Computational Investigation of Dye-Sensitized Solar Cells

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Abstract

Interfaces between semiconductors and adsorbed molecules form a central area of research in surface science, occurring in many different contexts. One such application is the so-called Dye-Sensitized Solar Cell (DSSC) where the nanostructured dye-semiconductor interface is of special interest, as this is where the most important ultrafast electron transfer process takes place. In this thesis, structural and electronic aspects of these interfaces have been studied theoretically using quantum chemical computations applied to realistic dye-semiconductor systems. Periodic boundary conditions and large cluster models have been employed together with hybrid HF-DFT functionals in the modeling of nanostructured titanium dioxide.

A study of the adsorption of a pyridine molecule via phosphonic and carboxylic acid anchor groups to an anatase (101) surface showed that the choice of anchor group affects the strength of the bindings as well as the electronic interaction at the dye-TiO$_2$ interface. The calculated interfacial electronic coupling was found to be stronger for carboxylic acid than for phosphonic acid, while phosphonic acid binds significantly stronger than carboxylic acid to the TiO$_2$ surface.

Aromatic and electronic structure of realistic dye-semiconductor interfaces were reported for Ru$^{2+}$-bis-terpyridine dyes on a large anatase TiO$_2$ cluster and perylene dyes on a periodic rutile (110) TiO$_2$ surface. The results show strong influence of anchor and inserted spacer groups on adsorption and electronic properties. Also in these cases, the phosphonic acid anchor group was found to bind the dyes significantly stronger to the surface than the carboxylic acid anchor, while the interfacial electronic coupling was stronger for the carboxylic anchor. The estimated electron injection times were twice as fast for the carboxylic anchor compared to the phosphonic anchor. Moreover, the electronic coupling was affected by the choice of spacer group, where unsaturated spacer groups were found to mediate electron transfer more efficiently than saturated ones.

Keywords: titanium dioxide, anatase, rutile, pyridine, perylene, nanostructured, interface, electronic coupling, electron injection, quantum chemistry, phosphonic acid

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Abbreviations

AO  Atomic Orbital
B3LYP  Three-parameter hybrid functional
bpy  2,2’-bipyridine
CB  Conduction Band
DFT  Density Functional Theory
DOS  Density of States
DSSC  Dye-Sensitized Solar Cell
ECP  Effective Core Potential
ET  Electron Transfer
eV  Electron Volt
fs  Femtosecond, \(10^{-15}\) s
FWHM  Full Width at Half Maximum
HF  Hartree-Fock
HOMO  Highest Occupied Molecular Orbital
KS  Kohn-Sham
LCAO  Linear Combination of Atomic Orbitals
LUMO  Lowest Unoccupied Molecular Orbital
MLCT  Metal-to-Ligand Charge Transfer
MO  Molecular Orbital
N3  Ru(4,4’-dicarboxy-2,2’-bipyridine)2(NCS)2
nm  Nanometer, \(10^{-9}\) m
PDOS  Projected Density of States
Pe  Perylene
Ph  Phenylene
Py  Pyridine
SCF  Self-Consistent Field
TD-DFT  Time-Dependent DFT
tpy  2,2’:6’,2”-terpyridine
VB  Valence Band
VDZ  Valence Double Zeta
Å  Ångström, \(10^{-10}\) m
1 Introduction

The modern civilization is full of technical challenges. Every day, new questions and problems appear from all possible fields. The laws of physics provide equations that can describe and explain what is going on, within the given mathematical model. Scientific computation is the bridge between theory and reality. The computational engineer constructs and evaluates models of the real problem, with the ambition to solve the modeled problem as accurately as possible. This often leads to quite large problems and some equations are difficult or even impossible to solve. Thanks to the rapid development of the modern computer resources, which have increased dramatically for many years, efficient parallelization algorithms and advanced computer architectures have continued to open up the field of computations. Larger problems can be considered, more and more realistic models can be used and equations can be solved effectively and accurately.

One area that is growing fast is computational chemistry. The quantum chemical computations deal with problems on the molecular, atomic, and subatomic level, such as chemical reactions, molecular geometries and electronic structures. In this thesis it is demonstrated how such computations can be used to obtain detailed information about physical and chemical properties and for valuable guidance in the development of applications of common interest.

One of the most important problems for mankind to solve is how to cope with our extreme demand of energy. Today, fossil fuels are the world’s primary energy resource. Heat is produced by combustion of these fossil fuels (coal, oil, natural gas), followed by pollution and global warming. This is an environmental-unfriendly energy resource that sooner or later will be depleted. Heat can also be produced in nuclear power plants, which today is the most efficient way to produce energy, but this also produces radioactive waste as by-product. Renewable fuels such as biomasses can also be used, but they also have by-products and wastes. The energy needed to produce and transport the biomass should however also be considered, which makes these resources rather expensive.

The heat is often used to generate electricity, because it is a very convenient form of energy that can be converted to many other forms of energy. Electricity can also be produced by mechanical motion, taken from e.g. hydro power, ocean waves or wind power in large scale generators. Another example is the fuel cells, where chemical reactions are used to create elec-
tricity. Electricity can also be produced by using the sun, the largest energy resource. Solar energy is an unlimited and clean energy that can be directly converted to electricity in photovoltaic ("light-to-electricity") cells without pollution, noise, or mechanical parts.

The idea to convert solar light directly to electricity is not new. Stable and efficient solar-electricity conversion cells have been on the market for several years. The conventional solar cell is, however, expensive for large-scale production, and it takes years to collect the same amount of energy that is consumed in the building process. The development of new types of solar cells, especially small thin film solar cell, has during the last decades made a lot of progress regarding efficient solar-electricity conversion. However, high purity requirements make the thin film solar cells expensive, and they are still far from an economical alternative to the electricity produced in hydro or nuclear power plants.

Another very promising way to harvest the solar energy has recently been extensively studied. The concepts are taken from the green plants, i.e. it mimics the process in photosynthesis, where the absorption of light is separated from the charge transport. This solar cell, introduced by Grätzel and co-workers, uses a nanostructured semiconductor (TiO₂) combined with dye molecules and is called the dye-sensitized solar cell (DSSC). By letting dye molecules be responsible for the light absorption, the cell can be built from cheap and easily produced components, and still be sensitive to the major visible part of the solar spectrum. The principal functions of the DSSC are shown in Figure 1.

![Figure 1](image)

*Figure 1.* The dye absorbs light and injects the excited electron into the TiO₂, where it is transported to the back-contact and then out to the load. The electron is returned to the cell through a counter-electrode. The electron is transferred through an electrolyte and then back to the dye. Then the dye is regenerated and the circle is closed.
This system, which can be made very cheaply, has a great potential to be a serious, low cost, non-toxic and unlimited solar-electricity energy resource. The future development of the DSSC requires a deeper understanding of the involved processes. The system is indeed very complex and involves physical, organic and inorganic chemistry as well as surface science. The huge potential and tuning possibilities makes this system fascinating and is keeping researchers in various fields occupied.

Some of the most important processes in this system take place on a microscopic level, involving molecular and electronic properties. The electron injection from the dye molecule into the semiconductor is said to be the heart of the cell performance, and it can take place on an ultrafast femto-second timescale. The mechanism for this fast electron transfer is not completely understood. Modeling of the electronic properties of the interacting dye and semiconductor, which are relevant for these processes, requires an accurate quantum mechanical description. Quantum chemical calculations on realistic models can give information of properties such as structure and stability for interacting components, which can be a valuable complement to experiments, and a useful help in the understanding of the involved processes. It can also be used as a valuable tool and guidance for developing new components in the search of efficient, stable and high performing DSSC.

In this thesis, quantum chemical calculations are used to provide electronic and structural information of the interface between realistic dye molecules and the semiconductor. Particular attention has been given to the possibility of using phosphonic acid as an anchor group (which binds the dye to the surface), and its influence of the stability and electron transfer performance of DSSC. The influence of inserted spacer groups between the dye and the anchor group is also investigated.

In chapter 2 the ideas and theory behind the quantum chemical calculations are discussed. A more detailed discussion of the individual parts of the DSSC and involved processes and models will be given in chapter 3. The computational details will be presented in chapter 4. Summary of results from the separate articles is made in chapter 5, which is followed by conclusions.
2 Quantum chemical methods

Nature itself on a micro- or macroscopic scale can be described by equations and simulated with computational algorithms. The thing with matter in nature is that it may behave as particle and as waves at the same time. This results in phenomena that cannot be explained in a classical context, such as discrete energies, particle interference, and tunneling. These phenomena are crucial when describing processes at the atomic and subatomic level. This is the case when dealing with processes and properties in a photoelectrochemical system as the DSSC. An accurate description of these systems requires quantum mechanics, and the central equation is the Schrödinger equation.4

2.1 Schrödinger equation

The solution to the Schrödinger equation gives a wavefunction $\Psi$. All physical properties of the system can then be extracted from this wave-function. The time-dependent Schrödinger equation for a particle described by the wavefunction $\Psi$ and moving in a potential $V$ is a linear differential (2nd order partial differential) equation:

$$i\hbar \frac{\partial \Psi(r,t)}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi(r,t) + V \Psi(r,t),$$

where $\Psi$ is the wavefunction, $r$ the position and $t$ time. $\nabla^2$ is the Laplace operator, $V$ the Potential energy operator and $\hbar$ is the Planck’s constant divided by $2\pi$. The Hamiltonian operator is defined as:

$$H = \left[ -\frac{\hbar^2}{2m} \nabla^2 + V \right],$$

i.e. the sum of the kinetic and potential energy operators. The time-independent Schrödinger equation, which is an ordinary differential equation, can be expressed in the form of an eigenvalue equation:

$$H_{tot} \Psi_{tot} = E_{tot} \Psi_{tot},$$

$E_{tot}$ and $\Psi_{tot}$ are eigenvalues and corresponding eigenvectors of the total Hamiltonian operator $H_{tot}$, respectively.
The systems in quantum chemistry refer to atoms and molecules, which consist of a number of nuclei and electrons. The total energy for this kind of system has five contributions: kinetic energies of each nuclei and electron \((T_e\text{ and } T_n)\), attraction between each electron and nuclei \((V_{en})\), internuclear and interelectronic repulsion potential energy \((V_{ee}\text{ and } V_{nn})\).

### 2.2 Born-Oppenheimer approximation

Since the electrons are so much lighter and faster than the nuclei they can be treated as if they instantly are adjusting according to the nuclear positions, which are in their point of view fixed. This is the Born-Oppenheimer approximation \(^5\) and the wavefunction \(\Psi_{tot}\) is accordingly separated into \(\Psi_{el}\) and \(\Psi_{nuclei}\). The electrons are treated as moving in a nuclear potential field and the remaining equation is called the electronic Schrödinger equation:

\[
(H_{el} + V_{nn})\Psi_{el}(r,R) = E_{el}(R)\Psi_{el}(r,R), \tag{2-4}
\]

where \(r\) is the position of the electrons and \(R\) the nuclear positions. In chemical applications it is often sufficient to concentrate on the electronic wavefunction. The constant nuclear-nuclear potential \(V_{nn}\) can be added after the electronic problem is solved and the solution to the electronic Schrödinger equation creates a potential energy surface (PES) upon which the nuclei can move. The lowest point on the surface corresponds to the optimized geometry. Removing the subscripts, \(H=Te+Vee+Ven\), \(\Psi=\Psi_{el}\), and \(E=E_{el}\), we can write the electronic Schrödinger equation in the simple form:

\[
H\Psi = E\Psi. \tag{2-5}
\]

Multiplied with complex conjugate and integrated over space:

\[
\int \Psi^* \Psi dv H = \int \Psi^* \Psi dv E, \tag{2-6}
\]

\(E\) is scalar and can be taken outside the integration:

\[
E = \frac{\int \Psi^* \Psi dv H}{\int \Psi^* \Psi dv}. \tag{2-7}
\]

The exact wavefunction is in practice often impossible to find, but one can obtain approximate solutions that approaches the exact solution. This is done via the variational theorem that states that an approximate wavefunction always leads to an energy higher than the exact. With a normalized wavefunction \(\int \Psi^* \Psi dv = 1\), the energy is written:

\[
E_{exact} = \int \Psi_{exact}^* H \Psi_{exact} dv \leq \int \Psi_{approx}^* H \Psi_{approx} dv = E_{approx}. \tag{2-8}
\]
The remaining problem is to find an appropriate trial wavefunction that can be varied.

### 2.3 Hartree-Fock method

To solve the electronic Schrödinger equation for a molecular system containing many electrons, the wavefunction can, if electron-electron interaction is neglected, be expressed as a set of one-electron wavefunctions (spin-orbitals). Each with the one-electron Hamiltonian:

$$ h_i = T_i + \sum_{n} V_{in}, \quad 2-9 $$

$T_i$ is the kinetic energy operator and $V_{in}$ the electron-nuclei potential energy operator. Then the equation can be solved for independent one-electron systems:

$$ h_i \phi_i = \varepsilon_i \phi_i, \quad 2-10 $$

where $\phi_i$ denotes the one-electron spatial eigenfunctions and $\varepsilon_i$ the corresponding energies. Note that this system contains no electron-electron interaction so far.

The spatial function is however not enough to describe an electron, and a function for its spin has to be added. Slater introduced a way to form a many-electron wavefunction by linear combination of products of one-electron spatial and spin functions in a way that accounts for anti-symmetry and the Pauli exclusion principle. The $N$-electron wavefunction in Slater determinant form is written as:

$$ \Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(1) & \chi_2(1) & \cdots & \chi_N(1) \\ \chi_1(2) & \chi_2(2) & \cdots & \chi_N(2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(N) & \chi_2(N) & \cdots & \chi_N(N) \end{vmatrix}, \quad 2-11 $$

where $\chi$ is the spin-orbital function, i.e. the product of spatial orbital and spin function. Note that this determinant contains no unoccupied orbitals.

For computational purpose and for simplicity, the spin-orbital will be presented in the closed shell approach, i.e. all electrons are spin paired. Then the set of coupled differential equations can be written as the Hartree-Fock equations:

$$ f_i \phi_i = \varepsilon_i \phi_i, \quad 2-12 $$
where $\epsilon_i$ denotes the one-electron eigenvalues, $\phi_i$ the corresponding eigenfunctions and $f_i$ is the Fock operator:

$$
 f_i = \hbar^2 + \sum_{j=1}^{N} \left( J_{ji}(1) - K_{ji}(1) \right).
$$

The summation is the average potential between the electron and the other $(N-1)$ electrons. The $(1)$ denotes that this is an operator involving coordinates of a single electron. $J$ is the coulomb term, which is the electrostatic repulsion between electrons, and $K$ is the electron exchange term. Since two electrons with same spin cannot occupy the same volume in space, there is a reduced probability of finding two electrons with the same spin close to each other. This is the exchange energy and it is calculated exact in Hartree-Fock (HF) due to the determinant form of the wavefunction.

However, HF is an approximation, where each electron is placed in an orbital and each electron is adjusted according to an average field of the other $(N-1)$ electrons. Consequently, the electrons are allowed to be distributed much closer than if they would have been distributed by energy minimization according to each individual electron. The HF method will therefore always overestimate the energy. The overestimation is defined as the correlation energy, $E_{\text{corr}} = E_{\text{exact}} - E_{\text{HF}}$. Further, the sum of the one-electron eigenvalues is not the total energy. The electron-electron interaction is counted twice when summing the one-electron energies and has to be compensated by reducing half of the total interaction. The total energy is then written:

$$
 E_{\text{HF}} = \sum_i \epsilon_i - \sum_i \sum_j \frac{1}{2} (J_{ij} - K_{ij}).
$$

The solution to the HF equations, the molecular orbitals, are eigenfunctions representing spatial distribution, each corresponding to an energy level. These orbitals are filled with 2 electrons each, from the orbital with lowest energy, until every electron in the system is distributed. The N orbitals with the lowest eigenvalues give the lowest possible total energy of the system, i.e. the system is optimized for its ground state. The remaining empty orbitals are referred as virtual orbitals. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are of particular interest.

The Molecular Orbitals (MO), occupied by the electrons, are rather complicated mathematical functions. They can however be constructed from a Linear Combination of Atomic Orbitals (LCAO):

$$
 \phi_i = \sum_{\mu} C_{i\mu} \phi_{\mu},
$$
where $C_{\mu}$ is the expansion coefficient and $\phi_\mu$ the Atomic Orbitals (AO). The AOs are e.g. the eigenfunctions of the solvable one-electron hydrogen atom equation (1s, 2s, 2p, 3s, 3p,...). By using LCAO, one can form a trial wavefunction with known functions, only the coefficients are unknown. Integration over all space yields the Roothaan-Hall equation:\textsuperscript{11,12}

$$F = S C e,$$  \hspace{2cm} 2-16

where $F$ denotes the Fock matrix, $S$ the overlap and $C$ the expansion coefficients. The matrix elements are:

$$F_{\mu\nu} = \int \phi_\mu^* f \phi_\nu dV$$ \hspace{0.5cm} and \hspace{0.5cm} $$S_{\mu\nu} = \int \phi_\mu^* \phi_\nu dV.$$ \hspace{2cm} 2-17

The equation can be viewed as a minimization problem, where, according to the variational theorem, a better wavefunction corresponds to a lower energy. The equation can then be solved iteratively by a procedure where the expansion coefficients are determined by minimizing the energy, with respect to the choice of coefficients. This procedure is known as the Self-Consistent Field (SCF) approach.

### 2.4 Basis set approximation

The set of mathematical functions that constructs the MO in the LCAO is called a basis set. The Hartree-Fock limit would be reached if an infinite basis set was used for constructing the wavefunction but this is technically and practically impossible. The bigger the basis set is, the more flexible spatial space is allowed for the electrons, and it accurately represents the MO, but at expense of consumed computer resources. The AOs can be taken as the hydrogen AOs and Slater-Type Orbitals (STO) but e.g. Gaussian-type functions have several mathematical advantages. Besides providing analytical integrals, one key advantage is that a Gaussian function (contracted) can be formed by a linear combination of other Gaussian functions (primitives). A contracted basis set of at least three primitive Gaussians can be made very similar to the AO by fitting its coefficients and exponents.

The chemically most active electrons, responsible for the formation and breaking of bonds, are the so-called valence electrons. It is advantageous to treat these with extra spatial freedom. This can be done by using more than one single (contracted) basis function for the valence electrons. In the split-Valence Double-Zeta (VDZ) basis there is one contracted basis function with a number of primitives for the core electrons and two contracted basis functions for the valence electrons.

Basis functions with more spatial and angular flexibility can also be included. This can significantly improve the accuracy and they are called polarization functions.
With larger system the number of atoms grows, and so does the number of electrons. Hence, the number of expansion coefficients to solve grows very fast. Clearly, there is a point of keeping the basis set as small as possible but still try to describe the chemistry as accurately as possible. However, by including these additional and sometimes necessary functions, as split valence and polarization, the size of the calculation grows substantially.

When calculating system with heavier atoms, a large basis set can easily be too expensive, due to the number of electrons. However, most of the electrons are core electrons and an efficient way to lower the number of coefficients to adjust is to use an Effective Core Potential (ECP). Then the description of the core electrons is included in the description of the nucleus, which can include, besides a reduced point charge, electron exchange energy and correlation energy, as well as relativistic effects. For further reading, the reader is referred to refs. 13 and 14.

2.5 Density functional theory

Instead of using the wavefunction with spin and spatial coordinates for every single electron, another theory can be considered. The Density Functional Theory (DFT) is a computationally efficient way of including electron correlation. The system is described by an electron density, rather than a sum of independent electrons, and the Hamiltonian is then only dependent on position and atomic number of the nuclei and the total number of electrons. The governing equation is still the electronic Schrödinger equation but the total energy of the system is expressed as a function of the electron density $\rho(r)$:

$$E[\rho(r)] = T[\rho(r)] + E_{ne}[\rho(r)] + E_{ee}[\rho(r)],$$

where $E$ is the total energy, $T$ the total kinetic energy, $E_{ne}$ the nuclear-electron attraction and $E_{ee}$ the electron-electron repulsion. Note that there is no reference to the wavefunction.

For a uniform gas of non-interacting electrons, Kohn-Sham (KS) introduced the one-electron waveequation:

$$ \left[-\frac{\nabla^2}{2} + V_{\text{nuc}}(r) + \int \frac{\rho(r')}{|r-r'|}dv' + V_{\text{xc}} \right] \phi_i(r) = \epsilon_i \phi_i(r),$$

where $\phi_i$ are the KS-orbitals which have no physical interpretation. However, the KS-orbitals can be solved in same variational SCF methodology as in Hartree-Fock and are used for calculating the electron density:

$$\rho = \sum_i^N |\phi_i|^2.$$
The \( V_{xc} \) denotes the exchange-correlation potential and is the functional derivative of \( E_{xc} \), which contains both exchange and correlation, energy:

\[
V_{xc} = \frac{dE_{xc}}{d\rho}.
\]

2.21

DFT is an exact theory and the only approximation is due to that \( E_{xc} \) is unknown. The basis sets for these KS-orbitals have fewer requirements than those in Hartree-Fock, they are not needed for calculating exchange and Coulomb interaction which are the most work consuming part of the Hartree-Fock method. This, and the fact that DFT account for electron correlation, make DFT very useful for larger systems. However, the crucial task in DFT is to find an accurate \( E_{xc} \) functional. The most popular exchange-correlation functional is the B3LYP functional.\(^{18,19}\) It consists of several functionals, including the HF exchange (\( E_{ex} \)), in a three-parametric scheme.

2.6 HF vs. DFT

Hartree-Fock is a theory that is an approximation of the reality but solved exactly. DFT is an exact theory but the solution is an approximation.

The HF energy is calculated as an expectation value of the Hamiltonian acting on a Slater determinant, which gives the exact exchange energy but leads to computing four-index integrals. The correlation energy is neglected.

In DFT, the energy is a functional of the density, which is calculated from the KS-orbitals. Since the exchange and correlation energy are accounted for in the \( E_{xc} \) functional, there is no need for the Slater determinant form and only 2-index integrals has to be computed. DFT scales as \( N^3 \) and HF as \( N^4 \), where \( N \) is the number of basis functions. HF optimizes wavefunctions, DFT optimizes density and both obtain a solution to the ground state.

Conclusively, DFT is a cost-effective way to include electron correlation and suitable for big systems. The convergence of HF is remarkable stable and the solution provides a very accurate wavefunction that can be used for evaluating all possible properties. The hybrid methods mix these theories which results in a very accurate and useful solution. The exact exchange is contributed from HF and the correlation from DFT.

2.7 Excited states

An excited state is a state where at least one electron is in a higher energy level compared to the ground state. Information and conclusions of excited states can be drawn by examining the occupied and virtual states in the standard DFT and HF ground state calculations, where the energy differences
between the occupied and unoccupied levels resemble the excitation energies. To get more reliable information about the excited states one has to go beyond HF and DFT.

The time-dependent DFT (TD-DFT) is an extension of DFT that handles electronic excited states. Physical properties such as absorption spectra can easily be calculated. For the extraction of the excited states, the system is simply subjected to an external time-dependent electric field that is treated as a small perturbation within a linear response theory. The perturbation can for instance be atomic motions or light.

Excitation energies can then be calculated without computing all the excited-state wavefunctions, they are simply determined by poles of the response function. In a variational form, each excitation energy and associated oscillator strength (transition probability) can then be calculated iteratively. For instance, the molecule interaction with light can be modeled by the interaction with an electric field with frequency \( \omega \), e.g. \( E = E \cos(\omega t) \). The response function (frequency-dependent polarizability) can then be written as:

\[
\mathcal{A}(\omega) = \sum_{i} \frac{f_i}{((E_i - E_0)^2 - \omega^2)},
\]

where \( E_0 \) is the ground state energy, \( E_i \) the excitation energy and \( f_i \) associated oscillator strength:

\[
f_i = \frac{2}{3} (E_i - E_0) \left\langle \left| \psi_i \right| \left| \psi_0 \right\rangle \right|^2.
\]

The vertical excitation energy from the ground state to excited states \( i \) are calculated as:

\[
h \omega = E_i - E_0.
\]

TD-DFT gives a good first estimation of physical processes such as photoeexcitation, for which information about the excited states is wanted. However, since the virtual orbitals in general are quite poor, this method should be handled with care and only be used for the lowest excitations. For a deeper understanding of TD-DFT, readers are referred to refs. 21 and 22.

### 2.8 Periodic calculations

The electronic calculation for a molecule provides a set of molecular orbitals with corresponding orbital energies. In a solid, the molecule can, however, be infinitely extended in one or more directions. Nearly degenerate energy levels originating from all atoms form dense energy bands, as shown in
Solving the Schrödinger equation for a system of an almost infinite number of atoms in the same way as described in HF leads to an infinite number of particles and basis functions, resulting in a matrix of infinite dimension to be solved in the Roothaan-Hall equation. To avoid this problem, the system can be treated as the crystals in solid-state physics, where crystals are formed of periodically repeated atoms or other units.24

The structures of solid-state crystals are described in terms of a lattice, which is a translation vector \( \mathbf{g} \) and a basis, which is the repeated unit. This lattice is mapped into the reciprocal lattice, which is in the Fourier space, with a reciprocal lattice vector (wave vector \( \mathbf{k} \)).

The wavefunction, which is constructed from crystal orbitals extended throughout the entire crystal, has to fit the periodicity of the lattice. So-called Bloch functions with appropriate periodicity can be formed from the atomic orbitals:

\[
U_\mu(r; k) = \sum_\mathbf{g} e^{i\mathbf{g} \cdot \mathbf{r}} \phi_\mu(r - \mathbf{g}).
\]

These Bloch functions are used in the LCAO expansion:

\[
\phi_i(r; k) = \sum_\mu C_{i\mu} U_\mu(r; k),
\]

where \( C_{i\mu} \) is the expansion coefficients.

In the SCF procedure, the Roothaan-Hall equation is solved for each \( \mathbf{k} \):

\[
F(\mathbf{k})C(\mathbf{k}) = S(\mathbf{k})C(\mathbf{k})\varepsilon(\mathbf{k}).
\]

Every value of \( \mathbf{k} \) corresponds to an energy, then total energy is written \( E=E(\mathbf{k}) \) and the continuous bands of energies, band structures, can be described properly. Each \( \varepsilon(\mathbf{k}) \) is corresponding to an energy level from a certain MO in the repeated unit cell and describes how it varies with the wave-vector \( \mathbf{k} \) (as it varies within a 3-dimensional zone called the Brillouin zone). For example, a one-dimensional chain of hydrogen atoms creates a band structure where the energy varies from the most bonding combination to the most antibonding combination of the s-functions, see Figure 3. Instead of
representing all values of $k$, the $\epsilon(k)$ usually is plotted along a certain direction in the reciprocal space, connecting some special points e.g. $\Gamma$ (0,0,0), $X$ ($\pi/a,0,0$), $M$ ($\pi/a,\pi/a,0$).

Since every MO in the unit cell corresponds to a band structure and there can be many bands in the total band structure, it is much more convenient to look at all the levels in a certain energy interval. The density of state (DOS) is proportional to the number of levels with energy $E$ (within a small interval) and the DOS for a typical band structure is showed Figure 3. Summing over all bands gives the total DOS. The total DOS can also be divided up among the atoms or orbitals. For example, the projected density of states (PDOS) can be constructed by selecting parts of the MOs with LCAO coefficients at a certain atom or atoms.

Figure 3. Schematic picture of a band structure $E(k)$ and corresponding DOS. The filled and unfilled circles are representing s-functions of a one-dimensional chain of hydrogen atoms, forming bonding and antibonding combinations.
3 Dye-sensitized solar cell

The solar cell is a photovoltaic “light-to-electricity” cell, which under illumination excites electrons from a low-energy level into a high-energy level. Thereafter the electrons are transferred, via an external load, back to its initial low-energy state. During the last decade much effort has been put into the development of thin film solar cells, which has resulted into a quite effective light-to-energy conversion performance. However, requirements of high purity and certain optical properties of the semiconductor p-n junctions make the thin film solar cell rather expensive to produce. The solar cell discussed in this thesis, the DSSC, is of another type, where the semiconductor is sensitized to light by adsorption of dye molecules.

The idea behind the DSSC is to mimic one of the energy producing processes in nature, the process of photosynthesis in plants. This concept was first developed by Grätzel and co-workers and the DSSC is therefore sometimes called the Grätzel solar cell. The DSSC is built up by a nanostructured semiconductor, sensitizing dye molecules and an electrolyte. These semiconductors are cheap and chemically stable, but, due to their wide band gaps, they absorb only a small fraction of the solar emission. By letting the dye molecules be responsible for the absorption, the cell can be made sensitive to the visible part of the solar spectrum. The dyes are acting like antennas, which capture the energy of the sunlight, and the absorption leads to excitation of an electron from a low-energy state into a high-energy state of the dye. The excited electron can then rapidly be injected into the semiconductor. The following charge transfer, to the back-electrode, takes place in the semiconductor, and in this way the absorption is separated from the charge transport. This concept, letting the process of light absorption be separated from the charge transport, differentiates this type of solar cells from the conventional silicon based solar cell.

The detailed functions of the DSSC, see Figure 4, are as follows. The dye (D) absorbs light, and thereby undergoes photoexcitation to an excited state (D*). The excited electron is then injected into the conduction band (CB) of the semiconductor, and the dye ends up in its oxidized state (D'). The electron is transferred by the semiconductor to the back-contact and through the external load back to the counter-electrode where it reduces the oxidized species of the electrolyte (E'/E). At the same time the oxidized dye accepts an electron from the reduced species of the electrolyte and returns to its ground state (D), and the circuit is closed.
The function of these devices is traced down to the molecular level and the performance of the cell mainly depends on the positions and structures of the energy levels in the dye, semiconductor and the electrolyte. The maximum output voltage ($\Delta V$) is the difference between the Fermi energy ($E_F$) and the redox potential of the electrolyte ($E_{\text{red}}/E_{\text{ox}}$). The complexity of the DSSC enhances the tuning possibilities of the system. By replacing and combining different components, the system can be tuned for the desired performance. However, even if the molecular and electronic structures of the separate parts are well understood, the interfaces between these parts are largely unknown and the combined system may not give the wanted performance. The DSSCs also have a number of other requirements to meet, such as stability of the combined system and the separate components in their different states. Moreover, the cell should have a long lifetime and have high photoelectrical performance. One of the best performing photovoltaic cells, with respect to solar-to-electric power conversion and long term stability, is constructed of nanocrystalline TiO$_2$ film sensitized by a ruthenium polypyridine dye$^{3,26}$ and will be discussed in more detail in section 3.2.

However, the potential of DSSCs is far from being fully exploited, and the desire to improve the performance requires a deeper understanding of the involved processes. The electron transfer from dye into the semiconductor is one of the most important processes in these devices.

The molecular and electronic structures of the interface are of huge importance for understanding and controlling the mechanism of the electron transfer across the interface. The enlightenment of this basic mechanism is crucial for designing and building stable, efficient solar cells that can compete with the energy resources of today.
3.1 Semiconductor

Semiconductors are often classified with respect to their electrical conductivity, that is, the ability to transfer charge and the number of mobile electrons.\(^{24}\) The electrons in a molecule are occupying discrete molecular orbital energy levels. In a solid, every interacting atom introduces new molecular energy levels, and due the huge number of atoms, these close lying levels form bands. There is a lower band, the valence band (VB), which is partially filled with electrons and an upper band, conduction band (CB), which is essentially empty. The semiconductor is also characterized by the band gap, the energy \((E_g)\) that separates the valence and the conduction band, where no available states exist for the electrons. The highest filled energy level (at absolute zero, 0 K) is defined as the Fermi level \((E_F)\) and is responsible for the chemical potential.\(^{2}\) If the Fermi level lies near the valence band and separated to conduction band by only a small band gap the electrons are very mobile and the solid is a conductor. If the Fermi level lies right above the valence band, and in a large band gap, the solid is an insulator. However, if the band gap is small enough and the Fermi level are close to the conduction band there is a possibility for electrons to reach and populate the conduction band at the expense of the previously filled valence band and the solid becomes a semiconductor. The holes in the valence band and the corresponding electrons in the conduction band are the charge carriers.

3.1.1 Transition metal oxides

The semiconductors used in the DSSC systems are wide band gap transition metal oxides.\(^{1-3,25}\) They are cheap and both thermally and photochemically stable, but due to the wide band gap they absorb only the UV part of the solar light. Transition metal atoms are characterized by partially filled d-orbitals and they can acquire several different oxidation states, often by loss of s-electrons before d-electrons. A metal complex consists of a central metal ion surrounded by ligands. The coordination of the metal complex is defined as the number of these, often symmetrically surrounding, ligands. The transition metal oxides thus have oxygen ions as ligands, and the oxygen can also acquire different oxidation states. Metal oxides usually have, due the highly regular atomic structure, full coordination of all the atoms. The bonding in these materials is, however, rather complicated and has both ionic and covalent character.\(^{27-29}\)

3.1.2 Titanium dioxide

The technical applications of titanium dioxide \((\text{TiO}_2)\) range from white pigments in paint and toothpaste to catalyst for water splitting.\(^{30}\) \(\text{TiO}_2\) is chemically stable in different environments as well as stable toward photo-
oxidation. In addition, it is non toxic and relatively easy and cheap to produce. Titanium dioxide has therefore been popular by both experimentalist and theoreticians as a model system for the surface science of metal oxides.\textsuperscript{1}

The use of nanostructured semiconductors as electrodes is one of the main components in the dye-sensitized solar cell and nanostructured TiO\textsubscript{2} has frequently been used in the most efficient DSSC systems.\textsuperscript{1,3} Nanostructured TiO\textsubscript{2} consists of interconnected 2-50 nm particles in electric contact. The resulting huge internal surface area magnifies the light harvesting ability by a factor of 1000 and offers a manifold of adsorption sites.\textsuperscript{1,3}

TiO\textsubscript{2} is fully coordinated in its bulk structure, i.e. 6-fold coordinated titanium atoms and 3-fold coordinated oxygen atoms. TiO\textsubscript{2} has three major crystalline structures; rutile, anatase and brookite. Nanocrystalline TiO\textsubscript{2} films are commonly comprised of particles of anatase or a mixture of anatase and rutile. The rutile is the most stable of the three structures and also the most extensively investigated form of TiO\textsubscript{2}. However, electrodes in photovoltaic cells are often based on anatase and the (101) surface of anatase is the thermodynamically most stable surface.\textsuperscript{2,29}

The large band gap of TiO\textsubscript{2} separates the fully occupied O 2p valence band and the empty Ti 3d conduction band, see Figure 5, and is smaller for rutile than anatase. The experimental bulk band gap is 3.0 and 3.2 eV for rutile and anatase, respectively.\textsuperscript{31,32} The band gap is expected to increase for smaller nanoparticles, which are used in photoelectrochemical cells, and is 3.4 eV for 2.4 nm anatase nanoparticles.\textsuperscript{33} Several theoretical investigations concerning TiO\textsubscript{2} have been performed.\textsuperscript{29,34-38}

![Figure 5. Schematic picture of the valence band, conduction band and band gap of TiO\textsubscript{2}. The lower part of the conduction band consists of Ti 3d-orbitals and the upper part of the valence band of O 2p-orbitals.](image)

### 3.2 Dye molecules

The adsorption of different molecules and atoms on a metal oxide surface, such as TiO\textsubscript{2}, can substantially affect the properties of the surface and
thereby the function of the system can be profoundly modified. Due to both fundamental and applied research interests, there are many investigations on small molecules attached to surfaces reported, especially with hydrogen, oxygen, and water as adsorbates. The interaction between larger adsorbates and surfaces are possibly even more important because of the large number of applications. The adsorption of dye molecules on semiconductor surfaces is particularly interesting for the photochemical applications.

3.2.1 Function and properties

In dye-sensitized photochemical devices, the dye molecules are responsible for the optical properties of the systems. That is, they should absorb a large part of the solar light. In addition, the dye should be strongly attached to the semiconductor and give an efficient electron injection into the conduction band of the semiconductor. Other required properties of the dyes are that they should be stable in ground and oxidized state and endure repeated oxidation and regeneration. Moreover, they should not be degraded by the semiconductor. In fact, the kinetic and energetic behavior of the electron in different steps of the process determines the efficiency of the cell. Electron transfer from the excited dye into the semiconductor has to be very fast to prevent the reduction of the oxidized dye. The back reaction from the semiconductor to the oxidized dye also has to be slow, and the regeneration of the dye must take place at the electrolyte, and not via a recombination, to obtain a closed circuit.

Many different compounds have been screened for sensitization of semiconductors, both organic dyes, for which some have become models used for the elucidation of the electron transfer process, i.e. perylene, and different transition metal complexes. By varying either the metal or the surrounding ligands the metal compounds can be tuned for the photophysical and electrochemical properties. Complexes with ruthenium have been found to perform very well since the ruthenium metal can coordinate a number of ligands, forming colored compounds excellent for photoinduced reactions in visible light. Ruthenium complexes with polypyridine ligands have shown very good performance, including especially the so-called N3 dye, see Figure 6, which today is, one of the most efficient sensitizing dyes.
Photoinduced excitations in the Ru-polypyridine complexes have shown Metal-to-Ligand Charge Transfer (MLCT) character. Further investigations indicate that the Highest Occupied Molecular Orbital (HOMO) is localized on the Ru metal, but that the Lowest Unoccupied Molecular Orbital (LUMO) is delocalized on the bipyridine ligands.\textsuperscript{44-47} It can be seen in Figure 7, that the HOMO of the N3 dye corresponds to a Ru 4d-type and isothiocyanato (NCS) $\pi^*$-orbital, and that the LUMO consists of carboxylic and bipyridyl $\pi^*$ contributions. The energy of this unoccupied level matches the conduction band of the semiconductor, which is required for an efficient electron injection.

Another way to tune the properties of the dye (besides metal or ligand substitution) is to insert one or more spacer groups between the dye and the surface. One purpose of this strategy is to prevent the back reaction (recombination) by creating a well separated charge-separated state. By inserting one or
more spacer groups between the dye and the semiconductor the distance can be altered in a way to minimize the back reaction without losing the fast efficient charge injection. These groups are called spacer groups or bridges and can be saturated, unsaturated, rigid or flexible. For example, insertion of saturated spacers would give a weakening of the electronic coupling which would be expected to slow down the injection rate. Typical spacer groups are phenylene and methylene. Spacer groups can also be used for a more geometrical structural control, for example forcing a more upright position of the dye perpendicular to the surface for preventing recombination. The possibility of fixing and altering the distance and thereby controlling the electronic contact has made the use of spacer groups become a method for understanding the electron transfer processes over the interface.

Clearly, the electronic structure of the compound is of great interest as it provides information about the energy levels and the nature of the orbitals. The HOMO of the dye is related to the electrochemical potential, and the LUMO is related to the absorption. However, these electronic properties for the isolated dye might change upon adsorption. For a complete picture these properties have to be evaluated for the combined system, where the dye is absorbed on the surface.

3.2.2 Anchor groups

Some dyes can be directly connected to the surface but more convenient is to let smaller functional groups be responsible for the chemical bonding to the surface. Dyes, and adsorbates in general, can bind to a surface through one or more of these groups called anchor groups. Then there is a well defined adsorption geometry at the interface assuring a strong adsorption. The anchor group in a DSSC system has to be stable with strong adhesion to the surface and at the same time be working as an efficient charge shuffle. Moreover, the anchor should provide a strong electronic coupling between a discrete electron donating orbital of the excited dye and the continuous levels of the electron-accepting semiconductor. The efficient ruthenium polypyridine complexes are almost exclusively based on carboxylic acid anchoring to TiO$_2$ that has therefore been the subject of many investigations. Carboxylic acids bind strongly to the surface and give a good electronic coupling over the dye-semiconductor interface. A severe problem with carboxylic acid is that it undergoes desorption in the presence of water, which is a huge drawback as a component for the solar cell application. However, phosphonic acid (HPO$_3$H$_2$) is another promising candidate as an anchor group that can be used to bind a wide range of molecules to TiO$_2$ surfaces. In fact, it has been shown to bind more strongly than carboxylic acid. The bindings of carboxylic acid are well explored whereas the bindings of phosphonic acid, until now, have not been investigated theoretically.
3.2.3 Adsorption geometry
The different types of adsorption are divided into molecular or dissociative adsorption. There are several different binding possibilities for an adsorbate that binds to a metal oxide surface through bonds between adsorbate oxygen atoms and surface metal atoms. The coordination can be either mono-, bi- or tridentate, depending on how many oxygen atoms the molecule use to coordinate to the surface metal atom. When there are several metal-oxygen bonds, the adsorption modes can also be distinguished by the number of metal atoms involved (1M, 2M, etc.) in the adsorption process. Figure 8 schematically shows some of the possible structures relevant for adsorption of phosphonic and formic acid.

![Figure 8. Examples of adsorption modes for HPO3H2 and HCOOH when bound to TiO2.](image)

The adsorbate may induce surface relaxations due to a partly restored full coordination of the surface atoms involved in the adsorption. These surface atoms will relax outwards. The type of binding to a metal surface may vary due to structural differences in the surface, dyes, and the binding group. Experimentally, the binding can also depend on environmental factors such as solvent or pH. Several binding modes can also be expected to be present simultaneously. Large adsorbates, as the dye molecules, may bind through several anchor groups. The binding of these separate anchor groups may restrict the number of possible adsorption geometries. The knowledge of the binding mode, geometry and strength is crucial for developing efficient DSSC systems. The interaction of the dye, anchor group and surface is of fundamental importance, since it determines the geometrical and electronic coupling.

3.3 Dye-surface interface
For building future efficient devices, consisting of photochemically active molecules on semiconductor nanoparticles, the interfaces are indeed very important. The energy matching between the different components at the interfaces sets the overall performance of the DSSC. Knowledge of the dye-semiconductor interface is in particular crucial, because the photoin-
duced charge transfer across the dye-semiconductor interface is the fundamental process that drives the dye-sensitized solar cell.

### 3.3.1 Model systems

As mentioned earlier, the promoted electron in the excited state of the, so far, best performing dye N3 is generally delocalized on the bipyridine rings and the carboxylate anchor group, see Figure 7. The interaction of the LUMO (\(\pi^*\)-orbital, localized on the bipyridine rings), and the surface conduction band would be a first step for investigating the photoinduced electron transfer in dye-surface systems. Aromatic adsorbates, such as pyridine are also interesting for pedagogical reasons because the electron interaction with the surface can easily be studied. Pyridine and isonicotinic acid have therefore been used as simple models of the ruthenium dye, where bisonicotinic acid is also the actual binding ligand of the N3 dye and pyridine with a carboxylate anchor is simply the “half” of that. The adsorption of these relatively small molecules on a semiconductor results in model systems that can be studied using quantum chemical calculations, which is very useful for a deeper understanding of the dye-surface interaction in realistic DSSC systems. There are several investigations of these systems that can be found in e.g. refs. 56-61. Another common model of a dye-semiconductor interface is the perylene-TiO₂. Perylene is a chromophore with favorable properties such as energy levels well aligned with the bands of TiO₂ for an appropriate HOMO-LUMO photoexcitation followed by an injection. The perylene-TiO₂ interface has therefore been widely used for fundamental studies of interfacial electron transfers and for example Willig et al. have used ultrahigh vacuum techniques to investigating how different parameters influence the interfacial electron transfer. However, the electron transfer process in the DSSC, which is accomplished at the dye-semiconductor interface, and is the most important process in these photochemical systems, is still not well understood.

### 3.3.2 Electron transfer processes

In an efficient DSSC the excitation of the dye has to be followed by a fast Electron Transfer (ET) into the semiconductor. The injection (transfer) times have been measured for these systems using pump-probe spectroscopy. Ultrafast electron injection from excited states into the substrate band, observed with increased time resolution, is now believed to occur even on a sub-10 fs timescale. The heterogeneous electron transfer from a single donor excited state of the dye molecule into several acceptor states of the substrate is far more complicated than the molecular state-to-state (homogeneous) transfer described by the Marcus theory. Marcus theory considers a motion along some reaction coordinate, where a weak coupling appears at a
crossing point between the reactant and product, and is well suitable in sys-
tems having well defined reactant and products. In the dye-semiconductor
ET there is instead a continuum of acceptor states and the description there-
fore has to goes beyond Marcus.

It is attractive to use quantum mechanical models for these processes and
especially a dynamic approach, considering motions of electrons and atoms.
The dynamics are described by the time-dependent Schrödinger equation,
see section 2.1. There are many ways to model the Hamiltonian. Most often
it is separated (according to Born Oppenheimer approximation described in
section 2.2) into one purely electronic part and one part treating the nuclear
and electronic-vibrational (the non-adiabatic interaction) degrees of freedom.

For a time-dependent perturbation treatment of a single state interaction
with a group of final states the electron transfer rate can be taken from the
Fermi’s Golden Rule:69

\[ k_{ET} = \frac{2\pi}{\hbar} |V_{da}|^2 \rho(E_a). \]  

Separation of electronic and vibrational couplings (within Frank Condon and
Born Oppenheimer approximation):

\[ k_{ET} = \frac{2\pi}{\hbar} \left( |\langle \psi_a | H_{el} | \psi_d \rangle|^2 \langle d_{vib} | a_{vib} \rangle^2 \rho(E_a) \right). \]  

where \( a \) represent acceptor states, \( d \) donor state, \( \rho(E_a) \) the density of acceptor
states and \( V_{da} \) the perturbation potential. In the weak coupling, this can be
seen as small perturbation to the uncoupled system. Systematic investiga-
tions have been performed on the dependency of density of accepting states
in the semiconductor and the dependency of electronic coupling.70-75 For
several dye-sensitized solar cell systems vibrational coherences (vibrational
wavepackets) are often detected76 but this is not considered in this thesis.

A fully quantum dynamical approach for this interfacial electronic trans-
fer is computationally very demanding and is not possible to be fully utilized
in the dye-surface system. Several different theoretical models and ap-
proaches for simulating this ET have been presented, for example, pure elec-
tronic dynamics, using tight-binding parameterization77 or \textit{ab initio} DFT
molecular dynamic for semi-empirical ET calculations on catechol-TiO\(_2\).78
Nuclear dynamics have been incorporated classically or quantum mechani-
cally and often with the use of harmonical vibrations. For example, Prezhdo
\textit{et al.} have performed \textit{ab initio} nonadiabatic molecular dynamics (NAMD)
using plane waves DFT and propagation via TD-DFT with vibrations con-
sidered using classical and semiclassical mechanics.60,61,79 Willig \textit{et al.} have
a fully quantum treatment with electronic-vibrational coupling employing a
Fano-Anderson type Hamiltonian.72,80-82 Related work by Thoss \textit{et al.} con-
sidered the electronic as well as the vibrational degree of freedom quantum
mechanically at the same time and involved different methods as a self-consistent hybrid method.\textsuperscript{83}

Most of the approaches above utilize calculated electronic structures, which preferably would be obtained by accurate quantum calculations, to evaluate the electronic coupling between the dye and the surface, in order to determine the rate of the electron transfer. The results indicate that both transfer rates and mechanisms are largely determined by the interfacial electronic interaction between the donor and acceptor states of similar energies.\textsuperscript{29,57,84} So far, this approach has been limited to use small model systems or using low-level calculations.

Our approach focuses on the electronic structure of realistic and very large models that are calculated with very accurate quantum chemical methods, which in combination manages to mimic reality. Then quantitative information of the density of states and interfacial electronic couplings can be provided.

3.3.3 Electronic coupling

As mentioned above the ultrafast electron transfer across the dye-semiconductor interface is believed to be governed by a strong electronic coupling between the excited state of the dye and the conduction band of the semiconductor. Assuming that the photoinduced excited state in these systems are primarily HOMO-to-LUMO excitations in the dye, the interaction of interest for the electron transfer is the interaction of the dye LUMO with the empty conduction band of the semiconductor. The nature of the electron coupling can be viewed from the calculated electronic structure by examining the interfacial orbital mixing. A weak coupling would show a localized orbital on the donor, and a strong coupling would show a delocalized orbital over both the donor as well as the acceptor.

For a more quantitative picture of the electronic coupling, adequate electron transfer theory has to be used and thereby also the rate of the electron transfer can be obtained from the electronic structure calculations.

A prominent theory for the ultrafast electron transfer in the dye-semiconductor systems, particularly due to the manifold of acceptor levels in these systems, is the Newns-Anderson model.\textsuperscript{55,86} It was developed for metal surfaces and considers the interaction between an adsorbed atom and a metal surface in terms of energy shift and broadening of the adsorbate atomic energy level. By extending this model to the description of organic adsorption on metal oxides the rate of the electron transfer over a dye-semiconductor interface can be estimated from calculated electron structure.

In this approach, the PDOS is used to evaluate the electronic coupling between the excited state of the adsorbate and the conduction band of the semiconductor. For a weak interaction the levels remain distinguishable and sharp, but as the coupling strength increases the level splits into an effective
band of levels, with a spread in energy. According to the Newns-Anderson model, the adsorption of a molecule at a metal surface is characterized by an energy shift $\Delta E_i$ of the electronic level $i$ and a lifetime broadening $\hbar \Gamma_i$. The lifetime broadening reflects the decay of a molecular state resonantly coupled to a continuum of final states and has a typical Lorentzian distribution in energy:

$$L_{\text{LUMO}}(E) = \frac{1}{\pi} \frac{\left( \frac{\hbar \Gamma}{2} \right)}{(E - E_{\text{LUMO}})^2 + \left( \frac{\hbar \Gamma}{2} \right)^2},$$

where $L_{\text{LUMO}}$ denotes the distribution of the LUMO level. By using calculated PDOS, projected on the adsorbate, for the different levels, the lifetime broadenings of that level can be estimated. The Full Width at Half Maximum (FWHM) of the PDOS can then be taken as a measure of the lifetime broadening, $\hbar \Gamma$, and the lifetime $\tau$ can then be estimated by $\tau = \hbar / \hbar \Gamma$, or in convenient units $\tau (\text{fs}) = 658 / \hbar \Gamma (\text{meV})$, see section 4.1 for more details.

The orbital level involved in the photoinduced electron transfer and its lifetime broadening when adsorbed on the semiconductor is of particular interest. The estimated injection time can then be directly compared to experimental studies of ultrafast electron injection times.$^{84,87}$
4 Computational details

All attempts at theoretical investigations of dye-semiconductor interfaces have to undergo serious considerations of which models and methods to be employed. The computational cost has to be weight against the accuracy of the method and the model has to be large enough to reproduce properties of the real system. In this thesis two quite different approaches, with their own advantages and drawbacks, have been used.

4.1 TiO$_2$ models

4.1.1 Periodic calculations
The periodic boundary approach is very suitable for bulk, surface, and adsorption studies of metal oxides. The periodical calculations in this thesis were carried out using periodic hybrid \textit{ab initio} HF-DFT calculations, as implemented in the CRYSTAL98 and CRYSTAL03 programs. The CRYSTAL03 program offers a geometry optimization tool, extremely useful for surface adsorption studies.\textsuperscript{88}

The periodical TiO$_2$ models are in this thesis referred to as (TiO$_2$)$_{2D}$, and the anatase and rutile unit cells are created the same way. A two dimensional slab is first constructed by cleaving the expanded bulk crystal structure twice, parallel to the surface plane of interest. The final orthogonal unit cell, the supercell, of sufficient size is then constructed and periodically repeated in the x- and y-directions.

To avoid undesired interaction over the boundaries the size of the slab in adsorption studies has to be carefully chosen. The computational cost grows rapidly with the size of the slab, which can be very critical when studying larger adsorbates as the realistic dyes presented in this thesis.

For analyzing the electronic interaction between the adsorbates and the semiconductor it is necessary to extract the energy levels with contributions from the adsorbate. The PDOS is very useful and can project the DOS onto the adsorbate atoms. The \Gamma-points of the atom-centered Molecular Orbitals (MO) are displayed by using the output from the CRYSTAL98 program with the XCrysDen program.\textsuperscript{89} Molecular illustrations are made with the Moviemol program\textsuperscript{90} and plots using the software Grace-5.1.18.\textsuperscript{91}
The electronic coupling and the estimated electron transfer rate of the photoinduced interfacial electron transfer are obtained from the electronic structure calculations. The interaction of the dye LUMO is characterized by an energy shift $\Delta E$ and a lifetime broadening $\hbar \Gamma$ as described in section 3.3.3. The adsorbate PDOS, identified as the adsorbate LUMO (excited state of the adsorbate), is fitted to a Lorentzian distribution, with respect to $E_{LUMO}$ and $\hbar \Gamma$, by the non-linear fitting module included in the program Grace-5.1.18. Note that in Paper II the FWHM width of the adsorbate PDOS was taken as a measure of the lifetime broadening $\hbar \Gamma$. The estimated electron transfer time is obtained from the lifetime broadening through $\tau(\text{fs})=658/\text{FWHM(meV)}$.

4.1.2 Cluster calculations

Matter in the form of clusters is the intermediate between small molecular and bulk states. Nanocrystals of ionic and semi-ionic compounds are examples of real-life clusters. A cluster model refers to a model of a solid or surface created simply by cutting out a suitable piece of the solid. The piece should be big enough to keep the properties of a solid and here it is of course desirable to reach the size of the 2-50 nm particles used in the dye-sensitized solar cells. Due to computational costs the size is today limited to at most a few nanometers in diameter. Small clusters usually have problems with missing ionic pairs and dangling bonds at the edges and are normally compensated by including point charges and small molecules as water at the edges. The TiO$_2$ clusters in this thesis are instead of the so-called bare clusters type, and are built in the following procedure. A suitable piece was cut from an anatase crystal structure unit cell, expanded in 3D, by systematically removing Ti and O atoms keeping the cluster stoichiometric, charge neutral and with as high coordination as possible for all atoms. In this way both the ionic and covalent effects are taking into account, which are required for keeping the electronic properties properly.

The cluster models are referred to as (TiO$_2$)$_n$ and the subscript $n$ indicates the number of TiO$_2$ units. The computational cost grows however very fast with the size of the cluster. Fortunately, a larger adsorbate does not require a larger cluster, and once a cluster is found suitable for modeling nanocrystals and at the same time computational reasonable there are no restrictions on the size of the adsorbate.

The molecular calculations in this thesis were carried out using the Gaussian03 program. For a visual resemblance to the DOS of a solid a constructed effective density of states (DOS) is obtained by a 0.3 eV artificial Gaussian broadening of the individual MO levels. Molecular illustrations were made with MOLEKEL, and graphs and remaining plots were made using Grace-5.1.18.
For analyzing the electronic interaction between the adsorbates and the semiconductor in the complete system it is necessary to extract the energy levels with contributions from the adsorbate. Unfortunately, the PDOS is not available for the cluster calculation. It is however simply extracted in a similar manner from calculated basis set expansion coefficients in the LCAO:

\[ p_i = \sum_{j}^A (e_{ij}^d)^2 / \sum_{j}^A (e_{ij}^d)^2, \]

where \( p_i \) is the adsorbate portion of MO \( i \) with orbital energy \( \varepsilon_i \), \( n \) is the number of basis functions and \( e_{ij}^d \) is the expansion coefficients centered on adsorbed atom \( A \).

The electronic coupling and the estimated electron transfer rate are obtained from the electronic structure calculations were the interaction of the dye is characterized by an energy shift \( \Delta E \) and a lifetime broadening \( h\Gamma \), as described in section 3.3.3. The dye LUMO levels are of particular interest for the photoinduced excited state interaction with the empty conduction band of the semiconductor. The MOs that contain adsorbate portions equivalent to that of the isolated adsorbate LUMO, the LUMO(ads) levels, are therefore identified and collected such that \( \sum p_i \approx 1 \). The center of the LUMO(ads) distribution, \( E_{\text{LUMO}}(\text{ads}) \), is obtained by a weighted average,

\[ E_{\text{LUMO}}(\text{ads}) = \sum_i p_i \varepsilon_i. \]

The adsorption induced energy shift are:

\[ \Delta E = E_{\text{LUMO}}(\text{ads}) - E_{\text{LUMO}}(\text{free ads}), \]

where the value of \( E_{\text{LUMO}}(\text{free ads}) \) is obtained from a separate electronic structure calculation of the free adsorbate. The width of the broadening, \( h\Gamma \), is taken as the mean deviation of the LUMO(ads) levels,

\[ h\Gamma = \sum_i p_i |\varepsilon_i - E_{\text{LUMO}}(\text{ads})|. \]

A Lorentzian distribution is then constructed to display the final energy distribution of the adsorbate states. The estimated electron transfer time is obtained from the lifetime broadening through \( \tau(\text{fs}) = 658/h\Gamma(\text{meV}) \).

4.2 Adsorption

For adsorption studies a geometry optimization of the adsorbate and the TiO\textsubscript{2} is of course desirable. This is, however, computationally demanding and for large adsorbate-substrate systems stepwise or partial relaxation is often employed.
For the adsorption of the anchor groups in this thesis, all final geometries were fully optimized, i.e. all atoms in both adsorbate and substrate were allowed to relax. The adsorption of the larger adsorbates were in the periodic studies mostly results of a fully relaxed calculation. A full relaxation of the complete adsorbate-(TiO$_2$)$_{46}$ was however not feasible and partial relaxations were adopted. The orientation of the dye relative to the TiO$_2$ surface was determined by the direction of the non-bonded hydrogen of the anchor group, and the rotation of the dye was determined by the direction of the double bonded oxygen of the acid entity in the free dye.

The adsorption energies were calculated by computing the difference in energy between the total energy of the combined system of substrate and adsorbate and the clean TiO$_2$ surface plus the adsorbate molecule in the gas phase, $E_{\text{ads}} = E[\text{TiO}_2] + E[\text{Adsorbate}] - E[\text{Adsorbate@TiO}_2]$. A positive value thus indicates stable adsorption.

### 4.3 Functional and basis set

The B3LYP functional$^{18,19}$ was used in all calculation performed by the author. This functional has proven successful for molecular system as well as condensed phase studies$^{97,98}$ and appears to be a good choice for studies of molecular adsorbates at metal oxides. The basis set was an atom-centered Gaussian basis set of VDZ quality (for Ti 41G$^{99}$ plus a shell of sp polarization functions$^{100}$ and O, P, N, C and F 31G$^{101}$), where the core electrons were replaced by ECPs.$^{102}$ This basis set is much faster than other common Gaussian basis sets and has been successfully used in several similar studies.$^{29,103}$ The exponent of an additional d-function for the P atom, 0.55, was taken from the polarization function of the 6-31G(d,p) basis set,$^{104}$ which significantly improves the description of P-O bonds. For the single point calculations of the cluster an additional diffuse sp shell (exponent 0.15) was added on the oxygen atoms$^{49}$ (VD(T)Z). Ruthenium was described by the LANL2DZ ECP and basis set,$^{105,106}$ and hydrogen by the standard 6-31G basis set.$^{104}$
5 Results

Detailed structural and electronic properties of large realistic dye-semiconductor interfaces are here presented. For validation and comparison, the presented results have been obtained by using different approaches, models and quantum chemical methods.

5.1 TiO$_2$

Periodic boundary conditions have been used for the anatase (101) surface in Papers I and II and for the rutile (110) surface in Paper V. A broad range of TiO$_2$ clusters and nanocrystal models with diameters up to 2 nm were examined in Paper III. In Papers III and IV the sensitization of a large cluster of 46 TiO$_2$ units was in particular carefully exploited.

5.1.1 Anatase bulk and the (101) surface

Geometry
The 2×1 orthogonal (101) anatase surface unit cell, used in Papers I and II, was constructed with dimensions $a=7.666$ Å and $b=10.298$ Å along the [010] and [−101] axes, respectively. The slab is about 6 Å thick, which corresponds to 12 layers of different atomic-coordinate values along the direction perpendicular to the (101) surface (the z-axis). This surface unit cell, (TiO$_2$)$_{2D}$, contains 16 titanium and 32 oxygen atoms, see Figure 9, and is periodically repeated in the x- and y-directions.

Figure 9. The relaxed anatase (101) (TiO$_2$)$_{2D}$ surface unit cell.
In Paper III several TiO$_2$ cluster models were investigated, using different methods, in terms of structural and electronic properties. The number of TiO$_2$ units ranged from 2 to 68, which allows, in particular, the transition from molecular to crystal properties to be investigated in greater detail. The degree of structural reorganization is found to largely depend on the quality of the computational method.

The large, bare, and charge neutral (TiO$_2$)$_{46}$ cluster was considered as a good candidate for modeling nanostructured TiO$_2$ particles and therefore sensitized in Papers III and IV. It has a quite large (101) surface suitable for accommodating the absorption sites. The maximum Ti and O atom distance is calculated to be 15.4 Å, i.e. the cluster is truly nanosized. In the (TiO$_2$)$_{46}$ starting crystal structure most of the atoms are under-coordinated, and therefore the geometry optimization causes considerable structural relaxation in the optimized structure creating an almost spherical geometry, as can be seen in Figure 10.

![Figure 10](image)

*Figure 10. The unrelaxed anatase (TiO$_2$)$_{46}$ cluster (a), and the geometry of the optimized bare (TiO$_2$)$_{46}$ cluster, in side (b) and top (c) view, respectively. The fully coordinated Ti and O atoms are highlighted in b and c by the Ball and Stick representation.*

Analogous to the relaxation of the periodic surface, the coordinatively unsaturated Ti and O atoms go inwards and the saturated Ti and O atoms go outwards relative to the surface plane, respectively, upon relaxation. Contrary to the surface of the periodic slab, which is stabilized in the x- and y-directions, the anatase (101) surface section in the (TiO$_2$)$_{46}$ cluster has a large number of edge atoms with a high degree of dangling bonds. This gives rise to highly reactive surface sites, so-called Ti=O defect sites. These oxygen atoms originate from the surface row of two-fold coordinated oxygens in the anatase (101) surface, denoted 2c-O in Figure 9, which are considered to be the chemically most active oxygen atoms of the surface which were taken to participate in the monodentate adsorption of anchor acids.
Electronic structure

The periodic anatase bulk and surface band gap is calculated to 3.4 eV and 4.0 eV, respectively. The results are consistent with experimental bulk band gap of 3.2 eV and in reasonable agreement with 3.4 eV for 2.4 nm particles. In Paper III and in the right panel of Figure 11 it is shown that the calculated band gap decreases monotonically from around 5 eV to 4.6 eV when going from 16 to 60 TiO₂ units in the cluster. For example, the band gap of the (TiO₂)₄₆ is calculated to be 4.7 eV and the optical band gap is calculated to be 4.0 eV. The shape of the clusters also seems to affect the band gap. The (TiO₂)₆₈ cluster clearly breaks the trend of a gradually decreasing band gap, which is attributed to its slab-like shape without a bulk-like core.

The calculated anatase (TiO₂)₂D surface and all calculated nanoparticles (TiO₂)₁₆ – (TiO₂)₆₈ exhibit a broad, filled valence band and a broad, empty conduction band, separated by a defect-free band gap, as can be seen in Figure 11.

![Figure 11. In left panel, DOS for anatase bulk (top) and anatase (101) (TiO₂)₂D surface (bottom). In the right panel, effective DOS for anatase clusters (TiO₂)₁₆ – (TiO₂)₆₈ obtained by a 0.3 eV artificial Gaussian broadening of the individual MO levels.](image)

The top of the valence band essentially consists of oxygen 2p-orbital character, whereas the conduction band is mainly of titanium 3d-orbital character. While the DOS of (TiO₂)₂D has energy levels which are continuous, and although the (TiO₂)₄₆ is a quite large cluster, the DOS of the (TiO₂)₄₆ is limited to discrete levels separated by a finite width. At the bottom of the conduction band these levels are most sparse. This is a realistic behavior for a
small particle exhibiting so-called quantum size effects, where the bands are not fully developed resulting in sparse discrete levels and increased band gap. The size and shape of the cluster has shown to have strong influence on these quantum size effects, and a thin cluster may therefore not be an ideal model for a nanocluster.

The position of the HOMO and LUMO levels was found to be very sensitive to the choice of computational methods and sizes of the cluster but the band gap was found to be quite stable. The LUMO of the clusters was found to be situated higher up in energy than the LUMO of the periodic surface and resulting in larger band gap. The energetically higher position of LUMO for the clusters was found to be critical when studying dyes having a lowest excited level positioned near the band edge.

5.1.2 Rutile bulk and the (110) surface

Geometry

The (110) rutile (TiO\textsubscript{2})\textsubscript{2D} surface unit cell was constructed of a 3×2 orthogonal surface slab with dimensions a=9.0465 Å and b=13.0976 Å in the [001] and [1-10] directions, respectively. The thickness is about 6 Å, corresponding to 10 layers of different atomic-coordinate values along the direction perpendicular to the surface (the z-axis), in literature this is often referred to as a two-layer thick slab. This surface unit cell, (TiO\textsubscript{2})\textsubscript{2D}, contains 24 titanium and 48 oxygen atoms and is periodically repeated in the x- and y-directions. In the relaxed surface structure, displayed in Figure 12, the coordinatively unsaturated Ti and O atoms have relaxed downwards and the saturated Ti and O atoms have relaxed upwards perpendicular to the surface plane.

Figure 12. The relaxed rutile (110) (TiO\textsubscript{2})\textsubscript{2D} surface unit cell.
Electronic structure
The calculated bulk band gap of 3.2 eV and surface band gap of 3.7 eV for the clean 3×2 rutile surface unit cell are slightly smaller than the band gaps of anatase. The result is consistent with experimental rutile bulk band gap of 3.02 eV.31

The calculated DOS of rutile is very similar to DOS calculated for anatase with a broad, filled valence band and a broad, empty conduction band, separated by a defect-free band gap, see Figure 13. The top of the valence band essentially has oxygen 2p-orbital character, whereas the conduction band is mainly of titanium 3d-orbital character.

![Figure 13. DOS for rutile bulk (top) and (110) (TiO₂)₂D surface (bottom).](image)

5.2 Anchor group adsorption
The adsorption of phosphonic acid on TiO₂ surfaces has a broad range of applications including the DSSC systems. The phosphonic acid (HPO₃H₂) offers a serious alternative as an anchor group that can be used for binding a variety of organic or inorganic molecules to the surface, in competition with the extensively investigated formic acid (HCOOH).

The adsorption of phosphonic and formic acid was investigated for binding to the anatase (101) surface, in Papers I and II, and to the rutile (110) surface, in Paper V, using periodic B3LYP computations. The adsorption of phosphonic and carboxylic acid was also studied in Papers III and IV for binding to an anatase nanocrystal, modeled by the anatase (TiO₂)₄₆ cluster using molecular B3LYP computations.
5.2.1 Phosphonic acid

Adsorption properties

There are several molecular monodentate and dissociative bidentate adsorption modes found in Paper I with calculated adsorption energies exceeding 40 kcal/mol. According to the calculations, the most stable adsorption arrangement is a molecular monodentate configuration. The structure was re-optimized in Paper II (see Figure 14, left) with a calculated adsorption energy of 49 kcal/mol. The most stable dissociative adsorption is a 2M-bidentate configuration with an adsorption energy of 44 kcal/mol.

![Figure 14. Surface section of HPO3H2 adsorbed on the anatase (101) surface of (TiO2)2D (left) and (TiO2)46 (right) via a monodentate binding. Selected bond distances of the fully optimized anchor and semiconductor geometries are given in Å.](image)

The geometry of the phosphonic acid anchored on the pre-optimized (TiO2)46 cluster was calculated in Paper III, and the fully optimized structure is shown in Figure 14 (right). The monodentate binding mode, found to be favored in the periodic study, was used as a prototype adsorption mode. The computed adsorption strength of 82 kcal/mol is noticeable larger than the corresponding periodic results, which can be ascribed to a larger reactivity of the cluster surface.

The geometry of HPO3H2 adsorbed to the cluster model is highly similar to the geometry obtained periodically. However, since there are large differences concerning Ti-O bond lengths and reorganization of the surface in the (TiO2)46 and (TiO2)2D models, there are also differences in the adsorbate-substrate bonds. Due to the unsymmetrical structure of the (TiO2)46 surface, the bonding of the two hydroxyl groups is not as symmetric as the bonding in the periodic model.

Further investigation reveals relaxation of the surface atoms that is connected with their restored bulk coordination. The Ti atom that is active in the adsorption changes in principle from being 5-fold to 6-fold coordinated and the adsorption results in an elongation of the bonds to its surrounding O atoms. Moreover, the Ti atom is lifted up from the surface, which results in a change of the Ti-O distance to the oxygen underneath the Ti atom from 1.83 Å (clean surface) to 2.06 Å, similarly to what was seen in the periodic study.
Compared to the anatase surface there are fewer possible unique binding modes for the adsorbate to bind to the rutile surface. The binding modes of the phosphonic anchor at anatase were used in Paper V as prototype adsorption modes at rutile and a complete search for the most favorable binding mode of the phosphonic acid was not performed. The adsorption of phosphonic acid on a 3×1 (TiO$_2$)$_{2D}$ surface unit cell is shown in Figure 15. The monodentate binding mode was found to be favored on the two-layer thick slab, with the calculated adsorption energies of 46 and 40 kcal/mol in the monodentate and bidentate binding mode, respectively. The adsorption energies of the phosphonic acid on the 3×2 (TiO$_2$)$_{2D}$ surface unit cell were 49 (monodentate) and 46 kcal/mol (bidentate).

Figure 15. Surface section of HPO$_3$H$_2$ adsorbed on the rutile (110) 3×1 (TiO$_2$)$_{2D}$ surface unit cell via a monodentate binding (left), and a bidentate binding (right). Selected bond distances of the fully optimized anchor and semiconductor geometries are given in Å.

However, the slab thickness of the rutile (110) surface has recently been shown to significantly influence the adsorption energies, and a thickness of at least four layers was found to be required for reliable adsorption energies of formic acid on the rutile (110) surface. Adsorption of phosphonic acid on a 4-layer thick slab was therefore investigated, which is the double thickness of the 3×1 (TiO$_2$)$_{2D}$ surface unit cell. The adsorption energies were 56 and 60 kcal/mol for monodentate and bidentate binding mode, respectively. Hence, the phosphonic acid is in these calculations suggested to bind to the rutile (110) surface in a favored bidentate binding mode, although the difference is small.

Electronic structure

In all the calculated electronic structures of HPO$_3$H$_2$-(TiO$_2$) the anchor group MO levels are all well merged into the substrate valence band and conduction band, indicating strong electronic coupling to the surface. The adsorption of the anchor groups does not shift or change the size of the band gap much, compared to the corresponding clean surface.
5.2.2 Formic acid

**Adsorption properties**
The adsorption strengths of HCOOH on anatase (101) \((\text{TiO}_2)_{2D}\) surface were found to be weaker than 30 kcal/mol (the Paper I). The examined adsorption modes are very similar to the most stable modes of phosphonic acid. The monodentate binding gives the most stable configuration with calculated adsorption energy of 29 kcal/mol and is shown on the left in Figure 16. The dissociative 2M-bidentate binding mode has an adsorption energy of 22 kcal/mol and the relative adsorption energy between these most stable monodentate and bidentate binding mode is in agreement with other studies.\(^{48}\)

The geometry of formic acid anchored on the pre-optimized \((\text{TiO}_2)_{46}\) is reported in Paper III, and the fully optimized structure is shown in Figure 16 (right). The calculated adsorption strength of 42 kcal/mol is, as for HPO\(_3\)H\(_2\), noticeably larger than the corresponding periodic results and ascribed to a larger reactivity of the cluster surface. The adsorbate-substrate bonds are approximately 0.15 Å shorter for binding to the cluster model (2.07 and 1.35 Å compared to the periodic 2.21 and 1.50 Å). Similarly to the adsorption of HPO\(_3\)H\(_2\), the Ti-O distance to the oxygen underneath the Ti atom changes from 1.83 Å (clean surface) to 2.02 Å due to restored bulk coordination.

![Figure 16. Surface section of HCOOH adsorbed on the anatase (101) surface of \((\text{TiO}_2)_{2D}\) (left) and \((\text{TiO}_2)_{46}\) (right) via a monodentate binding. Selected bond distances of the fully optimized anchor and semiconductor geometries are given in Å.](image)

The greater adsorption strength of phosphonic acid compared to formic acid, calculated for adsorption on both \((\text{TiO}_2)_{2D}\) and \((\text{TiO}_2)_{46}\), is in good agreement with experimental observations regarding differences in the long-term stability between the two different anchor groups.\(^{51-54}\)

Possible adsorption geometries of formic acid adsorbed at the rutile (110) surface were studied in Paper V, see Figure 17. The calculated adsorbate-substrate bonds are found to be slightly longer than those for formic acid adsorbed on anatase.
Figure 17. Surface section of HCOOH adsorbed on the rutile (110) $3\times 1$ (TiO$_2$)$_{2D}$ surface unit cell via a monodentate binding (left), and a bidentate binding (right). Selected bond distances of the fully optimized anchor and semiconductor geometries are given in Å.

The adsorption energies of the carboxylic acid on the $3\times 2$ (TiO$_2$)$_{2D}$ surface unit cell were 35 kcal/mol and 25 kcal/mol, for monodentate and bidentate adsorption mode, respectively. The relative adsorption energies (36/25 kcal/mol) are in good agreement with the relative adsorption energies (21/16 kcal/mol) calculated in ref. 107. In this reference the monodentate mode was found to be slightly favored for a two-layer thick slab but the bidentate mode was found favored for a 6-layer thick slab and the conclusion was that formic acid is adsorbed on the rutile (110) surface in a bidentate mode. The same conclusions can also be drawn from the present calculations.

A comparison of the calculated adsorption energies of the formic acid and the phosphonic acid reveals that the binding of phosphonic acid also to the rutile (110) surface is much stronger than that of formic acid.

Electronic structure
As for the phosphonic acid, all the calculated electronic structures have anchor group MO levels that are well merged into the substrate valence band and conduction band, indicating strong electronic coupling to the surface. The adsorption of the anchor groups does not shift or change the size of the band gap much compared to corresponding clean surface.

5.3 Dye-TiO$_2$ interfaces
Several different dye-TiO$_2$ interfaces have been studied. The dyes are attached via phosphonic or carboxylic acid to a periodic or cluster representation of TiO$_2$. In several cases a spacer group has been inserted between the dye and the surface. An overview of the dyes, discussed in this chapter is shown in Figure 18.
5.3.1 Pyridine bound to TiO$_2$

The adsorption of pyridine on the anatase (101) surface via carboxylic or phosphonic acid was investigated with periodic boundary conditions in Paper II and using a large (TiO$_2$)$_{46}$ cluster in Paper III by means of hybrid HF-DFT calculations. Pyridine adsorption on TiO$_2$ is an interface model of the adsorption of the Ru-dye N3 on TiO$_2$, commonly used in DSSC systems. Pyridine is the binding half of the ligand of the Ru-dye, and the $\pi^*$ LUMO level of pyridine coincides with the LUMO level of the Ru-dye which is involved in the photo-induced MLCT process. This makes pyridine adsorption on the TiO$_2$ surface a suitable model for theoretical investigations of the fundamental electron transfer properties of aromatic-metal oxide interfaces.

**Adsorption properties**

The pyridine ring was added to the anchor group-TiO$_2$ structures that were optimized in Papers I and III. For the periodic framework in Paper II the final structure was obtained by a full geometry optimization of the combined adsorbate-(TiO$_2$)$_{2D}$ system. The bond lengths and rotation of the pyridine ring calculated in Paper II, were used in Paper III for mounting the pyridine ring on the hydrogen atom of the anchor group adsorbed on the anatase (TiO$_2$)$_{46}$ cluster, with no further optimization.

In the periodic adsorption study performed in Paper II, the pyridine-4-phosphonic acid (Py-PO$_3$H$_2$) is found to bind substantially more strongly to the anatase (101) surface than isonicotinic acid (Py-COOH). For both adsorbates the monodentate mode is the strongest binding mode, with adsorption energies of 49 and 30 kcal/mol for Py-PO$_3$H$_2$ and Py-COOH, respectively. The strongest bidentate binding modes have adsorption energies of 44 and 22 kcal/mol for Py-PO$_3$H$_2$ and Py-COOH, respectively. For pyridine adsorbed on the large (TiO$_2$)$_{46}$ cluster in Paper III in the monodentate binding
mode, the adsorption energies are 82 and 42 kcal/mol for Py-PO$_3$H$_2$ and Py-COOH, respectively. Again, larger adsorption energies were obtained in the cluster study and are ascribed to a larger reactivity of the cluster surface than of the periodic surface.

The calculations in Papers II and III show that the adsorption energies for only the anchor group adsorbed at the anatase surface are less than 2 kcal/mol different from the binding energies of the complete adsorbates with pyridine. It is also notable that even after the full optimization with pyridine in Paper II, the bond lengths to the surface are almost unaltered. The results therefore show that calculations of the adsorption geometry and strength of the bindings of the anchor group itself to the surface may provide a good description also of the binding of larger molecules to the surface using that anchor group.

**Electronic structure and coupling**

The electronic structures calculated in Papers II and III are qualitative very similar. It is evident that the adsorbates introduce occupied molecular levels in the band gap that are very sharp, see Figure 19. The HOMO for all systems is mainly a nitrogen lone pair orbital of $\sigma$ character with no significant coupling to the surface (note: not a $\pi$-orbital as claimed in Paper II).

![Figure 19. Calculated total DOS (top) and adsorbate projected DOS (PDOS) (bottom) for Py-PO$_3$H$_2$ adsorbed on anatase in monodentate binding mode.](image)

The Py-COOH LUMO is in the gas-phase a $\pi^*$-orbital delocalized over the pyridine ring and carboxylic anchor, whereas for the Py-PO$_3$H$_2$ LUMO, only part of the oxygens on the phosphonic group contribute to the conjugated system. In the adsorbate-surface systems, the Py-PO$_3$H$_2$ LUMO mixes with TiO$_2$ orbitals higher up in the conduction band in comparison to the Py-COOH LUMO, which mix with TiO$_2$ orbitals energetically lower down in
the conduction band. The levels which are obtained by mixing the discrete adsorbate LUMO with levels in the conduction band are collectively referred to as LUMO(ads). The conduction band edge of the (TiO\textsubscript{2})\textsubscript{46} cluster lies energetically higher in the conduction band than of the periodic (TiO\textsubscript{2})\textsubscript{2D}, leading to a position of the carboxylic LUMO(ads) level which is energetically situated critically close to the conduction band edge.

For all systems, the visualized LUMO(ads) demonstrate strong coupling over the interface, where the LUMO(ads) is delocalized over the adsorbate and the entire substrate, and is not only localized on the Ti 3d-orbital contribution close to the adsorbate. This can be seen in Figure 20 and Figure 21 where a selected LUMO(ads) level is shown for Py-PO\textsubscript{3}H\textsubscript{2} adsorbed at the different anatase (101) surfaces.

*Figure 20.* Calculated Γ-point LUMO(ads) for Py-PO\textsubscript{3}H\textsubscript{2} adsorbed on the anatase (TiO\textsubscript{2})\textsubscript{2D} (101) surface in monodentate binding mode.

*Figure 21.* Calculated LUMO(ads) for Py-PO\textsubscript{3}H\textsubscript{2} adsorbed on the anatase (TiO\textsubscript{2})\textsubscript{46} (101) surface in monodentate binding mode.
The calculated PDOS (Papers II and III) show a clear difference between the interactions of the LUMO(ads) with the TiO$_2$ conduction band for the Py-PO$_3$H$_2$ and Py-COOH. The estimated injection times for the (TiO$_2$)$_{2D}$ systems are in a sub-40 fs regime but the injection times for the Py-COOH are found to be approximately twice as fast as those for the Py-PO$_3$H$_2$, irrespective of binding mode. It can be noted that the injection times for Py-COOH are very close to the nonadiabatic transfer time of 19 fs obtained by elaborate ab initio MD simulations for this acid on a rutile surface. The estimated injection times for the (TiO$_2$)$_{46}$ systems are slightly faster, in a sub-20 fs regime, and are in good agreement with the periodic findings that the carboxylic anchor gives rise to significantly faster injection times.

5.3.2 Ru$^{II}$(tpy)$_2$ bound to anatase TiO$_2$

In Paper IV, the structural and electronic properties of a nanoparticle sensitized by a set of Ru$^{II}$(tpy)$_2$ dyes have been investigated by the means of hybrid HF-DFT calculations. There is a huge interest in the use of Ru-polypyridine complexes, such as N3, for sensitization. Complexes based on the 2,2′:6′,2″-terpyridine (tpy) ligand are attractive alternatives to the more widely studied complexes based on 2,2′-bipyridine (bpy) ligands. The tpy ligand offers the possibility of forming linear dye complex structures from the central pyridyl in each tpy ligand.

The Ru$^{II}$(tpy)$_2$ dye was bound to the anatase surface via phosphonic or carboxylic acid and a phenylene (Ph) spacer was inserted for spatial separation of the dye and surface. The anatase nanocrystal was modeled by the large anatase (TiO$_2$)$_{46}$ cluster and the investigated interfaces are referred to as Ru$^{II}$(tpy)$_2$-PO$_3$H$_2$-(TiO$_2$)$_{46}$, Ru$^{II}$(tpy)$_2$-Ph-PO$_3$H$_2$-(TiO$_2$)$_{46}$, Ru$^{II}$(tpy)$_2$-COOH-(TiO$_2$)$_{46}$, and Ru$^{II}$(tpy)$_2$-Ph-COOH-(TiO$_2$)$_{46}$. The effects of anchor and spacer groups were investigated regarding calculated geometries, electronic structures, and spectral properties. In particular, the interfacial electronic structures between the dyes and the TiO$_2$ surface were investigated in terms of MO, DOS, estimated electronic coupling strengths and injection times, as well as calculation of the lowest electronic excitations. For computational reasons, mainly because of an unphysical shifting of the energies due to charge interactions of a charged dye and a neutral surface, the description of the dye comprised two counter ions (PF$_6^{-}$). This was shown to efficiently balance the positive charge of the ruthenium ion.

**Adsorption**

Due to previous findings, that the adsorption geometries of an adsorbate are mainly determined by the robust adsorption geometries of the anchor group itself, the dyes were mounted on the anchor-(TiO$_2$)$_{46}$ cluster, optimized in Paper III, with no further optimization. The orientation of the dye relative to the TiO$_2$ surface was determined by the direction of the non-bonded hydro-
gen of the anchor group, and the rotation of the dye was determined by the direction of the double bonded oxygen of the acid entity in the free dye. The adsorption energies are 81 and 82 kcal/mol for Ru(II)(tpy)_2-PO_3H_2-(TiO_2)_46 and Ru(II)(tpy)_2-Ph-PO_3H_2-(TiO_2)_46, respectively, and 38 and 39 kcal/mol, for Ru(II)(tpy)_2-COOH-(TiO_2)_46 and Ru(II)(tpy)_2-Ph-COOH-(TiO_2)_46, respectively. The adsorption energies of the dyes adsorbed on the TiO_2 nanoparticle are highly similar to those when only the anchor groups are adsorbed, with a much stronger binding for the phosphonic anchor.

Figure 22. Total DOS (black curve and grey lines) and adsorbate (red) and PF_6^-(blue) projected DOS for (a) bare (TiO_2)_46, (b) Ru(II)(tpy)_2-PO_3H_2-(TiO_2)_46 excluding counter ions, (c) Ru(II)(tpy)_2-PO_3H_2-(TiO_2)_46, (d) Ru(II)(tpy)_2-Ph-PO_3H_2-(TiO_2)_46, (e) Ru(II)(tpy)_2-COOH-(TiO_2)_46 and (f) Ru(II)(tpy)_2-Ph-COOH-(TiO_2)_46, including counter ions.

Electronic structure and coupling
The DOS for Ru(II)(tpy)_2-PO_3H_2-(TiO_2)_46 in Figure 22b shows that without the charge balancing counter ions, the adsorbate introduces unoccupied levels, and not occupied, in the band gap, which is a totally unphysical result not
expected for sensitization of the substrate. It was concluded that counter ions have to be included in the description of the dye and it was also shown that the adsorption, photoexcitation and electron injection processes were not affected by the counter ions. The reported DOS and PDOS for Ru\(^{II}\)(tpy)\(_2\)-PO\(_3\)H\(_2\)-(TiO\(_2\)\(_{46}\)), Ru\(^{II}\)(tpy)\(_2\)-Ph-PO\(_3\)H\(_2\)-(TiO\(_2\)\(_{46}\)), Ru\(^{II}\)(tpy)\(_2\)-COOH-(TiO\(_2\)\(_{46}\)), and Ru\(^{II}\)(tpy)\(_2\)-Ph-COOH-(TiO\(_2\)\(_{46}\)) are shown in Figure 22c-f.

In accordance with the very purpose of the sensitization of the semiconductor, all four adsorbates introduce occupied levels in the lower region of the substrate band gap. These levels become the highest occupied levels in their respective systems, and unanimous for all system, the five highest occupied levels correspond to the five highest occupied levels of the free adsorbate. They are, as exemplified by the HOMO of Ru\(^{II}\)(tpy)\(_2\)-PO\(_3\)H\(_2\)-(TiO\(_2\)\(_{46}\)) shown on the left in Figure 23, all entirely localized on the adsorbates, and the three highest occupied levels are Ru 4d-orbitals.

The LUMO(ads) levels for Ru\(^{II}\)(tpy)\(_2\)-PO\(_3\)H\(_2\)-(TiO\(_2\)\(_{46}\)) are situated in the conduction band and well above the conduction band edge, as seen in the PDOS plot in Figure 22c. Moreover, the levels are spread over a significant portion of the substrate band, with a significant coupling to the TiO\(_2\). The lowest LUMO(ads) levels for Ru\(^{II}\)(tpy)\(_2\)-COOH-(TiO\(_2\)\(_{46}\)) are however located at the edge of the conduction band in a region with large substrate level spacings. This means that there are no lower and few higher unoccupied TiO\(_2\) levels to couple to, which leads to the lowest LUMO(ads) levels being spread out on a large region of few but widely separated levels instead of being spread out on a large region of several narrowly spaced levels. In this situation, the LUMO(ads) does not properly fulfill the criteria of being in the wide band limit, which probably makes the calculated interfacial electronic coupling more sensitive to the local geometry at the interface. The LUMO(ads) for all systems are very similar to the LUMO of the free dyes with orbital contributions on the Ru atom, tpy ligand, anchor group, and the spacer groups, and have also contributions delocalized over the substrate, see Figure 23. This indicates strong electronic coupling over the interface.

Figure 23. HOMO of Ru\(^{II}\)(tpy)\(_2\)-PO\(_3\)H\(_2\)-(TiO\(_2\)\(_{46}\)) and selected LUMO(ads) level of Ru\(^{II}\)(tpy)\(_2\)-PO\(_3\)H\(_2\)-(TiO\(_2\)\(_{46}\)), Ru\(^{II}\)(tpy)\(_2\)-COOH-(TiO\(_2\)\(_{46}\)), Ru\(^{II}\)(tpy)\(_2\)-Ph-PO\(_3\)H\(_2\)-(TiO\(_2\)\(_{46}\)), and Ru\(^{II}\)(tpy)\(_2\)-Ph-COOH-(TiO\(_2\)\(_{46}\)).
A quantitative measure of the strength of the electronic coupling is the electron injection time, estimated from a constructed Lorentzian lifetime broadening of the calculated LUMO(ads) level. The injection times were for all systems in the sub-200 fs regime with a clear distinction between the anchor groups where the carboxylic acid facilitates much faster injection times. The insertion of the phenylene spacer groups was found to more than double the injection time.

5.3.3 Perylene bound to rutile TiO$_2$

The adsorption of perylene (Pe) on TiO$_2$ surface is often used as a model for theoretical and experimental investigations of fundamental electron transfer properties of aromatic-metal oxide interfaces and there are experimentally measured injection times available for direct comparison.\textsuperscript{87} The organic dyes have several advantages as photosensitizers and are interesting alternatives to the transition metal dyes. They can be produced more cheaply and have large absorption coefficients, due to intramolecular $\pi$-$\pi^*$ transitions. The photon absorption range can be modified by inserting spacers groups, as the ethenylene unit (-CH=CH-), which extends the $\pi$-system.

The adsorption of perylene on the rutile TiO$_2$ (110) surface via phosphonic and carboxylic acid was studied in Paper V using periodic B3LYP calculations. The insertion of saturated (-CH$_2$-) and unsaturated (-CH=CH-) spacer groups between the perylene and the anchor groups were also studied. The resulting interfaces are referred to as Pe-PO$_3$H$_2$-(TiO$_2$)$_{2D}$, Pe-CH$_2$-PO$_3$H$_2$-(TiO$_2$)$_{2D}$, Pe-CH$_2$-CH$_2$-PO$_3$H$_2$-(TiO$_2$)$_{2D}$, Pe-CH=CH-PO$_3$H$_2$-(TiO$_2$)$_{2D}$, Pe-COOH-(TiO$_2$)$_{2D}$ and Pe-CH=CH-COOH-(TiO$_2$)$_{2D}$. The influence of anchor and spacer groups on adsorption properties, electronic structure and electronic couplings were investigated. In particular, the use of phosphonic acid as anchor group was carefully investigated, and the final structures were obtained by a full geometry optimization of the combined adsorbate-substrate system.

**Adsorption properties**

The adsorbate-substrate bond lengths are very similar to the adsorbate-substrate bond lengths for adsorption of only the anchor group. The bond length for the different dyes anchored with the same anchor group are also very similar, as can be seen in the optimized geometries for Pe-PO$_3$H$_2$-(TiO$_2$)$_{2D}$ and Pe-CH=CH-PO$_3$H$_2$-(TiO$_2$)$_{2D}$, shown in Figure 24.

Perylene is found to bind substantially more strongly to the rutile (110) surface via the phosphonic acid than isonicotinic acid. The adsorption energies are comparable to those for the anchor group alone, with adsorption energies of 50-52 kcal/mol and 17-22 kcal/mol for the perylene dyes bound via the phosphonic and carboxylic acid, respectively. The results show, well in agreement with the previous conclusions, that calculation of the adsorp-
tion geometry and binding strength of the anchor group alone to the surface may provide a good indication also of the binding of larger molecules to the surface using that anchor group.

Figure 24. Optimized geometry of Pe-PO₃H₂ (left) and Pe-CH=CH-PO₃H₂ (right) adsorbed on the rutile (110) (TiO₂)₂D surface unit cell. Selected bond distances are given in Å.

Electronic structure and coupling
The reported DOS and PDOS are presented in Figure 25 for the clean and dye-sensitized rutile surfaces. The DOS contains broad substrate valence and conduction bands, separated by a wide band gap. The perylene dyes introduce very sharp occupied molecular levels in the band gap. The HOMO for all systems is a perylene π-orbital with no coupling to the surface, as can be seen for Pe-PO₃H₂-(TiO₂)₂D in Figure 26.

The perylene LUMO is in the gas phase delocalized over the perylene ring system and also extended over the whole carboxylic acid but only partly on the phosphonic acid. This delocalization is also extended over inserted unsaturated spacers, however broken for inserted saturated spacer groups. The degree of delocalization influence the level alignment and also the electronic interaction over the interface, where an extended delocalization results in a lowering of the LUMO level and at same time favors strong electronic coupling to the surface. This can be seen by the PDOS shown in Figure 25, where the LUMO(ads) for Pe-COOH-(TiO₂)₂D lies lower than the LUMO(ads) for Pe-PO₃H₂-(TiO₂)₂D. Moreover, the LUMO(ads) for the unsaturated spacer are even further down in the conduction band while the LUMO(ads) for the saturated spacers are further up.

Visualized LUMO(ads) for Pe-PO₃H₂-(TiO₂)₂D, Pe-CH=CH-PO₃H₂-(TiO₂)₂D, Pe-COOH-(TiO₂)₂D and Pe-CH=CH-COOH-(TiO₂)₂D, demonstrate strong coupling over the interface. The LUMO(ads) are delocalized over the adsorbate and the entire substrate, and it is not only localized on the Ti cen-
ters close to the adsorbate. This is shown in Figure 26 (right) for the delocalization of LUMO(ads) for Pe-PO₃H₂ adsorbed at the rutile (110) surface.

Figure 25. Total DOS (black curve and grey lines) and PDOS (red) for (a) (TiO₂)₂D, (b) Pe-PO₃H₂-(TiO₂)₂D, (c) Pe-CH₂-PO₃H₂-(TiO₂)₂D, (d) Pe-CH₂-CH₂-PO₃H₂-(TiO₂)₂D, (e) Pe-CH=CH-PO₃H₂-(TiO₂)₂D, (f) Pe-COOH-(TiO₂)₂D and (g) Pe-CH=CH-COOH-(TiO₂)₂D.

The PDOS show a clear difference between the LUMO(ads) interactions with the TiO₂ conduction band for the perylene dyes bound via the phosphonic acid and the dyes bound via carboxylic acid, with significantly stronger couplings for the carboxylic acid. There is also a substantial weak-
ening of the coupling for the dyes with saturated spacer groups, resulting in very narrow LUMO(ads) peaks.

Figure 26. Calculated Γ-point HOMO (left) and LUMO(ads) (right) for Pe-PO₃H₂ adsorbed at the rutile (TiO₂)₂D (110) surface in monodentate binding mode.

The shift and broadening of the dye LUMO level when interacting with the rutile conduction band are presented in Table 1 along with calculated and experimental injection times.¹⁰⁸ The calculated and experimental results show the same systematic trend and, the calculated and experimental results agree on an absolute scale within a factor of roughly two. The results show that the injection times of perylene bound via carboxylic acid are much faster than those of phosphonic acid. The unsaturated spacer group is found to be an efficient mediator of electron transfer with calculated injection times of only a factor two slower than the perylene without spacer groups.

Table 1. Electronic interaction between perylene dyes LUMO and TiO₂ conduction band. Calculated adsorbate LUMO energies, the shift (ΔE) and broadening (hΓ) of adsorbate LUMO, and estimated and experimentally determined injection times.

<table>
<thead>
<tr>
<th></th>
<th>E_{LUMO}(ads)</th>
<th>ΔE</th>
<th>hΓ (meV)</th>
<th>τ_{ads} (fs)</th>
<th>τ_{eq} (fs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pe-PO₃H₂-(TiO₂)₂D</td>
<td>-2.5</td>
<td>-0.20</td>
<td>49</td>
<td>14</td>
<td>23.5</td>
</tr>
<tr>
<td>Pe-CH=CH-PO₃H₂-(TiO₂)₂D</td>
<td>-2.8</td>
<td>-0.39</td>
<td>26</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>Pe-COOH-(TiO₂)₂D</td>
<td>-2.9</td>
<td>-0.32</td>
<td>225</td>
<td>3</td>
<td>8.4</td>
</tr>
<tr>
<td>Pe-CH=CH-COOH-(TiO₂)₂D</td>
<td>-3.0</td>
<td>-0.37</td>
<td>113</td>
<td>6</td>
<td>13.5</td>
</tr>
</tbody>
</table>

¹ Energies of LUMO(ads) and ΔE are reported in eV. ² ΔE = E_{LUMO}(ads) – E_{LUMO}(free ads).
³ Injection times by pump-probe time-resolved two-photon photoemission spectroscopy under ultra-high vacuum conditions, taken from ref. 108.
6 Conclusions

The interface between realistic dyes and nanostructured TiO$_2$ interfaces has been investigated using hybrid HF-DFT calculations in order to elucidate structural and electronic properties of the dye-sensitized solar cell at the molecular level.

The structures and adsorption energies of several adsorption modes for phosphonic acid on TiO$_2$ anatase (101) surfaces have been calculated using periodic boundary conditions. The overall strongest adsorption according to the calculations is a monodentate geometry. The adsorption of phosphonic acid is calculated to be significantly stronger compared to adsorption of formic acid. The same conclusion was found in the adsorption study of phosphonic and carboxylic acid on a large (TiO$_2$)$_{46}$ nanocrystal model. These results agree with experimental work that shows that phosphonic acid can be used as an anchor group to bind a variety of organic and transition metal dyes to TiO$_2$ surfaces with greater stability compared to the currently most frequently used carboxylic acid anchor group.

The adsorption properties for pyridine adsorbed on TiO$_2$ anatase via phosphonic or carboxylic acid anchor group have also been computed using periodic calculations. Both monodentate and bidentate adsorption modes have been considered. The adsorption of pyridine-4-phosphonic acid is found to be significantly stronger than that of isonicotinic acid. This result is irrespective of binding mode, and agrees well with the results for the binding of the anchor groups by themselves. In fact, the adsorption properties of pyridine are largely determined by the robust adsorption properties of the anchor group. Consequently, the geometries of the adsorbed anchor groups obtained in this thesis can be used for further investigations of larger adsorbates.

The presented electronic structures and visualized molecular orbitals, obtained by using a periodic anatase surface as well as a large anatase cluster, give a detailed picture of the electronic interaction between TiO$_2$ and a pyridine ring attached by the different anchor groups. This was performed using a periodic anatase surface as well as a large anatase cluster. The LUMOs demonstrate strong mixing of adsorbate and substrate orbitals, and strong interfacial electronic coupling is confirmed by a detailed analysis of the adsorbate contributions to the DOS. Theoretically estimated injection times are found to depend more strongly on the choice of anchor group than on the
binding mode, and are calculated to be more than twice as fast for isonicotinic acid than for pyridine-4-phosphonic acid.

Atomistic and electronic structures of large realistic dye-TiO₂ interfaces are reported. A large anatase cluster have been sensitized by a set of Ru¹¹-bis-terpyridine dyes attached to TiO₂ by phosphonic or carboxylic acid anchor groups, with and without a phenylene spacer group. Moreover, the perylene-TiO₂ system has been studied by adsorption of perylene dyes on a periodic rutile (110) surface via phosphonic and carboxylic acid anchor groups and with saturated or unsaturated spacer groups. The results show strong influence of the both anchor and spacer groups on adsorption and electronic properties. The adsorption properties of the dyes are found to be largely determined by the robust adsorption properties of the adsorbed anchor group itself. Also in these cases, the phosphonic acid anchor group binds the dyes significantly stronger to the surface than the carboxylic acid anchor group, while the calculated interfacial electronic coupling is stronger for the carboxylic acid than for phosphonic acid. Estimated electron injection times for the carboxylic acid are twice as fast as for the phosphonic acid. This shows that the anchor group can play an important role by governing electronic coupling and thus function as a mediator in the surface electron transfer processes. The electronic couplings are significantly influenced by the spacer groups, where the unsaturated spacer groups were found to mediate electron transfer more efficiently than the saturated ones. The injection times for dyes with unsaturated spacer groups are calculated to be within a factor of two slower than the injection times without spacer groups, but the injection times for dyes with saturated spacer groups are calculated to be at least a factor 5 slower than the injection without the spacer groups. For the perylene-TiO₂ system, the estimated injection times can be directly compared with experimental results. Within a series of adsorbates, the calculated and experimental results show the same systematic trend, and on an absolute scale, the calculated and experimental results agree within a factor of roughly two.

Conclusively, the results presented in this thesis give a detailed picture of the dye-TiO₂ interface. The decisive role of the anchor group on adsorption properties and electronic couplings is highlighted and clarified. Finally, the thesis shows that TiO₂, sensitized by realistic transition metal dyes or organic dyes now can be studied theoretically on the molecular and electronic level. This can be used as an important part of the development of the DSSC.


En ny typ av solcell som kallas Grätzel-solcellen är mycket lovande och forskning kring dess effektivisering och kommersialisering pågår runt om i världen. Principen bakom denna solcell är hämtad från naturen och härmar klorofyllets funktion i fotosyntesen, där de gröna bladen fångar upp solljus som omvandlas till energi. I traditionella solceller används halvledarmaterial till att både fånga upp solljus och att leda ström till elektroden. Höga krav ställs på dessa halvledare (ofta kisel) som är relativt dyra att framställa. I Grätzel-solcellen låter man istället halvledaren enbart ägna sig åt att leda strömmen och låter istället ett noga utvalt färgämne ta hand om solljusupptagningen. Dessa solceller är lämpliga för massproduktion eftersom man kan använda halvledare i form av nanostrukturerad metalloxid som är mycket
billigare och enklare att producera. Den nanoporösa formen i dessa material gör att den totala ytan som kan fånga upp solljus blir tusentals gånger större, vilket höjer kapaciteten avsevärt. På grund av principen att göra nanostrukurerade halvledare känsliga för ljus, dvs. sensiterade, kallas solcellen ofta för färg-sensiterad solcell.


Solcellens funktion visas schematiskt i Figur 27: (1) Färgämnet tar upp solljus och exciteras, dvs. en elektron lyfts till en högre energinivå. (2) Den exciterade elektronen förs (injiceras) över till halvledaren och transporterar genomb nätverk av sammankopplade titandioxidnanopartiklar till bakkontakten. (3) Elektronen vandrar genom en yttre krets, där man kan ta ut en spänning, till motelektroden. (4) Genom en elektriskt ledande vätska transporterar elektronen tillbaka till färgämnet och kretsen är slut.

Solcellen är ett mycket komplext system med många olika komponenter på molekylär skala. Solcellens kapacitet styrs av hur komponenternas elektroniska nivåer matchar, s.k. molekylär elektronik. Den effektivaste Grätzel-solcellen idag konverterar 10-11% av ingående solljus till elektricitet. Den teoretiskt maximala verkningsgraden är ca 30% men det har visat sig svårt att optimera solcellen ytterligare.

Gränssnittet mellan färgämne och halvledare, se Figur 27, har visat sig vara av stor betydelse för solcellens kapacitet och är därför särskilt intres-


Färgämnen binds ofta till halvledaren genom s.k. förankringsgrupper som ska binda färgämnet hårt till ytan men samtidigt inte förhindra den effektiva elektronöverföringen. De för närvarande effektivaste färgämnenanvänder karboxylsyra (-COOH) som förankringsgrupper vilken ger snabba injektionstider. Däremot är förankringen instabil i vattenlösning vilket är en stor nackdel som komponent i en solcell som skall kunna stå emot väder och vind. Fosfonsyran (-PO$_3$H$_2$) är däremot en god kandidat som har visat sig binda mycket starkare till halvledarytan och är inte vattenlös. Mellanrumsgrupper kan också placeras mellan förankringsgruppen och färgämnet för att bl.a. fixera färgämnets orientering mot ytan men också för att förhindra att den injicerade elektronen hoppar tillbaka till färgämnet.

I denna avhandling har kvantkemiska beräkningar använts för att studera gränssnittet mellan färgämne och titandioxid. Beräkningarna ger detaljerad information om materialens molekylära och elektroniska struktur, t.ex. hur färgämnet binder till ytan och hur färgämnets energinivåer matchar halvleddans energiband. Den elektroniska kopplingen mellan färgämne och yta och injektionstider för den snabba elektronöverföringen över gränssnittet har beräknats för flera gränssnitt. Effekten av olika förankrings- och mellanrumgrupper vid adsorption av färgämne på titandioxidytan har undersömts med avseende på adsorptionsgeometrier och energier, och hur elektronstruktur och den elektroniska kopplingen förändras vilket påverkar den ultra-
snabba injektionstiden. Vidare har en metod att kvantitativt uppskatta den elektroniska kopplingen mellan färgämnets exciterade elektroniska nivån och titandioxidens ledningsband använts. De uppskattade injektionstiderna kan då jämföras med experimentellt uppmätta tider.


Titandioxid har tre kristallstrukturer varav de två vanligaste, anatas och rutile, har studerats här. Genom att använda periodiska randvillkor har en mycket realistisk elektronstruktur för titandioxid kunnat beräknas. Den periodiska beräkningsmetoden lämpar sig mycket bra för studier av ytor och adsorption av molekyler på ytor. Vid större adsorbat kan icke-periodiska supermolekyler, s.k. kluster, vara mer lämpliga modeller. Dessa kluster påminner mycket om nanokristallerna och byggs upp av lämpligt antal 

Periodiska beräkningar har gjorts för adsorption av perylen på en rutileyt och resultaten visar hur olika förankrings- och mellanrumsgrupper påverkar adsorptions- och elektroniska egenskaper. Injektionstider har dessutom jäm-

Sammanfattningsvis ger dessa beräkningar en mycket detaljerad bild av gränssnittet mellan färgämnen och titandioxid. Förankringsgruppernas avgörande roll för adsorptionsegenskaper och elektronisk koppling har utretts. Avhandlingen visar att sensitering av TiO₂-nanopartiklar med realistiska färgämnen, både övergångsmetallkomplex och rent organiska färgämnen, både övergångsmetallkomplex och rent organiska färgämnen, nu kan studeras teoretiskt på den molekylär och elektronstruktur-nivå. Detta kan användas som en viktig del i utvecklingen av den lovande Grätzel-solcellen.
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My Family and Friends are not forgotten. Thanks for being Family and Friends. And, if anyone still doesn’t have a clue what I’ve been doing, no worries…

\m/
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