BSSE between these two methods is
generally less than 0.001 eV/molecule, where the magnitude of the BSSE correction was $\sim 0.11$
eV/molecule. Therefore, the BSSE correction was performed with the molecules (associated or
dissociated) acting as a single unit. The water molecule single-point energies both with and
without the BSSE correction were performed in the same unit cell as the combined TiO$_2$+H$_2$O
system and without the contribution from the external electric field, so as not to double-count
that contribution in the energy subtraction. The energy change of the BSSE with respect to
changes in the field (and also geometry) was overall low, varying by less than 0.01 eV/molecule
over the electric field window. This gives reason to ignore the electric field contribution to the
BSSE correction, but we chose to perform it anyway as a function of electric field rather than
use a single BSSE correction value for each adsorption scenario.
Figure 5.6: Top-view of the dissociated monomer (a), half-monolayer (b), monolayer (c), and “mixed” monolayer (d) H$_2$O coverages (in ball-and-stick representation) studied on the TiO$_2$ model surface (shown in vdW spheres representation) in the zero-field limit.

A presentation of $E_{\text{ads}}$ for the range of external electric fields under study is made in table 5.7 for the PBE and opt-B88 functionals. We find a nearly universally increasing trend in the adsorption energies as $E_{\text{ext}}$ increases from $-0.257$ to $+0.257$ eV. The magnitude of the energies is representative of chemisorption. For the PBE functional, the relative stability of adsorbed water follows: $E_{\text{ext}} < 0$: $E_{ML} > E_{\frac{1}{2} ML} > E_{\frac{3}{2} ML}$; $E_{\text{ext}} \geq 0$: $E_{ML} > E_{\frac{1}{2} ML} > E_{\frac{3}{2} ML}$. For opt-B88, the ordering tends toward: $E_{ML} > E_{\frac{3}{2} ML} > E_{\frac{1}{2} ML}$ for all electric field magnitudes, excepting the notable outlier case at $E_{\text{ext}} = -0.257$ where the adsorption energy for the water monomer is nearly $0.250$ eV below where it is expected. If that outlier is neglected, the slope of the adsorption energy vs. electric field curve for the opt-B88 monomer case is $15.6$ meV/eV (bias), very close to the PBE value. We also make the curious observation that at $E_{\text{ext}} = +0.193$ V/Å, the monolayer and monomer adsorption energies are nearly degenerate for both PBE and opt-B88, being within $0.004$ eV/molecule of each other.

The adsorption energies for PBE are generally $220-300$ meV lower than those of opt-B88. A look back at figure 3.15 implies that the reason for this increase may be due to the smaller bandgap and how more bonding states are available near the conduction band edge for bonding to the Ti5c atom. Since the underlying Ti5c–Ou bond is slightly stretched with increasing field and the general trend of Ti–O$_2$H$_2$O bond lengths is to decrease to a larger degree for opt-B88 rather than PBE, there is reason to conclude that the basis function overlap becomes more substantial between the Ti5c and O$_2$H$_2$O atoms for opt-B88 which directly leads to stronger bonding. Additionally, there is probably another component to the energy increase where the nature of the non-local correlation in the vdW-DF itself leads to stronger bonding between transition metal atoms and water molecules. [148]

In addition to the monomer, half-monolayer, and monolayer associatively-adsorbed water
Table 5.7: Adsorption energies (eV/molecule) for the associatively-adsorbed $\frac{1}{8}$ monolayer (monomer), $\frac{1}{2}$, monolayer, and 1 monolayer water coverages on the rutile (110) TiO$_2$ four-trilayer slab with the PBE and opt-B88 functionals as shown in Fig. 5.3.

<table>
<thead>
<tr>
<th>$E_{ext}$ (V/Å)</th>
<th>PBE</th>
<th>opt-B88</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\frac{1}{8}$ ML</td>
<td>$\frac{1}{2}$ ML</td>
</tr>
<tr>
<td>+0.257</td>
<td>0.858</td>
<td>0.775</td>
</tr>
<tr>
<td>+0.193</td>
<td>0.873</td>
<td>0.737</td>
</tr>
<tr>
<td>+0.129</td>
<td>0.790</td>
<td>0.734</td>
</tr>
<tr>
<td>+0.064</td>
<td>0.749</td>
<td>0.722</td>
</tr>
<tr>
<td>+0.032</td>
<td>0.704</td>
<td>0.709</td>
</tr>
<tr>
<td>0.000</td>
<td>0.689</td>
<td>0.693</td>
</tr>
<tr>
<td>-0.032</td>
<td>0.679</td>
<td>0.690</td>
</tr>
<tr>
<td>-0.064</td>
<td>0.668</td>
<td>0.672</td>
</tr>
<tr>
<td>-0.129</td>
<td>0.650</td>
<td>0.666</td>
</tr>
<tr>
<td>-0.193</td>
<td>0.637</td>
<td>0.658</td>
</tr>
<tr>
<td>-0.257</td>
<td>0.622</td>
<td>0.654</td>
</tr>
</tbody>
</table>

Slope (meV/V$_{bias}$) | 15.8 | 7.1 | 6.5 | 22.8 | 11.4 | 12.0

Simulations, we also perform simulations of the dissociated water monolayer, where there is an OH molecule adsorbed on the Ti5c site and an H atom adsorbed on the neighboring bridge oxygen site and mixed adsorption, where the Ti5c sites are fully covered by an alternating chain of associatively and dissociatively-adsorbed water molecules. These arrangements are shown graphically in figure 5.6. The intent here was to reproduce the well-studied result that water is favored to adsorb in the associative state on the clean TiO$_2$ surface. The adsorption energies per molecule are charted in table 5.8 for the PBE and opt-B88 functionals. The dissociative monolayer’s adsorption energy with the PBE functional, attains two minima, equally spaced at $\pm 0.064$ eV while increasing toward the zero field limit and also with increasing field magnitude. Meanwhile, the mixed monolayer shows behavior halfway between the associative and dissociative case: an adsorption energy minima occurs when $E_{ext}=-0.064$ but the energy rises slightly in either field direction up to the extrema. The trends in adsorption energy for the opt-B88 functional under mixed and dissociated monolayer coverage, obey much more regular trends. The adsorption energy of the dissociated and mixed monolayer increase from $E_{ext} = -0.257 \rightarrow +0.257$ eV/Å but the rate of increase is much lower than in the associated monomer situation.

The main conclusion from this analysis is that an increase of $E_{ext}$ in the positive direction
Table 5.8: Adsorption energies (eV/molecule) for the associatively-adsorbed, dissociatively-adsorbed, and mixed monolayer on the rutile (110) TiO$_2$ four-trilayer slab with the PBE and opt-B88 functionals as shown in Fig. 5.4. The final row is the slope of the data fitted to a linear trend.

<table>
<thead>
<tr>
<th>$E_{ext}$ (V/Å)</th>
<th>PBE</th>
<th>opt-B88</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.257</td>
<td>0.894</td>
<td>0.695</td>
</tr>
<tr>
<td>0.193</td>
<td>0.877</td>
<td>0.684</td>
</tr>
<tr>
<td>0.129</td>
<td>0.868</td>
<td>0.487</td>
</tr>
<tr>
<td>0.064</td>
<td>0.850</td>
<td>0.469</td>
</tr>
<tr>
<td>0.032</td>
<td>0.839</td>
<td>0.471</td>
</tr>
<tr>
<td>0.000</td>
<td>0.832</td>
<td>0.481</td>
</tr>
<tr>
<td>-0.032</td>
<td>0.827</td>
<td>0.479</td>
</tr>
<tr>
<td>-0.064</td>
<td>0.815</td>
<td>0.461</td>
</tr>
<tr>
<td>-0.129</td>
<td>0.817</td>
<td>0.505</td>
</tr>
<tr>
<td>-0.193</td>
<td>0.786</td>
<td>0.493</td>
</tr>
<tr>
<td>-0.257</td>
<td>0.788</td>
<td>0.525</td>
</tr>
</tbody>
</table>

Slope (meV/V$_{bias}$) | 6.5 | 9.5 | 2.7 | 12.0 | 2.8 | 5.0

will increase the adsorption energy of adsorbed water species on TiO$_2$. And this effect tends to be larger for opt-B88 than for PBE. A positive $E_{ext}$ will change the charge polarization of the surface slab so that the top surface where H$_2$O is adsorbed will be depleted of elections which are pushed to the opposite slab surface. Then, the lone pairs on the water molecule have a greater electrostatic interaction with the holes at the Ti5c sites. We also conclude that electron correlation plays a role whenever dissociative adsorption is involved under $E_{ext}$ because of the different response to the field, and that the opt-B88 functional which includes electron correlation explicitly in the density functional predicts higher energies of water adsorption than PBE which is likely due to an increased number of low-lying conduction band Ti3$d$ states available for bonding in addition to the nonlocal electron correlation effects.

Comparisons of the energy values obtained here with previous results in the literature are mostly good for PBE. One PW-DFT study with found adsorption energies of 0.77 and 0.66 eV/molecule for the associatively adsorbed monolayer and half-monolayer on a four-trilayer slab, and energies of 0.65 eV/molecule for the mixed monolayer case for PBE. [22] This is the same energy ordering that we see, with the addition that the energy differences are nearly equal as well at about 0.05 eV/molecule, with our results being larger. Tilocca et al. used PAW-DFT to find PBE adsorption energies of 0.76 and 0.66 eV/molecule using a four-layer
slab with the single bottom layer fixed in space. [91] Another PW-DFT study with a four-trilayer slab (with two fixed bottom layers) found the adsorption energies to be 0.82, 0.63, and 0.77 eV/molecule for the associative, dissociative and mixed monolayers, respectively. [24]. Although the energies obtained in that study are remarkably close to our results for PBE in the zero field limit, we obtain lower energies for dissociated and mixed H$_2$O monolayers by 0.15 and 0.06 eV/molecule, respectively. There exist plenty of surveys of this problem in the literature that achieve qualitative results generally similar to those presented here, but either use a different exchange-correlation functional or model slab setup which prevents a direct comparison of energies. [23, 25, 149] Experimental values of the H$_2$O barrier to desorption have been reported to be 0.73–0.74 eV from TDS measurements at low coverages [146, 150], and 0.83 eV for higher coverages of $\sim \frac{1}{3}$ ML from a modulated molecular-beam study. [151] This signifies that our PBE results are close to what is expected to be observed while the opt-B88 predicts higher barriers.

The work function of the TiO$_2$ slab changes in response to the addition of an adsorbate. The associatively-adsorbed monolayer reduces the work function of the clean surface by 0.65 eV for PBE and 0.76 for opt-B88 in the zero-field case. A monolayer of dissociatively adsorbed water reduces the work function by 0.16 eV for PBE and 0.81 eV for opt-B88 in the same zero-field case. The result for PBE compares neatly to the experimental work of Onda et al. [105] where the work function of the surface is depressed by $\sim$ 0.6 eV as a water monolayer is adsorbed onto the clean surface, although our results predict a higher TiO$_2$-H$_2$O work function magnitude of 5.4; 5.6 eV (PBE; opt-B88) compared with their 5.1 eV. The work function decrease is expected to be smaller for the dissociated water adsorption rather than the associative case, and the opt-B88 functional has difficulty predicting that trend.

5.4.3 Electrostatics

This section analyzes a selection of the simulation results to observe how the charge is being redistributed upon several factors: the adsorption of water itself, the application of the electric field, and the choice of exchange correlation functional. The movement of charge helps us to determine the main contributions to the net polarization of the slab. The magnitude of the $yz$-plane-averaged electron charge density near the plane of the water molecule oxygens for both PBE and opt-B88 is $\sim$ 0.04 $e$/bohr$^3$, while the charge density at the midpoint of the water
Figure 5.7: Side-view of the plot of the charge density difference $n_{\delta,ads}$ between the H$_2$O monolayer adsorption system at the indicated electric field strength and the surface slab and water molecules at the relaxed geometry of the composite system, calculated with the PBE xc-functional and the BC2 ESM condition. Ti–O bonds were removed for clarity. Yellow and blue regions correspond to an accumulation and depletion of electrons, respectively. The isosurface level is at 0.001e/bohr$^3$.

The molecule’s internal O–H bonds is close to $\sim 0.2$ e/bohr$^3$, which gives us a simple benchmark for comparison of charge magnitudes.

To establish the nature of charge rearrangement in water-adsorbed TiO$_2$ slabs, we use a reformulated version of the charge density difference previously described in equation 3.9:

$$n_{\delta,H_2O} = n_{TiO_2+H_2O} - n_{TiO_2} - n_{H_2O}$$

so that the quantity we would like to observe graphically is the adsorption-induced charge density difference. Figure 5.7 shows $n_{\delta,H_2O}$ for the extrema of $E_{ext}$ and the zero-field limit for PBE. Yellow regions correspond to areas where electrons are accumulated after adsorption and blue regions correspond to a depletion of electrons. The isosurface level is at 0.001e/bohr$^3$ and the maximum value on the numerical grid is close to $\sim \pm 0.02$ in most cases. The figure shows nearly identical results for $n_{\delta,H_2O}$ as a function of $E_{ext}$ and opt-B88 (not shown) also shows a negligible difference between the different external electric fields on $n_{\delta,H_2O}$. The only discernible electron redistribution lies around the water molecules themselves, the bridging and surface Oxygen atoms and the Ti5c sites on the surface. It is clear that electronic density moves away from the area lying above the water molecule’s plane in the $x$-direction and the hydrogen molecule closes to the bridging Oxygen, and accumulates in-between the water oxygen and the Ti5c site and on the bridging oxygen atom itself.
Another analysis we performed tracks the changes in the charge density as the field is applied, with respect to the zero-field limit. In this case, the analysis is performed with identical geometries (i.e. the zero-field charge density is not in its atomic ground state) to minimize the impact of the pseudopotential that was recorded earlier for clean slabs in figures 5.3-5.4. The field-modulated electron charge density difference is thus:

\[ n_{\delta, E} = n_{\text{TiO}_2 + \text{H}_2\text{O}, E} - n_{\text{TiO}_2 + \text{H}_2\text{O}, E=0} \]  

(5.2)

Unsurprisingly, the characteristic shapes of the charge density rearrangement in \( n_{\delta, E} \) become larger as the field magnitude is increased. In figure 5.8 we plot \( n_{\delta, E} \) for the PBE and opt-B88 functionals for \( E_{\text{ext}} = \pm 0.257 \text{ V/Å} \). The isosurface level is at 0.0001\( e/\text{bohr}^3 \), while the maximum value of \( n_{\delta, E} \) on the numerical grid is approximately \( \pm 0.008 |E_{\text{ext}}| \), or 0.002 \( e/\text{bohr}^3 \) for the \( E_{\text{ext}} = \pm 0.257 \text{ V/Å} \) results shown in the figure.

The charge rearrangement \( n_{E} \) occurs over the whole slab, polarizing mainly the \( p \) orbitals of Oxygen and Titanium, especially near both surfaces. The lobes of charge density difference are very close to being exactly the inverse of one another for opposite \( E_{\text{ext}} \) of the same strength. Although the rearrangement of charge is about one order of magnitude weaker for \( n_{\delta, E} \) compared to \( n_{\delta, \text{H}_2\text{O}} \), it is highly directional and spread over the whole unit cell. Relating these results back to the difference in dipole moment \( \Delta p \) in table 5.6, we obtain a consistent picture of how the adsorbed water and applied field work together to polarize the unit cell. The zero-field limit value of \( \Delta p \) is 2.232 D for PBE and 2.546 D for opt-B88, essentially due only to rearrangement of charge around the water molecule, which is the dominant effect. Then, as the electric field is swept, regions of electron depletion and accumulation appear in the combined in a manner in the direction of the dominant dipole (the + field direction and - field direction, respectively). The overall influence of the electric field on the net dipole difference is smaller than the adsorption effect, a picture consistent with the visuals shown here.

5.4.4 Electronic Structure

There has been relatively little work examining the effect of water adsorption on the electronic structure of the TiO\(_2\) surface, despite the considerable amount of work on energetics, geometries and dynamics. This section will use an analysis of the local and projected density of states to discern differences in the description of molecular adsorption of water on TiO\(_2\) resulting from the exchange-correlation functional and the applied electric field.
Figure 5.8: Side-view of the plot of the charge density difference $n_{\delta,E}$ between the H$_2$O monolayer adsorption system at the indicated electric field strength and a system with identical configuration except with zero electric field, calculated with PBE (top) and opt-B88 (bottom). Ti–O bonds were removed for clarity. Yellow and blue regions correspond to an accumulation and depletion of electrons, respectively. The isosurface level is at $0.0001e$/bohr$^3$. 

$n_{\delta,E}$  \hspace{1cm} E=-0.257 V/Å  \hspace{1cm} E=+0.257 V/Å
The local density of states (LDOS) is a space-resolved measure that describes the density of states, which can be used to interpret STM results or to otherwise spatially probe the electronic characteristics of a system on a sub-Angstrom scale. In the SIESTA code, the LDOS is formally the DOS weighted by the amplitude of the corresponding wavefunctions at different points in space. The code essentially picks out the portion of the electronic charge density that arises from electron states inside a particular energy window. We perform this analysis to obtain a spatial sense of how the electron states in the valence band behave, and if the adsorption of water appreciably changes the results found for the surface in section 3.3.3, which marked a sharp contrast in the LDOS for a TiO$_2$ slab with one layer of molecularly adsorbed water (on the right of the slab) is shown in figure 5.9. The energy window of each LDOS plot is 0.250 eV, the windows start at the valence band maximum at the top of the page and end at 3 eV below the conduction band at the bottom. The isosurface level is set to 0.004 states/bohr$^3$. The LDOS plot shows a result similar to figure 3.14 where the majority of the electron states at the valence band edge are located at the fixed end of the slab, and the downshift in energy levels on the opt-B88 side of the LDOS plot is visible in space. For example, the energy range 1250-1500 meV below the valence band contains states with significant population across the entire model slab (but not the H$_2$O molecules) but at that same energy range the valence states only propagates halfway through the slab for opt-B88, encompassing only the fixed region. An appreciable population of states begins to accumulate on the adsorbed water molecules at about 1750 meV below the valence band yet this takes place at 2750 meV below the valence band when the opt-B88 functional is used. The LDOS within $\sim 1$ eV of the conduction band edge (not shown) lies predominantly in the top two trilayers of the model slab almost entirely contributed by Ti3$d$ orbitals, and the second trilayer from the top has the larger contribution, similar to the result obtained for m×n TiO$_2$NWs where m or n (or both) is odd. We recall that the main source of this downshift is due to the fixing of the two bottom layers of the slab, as described in section 3.3.3.

The next series of plots investigates the projected density of states on a number of atoms and orbitals of interest with regard to the associatively adsorbed water monolayer on TiO$_2$ (110). The purpose is to determine the effect of the external field on electronic states. Figures 5.10-5.11 show the PDOS for the clean TiO$_2$ slab (a) and the water monolayer-adsorbed slab in three different equally spaced electric field strengths for PBE and opt-B88, respectively. With the clean TiO$_2$ slab as a reference, it is clear how the application of the field induces a progressively
Figure 5.9: Side-view of H\textsubscript{2}O monolayer adsorption simulation cells calculated with the PBE (left) and opt-B88 (right) xc-functionals in the zero-field limit. Ti–O bonds were removed for clarity. The yellow isosurface is the LDOS, drawn at a constant 0.004 states/bohr\textsuperscript{3}, calculated between the energy intervals indicated at left starting at the valence band maximum at the top and going deeper into the valence band towards the bottom of the series.
greater downshift in the electronic levels of all states not at the immediate valence band edge in figure 5.10 as the external field becomes more negative. It as known that the states close to the valence band edge are entirely contributed by the bulk-like O2p states from the PDOS analysis in chapter 3.3.3 and the previous LDOS plots. The states less than ~ 0.25 eV from the conduction band edge also appear to be pinned in place, keeping the magnitude of the gap equal with respect to the applied field but the Ti3d peak above it in energy does shift upwards or downwards depending on the applied field direction. The prominent Obr peak near -2 eV spreads out and reduces in energy. The PDOS in figure 5.11 for the opt-B88 functional however, shows markedly different behavior than for PBE. First, the conduction band edge is not pinned in place as the external field changes in the positive direction, so the bandgap of the system is changing in response to the applied field. This hints at the other difference from the previous plot, that there appears to be no downshift in energy as the $E_{ext}$ points in the negative direction.

To determine the effect of adsorption and the electric field on the electronic states belonging to the adsorbed water on the TiO$_2$ surface, the DOS is projected over the water orbitals and
Figure 5.11: PDOS of the clean 2 × 1 TiO₂ slab in the zero-field limit (a) and the associatively adsorbed H₂O-monolayer TiO₂ slab (b)-(d) with electric field indicated for the opt-B88 functional. Line indicators are identical to fig. 5.10.

compared to H₂O in its free state. This is shown for the PBE functional in figure 5.12, where (a) shows the PDOS of the top of the surface slab, (b) is the water molecule in gas phase, shifted to a common vacuum level to the H₂O+TiO₂ slab, and the three plots beneath it show the PDOS of each water molecule and the total contribution from all the water as a function of field strength. The water molecule mostly has contributions to the PDOS stemming from the Oxygen atoms, and in the case of the 1b₂ state at ∼-9 eV the hydrogen contributes about 25% to the PDOS. The δ-function like energy levels of the free water molecule are noticeably split upon adsorption for the 3a₁ state near -5.5 eV and the 1b₂ state. The highest water energy peak (1b₁) for the free molecule spreads out over a large 4 eV energy window for the water-adsorbed slab, and that the two water molecules contribute more or less equally to this state. This becomes less true deeper in the valence band, where the difference in the PDOS peaks. The degeneracy-breaking between H₂O–1 and H₂O–2 becomes clear in the low-energy water state as the different contributions from each molecule (pink and blue dash-dotted lines in figure 5.11 change as the electric field is applied. We note that the contribution of each water molecule is not a single peak either, that the admixture of states is due to their interaction...
through hydrogen bonds, and there are no TiO$_2$ states to interfere with this state in a nearby energy window. Likewise, the spreading of the intermediate water state between $\sim 6$ and $-5$eV is mostly due to interactions between the surface O and Ti atoms with the water oxygen and the wide spreading of the highest water state is due to the interaction of the hydrogen molecules with the entire first trilayer of the surface, including the bridging oxygen atoms.

The response of the electronic levels for opt-B88 is similar to that of the PBE functional except that the downshift of the electronic states as the field becomes more strongly negative is not observed. In figure 5.13, the water molecule PDOS is shown over the range of external field strengths. The shift of the peak positions is confirmed to be linear for the positive field direction, yet the distance between the $1b_2$ peaks and also the relative populations between the energy states is observed to change in a nonlinear manner. As mentioned before, this effect must be entirely due to field-induced geometric effects internal to the structure of the two water molecules since there are no substrate states to mix with in that energy region. The rest of the states higher in the valence band have a similar profile as a function of the applied field and are

Figure 5.12: PDOS of the the associatively adsorbed H$_2$O-monolayer TiO$_2$ slab in the zero-field limit (a), a single isolated water monomer in the $2 \times 1$ simulation cell (b), and the associatively adsorbed H$_2$O-monolayer TiO$_2$ slab (c)-(e) with electric field indicated for the PBE functional. In (c)-(e) the PDOS of the H$_2$O molecule with index 1 is blue dash-dotted line, the PDOS of the H$_2$O molecule with index 2 is pink dotted line, and their sum is the black solid line.
less effected by the internal geometry of the water-water subsystem, dominated by electronic effects in the substrate.

In summation, the choice of exchange functional influences the solution of the DFT Hamiltonian and sometimes the effect of the choice of that functional on the electronic states can be large which transform into geometric and energetic properties under analysis. The relatively unstudied opt-B88 functional seems to suffer from a poorer description of electronic states inside a model slab with the two bottom trilayers fixed in space with the SIESTA method, shifting the electronic levels of all states corresponding to free geometries down in energy by 0.7 eV. In response to an electric field, it is expected that a bias voltage will also shift the electronic levels proportional to the applied field, but that trend sees an extinction in the opt-B88 functional for reverse-biased slabs. The states corresponding to the adsorbed water in a monolayer configuration greatly spread out in the valence band due to interactions between the water electronic states and the substrate.

Figure 5.13: PDOS of the the associatively adsorbed H₂O-monolayer TiO₂ slab with electric field indicated for the opt-B88 functional. Line indicators are identical to fig. 5.12c-e.
5.5 Conclusion

DFT simulations were performed with PBE and the self consistent van der Waals opt-B88 functional for biased four-trilayer rutile TiO$_2$ slabs with and without water adsorption. The model slab geometry was sandwiched between two metal-like medium in the BC2 ESM boundary condition with 10 Å of vacuum (7 Å in the Kohn-Sham cell) on each between the ESM region and the simulation slab. A $2 \times 1$ surface unit cell was used to model water monolayer and half-monolayer adsorption, while a $4 \times 2$ cell was used to model water monomer adsorption.

For the clean surface (without adsorbed molecules), a strong, but not complete, quenching of the electric field was observed in the TiO$_2$ slab while the field in the vacuum region was enhanced, and this was the expected result. The atomic bond lengths and geometries of the atoms and were found to be dependent on the electric field in most cases. The hydrogen bonds and tilt angles responded greatly to the applied field, while the Ti–O distances, water O–O distances, and inter-trilayer distances had a weaker response. The choice of functional had a small effect in the response of the geometries of the water molecules to the field, and the distance displacements for the opt-B88 functional were generally larger than PBE, especially with regard to the surface hydrogen bond network. The adsorption energies of the water molecules on the model slab were found to be similar magnitudes and stability-ordering as a function of coverage to previous literature results for PBE. The opt-B88 predicted a near-unilateral 230 meV increase of adsorption energy per molecule, and the applied electric field and magnitude increased the adsorption energy as the field became larger in the $+x$ direction and vice versa. The energetic response of the water molecules to the applied field was strongest in the associative adsorption case compared to the dissociated or mixed ($\frac{1}{2}$ ML associated, $\frac{1}{2}$ ML dissociated) adsorption case, with the change in energy per unit Volt of electrical bias being larger for the opt-B88 slabs for associative adsorption and PBE for dissociative and mixed adsorption. The adsorption energies for the monolayer coverage of water were the most exothermic, with dissociative adsorption the least exothermic. The predicted work functions for opt-B88 were lower in magnitude than PBE for the water-adsorbed surfaces, excepting the dissociative. The molecular adsorption of water reduces the work function compared to the clean surface by 0.65 eV and 0.76 eV for the PBE and opt-B88 functionals, respectively, and dissociative adsorption reduces it by 0.16 eV and 0.81 eV, respectively.
The effect of adsorption and the bias voltage on the electrostatic charge distribution of the model interface was mostly intuitive. The charge rearrangement of the model slab due to chemisorption of H\textsubscript{2}O is nearly entirely screened by the first surface trilayer and thus does not penetrate deeply into the bulk region. This charge rearrangement does not appreciably depend on the applied field. The induced charge stemming from the applied field alone indeed scales with the field magnitude and creates a net polarization across the entirety of the slab, and PBE and opt-B88 behave essentially identically in these respects. This is another way of saying the order of the magnitude of potential difference induced from chemisorption, the potential induced from the applied field, and the xc-potential follow: $V_{\text{ads}} > V_E \gg V_{xc}$. The electronic structure of the adsorbate+TiO\textsubscript{2} system displays similar behavior to the clean slabs where a large downshift of all electronic levels corresponding to unfixed atoms is observed in both the valence and conduction band. A shift upwards in energy for the electronic levels for both functionals in the positive direction of the electric field was observed, but the reverse was seen only for PBE. Finally, the degeneracy in the electronic states belonging to the adsorbed water molecule beneath the valence band are due to geometric effects rather than interactions in the substrate, and the relative ordering of energies of levels corresponding to each water molecule shifts with the applied field. In this respect, the geometric, energetic, electrostatic, and electronic structure effects of the TiO\textsubscript{2}–H\textsubscript{2}O interface using the ESM BC2 boundary condition with an external electric field and the opt-B88 functional are brought into the light of day, indicating that this functional is probably not well-suited for this interface and strong asymmetry because of its strong downshift in electronic states (from the fixing of the bottom two layers of the slab), its adsorption energies for water molecules that do not fit experiment, predicts unruly behavior of the electronic structure response of the system to an applied electric field, and is on the whole more computationally expensive. This is not to say that the opt-B88 functional is a poor descriptor of physics at the nanoscale, but for this system it has serious shortcomings.
Conclusions and Outlook

The construction of a suitable model of the rutile TiO$_2$ (110) surface with adsorbed water and the analysis of its properties in response to an applied electric were the main foci of this thesis, which was performed with the density functional theory code SIESTA. The recent van der Waals density functional opt-B88 was employed to determine if the description of the system was enhanced compared to GGA-PBE and the effective screened medium theory was used to create non-periodic unit cells amenable to the simulation of a physically-consistent bias voltage in the DFT simulation.

6.1 TiO$_2$ Nanowires

Recent interest in nanowires fashioned from TiO$_2$ have begun to find applications in novel technologies, especially batteries and dye-sensitized solar cells. The ability to grow self-assembled, high-aspect ratio nanowires engineered to have specific electronic characteristics with atomic-level precision is highly attractive, opening the door for fascinating new devices.

A survey of the structure-property relationships of TiO$_2$ nanowires with rectangular cross section performed with GGA-DFT found that the presence of a direct bandgap arises from an odd number of surface layers in either or both confinement directions which enforce mirror planes onto the electronic states rather than $C_2h$ symmetry. The formation energy analysis showed that the even $m \times n$ NWs, with indirect bandgaps, tend to have the lowest formation energies per formula unit, a trend that favors larger nanowires. An analysis of interlayer distances, COOP and LDOS plots concluded that the nanowires are composed of series of interacting dual trilayer, with have the weakest coupling between the second and third layer from each surface. The origin of the nature of the direct bandgap from odd and mixed parity nanowires comes
from a downshift in the low-lying conduction bands due to the quantum confinement-induced localization of the LUMO wavefunction along each confinement direction.

As nanowire fabrication processes become more precise, it is plausible that atomic-level control over nanostructures can be executed to make devices with specific electronic characteristics, and studies of structure-property relationships can direct and inform the ultimate usefulness of these nanostructures in devices.

6.2 The TiO$_2$–H$_2$O Interface

The fundamental surface chemistry of the TiO$_2$–H$_2$O interface is a timely problem that has appears in various applications, including water photocatalysis, sensing, and fuel cell anodes. The purpose of this study is to compare the GGA and vdW-DFT methods in how they describe the physics at the surface at electrical bias. The TiO$_2$–H$_2$O interface is simulated using a four-trilayer slab model with the bottom two layers fixed with the ESM metal-slab-metal (BC2) boundary condition, and adsorbed water molecules in a monomer, half-monolayer, and monolayer associative adsorption pattern and a mixed or fully-dissociated monolayer. A relatively strong external electric field is applied to the cell in a series of simulations in order to determine trends in the equilibrium geometries, energetics, electrostatics, and electronic structure while observing how the choice of exchange-correlation functional affects those descriptions.

PBE and opt-B88 are in good agreement with each other regarding bulk properties of TiO$_2$ including crystal structure parameters, cohesive energy, bulk modulus, electronic band structure and density of states. Calculations of the surface bond lengths and inter-trilayer distances of the TiO$_2$ (110) surface with PBE and opt-B88 were are also very close to one another, and showed negligible effects with regards to the choice of ESM boundary condition. The surface energies of the opt-B88 slab were much larger than PBE. The work functions for PBE and opt-B88 converged to 0.15 eV of each other but the opt-B88 bandgap was 0.7 eV smaller than PBE for the slab with fixed bottom two trilayers, a primary indicator of trouble in the electronic structure of that system. Indeed, a study of the PDOS revealed a $\sim$ 0.7 eV downshift in electronic levels in all states arising from atoms not on the bottom-most fixed TiO$_2$ trilayer, which in turn was due to the fixing of the bottom two layers of the slab model. The fully-relaxed PBE and opt-B88 slabs had very close bandgaps, to within 0.1 eV. A COOP analysis showed interlayer binding between the second and third trilayer to be weaker the first and second trilayer for PBE and
opt-B88. The geometric properties of the water molecule and dimer were computed with PBE and opt-B88 in good agreement to results from the literature.

Adding an external field to the ESM BC2 computational setup made the electrostatic potential perform as expected from elementary theory, introducing an unambiguous bias voltage on the two sides of the model slab. The structural effect of the external field on the TiO$_2$ slabs lengthened or contracted Ti–O bonds perpendicular to the surface and changed other bond lengths. The opt-B88 and PBE functionals both made some of these bond lengths and characteristics for the relaxed geometries of various coverages of water increase or decrease linearly as a function of the field, while some geometric parameters, took on a nonlinear relationship with the applied field. The geometry of the hydrogen bond network (or single hydrogen bonds) had a strong response to the external field.

Observations of charge rearrangement as a result of the applied field and adsorption indicated that the adsorption had a strong effect of polarizing the top surface layer of the model slab and the electric field had a weaker effect of polarizing the entire slab, especially the surfaces. The adsorption energies for water were most exothermic in the associative adsorption case and weakest in dissociative adsorption with the external electric field increasing the adsorption energy as it increased in the positive direction. Opt-B88 predicted stronger adsorption than PBE by 0.23 eV. Associative adsorption depressed the work function more than dissociative adsorption for PBE while for opt-B88 they were nearly equal. The effect of the electric field on the electronic states tended to push most states upward or downward in energy in the same direction as the field, and this trend was mostly linear for PBE. The widening and closing of the bandgap in response to the field is observed for opt-B88 as well.

The opt-B88 functional is determined to have major flaws in the study of this interface. This is actually a blessing because these types of limitations allow investigators to distinguish between the intrinsic properties of a system under simulation and how observations of those properties may arise from a poor description of the physics in its ab initio treatment.

6.3 Outlooks

I have focused exclusively on stoichiometric surfaces and nanowires that can be constructed directly from the bulk rutile TiO$_2$ crystal in this work. In contrast, most of the interesting catalytic properties in rutile TiO$_2$ are connected with the presence of oxygen vacancy on the
It would be interesting to understand how the properties of the TiO$_2$ surfaces and nanowires may be modified by surface functionalization, which invariably occurs in realistic growth and fabrication environment. Experimentation with these properties, in nanowires and surfaces alike, may advance the state of knowledge as to what simulation setup yields the quickest convergence to known properties while not introducing any undesirable artifacts in the electronic structure or energies.

Future directions for the work on the TiO$_2$-H$_2$O interface include *ab initio* molecular dynamics situations to investigate thermodynamic properties of the interface, especially in the limit of multilayers of water or full liquid water simulations. In addition, there has been a recent update to the ESM formalism whereby the dielectric permittivity can be varied smoothly which affords an even greater degree of flexibility and usefulness to the ESM formalism. [152] The ESM boundary condition of a screened dielectric medium (like water) was not available in the freely-available SIESTA code at the time of writing this thesis, and this avenue of research would be useful in the simulation of ensemble-scale physics with charged cells. Finally, a limitation in this study was the inability to obtain vibrational properties for the chemisorbed H$_2$O due partly to erratic behavior approaching convergence in the maximum forces on atoms with the (now vastly outdated) development trunk version of SIESTA. As the ESM method gains wider use and the developer community increases, I believe that the capabilities of these computer codes will be able to allow theoreticians to inform experimentalists and interpret their results far better than is possible now.

As for the aspect of the use of vdW-DFT on the recovery of accurate surface chemistry from first principles, there are definite trade-offs that come with the territory. First, vdW-DFT simulations require more memory and computer effort to solve, and in my opinion, are more difficult to converge to a satisfactory electronic ground state. Second, it appears through this work and others that the advantages to using vdW-DFT strongly depend on the system under study and the dominant forces and energetics within. In this work, the nearly 1 eV downshift of the electronic levels corresponding to unfixed atoms is clearly an undesirable trait. This is not to say that it is useless to study any particular material or interface with vdW-DFT, far from it! The scientific record needs these trials to determine how to improve these functionals in the ultimate search for a facile, low-effort solution that is “mostly correct, nearly all of the time” even for systems that contain exotic physics. Finally, as Moore’s law marches on and computer power increases, particularly with the advent of new massively GPU-parallelized simulations,
the computational complexity of systems that humanity can study atomistically will approach boundless heights.
Appendices
Appendix A

Shape-tunable properties of silicon nanowires

Silicon nanowires (SiNWs) have been studied extensively in recent years as promising building blocks for future nanoscale devices due to their compatibility with current CMOS technology, with many applications having been demonstrated as e.g., field-effect transistors,[153], thermoelectric materials,[154], electromechanical devices,[155], and chemical and biological sensors.[156] The interests in SiNWs also arise from their novel electronic and optical properties due to quantum confinement,[157, 158, 159] which can be modified through precise control of the growth orientation, surface passivation, and nanowire stoichiometry during growth and fabrication processes. The production of H-terminated SiNWs in the diameter range of 1 – 5 nm in bulk quantities[160, 161] has stimulated a number of computational studies on the structure-property relationship of these quasi-1D nanostructures. An important observation, of relevance to the development of Si-based photonic devices, is the possibility of obtaining direct band gap for small diameter SiNWs of different growth orientation,[162, 163, 164, 165, 166, 167] which deviates considerably from the bulk Si.

Since the H passivation of the surface dangling bonds leads to bulk-like tetrahedral Si configuration even for small diameter SiNWs, the confinement-induced direct band gap formation in SiNWs can be understood from the folding of the bulk Si band. [162, 166, 168] For [100] and [110] SiNWs, parts of the six equivalent conduction band minima can be projected onto the Γ point of the 1D Brillouin zone with an upward shift in energy level induced by confinement. The amount of upshift is smaller than that of the projection of the remaining conduction band minima because of the larger effective mass in the confinement plane, leading to a direct band gap significantly larger than that of the Bulk Si at decreasing wire diameter. In contrast, for
[111] and [112] SiNWs, there is no conduction band minima which can be projected onto the Γ point. They are thus expected to exhibit an indirect band gap at large diameters. Previous work has shown that an indirect to direct transition can occur for [111] SiNWs as diameter decreases to ≤ 2 nm, but the difference between the indirect and direct gaps remains very small. Much less attention has been paid to [112] SiNWs [128, 169, 170], although they are the most abundant SiNWs grown by the oxide-assisted growth process [160]. In addition, most previous studies considered just SiNWs with heuristically chosen structures.

Recent computational study combining genetic algorithm optimization with density functional theory (DFT) [171] has shown that the H-terminated [112] SiNWs can take stable structures with a rectangular cross section bounded by monohydride {110} and {111} facets with dihydride bridges at the corner, or the {111} facets may acquire trihydride termination, although only the trihydride-passivated [112] SiNWs have been experimentally observed and experimental measurements of band gap are available for them. [160] Two recent works [172, 173] have suggested that an indirect to direct band gap transition for monohydride [112] SiNWs may be induced by varying the cross sectional aspect ratio, which call for further study. In this paper we present a systematic first-principles investigation on the shape-tunable electronic properties of the [112] SiNWs for both monohydride (mh-SiNWs) and trihydride (th-SiNWs) passivation.

Our DFT calculations are performed using the SIESTA code [49] with the Perdew-Burke-Ernzerhof functional within the generalized gradient approximation (GGA) [41] and norm-conserving pseudopotential [47]. We used the double-zeta plus polarization optimized basis set and a real-space mesh cutoff of 350 Ry. A vacuum region of at least 13 Å is employed in the lateral directions to eliminate the interaction between the image SiNWs in neighboring cells within the supercell method. The Brillouin zone was sampled using a 1 × 1 × 24 Monkhorst-Pack k-point mesh. Structure relaxations are performed to reduce the force on each atom to below 0.01 eV/Å. The lattice constant along the wire axis (chosen as the z axis) is optimized by minimizing the uniaxial stress. Tests have also been performed to ensure that the results are fully converged using both plane-wave pseudopotential [174] and all-electron Gaussian orbital methods. [175] Although it is well known that the DFT calculations systematically underestimate the band gap, recent quasi-particle calculation using the GW approximation for SiNWs, [162, 168] which is computationally expensive, has indicated that the general trend of band gap variation and band dispersion close to the gap region are well reproduced by the DFT calculations. This
Figure A.1: (Color online) Indirect-direct band gap difference $\Delta$ versus cross sectional area (left figure) and aspect ration (right figure) for monohydride (upper figure) and trihydride (lower figure) [112] trihydride SiNWs. (b) Indirect-direct band gap difference $\Delta$ versus cross sectional area (left figure) and aspect ration (right figure) for trihydride [112] SiNWs. The geometry of the SiNWs is denoted $A_nB_m$ and characterized by the number of layers $n$ ($m$) parallel to the \{111\} (\{110\}) facet. The dashed line represent the nanowire series of $A_5B_m$, $B = 2 - 5$. The inset shows the top view of the atomic structure of the monohydride $A_5B_2$ SiNW. The horizontal line at $\Delta = 0$ denotes indirect to direct transition.

makes possible a reliable investigation on the indirect to direct band gap transition for [112] SiNWs with moderate computational costs.

We use the notation $A_nB_m$ to classify the [112] SiNWs of different shape, where the labels $A$ and $B$ represent the \{111\} and \{110\} facets respectively, while the indices $n$ and $m$ characterize the number of layers parallel to the \{111\} and \{110\} facets (see Fig. A.1). The wires studied here correspond to $n = 2 - 7$ and $m = 2 - 5$. The cross sectional aspect ratio is defined as the ratio between the lateral dimension of the \{111\} and \{110\} facets projected onto the $xy$ plane. An increasing aspect ratio thus correlates with an increasing ratio of $m/n$ (see the insets of Fig.A.1). For all the [112] SiNWs studied, the valence band maximum (VBM) is located
Figure A.2: Electron (upper figure) and hole (lower figure) effective masses for mh-SiNWs and th-SiNWs. For both mh-SiNWs and th-SiNWs, the hole (electron) effective masses converge to essentially identical values at increasing cross sectional area (aspect ratio).
at the Γ point. To quantify the indirect to direct band gap transition, we define an energy
difference $\Delta$ between the energy of conduction band bottom at the Γ point and the conduction
band minimum near the Brillouin zone boundary ($X$ point). Therefore a positive $\Delta$ denotes an
indirect band gap and a negative $\Delta$ denotes a direct band gap with indirect to direct transition
occurring at $\Delta = 0$.[172]

The shape-induced indirect to direct band gap transition is shown clearly in Fig. A.1, where
we plot four series of [112] SiNWs corresponding to $A_n B_2, A_n B_3, A_n B_4$ and $A_n B_5$ for both
monohydride and trihydride passivation, where $n = 2 - 7$. The same set of data points could
also be plotted with the indices exchanged, e.g., the dashed line represents the nanowire series of
$A_2 B_m$ with $m = 2, 3, 4, 5$. For both monohydride and trihydride passivations, the [112] SiNWs
exhibit a direct band gap at decreasing $\{111\}$ to $\{110\}$ facet ratio with the transition point
occurring at $\approx 0.5$, independent of the cross sectional area. Although similar indirect to direct
transition was observed by Lu et al.[172] for the case of mh-SiNWs, these authors attribute
the transition mechanism to the different contribution to conduction band density of states
by the Si atoms on the $\{111\}$ and $\{110\}$ facets. Since the trihydride passivation of the $\{111\}$
facets modifies substantially the facet atomic structure, the similar pattern of indirect-to-direct
transition for mh-SiNWs and th-SiNWs suggests instead a mechanism based on the contribution
from the interior atoms. This is further evidenced by examining the electron and hole effective
masses as a function of the cross sectional area and aspect ratio for both mh-SiNWs and th-
SiNWs. As shown in Fig. A.2, we found that the electron effective masses for both mh-SiNWs
and th-SiNWs converge to essentially identical values at increasing aspect ratio, corresponding
to the indirect band gap region. But the hole effective masses for both mh-SiNWs and th-SiNWs
converge to essentially identical values with increasing cross sectional area, independent of the
aspect ratio.

Examining the electronic band structure variations across the different series of SiNWs
shows that the energy levels of the conduction band minimum (CBM) close to the Brillouin zone
boundary change little relative to the valence band maximum (VBM). To reveal the mechanism
of the observed indirect-to-direct transition, we analyze therefore the nature of the wavefunction
of the conduction band bottom at the Γ point. In Fig. A.3 we show the wave function plots
for four mh-SiNWs, corresponding to the beginning ($A_2 B_2$) and end ($A_7 B_2$) of the series $A_n B_2$
and the beginning ($A_5 B_2$) and end ($A_5 B_5$) of the series $A_5 B_m$. The wave function plots for
the corresponding th-SiNWs show similar distribution. We found that the wave functions of
Figure A.3: (Color online) Wave function plots of monohydride SiNWs corresponding to conduction band bottom at Γ point for $A_2B_2$ (a), $A_7B_2$ (b), $A_5B_2$ (c) and $A_5B_5$ (d) SiNWs. Both the top view and side view are shown here. The blue and darker (yellow and lighter) region represents the positive (negative) part of the wavefunction. Going from $A_2B_2$ (a) to $A_7B_2$ (b), the confinement effect due to $\{111\}$ facet weakens and the SiNWs change from indirect to direct band gap. Going from $A_5B_2$ (c) to $A_5B_5$ (d), the confinement effect due to $\{110\}$ facet weakens and the SiNWs change from direct to indirect band gap.
Figure A.4: (Color online) Relative stabilities of [112] SiNWs: The free energy of formation per Si atoms for four mh-SiNWs and three th-SiNWs was plotted as a function of the hydrogen chemical potential. The symbols appended to the end M and T denote monohydride and trihydride respectively. To aid visualization, the ordering of the labels from top to bottom in the legend has been chosen to coincide with the ordering of the free energy at large H chemical potential $\mu_H$. 
the conduction band bottom at Γ point arise from hybrized p-orbitals of the interior Si atoms and extend normal to the \{110\} facets. The sign of the wavefunction alternates in the direction perpendicular to \{110\} facet but does not change in the direction perpendicular to the \{111\} facets. This leads to an anti-bonding state in the confinement direction corresponding to \{110\} facets but a bonding state in the confinement direction corresponding to \{111\} facets. Therefore as we move from \(A_2B_2\) to \(A_7B_2\), the confinement effect from the \{110\} facet reduces leading to down-shift of the energy level of conduction band at Γ point, and the SiNWs change from indirect to direct band gap. As we move from \(A_5B_2\) to \(A_5B_5\), the confinement effect from the \{111\} facet reduces leading to up-shift of the energy level of CBM at Γ point, and the SiNWs change from direct to indirect band gap. Since the confinement effect of the \{110\} facets is stronger than that of the \{111\} facets, the SiNWs will move to the indirect band gap region when the number of layers \((m)\) parallel to the \{110\} facet is sufficiently large, and the energy difference \(\Delta\) eventually converges to a value close to the difference between the direct and indirect band gap obtained from the bulk Si band structure projected onto the [112] direction. The last series \(A_n B_5\) in Fig. A.1 show clearly this trend. The wave function corresponding to the VBM at Γ point for both mh-SiNWs and th-SiNWs (not shown here) was found to arise from hybridized sp\(^3\)-orbitals extending along the neighbor Si-Si bond and is delocalized throughout the interior Si atoms. This explains why the hole effective mass converges to essentially identical values with increasing cross sectional area for both mh-SiNWs and th-SiNWs.

The nature of the wavefunction of conduction band bottom at Γ point also explains naturally the strain dependence of the [112] SiNWs band structure and a subtle difference between the monohydride and trihydride SiNWs. Examining the variation of the wave function along the nanowire axis shows a bonding configuration for the conduction band state at Γ between adjacent unit cells, with no nodal plane perpendicular to the axial direction. When applying a compressive uniaxial strain which reduces the lattice constant, we expect a down-shift in the energy level of the conduction band bottom at Γ point, leading to a reduced energy difference \(\Delta\). For the case of monohydride [112] SiNWs, this was indeed observed by Huang et al.\[173\]. Our results here also suggest that a similar scenario could apply to the th-SiNWs. On the other hand, a careful examination of the indirect to direct band gap transition plotted in Fig. A.1 reveals subtle differences between mh-SiNWs and th-SiNWs: As we vary along the series from \(A_2B_m\) to \(A_7B_m\) for \(m = 2 - 5\), the energy difference \(\Delta\) changes with a larger amount number for the monohydride SiNWs as the number of layers \(n\) parallel to the \{111\} facets increases.
But as we vary along the series from $A_nB_2$ to $A_nB_5$ for $n = 2−7$ (as indicated by the dashed line in Fig. A.1 where $n = 5$), the energy difference $\Delta$ changes instead with a larger amount for the trihydride SiNWs as the number of layers $m$ parallel to the $\{110\}$ facets increases. This is because that trihydride passivation occurs only at the $\{111\}$ facets. The strong H-Si bonds at the trihydride $\{111\}$ facets weaken the Si-Si bond and leads to a slightly larger Si-Si bond length perpendicular to the $\{111\}$ facets, which in turn induces a slightly shorter Si-Si bond length perpendicular to the $\{110\}$ facets. Consequently the confinement effect due to the $\{110\}$ facets are stronger for the th-SiNWs leading to larger variation in $\Delta$ as the number of layers $m$ parallel to the $\{110\}$ facets increases, while the confinement effect due to the $\{111\}$ facets are stronger for the mh-SiNWs leading to larger variation in $\Delta$ as the number of layers $n$ parallel to the $\{111\}$ facets increases.

To determine the relative stability of the [112] SiNWs of different shape and surface passivation, we calculated the free energy of formation $\Omega$ as a function of the hydrogen chemical potential $\mu_H$ following Northrup\textsuperscript{[176]}

\begin{equation}
\Omega = E^{tot} + E_{ZPE} - n_{Si}\mu_{Si} - n_H\mu_H
\end{equation}

where $E^{tot}$ is the total energy of SiNWs, $E_{ZPE}$ is the zero-point energy of Si-H vibrations, $n_{H(Si)}$ is the number of H (Si) atoms. We use the bulk energy for $\mu_{Si}$ and measure $\mu_H$ relative to the value where the $SiH_4$ molecule can be formed from a reservoir of H and bulk Si without energy cost.\textsuperscript{[176]} We calculated the Si-H vibrational frequency from a series of cluster calculations mimicking the atomic structure of the passivated [112] SiNWs using Gaussian 03 code.\textsuperscript{[175]} which converges quickly with increasing cluster size (0.21 eV per H-Si bond). Representative results for both mh-SiNWs and th-SiNWs are shown in Fig. A.4, which confirm that direct band gap [112] SiNWs can indeed form at higher H chemical potential. Specifically, the direct band gap trihydride $A_4B_2/A_6B_2$ and monohydride $A_7B_2$ SiNWs have lower free energy of formation than the indirect band gap trihydride $A_4B_5$ and monohydride $A_2B_5/A_5B_5$ SiNWs at higher H chemical potential. These high $\mu_H$ conditions exist when the SiNWs are exposed to atomic H which is generated from $H_2$ gas at appropriate growth conditions.\textsuperscript{[177, 178]} Note that although the $\{110\}$ facet is energetically less favorable to form than $\{111\}$ facet from the total energy $E^{tot}$ calculations,\textsuperscript{[161, 172]} our calculation of free energy of formation $\Omega$ show that it is indeed thermodynamically possible to achieve [112] SiNWs with predominatly $\{110\}$ facets at experimentally relevant passivation environments.
In conclusion, we have shown for the first time using first-principles DFT calculation that an indirect to direct band gap transition can be induced in both monohydride and trihydride [112] SiNWs solely by varying the cross sectional aspect ratio. We show that this transition is caused by the different confinement effects on the conduction band state at Γ point from the \{111\} and \{110\} facets enclosing the nanowire. We suggest that as-grown direct band gap [112] SiNWs are thermodynamically possible by analyzing the free energy of formation.

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Appendix B

Water adsorption on silicon nanowires

The interaction between water and other materials is perhaps the most important interfacial phenomenon, with broad implications in such areas as corrosion, catalysis, electrochemistry, and biology.[180] With the rapid development of nanotechnology in environmental and sustainable energy applications[181], a thorough molecular-level understanding of the structure and properties of water at the interface with various nanostructures will be timely and essential.

Compared to water adsorption on single-crystal surfaces[180, 182], studying interfacial water in nanomaterials presents new challenges due to the reduced symmetry and typically larger size, which generally leads to a more complicated potential energy surface underlying the water-nanostructure interaction. In addition, the more opened structure of nanomaterials suggests that van der Waals (vdW) forces due to the nonlocal correlation between atoms separated by regions with low electron density may not be neglected in studying interfacial water, which is not addressed by the current density functional theory (DFT) in the generalized gradient approximation (GGA).[183]

The first step towards understanding interfacial water in nanomaterials is to determine the binding site/orientation of individual water molecules, the nature of the interfacial binding, and the diffusion path of water molecules across the surface of nanostructures, which govern the subsequent formation of water clusters and monolayers.[184] In this paper we present a DFT study of the structure and energetics of water monomer adsorbed onto the surfaces of hydrogen-passivated silicon nanowires (h-SiNWs), where the vdW interaction is taken into account using a semi-empirical dispersion correction (vdW-DFT). The availability of small-diameter h-SiNWs in bulk quantities[160] has stimulated many works on their novel electronic, thermoelectronic,
and electromechanical properties in recent years[153, 154, 185], thereby paving the way for future energy applications.[155]

The h-SiNWs chosen for our study were a [110]-oriented h-SiNW with a hexagonal cross section bounded by monohydride (111) facets and canted dihydride (100) facets, and a [112]-oriented h-SiNW with a rectangular cross section and monohydride passivation bounded by (110) and (111) facets with diameters of ∼ 2 nm (Fig. B.1), which are representative of stable structures with low formation energy from DFT calculations.[163, 171, 179] Experimentally the [110] and [112] growth orientations have been found to be the most abundant for nanowires of diameter smaller than 10 nms.[153, 154, 160, 185]

Our DFT-GGA calculations are performed using the SIESTA code[49] with the Perdew-Burke-Ernzerhof (PBE) functional[183] and Troullier-Martins norm-conserving pseudopotential.[47] We use the standard double-zeta plus polarization (DZP) basis for the h-SiNWs. To improve the accuracy in binding energy calculation, the standard DZP basis for the water molecule was augmented by one set of diffuse functions on both the H and O atoms (DZP+), where the radial cutoff and orbital exponent were optimized variationally using the simplex algorithm as implemented in SIESTA.[49] Benchmark calculations on water monomer and dimer with the DZP+
Table B.1: Adsorption energy $E_{\text{ads}}$ at the least favorable (low) and most favorable (high) adsorption sites on each facet of the [110] and [112] h-SiNWs from DFT calculations with ($E_{\text{DFT-D}}$) and without ($E_{\text{PBE}}$) dispersion-correction, the corresponding minimum distance between water H atoms and surface H atoms ($d_{H-H}$), and the tilt angle of the water molecule plane relative to the facet.

<table>
<thead>
<tr>
<th>Orientation</th>
<th>Facet</th>
<th>$E_{\text{ads}}$ ($eV$)</th>
<th>$E_{\text{PBE}}$ ($eV$)</th>
<th>$E_{\text{DFT-D}}$ ($eV$)</th>
<th>$d_{H-H}$ (Å)</th>
<th>Tilt Angle ($^\circ$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[110]</td>
<td>(100)</td>
<td>Low</td>
<td>0.027</td>
<td>0.051</td>
<td>2.059</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td></td>
<td>High</td>
<td>0.054</td>
<td>0.076</td>
<td>2.061</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>(111)</td>
<td>Low</td>
<td>0.030</td>
<td>0.043</td>
<td>2.003</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td></td>
<td>High</td>
<td>0.043</td>
<td>0.061</td>
<td>2.033</td>
<td>66</td>
</tr>
<tr>
<td>[112]</td>
<td>(110)</td>
<td>Low</td>
<td>0.027</td>
<td>0.058</td>
<td>1.924</td>
<td>42</td>
</tr>
<tr>
<td></td>
<td></td>
<td>High</td>
<td>0.040</td>
<td>0.077</td>
<td>2.021</td>
<td>75</td>
</tr>
<tr>
<td></td>
<td>(111)</td>
<td>Low</td>
<td>0.045</td>
<td>0.056</td>
<td>1.897</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td></td>
<td>High</td>
<td>0.055</td>
<td>0.074</td>
<td>2.045</td>
<td>56</td>
</tr>
</tbody>
</table>

basis give a water molecule dipole moment of 1.918 D, and a hydrogen bond energy of 0.23 eV with the O-O distance of 2.89 Å, in good agreement with calculations using a large gaussian basis set.[2]

In this work the vdW interaction is taken into account using the semi-empirical DFT-D method of Grimme[57], where the total energy is given by $E_{\text{DFT-D}} = E_{\text{PBE}} + E_{\text{disp}}$. $E_{\text{PBE}}$ is the usual self-consistent Kohn-Sham energy as obtained from the PBE exchange-correlation functional. $E_{\text{disp}}$ is an empirical dispersion correction given by:

$$E_{\text{disp}} = -s_6 \sum_{i=1}^{N_{\text{at}}-1} \sum_{j=i+1}^{N_{\text{at}}} \frac{C_{ij}^6}{R_{ij}^6} f_{\text{damp}}(R_{ij})$$

where the damping function $f_{\text{damp}}(R_{ij}) = \frac{1}{1+e^{-a(R_{ij}/R_{r}-1)}}$ is used to avoid near-singularity at small atomic pair distance $R_{ij}$, and $R_r$ is the sum of atomic vdW radii. The vdW coefficients for atomic pairs $C_{ij}^6$ are obtained from the individual atomic value via geometric mean $C_{ij}^6 = \sqrt{C_i^6 C_j^6}$, which in turn is derived from the London dispersion formula with DFT calculation of atomic polarizability.[57] Although in principle a self-consistent vdW-DFT calculation could be performed[186, 187], the DFT-D method provides a simple and accurate alternative scheme for incorporating vdW effects in non-metallic systems and is well suited for studying interfacial water.

A supercell scheme of $a \times b \times nc$ was used in the water monomer calculation, where $n=2$ (3) for [112] ([110]) h-SiNW with a lattice constant along the wire axis of $c=6.61$ Å ($c=3.89$ Å) respectively. The size of the simulation box in the lateral direction $a, b$ is chosen so that a
vacuum region of at least 13 Å is employed to eliminate the interaction between the neighboring images. The Brillouin zone was sampled using a $1 \times 1 \times 6$ Monkhorst-Pack k-point mesh. Geometry optimizations were performed using the conjugate gradient method with a maximum force tolerance of $0.008 \text{ eV/Å}$ and a energy mesh cutoff of 350 Ry. The water monomer adsorption geometry is found by performing structure optimizations for a variety of initial adsorption sites and orientations of the water molecule, chosen randomly on each facet of the h-SiNWs. The binding energies $E_{\text{ads}} = E_{\text{SiNW}} + E_{\text{H}_2\text{O}} - E_{\text{H}_2\text{O}/\text{SiNW}}$ were then calculated using counterpoise correction\cite{53} to eliminate the basis-set-superposition-error (BSSE) due to the use of local atomic basis sets.

From this extensive set of calculations a large number of locally stable adsorption geometries were found for both [112] and [110] h-SiNWS, reflecting the reduced symmetry and correspondingly more rugged potential energy landscape of the h-SiNWs. All the adsorption sites are characterized by a small binding energy in the range of $0.043 - 0.077 \text{ eV}$, corresponding to the weak physisorption limit. For such weak interfacial interactions, the vdW interaction is significant in determining the absolute magnitude of the binding strength (Table 1), but its effect on the relative adsorption energy at different adsorption sites is much smaller and is not sensitive to the facet orientation. The overall magnitude of vdW correction ($\sim 0.02 - 0.03 \text{ eV}$) in adsorption energy agrees well with results for water adsorption on the bulk H-terminated Si surfaces computed using a plane-wave implementation of the self-consistent vdW-DFT method.\cite{188}

The weak binding strength suggests that electronic orbital overlap across the interface is not relevant in determining the adsorption geometry. This is confirmed by examining the projected density of states (PDOS) onto the p-orbitals of water O atom\cite{180}, where the shift in the peak position corresponding to the lone-pair orbital of the water molecule is indeed negligible upon adsorption. This is in contrast to water adsorption on transition and noble metal surfaces, where it is found that the orbital interaction between the metal d-band and water lone-pair orbital leads to a nearly flat adsorption orientation at the on-top site.\cite{189, 190}

The adsorption geometries differ mostly in the orientation of the water molecule. Only at the least favorable adsorption site we have a configuration corresponding to one hydrogen-up/one hydrogen-down (Fig. B.2b), for all other cases the adsorption orientation corresponds to oxygen-up/two hydrogen-down with the two water H atoms bridging two nearest-neighbor surface H atoms at the most favorable adsorption site, although the tilt angle between the facet and water plane may differ up to 50 degrees (Table 1). The adsorption geometry of a water monomer can
be understood from the delicate balance between electrostatic interactions involving the static water dipole, the partial charges on the surface H atoms, the surface Si atoms, and the interior Si atoms of the h-SiNWs. Consequently the inclusion of vdW correction due to dynamic dipole-dipole interaction does not change the qualitative picture of water adsorption.

This is analyzed by examining both the charging state of the h-SiNWs through the Mulliken population analysis and the charge redistribution (polarization) upon water adsorption through the spatial distribution of the charge density difference between the adsorption system and its components. Results from Mulliken population analysis show that for both [112] and [110] h-SiNWs, the surface H and its neighbor Si atoms are positively charged while the interior Si atoms are negatively charged. This net electron transfer from the surface to the interior of the h-SiNWs is less pronounced for the [110] h-SiNWs due to the more localized nature of their occupied states which center on the interior Si-Si bond.[163, 179] Consequently the net positive charge on the surface Si atoms (an average of 0.05 e) for the [110] h-SiNW is substantially larger than the surface H atoms (an average of 0.004 e), while the corresponding values for the [112] h-SiNW are 0.03 e and 0.01 e respectively. The orientation dependence in the average partial charge on the interior Si atoms (−0.044 e and −0.027 e for [112] and [110] h-SiNWs respectively) is weaker.

Such charge distributions in the h-SiNWs favor the oxygen-up/two hydrogen-down config-
Figure B.3: Right figure (left figure) shows potential energy surface scan for a water molecule diffusing along the axis (along the circumference) of the [112] h-SiNW on both the (110) and (111) facets.

Figure B.4: Right figure (left figure) shows potential energy surface scan for a water molecule diffusing along the axis (along the circumference) of the [110] h-SiNW on both the (100) and (111) facets.

Figure B.5: Potential energy surface scan for water molecule rotating around the x, y, and z axis on the (110) (left figure) and (111) (right figure) facets of the [112] h-SiNW.
uration as the much smaller radius of the H atoms allows the water to approach the nanowire surface through the groove between neighboring rows of surface Si atoms, thereby maximizing the Coulomb attraction between the postively charged water H atoms and the negatively charged nanowire bulk while keeping the negatively charged water O atoms away from the interior Si atoms. To minimize the Coulomb repulsion between the water H atoms and the surface H and Si atoms, the water molecule occupies the bridge sites. By examining the charge density difference plot (Fig. B.2) and the Mulliken population analysis after adsorption, we find that upon water adsorption, there is a back-donation of electrons both from the surface Si atoms to the surface H atoms facing the water molecule and from the water O atom to the water H atoms. This leads to less positively charged surface H and water H atoms reducing their Coulomb repulsion. Although the charging state in the interior of the nanowire is not affected, the less negatively charged water O atom leads to reduced Coulomb repulsion. Due to the much smaller partial charge on the surface H atoms of the [110] h-SiNW, the difference in $d_{H-H}$ at the least and most favorable adsorption sites is much smaller than that of the [112] h-SiNW (Table B.1).

To analyze the water monomer diffusion across the surface of h-SiNWs, we perform a potential energy surface (PES) scan along selected high-symmetry directions on the high-dimensional PES, corresponding to water monomer diffusion both parallel and perpendicular (along the circumference) to the nanowire axis (Figs. B.3 and B.4). The starting point of the PES scan represents the most favorable water adsorption site on the corresponding facet. Results from both DFT calculations with (DFT-D) and without (PBE) dispersion correction were shown for comparison. Consistent with our previous analysis, including the vdW correction has essentially no effect on the water diffusion path.

For both h-SiNWs, the magnitude of diffusion barrier can be much larger than that deduced from the binding energy difference at different adsorption sites. There is also a large anisotropy between different facets in the barrier for diffusion parallel to the nanowire axis, which can be understood from the different lattice structure of the surface H atoms (Fig. B.1). The surface H atoms on the (111) facet of both the [112] and [110] h-SiNWs form a triangular lattice, but their orientations relative to the nanowire axis are different. For water diffusing along the axis on the (111) facet of the [112] h-SiNW, a large barrier occurs when the water molecule moves from the bridge site to an on-top site due to the Coulomb repulsion between the surface H and water H atoms. Such on-top adsorption will not occur for water diffusing along the nanowire
axis on the (111) facet of the [110] h-SiNW, leading to a much smaller diffusion barrier. In contrast, parallel diffusion on the (100) facet of the [110] h-SiNW results in a large barrier. This is due to the canted dihydride passivation pattern on the (110) facet which leads to alternating low and high rows of surface H atoms perpendicular to the nanowire axis. The facet anisotropy is reduced substantially for water diffusing along the circumference of the h-SiNWs, which can be understood similarly from analyzing the change in $d_{H-H}$ during the diffusion.

The weak binding strength and its relative insensitivity to the water adsorption site is often suggested as the microscopic origin of a hydrophobic surface, where water clusters and monolayers may form without water being adsorbed in registry with the surface lattice structure. But to facilitate cluster and monolayer formation, the individual water molecules need to adapt its orientation to maximize hydrogen bonding with neighbor molecules without incurring a potential energy penalty.[180] Therefore we also performed a PES scan for water monomer rotation starting from the most favorable adsorption geometry on each facet. The results for the [112] h-SiNW were shown in Fig. B.5, where the water O atom is fixed during the rotation. For adsorption on the (110) facet, the water plane lies nearly perpendicular to the facet at the most favorable adsorption site (Table 1). Rotation around both the x and z axis corresponds to the cart-wheel mode, which lead to a larger barrier than rotation around the y axis (the facet normal). For adsorption on the (111) facet, the water plane becomes more flat with the three rotational modes leading to qualitatively similar shape in the PES scan. Note that the barrier for rotation is generally much less than that for diffusion. Consequently the water molecule can readily adapt its orientation to maximize hydrogen bonding with its neighbors, thereby facilitating water cluster and monolayer formation at room temperature and lower.[180]

In conclusion, we have studied the structure and energetics of water monomer adsorption onto the h-SiNWs of different shape and growth orientation using DFT calculations with dispersion correction. Our results show that water adsorption on the h-SiNWs is in the weak physisorption limit leading to a hydrophobic surface, which is not affected qualitatively by including the vdW correction. The study of water monomer adsorption represents the first step towards a fundamental molecular-level understanding of the wetting properties of silicon nanowires.

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