Understanding Fundamental Processes in TiO$_2$: Electronic and Interface Properties from First Principles

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Abstract

This work provides a detailed understanding of the behavior of titanium dioxide from an atomistic point of view, by employing state-of-the-art electronic structure methods. Special attention is paid to the processes that are relevant for renewable energy applications, such as dye sensitized solar cells (DSSC) and photocatalytic devices. Different system sizes, defect concentrations and computational strategies have been systematically tested to obtain unbiased results.

Investigation of the behavior of excess electrons in the undoped and defect free bulk material confirm charge trapping in the two most common oxide polymorphs (anatase and rutile), with formation of a polaron that extends for several lattice constants in anatase. Electrons are more strongly localized in rutile than in anatase, with an energy difference of 0.5 eV consistently obtained with different methods, including hybrid density functional theory (hybrid DFT) and the random phase approximation (RPA). Computed activation energies for polaron hopping and delocalization clearly show that anatase and rutile might have different charge transport mechanisms: in rutile, only hopping is likely, whereas in anatase hopping and delocalization are competing, resulting in anisotropic conduction-band-like and thus enhanced transport.

Interface effects have a substantial impact on the material properties: it is demonstrated that the first subsurface oxide layers retain the full coordination of the bulk environment, but are geometrically less constrained, allowing stabilization of both excess electrons and intercalated species, such as Li⁺ cations. Subsurface intercalated ions act as pinning centers for adsorbates, and the combined effect of adsorbate pinning and enhanced electron localization constitute a reservoir of shallow trap states in the proximity of the adsorbed donor molecules, likely to facilitate charge transfer mechanisms. Intermolecular interactions are also fundamental, influencing the binding strength and the long term stability of surface adsorbates: the presence of a liquid acetoniitrile solvent lowers the activation energy for acetic acid desorption to 0.53 eV, assisting the molecule detachment. The mobility of surface species is also influenced by the presence of neighboring adsorbates, as bridging water molecules or acetate moieties can facilitate the proton transfer on the surface. Comparison of TiO₂ and Al₂O₃ hydrogenation reveal an important difference in the behavior of the two oxides: the H₂ molecule is homolitically split on the anatase interface, with electron transfer to the metal cations and creation of a defect state. H₂ is instead heterolitically split when Al₂O₃ is studied, and the reducing moiety remains confined at the oxide interface, with a limited mobility.
Sommario

Questa tesi fornisce una visione dettagliata del comportamento del biossido di titanio da un punto di vista atomistico, grazie all’impiego di tecniche di calcolo della struttura elettronica. Particolare attenzione è rivolta ai processi rilevanti nelle applicazioni per lo sfruttamento di energie rinnovabili, come le celle di Grätzel o i dispositivi fotocatalitici. Varie possibili dimensioni del sistema in analisi, diverse concentrazioni di difetti e strategie di calcolo sono state sistematicamente testate allo scopo di ottenere un risultato privo di errori.

Un’analisi del comportamento degli elettroni in eccesso nell’ossido privo di difetti conferma che le cariche risultano localizzate nei due polimorfi più diffusi (anatasio e rutile), con formazione di un polarone che, nel caso dell’anatasio, si estende per la lunghezza di diverse celle cristalline. Gli elettroni risultano più stabilmente localizzati nel rutile che nell’anatasio, con una differenza in energia di circa 0.5 eV, calcolata coerentemente con diversi metodi, compresa la teoria del funzionale di densità (DFT) e la random phase approximation (RPA). Le energie di attivazione calcolate per la migrazione e la delocalizzazione degli elettroni indicano che anatasio e rutile dimostrano diversi meccanismi di trasporto elettronico: nel rutile è possibile solo un trasferimento adiabatico della carica tra centri di localizzazione adiacenti. Nell’anatasio questo meccanismo è invece in competizione con una delocalizzazione della carica, che risulta in una mobilità analoga a quella nella banda di conduzione del materiale, e quindi, in un incremento del trasporto, che risulta anisotropico.

Gli effetti della presenza di un’interfaccia sulla proprietà del materiale sono sostanziali: questo studio dimostra infatti che gli atomi al di sotto della superficie mantengono la piena coordinazione dell’ossido cristallino, ma permettono una maggiore stabilizzazione sia di elettroni in eccesso sia di altre specie intercalate, come ad es. cationi Li+. I cationi intercalati sotto la superficie agiscono inoltre come punti di ancoraggio per eventuali molecole adsorbite all’interfaccia. La combinazione di questi due fenomeni risulta nella formazione di una riserva di stati di localizzazione in prossimità delle specie riducenti adsorbite sulla superficie, così da facilitare il trasferimento di elettroni all’ossido. Anche le interazioni intermolecolari sono rilevanti, dal momento che influenzano la stabilità delle molecole adsorbite sulla superficie: la presenza di acetonitrile come solvente liquido riduce l’energia di attivazione per il desorboimento di una molecola di acido acetico a 0.53 eV, facilitando il processo. Anche il trasferimento di protoni all’interfaccia è notevolmente facilitato dalla presenza di molecole adsorbite nelle vicinanze, che agiscono come intermedi durante il trasferimento. Un confronto tra l’idrogenazione degli ossidi di titanio (TiO₂) e alluminio (Al₂O₃) rivela un’importante differenza tra i due materiali: la molecola di idrogeno (H₂) si suddivide in due singoli atomi, cioè in due protoni, che rimangono all’interfaccia, e due elettroni, che sono trasferiti all’ossido. Al contrario, sull’ossido di alluminio H₂ si dissocia in un protone e uno ione H⁻, che trattiene i due elettroni all’interfaccia, limitando la mobilità delle specie riducenti.
Acknowledgement

First of all, I would like to thank Professor Joost VandeVondele for giving me the opportunity to carry out my Ph.D project in the Nanoscale Simulations group. He has always been available for a discussion and to provide fundamental advice on many issues for my research.

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This thesis is divided into six main chapters. The variety of possible fields of TiO$_2$ applications, including devices for renewable energy conversion, that motivate this doctoral work, is presented in the Introduction. After an overview of the main oxide properties, the operating principles of dye sensitized solar cells and photocatalytic water splitting devices are discussed, with a description of the system components and their interplay, focusing on the role of the substrate. State of the art theoretical results are also reported, along with the main challenges concerning TiO$_2$ modelling. The second part of the first chapter is focused on the fundamentals of the electronic structure methods adopted in this work, emphasizing the crucial aspects related to modelling of semiconductor materials. Computation of reaction energies and profiles is an essential part of this work, and the relative computational strategies are also reported. The following four chapters provide a detailed description of the computed system properties: the electron localization behavior in the oxide, relevant for both DSSC and photocatalytic application, is analyzed in detail in Chapter 2. RPA calculations are applied for the first time to crystalline systems composed of hundreds of atoms, and a refined value of the polaron formation energy and mobility is obtained. Chapter 3 is instead focused on adsorption of functional molecules on the anatase (101) surface, and on the reversibility of the interaction. Entropic and solvent effects are also taken in consideration. Chapters 4 and 5 investigate adsorption and intercalation of lithium and hydrogen across the oxide interface. Both species are often present as additives (Li ions in DSSCs) or active components (H$_2$ in photocatalysis), and influence the oxide reactivity and electronic structure. Another relevant material for catalytic applications, Al$_2$O$_3$, is also presented and investigated in the fifth chapter, and its behavior is compared to the performance TiO$_2$. The concluding chapter summarizes the main results in a short discussion for material development and future outlook.
1.1 Background and Motivation

This doctoral thesis is motivated by the increasing need of a continuous and reliable energy supply, a key issue for achieving long-term economic and political stability. In fact, the world primary energy consumption grew by 2.5% in 2011, surpassing the level of $5 \times 10^{20}$ J per year, and it is expected to further increase in the future, due to population and economic growth[1]. Public concern over the environmental damage caused by massive consumption of non-renewable fossil fuels encourages research and development towards renewable forms of energy. The amount of Solar energy striking the earth in one hour ($4.3 \times 10^{20}$ J) is roughly equivalent to the planet’s yearly energy consumption and it is then logical to consider it as a significant resource. Solar power can be directly harvested in a few different ways, ranging from domestic water heating to the complex devices for direct conversion of sunlight to electrical energy using photovoltaic cells. Even if this technology is currently insufficient to fully power our modern society, it has some major advantages over other renewable energy sources: its versatility and relatively low cost makes it suitable for employment in urban and densely populated areas, as opposed to wind or hydropower, that require large areas, significant landscape modifications and high setup and maintenance costs. Most commercial solar cells are based on crystal silicon or thin films technologies (including amorphous silicon), whose low production cost makes them almost competitive with electricity production from fossil fuels. A widespread use of those devices is however limited by the low abundance, and in some case toxicity, of the component materials, and relatively limited operating range. The Dye Sensitized Solar Cell (DSSC) technology represents a promising alternative, with lower production and materials costs and enhanced robustness and efficiency in non optimal light and temper-
1. Introduction

ature conditions. A further increase in efficiency is however necessary for intensive, large scale applications. DSSCs have a complex architecture, and, while a great part of the components of the original concept has been replaced by novel materials, the semiconducting TiO\textsubscript{2} substrate, connecting the photoactive elements to the electrode, has basically remained unaltered. Solar light could not only be employed for direct conversion in electrical energy, but also for fuel production in photochemical reactions, for example H\textsubscript{2}. The concept of an alternative fuel as hydrogen, to power highly efficient, emission-free fuel cells is still in its infancy, but fuel cell vehicles and stationary applications are beginning to enter the consumer market in localized regions around the world. Steam reforming currently accounts for the majority of the hydrogen produced. Water electrolysis can be alternatively performed, but this method is much more energy intensive. Hydrogen generation from photocatalytic water splitting (or solar hydrogen) would provide an environmentally friendly fuel, both in terms of production and utilization. This technology can be ideally commercialized in areas where sunlight and water are abundant, but it would also allow producers to actually export solar energy. As for dye cells, the titanium dioxide support is a core element of photocatalytic devices.

For both applications, titanium dioxide represents the best available compromise between electronic structure, long term stability and cost. TiO\textsubscript{2} is in fact resistant to (photo)corrosion, is present in abundant reserves around the world and has a substantially lower cost than other photosensitive materials. Additionally, its activity and photosensitivity can be increased or altered via doping or surface modification and with specific material synthesis processes. Achieving a good understanding of the oxide behavior is therefore an essential aspect, motivating the detailed characterization of its interface and electronic properties presented in this thesis.

1.2 TiO\textsubscript{2}: Properties and Applications

1.2.1 A Versatile Material

In recent years, titanium dioxide, commonly known as titania, has been one of the most thoroughly investigates materials, for its versatility in a variety of applications. One of the main uses of this compound is as white pigment in coatings, pharmaceuticals and cosmetics, due to its stability, brightness, high refractive index and resistance to discoloration when exposed to UV radiation\cite{2}. Its biocompatibility makes TiO\textsubscript{2} an important component for surgery and dental implants \cite{3, 4}, while its photocatalytic activity can be exploited to
produce reactive species and obtain disinfectant surfaces or self-cleansing air filters\cite{5, 6}. A growing branch of TiO$_2$ research actively focuses on its use in solar devices for hydrogen or electrical energy production\cite{7, 8, 9}. Electron transport in the oxide is usually an essential aspect for most of its relevant applications, motivating a detailed characterization of its electronic properties.

The presence of intrinsic defects or doping species is also an important aspect to address. As an example, the operating principle of TiO$_2$ based sensors relies on the presence of oxygen vacancies, that correlate the electrical resistivity of the material to the oxygen content of the atmosphere\cite{10, 11}. Cationic effects on the energetics of nanocrystalline TiO$_2$ films has been extensively studied: it was demonstrated that, in aprotic solvents, the introduction of cations shifts the energy levels of the oxide towards more positive potentials, enhancing the efficiency of solar devices\cite{12}. Also oxygen and humidity sensors benefit from the presence of Li$^+$ cations, that enhance the device sensitivity\cite{13}. Investigation of Li$^+$ intercalation in titania is also of interest for energy storage, as TiO$_2$ is an eligible electrode material for Li-ion batteries\cite{14, 15}.

This chapter focuses on two of the most promising applications of titanium dioxide in the field of energy storage and conversion, that motivate the detailed study of the material presented in this thesis. The first two sections describes the crystal structure of the two main TiO$_2$ polymorphs and the most common reducing defects. The Dye Sensitized Solar Cells technology is then reviewed, with a detailed description of the principal device components and of their interplay, followed by a presentation of photocatalytic applications and of the most recent advances in the field. The concluding section presents the principal results achieved with theoretical modelling strategies, for both bulk and interface structures.

### 1.2.2 Crystal Polymorphs

Three major oxide crystal structures exist: rutile, anatase and brookite. Only rutile and anatase, however, are normally utilized in applications\cite{2}. Their structure is illustrated in Figure 1.1. Reported bulk parameters were obtained from Ref\cite{16}.

Both rutile and anatase crystals are based on an slightly elongated octahedral TiO$_6$ moiety, i.e. a titanium cation (with formal charge +4), surrounded by 6 oxide anions. In both structures, the oxide anions are threefold coordinated. In rutile, neighboring TiO$_6$ moieties share one edge along the [110] and symmetric directions, forming columns of edge sharing octahedra. Such columns are stacked so that octahedra in adjacent columns share corners, and their long axis is flipped by 90 degrees. Parallel channels along the [001] direction run through the columns (Figure 1.2). In anatase, the
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(a) Rutile

(b) Anatase

<table>
<thead>
<tr>
<th>Rutile</th>
<th>D_{4h}^{14}</th>
<th>P4_2/mnm</th>
<th>a=b/Å</th>
<th>4.587</th>
</tr>
</thead>
<tbody>
<tr>
<td>c/Å</td>
<td>2.954</td>
<td>Ti-O distance/Å</td>
<td>1.946 ; 1.976</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Anatase</th>
<th>D_{4h}^{19}</th>
<th>I4_1/amd</th>
<th>a=b/Å</th>
<th>4.587</th>
</tr>
</thead>
<tbody>
<tr>
<td>c/Å</td>
<td>2.954</td>
<td>Ti-O distance/Å</td>
<td>1.946 ; 1.976</td>
<td></td>
</tr>
</tbody>
</table>

Figure 1.1: Ball-and-Stick model of the rutile (a) and anatase (b) unit cells, seen along the [010] direction, with relevant lattice parameters and Ti-O bond lengths (in Å). Color coding: Grey=Titanium, Red=Oxygen

octahedral moieties are stacked with the long axis along the [001] crystal direction, and share edges along the [100] and [010] directions. Anatase octahedra are also significantly distorted, with the shorter Ti-O bonds out of the equatorial [001] plane.

Calcination of titanium salts at moderate temperatures forms predominantly anatase, that is converted to rutile at higher temperatures [17]. Even if the rutile crystal phase is the most stable form at all the temperatures, the anatase phase is often preferred due to its higher performance in photocatalytic devices [18, 19, 20]. Anatase has in fact a larger bandgap and an higher conduction band edge energy. This leads to a higher Fermi level and $V_{oc}$ in DSSCs for the same conduction band electron concentration. Anatase is also the preferred form for catalytic applications, due to its higher surface area than rutile [17] and to the longer lifetime of the photoexcited carriers [21].

Transmission electron microscopy measurements revealed that crystalline anatase particles are formed exposing mainly the (101) surface [22]. The surface energies of the (101), (100), (001) and (101) surfaces of anatase were also investigated in one of the first theoretical studies of TiO$_2$ interfaces [23].

The equilibrium shape of the anatase crystal exhibits (100)/(010) and (101)
1.2. TiO$_2$: Properties and Applications

(a) Rutile, along 100 direction  
(b) Rutile, along 001 direction  
(c) Anatase, along 100 direction  
(d) Anatase, along 001 direction

Figure 1.2: Tridimensional models of the rutile and anatase crystals, showing the stacking of the TiO$_6$ octahedra. Empty channels can be noticed along the [001] rutile direction and along the [100] direction (and equivalent [010] direction) of anatase.

interface planes, which are also found in powder materials. Consistently with experimental evidence, the (101) surface was computed to be thermodynamically most stable[24], even more stable than any of the rutile surfaces. It is therefore adopted in the following chapters as the prototypical TiO$_2$ interface.

A detailed account of the most recent modelling results for the TiO$_2$ phases is reported in Section 1.5

1.2.3 Electronic Structure and Defects

Titanium dioxide is a semiconductor material, with a valence band formed of 2$p$ orbitals of the oxygen anions, while the conduction band is formed of empty 3$d$ states of the Ti cations, as shown in Figure 1.3. The difference between the energy at the top of the valence band ($E_V$) and at the bottom of the conduction band ($E_C$) is the so called electronic band gap, that can be measured by photoemission experiments and is related to a one-particle descript-
1. Introduction

Figure 1.3: Anatase density of states (DOS) diagram, showing the oxide valence and conduction band. Black, continuous line: occupied states (valence band). Black, dashed line: unoccupied states (conduction band). Left Side: O contribution to the DOS. Yellow: O 2p orbitals. Right Side: Ti contribution to the DOS. Blue: Ti 3d orbitals. Green: Ti 3f orbitals.

...tion. The optical band gap is instead given by light absorption experiments, and is intrinsically characterized by the copresence of an excited electron and of the corresponding hole. Different experiment types can then provide information on two different physical quantities: while there is general agreement on the optical TiO₂ gap (3.2 eV), an exact value of the electronic gap for anatase proves to be more difficult to determine, and is estimated to be around 3.7-3.9 eV [25].

TiO₂ is easily reducible, leading to the creation of color centers and evident color shift from transparent to blue and, eventually, black[26]. The presence of such defects enhances the material conductivity, and, as suggested by recent studies, modulates important properties such as light absorption and photocatalytic reactivity and selectivity [27, 28]. Reduction can be achieved within a single phase, with formation of point defects in the crystal lattice. Some of the most common reducing defects are:

i) Ionized Oxygen Vacancies: oxygen anions missing from the lattice site.

\[ O_\circ \Leftrightarrow V_O^{**} + 2e' + \frac{1}{2}O_2 \]

ii) Ionized Metal Interstitials: metal cations in an interstitial site. Can be either self-interstitials (i.e. Ti cations) or hetero-interstitials, as, for example Niobium or Lithium.

\[ 2O_\circ + Ti_{Ti} \Leftrightarrow Ti_i^{***} + 4e' + O_2 \]
\[ Li \Leftrightarrow Li_i^* + xe' \]
iii) **Excess Electrons or Electron-Hole pairs**: injected from neighboring reducing species, as is the case for DSSCs, or generated upon light excitation, as for applications in water photolysis.

\[
[DyeMolecule]^* \rightleftharpoons [DyeMolecule]^+ + e'_\text{TiO}_2 \\
h\nu \rightleftharpoons e'_\text{TiO}_2 + h^*_{\text{TiO}_2}
\]

The balance of defects is quite complex and depends on temperature, gas pressure and material preparation technique (i.e. quenching, presence of impurities). The defect diffusion mechanism is also different: vacancies migrate via an oxygen site exchange mechanism, while excess metal ions diffuse in the interstitial cavities[2]. In addition, the excess electrons (e') originating from the ionized defects can either spread over several Ti centers, with small or negligible lattice distortion, or localize on an individual Ti cation, with formation of a polaron, i.e. a formal 3+ center and corresponding lattice distortion[29]. Depending on the localization of the electron, two main possible charge migration mechanisms can be considered: a hopping mechanism, for localized charges, and a conduction band-like mechanism, if the charge is delocalized[30]. The two mechanisms are regulated by different dynamics, so that, to correctly evaluate charge mobility, and therefore the material conductivity, a good understanding of the exact nature of the excess electrons is necessary.

### 1.3 Dye Sensitized Solar Cells

Dye sensitized solar cells (DSSC) provide a technically and economically alternative concept to present day p-n junction photovoltaic devices, due to potential low cost, manufacturing and design flexibility and potential to partially overcome the thermodynamic limits affecting single p-n junction devices. Since the publication of the key paper by O’Regan and Grätzel at the beginning of the 1990s[8], the dye sensitized solar cell efficiency underwent a rapid climb, followed by a slow settlement at around 10-12% in recent years[31], with a record performance of ~15% reported in 2013[32]. Therefore, to make DSSCs devices competitive with other solar cell technologies, the demand for further insight is still strong.

### 1.3.1 Operating Principle

A schematic presentation of the operating principles of the DSSC is given in Figure 1.4. The core of the device consists of a mesoporous semiconductor
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Figure 1.4: Schematic representation of the energy levels and device operation of DSSCs (adapted from Ref.[33]).

substrate, usually composed of TiO₂ nanoparticles, on which a monolayer of dye molecule is adsorbed. Upon light excitation, dyes inject electrons into the oxide conduction band, and are in turn regenerated by reducing species present in the surrounding electrolyte. The most common electrolyte employed in DSSCs is a liquid solvent (or solvent mix), containing the I⁻ /I₃⁻ redox couple[34, 35, 36] as dye regenerator.

The overall solar-to-electrical energy conversion efficiency (η) for a solar cell is given by the photocurrent density measured at short-circuit (J_{sc}), the open-circuit photovoltage (V_{oc}), the fill factor of the cell (FF) and the intensity of the incident light(P_{in}):

$$\eta = \frac{J_{sc}V_{oc}FF}{P_{in}}$$

The fill factor can assume values between 0 and less than 1 and is defined by the ratio of the maximum power (P_{max}) of the solar cell per unit area divided by the V_{oc} and J_{sc}:

$$FF = \frac{P_{max}}{J_{sc}V_{oc}}$$

The maximum power is obtained as the product of the photocurrent and photovoltage at the voltage where the power output of the cell is maximal.

1.3.2 Photosensitizers

The photosensitizer plays a fundamental role in the device operation. It is normally provided with functional groups (-COOH, -H₂PO₃, -SO₃H), acting as anchors to bind the light harvesting unit to the semiconducting oxide [37]. In addition to the requirements of photo, electrical and thermal stability, the
structure of the sensitizer is optimized in order to either avoid unfavorable dye aggregation or to control it to improve the device performance [38]. Many different light harvesting units have been proposed and investigated in the past: the most common are metal complexes, often Ru(II) complexes, in which light adsorption is due to a metal to ligand charge transfer mechanism. The ligands normally have also the additional role of i) anchor the light harvesting unit to the oxide and ii) extend and tune the light adsorption spectrum.

A wide range of possible ligands have been explored in the years, to increase the molar extinction coefficient, control dye aggregation on the semiconductor, and optimize the redox potential of the photosensitizer [39, 40]. The N3 and N719 dyes (Figure 1.5) are now considered as standard reference for performance and stability testing of novel ligand molecules [9].

Other studies have focused on overcoming the limited spectral adsorption of Ru(II) based dyes, by investigating other metal centers (Os, Re, Fe, Pt, Cu), different ligand structures (porphyrins, phthalocyanines) [41] or metal-free organic dyes, mostly with a donor–π–acceptor structure [42, 43]. Organic dyes are particularly promising due to the design flexibility and lower cost and environmental issues, if compared to transition metal complexes. In addition, they often have an higher molar extinction coefficient than metal complexes, which makes them suitable for thin film DSSC devices. A significant improvement in DSSC performance, up to ~15% PCE, to was recently obtained by Grätzel and co-workers with a novel approach based on hybrid perovskites (CH$_3$NH$_3$PbX$_3$, X=Cl, Br, I) as a light harvesting phase covering the semiconductor oxide [44, 32].

The adsorption modes of dyes on semiconductor surfaces are very important for the DSSC efficiency and stability, as desorbed dyes can lead to an

![Figure 1.5: Metal-ligand complexes used as reference sensitizer in dye sensitized solar cells. Panel (a): cis – diisothiocyanato – bis(2,2 – bipyridyl – 4,4 – dicarboxylicacid) ruthenium(II), or N3 dye. Panel (b): cis – diisothiocyanato – bis(2,2 – bipyridyl – 4,4 – dicarboxylato)ruthenium(II)bis(tetrabutylammonium), or N719 dye.](image-url)
unwanted filter effect, dye degradation and decrease of the counter electrode performance\cite{45}. Different binding geometries and their relative stabilities are thoroughly investigated in Chapter 3.

1.3.3 Solvents and Additives

Liquid electrolytes were the first to be introduced and developed in DSSCs. Key requirements for the basic solvent/mix of solvents are chemical stability and low viscosity, to facilitate transport mechanisms. In addition, it should not cause dye dissolution or detachment from the semiconductor and have good solvating properties for the redox couple and the additives usually employed to improve the materials properties. Water and protic solvents are likely to cause hydrolysis of metal complexes, and therefore are not usually employed in standard DSSCs. A large number of possible organic solvents have been investigated: among them, nitriles are chosen to obtain an higher boiling point and minimize solvent evaporation\cite{9}. While $3-\text{methoxypropionitrile}$ shows good performance and is one of the most common electrolyte solvents, record cells were created employing $\text{acetonitrile}$ (ACN), which therefore is considered as a standard for electrolyte research.

To overcome leakage problems, as well as the system instability due to the corrosive nature of the electrolyte solution, various types of quasi-solid/solid-state electrolytes have been developed during the past two decades\cite{46, 47}. Devices relying on such materials are often referred to as solid-state DSSCs (ss-DSSCs), and do not contain a dye regenerating redox couple, but the dye regeneration is achieved via an hole hopping mechanism through the electrolyte to the counter electrode. One of the limiting factors in using (quasi)solid electrolytes is that they demonstrate poor pore filling properties, and thus do not penetrate enough to completely contact all the sensitized surface \cite{48}. A promising candidate to overcome this limit is the

\begin{figure}[h]
\centering
\includegraphics[width=0.8\linewidth]{figure16.png}
\caption{2,2',7,7'-tetrakis(N,N-di-p-methoxyphenylamine) - 9,9' - spirobifluorene, or spiro-MeOTAD, a reference electrolyte for solid-state DSSCs.}
\end{figure}
so called spiro-OMeTAD molecule (Figure 1.6), deposited as an amorphous phase on the sensitized oxide, yielding a pore filling factor of 60-80% [49]. However, solid state-DSSCs still demonstrate incomplete light harvesting and lower internal quantum efficiency, resulting in lower current densities than liquid-based DSSCs. Development of new transport models, designs and hole transporting materials are therefore required to improve the performance of solid state devices for practical application [33].

Device performance in DSSCs can be improved in different ways: the most common one is to add a mixture of additives to the electrolyte solution. For example, the cation concentration at the semiconductor/electrolyte interface exerts a profound influence on the mechanism and efficiency of the electron transfer reactions, as discussed in an exhaustive review presented by Watson and Meyer [12]. Improved DSSCs performance (both liquid and solid state devices) in the presence of cations may depend on a series of factors:

i) Energetics of the semiconductor film.
   Li+ cations alter the conduction band level of the oxide ($E_{cb}$), shifting it towards more positive potentials and therefore enhancing the electron injection efficiency from the excited dye molecule. Increasing the Li+ concentration from 0 to 1 M lowers $E_{cb}$ by more than 1 eV. This effect is reversible [50].

ii) Energetics of the dye orbitals.
   While the reduction potential of the sensitizer molecule is almost pH-independent in solution, a pH dependency is observed when the dye is attached to the TiO$_2$ surface [51].

iii) Influence of cations on the sensitizer surface-attachment geometries and equilibrium.
   It was deeply investigated for protons during the early development of dye cells, with pH dependence studies. Dye desorption was observed at basic pH, highlighting the influence of protons on the attachment equilibrium [12]. Theoretical and (ATR)-IR results also provide support for a protonation-dependent binding equilibrium of the N3 sensitizer dye molecule [52]. An account of the possible influence of other cations is, at present, missing.

iv) Electron injection efficiency and dynamics.
   It depends on the energetic shifts described in the above i) and ii) points, but also on the dye quantum yield and excited state lifetime, that depend on the environment and thus on the presence of cations [53]. However, those states are particularly difficult to characterize and correlate with the cation presence.

v) Charge recombination efficiency and dynamics.
As for electron injection, also charge recombination has many components. The fast component is interestingly independent of pH or cations, even if the energetics and thus the driving force are influenced by pH. So it can be said that the fast component is driving-force independent [54].

vi) Iodide oxidation.
Cation dependent I- oxidation has been reported: an increase in Li+ concentration leads to a faster I- oxidation. Probably cation adsorption facilitates ion pair formation on the TiO$_2$ surface, which greatly accelerates the oxidation rate[55].

Among the factors reported above, the energy shift in the semiconductor band edge towards more positive potentials is dominant (point i) and very often reported. Another additive, 4-tert-Butylpyridine (TBP), was first applied in liquid-based DSSCs by Grätzel and co-workers in 1993 [56], in combination with LiI-based electrolytes, demonstrating a remarkable increase in $V_{oc}$. It was shown[57] that TBP plays a role in reducing recombination phenomena, by shifting the titania band edge towards higher energies. So, although TBP and Li$^+$ ions have opposite effects on the conduction band and trap states, and thus on the kinetics of electron injection and recombination, they are commonly combined as additives in solar cell electrolytes. Additional organic co-adsorbents can be introduced to improve the overall device performance: in 2012, a remarkable solar-to-electrical power conversion efficiency of 11.4 % was achieved by Han et al. [58], by adding novel donor-$\pi$-acceptor molecules to the overall device architecture. Such molecules were designed to adsorb on the oxide surface, from where they effectively overcome the competitive light absorption by the $I^-/I_3^-$ redox couple, avoid dye aggregation, and reduce charge recombination.

The replacement of the traditional $I^-/I_3^-$ redox couple with other compounds, that deliver higher $V_{oc}$ values, is another valuable strategy to obtain high device performances. A promising substitute has proven to be the Co(II/III)-based redox couple, if used in presence of specifically tailored dyes, designed to reduce the high charge recombination rate that limits the use of Cobalt complexes: in this way, the record performance of 12.3% for liquid-based device was obtained in 2011 by Grätzel et al [31].

### 1.3.4 Role of the semiconductor

On a smooth semiconductor substrate, a monolayer of sensitizer molecules adsorbs less than 1% of incident light, and attempts to employ multilayers of dyes generally prove unsuccessful [8]. Only by increasing the overall device
surface area, a larger number of dye molecules can be adsorbed directly at the interface between semiconductor and electrolyte, so that the light harvesting efficiency is increased. The use of a nanostructured, mesoporous electrode, has therefore been crucial to make the practical application of dye cells feasible.

Many binary metal oxides have been considered as substrate (ZnO, SnO₂, Nb₂O₅)[59, 60, 61], as well as ternary compounds (SrTiO₃, Zn₂O₄)[62] and core-shell particles (ZnO coated TiO₂)[63]. However, TiO₂, the originally proposed DSSC substrate, still gives the highest performance[64].

State-of-the-art cells have a complex semiconductor architecture, composed of different layers:

i) A thick coating TiO₂ layer (~ 50nm), that prevents contact between the electrolyte and the glass electrode.

ii) The active layer, composed of nanometric TiO₂ particles (~ 20nm) covered in light harvesting molecules.

iii) A thin, ultrapure coating of TiO₂, increasing the overall roughness of the system and therefore dye adsorption.

iv) An upper light scattering layer, with sub-μm sized pores.

The nanocrystals of the active layer are not electronically doped and the electrons photoinjected from the dye molecules are charge compensated by the ions in the electrolyte. The particles, therefore, do not have an internal electrical field and do not display any significant band bending. In such conditions, electron transport occurs by diffusion, driven by a concentration gradient[65]. The measured value of the diffusion coefficient in the nanostructured electrodes is orders of magnitude lower than that determined for single-crystalline TiO₂ anatase (~ 0.4 cm²s⁻¹)[18]. These observations can be explained with a trapping model [66], that includes the presence of localized trap states below the conduction band, from which they can escape by thermal activation.

Experimental results show trap states of different nature, ranging from shallow traps to electronic states well below the conduction band edge. The origin of the trap states is probably due to a series of different factors: defects located at the semiconductor/electrolyte interface, at the grain boundaries or in the deeper bulk-like layers, or coulomb trapping due to local field effects[67, 68]. The nature, location and density of defect states depends on the nanoparticle size, with bigger nanoparticles demonstrating lower trap state density and increased electron diffusion coefficients. On the other hand, as discussed above, smaller nanoparticles exhibit a larger surface area, with higher light harvesting efficiencies. Tailoring the nanocrystal size in order to achieve a good balance is therefore crucial for improving the device performance.
1.4 TiO$_2$ for Catalytic Applications

1.4.1 Photocatalytic Mechanisms

On of the major application of TiO$_2$ is in photocatalysis: UV photoexcitation of the oxide results in the formation of an electron-hole pair, as demonstrated by electron paramagnetic resonance spectroscopy (EPR)[69], photoluminescence (PL)[70], and O$_2$ photodesorption[71].

\[
\text{TiO}_2 \xrightarrow{h\nu} e^-_{\text{TiO}_2} + h^+_{\text{TiO}_2}
\]

The resulting charge carriers undergo a series of trapping and recombination steps, but at least part of them migrates to the surface, where they are available for a reaction with adsorbed species[72], as illustrated in Fig. 1.7. Charge carriers reaction with surface adsorbed organic molecules normally causes the formation of radical species, eventually leading to complete degradation into CO$_2$ and H$_2$O. This photocatalytic decomposition of polluting compounds is applied in wastewater treatment, for the production of self-cleaning filters employed in the automobile and construction industries, and to coat surfaces with an antibacteric material that can be activated by UV light [73, 74].

A similar mechanism is also employed for photocatalytic water splitting, in order to produce H$_2$, which, used as fuel, possibly constitutes another important source of renewable, carbon-free energy[75]. However, the role of the charge carriers is different in the two cases [7]. In photocatalytic water/air purification, valence band (VB) holes are normally the key elements that induce radicalization, oxidation and decomposition of contaminants. On the other hand, when photocatalysis is applied to perform water-splitting for the production of hydrogen, the reducing CB electrons become important as their role is to reduce protons to hydrogen molecules. The CB
level should be more negative than the hydrogen evolution level $E_{H_2/H_2O}$ to initiate hydrogen production. In general, this is the case, so that water photolysis is electrochemically feasible, but $H_2$ evolution on clean TiO$_2$ surfaces is hindered by the presence of a large overpotential, and the clean, unaltered oxide surface results inert. Continuous efforts have been made to promote the photocatalytic activity as well as to enhance the visible light response. As an example, the use of hole scavengers or sacrificial reagents (e.g. EDTA, ethanol, methanol, lactic acid) can enhance the photocatalytic electron/hole separation resulting in higher quantum efficiency[76]. Electron donors are consumed during the photocatalytic reaction and continued addition of such compounds is required to sustain hydrogen production. Noble metals (Pt, Au, Rh, Ni, Cu) have also been reported to be very effective for enhancing TiO$_2$ photocatalysis [77, 78]. As the Fermi levels of these noble metals are lower than that of TiO$_2$, photo-excited electrons can be transferred from the oxide to surface adsorbed metal particles, resulting in efficient carrier separation.

1.4.2 Black TiO$_2$ for Photocatalysis

One of the major limiting factors in the use of TiO$_2$ for solar light based photocatalysis is its relatively wide band gap, that makes it only active under UV light. Band structure modification, as sensitization with smaller gap semiconductors or elemental doping is thus fundamental to improve the solar light utilization efficiency. In particular, ad hoc reduced TiO$_2$ (or "Black TiO$_2"$, see section 1.2.3) is a promising candidate for solar based catalysis, thanks to its high absorption of visible/infrared radiation [79]. Dopants introduce electronic states in various positions in the band gap of TiO$_2$ and lead to different degrees of modification in electrical conductivity[28]. The use of hydrogen gas as doping agent is particularly convenient for its low molecular weight, and thus higher mobility, and, in comparison to other reducing agents, ultra-high-purity hydrogen can also avoid the possibility of integrating dopants from the reducing agent or solvent into the TiO$_2$ structure. Employing hydrogen as a dopant for TiO$_2$, to be adopted for photocatalytic water splitting for $H_2$ gas production might seem counterintuitive, but several studies demonstrate that hydrogen-treated TiO$_2$ is much more active for solar light driven reactions, increasing in the overall device efficiency. Such improvement can be attributed to increased optical absorption of the material (Figure 1.8), but also to the presence of surfacial Ti-H bonds, with a key role in electron-hole separation[80].

A possible TiO$_2$ hydrogenation method is exposure of the amorphous oxide to an high-pressure, hydrogen rich atmosphere at elevated temperature. This is however of little effect for crystalline titania, that on the other hand shows the best photocatalytic activity[81]. Another hydrogenation strategy,
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(a)

Figure 1.8: Panel (a): UV-vis adsorption spectrum of undoped and H-treated TiO$_2$, demonstrating the higher adsorption efficiency of the doped material. Panel (b): time dependent hydrogen evolution efficiency upon visible light irradiation, showing the consistently better performance of the doped material. Image obtained from Ref.[80]

achievable also in milder conditions and also suitable for crystalline materials is to rely on hydrogen spillover i.e. transfer of an hydrogen atom from a noble metal nanoparticle (Pt, Pd, Rh, Ru) to the oxide surface. The H$_2$ molecule is at first chemically adsorbed and dissociated on the metal, and then the atomic H species migrates to the oxide support. In the case of TiO$_2$, spillover of hydrogen to the support results in full or partial reduction of the oxide and surface protonation. After the initial reduction of a Ti$^{n+}$ cation to a Ti$^{(n-1)+}$ cation at the metal-support interface, electrons can move over the surface or into the bulk of the compound. At the same time, protons can move between neighboring oxide ions, either concurrently with the electron migration or incoherently, depending on the interaction strength of the two charges. When the reduction moves away from the metal-support interface, the reoxidized metal cation at the periphery of the metal particle can be reduced by another H atom. The extent of the reduction of the metal oxide depends on the activation energy of the proton and electron migration, so that a careful understanding of the transfer mechanism and energetics is important.

1.5 TiO$_2$ Modelling: State of the Art

1.5.1 Advantages of first Principles Modelling

From the overview given in Section 1.3 and 1.4 , it appears clear that the introduction of specifically designed additives, co-adsorbents and dopants plays an important role in enhancing the overall performance of TiO$_2$ based devices.
In this context, an atomistic model for the different components of the system provides a better understanding of their interplay and proves to be a fundamental tool to rationalize and suggest new strategies for future development. In addition, modelling the main interactions in an electrochemical device as dye cells or photocatalytic systems, requires one to model electron transfer phenomena, making an explicit treatment of electrons by a proper quantum chemical treatment mandatory. In order to set up an approach to screen novel candidates, any method introducing empirical parameters not straightforwardly extendable to novel materials has to be excluded. Considering the high complexity of the systems to be modeled, DFT-based methods appear as a natural choice due to their appealing performance to accuracy ratio [82]. One of the most common approaches to computational modelling is to adopt a stepwise procedure [83], where one first needs to accurately simulate the individual system components. In this way the correct geometrical structures can be computed, as well as the semiconductor conduction band energy and/or density of states, band gap and optical absorption spectra. Single elements are then combined together, starting from a minimal model consisting of the semiconductor and one defect, dopant or surface adsorbate. Increasing the number of system components yields a more realistic system representation, but it will also increase the simulation complexity, with a variety of configurations and interactions to take into account.

As a consequence of its technological relevance, extensive theoretical investigation and modelling of TiO\(_2\) was carried out in the past decades. The existing literature can be divided into two main topics, that will be discussed in the following sections:

i) Investigation of the bulk TiO\(_2\) properties, for intrinsic or doped systems, usually modelled with full 3d periodicity.

ii) Investigation of interfacial TiO\(_2\) reactivity, using a slab model, normally employing single probe molecules.

### 1.5.2 Bulk TiO\(_2\) from ab Initio

One of the most interesting and challenging aspects of TiO\(_2\) is its complex and varied electrochemistry, that depends on the crystal phase, but also on the doping level and on the system treatment. Intense investigations of the two common TiO\(_2\) phases, anatase and rutile, have lead to contrasting results regarding charge mobility and defect properties. Excess electrons generated by impurities, defects or photoexcitation can either localize on an individual Ti cation, inducing a formal 3+ charge and a corresponding lattice distortion, or spread over several Ti centers, with small or negligible lattice distortion. Mobility, EPR and lattice vibration studies report evidence
for the existence of small polarons in rutile [30, 84, 85], confirmed by DFT results [86, 87, 88, 89]. Other works emphasize the possibility of a dual behavior of rutile, with the delocalized solution almost energetically equivalent to self-trapped electrons [29, 90]. The situation is more complex in anatase, with both theoretical and experimental works reporting charge delocalization over several titanium lattice ions [91, 86, 88, 87], while other describe stable small polarons [92, 93]. A recent experimental paper also proposes a dual charge behavior, as a function of the dopant concentration [94]. The dependence of the nature of the solution on the defect type and concentration is therefore crucial to the discussion. So far, the computational effort required to carry out accurate \textit{ab initio} simulations of realistic TiO$_2$ systems limited theoretical studies to a small number of atoms and consequently, when introduced, high impurity concentrations. A consistent model for predicting the material behavior independently of the system size has yet to be provided. It is also important to emphasize that standard DFT functionals (local density or general gradient approximations) often fail in computing the electronic structure of metal oxides. A more detailed description is given in Section 1.6.4. A similar problem arises in the simulation of highly conjugated organic molecules [83], such as some of the most common donor-$\pi$-acceptor dyes and polymeric electrolytes, that are at the basis of the promising solid-state-DSSC technology. While the adoption of the DFT+U method, which replaces the onsite Coulomb interaction within the chosen functional with a Hubbard term by means of a tunable parameter (U), has proven to be successful for opening the TiO$_2$ band gap between occupied and unoccupied states [95], the problem of providing a unified modelling of the electronic structure and excited states of the joint dye/electrolyte/semiconductor interface is still unsolved and will require a more dedicate approach based on post GGA descriptions.

1.5.3 Interface Models: Anatase (101)

Regarding interface modelling, initial studies concentrated on the Rutile phase, and to day, rutile (110) is one of the most studied single crystal surfaces. Its $1 \times 1$ termination is considered a prototypical metal oxide interface. This is also partially due to the higher availability of highly pure rutile crystals, so that for rutile, a larger amount of experimental data is available for comparison with modelling results. However, as explained in Section 1.2.2, the anatase phase is often preferred in applications, due to its better performance. A good description of the anatase surface can be obtained by adopting a \textit{slab model}: the system is built so that the (101) surface of the crystal lays perpendicular to the z direction and it is exposed to the environment, while the x and y directions are periodically repeated, in order to better resemble
the bulk properties, as shown in Figure 1.9. Even if the anatase (101) inter-
face undergoes a certain level of relaxation, the original bulk structure is ba-
sically retained (cfr. Figure 1.10). The clean surface has a characteristic saw-
tooth profile, that exposes, along the [010] direction, alternating rows of five-
fold and sixfold coordinated titanium cations, as well as twofold and three-
foldcoordinated oxide anions. The reactivity of the (101) interface was tested 
with adsorption of a range of small molecules, such as hydrogen[96, 97], 
water[98, 99, 100, 101], acetonitrile[102, 103], methanol[104, 105], formic acid 
[106, 107], pyridine[108], phosphonic acids[109] and metal atoms [110]. In
general, the interface structure is not perturbed by the interaction with the adsorbates, that in turn, can retain their molecular form (water, acetonitrile) or dissociate (acid molecules). However, to correctly compare and relate theoretical and experimental data, realistic model systems have to be considered, taking into consideration the adsorbate concentration and addressing the role of solvent molecules (if present). A comprehensive study of the TiO₂-adsorbate-solvent interface, including explicit treatment of the surrounding liquid molecules and free energy calculations of the adsorption-desorption processes on the surface is challenging, and will be presented in this work.

1.6 DFT Fundamentals

In recent years, Density Functional Theory (DFT) has become a popular tool for modelling both molecular and solid state systems. As introduced in the previous chapter, this is mainly due to the good balance between computational cost and accuracy, allowing to treat systems up to a few thousand atoms without resorting to empirical parameters. Aided by the increased availability and power of computational resources, a variety of simulation packages has been developed and made available. The relevance of DFT was also recognized with a Nobel Prize in Chemistry awarded in 1998 to Walter Kohn "for his development of the density functional theory" and John A. Pople "for his development of computational methods in quantum chemistry".

This section presents some of the fundamental aspects of DFT, with particular focus on its application and limits as a modelling tool for semiconductors. Strategies to overcome such limits are presented in the second part, while the last section is dedicated to methods for computing activation energies in chemical reactions.

1.6.1 Hohenberg-Kohn Theorems

As the name suggests, the main aspect of Density Functional Theory is the description of a system of interacting electrons through a single variable, the electron density. This concept was already introduced by Thomas and Fermi in the 1920s, and theoretically formalized in 1964 with the two Hohenberg-Kohn theorems[111].

I- The electron density \( \rho(r) \) determines the external potential, within an additive constant.

Since the Hamiltonian (\( \hat{H} \)) is specified by the external potential (\( \hat{V}_{\text{ext}} \)) and by the total number of electrons (N), that can also be computed from the density by spatial integration, it follows that the electron den-
sity uniquely determines the Hamiltonian operator, and thus, the system wave functions ($\Psi$). The electron density can therefore be used as a variable to solve the Schrödinger equation and compute the electronic properties of a N-electron system.

II- For any positive definite trial density $\rho_t$ such that:

$$\int \rho_t(r) dr = N$$

then:

$$E[\rho_t] \geq E_0$$

where $E_0$ is the exact ground state density and $E[\rho_t] = \langle \Psi_t | H | \Psi_t \rangle$

This theorem establishes a variational principle, stating that the density for which the energy functional reaches the global minimum has to be the ground state density. In other words, the ground state energy corresponds to the minimum of some density functional $E[\rho]$ subject to the constraint that the density contains the correct number of electrons.

1.6.2 The Energy Functional

From the theorems in the above section it is established that there is a functional $E[\rho]$, which, if its form were known, could be minimised to obtain the exact ground state density and energy.

From the Schrödinger equation:

$$\hat{H} \Psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N) = E \Psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)$$

$$\hat{H} = -\frac{1}{2} \sum_i \nabla_i^2 + \hat{V}_{ext} + \sum_{i<j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

it can be seen that the energy functional contains three terms: kinetic energy, interaction with an external potential and electron-electron interaction. The energy functional $E[\rho]$ may therefore be written as the sum of such contributions:

$$E[\rho] = T[\rho] + V_{ext}[\rho] + V_{ee}[\rho]$$

If those terms are known, direct minimization of the energy would be possible. However, only the interaction with an external potential can be exactly computed:

$$V_{ext}[\rho] = \int \hat{V}_{ext} \rho(\mathbf{r}) d(\mathbf{r})$$
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The kinetic and electron-electron interaction are unknown, and have to be approximated. This is the reason why DFT is in principle an exact formalism, but becomes approximated in practice.

A good way to approximate those terms was introduced by Kohn and Sham, who proposed a different partitioning of the energy functional, based on a fictitious system of N non-interacting electrons. Such system is described by a single determinant wavefunction in N orbitals \( \phi_i \). The kinetic energy of this system \( T_s \) is known exactly:

\[
T_s[\rho] = -\frac{1}{2} \sum_i^N (\phi_i | \nabla^2 | \phi_i)
\]

Additionally, the classical Coulomb term, which is a component of the electron-electron interaction term can also be computed. This term is also called Hartree energy.

\[
V_H[\rho] = \frac{1}{2} \int \rho(r_1)\rho(r_2) \frac{|r_1 - r_2|}{r_1 - r_2} dr_1 dr_2
\]

The energy functional can be rearranged:

\[
E[\rho] = T_s[\rho] + V_{ext}[\rho] + V_H[\rho] + E_{xc}[\rho]
\]

Where all the terms can be exactly computed, except for the exchange and correlation functional, which includes the error made i) in considering the kinetic energy of a non-interacting electron system \( T_s \) and ii) in considering a classical Coulomb term to approximate the electron-electron interaction.

\[
E_{xc}[\rho] = (T[\rho] - T_s[\rho]) + (V_{ee}[\rho] - V_H[\rho])
\]

Exchange arises from antisymmetry due to the Pauli exclusion principle, and correlation accounts for the remaining many-body effects that need many determinants to be fully described. However, the form of exchange-correlation in terms of the density remains unknown and it is necessary to use approximations.

1.6.3 Approximations for the Exchange and Correlation Functional

A variety of approximations for \( E_{xc}[\rho] \) has been developed, and selecting one or the other depends on the focus and the aim of a particular study. In this context, comparison with experimental data and with results from more accurate theory is important, as well as knowledge of derivation and structure of a particular functional.

One of the simplest approaches is the Local Density Approximation (LDA). It is based on the assumption that the exchange and correlation functional
of an inhomogeneous system can be approximated as a simple function of the local charge density.

$$E_{xc}[\rho] \approx E_{xc}^{LDA}[\rho] = \int \rho(\mathbf{r}) \epsilon_{xc}(\rho(\mathbf{r})) d\mathbf{r}$$

For a given local density $\rho(\mathbf{r})$, $\epsilon_{xc}(\rho(\mathbf{r}))$ is taken to be the exchange and correlation energy of an uniform gas with density $\rho$, and can be separated in exchange and correlation contributions. In practice, the energy density of the inhomogeneous material is assigned a value from the known exchange-correlation energy density of the homogeneous electron gas, with no regard to location or variations of the inhomogeneous density. Despite its simplicity, LDA has proven in many cases to be a good approximation to compute crystal systems structures and vibrational frequencies. However, this approach is adequate only for systems with slowly varying densities, and performs poorly for molecular systems. It was proven that it overestimates binding energies, and consequently, energy barriers in diffusion and chemical reactions result biased.

An extension of LDA is the General Gradient Approximation (GGA), that also takes into account the gradient of the electronic density, and thus its local variations (semi-local approach).

$$E_{xc}[\rho] \approx E_{xc}^{GGA}[\rho] = \int \rho(\mathbf{r}) \epsilon_{xc}(\rho, \nabla \rho) d\mathbf{r}$$

The exact form of $\epsilon_{xc}(\rho, \nabla \rho)$ is unknown, and a number of different approximated functionals were developed to include the gradient. Among those, the one developed by Perdew, Burke and Ernzerhof (PBE functional) [112] is one of the most frequently adopted in the physics and solid state community. The BLYP functional, that combines the exchange functional firstly developed by Becke[113] with the correlation functional by Lee, Yang, and Parr [114] is instead widely employed for DFT calculations in the chemistry community. With respect to LDA, GGA-based functionals improves significantly on the description of the binding energy of molecules[115, 116], energy barriers[117] and structural energy differences[118].

### 1.6.4 Limits of DFT

Despite its popularity, conventional local and semi-local DFT is not applicable to all chemical systems. This is not due to a flaw in the theory, but to the limits of the approximations introduced in the exchange-correlation term. In addition, a systematic approach for constructing functionals is currently missing, so that there is no universal way to evaluate functional performance or to achieve a guaranteed improvement.

Two main sources of error are present:
i) Delocalization error: dominating Coulomb term that forces charges apart.

This issue becomes clear when computing the dissociation energy of an $H_2^+$ cation: even if the equilibrium bond length is described correctly, the dissociation barrier is much lower than the physical value and the resulting dissociated state consists of two H atoms with half an electron each. In more formal terms, the exact energy of an atom as a function of its charge is a straight line between integer charge values, due to the discrete nature of the electrons. However, approximate functionals are incorrectly convex between the integers, predicting a lower energy for fractional charges[119]. Amongst other possible errors deriving from such behavior, excess charges, such as electrons or holes, result to be overly dispersed. In addition, the band gap of materials is underestimated, introducing errors in computing the electronic properties of semiconductors [120].

ii) Nondynamic correlation error.

Approximate functionals describe covalent bonds relatively well near the equilibrium distance, but their energy is severely underestimated upon dissociation. This is due to a violation of the constancy condition, i.e. the condition that systems with any fractional occupation of degenerate spin states should have an energy equal to the integer-spin states. In fact, approximate functionals do not accurately describe the interaction between the degenerate spin-up and spin-down states, and massively overestimate the energy of fractional-spin states with respect to integer-spin states [121]. Such behavior leads to errors in presence of degenerate (or near degenerate) states, and is a crucial source of error in treating transition metal dimers or in computing magnetic properties, that rely on the accurate computation of single and triplet states.

1.7 Strategies for Modelling Semiconductor Materials

1.7.1 Hybrid Functionals

One of the most popular approaches for a better description of semiconducting materials is the use of Hybrid Functionals. They are constructed by mixing contributions from (semi-)local DFT functionals with exact exchange from the Hartree-Fock (HF) theory. It is in fact known that the exchange energy of electrons with the same spin, which is direct consequence of the Pauli principle, is the predominant contribution to the total exchange correlation energy (85-95%). Therefore, it would be reasonable to expect good results if the semilocal exchange functional is replaced with an exact (Hartree-Fock) equation for exchange energy $E_x$ and further modeled with
the density functionals relative to the small “residue” i.e. the Coulomb correlation energy $E_c$.

$$E_{xc} = E_x + E_c$$

$$E_{xc}^{exact} = -\frac{1}{2} \sum_{\sigma=\alpha,\beta} \sum_{\text{occ}} \int \frac{\phi_{i\sigma}(\mathbf{r})\phi_{j\sigma}(\mathbf{r})\phi_{j\sigma}(\mathbf{r}')\phi_{i\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$$

With $i, j$ = indices of the occupied orbitals and $\alpha, \beta$ = spin indices. However, constructing an exchange and correlation functional in the form:

$$E_{xc} = E_{xc}^{exact} + E_c$$

is suitable only for single atoms and ions, and provide a poor description of chemical bonds in molecules [122, 123]. This is because, even if $E_{xc}^{exact}$ is free of any non-physical self-interaction (or delocalization) error, it also does not contain any nondynamic correlation, that conversely, is taken (at least partially) into account in the semilocal DFT exchange functionals. A better solution is therefore finding a balance between the elimination of self-interaction and the inclusion of the nondynamic correlation. Such result is achieved with hybrid functionals, that in the simplest form, are a linear combination of DFT and HF contributions.

$$E_{xc}^{hybr} = a_0 E_{xc}^{exact} + (1-a_0) E_{x}^{DFT} + E_{c}^{DFT}; \quad 0 \leq a_0 \leq 1$$

Amongst all the various functionals introduced in the years, the PBE0 functional [124] has this simple form, with $E_{x}^{DFT} = E_{x}^{PBE}$ and $a_0 = \frac{1}{4}$. Another popular functional is the more complex B3LYP functional, that relies on three numerical parameters (B3) in combination with the LYP correlation functional[125].

While this functionals prove reliable for the study of molecules, convergence issues arise in the case of solid state calculations, carried out in full 3D or 2D periodicity. This is due to the ‘self-exchange’ interaction of an electron with its replica image in the neighboring cells. In order to avoid such issue, the PBE0 functional can be combined with a truncated Coulomb operator (TC), ensuring rapid convergence at distances bigger than a chosen cutoff radius ($R_c$)[126].

$$g_{TC}(r_{12}) = \begin{cases} 
\frac{1}{|r_1 - r_2|}, & |r_1 - r_2| \leq R_c \\
0, & |r_1 - r_2| \geq R_c 
\end{cases}$$

The HSE (Heyd-Scuseria-Ernzerhof) exchange-correlation functional[127, 128] is instead based on an error function-screened Coulomb potential, with a decaying behavior at large distances.

$$E_{xc} = a_0 E_{x}^{exact,SR}(\omega) + (1-a_0) E_{x}^{PBE,SR}(\omega) + E_{x}^{PBE,LR}(\omega) + E_{c}^{PBE}$$
In this case, in addition to the mixing parameter ($\alpha_0$), there is also an adjustable parameter ($\omega$) controlling the range of the interaction. Hybrid DFT functionals rely on the computation of the exact Hartree-Fock exchange, that is computationally demanding for large systems. Even if the use of a truncated or screening potential reduces the dependence of the computational cost on the system size to a mere quadratic, or in some cases, linear relation, the same can not be said for the quality of the basis functions used to expand the Kohn-Sham orbitals (i.e. the basis set). In fact, the computational cost increases with the fourth power of the number of (primitive) basis functions per atom. This is an important issue, since high-quality results not only require accurate functionals but also good quality basis sets, i.e. basis sets with a large number of basis functions. To make hybrid calculations feasible also for condensed-phase calculations, a possible alternative is to use an auxiliary density matrix method (ADMM) to evaluate the the expensive nonlocal part of the functional (the Hartree-Fock term), while all other energy components are computed with the primary (original) density matrix [129]. The ADMM will be constructed to allow a rapid evaluation of the HFX energy. A correction term is also added to the exchange and correlation functional, to take into account the difference between auxiliary and primary density matrices and ensure that the quality of the calculation is influenced as little as possible by the quality of the ADMM.

One of the major drawbacks of hybrid functionals is their dependence on external parameters, that have to be determined by comparison with experimental data or higher levels of theory. In some cases, variation of the type of functional (e.g. B3LYP vs. PBE0) or even of the mixing parameter ($\alpha_0$) will lead to different and, at times, contrasting results [130], so that an accurate selection of the functional and screening of different properties before fixing the mixing parameters is required to achieve reliable results.

**1.7.2 The EXX-RPA method**

To improve the performance and predictivity of hybrid functionals, comparison with higher levels of theory is sometimes required. Such methods are focused on more accurately computing the electron correlation energy, that is only approximated with (semi)local or hybrid DFT calculations. Amongst all the possible methods to more accurately compute the correlation, the Random Phase Approximation (RPA) is emerging as an attractive alternative, with important advantages. In fact, it includes long-range dispersion[131] (that semilocal functionals neglect), it is non perturbative, and then can be applied to small or zero-gap materials (semiconductors, metals)[132] and it does not rely on any parameterization. The RPA correlation energy is exactly given by the difference of correlated and uncorrelated electronic zero point vibrational energies. In practice, the RPA total energy
1.7. Strategies for Modelling Semiconductor Materials

is typically evaluated in a post-Kohn-Sham fashion[133], i.e. using Kohn-Sham orbitals from a precedent DFT calculation (GGA, hybrid), and can be computed by solving the problem[134]:

$$
\begin{pmatrix}
A & B \\
-B & -A
\end{pmatrix}
\begin{pmatrix}
X \\
Y
\end{pmatrix} = \begin{pmatrix}
X \\
Y
\end{pmatrix} \omega
$$

The dimension of all the matrices is \((N_{occ} \cdot N_{virt}) \times (N_{occ} \cdot N_{virt})\), with \(N_{occ}\) total number of occupied orbitals (indices \(i, j\)...) and \(N_{virt}\) total number of virtual orbitals (indices \(a, b\)...). The \(\omega\) matrix contains the excitation energies \((\omega_i)\) corresponding to the excitation eigenvectors \((X^i, Y^i)\). The \(X, Y\) excitation vectors satisfy:

\[XX^T - YY^T = 1\]

While the \(A, B\) matrices are defined as:

\[A_{ia,jb} = (\epsilon_a - \epsilon_i) \delta_{ij} \delta_{ab} + (\langle ia | jb \rangle)\]

\[B_{ia,jb} = \langle ia | jb \rangle\]

With \(\epsilon = \) Kohn-Sham orbital energy and \(\langle ia | jb \rangle = \) two electron integral in the notation : \(\langle pq | rs \rangle = \int \int \phi_p(r_1)\phi_q(r_2)\phi_r(r_1)\phi_s(r_2)dr_1dr_2\).

The equation for computing the RPA correlation energy is then given by [135]:

\[E^{C_{RPA}} = \frac{1}{2} Tr(\omega - A) = \frac{1}{2} Tr(M^{1/2} - A)\]

\[M = (A - B)^{1/2} - (A + B)(A - B)^{1/2}\]

While the exchange energy is accounted by the exact exchange:

\[E_x = \frac{1}{2} \sum_{ij} \langle ij | ij \rangle\]

The exchange energy has the same form as the exact Hartree-Fock exchange energy introduced in the previous section, but the two values differ in practice, due to the deviation between the Hartree-Fock and the Kohn-Sham orbitals. Together, the exchange and correlation energies defined above define the EXX+RPA method.

A central obstacle for a widespread application of RPA is its relatively high computational cost, if compared to lower level approaches (as GGA or hybrid DFT). In fact, only the most recent advances in the field reduced the formal computational cost from \(O(N^6)\) to \(O(N^4)\), relatively to the system size[133, 136, 137]. Even if a very recent paper demonstrates a promising cubic scaling behavior[138], RPA calculations remain usually feasible for limited numbers of atoms. To avoid unnecessary consumption of computational resources it is therefore advisable to carry out a first structure relaxation with a lower level of theory. In the current EXX-RPA implementation,
1. Introduction

Energy gradients are not available, so that a single point EXX-RPA energy calculation is to be performed on a preliminarily geometry optimized structure. In addition, since EXX-RPA uses KS orbitals from preceding DFT calculations as an input, the result dependence on the starting level of theory has to be carefully assessed. Nevertheless, RPA can prove an useful tool to evaluate the performance of different DFT functionals, and is particularly useful to lower the parameter dependence that affects the results of some hybrid DFT calculations.

1.8 Calculation of Reaction Energies

Computation of the energy barrier to overcome for a given chemical reaction, and therefore its rate, is often a crucial issue in computational chemistry. In the case of TiO$_2$, activated processes may involve phenomena in the bulk, such as the migration of a defect between sites, or surface events, like the adsorption of a given molecule on the substrate. A variety of computational strategies have been developed in the past decades, with different strategies and weaknesses: some methods, such as the metadynamics technique[139], yield a representation of the free energy surface, while others, as the activation-relaxation technique [140], focus on the prediction of a single energy barrier between reactant and product state. In the following sections two of the most relevant approaches are presented in detail. Advantages and possible applications in TiO$_2$ calculations, that motivate their selection for this work, are also presented.

1.8.1 Nudged Elastic Band

The Nudged Elastic Band (NEB) method was developed by Jónsson and co-workers to compute the lowest energy path between the reactant and product basins[141]. The basic assumption of the method is that both the reactant and product states are known. A number of replicas of the system is then prepared and initially located equidistantly on the linear path between reactant and product, obtained by linearly combinating the reactant and product coordinates. The position of the replicas is then relaxed from the linear path towards the minimum energy path, with the following strategy:

i) The replicas are connected by harmonic springs, that keep them almost equally spaced. From this concept comes the name “Elastic Band”. The elastic forces are allowed to act only in the direction parallel to the local tangent.

ii) Each replica experiences the gradient of the potential energy surface, driving them towards the minimum energy path. The gradient forces
are allowed to act only in the direction perpendicular to the local tangent.

As a consequence of such balance, the gradient forces move the elastic band laterally, until the minimum energy path is reached (i.e. no perpendicular forces acting on the band of replicas), while the parallel forces prevent the band from collapsing into the reactant or products basin. This concept is illustrated in Figure 1.11.

The force projection and decomposition is an essential feature of the NEB,

\[
\tau_i = \frac{\mathbf{R}_i - \mathbf{R}_{i-1}}{|\mathbf{R}_i - \mathbf{R}_{i-1}|} + \frac{\mathbf{R}_{i+1} - \mathbf{R}_i}{|\mathbf{R}_{i+1} - \mathbf{R}_i|} ; \quad \hat{\tau} = \frac{\tau}{|\tau|}
\]

The total force acting on an image is the sum of the spring force along the local tangent and the true force perpendicular to the tangent.

\[
\mathbf{F}_i = \mathbf{F}_i^\| - \nabla V(\mathbf{R}_i)|_\perp
\]

When the perpendicular component of the spring force is not included, in some cases the path might form kinks in the region where the parallel component of the NEB is large compared to the perpendicular component. In
order to reduce the kinks the so-called improved tangent NEB (it-NEB) was developed. The improved method is based on a new definition of the local tangent, based only on the image $i$ and on the adjacent image with the highest energy. Another drawback of the conventional NEB method is that, given the equal spacing of the image replicas, is not always possible to exactly estimate the energy of the saddle point. This occurs in particular if the energy barrier is narrow if compared to the length of the NEB, because few images will be located in the proximity of the saddle point. The climbing image NEB (ci-NEB) is another possible modification of the NEB method, that retains information about the shape of the minimum energy path, but it also ensures rigorous convergence to the saddle point. After a few iterations with the regular NEB, the image with the highest energy $i_{\text{max}}$ is identified. In the following iterations, the force acting on such image is given by:

$$F_{i_{\text{max}}} = -\nabla V(R_{i_{\text{max}}}) + 2\nabla V(R_{i_{\text{max}}}) ||$$

This is the full force due to the potential with the component along the elastic band inverted, so that this image moves up the potential energy surface until the saddle point. The maximum energy image is not affected by the spring forces, while the other images are, defining the reaction coordinate around the saddle point. Two or more climbing images can be specified if the MEP appears to have two or more high maxima that are close in energy. The only issue is to have enough images close to the climbing images to get a good estimate of the reaction coordinate.

One of the main advantages of the NEB method is that it is robust and relatively simple, as the only requirement is the geometry reactant and product states, without knowledge of the complete potential energy surface. However, if multiple reaction paths are possible, an approximate idea of the reaction mechanism is also necessary. This is because, in some cases, the starting linear path, built from only reactant and product state, may be a too coarse approximation, leading to a band relaxation towards a reaction path that is not the actual minimal energy path (MEP). A visual interpretation of this concept is shown in Figure 1.12. In this case, the introduction of an extra known point, along the hypothesized MEP between reactant and product state is helpful for a better approximation of the starting path from where to relax the band calculation. The advantage of the NEB implementation is that the extra intermediate points are not kept fixed, but relaxed along with the rest of the elastic band. An exact knowledge of the intermediates geometry is therefore not strictly necessary. In the case of the migration of defects between equivalent lattice sites in TiO$_2$, a rough reaction path is easy to hypothesize and intermediate states can be constructed. If multiple reaction paths are possible, as it occurs for adsorption or movement of molecules on an anatase slab, multiple NEB profiles can be defined by specifying different intermediates. The path with the lowest saddle point would
1.8. Calculation of Reaction Energies

Figure 1.12: Illustration of the NEB limitation: if multiple reaction paths are possible, relaxation of the elastic band starting from the mere linear interpolation between reactant and product states might result in convergence towards a path that is not necessarily the lowest energy path.

...then correspond to the preferred reaction mechanism.

1.8.2 Thermodynamic Integration

Another relevant parameter in computational chemistry is the free energy difference between reactant and product state. This quantity can not be computed with techniques relying on potential energy minimization (such as the NEB method), because these methods do not take into account entropic contributions. Since thermal quantities can not be directly measured in a simulation, a possible strategy is to select a different quantity, that is a derivative of the free energy and could be measured in a simulation. Integration of the chosen quantity along a reversible path between reactant and product would yield the free energy difference of the reaction. This technique is called Thermodynamic Integration (TI)[144]. The advantage of simulations is that the integration is not limited to a physical quantity, but can be carried out over any parameter that characterizes the path. In more rigorous terms, for a given parameter $\lambda$ that describes the Hamiltonian ($H$) of the evolving system (e.g. with a linear relation):

$$H(\lambda) = (1 - \lambda)H_I + \lambda H_{II}$$

with $H_I = \text{describing the initial state (system I)}$ and $H_{II} = \text{describing the final state (system II)}$, so that:

$$\begin{cases} 
\lambda = 0 \ ; \ H(\lambda) = H_I \\
\lambda = 1 \ ; \ H(\lambda) = H_{II}
\end{cases}$$
The free energy difference ($\Delta F$) between system I and II can be obtained by:

$$
\Delta F = (F_{\lambda=1}) - (F_{\lambda=0}) = \int_{\lambda=0}^{\lambda=1} d\lambda' \langle \frac{\partial H(\lambda)}{\partial \lambda'} \rangle_{\lambda'}
$$

Where $\langle ... \rangle_{\lambda'}$ is a statistical average over the equilibrium ensemble corresponding to the value $\lambda'$. This formalism is quite useful, because it expresses the free energy difference in terms of an ensemble average, which can be directly computed in a simulation.

Thermodynamic integration can also be used to compute reaction and activation energies along a reaction path defined by varying a reaction coordinate ($\xi$), that constitutes the chosen thermodynamic integration variable. Some simplifications in the computation can then be made:

i) By using the “Blue Moon Ensemble” [145], the statistical average over an equilibrium ensemble can be replaced by a time average over a constrained trajectory, with the reaction coordinate fixed at special values $\xi(r) = \xi'$. The basic equation then becomes:

$$
\Delta F = (F_{\xi=1}) - (F_{\xi=0}) = \int_{\xi=0}^{\xi=1} d\xi' \langle \frac{dF}{d\xi'} \rangle_{\xi'}
$$

with:

$$
\frac{dF}{d\xi'} = \frac{(Z^{-1/2}[-\Lambda + k_B T G])_{\xi'}}{(Z^{-1/2})_{\xi'}}
$$

$\Lambda$ is the Lagrange Multiplier used to impose the constraint. Z and G are, respectively a re-weighting and geometric correction factor.

ii) In the special case that the chosen reaction coordinate is a simple distance constraint between two nuclei $\xi(r) = |R_I - R_J|$ the parameter Z is a constant and $G = 0$ [146]. This further simplifies the Thermodynamic Integration equation to a form that allows direct computation of the free energy difference and profile with the sole knowledge of the time average of the Lagrange Multiplier used to impose the constraint.

$$
\Delta F = (F_{\xi=1}) - (F_{\xi=0}) = \int_{\xi=0}^{\xi=1} d\xi' \langle \Lambda \rangle_{\xi'}
$$

In the following chapters, Thermodynamic Integration is adopted to investigate adsorption and movement of functional groups on the anatase surface, in presence of an explicit solvent. The presence of solvent surrounding the anatase surface is crucial for a realistic representation of a sensitized
solar cell device, because solvent molecules can compete with functional molecules for surface adsorption. In addition, solvent molecules will surround and interact with any desorbed functional moiety, altering the overall system stability and therefore influencing the computed energy differences. Thermodynamic Integration reveals quite useful for application in computing reaction energies in presence of a liquid solvent, that requires careful assessment of thermal contributions. In fact, if a liquid-phase reaction is analyzed by the NEB method, each replica of the system would be relaxed according only to the gradient of the potential energy surface. The resulting path would be consisting of a series of replica images with a frozen, crystal like, solvent, leading to non realistic reaction energies.

On the other side, Thermodynamic Integration is a fairly complex technique, that requires not only knowledge of the reactant and product state, but also the definition of a reaction coordinate ($\zeta(r)$) as the integration variable. The chosen reaction coordinate should unequivocally describe the evolving system, and, at the same time, should be a linear combination of distances between nuclei, to benefit from the simplification of the $Z$ and $G$ parameters. The selection of a valid reaction coordinate is therefore not easy, and a relatively good knowledge of the reaction mechanism is required. In addition, TI is computationally quite expensive, because for a good integration, the time average of the Lagrange multiplier with constrained reaction coordinate $\langle L \rangle_{\zeta'}$ should be computed at least three times: the initial state (lower integration limit), the final state (upper integration limit) and one point in between. Each time average is obtained from an independent Molecular Dynamics simulation and, ideally, the number of required time averages for an accurate calculation is more than three, dramatically increasing the overall computational cost. Given the computational complexity and cost, an investigation of all possible reaction paths is quite time consuming, so that, in many cases, it is advisable to resort to Thermodynamic Integration only after a preliminary screening with simpler models and techniques.
Chapter 2

The Nature of Excess Electrons in Anatase and Rutile from hybrid DFT and RPA

In this chapter the behavior of excess electrons in undoped and defect free bulk anatase and rutile TiO$_2$ is investigated by state-of-the-art electronic structure methods including hybrid density functional theory (DFT) and the random phase approximation (RPA). Consistently with experiment, polaron formation is observed in both anatase and rutile treated with hybrid DFT, even if with different trapping energies and relevant concentration effects. EXX-RPA results are also reported, demonstrating a considerably lower dependence of the polaron formation energy on the chosen starting functional. At a second stage, charge mobility in the two polymorphs is investigated, showing that anatase and rutile might have different charge transport mechanisms. These calculations serve also as a benchmark and suggest RPA on top on hybrid orbitals (PBE0 with 30 % Hartree-Fock exchange), as a suitable method to study the rich chemistry and physics of TiO$_2$.

2.1 Polaron Trapping Energy from Hybrid DFT

As a starting point, to validate our computational setup, we demonstrate that hybrid functionals (truncated PBE0 and HSE06, introduced in Chapter 1.7.1) provide a qualitatively correct description of both crystal phases in the absence of an excess electron. Table 2.1 reports structural parameters for neutral anatase and rutile, demonstrating excellent agreement between experimental data and the computational setup.
In presence of an excess electron, hybrid functionals, contrary to the generalized gradient approximation (GGA), can yield both localized and delocalized solutions. The localized electronic states are accompanied by a relaxation of the surrounding atoms, so that a polaron is formed. Increasing the percentage of Hartree-Fock exchange (%hfx) in the hybrid functional favors localization. In both anatase and rutile, the delocalized and polaronic solution can coexist for a rather wide range of %hfx, as shown in Figure 2.1. There is an energetic barrier between these two states, as shown by Nudged Elastic Band (NEB) calculations and reported in Figure 2.2.

For small fractions of exchange, the polaronic solution is metastable, and ultimately only the delocalized solution can be found. For large fractions of exchange, the delocalized solution is metastable, and ultimately only the localized solution can be found. When the two states coexist, the polaron formation energy ($E_{pol}$) is computed as the energy difference between the geometries of the localized ($E_{loc(N+1)}$) and the fully delocalized ($E_{deloc(N+1)}$) solution [86]:

$$E_{pol} = E_{loc(N+1)} - E_{deloc(N+1)}$$

As shown in Fig. 2.1, a linear relation with similar slope is observed between %hfx and $E_{pol}$ for both anatase and rutile. On the contrary, if the lattice deformation energy is computed as the energy difference between the delocalized (perfect crystal) and polaron geometry, in absence of excess electrons:

$$E_{deformation} = E_{crystal(N)} - E_{polaron(N)}$$

the result is more or less independent of the chosen functional, and is around 0.6 eV for anatase and 0.7-0.9 eV for rutile (Figure 2.2).

Consistent with the results by Setvin et al. [86] and by Sezen et al. [89], the
2.1. Polaron Trapping Energy from Hybrid DFT

Figure 2.1: Panels (a) and (b): polaron trapping energy computed for various system sizes and hybrid functionals, with varying fractions of %hfx. Anatase: 3x3x1 (red), 6x6x2 (black), 6x6x4 (Green), 9x9x2 (Blue). Rutile: 3x3x4 (red), 6x6x8 (black). Panels (c) and (d): convergence of $E_{pol}$ in anatase, with increasing cell size at fixed % hfx (PBE0 functional, 30% hfx). Each system size is labeled with three digits, representing the repetition of the anatase unit cell in the x, y and z direction. Cell parameters: $x, y = 3.782; z = 9.502$ Å

The polaron formation energy in rutile is larger than the one in anatase. However, the exact fraction of exchange at which the transition from a metastable to a stable polaron solution is obtained depends strongly on the polymorph.
2. The Nature of Excess Electrons in Anatase and Rutile from hybrid DFT and RPA

Figure 2.2: Blue curves: NEB profiles for the delocalized-localized transition in anatase and rutile with one excess electron, obtained with the truncated PBE0 functional and different amounts of %hfx. Black curves: Energetic cost of the corresponding lattice deformation as obtained for the neutral system. R.C. = \( d(Ti_c - O_{eq})_{Nth\, replica} - d(Ti_c - O_{eq})_{perfect\, lattice} \).

and system size. Indeed, doubling the edges of the cubic unit cells of anatase and rutile from \( \sim 10 \) to \( \sim 20 \) Å, a clear stabilization of the localized solution, by \(-0.27\) eV for anatase and \(-0.16\) eV for rutile is observed. Note that system size and excess electron concentration are directly related. Further increases in system size lead to smaller energy shifts, a few tens of meV, but note that the convergence of \( E_{pol} \) with respect to the system size is not monotonic, with an oscillatory behavior, as shown in Figure 2.1(c) and (d).
For standard functionals such as PBE0 (Figure 2.1) and HSE06 (Figure 2.3), both with 25% hfx, stable polarons are observed in anatase only in the larger unit cells, while charge trapping in smaller system is metastable. The tendency to delocalize at high concentration (i.e. small unit cells) is in agreement with experimental results by Moser et al. [94] which describe a transition from polaronic to diffusive as a function of electron concentration. The instability of anatase polarons observed in smaller unit cells is also found in earlier studies on smaller TiO$_2$ systems treated with the HSE06 hybrid functional[88] and DFT+U$c_{RPA}$ [86], that reported stable polarons in rutile but not in anatase. On the other hand, a B3LYP (20% hfx) investigation of a $\sqrt{2} \times \sqrt{2} \times 1$ anatase cell yielded stable polarons in a relatively small system (98 atoms) [93]. The latter finding could not be reproduced by us, also after performing structural relaxation of the polaron with the same B3LYP functional and all electron basis sets similar to the ones reported in the study. The use of the Quantum ESPRESSO plane wave code[147] yields values of $E_{pol}$ consistent with the CP2K results (cfr. Table 2.2). For example, for PBE0(25% hfx) the polaron stabilization energies agree to within less than 0.1eV. We conclude that a 6x6x2 anatase simulation cell (864 atoms) might provide a fair balance between accuracy and computational cost, and that system size corrections might be important if smaller simulation cells are employed.
2. The Nature of Excess Electrons in Anatase and Rutile from Hybrid DFT and RPA

Table 2.2: Energy difference between a polaronic and delocalized geometry in presence of an excess electron \((\Delta E = E_{\text{loc}} - E_{\text{deloc}})\), for a provided polaron geometry, computed with both the CP2K and Quantum ESPRESSO codes. Employed is a small anatase \(3 \times 3 \times 1\) system, to facilitate benchmarking and comparing different functionals, basis sets and codes. Negative values indicate stable polaron geometries, positive values indicate metastable polaron geometries.

<table>
<thead>
<tr>
<th>BASIS_SET</th>
<th>FUNCTIONAL</th>
<th>(\Delta E / eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cc-TZ</td>
<td>tr-PBE0(40% hfx)</td>
<td>-0.49</td>
</tr>
<tr>
<td></td>
<td>tr-PBE0(25% hfx)</td>
<td>0.23</td>
</tr>
<tr>
<td></td>
<td>B3LYP(20% hfx)</td>
<td>1.20</td>
</tr>
<tr>
<td></td>
<td>ADMM cc-TZ</td>
<td></td>
</tr>
<tr>
<td></td>
<td>tr-PBE0(40% hfx)</td>
<td>-0.49</td>
</tr>
<tr>
<td></td>
<td>tr-PBE0(25% hfx)</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td>B3LYP(20% hfx)</td>
<td>1.21</td>
</tr>
<tr>
<td>Ti_{86-411(d31)}G and O_{8-411dJ}[149, 150]</td>
<td>B3LYP(20% hfx)</td>
<td>0.84</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Quantum ESPRESSO[147]</th>
<th>FUNCTIONAL</th>
<th>(\Delta E / eV)</th>
</tr>
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<tbody>
<tr>
<td>'vcut_spherical'</td>
<td>PBE0(25% hfx)</td>
<td>0.29</td>
</tr>
<tr>
<td>'vcut_spherical'</td>
<td>B3LYP(20% hfx)</td>
<td>0.92</td>
</tr>
<tr>
<td>'gygi-baldereschi'</td>
<td>PBE0(25% hfx)</td>
<td>0.27</td>
</tr>
<tr>
<td>'gygi-baldereschi'</td>
<td>B3LYP(20% hfx)</td>
<td>0.87</td>
</tr>
</tbody>
</table>

Simulation Parameters
- \(\text{ecutwfc}\): 150
- \(\text{ecutfock}\): 400
- \(\text{conv_thr}\): 1d-6
- \(\text{mixing_beta}\): 0.3

2.2 Polaron Geometry

To rationalize the observed behavior, it is instructive to characterize in more detail the shape of the polarons in both anatase and rutile. As shown in Fig. 2.4, the lattice relaxation is only weakly dependent on the % hfx employed, in both rutile and anatase. Precise values of bond length and atomic displacement with varying %hfx are reported in Table 2.3. General geometrical observations can thus be made at the hybrid DFT level, and these geometries can be used for single point energy calculations at a higher level of theory.

The anatase polaron structure is characterized by an anisotropic distortion of the coordination environment of the charge localization center \((Ti_c)\), with the equatorial oxygen bonds bonds more elongated than the axial bonds. Nearest neighboring Ti cations are attracted without preferential direction. The corresponding lattice relaxation extends within a diameter of 15.2 Å along the [100] and [010] directions, in a range corresponding to more than...
2.2. Polaron Geometry

Figure 2.4: Panels (a),(b),(c),(d): polaron structure for anatase and rutile, respectively along the anatase (001) and (010) and rutile (001) and (110) planes. Blue = central Ti atom, Red = displaced O anions, Grey = displaced Ti cations. The radius of the spheres increases with the atomic displacement. The crystal unit cell is displayed in black dashed lines. Panels (e), (f): distance between the central Ti atom and its nearest neighbors (n.n.) as a function of fraction of Hartree-Fock exchange (%hfx) for anatase and rutile respectively. Black = $d(Ti_cO_{eq})$, blue = $d(Ti_cO_{ax})$, green = $d(Ti_cTi_{ax})$, red = $d(Ti_cTi_{eq})$.

four unit cells (anatase [100] and [010] lattice vector = 3.784 Å)[16]. In this case, it is customary to use the term large polaron or Fröhlich polaron when referring to systems in which the radius of the polaron is much larger than the
2. The Nature of Excess Electrons in Anatase and Rutile from hybrid DFT and RPA

Table 2.3: Variation in the inter atomic distance (in Å) between the electron localization center, $T_{lc}$, and its nearest neighbors, as a function of the amount of exact exchange in the tr-PBE0 functional.

<table>
<thead>
<tr>
<th></th>
<th>Anatase</th>
<th></th>
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</thead>
<tbody>
<tr>
<td></td>
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<td>$T_{lc} - O_{ax}$</td>
<td>$T_{lc} - Ti_{eq}$</td>
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<table>
<thead>
<tr>
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<td>% hfx</td>
<td>$T_{lc} - O_{eq}$</td>
<td>$T_{lc} - O_{ax}$</td>
<td>$T_{lc} - Ti_{eq}$</td>
</tr>
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<tr>
<td>e5</td>
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<td>-2.85E-02</td>
<td>-2.60E-02</td>
</tr>
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<td>-2.88E-02</td>
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<td>2.97E-02</td>
<td>-3.07E-02</td>
<td>-2.02E-02</td>
</tr>
</tbody>
</table>

The lattice constant of the material and a large number of lattice sites is involved [151]. The lattice relaxation along the [001] direction is smaller and decays within a diameter of 8.6 Å, so that in this direction the polaron dimension is comparable to a single lattice vector (9.512 Å)[16]. Recent experimental observations of polarons in anatase by Moser et al. [94] and by Setvin et al. [86] indeed report a strong anisotropy and a spatial extension of 12-25 Å along the [010] direction, in good agreement with these calculations. The rutile polaron structure is more localized, but more pronounced. The overall magnitude of the atomic displacement is almost twice the one of anatase and the anisotropy is stronger with an elongation of the equatorial bonds almost five times the elongation of the axial bonds. The lattice distortion is thus mainly along the (110) plane. The lattice relaxes within a diameter of 9.8 Å in the [100] and [010] direction (unit cell 4.593 Å)[16], and within 11.8 Å in the [001] direction (unit cell 2.958 Å) [16]. Despite the clear anisotropy of the coordination environment, the symmetry of all four axial bonds and of the two equatorial bonds is maintained in both anatase and rutile, consistently with the overall symmetry. The GGA+U approach by Deskins et al [152] lead to similar values of the bond elongations, but, in particular for anatase, yielded an asymmetric distortion of the TiO$_6$ octahedron. Finally, we emphasize that the polaron dimensions are sizeable, extending beyond the commonly employed simulation cells, i.e. 3x3x1[153] or 3x3x2[152] for anatase and 3x3x3[152] or 3x3x4[29, 89] for rutile. These
longer range lattice relaxations contribute to the polaron stabilization, and
must be taken into account for precise estimates of the polaron formation
energy.

2.3 RPA Polaron Stability

The sensitivity of the polaron formation energy to the fraction of exchange
is unfortunate, but confirms expectation and earlier results[130, 154]. Ulti-
mately, more advanced electronic structure methods are required to address
this issue in a more satisfactory way. Here, we explore methods that include
virtual orbitals, the so called 5th rung on DFT.

We focus on the random phase approximation (RPA), introduced in Chap-
ter 1.7.2. Its non-perturbative nature makes it suitable for systems with
small band-gaps, such as the the current system, where the electronic gap
between the excess electron and the conduction band is small in the de-
localized state. This is one reason why perturbative approaches such as
second-order Möller-Plesset (MP2) theory[155] and double hybrids[156] are
less suitable for this system. In addition, the latter two approaches are based
on a large amount of Hartree-Fock exchange, which makes the fully delo-
calized state metastable with respect to a localized electronic solution, even
on the perfect crystal lattice, as shown in Table 2.4.

The computational cost of this class of methods has long prohibited their
use for larger condensed phase systems, but recent progress, in particular
the RI-GPW method for wavefunction correlation[157, 136], has radically
changed this state. Here, we treat TiO$_2$ systems with up to 216 atoms with

Table 2.4: HF, MP2 and DH energy difference between $E_{\text{loc,relax}}$ = localized charge with
a consistent lattice relaxation (polaron) and $E_{\text{loc,perf}}$ = localized charge with a perfect (non
relaxed) lattice geometry. The fully delocalized solution $E_{\text{deloc,perf}}$ can not be obtained with those
methods, due to the high amount of %hfx introduced. Therefore $E_{\text{pol}} = E_{\text{loc,relax}} - E_{\text{deloc,perf}}$
can not be computed.

<table>
<thead>
<tr>
<th>Charge</th>
<th>Geometry</th>
<th>Charge</th>
<th>Geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{\text{loc,relax}}$ (polaron)</td>
<td>localized</td>
<td>relaxed (polaron distortion)</td>
<td>localized</td>
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<tr>
<td>$E_{\text{loc,perf}}$</td>
<td>localized</td>
<td>delocalized (perfect lattice)</td>
<td>delocalized</td>
</tr>
<tr>
<td>$E_{\text{deloc,perf}}$</td>
<td>delocalized</td>
<td></td>
<td>delocalized</td>
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</table>

Anatase

<table>
<thead>
<tr>
<th>$E_{\text{loc,relax}} - E_{\text{loc,perf}}$ / eV</th>
<th>$E_{\text{loc,relax}} - E_{\text{loc,perf}}$ / eV</th>
<th>$\Delta E_{\text{rutile-anatase}}$ / eV</th>
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<td>HF</td>
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<td>-1.22</td>
</tr>
<tr>
<td>MP2</td>
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<td>-0.84</td>
</tr>
<tr>
<td>DH</td>
<td>-0.41</td>
<td>-0.78</td>
</tr>
</tbody>
</table>
2. The Nature of Excess Electrons in Anatase and Rutile from Hybrid DFT and RPA

good quality basis sets (~9500 functions). Nevertheless, the finite size effects discussed in the previous section should be kept in mind. Furthermore, these 5th rung calculations are single point calculations so a polaron geometry as obtained with a particular hybrid must be employed. As shown in Table 2.5, all geometries lead to similar energetics, which confirms our earlier analysis stating that the geometry is relatively insensitive to the precise nature of the hybrid functional. The following analysis therefore employs geometries obtained at 35%hfx.

In our computational setup, RPA is a post self-consistent approach, starting

<table>
<thead>
<tr>
<th>Method</th>
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<th>30</th>
<th>31</th>
<th>32</th>
<th>33</th>
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<td>0.54</td>
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<td>0.30</td>
<td></td>
<td>0.35</td>
<td></td>
<td>0.36</td>
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<tr>
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<td>0.18</td>
<td>0.19</td>
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<td>0.20</td>
<td>0.21</td>
<td>0.21</td>
<td>0.21</td>
<td>0.21</td>
</tr>
<tr>
<td>trPBE0 (35% hfx)</td>
<td>-0.17</td>
<td>-0.19</td>
<td>-0.19</td>
<td>-0.20</td>
<td>-0.20</td>
<td>-0.20</td>
<td>-0.20</td>
<td>-0.20</td>
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</tr>
<tr>
<td>trPBE0 (40% hfx)</td>
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<td>-0.41</td>
<td>-0.42</td>
<td>-0.43</td>
<td>-0.43</td>
<td>-0.43</td>
<td>-0.44</td>
<td>-0.44</td>
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<td>0.35</td>
<td>0.39</td>
<td>0.40</td>
<td>0.42</td>
<td>0.43</td>
<td>0.44</td>
<td></td>
</tr>
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<td>-0.02</td>
<td>-0.02</td>
<td>-0.02</td>
<td>-0.02</td>
<td>-0.01</td>
<td></td>
<td></td>
</tr>
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<td>-0.12</td>
<td>-0.12</td>
<td>-0.12</td>
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<td>-0.11</td>
<td>-0.11</td>
<td>-0.10</td>
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<tr>
<td>RPA-trPBE0 (35% hfx)</td>
<td>-0.21</td>
<td>-0.22</td>
<td>-0.22</td>
<td>-0.22</td>
<td>-0.22</td>
<td>-0.22</td>
<td>-0.22</td>
<td>-0.22</td>
<td>-0.21</td>
</tr>
<tr>
<td>RPA-trPBE0 (40% hfx)</td>
<td>-0.23</td>
<td>-0.24</td>
<td>-0.24</td>
<td>-0.24</td>
<td>-0.24</td>
<td>-0.24</td>
<td>-0.24</td>
<td>-0.24</td>
<td>-0.23</td>
</tr>
</tbody>
</table>

with orbitals obtained from a preliminary self-consistent calculation with a parent functional. The sensitivity of the energetics with respect to the parent functional, here the fraction of exchange employed, must thus be quantified. Anticipating our results, hybrid functionals provide a better starting point than GGA functionals, an observation that has also been made for GW calculations for molecular systems [158] and non metallic solids [159]. Most importantly, at the RPA level, the dependence of the energetics on the precise composition of the hybrid parent functional is relatively weak. The results are summarized in Fig. 2.5.
2.3. RPA Polaron Stability

![Graph showing polaron formation energies in anatase and rutile](image)

**Figure 2.5:** Panels (a) and (b): Polaron formation energies in anatase and rutile, with unit cells of 108 and 216 atoms respectively, computed with hybrid DFT (black) and RPA (red) for varying amounts of %hx. The sensible RPA-0% (GGA) is to be neglected, due to the fact that GGA calculations do not yield a localized solution for the polaron geometry.

In rutile, RPA yields a polaron formation energy that is essentially independent of %hx and, even starting from GGA orbitals, a stable polaron is predicted. This is a significant improvement over the hybrid functionals, where a mere 10% change in %hx changes the energy by nearly 0.5 eV.

In anatase, RPA requires hybrid orbitals as a starting point to predict localization, because the GGA orbitals and eigenvalues are too different from the physical solution. In particular, while for rutile GGA calculations yield a localized solution for the polaron geometry and a delocalized solution for the perfect crystal geometry, GGA calculations for anatase yield a delocalized solution for both the perfect crystal and polaron geometry, most probably due to the less pronounced lattice distortion in anatase polarons. For this reason, computing the energy difference between RPA-GGA localized and delocalized solutions to give \( E_{pol} \) is not meaningful, and RPA-GGA data for anatase are to be neglected. In the case of anatase hybrid calculations, the localized and localized solutions are well distinct, and \( E_{pol} \) can be correctly evaluated. For RPA-hybrid calculations, a 20% increase of %hx changes the RPA polaron formation energy by only 0.2 eV, while the corresponding hybrid results changes qualitatively and by roughly 0.8 eV. Taking the correction for size effects into account, around 0.27 eV for anatase and 0.16 for rutile, the polaron is predicted to stable at the RPA level also for only 20%hx in the parent functional. The difference in polaron formation energy between the polaron in anatase and rutile is predicted to be roughly...
2. The Nature of Excess Electrons in Anatase and Rutile from hybrid DFT and RPA

0.6 eV for the unit cells studied, i.e. 0.5 eV after correction for size effects. This difference is relatively independent of %hfx already for standard hybrid functionals, and is robustly predicted with RPA on top of the hybrid functionals. This makes clear that the polaron is very stable in rutile, while in anatase the excess electron will be polaronic but could adopt conduction-band like behavior at higher concentration, or with a small activation energy. As we discuss in the following, this might have important implications for the charge transport in these materials, explaining the higher conductivity in anatase and the improved performance in photoelectrochemical devices [18, 19, 20].

2.4 Electron Mobility

Charge migration can occur either via a polaron hopping mechanism, or via a conduction band like mechanism with delocalized electrons. For the hopping mechanism two regimes can be considered: nonadiabatic hopping, which results from a small electronic coupling between the initial and final state, and adiabatic hopping, which results from a strong electronic coupling.[160] The nonadiabatic hopping is characterized by a reaction profile that closely resembles the intersection of two parabolas, while the strong coupling in the adiabatic regime lowers the energy of the transition state and smoothens the energy profile. In the hopping regime, electron mobilities can be estimated from the rate of hopping by applying the Marcus-Emin-Holstein-Austin-Mott theory[160, 161] and the Einstein relation[162]:

\[
k_{el} = v_n \exp\left(-\frac{\Delta G^*_a}{k_BT}\right) \quad \text{Adiabatic hopping}
\]

\[
k_{el} = \frac{2\pi}{\hbar} |V_{ab}|^2 \frac{1}{\sqrt{4\pi\lambda k_BT}} \exp\left(-\frac{(\lambda^2)}{4\lambda k_BT}\right) \quad \text{Nonadiabatic hopping}
\]

\[\Delta G^* = \lambda / 4\]

\[D = R^2 n k_{el}\]

\[\mu = \frac{eD}{k_BT}\]

With \(v_n\) = typical frequency for nuclear motion [152]; \(V_{AB}\) = electron coupling element [152]; \(R\) = distance between transfer sites; \(n\) = number of neighboring electronic accepting sites. \(R\) and \(n\) values for the different possible migration directions in anatase and rutile are listed in Table 2.6

For the conduction band like mechanism, the mobility can not easily be estimated. The process consists of an initial activated event to delocalize the electron, followed by transport over an unknown, but potentially large
2.4. Electron Mobility

<table>
<thead>
<tr>
<th>Path</th>
<th>R / Å</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
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<td>2.91</td>
<td>2</td>
</tr>
<tr>
<td>Rutile[111]</td>
<td>3.57</td>
<td>8</td>
</tr>
<tr>
<td>Anatase[100]</td>
<td>3.03</td>
<td>4</td>
</tr>
<tr>
<td>Anatase[201]</td>
<td>3.78</td>
<td>4</td>
</tr>
</tbody>
</table>

Table 2.6: Parameters that influence electron mobility in the hopping regime. $R =$ distance between transfer sites and $n =$ number of neighboring accepting sites.

distance, and subsequent localization. For the same activation energy, this will result in larger mobility.

The mobility is not necessarily isotropic, as the nearest Ti(4+) neighbors of a Ti(3+) localization center can be located along the [001] and [111] directions in rutile and the [100] and [201] directions in anatase, as illustrated in Fig.2.6. The pathways for polaron hopping and delocalization have been computed with the improved tangent nudged elastic band (it-NEB) method [141, 142], employing the hybrid PBE0 functional for geometric relaxation. After NEB convergence, RPA has been applied on all the configurations of the path. Even if the precise values of the activation energy depends on the computational method, a number of observations can be made.

For rutile, it is clear that charge migration will be hopping, since the corresponding activation energy (see Table 2.7) is significantly smaller than the activation energy needed to completely delocalize the excess electron. The [001] migration direction is characterized by the lowest activation energy.

<table>
<thead>
<tr>
<th>Path</th>
<th>$E_{act}[001]$</th>
<th>$E_{act}[111]$</th>
<th>$E_{act} [loc - deloc]$</th>
<th>$\mu_{hop}[001]$</th>
<th>$\mu_{hop}[111]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anatase</td>
<td>$E_{act}[201]$</td>
<td>$E_{act}[100]$</td>
<td>$E_{act} [loc - deloc]$</td>
<td>$\mu_{hop}[201]$</td>
<td>$\mu_{hop}[100]$</td>
</tr>
<tr>
<td>PBE0 (35%hfx)</td>
<td>0.23</td>
<td>0.23</td>
<td>0.21</td>
<td>1.55 $\times 10^{-6}$</td>
<td>9.96 $\times 10^{-7}$</td>
</tr>
<tr>
<td>RPA (PBE0 35%hfx)</td>
<td>0.17</td>
<td>0.14</td>
<td>0.22</td>
<td>1.84 $\times 10^{-5}$</td>
<td>4.15 $\times 10^{-5}$</td>
</tr>
<tr>
<td>RPA (PBE0 20%hfx)</td>
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<td>0.09*</td>
<td>0.07</td>
<td>1.37 $\times 10^{-3}$</td>
<td>1.16 $\times 10^{-1}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Path</th>
<th>$E_{act}[001]$</th>
<th>$E_{act}[111]$</th>
<th>$E_{act} [loc - deloc]$</th>
<th>$\mu_{hop}[001]$</th>
<th>$\mu_{hop}[111]$</th>
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</thead>
<tbody>
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<td>$E_{act}[001]$</td>
<td>$E_{act}[111]$</td>
<td>$E_{act} [loc - deloc]$</td>
<td>$\mu_{hop}[001]$</td>
<td>$\mu_{hop}[111]$</td>
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<tr>
<td>PBE0 (35%hfx)</td>
<td>0.26</td>
<td>0.39</td>
<td>0.81</td>
<td>4.61 $\times 10^{-6}$</td>
<td>1.48 $\times 10^{-7}$</td>
</tr>
<tr>
<td>PBE0 (20%hfx)</td>
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<td>0.25</td>
<td>3.37 $\times 10^{-1}$</td>
<td>2.14 $\times 10^{-4}$</td>
</tr>
<tr>
<td>RPA (PBE0 35%hfx)</td>
<td>0.11*</td>
<td>0.70</td>
<td>0.60</td>
<td>2.25 $\times 10^{2}$</td>
<td>1.06 $\times 10^{-1}$</td>
</tr>
<tr>
<td>RPA (PBE0 30%hfx)</td>
<td>0.07*</td>
<td>0.73</td>
<td>0.73</td>
<td>7.31 $\times 10^{-1}$</td>
<td>7.31 $\times 10^{-1}$</td>
</tr>
</tbody>
</table>

* adiabatic transfer

Table 2.7: Computed activation energies for the migration paths illustrated in Figure 2.6 and activation energy for charge delocalization in the corresponding computational approach. Hopping derived electron mobilities ($\mu_{hop}$) for each migration direction (T = 300 K), are also reported.
2. The Nature of Excess Electrons in Anatase and Rutile from hybrid DFT and RPA

![Diagram showing possible hopping directions for localized electrons and energy profiles](image)

**Figure 2.6:** Panels (a) and (c): Possible hopping directions for a localized electron in bulk anatase and rutile. Panels (b) and (d): Energy profiles for electronic hopping, in the [100] and [201] directions for anatase and in the [001] and [111] for rutile, with hybrid and RPA approaches. For PBE0 (35% hfx, black), PBE0 (20% hfx, green), RPA (35% hfx, blue), RPA (30% hfx, violet), and RPA (20% hfx, red). Dashed lines indicate the value of activation energy for charge delocalization in the corresponding approach. R.C. anatase [201] migration: $d_{(T1-O2)} - d_{(T2-O3)}$. R.C. anatase [100] migration: $d_{(T1-O1)} - d_{(T3-O1)}$. R.C. rutile [001] migration: $d_{(T1-O2)} - d_{(T2-O2)}$. R.C. rutile [111] migration: $d_{(T1-O1)} - d_{(T3-O3)}$.

roughly 0.15 eV below that of the [111] direction. This is consistent with the experimentally reported anisotropy in charge conductivity that is enhanced in the [001] direction [163]. Hybrid (PBE0-20% hfx) and RPA results suggest an adiabatic transfer in the [001] direction, characterized by an excess spin density that is evenly distributed between both Ti center at the transition state. A small amount of %hfx in the RPA parent functional (e.g. 20%
2.4. Electron Mobility

hfx) leads to an underestimated transition state energy, with an unphysi-
cal minimum (see Figures 2.6 (d) and 2.7), reminescent of the known RPA
overcorrelation in H$_2^+$ dissociation[164, 165]. This problem is less severe if
the excess electron is not symmetrically delocalized and if a larger % hfx
is employed in the parent functional (e.g. 35% hfx). Migration along the

Figure 2.7: Comparison of the NEB profiles for the [001] electron hopping in rutile, computed
with the truncated PBE0 functional and RPA, at different amounts of %hfx. Dashed lines
indicate profiles affected by RPA overcorrelation.

[111] direction is nonadiabatic, and since it is energetically less favored, a
detailed RPA investigation was not carried out. The computed activation
energies are in qualitative agreement with previous theoretical investiga-
tions of charge mobility in rutile [152, 29], with RPA providing a deeper
insight in the charge transport mechanism, suggesting an adiabatic transfer
between two Ti centers, and mobility values in good agreement with
experimental data (i.e 1.06 × 10$^{-1}$ cm$^2$V$^{-1}$s$^{-1}$ with RPA-30%hfx vs. ∼0.1-1
cm$^2$V$^{-1}$s$^{-1}$ from Hall measurements)[166, 163].

For anatase, hybrid calculations predict a nonadiabatic hopping mechanism
with similar activation energies along the [100] and [201] directions, while
RPA predicts an adiabatic mechanism with an anistropy that favors migra-
tion along [100].

Note that the activation energies for hopping are slightly larger in anatase
than rutile, which is reflected in larger estimated hopping mobilities in ru-
tile than in anatase. However, an important difference to rutile is the fact
that the activation energy for hopping is comparable to the one for charge
delocalization. This is consistently observed with both hybrid and RPA cal-
culations. The activation energy for charge delocalization will increase for
larger models or reduced excess electron concentration, while it was verified
2. The Nature of Excess Electrons in Anatase and Rutile from Hybrid DFT and RPA

![Figure 2.8: NEB profiles for the [001] electron hopping in rutile, with the truncated PBE0 functional (35% hfx). Black: 3 × 3 × 4 system, 216 atoms. Red: 6 × 6 × 8 system, 1728 atoms.](image)

that the activation energy for non-adiabatic hopping is not affected by the system size (see Figure 2.8). Even if the activation energy for delocalization is slightly larger than for hopping, it could still be the dominant mechanism for transport, given the typical differences in hopping and conduction-band-like mobility. Since delocalization involves multiple Ti centers in a given (001) plane, mobility will be specifically enhanced in that direction. Overall, our results confirm that polaron delocalization is indeed the likely reason for the higher charge mobility in anatase, especially at higher electron concentration, as well as the anisotropy of the mobility[18].

2.5 Conclusion

To conclude, the behavior of excess charges in undoped bulk anatase and rutile TiO$_2$ systems has been investigated by means of advanced DFT methods to overcome the limitations of semi-local approximations. We find that excess electron localization is predicted by hybrid functionals in both anatase and rutile, provided that the model is big enough (around 20 Å) to accommodate the long range lattice relaxation induced by polaron formation. This is particularly important in anatase, where the spatial extent of the polaron is larger. Applying, for the first time, RPA calculations to crystalline systems composed of hundreds of atoms, a refined value of the polaron formation energy is obtained, and the dependence of the result on the chosen hybrid functional is reduced. Wavefunctions obtained with hybrid functionals are nevertheless required as a starting point for the RPA calculations. Fifth
2.6. Computational Methods

rung functionals that include a large % hfx, such as MP2 or double hybrids, appear less suitable for this system, as the delocalized state is not well described. The results confirm that the driving force for polaron formation is large in rutile and significantly weaker in anatase. The calculations also suggest that conduction-band-like transport is possible in anatase, while in rutile hopping will be dominant. Conduction is anistropic, and likely adiabatic. The activation energies for hopping are sensitive to the approach employed, but provide a good benchmark for selecting a suitable computational method. Based on this criterion, we suggest RPA(30%hfx) to be a suitable method for this system, which could used to investigate defects such as Oxygen vacancies, impurities and dopants. Particular care should be taken in treating highly symmetric (H$_2^+$ like) charge distributions.

2.6 Computational Methods

All calculations have been carried out with the CP2K program package [148], based on the hybrid Gaussian and plane wave (GPW) scheme[167, 168]. A plane wave density cutoff of 600 Ry and periodic boundary conditions have been adopted. Hybrid calculations have been carried out both with the truncated PBE0 (trPBE0) functional [124, 126] and with the HSE06[127, 128] functional. As recommended, a cutoff radius of half the smallest simulation cell (4.5 Å) has been chosen and consistently used for all calculations with the trPBE0 functional. Convergence has been verified in a larger cell using a truncation radius of 6 Å, yielding small differences in the polaron formation energies. HSE06 calculations employ $\omega = 0.11 \alpha_{\text{hxc}}^{-1}$. RPA calculations[157, 136] have been applied on the eigenstates obtained by trPBE0 parent functional, for the nomenclature, RPA is prefixed to the functional name, so that RPA-trPBE0(25%) refers to RPA applied to the result of hybrid truncated PBE0 calculations with 25% hfx. The MP2 approach [155] is applied to a full Hartree-Fock reference determinant, while the PWPB95-D3 double hybrid functional employs 50% hfx exchange as defined in the original work[156]. The primary Gaussian basis set adopted in all calculations is a correlation consistent basis set of triple $\zeta$ quality, in combination with GTH pseudopotentials [169]. Large scale hybrid DFT calculations are performed with the auxiliary density matrix method (ADMM), which relies on an auxiliary basis for Hartree-Fock exchange.[129] Polaron energies for anatase and rutile systems, obtained with and without ADMM differ by 0.01eV or less. Fifth rung calculations do not employ ADMM, making the calculation of the Hartree-Fock exchange computationally much more demanding. A further auxiliary basis set is needed for the resolution of identity-based RPA and MP2 implementation[136]. Strict SCF convergence (i.e. $10^{-8}$) and a fine integration grid for RPA, 100 points within a Clenshaw-Curtis
integration scheme, in particular for the delocalized states, are required to obtain reliable polaron formation energies. Technically, these calculations can be challenging, requiring strict computational parameters to obtain accurately small energy differences on large and sensitive systems. For anatase, orthorombic systems with various dimensions including $11.346 \times 11.346 \times 9.502 \, \text{Å}^3$ (3 × 3 × 1 unit cells, 108 atoms), $22.692 \times 22.692 \times 19.004 \, \text{Å}^3$ (6 × 6 × 2 unit cells, 864 atoms), $34.0380 \times 34.0380 \times 19.004 \, \text{Å}^3$ (9 × 9 × 2 unit cells, 1944 atoms), and $22.692 \times 22.692 \times 47.510 \, \text{Å}^3$ (6 × 6 × 5 unit cells, 2160 atoms) have been studied. For rutile, orthorombic systems with dimension $13.782 \times 13.782 \times 11.836 \, \text{Å}^3$ (3 × 3 × 4 unit cells, 216 atoms) and $27.564 \times 27.564 \times 23.672 \, \text{Å}^3$ (6 × 6 × 8 unit cells, 1728 atoms) have been studied. One electron has been introduced in each system, yielding electronic concentrations ranging from $8.18 \times 10^{20} \, \text{e}^- \cdot \text{cm}^{-3}$ to $0.45 \times 10^{20} \, \text{e}^- \cdot \text{cm}^{-3}$. 

Chapter 3

Structure and Mobility of Acetic Acid at the Anatase (101) / Acetonitrile Interface

Acetic acid is one of the simplest molecules containing a carboxylic moiety, a common anchoring groups used to functionalize TiO$_2$-based devices. In this chapter, the behavior of acetic acid in proximity of the anatase (101) surface has been investigated by means of first-principles density functional theory (DFT) calculations, including explicit liquid solvent in the simulations. At first an investigation of the influence that slab size and presence of the solvent have on the relative energy of the many possible acetic acid binding modes is carried out to determine which modes are most stable. A study on proton diffusion paths and on the interconversion between adsorption modes is then presented, followed by a detailed investigation of the desorption process. Where significant, a comparison between the ‘explicit liquid’ environment and the more often employed ‘solvent monolayer’ environment has been carried out, highlighting the importance of solvent interactions.

3.1 Structure of the Solvated (101) Interface

As described in Chapter 1.2, TiO$_2$ anatase is the preferred phase for the nanoparticles employed in the mesoporous semiconductor layer of dye sensitized solar cells. On these nanoparticles, the (101) surface is dominant due to its lower surface energy. The model adopted is therefore based on a slab representation of the anatase (101) surface, which is a good approximation of the nanoparticle size (> 10nm). Acetonitrile (ACN) constitutes the basis of the most common electrolytic solutions employed in DSSCs, and has been
3. Structure and Mobility of Acetic Acid at the Anatase (101) / Acetonitrile Interface

![Figure 3.1](image_url): Representation of an acetic acid molecule adsorbed on the anatase (101) surface, in presence of explicit liquid acetonitrile solvent. The ordered structure of the first solvent layer in contact with the surface is clearly visible. Coordination numbers for surface anatase ions are indicated. Color coding: Silver=Titanium, Red=Oxygen, Blue=Nitrogen, Cyan=Carbon, Yellow=Hydrogen.

chosen to represent the explicit liquid solvent. At this stage, further additives have not been considered.

An acetic acid molecule has been introduced to model the binding group by which the sensitizing dye is anchored to the oxide surface. As illustrated in Figure 3.1, ACN molecules preferentially bind to the anatase (101) surface with the carbonitrile group pointing towards the five-fold coordinated Ti$^{2+}$ cations[102, 103], so that the first layer of solvent molecules in contact with the surface assumes a distinctive and ordered structure; on the other hand, carboxylic moieties can assume a range of different configurations[106, 108, 107, 170, 52] that are to be discussed in this chapter.

3.2 Adsorption modes of acetic acid on TiO$_2$

At first, we perform a careful analysis of our computational model and present the energy landscape of different adsorption modes of acetic acid to anatase TiO$_2$. A schematic representation of the different identified minima is displayed in Figure 3.2. The sensitivity of the adsorption energies with respect to surface size and first layer solvation effects has been care-
### 3.2. Adsorption modes of acetic acid on TiO$_2$

**Figure 3.2:** Most stable adsorption modes of the carboxylic moiety on the anatase (101) slab, from side view. 
- **A** and **B**: Molecular bridging with Hydrogen interactions.
- **C**: Molecular monodentate binding.
- **D, E**: Dissociative bridging with proton adsorption on the anatase surface.
- **F**: Dissociative bridging with proton insertion below the surface. Several possible locations for the proton have been tested (see SI) and the most stable is reported. The proton is pointing inwards and the three-fold coordinated oxygen atom to which the proton is bound relaxes accordingly.
- **G**: Dissociative ester linkage.

**Table 3.1:** Comparison of the gasphase adsorption energies of geometry A, D and F of Figure 3.2, establishing the importance of slab thickness. $x=10.227\,\text{Å}; y=3.782\,\text{Å}; z=3.513\,\text{Å}$

<table>
<thead>
<tr>
<th></th>
<th>E$_{ads}$ [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>slab 133</td>
</tr>
<tr>
<td><strong>A</strong></td>
<td>-114.3</td>
</tr>
<tr>
<td><strong>D</strong></td>
<td>-98.6</td>
</tr>
<tr>
<td><strong>F</strong></td>
<td>-105.8</td>
</tr>
</tbody>
</table>

Fully tested using a variety of possible setups. The results show that the thickness of the slab employed in these calculations has a serious impact on the relative stabilities. Moreover, a stable adsorption mode including a sub-surface proton has been identified which has not been predicted previously. A common model to study adsorbents on anatase TiO$_2$ is based on a 108 atom slab with a thickness of 3 layers. Comparing the relative stabilities of the different adsorption modes for this model with the larger 5-layer and 7-layer slab model (Table 3.1) a noticeable change in energies can be seen. Between the 133 and 135 model adsorption energies change up to about 20 kJ/mol. More importantly, this change is not a systematic shift of the energies but affects their relative stabilities as well. While the 3-layer model strongly favors **A** as most stable adsorption mode, the larger models predict almost the same stability for **A**, **D**, and **F**. This finding can be explained by the fact that a 3-layer model is not big enough to accommodate all lattice
3. Structure and Mobility of Acetic Acid at the Anatase (101) / Acetonitrile Interface

Table 3.2: Comparison of adsorption energies of the geometries illustrated in Figure 3.2 for increasing slab width and decreasing acid coverage.

<table>
<thead>
<tr>
<th></th>
<th>E$_{ads}$ / kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>gasphase</td>
</tr>
<tr>
<td>A</td>
<td>-125.0</td>
</tr>
<tr>
<td>A*</td>
<td>-133.7</td>
</tr>
<tr>
<td>B</td>
<td>-114.6</td>
</tr>
<tr>
<td>C</td>
<td>-72.1</td>
</tr>
<tr>
<td>D</td>
<td>-120.3</td>
</tr>
<tr>
<td>E</td>
<td>-120.5</td>
</tr>
<tr>
<td>G</td>
<td>-52.8</td>
</tr>
</tbody>
</table>

A* different monolayer model: (a) 5 ACN monolayer; (b) 19 ACN monolayer; (c) 23 ACN monolayer.

relaxations induced by acetic acid adsorbed on anatase, as shown in Figure 3.3. Increasing the slab thickness further to a 7-layer slab leads only to minor differences of about 2 kJ/mol. From these results it is obvious that a 3-layer model gives qualitatively wrong results and a 5-layer model is needed to obtain a reasonable compromise between accuracy and computational cost. At the Γ-point the size of the unit cell in the periodic directions could be important.

Table 3.3: Comparison of the gasphase adsorption energies of geometry A, D and F for increasing slab width and constant acid coverage.

<table>
<thead>
<tr>
<th></th>
<th>E$_{ads}$ [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1acid@slab133</td>
</tr>
<tr>
<td>A</td>
<td>-114.3</td>
</tr>
<tr>
<td>D</td>
<td>-98.7</td>
</tr>
<tr>
<td>F</td>
<td>-105.8</td>
</tr>
</tbody>
</table>

important. Energy convergence tests were therefore carried out by comparing the acetic acid adsorption energy for different slab sizes (in the periodic xy direction) and constant acid coverage. Results are reported in Table 3.3 and did not show a significant size effect, so that size, and thus k-point, convergence in the periodic directions is assumed.

Next, we focus on the influence of co-adsorbed ACN molecules on the adsorption energies. Again, size convergence of the model has been carefully tested to exclude artificial interactions (electrostatic or steric) induced by periodic boundary conditions. The effects we found were up to 7 kJ/mol from the smallest model to the biggest (Table 3.2). We find that the relative stabil-
3.2. Adsorption modes of acetic acid on TiO₂

A significant problem with the monolayer model arises because of the two different types of binding modes that the carboxyl groups can adopt. The monodentate modes (A, B, C, G) only occupy a single adsorption site in the monolayer while the bidentate modes (D, E, F) occupy two. Therefore two different definitions for the reference monolayer for the adsorption process are possible: the ideal monolayer with one ACN vacancy, which is only suitable for the monodentate binding modes, or a monolayer with two ACN vacancies. The latter model describes the bidentate modes well but leaves a vacant ACN adsorption site on the surface in case of monodentate binding. Hence an energy penalty of the order of the binding energy of a ACN to the surface (about 90 kJ/mol) has to be added to the bidentate modes if the energies of the system in contact with ACN vapor is being discussed. In case an explicit solvent model is chosen, the energy alignment of the different

Figure 3.3: Diagram reporting the displacement of the atoms of the anatase slab, for adsorption modes A and D compared to a clean slab of the same dimension.
binding types can not be easily evaluated as the shift is a combination of the binding energy of an acetonitrile from the liquid and the solvation energy of the different structures. Therefore deductions from the gas phase models to solvated system can only be made for sufficiently similar configurations (binding modes, dipoles, etc.). Even if the monolayer models are not perfect, they can give insight in the interactions of the acid with co-adsorbed ACN molecules and can account for sizable stabilization effects. This is observed for configuration G, in which the carboxylate group is partially pointing away from the surface. This geometry is metastable in the gas phase, but is stabilized by hydrogen interactions with the surrounding molecules if a monolayer of ACN is introduced.

3.3 Proton Binding Site Accessibility and Mobility

So far little attention has been paid to subsurface proton states due to the higher energy originally assigned to these configurations. In previous theoretical studies, subsurface Hydrogen insertion has always been reported as less stable compared to surface adsorption\[97, 96\]. Configuration F presented here differs from the ones previously investigated by the presence of the above co-adsorbed carboxylate moiety, that stabilizes the subsurface position. Although configuration F presents a stable adsorption mode, the formation depends on the accessibility of the subsurface proton site. A detailed investigation of possible intercalation pathways and proton diffusion pathways on and below the surface is therefore necessary. Starting from an adsorption mode in which the proton is placed on top of the anatase surface, configuration F can be reached by proton migration via many possible paths. All proton intercalation and diffusion processes involve mainly interactions with the surface atoms and small contributions from molecules that are located close to the anatase surface. Hence, the role of the liquid solvent above the first layer is assumed to be small and the monolayer description of the interface is employed. Exploring all possible pathways is beyond the scope of this work, therefore we restrict the simulations to the three pathways which we assume to require the smallest barriers. The pathways are illustrated in Figure 3.4 and reaction energies provided in Table 3.4

Proton migration into the anatase surface is a stepwise process transferring the migrating proton from one oxygen site to a neighboring one. Due to the strength of the O-H bond and to the fact that the surrounding anatase lattice is heavily deformed by the presence of the migrating proton, a high activation energy is required for most of the proposed paths. Only those involving a short-range proton migration and a small lattice distortion present
Table 3.4: Starting configurations and activation energies relative to the hydrogen intercalation paths shown in Figure 3.4 calculated for the '18ACN monolayer' environment, with the NEB method.

<table>
<thead>
<tr>
<th>Starting configuration</th>
<th>E\textsubscript{act} [kJ/mol]</th>
<th>ΔE [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Path1</td>
<td>D</td>
<td>207.4</td>
</tr>
<tr>
<td>Path2</td>
<td>E</td>
<td>118.3</td>
</tr>
<tr>
<td>Path3</td>
<td>B</td>
<td>72.3</td>
</tr>
</tbody>
</table>

an activation energy around 100 kJ/mol (see Table 3.4), thus the reaction is likely to proceed on the hour timescale at room temperature. As this energy is significantly higher than the barrier for interconversion between molecular configurations (see Figure 3.5), the lowest energy path will be the same for all of the configurations. In addition, configuration F is most stable, thus the reverse process always occurs with a higher energy cost.

The lowest energy path for direct intercalation is found to proceed via configuration B (Path3 of Figure 3.4). From the molecular adsorption mode B the proton is transferred to the interacting surface oxygen, and from there rotates into the surface and configuration F is formed. Interaction with the carboxylate moiety therefore assists intercalation, by allowing the proton to approach the final subsurface position without causing a big lattice distortion. The activation energy to reach that state from B is 72.3 kJ/mol. As mentioned earlier, the different acetic acid configurations can interconvert and hence the barrier for intercalation from e.g. the more stable configuration A has an activation energy of 93.5 kJ/mol and the reverse reaction 97.6kJ/mol. This is because, to reach the initial state B from A, an initial barrier of 36.2kJ/mol has to be overcome (see Figure 3.5). These findings indicate that proton intercalation will be the rate determining step the formation of the subsurface proton configuration F and that the carboxylate moiety is crucial for a low barrier intercalation process.

It is intuitive that the presence of a nearby co-adsorbed carboxylate moiety has an influence not only on the relative stability of various proton adsorption or insertion sites, but also the proton diffusion on top or below the anatase surface. For this reason, other possible proton migration paths have been investigated in presence of the co-adsorbed carboxylate moiety. These paths focus on proton diffusion completely above or below the surface edge, with no crossing between different layers (Figure 3.6).

Regarding subsurface proton migration, we note that the required E\textsubscript{act} for proton migration is 84.8kJ. This indicates that this type of subsurface diffusion should happen on a similar timescale as proton intercalation/deintercalation. However, the energy differences between initial and final position is about 20kJ/mol. Further calculations on more distant sites show that this trend continues. This can be easily understood from the electrostatic interaction
3. Structure and Mobility of Acetic Acid at the Anatase (101) / Acetonitrile Interface

![NEB profiles for subsurface proton insertion](image)

Figure 3.4: NEB profiles for subsurface proton insertion, starting from configuration D (Path1), E (Path2), and B (Path3), computed in presence of a co-adsorbed carboxylate moiety and of an acetonitrile monolayer. For clarity, ACN molecules are not shown. Position D and B can be reached from position A, as discussed in the following sections.

between the positively charged proton and the negatively charged acetate. Due to this stability gradient, protons are likely to remain in the proximity of the corresponding acetate. The other possible subsurface migration path (Path 5) studied exhibits a significantly higher barrier of >150 kJ/mol and therefore should not play a significant role in this system. As these are the only two escape routes for the proton, we do not expect to see a noticeable subsurface proton diffusion in this system.

Contrary the subsurface migration, proton migration above the anatase surface should be facilitated as a nearby carboxylate moiety might stabilize the
3.4. Electronic Properties of Subsurface Protons

As reported in Chapter 1.3, different binding modes and the presence of acidic protons affect important properties for a DSSC device (shift in the oxide electronic levels, increased electron injection/charge collection efficiency and increased amount of adsorbed dye molecules [171, 172, 173, 174]). Therefore, the electronic properties of the anatase slab in presence of a subsurface proton in combination with an excess electron have been investigated by hybrid calculations, adopting the tr-PBE0 functional. Results are shown in Figure 3.7. The excess electron tends to localize in proximity of the subsurface proton, on a Ti cation that acquires a formally (3+) valence. From the density of states calculations it can be seen that the fully localized electron represents a trap state in the band gap, located 1.19eV below the conduction band edge. Electron localization deeper in the slab is also possi-
3. **Structure and Mobility of Acetic Acid at the Anatase (101) / Acetonitrile Interface**

(a) **Path4** Subsurface diffusion 1: $E_{act} = 84.8 \text{ kJ/mol}$.

(b) **Path5** Subsurface diffusion 2: $E_{act} = 163.9 \text{ kJ/mol}$.

(c) **Path6** Diffusion above surface, no interaction: $E_{act} = 48.1 \text{ kJ/mol}$.

(d) **Path7** Diffusion above surface assisted by a carboxylate moiety $E_{act} = 19.4 \text{ kJ/mol}$.

**Figure 3.6:** NEB profiles for proton migration in presence of a co-adsorbed carboxylate moiety and of an acetonitrile monolayer, seen from top view.
3.4. Electronic Properties of Subsurface Protons

![Graph and image of a network structure]

**Figure 3.7:** Total density of states for the fully localized polaron (upper panel, electron charge in blue) and for the partially delocalized polaron (lower panel, electron charge in green). The projected DOS on Ti d orbitals is painted in red.

...ble, with a loss in stability of about 4 kJ/mol and no substantial change in the DOS distribution, as shown in Figure 3.8.

A more extended polaron, with the excess charge delocalized over several Ti atoms, is also observed. Such partially delocalized state is located somewhat higher in the band gap, 0.25eV below the CB edge. This state is only metastable and nearly iso-energetic with the localized state. Their relative stability may be significantly influenced by the nature of the exchange and correlation functional and on the amount of Hartree Fock exchange[130], but it appears that both solutions are possible.

The presence of a co-adsorbed carboxylate moiety does not alter the overall DOS distribution (Figure 3.9), even if the most stable position for the localized proton is found to be located deeper below the surface edge, probably because of the electrostatic repulsion and surface deformations due to the presence of the negatively charged carboxylate moiety. Hence, it can be stated that the presence of a subsurface proton, stabilized by the co-adsorbed carboxylate moiety, acts as a trap state for the excess electrons injected into the anatase slab, favoring charge localization. Such behavior may influence the electron injection dynamics and the overall device performance.
3. Structure and Mobility of Acetic Acid at the Anatase (101) / Acetonitrile Interface

Figure 3.8: Total density of states for the fully localized polaron localized in proximity of the subsurface proton (left panel) or deeper in the slab (right panel). The projected DOS on Ti d orbitals is painted in red.

Figure 3.9: Total density of states for the fully localized polaron, in presence of a coadsorbed acetate moiety (upper panel, electron charge in blue) and for the partially delocalized polaron (lower panel, electron charge in green). The projected DOS on Ti d orbitals is painted in red.

3.5 Surface Mobility of Acetic Acid

Following the activation energies computations for proton diffusion on the anatase surface, the possibility of acetic acid migration with the proton on top of the anatase slab has been investigated. In this case, solvent plays a fundamental role, by assisting partial detachment of the acid molecule,
filling up vacant binding positions and interacting with the molecule in its transition state. Hence a monolayer model for the solvent is not sufficient anymore to described the reaction path. Instead we have adopted an explicit solvent model and used the thermodynamic integration scheme (TI) to explore the free energy surface. The details of the reaction coordinate used for these simulations are shown in Figure 3.10. The most likely molecular movement studied is a geometry switch from configuration \textbf{A} to configuration \textbf{D} (Path8, Figure 3.5). During the MD run, a spontaneous exchange of protons takes place from the acid molecule adsorbed in configuration \textbf{A} (R.C.=-0.94 Å) to the surface and vice versa, so that the carboxylic moiety adsorbed in configuration \textbf{A} exists both in its dissociate and stability form, as illustrated in the lower panel of Figure 3.11. We observe that with respect to the solvent monolayer environment the relative stability of the two modes is slightly altered, with the bidentate configuration \textbf{D} stabilized in the liquid environment with respect to the monodentate configuration \textbf{A} by $\Delta E = 5.3$ kJ/mol (Figure 3.11). The activation energy for moving from configuration \textbf{D} to \textbf{A} is lowered by 5.9 kJ/mol for the reaction compared to the monolayer simulation ($E_{act}=14.7$ kJ/mol in the liquid environment vs 20.6 kJ/mol in the solvent monolayer environment, Figure 3.5 ). This shows that the presence of solvent molecules facilitates the interconversion of the structures.

A continuous sequence of switches in adsorption geometry and hydrogen diffusion steps (as described in the previous section) leads to an overall migration of the acid molecule along the [010] direction of anatase (101), as pictured in detail in Figure 3.12. The highest barrier to overcome along the studied migration path is at maximum of $E_{act}=19.4$ kJ/mol, so that a stepwise molecular diffusion on the surface, without complete detachment of the adsorbed carboxylate moiety, is easily feasible if the proton does not
3. Structure and Mobility of Acetic Acid at the Anatase (101) / Acetonitrile Interface

Figure 3.11: Upper panel: Free energy profile relative to Path8, obtained by Thermodynamic Integration. Lower panel: plot of the distance between the acidic proton and the surface (red) and between the proton and the carboxylate moiety (black) as a function of simulation time (0.5 fs/step), for R.C. = -0.50 Å (circled in red on the free energy profile). Spontaneous proton transfer between the acid and the surface (black/red crossover) is observed.

3.6 Acetic Acid Desorption

In this section the desorption process in presence of a liquid solvent is studied, establishing the strength of the interaction. Configuration A (Figure 3.2) was chosen as starting point for these simulations. As demonstrated in the previous sections, this geometry is energetically almost equivalent to the dissociative bridging configuration D and both modes can easily interconvert. The desorption process is necessarily associated with the adsorption of ACN molecules to fill the created vacancy in the monolayer. Therefore, an explicit solvent model is again needed in these simulations and the relative stabilities and barriers are obtained via TI.

The reaction coordinate employed in these simulations is shown in Figure 3.13 and accounts at the same time for acid desorption as well as ACN adsorption. The computed free energy profile is reported in Figure 3.14. We note that at the final point in the TI calculation, the acid molecule is fully detached from the anatase (101) surface, but a complete separation...
3.6. Acetic Acid Desorption

Figure 3.12: Upper panel: Energy diagram reporting the activation energies computed (in kJ/mol) for the stepwise migration of the acid molecule on anatase (101). Lower panel: Graphical representation of the migration process; for clarity, surrounding solvent molecules are not shown. As a reference, the initial detachment point is painted in black. **Step 1**: movement from configuration $D$ to configuration $A$. **Step 2**: Proton transfer from the surface to the molecule and rearrangement in a symmetric position. **Step 3**: movement from configuration $A$ to configuration $D$. For each series of steps, the overall displacement of the molecule is 3.79 Å along the [010] direction.

Figure 3.13: Representation of the two components of the reaction coordinate chosen for the desorption process; $R.C. = d(Ti_{surf} - N_{solv}) - d(Ti_{surf} - C_{acid})$. For clarity, co-adsorbed and surrounding solvent molecules are not shown from the interface is not yet achieved. The acid can be involved in multiple Hydrogen bonds with the nearby adsorbed acetonitrile molecules. Such
3. Structure and Mobility of Acetic Acid at the Anatase (101) / Acetonitrile Interface

![Figure 3.14](image)

**Figure 3.14:** Upper panel: Free energy profile relative to the detachment of an acetic acid molecule from the anatase (101) surface, obtained by thermodynamic integration. Mid and Lower Panel: plot of the distance between the acidic proton and the surface (red) and between the proton and the carboxylate moiety (black) as a function of simulation time, for a molecule partially attached to the surface (R.C.=2.2 Å circled in red on the free energy profile) and for a completely detached molecule (R.C.=-6.0 Å circled in black on the free energy profile). Spontaneous proton transfer between the acid and the surface (black/red crossover) is observed only if the molecule is partially attached to the surface and, even in this case, a preponderance of the protonated acid form is evident.

interactions strongly influence the stability of the detached acid molecule, making it difficult to precisely obtain its adsorption energy, i.e. the stability difference between the surface-adsorbed acid molecule and the solvated acid molecule. For the process studied, the obtained binding energy of acetic acid adsorbed in a molecular bridging configuration (configuration A of Figure 3.2) is $E_{\text{ads}} = 37.5$ kJ/mol. From the dissociative bridging configuration D this value increases to $42.8$ kJ/mol considering the $5.3$ kJ/mol stability difference between binding modes A and D derived earlier. The activation energies obtained for the desorption from A and D are $52.2$ kJ/mol and $57.3$ kJ/mol respectively.

It is important to note that the desorption mechanism presented requires the molecular acetic acid to be desorbed. As this requirement was not part of the reaction coordinate, this shows that a dissociative desorption has to have a higher barrier. As it can be seen in figure 3.14, in the early stages of the reaction, proton transfer from the surface to the acid molecule and vice
versa is possible, while this is not the case in the final state. This means that this mechanism can only occur in configurations where the the proton can be easily transferred to the acid. Therefore, the observation of a stable subsurface proton state can kinetically trap the acid on the surface and prevent desorption.

3.7 Conclusion

In this chapter, first-principles DFT calculations were performed to investigate the behavior of acetic acid molecules adsorbed on the anatase (101) surface, in presence of explicit acetonitrile liquid solvent. A systematic screening on different anatase slabs, with varying thickness and width, led to the conclusion that a slab thickness of at least 5 layers (about 17 Å) should be adopted to correctly evaluate the acid binding properties. A similar size dependence of the relative stability of different adsorption modes has been previously reported for water on the rutile (100) surface [175], supporting the need of a fully converged slab thickness to perform calculations.

The use of such a thick slab allowed us to discover a novel, more stable binding mode, characterized by proton insertion below the first layer of oxide atoms. Hybrid DFT calculations show that the subsurface proton insertion slightly distorts the anatase lattice and favors localization of excess electrons below the surface edge.

NEB calculations show that the presence of the above co-adsorbed acetate moiety assists proton intercalation, while subsurface proton migration remains limited. On the other hand, proton diffusion on top of the anatase surface is favored by the interaction with a nearby adsorbed carboxylate moiety.

Activation energies computed with the Nudged Elastic Band and Thermodynamic Integration method also demonstrate that, if the proton is adsorbed on top of the anatase slab, an acid molecule adsorbed on the surface in a less stable geometry can move towards the thermodynamically stable state, by partial detachment, rotation and re-adsorption on the surface. A stepwise sequence of changes in the acetic acid adsorption geometry can take place, leading to an overall diffusion of the molecule along the [010] direction, with a maximum activation energy of only $E_{\text{act}} = 19.4$ kJ/mol. The process of complete acetic acid desorption from the surface has been shown to require an activation energy, in presence of explicit liquid solvent, of $E_{\text{act}} = 51.0$ kJ/mol. The protonated acid form is dominant during the desorption process and, at the end, the molecule detaches from the slab in its protonated form. For this reason, proton deintercalation from the more stable subsurface state is essential for the acid detachment. Such process is characterized by an high activation barrier, so that the acetic acid molecule results effectively ‘pinned’
3. Structure and Mobility of Acetic Acid at the Anatase (101) / Acetonitrile Interface

to the surface if proton intercalation takes place. The performed simulations account for effects of the solvent explicitly, which might be overlooked or difficult to take into account in calculations adopting less advanced models. By direct comparison of the explicit solvent with ‘gasphase’ and ‘solvent monolayer’ environments, it was demonstrated that the adsorption energy differ by almost a factor of two between these models. Such quantitative results, which where obtained by ab initio MD calculations on a complex solid-liquid interface made up of 1400 atoms, could be used as a benchmark result to validate more expedient computational approaches. Future work should extend these results, both towards more realistic dyes, including bulky organic ligands and organo-metallic compounds, as well as towards explicit electrolytic solutions that contain the additives commonly employed in high efficiency devices. Finally, experimental verification of the subsurface proton state and a characterization of its influence on electron injection would further contribute to rationalizing the performance of dye sensitized solar cells.

3.8 Computational Methods

All density functional theory calculations were performed using the CP2K program package[148]. DFT calculations are based on the hybrid Gaussian and plane wave (GPW) scheme[167], with the Perdew-Burke-Emzerhof[112] exchange correlation functional and corresponding pseudo potentials[169, 176]. The plane wave density cutoff of 600 Ry and periodic boundary conditions have been employed. Dispersion interaction were included in the computation by means of an empirical analytical potential, using the Grimme D3 method[177], within a range of 15 Å. Standard coefficients and scaling factors for PBE and PBE0 functionals were adopted. Scaling factors for PBE are: s6 = 1.0; sr,6 = 1.217; s8 = 0.722. For PBE0: s6 = 1.0; sr,6 = 1.287; s8 = 0.928.

All the atomic species involved in the simulation were described with Gaussian basis sets of double-ζ quality[178]. Relative stabilities of the different binding modes have been computed for a variety of slab models to ensure size convergence of the slab and to test the effect of different environments. The parameters of the unitary cell adopted for building the different slabs are: x=10.227Å; y=3.782Å; z=3.513Å. The (101) interface under study is perpendicular to the z axis. Each slab presented in the text is identified by a three digit code, reporting its size in terms of repetitions of the unitary cell along the x, y and z direction. The tested slab sizes range from 10.227 × 11.346 × 10.540 Å³ (slab 133) up to 20.454 × 22.692 × 17.570 Å³ (slab 265). Three different environment models have been studied, the bare slab without any co-adsorbed ACN molecules,
a four and a five ACN monolayer. As only certain adsorption modes can accommodate a perfect five ACN monolayer an overall comparison of adsorption modes is only possible for the four ACN monolayer. Therefore only the four ACN results are discussed in this paper while the five ACN results are reported in the SI for completeness.

An investigation of the electronic properties of the system in its most stable configuration was carried out by hybrid-DFT calculations. The truncated PBE0 functional [124, 126] with 25% of Hartree-Fock exchange and a cutoff radius of 6 Å has been employed. For computational efficiency, the auxiliary density matrix method [129] was used. The cpFIT3 basis sets as provided by CP2K and a specially optimized basis (see SI) for Ti of similar quality [129] have been used as auxiliary basis for this method.

Minimum energy paths have been computed using the climbing image nudged elastic band (CI-NEB) method, introduced by Jónsson and co-workers[141, 142, 143]. The spring constant value for NEB calculations was set to 0.02.

Free energy profiles have been computed using the thermodynamic integration scheme based on molecular dynamics. All reaction coordinates have been defined as linear combinations of interatomic distances and therefore the computation of additional correction terms is not required[146]. The model in these calculations consisted out of the $20.454 \times 22.692 \times 17.570 \, \text{Å}^3$ slab to avoid a bias due to missing k-points and to obtain a better description of the solvent structure. For efficiency reason, four acid molecules have been included at each side of the slab. In this way 8 points of the TI could be computed simultaneously. The slab was enclosed into an orthorhombic unit cell of dimension $20.454 \times 22.692 \times 38 \, \text{Å}^3$ and surrounded by the explicit liquid environment, for a total of 1396 atoms. This setup was equilibrated at 300 K with a 50 ps (0.5 fs timestep) NVT simulation using forcefields from literature[179, 180, 102] and fixed acid positions. The constrained MD runs were carried out in the NVT ensemble at 300K, with a timestep of 0.5 fs for a total of 20000 steps (10 ps). The thermostating scheme of NVT runs was canonical sampling through a velocity rescaling algorithm (CSVR), as implemented in the cp2k package [181]. Error bars were calculated from independent averages over the Lagrange multipliers during the first half of simulation (upper limit) and during the second half of the simulation (lower limit), equilibration period excluded. The asymmetry of the error bars along the reaction path is due to the integration procedure, which, by convention, fixes the first integration point to zero.
Chapter 4

Excess electrons and Li atoms at the anatase (101) interface

Investigation of Lithium intercalated TiO$_2$ is relevant for application in Dye Sensitized Solar Cells, as the presence of Li-based additives is crucial for improved device performance, but also for sensors and battery application. In this chapter the stability, electronic structure and intercalation mechanism of Li-doped anatase is investigated with hybrid DFT. In particular, as the Li intercalation process results in the formation of interstitial Li$^+$ cations and Ti(III) centers, the interaction of the two species is taken in consideration for both a bulk and surface environment. The relevance of the upper (101) surface layers and the role of the solvent in the stabilization of Li atoms is also explored, as well as the possibility of cation segregation and its effect on surface adsorbates.

4.1 Anatase bulk properties

An investigation of the geometrical and electronic properties of defects in bulk anatase has the dual purpose of a) testing the validity of the employed method, by allowing comparison of the results with the more frequent studies on bulk materials and b) providing a set of bulk data that can directly be compared with the results of surface models. It is widely accepted that Li atoms intercalate in the distorted octahedral cavities of anatase TiO$_2$ [182, 183, 184, 110, 185]. Experimental and theoretical evidence [186, 187, 188, 185, 189, 110] support the notion of charge transfer from the intercalated Li atom to a Ti site. For this reason, the insertion of a Li atom in the anatase lattice can be related to the presence in the
4. Excess electrons and Li atoms at the anatase (101) interface

lattice of separated Li+ ions and excess electrons, and represented as[110]:

\[ TiO_2 + xLi^+ + xe^- \rightarrow Li_xTiO_2 \]

The geometrical and electronic properties of self-trapped electrons in anatase were investigated in greater detail in Chapter 2. Excess electrons in bulk anatase localize on Ti sites, generating a formal Ti(III) site. The associated lattice relaxation is anisotropic, with a stronger distortion in the (001) plane and maximal diameter \( \sim 15 \, \text{Å} \). Given the long range lattice relaxation, the polaron stability depends on the electron concentration, with a tendency to delocalize at high concentrations, probably due to the overlap of the polaronic distortion[94].

The charge localization (or trapping) energy on a Ti site is computed as:

\[ E_{\text{trap}} = E_{\text{loc}} - E_{\text{deloc}} \]

Where \( E_{\text{loc}} \) and \( E_{\text{deloc}} \) are the total energies for pure (or Li intercalated) TiO\(_2\) systems with, respectively, fully localized and delocalized excess electron charge and accordingly relaxed ionic lattice. Negative values of \( E_{\text{trap}} \) indicate stable polarons around the reduced Ti(III) center, while positive values imply metastable charge trapping and conduction band like behavior. In a \( 6 \times 6 \times 2 \) anatase supercell, the smallest cell in which the polaron overlap is negligible, the charge trapping energy can be estimated between -0.05 and -0.1 eV in absence of Li+ ions.

The long range lattice relaxation associated with charge localization plays a role also in Li intercalated systems, leading to system size effects: for higher Lithium concentrations, trapped charges are less stable (See Figure 4.1). To minimize size effects, a \( 6 \times 6 \times 2 \) anatase system, analogous to the one ef-
4.1. Anatase bulk properties

Effective for excess electrons, has to be adopted. Different combinations of

![Figure 4.2](image)

**Figure 4.2:** Charge trapping energy for Li intercalation in bulk anatase, as a function of \% hfx for the $6 \times 6 \times 2$ bulk system. Different charge localization positions: Red: Ti1; Blue and Cyan: Ti2 and Ti3; Green: Ti atom at 12 Å distance from the interstitial; Black: lone excess electron in absence of Li ions.

Li+/electron sites were tested: the energetically most favored combination is achieved when the electron is placed on a Ti center near the Li ion but not in the equatorial plane of the octahedron, as in Ti2 and Ti3 of Figure 4.2.

The influence of Li+ ion on charge localization is assessed by comparison to a system in which the Li+/electron couple is separated by several lattice constants. The comparison yields a stabilization for charges localized on position Ti1 of $3 \times 10^{-2}$ eV, while for charges localized on positions Ti2 and Ti3 the stabilization is $5 \times 10^{-2}$ eV. This result is fully consistent with what reported by Morgan et. al. [110], showing a destabilization of $\sim 5 \times 10^{-2}$ eV when the Li+/electron couple was separated by one or more lattice constants. Such small values of interaction between electrons and Li+ ions suggest that the charge localization energy is only marginally influenced by the presence of a nearby Li ion, and can be compared to the localization of a lone excess electron, shown in Figure 4.2.

Further testing on Li+ ion and electron mobility, carried out via the NEB method, confirms that the electron hopping and Li+ migration mechanisms are not influenced by the relative position of the two species (Figure 4.3).

The activation energy for Li+ migration between octahedral cavities in bulk anatase is 0.63 eV, both in absence and presence of a nearby electron, and is in agreement with other theoretical[110] and experimental[185] studies. Also the mechanism of electron hopping is not altered by the presence of an adjacent interstitial Li+ ion, with an activation energy of 0.23 eV, as for the migration of intrinsic anatase polarons. During both Li+ and electron migration, the relative position of the two species was constantly monitored, with no evidence of collective migration of ions and polarons, confirming the small interaction energy of the two species in bulk anatase.
4. Excess electrons and Li atoms at the anatase (101) interface

![Figure 4.3](image)

**Figure 4.3:** Panel (a): energy profile for electron hopping between equivalent Ti sites in bulk anatase, in presence (red) and absence (black) of an adjacent interstitial Li\(^+\) cation, computed with the PBE0 functional (35% hfx) in a \(6 \times 6 \times 2\) bulk system. Panel (b): energy profile related to Li migration in bulk anatase, computed with the PBE0 functional (35%hfx) in a \(6 \times 6 \times 2\) bulk system. Different sites for electron localization are considered. Red: delocalized charge. Green: localization of the charge near the Li\(^+\) path. Blue: localization of the charge far away from the Li\(^+\) path. Black, continuous: lone Li\(^+\) migration (PBE0-35% hfx level). Black, dashed: lone Li\(^+\) migration (PBE level).

4.2 Insertion of Li\(^+\) ions across the (101) interface

The first surface layers of anatase (101) provide more favorable Li\(^+\) binding and intercalation sites compared to the bulk material. Topsurface Li\(^+\) adsorption is most favorable when the ion interacts with the maximum possible number of topsurface oxide ions (i.e. 4), as reported by Olson et al.[189]. In the subsurface layer two non equivalent intercalation positions exist, as shown in Figure 4.4: calculations carried out on multiple system sizes confirm that the insertion cavity surrounded by 6 Ti\(_{6c}\) is energetically favored by \(\sim 4.5 \times 10^{-1}\) eV. In the following discussion, such position is named Li\(_{2a}\), while the other less favored configuration is named Li\(_{2b}\).

The destabilization of position Li\(_{2b}\) may be related to the contrasting effects of surface relaxation, normally driving the topsurface O\(_{3c}\) anions towards the vacuum region (i.e. away from the center of the slab), and the attractive interaction between the O\(_{3c}\) anions and the subsurface interstitial Li\(^+\) cation. The situation is instead reversed for configuration Li\(_{2a}\), in which the Li\(^+\) cation is bound to an oxygen anion that is normally slightly relaxed inwards (i.e. towards the center of the slab), so that the attraction of the Li\(^+\) cation is not competing against surface relaxation, but is instead enhancing it. The energy difference between the two cavities levels off in the other layers, as the two positions regain the symmetry of a bulk like environment.

As reported in Figure 4.5, the most favorable insertion position for Li\(^+\) ions is the Li\(_{2a}\) subsurface cavity. Cavities in deeper, bulk like layers are less favorable for Li\(^+\) intercalation. This result explains why maximal cation loading (i.e. LiTiO\(_2\)) can only be reached in small crystallites with higher
4.2. Insertion of Li+ ions across the (101) interface

![Figure 4.4](image)

**Figure 4.4:** Inequivalent subsurface positions. Blue arrows indicate the attractive interaction between the surface O\(_{3c}\) anion and the intercalated subsurface Li+ cations. Black arrows indicate the direction of O\(_{3c}\) relaxation due to surface relaxation.

<table>
<thead>
<tr>
<th>Position</th>
<th>PBE</th>
<th>PBE0-25%hfx</th>
<th>PBE0-35%hfx</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li1</td>
<td>-0.04</td>
<td>-0.06</td>
<td>-0.07</td>
</tr>
<tr>
<td>Li2a</td>
<td>-0.11</td>
<td>-0.11</td>
<td>-0.11</td>
</tr>
<tr>
<td>Li2b</td>
<td>+0.33</td>
<td>+0.40</td>
<td>0.41</td>
</tr>
<tr>
<td>Li3a</td>
<td>-0.04</td>
<td>-0.04</td>
<td>-0.04</td>
</tr>
<tr>
<td>Li3b</td>
<td>0.09</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>Li4</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

**Figure 4.5:** Lithium intercalation positions across the anatase [101] surface, and proposed intercalation path. The stability of the intercalated positions is computed in a \(2 \times 6 \times 7\) slab and normalized to the bulk-like intercalated Li4 position.

Surface to volume ratio than bulk anatase [190]. Analysis of different system sizes and Li+ concentrations (See Table 4.1 ) reveal that the surface effect is attenuated after the 2nd TiO\(_2\) layer, so that the 3rd subsurface layer (i.e. position Li4) can be assumed to have approximately bulk like behavior. Topsurface Li+ adsorption (Li1) is energetically disfavored compared to subsurface insertion (Li2b) by \(\sim 5 \times 10^{-2}\) eV.

If multiple Li+ ions are present in the system, subsurface segregation oc-
4. Excess electrons and Li atoms at the anatase (101) interface

Table 4.1: Stability difference of the Li intercalated positions with respect to the topsurface adsorption position, for increasing slab thickness and width and decreasing Li+ concentration.

<table>
<thead>
<tr>
<th>System</th>
<th>Periodicity</th>
<th>∆E_{surf} / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1st layer</td>
<td>2nd layer</td>
</tr>
<tr>
<td>slab133</td>
<td>xy</td>
<td>+0.21</td>
</tr>
<tr>
<td>slab135</td>
<td>xy</td>
<td>+0.11</td>
</tr>
<tr>
<td>slab137</td>
<td>xy</td>
<td>+0.05</td>
</tr>
<tr>
<td>slab139</td>
<td>xy</td>
<td>+0.07</td>
</tr>
<tr>
<td>slab255</td>
<td>xy</td>
<td>-0.11</td>
</tr>
<tr>
<td>slab257</td>
<td>xy</td>
<td>-0.13</td>
</tr>
<tr>
<td>slab259</td>
<td>xy</td>
<td>-0.10</td>
</tr>
</tbody>
</table>

∆E_{surf} = E_{nth layer subsurf} − E_{top surf layer}

curs: as reported for bulk crystals [191] Li+ ions tend to segregate in adjacent octahedral cavities rather than distributing in the system. Due to subsurface stabilization, segregation along the [010] crystal direction is favored, resulting in the formation of a subsurface row of Li+ atoms in adjacent cavities. The energy gain associated with Li+ segregation is assessed by comparison with a range of configurations in which the Li+ ions are dispersed in the subsurface layer (See Figure 4.6), and is quantified in $5 \times 10^{-2}$ eV.

It is assumed that the subsurface Li+ insertion proceeds through a path analogous to the one observed for the bulk migration, i.e. via multiple steps along a zigzag path. Insertion profiles and activation energies were obtained via the NEB method, and are reported in Figure 4.7. The total activation energy required to reach the most stable subsurface position (i.e. position Li2a) is 1.43 eV when the surface is exposed to the vacuum. The highest barrier to overcome for Li+ insertion is 1.22 eV and corresponds to the cation migration from the topsurface adsorption position to an intermediate intercalation position (i.e. position Li2b). The presence of an acetonitrile (ACN) monolayer, a solvent commonly used in sensitized solar cells, further destabilizes the topsurface adsorption position Li1 due to the unfavorable interaction between topsurface Li+ ions and the terminal methyl moiety of ACN. On the other hand, the subsurface Li2b position is slightly stabilized, being directly below the nitrile moiety. For this reason, the intercalation energy from position Li1 to Li2b is lowered to 0.47 eV, while the second intercalation step, from Li2b to Li2a, has a slightly higher activation energy (0.29 eV) with respect to the bare slab. Overall, solvent adsorption on anatase facilitates subsurface Lithium insertion in the most stable Li2a position, lowering the total activation energy to 0.76 eV. Solvent effects are significantly reduced below the first subsurface layer, with marginal effects on more deeply intercalated Li+ species.
4.3. Acetic Acid Pinning

The presence of topsurface/subsurface intercalated Li+ ions has an influence on the adsorption equilibrium of functional molecules. One of the most common anchoring groups for TiO$_2$ functionalization is the carboxylic/carboxylate moiety, that can be modeled with acetic acid, as discussed more in detail in Chapter 3. Among the possible adsorption positions, two are energetically more favored (Figure 4.9): dissociative bidentate adsorption, with two $Ti_{slab} - O_{acid}$ bonds, and a molecular adsorption, with...
4. Excess electrons and Li atoms at the anatase (101) interface

![Image](image_url)

**Figure 4.7:** NEB profile for Li+ intercalation and corresponding activation energies for both the bare slab (black line) and the solvent monolayer (red line) environment. NEB profiles are computed with PBE and in a less thick $2 \times 6 \times 5$ slab. Different slab thickness accounts for energy variations in the order of $10^{-2}$ eV between the $2 \times 6 \times 7$ and $2 \times 6 \times 5$ slab models.

<table>
<thead>
<tr>
<th>Path</th>
<th>$E_{act} / eV$</th>
<th>Bare slab</th>
<th>ACN Monlayer</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-2b</td>
<td>1.22</td>
<td>0.47</td>
<td></td>
</tr>
<tr>
<td>2b-2a</td>
<td>0.21</td>
<td>0.29</td>
<td></td>
</tr>
<tr>
<td>2a-3b</td>
<td>0.86</td>
<td>0.81</td>
<td></td>
</tr>
<tr>
<td>3b-3a</td>
<td>0.37</td>
<td>0.38</td>
<td></td>
</tr>
<tr>
<td>3a-4</td>
<td>0.67</td>
<td>0.68</td>
<td></td>
</tr>
</tbody>
</table>

one $T_{i_{slab}} - O_{acid}$ and one $OH_{acid} - O_{slab}$ bond. The stability of the two geometries is similar, in particular when a thick slab model, more similar to a nanoparticle, is used.

Different relative positions of Li+ cation and acetic acid moiety were tested (See Figure 4.8).

Overall, the presence of subsurface Li+ ions in the vicinity of the adsorbed moiety enhances the binding stability, by $\sim 1.1 \times 10^{-1}$ eV in the case of bidentate adsorption, and of $9 \times 10^{-2}$ eV for the molecular adsorption mode. In both cases, the stabilization effect is achieved only if the cation is present subsurface, and not when the Li+ is adsorbed on top of the surface, even in the vicinity of the acid moiety. An analysis of the system geometry reveals that subsurface Lithium ions tend to retain the energetically favored $T_{i_{slab}}$ environment (pos. **Li2a** of Figure 4.5), also in proximity of the acid moieties. For this reason, Li+ cations tend to segregate in the proximity of the adsorbed acid, but avoid to insert directly below the moiety (pos. **Li2b** of Figure 4.5), contrary to what it occurs when protons are inserted.
4.4 Excess electrons

As for Li+ ions, the presence of the [101] interface leads to a stabilization of localized charges in the topsurface and subsurface slab layers with respect to bulk polarons. The extent of the stabilization is such that, even when a relatively small amount of exact Hartree-Fock exchange is adopted, the charge trapping energy is negative, producing stable polarons, as reported in Fig-

![Diagram showing dissociative and molecular adsorption modes](image)

**Figure 4.8:** Energies of the tested combinations of Li+ ions and adsorbed acetic acid molecules on the 255 anatase surface. For each Li+ ion of any configuration, the insertion layer and the position on the slab are reported. Energies are normalized with respect to the energy of configuration m1 for the molecular adsorption mode and d1 for the dissociative adsorption mode.
4. Excess electrons and Li atoms at the anatase (101) interface

Figure 4.9: Most favorable Li⁺ intercalation positions in presence of a coadsorbed acetic acid moiety, in the molecular (a) and dissociative (b) forms.

Figure 4.10: Polaron trapping energy ($E_{\text{trap}}$) as a function of the charge localization position in the anatase (101) slab models ($2 \times 6 \times 7$ clean slab), for different amounts of % hfx. Energies are computed with respect to the bulk-like pos Ti5, in the middle layer of the slab.

<table>
<thead>
<tr>
<th>Position</th>
<th>$E_{\text{trap}} / \text{eV}$</th>
<th>$E_{\text{trap}} / \text{eV}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Absolute</td>
<td>Relative*</td>
</tr>
<tr>
<td></td>
<td>25%hfx 30%hfx 35%hfx</td>
<td>25%hfx 30%hfx 35%hfx</td>
</tr>
<tr>
<td>Ti1a</td>
<td>0.00 -0.26 -0.55</td>
<td>0.00 -0.04 -0.06</td>
</tr>
<tr>
<td>Ti1b</td>
<td>0.00 -0.24 -0.52</td>
<td>0.00 -0.02 -0.03</td>
</tr>
<tr>
<td>Ti2</td>
<td>-0.04 -0.27 -0.53</td>
<td>-0.04 -0.05 -0.04</td>
</tr>
<tr>
<td>Ti3</td>
<td>-0.03 -0.26 -0.53</td>
<td>-0.03 -0.04 -0.04</td>
</tr>
<tr>
<td>Ti4</td>
<td>-0.01 -0.23 -0.50</td>
<td>-0.01 -0.01 -0.01</td>
</tr>
<tr>
<td>Ti5</td>
<td>0.00 -0.22 -0.49</td>
<td>0.00 0.00 0.00</td>
</tr>
</tbody>
</table>

* relative to pos Ti5

On the other hand, when excess electrons are added to an anatase slab, but no lattice relaxation is allowed, the additional charge delocalizes in the deeper, bulk-like layers of the slab (Figure 4.11), where the Ti centers are more positively charged and interaction with the delocalized charge is more favorable. For this reason, the stabilization of localized excess electrons in
4.4. Excess electrons

the upper slab layers is most likely due to the lesser geometrical constraint of the surface atoms, that allow a better lattice relaxation around the Ti(III) center. This observation is confirmed by the fact that both positive (Li+ ions) and negative (excess electrons) charges are more stable at the interface, emphasizing the relevance of lattice relaxation for defect stabilization.

Due to the presence of the interface, not all the Ti cations of the anatase slab are equivalent. In particular, on top of the (101) surface, Ti cations can be in a 5-coordinated (Ti$^{5c}$) or in a 6-coordinated environment (Ti$^{6c}$). The overall polaron geometry, as described for bulk polarons in Chapter 2, is essentially maintained in the slab, with an anisotropic atomic relaxation mostly along the [100] and [010] directions. The main difference with respect to bulk polarons is observed when charges are localized on the under-coordinated Ti$^{5c}$. In this case, the Ti(III)-O bonds are shorter than in the bulk, as it occurs for the Ti$^{5c}$-O bonds of a defect free surface. The interface effect is attenuated at increasing localization depths.

For all the %hfx considered, the stabilization energy for the subsurface position with respect to the bulk can be estimated in $5 \times 10^{-2}$ eV for position Ti2 and $4 \times 10^{-2}$ eV for position Ti3. The stability of topsurface configurations (Ti1a and Ti1b) increases with the % of hfx adopted in the functional, so that the relative stability with respect to the subsurface localization positions depends on the computational model. However, higher level calculations, based on the Random Phase Approximation (RPA), carried out on a smaller $3 \times 3 \times 1$ slab, confirm that charge localization in the subsurface position Ti2 is more favored than localization in the topsurface Ti ions, regardless of the parent functional adopted (PBE0 with 25% and 35% hfx). Results for the...
4. Excess electrons and Li atoms at the anatase (101) interface

Figure 4.12: Difference in topsurface (Ti1a) and subsurface (Ti2) polaron energies, computed by RPA with different parent functionals (tr-PBE0 with varying amounts of %hfx). \( \Delta E = E_{Ti2} - E_{Ti1a} \). A comparison with results from hybrid calculations (tr-PBE0) is also reported. Red: 1 \times 3 \times 3 slab system. Black: 2 \times 6 \times 7 slab system.

RPA calculations are reported in Figure 4.12.

Step edges are one of the most common defects on the (101) anatase

<table>
<thead>
<tr>
<th>Position</th>
<th>( E_{\text{trap}} ) step edge / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25%hfx</td>
</tr>
<tr>
<td>Ti1</td>
<td>0.20</td>
</tr>
<tr>
<td>Ti2</td>
<td>0.04</td>
</tr>
<tr>
<td>Ti3</td>
<td>-0.05</td>
</tr>
<tr>
<td>Ti4</td>
<td>-0.04</td>
</tr>
<tr>
<td>Ti5</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Figure 4.13: Polaron trapping energy (\( E_{\text{trap}} \)) as a function of the charge localization position in the D step model (2 \times 6 \times 7 slab with steps along the [111] direction on both sides of the slab), for different amounts of % hfx. Energies are computed with respect to the bulk-like pos Ti5, in the middle layer of the slab.
4.4. Excess electrons

surface[192] and, with respect to the clean surface, exhibit different electronic properties[193]. Amongst all the possible step edges, one of the most stable is the one in which the edge is parallel to the [11\bar{1}] direction, often referred to as D type step[192]. The creation of a D type step affects the atoms of the first two layers of the interface, creating four different possible localization positions in proximity of the step: an under-coordinated \( Ti_{5c} \) topsurface position, a fully coordinated \( Ti_{6c} \) topsurface position at the step edge, and the corresponding atoms at the base of the step. The effect of the step is assessed by comparing the surface polaron energies to the energy of a bulk like polaron on a Ti atom deeper below the surface (Figure 4.13). Also in this case, subsurface polarons are stabilized by \( 5 \times 10^{-2} \) eV with respect to the bulk, with an additional stabilization of \( 1 \times 10^{-2} \) eV at the base of the step. Energy variations due to the adopted functional make it difficult to exactly quantify topsurface and step edge polaron stability. However, it is clear that surface polaron are less stable than subsurface ones, and are further destabilized by the presence of the step edge, by \( \sim 1.4 \times 10^{-1} \) eV. This result is at variance with what reported in a previous DFT study[193], that, however, confined the electron on one surface site and compared its stability to bulk data, without investigating other possible subsurface positions. 

Anatase polarons can not easily be visualized via STM imaging of the clean (101) surface, but are detected at step edges[86, 193]. This finding can be consistent both with the prediction of higher stability of edge polarons[86], and with the here reported existence of stable subsurface trap sites, that can easily be accessed by STM imaging only in proximity of step edges. Further theoretical investigation is therefore necessary to correctly assess the role of step edges in the overall anatase (101) behavior.

As for bulk polarons, surface charge localization is associated to a trap state in the semiconductor TiO\(_2\) band gap. In both the 25 and 35 % hfx cases, the

Figure 4.14: Density of states for the anatase 101 slab (grey - \( 2 \times 6 \times 7 \) slab) and bulk system (red - \( 6 \times 6 \times 2 \) bulk supercell). The diagrams are aligned so that the energy of the VB edge is equal to zero. The Ti(III) trap state is visible in the middle of the gap. Red: bulk system. Black: electron localized on slab, position \( Ti_{5} \). Blue: electron localized on slab, position \( Ti_{3} \). Green: electron localized on slab, position \( Ti_{1} \).
system band gap and the position of the bulk-like Ti(III) state match almost perfectly the ones computed for bulk systems, confirming the bulk like properties of the inner layers of the chosen slab model. While the system band gap strongly depend on the %hfx adopted, the relative difference between surface and bulk-like trap state is only slightly affected by the functional (+0.05 eV increase in the relative stability of the surface trap vs. +0.97 eV increase in the band gap) and can be quantified in $3.5 \times 10^{-1}$ eV (See Figure 4.14). Note that the $3.5 \times 10^{-1}$ eV shift between the gap states associated to topsurface and bulk like polarons is larger than the relative stability difference computed by comparing the total energy of the two systems ($4 \times 10^{-2}$ eV for PBE0-25%hfx and $6 \times 10^{-2}$ eV for PBE0-35%hfx).

The stabilization of localized excess charges in the (101) surface area, creating deep trap states, is consistent with recent theoretical work, treating Oxygen vacancies and Niobium doping with the HSE06 functional[194].

<table>
<thead>
<tr>
<th>Path</th>
<th>Starting position</th>
<th>Ending position</th>
<th>Hopping distance / Å</th>
<th>$E_{act}$ / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>bulk migration - 6 x 6 x 2 cell</td>
<td>Ti1a</td>
<td>Ti2</td>
<td>3.78</td>
<td>0.23</td>
</tr>
<tr>
<td>a</td>
<td>Ti1a</td>
<td>Ti1b</td>
<td>3.75</td>
<td>0.23</td>
</tr>
<tr>
<td>b</td>
<td>Ti4</td>
<td>Ti5</td>
<td>3.04</td>
<td>0.26</td>
</tr>
<tr>
<td>c</td>
<td>Ti1a</td>
<td>Ti1a*</td>
<td>3.81</td>
<td>0.53</td>
</tr>
<tr>
<td>d</td>
<td>Ti1a</td>
<td>Ti2</td>
<td>3.75</td>
<td>0.23</td>
</tr>
<tr>
<td>e</td>
<td>Ti1a</td>
<td>Ti1b</td>
<td>3.04</td>
<td>0.26</td>
</tr>
<tr>
<td>f</td>
<td>Ti4</td>
<td>Ti5</td>
<td>3.76</td>
<td>0.27</td>
</tr>
<tr>
<td>g</td>
<td>Ti1a</td>
<td>Ti1a*</td>
<td>3.81</td>
<td>0.53</td>
</tr>
</tbody>
</table>

**Figure 4.15:** Activation energies and reaction profiles for subsurface polaron migration in the 2 x 6 x 7 slab system, along different reaction paths, computed at 35% hfx.

if the presence of the (101) interface leads to a stabilization of the subsurface polarons, it has only a small effect on the overall activation energy for polaron migration, that is comparable to the bulk one (See Figure 4.15). However, even if the activation energy difference between bulk and surface charge mobility is limited ($4 \times 10^{-2}$ eV), such energy shift leads to a 10-fold change in the rate constant at room temperature ($k_{eq} \propto exp \left( \frac{-\Delta E_{act}}{kT} \right)$), yielding different hopping rates for surface and bulk like polarons. Similarly to bulk
4.5 Li+/electron interaction at the interface

The Li+/electron interaction is enhanced at the (101) interface, to become more than double than the bulk value. To assess the interface effect, three possible Li+ positions were taken in consideration: topsurface Li+ (position Li1), the most stable subsurface configuration (position Li2a) and the bulk like Li4 position. For each of those Li+ positions, a range of electron localization sites were investigated. The subsurface Li2a position is found to be the most stable for Li+ intercalation also in presence of an electron, either localized or delocalized.

As for bulk systems, the most favorable site for electron localization is on the Ti sites in proximity of the intercalated Li+ ion. Multiple Li insertion will therefore result in the creation of Ti(III) states at the interface region, in good agreement with surface sensitive XAFS experiments [195].

The subsurface Li+/electron interaction is $9 \times 10^{-2}$ eV, with slight variations of $1 \times 10^{-2}$ eV depending on the relative positions of Li+ and electron. A similar value for Li+/electron interaction is computed for topsurface Li+ ions ($1.1 \times 10^{-1}$ eV). Such interaction is double than values computed in bulk anatase ($5 \times 10^{-2}$ eV) and for deeply intercalated Li+ ions ($4.8 \times 10^{-2}$ eV). This behavior is partially due to the lower constraint of the surface atomic layers, so that the Ti(III)/Li+ centers are free to move closer than in bulk material. In addition, the electrostatic screening at the TiO$_2$ interface is reduced, due to the presence of the vacuum layer.

We remark that the magnitude of Li+/electron interaction, even if enhanced at the TiO$_2$ interface, can still be regarded as shallow charge trapping ($\sim 1 \times 10^{-1}$ eV). Therefore the presence of Li+ cations is not likely to strongly hinder electron mobility, but it rather stabilizes surface Ti(III) sites, constituting a series of likely acceptors. This could facilitate charge transfer from donor molecules in the surface area where Li species segregate, increasing quantum yields, as experimentally reported [196]. Additionally, the energetic distribution of potential Ti acceptor sites in proximity of the interface Li+ cations is also consistent with the greater degree of electronic disorder.
of CB states measured in DSSC devices in presence of Li+ based electrolytes [57].

4.6 Conclusion

This Chapter investigates the process of excess charges and Li+ ion intercalation across the TiO$_2$ anatase (101) interface, as it occurs in Dye Sensitized Cells and Li ion batteries. The use of a multi layered slab model (7 TiO$_2$ layers, roughly 1000 atoms) allowed to investigate the oxide behavior in a realistic interface model, with both surface and unconstrained bulk like layers in the same system. The interface properties were computed by direct comparison of surface and deeper, bulk like, layers of the same slab, so that the bias due to the comparison of different models and sizes is minimized. We remark that the choice of different density functionals yields consistent electron localization properties for subsurface layers, but affects results for the topsurface positions. For this reason, results obtained with different functionals should be compared, and possibly confirmed by the adoption of higher levels of theory, such as RPA. The first subsurface layer of the anatase (101) interface proves crucial for both Li+ cation intercalation and excess electron localization, due to the more favorable lattice relaxation than in the bulk material. This finding is in agreement with the fact that the use of finer anatase powders (higher surface to volume ratio) leads to an enhanced device capacity[184], thanks to improved charge storage. Li+ ion segregation in the first subsurface layer occurs in rows along the [010] crystal direction, in turn enhancing the interaction of nearby adsorbed molecules with the oxide, and consequently the binding equilibrium and the overall device stability. Additionally, the presence of Li+ ions in the proximity of coadsorbed moieties can constitute a reservoir of electron trap states, more likely to accommodate charges injected from donors. Despite the fact that the Li+/electron interaction is enhanced at the anatase interface, and doubled with respect to its bulk value, the charge trapping energy is around 0.1 eV, resulting in shallow trapping that is not likely to hinder electron migration. The exact charge trapping energy depends on the relative position of Li+ ions, adsorbates and localized electrons, so that a distribution of trapping energies and time scales for charge migration is expected. This is consistent with the slower electron kinetics, distributed over several time scales, reported in some studies [57].
4.7 Computational Methods

4.7.1 DFT simulations

*Ab initio* DFT calculations were carried out with the CP2K package [148], based on the hybrid Gaussian and plane wave (GPW) scheme [167, 168]. A plane wave density cutoff of 1200 Ry and periodic boundary conditions have been adopted. Bulk calculations were carried out in 3D periodicity, while slab calculations were performed in 2D periodicity, with a wavelet based Poisson solver [197]. GGA calculations were performed with the Perdew-Burke-Enzerhof [112] (PBE) exchange correlation functional, while hybrid calculations have been carried out with the truncated PBE0 (trPBE0) functional [124, 126], with varying percentages of exact Hartree-Fock exchange (hfx), ranging from 25% to 35% hfx. For TiO2, a cutoff radius of 4.5 Å, sufficient to ensure converged electronic properties in the trPBE0 calculations (See Table 4.2), has been chosen for all calculations with the trPBE0 functional. Dispersion interactions were included by means of an empirical analytical potential, using the Grimme D3 method [177], within a range of 15 Å. Standard coefficients and scaling factors for PBE and PBE0 functionals were adopted. The primary Gaussian basis set adopted in all calculations is of double ζ quality, in combination with GTH pseudopotentials [169]. The auxiliary density matrix method (ADMM), which relies on an auxiliary basis for Hartree-Fock exchange [129], was employed to speed up hybrid calculations. RPA calculations [157, 136] have been applied on the eigenstates obtained by the trPBE0 parent functional. Such fifth rung calculations rely on more accurate primary basis (correlation consistent, triple ζ quality) and on a further auxiliary basis, needed for the resolution of identity-based RPA implementation [136]. Fifth rung calculations do not employ ADMM, making the calculation of the Hartree-Fock exchange computationally much more demanding. Activation energies for ions and charge migration were computed with the improved tangent nudged elastic band (it-NEB) method.

### Table 4.2: Relative stability of the localized and delocalized electron solutions as a function of % hfx, for bulk anatase, $x_{Li} = 1.16 \times 10^{-3}$ and truncation radius (R.T.)

<table>
<thead>
<tr>
<th>%hfx</th>
<th>$\Delta E_{loc - deloc}$ R.T. 4.5 Å</th>
<th>$\Delta E_{loc - deloc}$ R.T. 6 Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.04</td>
<td>0.01</td>
</tr>
<tr>
<td>27</td>
<td>-0.06</td>
<td>-0.08</td>
</tr>
<tr>
<td>30</td>
<td>-0.21</td>
<td>-0.22</td>
</tr>
<tr>
<td>33</td>
<td>-0.36</td>
<td>-0.34</td>
</tr>
<tr>
<td>35</td>
<td>-0.47</td>
<td>-0.48</td>
</tr>
</tbody>
</table>
4. Excess electrons and Li atoms at the anatase (101) interface

[141, 142]

4.7.2 Models of the (101) interface

The presence of an interface alters the bulk geometrical and electronic properties of the anatase crystal, thus influencing the overall behavior of excess charges and intercalated Li species. Bulk properties were computed in a $6 \times 6 \times 2$ supercell, i.e. an orthorombic cell with edges $22.692 \times 22.692 \times 19.004$ Å, for a total of 864 atoms. For surface modelling, the adoption of a thick anatase slab (7 to 9 TiO$_2$ layers in the non periodic direction, for 20-25 Å thickness) is essential to correctly assess differences between bulk and surface properties. In fact, Ti and O atoms in the middle of slab of such thickness behave like bulk atoms, providing comparison to surface species, as long as the chosen slab is thick enough to allow differentiation of the two regions. In the modelled slabs, the (101) interface is perpendicular to the z axis. Parameters of the unit cell adopted for building different slabs are: $x = 10.227$ Å; $y = 3.782$ Å; $z = 3.513$ Å. Slabs are identified by a three digit code, corresponding to the repetitions of the unit cell along the x, y and z directions; as an example, the $2 \times 6 \times 7$ slab notation corresponds to a $20.454 \times 22.692 \times 24.591$ Å slab.

This approach is computationally more expensive than mimicking bulk behavior in a slab model by fixing the bottom layer(s) of the slab to the bulk geometry positions. However, this latter strategy, if not carefully tested, could yield unphysical results. In particular, if the bottom layers of the TiO$_2$ slab are fixed, the computed anatase band gap is smaller in the slab model than the computed bulk gap. Such result might lead to the biased conclu-

![Figure 4.16](image)

**Figure 4.16:** Ti $d$ orbital contribution to the total density of states for a (101) anatase slab model (size $2 \times 6 \times 7 = 20.4540 \times 22.692 \times 24.597$ Å). Black: total DOS. Red: 1st (surface) layer. Orange: 2nd layer. Green: 3rd layer. Blue: core (bulk like) layer. The energy diagram is aligned so that the energy of the VB edge is equal to zero.
4.7. Computational Methods

sion that surface states determine a smaller gap than bulk states. On the contrary, when all the surface atoms are allowed to relax to fully unconstrained positions, the band gap determined by the surface atoms is wider than the bulk band gap, as shown in Figure 4.16. This demonstrates that the electronic properties of the anatase system are distorted when the bond length and position of under-coordinated, surface atoms are constrained to the values of fully coordinated, bulk like ones. More realistic data might be obtained when the middle layers of a slab model are constrained to the bulk values, even if, also in this case, proper testing should be carried out to ensure the validity of the model.

Another common technique in surface modelling is the adoption of a fully periodic slab model, in which the surface of interest is exposed to a layer of vacuum (or solvent) of chosen thickness. The obtained structure is periodically repeated in space, alternating vacuum and crystal layers. Such approach does not require the introduction of specific Poisson solvers for the non periodic direction (the one perpendicular to the interface under study) and is widely adopted. The effect of alternating layers on the interface properties must however be carefully investigated, in particular when charged defects are present on the interface and vacuum is interposed between crystal slabs (no electrostatic screening). In particular, for the anatase (101) model in presence of Li+ ions, the thickness of the vacuum layer required to minimize the effect of vicinal interfaces is at least $\sim 50 \, \text{Å}$, and increases at higher defect concentration, as reported in Figure 4.17. In this case, to completely avoid the effect of neighboring interface, a 2D periodic model can be adopted: the interface of interest is still exposed to vacuum layer, but without periodic alternation of the interface/vacuum layers.

![Figure 4.17: Stability of Li+ intercalated in the first subsurface layer with respect to the top surface layer, for two different system sizes and increasing z parameter. Blue: slab137. Red: slab257. Dashed lines: difference in stability obtained with periodicity xy.](image-url)
Chapter 5

A closer look at TiO₂ Hydrogenation

TiO₂ is a frequently employed support in heterogeneous catalysis, in particular for hydrogenation reactions, along with other oxides, such as Al₂O₃, ZnO, ZrO₂, SiO₂. Depending on the support, there are large differences in performance, the origin of which remains, at present, to be fully understood. A comparison of TiO₂ and Al₂O₃ hydrogenation is therefore reported in this Chapter, pointing out relevant differences in the behavior of the two oxides that can influence the catalytic performance. In addition, as introduced in Chapter 1.2, reduced TiO₂ shows improved photocatalytic properties with respect to the non defective material, thanks to improved light adsorption and electrical conductivity. As an example, Li doping (discussed in Chapter 4) results in separated Li⁺ and Ti(III) centers, weakly interacting, so that the mobility of the electron trap state is similar to the one in absence of Li⁺ cations. However, as demonstrated in this Chapter, the behavior of hydrogenated TiO₂ surfaces is quite different, demonstrating that the nature and behavior of defective states influencing the oxide performance depends on the reduction route employed. A third section, focusing on spillover from Platinum clusters to the anatase support to achieve a controlled oxide reduction is also reported. In these calculations, a combination of GGA and hybrid DFT is adopted, depending on the material behavior to model. The parameter dependence of hybrid DFT is accounted for with a screening over different setups.

5.1 Hydrogenated Anatase

5.1.1 H₂ Adsorption Stability

As this Chapter deals primarily with TiO₂ hydrogenation in comparison to the behavior of other oxides, assessment of the interaction of H₂ with the
5. A closer look at TiO₂ Hydrogenation

Anatase surface is a first, fundamental step of the investigation. The adsorption energy of an Hydrogen molecule (H₂) on the anatase (101) interface is computed as:

\[ E_{ads,H₂} = E_{(2H,TiO₂)} - E_{(H₂,vacuum)} \]

With \( E_{(2H,TiO₂)} \) = energy of two H atoms adsorbed on anatase and \( E_{(H₂,vacuum)} \) = energy of H₂ in vacuum, not interacting with the anatase slab. Direct comparison to H₂ in vacuum phase avoids the bias due to the intrinsic instability of a single H atom in vacuum. The adsorption energy of a single H atom on anatase can then be computed as:

\[ E_{ads,H} = \frac{1}{2} E_{ads,H₂} \]

Different slab dimensions, relative positions of the two H atoms and spin multiplicity were considered. Corresponding adsorption energies are reported in Figure 5.1.

As already observed in the case of lithium intercalation, upon H₂ adsorption the oxide slab is reduced with transfer of two electrons to the substrate. Charge localization on TiO₂ depends on the level of theory adopted. PBE calculations result in a delocalized charge in the slab bulk. On the other
5.1. Hydrogenated Anatase

Table 5.1: Differential adsorption Energies for multiple H₂ molecules on a 267 TiO₂ slab.

<table>
<thead>
<tr>
<th>Total number of H₂ molecules (n)</th>
<th>%H₂ coverage per TiO₂ surface unit</th>
<th>Surface H₂ concentration cm⁻²</th>
<th>∆E_{ads,diff} eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>17%</td>
<td>8.6×10¹³</td>
<td>-0.39</td>
</tr>
<tr>
<td>3</td>
<td>25%</td>
<td>1.3×10¹⁴</td>
<td>-0.26</td>
</tr>
<tr>
<td>4</td>
<td>33%</td>
<td>1.7×10¹⁴</td>
<td>0.10</td>
</tr>
<tr>
<td>5</td>
<td>41%</td>
<td>2.2×10¹⁴</td>
<td>0.21</td>
</tr>
</tbody>
</table>

On the other hand, PBE0 calculations, that in general better reproduce the oxide electronic structure, lead to localized charges, whose stability with respect to delocalized electrons depends on the amount of %hfx in the functional. However, it is clear that in both cases system size plays a role: a larger oxide slab (i.e. lower H₂ concentrations) will reduce the overlap of polarons/delocalized electrons and yield more stable H₂ adsorption. On the contrary, smaller system sizes (i.e. higher adsorbates concentrations) result in lower adsorption energies. Computation of the differential adsorption energy for subsequent adsorption of multiple H₂ molecules on the oxide (ΔE_{ads,diff}), suggests that the limit concentration for H₂ exothermic adsorption is between 1.3×10¹⁴ and 1.7×10¹⁴ H₂/cm² TiO₂, as shown in Table 5.1.

\[ \Delta E_{ads,diff} = E_{2nH/TiO₂} - E_{(2n-2)H/TiO₂} - E_{H₂} \]

with \( n \) = total number of H₂ molecules adsorbed on the oxide, \( E_{2nH/TiO₂} \): total energy of \( n \) H₂ molecules adsorbed on the oxide (\( =2n \) H atoms), \( E_{H₂} \): total energy of an isolated H₂ molecule.

![Figure 5.2: Comparison of the excess spin density between surface adsorbed H and Li atoms, seen from top view, along the [101] direction. Panel (a): small protons (yellow) directly bind to a surface O anion, and the corresponding electron density (blue) is transferred to a nearest neighbor Ti center. Panel (b): Li (purple) intercalates between two O sites. While charge is still transferred to a neighboring Ti center, there is no evidence of orbital overlap.](image)
5. A closer look at TiO$_2$ Hydrogenation

5.1.2 On the Nature of the Hydrogen Induced Defect States

Even if TiO$_2$ reduction can be achieved with different methods, the nature of the doping species can influence the behavior of the defect state. A similar issue was addressed by Finazzi et al.[130], by comparing the electronic structure of reduced TiO$_2$ in presence of oxygen vacancies or hydrogen impurities. The study was however limited to bulk states, and did not take into account other possible dopants. In this section a comparison of the interaction of Lithium and Hydrogen with the anatase (101) surface is therefore carried out.

By comparing the excess spin density of the hydrogenated and lithiated interface, it is clear that the electronic structure of the two reduced systems is quite different. Lithium intercalates between two neighboring O$_{2c}$ anions, with no direct overlap between the Li$^+$ cation and the charge localized on the Ti(III) center. On the other hand, the smaller proton directly binds with a single O$_{2c}$ anion, and the localized charge on the Ti(III) center overlaps to the O$_{2c}$–H bond, suggesting a stronger charge interaction.

This assumption is confirmed by computing the interaction strength between surface adsorbed protons and localized electrons, with a comparison of the total energies of hydrogenated systems with different electron localization positions. The energies are referred to the configuration in which topsurface proton and localized electron are separated by several lattice constants in the horizontal direction parallel to the surface, and the localized electron is localized in the bulk like layers of the slab (configuration P7 of Figure 5.3). The total interaction between surface protons and Ti(III) centers can be quantified to be in the range 0.37-0.45 eV. When this value is compared to the surface stabilization of electrons in absence of nearby protons (0.02-0.06 eV) or even in presence of Li$^+$ cations (~0.1 eV, with slight variations depending on the relative position of Li$^+$/Ti(III) see Chapter 4), it becomes evident that interface electron trapping is much more pronounced in presence of surface protons than with Lithium doping. This finding confirms that reduced TiO$_2$ exhibits different properties depending on the method employed, so that the system performance can be tuned. It also proves the importance of theoretical modelling as a method to rationalize the material behavior and assist in the design of different devices.

5.1.3 Kinetics of the Hydrogen Dissociation Process

Even if hydrogen adsorption is exothermic, the TiO$_2$ surface shows little reactivity towards direct reduction in an hydrogen rich atmosphere. Theoretical modelling confirms this tendency, as the activation energy barrier associated to hydrogen adsorption and splitting on the clean anatase (101) surface is rather high.
5.1. Hydrogenated Anatase

<table>
<thead>
<tr>
<th>Relative H+/e- Position</th>
<th>$\Delta E_{int}$/eV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25% hfx</td>
</tr>
<tr>
<td>P1</td>
<td>-0.34</td>
</tr>
<tr>
<td>P2</td>
<td>-0.37</td>
</tr>
<tr>
<td>P2b</td>
<td>-0.06</td>
</tr>
<tr>
<td>P3</td>
<td>-0.12</td>
</tr>
<tr>
<td>P4</td>
<td>-0.12</td>
</tr>
<tr>
<td>P5</td>
<td>0.02</td>
</tr>
<tr>
<td>P6</td>
<td>0.02</td>
</tr>
<tr>
<td>P7</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Figure 5.3: Electron/proton interaction energy, with respect to a reference e/H+ configuration, in which the proton and electron are separated by several lattice constants (P7). Charge trapping values are computed for different amounts of %hfx, to reduce the functional dependence.

Two different $H_2$ dissociation mechanisms are possible: the first one (Panel (a) of Figure 5.4) involves adsorption of an $H_2$ molecule is at first adsorbed on a single $O_{2c}$ surface anion, and then transfer of one (or both) atoms on adjacent oxide anions. Depending on the vicinity and relative position of the surface oxide anions, the activation energy of this process varies between 2.0 and 2.5 eV [97]. Another possible mechanism (Panel (b) of Figure 5.4) involves a preliminary adsorption of an $H_2$ molecule in the interstitial positions along the parallel rows of $O_{2c}$ anions, and subsequent dissociation of the molecule, with proton transfer to neighboring anions. This reaction path was investigated with both GGA and hybrid DFT, and results are reported in Figure 5.4. The computed activation energy is 2.05 eV, with no relevant dependence on the chosen functional. Even if the system size and hydrogen concentration might slightly alter the activation energies, the energy cost for direct $H_2$ dissociation on TiO$_2$ is still quite high, explaining the low reactivity of the clean anatase surface. The presence of a coadsorbed metal cluster, from which $H$ atoms could spill over to the oxide support, might facilitate the hydrogenation process, and is treated in more detail in the following Section 5.3.
5. A closer look at TiO$_2$ Hydrogenation

![Figure 5.4: Two proposed mechanisms for hydrogen adsorption and dissociation on anatase (101). Relative activation energies are also reported. Black, dashed: Barrier for Mechanism 1 (from ref. [97]). Green: Mechanism 2, GGA, 133 slab. Blue: Mechanism 2, GGA, 265 slab. Red: Mechanism 2, PBE0-25%hfx, 265 slab. R.C = -2 H$_2$, gas phase. R.C > 2 H$_2$, surface adsorbed.]

5.1.4 Interface Charge Mobility

Oxide reduction does not always proceed via doping: as it occurs in dye sensitized solar cells, excess electrons can be injected in the material from a donor molecule. As reported in Chapter 4, in absence of strongly interacting neighboring species, the mobility of excess electrons at the anatase (101) interface can be assumed to be similar to bulk mobility, with an activation energy of 0.23 eV. A higher barrier is expected for topsurface migration between the two equivalent Ti$_{5c}$ positions (0.53 eV), so that alternative paths involving intermediate subsurface steps are favored. On the other hand, as reported in Chapter 3 and in other theoretical studies [97, 96], in absence of neighboring species, topsurface protons diffuse preferentially between neighboring O$_{2c}$ sites, with an activation energy of 0.6 eV in absence of neighboring species. Our calculations, carried out at both the PBE and PBE0 level, confirm a similar activation energy value (0.64 eV), which is however drastically reduced in presence of coadsorbed species that can act as a mediating bridge. One example of such mediation via acetic acid is reported in Chapter 3, but also water can act as a bridging molecule for proton transfer,
with an activation energy of 0.15 eV, as reported in Figure 5.5. The situation is however quite different when hydrogen atoms are adsorbed at the (101) interface, as a surface proton and a polaronic Ti(III) center are simultaneously created. Due to the rather strong interaction of electrons and protons, significant mobility variations are expected if compared to the migration of the single, isolated species. In fact, when both species are present on the anatase surface, the two combined charges (e-/H+) migrate concurrently with an activation barrier of 0.73 eV. The migration profile shows a first peak, corresponding to proton transfer between the two $O_{2c}$ centers, immediately followed by a barrierless electron transfer.

Contrary to what happens for proton migration, the presence of coadsorbed molecules, that could act as bridging mediator, has no effect on the combined charge migration, as illustrated in Figure 5.5. This behavior is due to the strong interaction between the surface adsorbed protons and the elec-
5. A closer look at TiO₂ Hydrogenation

electrons localized on the Ti(III) centers that makes charge separation energetically unfavorable. In addition, the steric hindrance of the Ti(III) centers forces coadsorbed molecules further away from the surface protons, thus increasing the distance between surface protons and bridging molecules that could facilitate the transfer.

5.2 H₂ adsorption on γ-Al₂O₃

5.2.1 Adsorption Stability

Hydrogenation reactions can also be supported on γ-Al₂O₃, and as for TiO₂, the oxide reactivity can be modified by control of the surface sites. Since the reaction efficiency is influenced by the chosen support, a comparison of the two oxide materials can provide useful insight for process optimization. In particular, even if Al₂O₃ is usually considered a nonreducible support [198], recent experimental results seem to confirm hydrogen spillover from a Pt cluster to the aluminum oxide surface and then transfer to a target species, with a selective reduction of targets depending on the distance from the metal cluster [199]. In this case, theoretical modelling could help explaining the hydrogen behavior on the non reducible oxide surface.

The Bohemite-based crystal structure of γ-Al₂O₃ proposed in Ref. [200] and then confirmed by theoretical calculations [201] was adopted in our model system. The bulk structure of the oxide and of its two most stable surfaces, (100) and (010) is reported in Figure 5.6. The crystal structure of alumina consists of aluminum ions in octahedral (75%) and tetrahedral coordination (25%), that have a determining role for the material reactivity[202]. In fact, even if the (001) surface is the most stable one [203], the (100) surface is the one exposing highly reactive Al₃c centers, with an undercoordinated tetrahedric geometry. Hydrogen adsorption was investigated on both surfaces: exothermic adsorption and hydrogen splitting is only observed on the second most stable (100) surface, and only when the undercoordinated Al₃c sites are involved in the interaction, confirming the importance of those sites for the material performance.

A list of all the possible hydrogen adsorption positions on the (100) surface and their energy is reported in Figure 5.7. In comparison to TiO₂, which can be easily reduced by electron transfer from surface adsorbed hydrogen atoms, on Al₂O₃ energetically favorable H₂ adsorption is achieved only through heterolytic splitting, with formation of a proton and of an H⁻ anion. The proton is preferentially located in a bridging position between two oxide anions (e.g. positions 1,3,5 or 6 of Figure 5.7). The hydride anion is instead bound to an under coordinated Al₃c site, with formation of an Al-H
5.2. H$_2$ adsorption on $\gamma$-Al$_2$O$_3$

Figure 5.6: Ball-and-stick model of $\gamma$-Al$_2$O$_3$. Panel (a): bulk crystal. Panel (b): detail of the (100) surface, exposing the tri- and five-coordinated Al atoms. Panel (c): detail of the (001) surface, exposing the four- and five-coordinated Al atoms. Red: Oxygen. Blue: Aluminum.

bond (e.g. positions 2 or 7 of Figure 5.7). Analysis of the spin density distribution and of the system total density of states (DOS, reported in Figure 5.8) show that there is no formation of trap states in the oxide band structure. This confirms that, even if hydrogen adsorption on the Al$_2$O$_3$ surface is energetically feasible, it will not result in reduction of the oxide cations, as electrons are not effectively transferred from the surface adsorbates to the support. The interaction of the reducing hydride moiety with the neighboring coadsorbed proton, computed by comparing the adsorption energies of configuration 5 and 6, is 0.7 eV, so that charge separation is energetically unfavorable, as it occurs for TiO$_2$.

5.2.2 Hydrogen adsorption mechanism

In this section the heterolytic H$_2$ splitting mechanism on the $\gamma$-Al$_2$O$_3$ (100) surface is investigated in order to assess the main differences with TiO$_2$ hydrogenation. The undercoordinated Al$_{3c}$ surface sites are quite reactive [202] and the adsorption mechanism and energetics can be influenced by the presence of other interface species. In most experimental setups, water is a common surface adsorbates: on Al$_2$O$_3$ (100) dissociative adsorption of water molecules takes place, with formation of a Al$_{3c}$-OH and O$_{2c}$-H bonds. The situation is instead different for TiO$_2$, since water adsorption on anatase
5. A closer look at TiO₂ Hydrogenation

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Position H1</th>
<th>Position H2</th>
<th>$E_{ads,H_2}$/ eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>1ᵃ</td>
<td>1</td>
<td>3</td>
<td>+0.46</td>
</tr>
<tr>
<td>2ᵃ</td>
<td>1</td>
<td>5</td>
<td>+0.48</td>
</tr>
<tr>
<td>3ᵇ</td>
<td>1</td>
<td>6</td>
<td>+0.83</td>
</tr>
<tr>
<td>4ᵇ</td>
<td>5</td>
<td>6</td>
<td>+0.42</td>
</tr>
<tr>
<td>5ᵇ</td>
<td>1</td>
<td>2</td>
<td>-1.26</td>
</tr>
<tr>
<td>6ᵇ</td>
<td>1</td>
<td>7</td>
<td>-0.57</td>
</tr>
<tr>
<td>7ᵇ</td>
<td>1</td>
<td>4 or 8</td>
<td>-0.01</td>
</tr>
</tbody>
</table>

a: homolytic H₂ splitting  
b: heterolytic H₂ splitting

**Figure 5.7:** Most relevant H₂ binding positions on γ-Al₂O₃ (100), from top view.

**Figure 5.8:** Total density of states TiO₂ and Al₂O₃, in presence of an adsorbed H₂ molecule. The energy of the states is normalized to the Valence Band energy. Black: total density of states. A reduced metal state is created in the case of TiO₂ (Ti(III) center), but not in the Al₂O₃ case. The DOS is computed with GGA, so that the band gap is not correctly reproduced, but a qualitative analysis of the charge behavior is still possible.
5.2. \( \text{H}_2 \) adsorption on \( \gamma\text{-Al}_2\text{O}_3 \)

(101) is molecular and occurs on the Ti\textsubscript{5c} centers, not influencing the \( \text{H}_2 \) adsorption sites. As water adsorption can compete for the reactive \( \text{Al}_2\text{O}_3 \) surface sites, hydrogen adsorption mechanism was investigated for the clean and water covered alumina slab. Results are reported in Figure 5.9.

The main difference with the TiO\textsubscript{2} case is the fact that, instead of homolytic

![Figure 5.9: Mechanism and energy profile for \( \text{H}_2 \) dissociation on the clean (red) and water covered (blue) \( \text{Al}_2\text{O}_3 \) (100) surface. Dashed lines indicate the stability of intermediate situations, in which the water coverage is not uniform and selected sites are available for \( \text{H}_2 \) adsorption. H R.C.=-4: \( \text{H}_2 \), detached. R.C.=1/1.5: \( \text{H}_2 \), adsorbed on the slab.](image)

hydrogen splitting, on the \( \text{Al}_2\text{O}_3 \) surface \( \text{H}_2 \) is at first coordinated to the Al\textsubscript{3c} center, and then a single proton is transferred to a neighboring O\textsubscript{2c} site (Figure 5.9). The energy barrier for this process is lower than the one for homolytic splitting, and, on the clean (100) slab occurs with a relatively low activation energy (0.65 eV). The preliminary coordination step is also evident along the reaction profile, as the energy of the approaching molecule is lowered with respect to the gas phase, by 0.19 eV.

If the alumina surface is fully covered in water, instead, hydrogen adsorption implies an energetic loss, and the activation barrier for the process is 1.02 eV. In addition, the presence of surface water also hinders the formation of the preliminary coordinated state, as the energy of the \( \text{H}_2 \) molecule is not altered upon approaching the oxide slab. Intermediate situations, in which the water coverage is not uniform, are also possible. In this case, the activation energy for hydrogen adsorption is influenced by the relative position of the approaching hydrogen molecule and surface adsorbates and by the availability of free sites.

5.2.3 Mobility of the Reducing Species

As reported in the previous sections, hydrogen adsorption on the \( \text{Al}_2\text{O}_3 \) surface results in the formation of Al\textsubscript{3c}-H and O\textsubscript{2c}-H bonds. There is no
net electron transfer to the oxide and the reducing species is confined at the (100) interface, so that the only possible charge transfer route will proceed with hydride migration between Al\textsubscript{3c} surface sites. Also in this case activation barriers for H- migration between Al\textsubscript{3c} sites were computed for the clean and hydrated Al\textsubscript{2}O\textsubscript{3} (100) surface. Results are reported in Figure 5.10 and 5.11.

On the clean surface, the lowest energy H- transfer between Al\textsubscript{3c} sites proceeds through an intermediate adsorption step on a Al\textsubscript{5c} site, with a net transfer along the [010] direction. Migration towards neighboring Al\textsubscript{3c} sites along the [100] direction is less favorable, as the distance between the sites is smaller, but has to be covered in a single step with no possibility of intermediate adsorption or coordination steps. Starting from the most stable H\textsubscript{2} adsorption position (configuration 5 of Figure 5.7), an activation energy of 1.09 eV is required for the transfer to the intermediate Al\textsubscript{5c} site, and then additional energy of 0.62 eV for the subsequent transfer to the target Al\textsubscript{3c} site. The total activation energy for the process is 1.32 eV. In absence of neighboring protons, the migration path proceeds via the same scheme, with an activation energy of 1.23 eV. However, the energy cost for overcoming the stabilizing effect of neighboring protons is 0.7 eV (energy difference between configuration 5 and 6 of Figure 5.7), so that the overall activation energy for H- movement, starting from the most stable H\textsubscript{2} adsorption position, is around 1.93 eV.

Since water adsorption on Al\textsubscript{2}O\textsubscript{3} is energetically favorable, it is highly probable to have coadsorbed H\textsubscript{2}O molecules, occupying neighboring Al sites. As
5.2. H$_2$ adsorption on γ-Al$_2$O$_3$

Figure 5.11: Energy profiles for H- transfer between Al$_{3c}$ centers, in presence of water coverage. The computed profile is shown as a dashed line, while the main features are put in evidence with points and a continuous line. Red: Al$_2$O$_3$ oxygen. Blue: Al$_2$O$_3$ aluminum. Orange: H$_2$O oxygen. Green: H$_2$O hydrogen. Yellow: H$_2$ hydrogen.

reported in Figure 5.11, due to the multiple interactions with the coadsorbed moieties, the reaction profile is more complex than on the clean slab. Two cases are possible, depending on the relative adsorption position of H$_2$ and H$_2$O molecules: the first case (strong interaction) is similar to what happens on the clean slab, with the H$_2$ molecule split to form Al$_{3c}$-H and O-H moieties. Neighboring protons, deriving from coadsorbed water molecules on Al$_{5c}$ sites, coordinate the H- moiety during the transfer between the Al$_{3c}$ sites, and the process has an activation energy of 1.57 eV. However, as it can be seen from Figure 5.11(a), the ending configuration, in which the relative positions of OH- and H- are inverted (i.e. Al$_{3c}$-OH bonds + Al$_{5c}$-H bonds) is more stable, by 0.55 eV. This is the weak hydrogen interaction case, in which all the most reactive Al$_{3c}$ sites are occupied by water molecules, so that the reducing H- moiety is more loosely bound to the Al$_{5c}$ sites. In this case, the activation energy for H- transfer between Al$_{5c}$ sites is 1.22 eV.

Investigation of the mobility of the reducing species on the Al$_2$O$_3$ surface is quite complex, due to the multiplicity of possible adsorption sites for both water and H$_2$. A complete summary of all the investigated activation energies for H- transfer is reported in Table 5.2. Despite the various possible migration paths and energy barriers, it is clear that the mobility of the reducing hydride species is much more limited if compared to the combined H+/e- migration on the anatase interface, with an almost double activation
energy barrier. The presence of neighboring species, assisting the migration between surface sites only have a marginal effect on the overall activation energy barriers.

Table 5.2: Summary of the investigated H- migration paths, in presence or absence of coadsorbed water molecules

<table>
<thead>
<tr>
<th>Environment</th>
<th>Starting configuration</th>
<th>Ending Configuration</th>
<th>$E_{act}$ / eV</th>
<th>$\Delta E$ / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clean slab</td>
<td>$\text{Al}_3\text{c}\text{-H, O}_2\text{c}\text{-H}$</td>
<td>$\text{Al}_3\text{c}\text{-H}$</td>
<td>1.32</td>
<td>+0.53</td>
</tr>
<tr>
<td>Clean slab</td>
<td>$\text{Al}_3\text{c}\text{-H}$</td>
<td>$\text{Al}_3\text{c}\text{-H}$</td>
<td>1.23</td>
<td>0</td>
</tr>
<tr>
<td>Water coverage*</td>
<td>$\text{Al}_3\text{c}\text{-H, Al}_5\text{c}\text{-OH}$</td>
<td>$\text{Al}_3\text{c}\text{-OH, Al}_5\text{c}\text{-H}$</td>
<td>1.57</td>
<td>-0.55</td>
</tr>
<tr>
<td>Water coverage*</td>
<td>$\text{Al}_3\text{c}\text{-OH, Al}_5\text{c}\text{-H}$</td>
<td>$\text{Al}_5\text{c}\text{-OH, Al}_5\text{c}\text{-H}$</td>
<td>1.22</td>
<td>0</td>
</tr>
</tbody>
</table>

* with water coverage, the presence of protonated O$_2$-H sites is assumed

5.3 TiO$_2$ reduction by Hydrogen Spillover

5.3.1 Kinetics of the Spillover Mechanism

By comparing hydrogen adsorption and migration on TiO$_2$ and Al$_2$O$_3$, it is clear that, even if the clean, dehydrated Al$_2$O$_3$ surface can be more reactive towards H$_2$ splitting, the mobility of the reducing species is quite limited. On the other hand, anatase can be more easily reduced and demonstrates higher charge mobility. Direct H$_2$ adsorption from the gas phase is however characterized by a rather high activation energy barrier, so that alternative reduction routes have to be considered. As introduced in Chapter 1.1, spillover from a surface adsorbed metal cluster can be employed to achieve a controlled oxide reduction. This section therefore investigates the spillover mechanism in more detail, in order to asses the kinetics of the process and determine which parameters can influence it.

A 13-atom Pt system (Pt$_{13}$), previously used to represent a highly dispersed platinum catalyst [204, 205], was employed to model the surface metal cluster. Thirteen also corresponds to the smallest number of Pt atoms necessary to build a cuboctahedron, often considered a relevant particle morphology. Adsorption of the cluster on the anatase TiO$_2$ surface was modelled by placing the 13 metal atoms, with three different possible geometries (cuboctahedron, amorphous 2 and 3 layered structure), on the oxide surface, and then letting the system evolve with a molecular dynamics (MD) simulation for approximately 5 picoseconds each at 700K. Cluster geometry samples were obtained at every 1000th MD step, and subsequently geometry relaxed. The lowest energy cluster geometry (i.e. amorphous 2 layered structure) was selected as a reasonable approximation for the metal geometry.
As the hydrogen adsorption energy is affected by the dimension of the oxide slab (Section 5.1) and possibly also by the dimension of the metal cluster, it is likely that system size will also influence the relative stability of the starting and ending state of the spillover process and its activation energy. Investigation of slab size effects indeed confirms that the dimension of the chosen oxide slab is crucial: increasing the slab thickness from 10.5 to 24.6 Å inverts the relative stability of the Pt-H and TiO$_2$-H solutions, yielding more favorable H$_2$ adsorption on the oxide than on the metal cluster. The activation energy for H spillover is also lowered, from 1.23 to 1.02 eV. On the other hand, when the hydrogen to metal ratio is less or equal to 1:1, the activation energy for spillover of a single H atom is not influenced by the chosen cluster size, as demonstrated by comparing a 13-atom and a 4-atom Pt cluster. To obtain results consistent with the bare oxide calculations, a 267 oxide slab is employed in combination with a Pt$_{13}$ cluster.

Two possible spillover mechanisms were investigated (Figure 5.12): i) pre-

![Figure 5.12: Possible spillover mechanisms. Panel (a): Dissociative H2 adsorption on Pt cluster and subsequent H transfer to TiO2. Panel (b): Coordimative dissociation of an H2 gas molecule in proximity of the Pt cluster, with transfer of one H atom to the oxide surface. Panel (c): Comparison of the activation energies of the two proposed mechanisms, for the same cluster size, oxide slab and number of coadsorbed H2 molecules. Blue: Mechanism 1. Red: Mechanism 2.](image)
Liminary hydrogen splitting on the Pt cluster and subsequent transfer of a single atom to the oxide (mechanism 1) or ii) one-step hydrogen splitting at the cluster edge, with transfer of a single H atom to the oxide (mechanism 2). For the same cluster size and hydrogen coverage on the cluster, the activation energies for transfer of a single hydrogen atom to the oxide surface is 1.02 eV (mechanism 1) and 0.98 eV (mechanism 2). Given the very similar activation energies of the two mechanisms a dominant one can not be clearly determined. The occurrence of mechanism 2 over mechanism 1 will most probably depend on the availability and accessibility of edge Pt sites, and therefore on the dimension and shape of the metal cluster.

Another factor that might influence the activation energy for oxide reduction is the hydrogen loading on the metal cluster. Higher hydrogen loading will reduce the accessibility of edge Pt sites for mechanism 2, and at the same time, might reduce the Pt-H interaction, favoring H transfer from the cluster to the oxide (mechanism 1). The adsorption energy for multiple H₂ molecules on the cluster was computed, in order to determine the maximum H loading for a Pt₁₃ cluster. The average H₂ adsorption energy for a Pt cluster covered with n H₂ molecules is computed as follows:

\[
\Delta E_{\text{ads,H}_2\text{ aver}} = \frac{E_{2nH/Pt\text{ cluster}} - E_{Pt\text{ cluster}} - nE_{H_2}}{n}
\]

With \(E_{2nH/Pt\text{ cluster}}\) = total energy of the hydrogenated cluster on the oxide surface, \(E_{Pt\text{ cluster}}\) = total energy of the clean cluster on the surface and \(E_{H_2}\) = energy of the single, gas phase H₂ molecule. As expected, the average

**Figure 5.13:** Panel (a): Dependence of the H₂ adsorption energy on the hydrogen coverage of the metal cluster. Panel (b): Dependence of the activation barrier for hydrogen spillover on the hydrogen coverage of the metal cluster. Green: 10 H₂ molecules on the cluster. Blue: 16 H₂ molecules on the cluster. Red: 24 H₂ molecules on the cluster.
adsorption energy decreases linearly with increasing H coverage of the Pt cluster, from -1.19 eV with 10 adsorbed H₂ molecules (i.e. 20 H atoms on the cluster) to -0.78 eV with 24 adsorbed H₂ molecules (i.e. 48 H atoms on the cluster). Higher coverage is difficult to achieve, as the addition of more H₂ molecules to the cluster results in immediate transfer of H atoms to the oxide surface. This behavior indicates weaker interaction of the adsorbed molecules with the metal cluster surface at increasing hydrogen coverage, and, for this reason transfer to the oxide surface, following mechanism 1, has a lower activation energy, as shown in Figure 5.13. The activation barrier for hydrogen spillover is in fact decreased from 1.02 eV (10 H₂ molecules on the cluster) to 0.45 eV (16 H₂ molecules) and finally, becomes negligible for 24 H₂ molecules on the cluster. In addition, at higher H coverage, more H atoms will be located at the metal cluster edge sites, in favorable position for transfer to the oxide surface, and, at the same time, limiting the available sites for mechanism 2 to occur. The partial pressure of Hydrogen in the system and the cluster deposition technique are therefore crucial factors influencing the shape and coverage of the metal nanoparticle, and thus the kinetics of the spillover process.

5.3.2 Oxide Reduction

To evaluate whether, during H spillover from the Pt cluster, the oxide slab is effectively reduced, density of states analysis was performed. The total density of states for the three main states of the spillover process, according to mechanism 1: i) a gas phase H₂ molecule not interacting with the hydrogenated Pt cluster, ii) the additional H₂ adsorbed and split on the metal cluster and iii) H₂ spilled over to the oxide slab. A comparison of the electronic structure for cases i) and ii) does not reveal significant alterations of the oxide energy bands, confirming that the first hydrogen adsorption and splitting step on the metal cluster does not affect the support oxide. With the following step, i.e. transfer of two H atoms from the Pt cluster to the anatase slab, an occupied Ti₃⁺ state appears in the oxide conduction band (Figure 5.14, upper right panel). This confirms that H transfer from the Pt cluster results in effective Ti reduction, with electrons being injected in the oxide valence band. This observation is also qualitatively confirmed by Mulliken charge analysis: the charge difference on Ti sites before and after H transfer from the Pt cluster is negative, confirming that electrons are transferred to Ti sites.
5.3 A closer look at TiO₂ Hydrogenation

**Figure 5.14:** Density of States analysis for a Hydrogen covered Pt₁₃ cluster on TiO₂ anatase. Top row: total (black) and occupied (blue) density of states. Bottom row: Ti (grey), Pt (light blue), O (red) and H (yellow) orbital contribution to the total density of states.

5.4 Conclusion and Outlook

In this chapter, the TiO₂ hydrogenation process is investigated and compared to results for the Al₂O₃ system. The main difference between the two oxides lies in the hydrogen adsorption and splitting mechanism: hydrogen adsorption on anatase (101) leads to an homolytic splitting of the molecule, resulting in protonation of the surface and electron transfer to the oxide cations, with formation of polaronic Ti(III) centers. The energy barrier associated with H₂ homolytic splitting on the anatase surface is higher than 2 eV, explaining the limited reactivity of clean TiO₂ surfaces towards gas-phase hydrogen. Spillover from a metal cluster is instead characterized by a lower activation energy (1.02 eV) that can be further lowered by modulating the hydrogen partial pressure in the system, as it changes with the hydrogen coverage of the metal cluster.

On the other hand, hydrogen adsorption on the Al₂O₃ reactive surface (100) will result in heterolytic splitting of the molecule, with transfer of a proton to a surface oxide anion and of an hydride anion to a surface Al₃c cation. Contrary to TiO₂, hydrogen splitting on the clean alumina surface involves a rather low activation energy (0.65 eV), but does not result in reduction of the oxide. The accessibility of surface sites and the presence of coadsorbates (particularly water), competing for adsorption on the same Al₃c site, can hinder hydrogenation on the alumina surface, so that thermal treatment
and vacuum conditions are critical in determining the material reactivity. The mobility of reducing species was also investigated: on TiO$_2$, the interaction between the surface proton and the localized electron is in the order of 0.5 eV, and the two charges move with a concerted mechanism and an activation barrier of 0.7 eV, not influenced by the presence of coadsorbed water molecules. On Al$_2$O$_3$, the reducing species is confined at the interface Al-H bond, and its mobility is limited by the availability of neighboring Al$_{3c}$ sites, and thus by the presence of competing adsorbates. Even if the Al$_2$O$_3$ surface structure is quite complex, in particular in presence of coadsorbates, the computed activation energies for hydride transfer between Al$_{3c}$ centers is much higher than the activation energy required for H transfer on the anatase surface (~ 1.5 eV, depending on the water coverage of Al$_2$O$_3$ vs. 0.73 eV for TiO$_2$, regardless of the water coverage), explaining one aspect in the different performance of the materials.

As reported in the previous chapters, system size effects are also relevant for the hydrogenation process, in particular for TiO$_2$, as the distortion caused by the localized electron centers can extend for several lattice constants. Size effects are instead negligible for the Al$_2$O$_3$ surfaces, as the reducing species is confined at the interface Al-H bond, and no polaronic centers on the oxide lattice are created.

Future work will focus on taking into account partial hydrogen and water pressures in the two systems, in order to quantitatively assess thermodynamic effects and achieve a better understanding of effect that the reaction conditions will have on the process. In addition, combinations of multiple defect sites and other coadsorbates is to be investigated, for obtaining a more realistic system representation.

### 5.5 Computational Methods

First principles DFT calculations were carried out with the CP2K package [148], based on the hybrid Gaussian and plane wave (GPW) scheme[167, 168]. A plane wave density cutoff of 800 Ry and periodic boundary conditions have been adopted. GGA calculations were performed with the Perdew-Burke-Enzerhof[112] (PBE) exchange correlation functional, while hybrid calculations have been carried out with the truncated PBE0 (trPBE0) functional [124, 126], with varying percentages of exact Hartree-Fock exchange (hfx), ranging from 25% to 35% hfx. A cutoff radius of 4.5Å, sufficient to ensure converged electronic properties in the trPBE0 calculations, has been chosen for all calculations with the trPBE0 functional. The auxiliary density matrix method (ADMM), which relies on an auxiliary basis for Hartree-Fock exchange[129], was employed to speed up hybrid calculations. Dispersion interactions were included by means of an empirical ana-
5. A closer look at TiO$_2$ Hydrogenation

Analytical potential, using the Grimme D3 method[177], within a range of 15 Å. Standard coefficients and scaling factors for PBE and PBE0 functionals were adopted. The primary Gaussian basis set adopted in all calculations is of double $\zeta$ quality, in combination with GTH pseudopotentials [169]. Validation of the computational setup was carried out for both TiO$_2$ and Al$_2$O$_3$, by comparison with experimental lattice parameters and bond lengths. Differences between computed and experimental parameters were generally less than 1%.

Activation energies for ions and charge migration were computed with the climbing image nudged elastic band (ci-NEB) method. [141, 143] Density of states analysis was carried out with a resolution of 0.03 eV.

In the modelled slabs, the interface under study is built to be perpendicular to the $z$ axis, facing a $\sim$20 Å vacuum layer, while the $x$ and $y$ directions are fully periodic. In the rotated set of coordinates, parameters of the unit cell adopted for building the different slabs are: $x=10.227$ Å; $y=3.782$ Å; $z=3.513$ Å for TiO$_2$ anatase and $x=8.068$ Å; $y=8.413$ Å and $z=5.587$ Å for $\gamma$-Al$_2$O$_3$. Slabs are identified by a three digit code, corresponding to the repetitions of the unit cell along the $x$, $y$ and $z$ directions: as an example, the anatase $2 \times 6 \times 7$ slab notation corresponds to a $20.454 \times 22.692 \times 24.591$ Å slab, while the alumina $2 \times 2 \times 3$ notation corresponds to a $16.14 \times 16.82 \times 16.74$ slab.
Chapter 6

Conclusion and Outlook

This thesis presents a detailed investigation of the electronic and interface properties of titanium dioxide, for application in DSSCs and photocatalytic devices.

The electronic properties of the two main oxide polymorphs, anatase and rutile, were determined and compared by treatment with hybrid functionals and a novel RPA-based approach. In both materials, excess electrons localize on the titanium cations, creating Ti(III) centers. The associated lattice distortion extends for several lattice constants, resulting in a large polaron. Variations in the system size and defect concentration will affect the polaron overlap and higher defect concentrations result in delocalized electrons, explaining the dual behavior observed in experimental measurements and suggesting the possibility of tuning of the charge localization properties with the defect concentration. The main difference between the two polymorphs is in the polaron formation energy and mobility: at similar defect concentrations, localized electrons are more stable in rutile than in anatase, by 0.5 eV. Anisotropic charge transfer is expected in both cases, but, while for rutile the main charge transfer mechanism is polaron hopping between Ti centers along the [001] direction, the activation energy required for charge hopping is similar to the one for charge delocalization, so that a conduction band like migration mechanism is also possible. Theoretical results confirm experimental data for rutile and propose a new perspective on the anatase properties, explaining its better performance in terms of charge mobility.

The second part of this thesis takes into account the interplay between different components of the functionalized oxide interface, demonstrating the relevance of intermolecular interactions. The presence of protons on the surface is an important parameter, influencing both the adsorption geometry and mobility of the functional molecules and the creation of electronic trap states. The role of the solvent, represented with a full atomistic model and sometimes overlooked in theoretical studies, determines the adsorption
6. Conclusion and Outlook

equilibrium of functional molecules, as it both competes for surface sites and stabilizes the detached fragments. This observations emphasize that, even if the sensitized oxide supports are the core of the solar cell or catalytical devices, the surrounding environment (i.e. solvent, pH, additives) is of importance for the long term stability and performance and should be carefully taken into consideration in the development phase.

The interaction of two different reducing species (lithium and hydrogen) with the oxide was investigated: adsorption of both on the TiO$_2$ surface result in formation of cations and oxide reduction, with formation of polaronic Ti(III) centers. The relevance of surface effects on the oxide properties is confirmed by the fact that polaron localization is enhanced at the interface, as the upper layers are less stiff and allow more favorable lattice relaxation. The interaction between lithium cations and Ti(III) centers is weak (0.1 eV) so that lithium doping of the oxide constitutes a reservoir of shallow trap states at the interface, without sizeable alteration of the charge mobility. Hydrogen doping results instead in a strongly bonded charge pair, that migrates collectively on top of the anatase surface. The nature and mobility of the electron trap state is therefore strongly influenced by the chosen doping component: doping with lithium or other alkali metal cations will facilitate charge injection from a donor species without sensible losses in the device performance. Hydrogen doping is instead more suitable for influencing the material properties in a deep and durable way, as it would be for example needed to improve the oxide light adsorption.

TiO$_2$ is not easily reduced by direct H$_2$ adsorption from the gas phase, as the barrier for H$_2$ splitting at the (101) interface is higher than 2 eV. Hydrogen spillover from a noble metal cluster is required and the process velocity can be modified by varying the H$_2$ partial pressure in the system. While TiO$_2$ hydrogenation results in an effective reduction of the oxide, with formation of trap states in the band gap, Al$_2$O$_3$ hydrogenation does not alter the material electronic structure. The Al$_2$O$_3$ surface reactivity can also be significantly altered by water adsorption, so that the reaction environment and the thermal sample pre-treatment have to be carefully controlled in order to achieve the desired behavior. The reducing species remains confined at the interface and has a lower mobility than on anatase, explaining the different material performance for application in catalysis: H atoms are quite mobile on the TiO$_2$ surface, so that Ti(III) centers are found also at several nm distance from the noble metal cluster. The mobility of the reducing species on Al$_2$O$_3$ is instead much lower and difficult to monitor, as hydrogenation of the material does not result in oxide reduction. Theoretical investigation of the oxide interfaces provided useful insight for rationalizing the difference in performance of the two materials, that can be exploited for specific applications, such as selective hydrogenation of target species.

In all the simulations performed, system size and defect concentration effects were observed. Even with the most recent method developments and
improved computer hardware, the system size to be modelled is still limited, in particular when computationally more intensive levels of theory as hybrid DFT and especially EXX-RPA calculations are adopted. As realistic defect concentrations are usually much lower than the modelled ones, system size effects have to be reported and taken into account during data processing and result evaluation.

This thesis evaluates model systems with a limited number of elements, in order to better assess the oxide properties and the interaction between single component pairs. A good understanding of the single intermolecular interactions, fundamental to rationalize the complex behavior of a multi-component system, has been obtained. This work thus constitutes a solid basis for more complicated simulation setups, increasingly combining more elements. Up to date computational resources were extensively employed in the present study. As it is likely that even more effort will be required for more complex systems, special attention would have to be devoted for developing a significative model system, balancing number of components and computational cost.


Appendix A

Publications and Contributions

Publications

- The mechanism of hydrogen spillover in heterogeneous catalysis: seeing is believing
  Waiz Karim, Clelia Spreafico, Armin Kleibert, Jens Gobrecht, Joost VandeVondele, Yasin Ekinci, Jeroen A. van Bokhoven
  Manuscript in preparation

- Excess Electrons and Interstitial Li Atoms in TiO2 Anatase: Properties of the (101) Interface
  Clelia Spreafico and Joost VandeVondele

- The nature of excess electrons in anatase and rutile from hybrid DFT and RPA
  Clelia Spreafico and Joost VandeVondele

- Structure and Mobility of Acetic Acid at the Anatase (101)/Acetonitrile Interface
  Clelia Spreafico, Florian Schiffmann and Joost VandeVondele

- Insight into cation disorder of Li$_2$Fe$_{0.5}$Mn$_{0.5}$SiO$_4$
  Marcella Bini, Stefania Ferrari, Doretta Capsoni, Clelia Spreafico, Cristina Tealdi and Piercarlo Mustarelli

- Lithium diffusion in Li1-xFePO4: the effect of cationic disorder
A. Publications and Contributions

Cristina Tealdi, Clelia Spreafico and Piercarlo Mustarelli

Presentations

- Is Oxide Hydrogenation equivalent to Reduction? Fundamental Differences between TiO2 and Al2O3 from DFT
  - 251st ACS National Meeting & Exposition; March 2016 - San Diego, California (US)

- Excess Electrons in TiO2: a Hybrid DFT and RPA Study
  - Swiss Computational Chemistry Society Spring Meeting: Materials; February 2015 - ETH Zürich; Zürich (CH)
  - 3rd TYC Energy Materials Workshop: Materials for Electrochemical Energy Storage; September 2014 - Thomas Young Centre; London (UK)
  - Junior Euromat 2014; July 2014 - EPFL Lausanne; Lausanne (CH)

Poster Contributions

- Is Oxide Hydrogenation equivalent to Reduction? Fundamental Differences between TiO2 and Al2O3 from DFT
  - 251st ACS National Meeting & Exposition; March 2016 - San Diego, California (US)

- The Nature of Defects at the TiO2 Anatase Interface
  - Workshop on Materials for Energy Storage; May 2015 - International Centre for Theoretical Physics - Trieste (IT)

- Excess Electrons in TiO2: a Hybrid DFT and RPA Study
  - Swiss Chemical Society Fall Meeting; September 2014 - University of Zürich; Zürich (CH)
  - Junior Euromat 2014; July 2014 - EPFL Lausanne; Lausanne (CH)
  - Platform of Advanced Scientific Computing Conference 2014; June 2014 - ETH Zürich; Zürich (CH)

- Free energy simulations of carboxylic acid ligands on anatase (101): Are dyes able to walk on the surface?
  - Swiss Association of Computational Chemistry Spring Meeting; Feb 2014; Basel (CH)
- Functional Oxides for Emerging Technologies Workshop; October 2013 - University of Bremen/BCCMS; Bremen (DE)

- Spring School in Computational Chemistry; March 2013 - CSC IT Center for Science; Espoo (FI)

- Swiss Association of Computational Chemistry Spring Meeting; Feb 2013; Bern (CH)