Theoretical Studies of Ground and Excited State Reactivity

POORIA FARAHANI
Abstract

To exemplify how theoretical chemistry can be applied to understand ground and excited state reactivity, four different chemical reactions have been modeled. The ground state chemical reactions are the simplest models in chemistry. To begin, a route to break down halomethanes through reactions with ground state cyano radical has been selected. Efficient explorations of the potential energy surfaces for these reactions have been carried out using the artificial force induced reaction algorithm. The large number of feasible pathways for reactions of this type, up to eleven, shows that these seemingly simple reactions can be quite complex. This exploration is followed by accurate quantum dynamics with reduced dimensionality for the reaction between Cl and PHCl. The dynamics indicate that increasing the dimensionality of the model to at least two dimensions is a crucial step for an accurate calculation of the rate constant. After considering multiple pathways on a single potential energy surface, various feasible pathways on multiple surfaces have been investigated. As a prototype of these reactions, the thermal decomposition of a four-membered ring peroxide compound, called 1,2-dioxetane, which is the simplest model of chemi- and bioluminescence, has been studied. A detailed description of this model at the molecular level can give rise to a unified understanding of more complex chemiluminescence mechanisms. The results provide further details on the mechanisms and allow to rationalize the high ratio of triplet to singlet dissociation products. Finally, a thermal decomposition of another dioxetane-like compound, called Dewar dioxetane, has been investigated. This study allows to understand the effect of conjugated double bonds adjacent to the dioxetane moiety in the chemiluminescence mechanism of dioxetane. Our studies illustrate that no matter how complex a system is, theoretical chemistry can give a level of insight into chemical processes that cannot be obtained from other methods.

Keywords: Chemical Reactivity, Computational Chemistry, Dynamics, Ground and Excited States, Chemiluminescence, Atmospheric Chemistry

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To all those with whom I have shared hunger and cold, and the loneliness that gnaws and gnaws. To the good people with ideas, that perished at personal contact. To the ones who die before giving up...
This thesis is based on the following papers.

I  **Breakdown of Halomethanes by Reactions with Cyano Radicals**  

II  **Ab initio Quantum Mechanical Calculation of the Reaction Probability for the $\text{Cl}^- + \text{PH}_2\text{Cl} \rightarrow \text{ClPH}_2 + \text{Cl}^-$ Reaction**  

III  **Revisiting the Non-Adiabatic Process in 1,2-Dioxetane**  

IV  **Theoretical Study of the Chemiluminescence Mechanism of the Dewar Dioxetane**  
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Addional Publications not Included in This Thesis

i. A Two-Scale Approach to Electron Correlation in Multiconfigurational Perturbation Theory

ii. A Combined Computational and Experimental Study of the $[Co(bpy)_3]^{2+/3+}$ Complexes as a One-Electron Outer-Sphere Redox Couple in a Dye-Sensitized Solar Cell Electrolyte Media

iii. A Combined Computational and Experimental Study of the Hydrogen Bonding with Chlorine Ion in a Crab-claw Like Site of a New Chromium Schiff Base Complex
    Mahmoud Zendehdel, Narges Yaghoobi Nia, Mojtaba Nasr-Esfahani and Pooria Farahani. RSC Advances (2014), (submitted)
The Author’s Contribution to the Papers in This Thesis

I Performed preliminary investigation of the PES and was involved in the design of the research study. From the stationary points computed by the AFIR algorithm, carried out the energy calculations and analyzed the data. Contributed in the writing of the manuscript.

II Performed the electronic structure calculations and analyzed the results.

III Performed the electronic structure calculations, analyzed the results and characterized the reaction mechanism. Wrote parts of the manuscript.

IV Designed the research study, carried out the calculations, analyzed the results and prepared the manuscript.
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Abbreviations

BL  Bio luminescence
AFIR  Artificial Force Induced Reaction
AIMD  Ab Initio Molecular Dynamics
ANO  Atomic Natural Orbital
BO  Born-Oppenheimer
CASSCF  Complete Active Space Self-Consistent Field theory
CC  Coupled Cluster
CI  Configuration Interaction
CIx  Conical Intersection
CL  Chemiluminescence
CRP  Cumulative Reaction Probability
CT  Charge Transfer
DFT  Density Functional Theory
GGA  Generalized Gradient Approximation
HF  Hartree-Fock
HLC  Higher Level of Correction
HOMO  Highest Occupied Molecular Orbital
IRC  Intrinsic Reaction Coordinate
ISC  Intersystem Crossing
KIE  Kinetic Isotope Effect
LDA  Local Density Approximation
LE  Local Excitation
LUMO  Lowest Unoccupied Molecular Orbital
MCSCF  Multiconfigurational Self-Consistent Field theory
MEP  Minimum Energy Path
PES  Potential Energy Surface
QCI  Quadratic Configuration Interaction
RHF  spin Restricted Hartree-Fock
SCF  Self-Consistent Field
SOC  Spin-Orbit Coupling
TC   Transition Complex
TST  Transition State Theory
UHF  spin Unrestricted Hartree-Fock
1. Introduction

“What we call the beginning is often the end. And to make an end is to make a beginning. The end is where we start from.”

T. S. Eliot

Chemistry is the central science inasmuch as it is related to many areas of human curiosity. Theoretical chemistry answers the fundamental questions of chemistry based on principles of physics. One of the most important questions is to understand chemical reactivity. A large number of chemical reactions important in our daily life take place in ground states. The ground state refers to the lowest energy state of the system and it is basically simpler to understand and study than any other state. However, these kinds of chemical processes can be very complex, despite seeming simple. Another type of chemical phenomenon is the fascinating class of reactions that involve light. These reactions implicate an excited state which is any state with greater energy than the ground state. These processes are even more complicated to describe and study than ground state reactions. The aim of this thesis is to explore how theoretical chemistry can be used to understand ground and excited state reactivity.

Theoretical chemistry is a tool to describe the chemical reactivity based on principles of physics. It applies both quantum and classical mechanics to give a good account of chemical observations. The quantum theory is based on the time-independent and the time-dependent Schrödinger equations. Applying these equations, one can, in principle, compute the chemical properties of any system in any state. This gives a level of insight into chemical processes that cannot be obtained from other methods. One example is transition states (TS) that determine the rate of the chemical reactions. These stationary points are relatively easy to compute and can be studied with similar accuracy to stable molecules. Another example of the advantage of theoretical chemistry is that the short-lived excited states can be treated at the same level as the ground states. These facts, make theoretical chemistry a unique tool to understand the mechanisms of these processes at the molecular level.

Theoretical chemists would generally like to carry out their investigation to the highest possible accuracy. However it is in practice possible only for very small systems due to the computational power and time requirements.
Nevertheless, depending on which question should be answered for a specific system, the required level of accuracy can be different. On the other hand, as scientists we endeavor to knit inseparable theoretical and experimental parts of science into a coherent structure which represents accurately the nature of processes. Therefore, an important task for a theoretical chemist is not only to apply correct methodologies on specific systems to get the right answers, but also to demonstrate the relation to the experimental observations. In this thesis we investigate how these goals can be accomplished for a few selected ground and excited state reactions.

The ground state reactivity has been selected to begin our journey, since these types of reactions are the simplest models in chemistry to study and understand. One of the interesting examples is the accumulation of chlorofluorocarbons (CFCs) in the atmosphere which leads to ozone depletion.\[1\] Therefore there is a significant interest to model the CFC stability. This requires an understanding of reaction pathways for many different atmospheric processes. To exemplify how these reaction pathways can be efficiently explored, various feasible pathways for the reaction between halomethanes and the cyano radical have been studied, one of which is the nucleophilic substitution (\(S_N^2\)) reactions:

\[
\text{CX}_3\text{Y} + \text{CN} \cdot \rightarrow \text{CX}_3\text{CN} + \text{Y} \cdot ,
\]

(1.1)

where X = F, H and Y = Cl, Br. The cyano radical (\(-\text{C}≡\text{N}\)) is an important atmospheric species, since it can be found in significant amounts due to the combustion of biomass. In the proposed mechanism, the cyano radical forms a C−C bond when it replaces the leaving group. \(S_N^2\) reactions are generally considered as one of the simplest examples of chemical reactions. This one-step reaction mostly occurs when a halogen atom, an electronegative stable leaving group is attached to an aliphatic sp\(^3\) carbon. Nucleophilic attack on the halogenated carbon leads to a TS which is the direct pentacoordinate TS.

Our results indicate that the mechanism of such systems can be quite complex. To be able to explore the large number of different pathways efficiently, a special computational algorithm, the artificial force induced reaction (AFIR), has been employed.\[2\] Among the eight discovered pathways, two correspond to hydrogen abstraction, similar to the “roundabout” mechanism proposed by Hase et al., for F\(^-\) + CH\(_3\)I.\[3\] This illustrates how complex a seemingly simple \(S_N^2\) reaction can be. However, there are still some factors, like the rate constant and the product distribution of a chemical reaction, which cannot be accurately described only by the potential energy surface (PES).

In spite of the ubiquitous application of classical molecular dynamics, in which the nuclear motions are governed by classical equations of motion, some factors like tunneling and zero-point energy, as well as all kinds of interference phenomena need a quantum treatment of the nuclei. Quantum molecular dynamics, is a modern systematic approach to study the vibrations, interactions, and the rates of reactions. This gives a level of detail into the
chemical processes that cannot be obtained from other methods. Once we have discovered all the feasible pathways of a reaction, one needs to implement quantum dynamics simulation on the most favorable pathway. To start our dynamics study, the symmetric $S_N2$ reaction at the phosphorus center has been studied as a prototype:

$$PH_2Cl + Cl^- \rightarrow ClPH_2 + Cl^-,$$

which is the reaction in its class with the least number of atoms. $S_N2$ reactions at phosphorus center play a key role in organic and biological processes such as DNA replications,[4] as well as in medical treatments.[5] The dynamics of these types of reactions can be quite complex. The reaction proceeds through a transition complex (TC) well instead of a transition state barrier.[6] For an accurate description of the bimolecular rate constant, we have used a quantum mechanical description for the nuclei. By using a reduced order modeling approach on both one- and two-dimensional PES for the reaction (1.2), the effect of increasing the dimensionality can be clearly seen, e.g., the effect of transition well resonances. This contribution shows how an exact description of the molecular quantum dynamics can provide significant additional understanding of the dynamics of these elementary chemical processes.

Throughout our ground-state projects we have considered multiple pathways on a single PES. In the next part of the thesis, various feasible pathways on multiple surfaces have been investigated. A very fascinating phenomenon is chemiluminescence, the phenomenon in which a chemical reaction that initially proceeds on a ground state generates a light-emitting product. The same chemical reaction observed in living organisms is referred to as bioluminescence. This phenomenon is used as a practical tool in biotechnological applications, e.g., as a research tool in genetic engineering with the use of reporter genes or DNA sequencing using pyrosequencing.[7] The bioluminescence, which can be easily seen in firefly beetles for instance, involves a substrate, called luciferin, and an enzyme, called luciferase. When luciferin is oxidated, a four-membered ring peroxide compound moiety, called 1,2-dioxetane, will be produced. Despite significant theoretical and experimental efforts that have been performed to understand the mechanism of simple models of this class of reactions, it is not known in detail. In the next stage, of our journey, the ground and excited state processes in 1,2-dioxetane have been studied.

The thermal decomposition of 1,2-dioxetane can be considered as the simplest model of chemi- and bioluminescent systems:

$$C_2H_4O_2 \rightarrow 2CH_2O + h\nu.$$  

This peroxide compound is a common functional group in these systems, since the chemi- or bioluminescence reaction occurs through an oxygen bond breaking process. Therefore, a detailed description of this model at the molecular level can give rise to a unified understanding of more complex chemiluminescence mechanisms, e.g., dioxetanone and dioxetanedione. In this project, three
different proposed mechanisms have been studied and compared. We also put
some efforts in understanding the large triplet/singlet ratio of the chemilumi-
nescence which was reported by Adam and Baader.[8] To be able to study
the excited state chemistry of 1,2-dioxetane in detail, an exploration of the
multiple PESs has been performed at multiconfigurational levels of theory. In
addition, \textit{ab initio} molecular dynamics was applied to simulate the dynamical
behavior in the bond breaking region. Our results clearly show how complex
a seemingly simple model of such excited state reactions can be. This gives
the opportunity to apply a similar approach to more complicated excited state
reactions.

An observed light emission through thermal decomposition of Dewar ben-
zene was suggested to be dependent of the presence of oxygen.[9] Drawing
from the previous knowledge of chemiluminescence processes, the most likely
candidate for the light emission would be decomposition of so-called Dewar
dioxetane. Dewar dioxetane is a composition of 1,2-dioxetane and butadiene.
The dioxetane moiety in this molecule leads us to consider the same mech-
anism as 1,2-dioxetane, however O–O bond breaking leads to isomerization
rather than decomposition:

\[ C_6H_6O_2 \rightarrow C_6H_6O_2 + h\nu \]  

Using our knowledge of 1,2-dioxetane leads us to characterize and compare
the effects of the presence of \( \pi \) conjugation in the mechanisms of these critical
reactions. This is an excellent example of how theoretical chemistry is able to
describe the effects of substituents in a level of detail that cannot be reached
using any other method.

The articles presented in this thesis deal with the application of theoreti-
cal chemistry. Our study illustrates that no matter how complex a system is,
finding the best method is the most crucial task for a theoretical chemist. In
the next chapter, a background of the chemical reactivity in both ground and
excited states is brought. In Chapter 3 a brief account is given about the the-
eoretical foundations of the methods used. The exploration of the PES of the
reactions between haloalkanes and cyano radical are discussed in Chapter 4,
and the reactivity of different haloalkanes containing hydrogen and fluorine is
explained. To understand in detail how the shape of the PES affects the rate
constant of the \( S_N2 \) at phosphorus center, the dynamical effects on the reaction
rate are outlined in Chapter 5. In Chapter 6, the thermal decomposition mech-
anism of isolated 1,2-dioxetane is investigated. The thermal decomposition of
Dewar benzene is studied in Chapter 7. Finally, a summary of how theoretical
chemistry can be applied to understand chemical reactivity is presented.
2. Chemical Reactivity

“The scientist is not a person who gives the right answers, he’s one who asks the right questions.”
Claude Lévi-Strauss

In chemistry, a key question to answer is why and how a chemical reaction occurs. To do so, one needs to understand what happens when molecules interact with each other and their surrounding. Determining the reaction mechanism requires additional information about the thermodynamic stability of the molecules and their reaction rates. Both of these factors can be explained considering how the potential energy of the system changes during the reaction. The PES is the potential energy as a function of the positions of all the atoms partaking in the process. In this chapter a brief explanation of how the shape of the PES affects the reactivity of systems in both ground and excited states is given.

2.1 Ground State Reactivity

A large number of chemical reactions take place in the electronic ground state. Stable molecules represent minima on the ground state PES. As the reaction occurs, some bonds are being formed and some are broken, and the potential energy rises to a maximum, which corresponds to an activated complex. The geometry at this point is called the transition structure. At the transition structure the reactant molecules have come into a degree of closeness and distortion in which a small further action, makes the system fall into the new minimum of the potential surface with rearranged positions of the atoms. The minimum energy pathways connecting minima describe the reaction mechanisms. The highest points along these pathways are the TSs and the path with the lowest energy TS is the most feasible pathway.

To exemplify these concepts, we consider a simple bimolecular process like an $S_N^2$ reaction:

$$A + BC \rightarrow AB + C.$$  \hspace{1cm} (2.1)

At the beginning of the collision the distance between A and B ($R_{AB}$) is infinite and $R_{BC}$ equals to the BC equilibrium bond length. When the reaction
is terminated successfully $R_{AB}$ is equal to the AB equilibrium bond length and $R_{BC}$ is infinite. The plot of the total energy of this system versus the bond distances $R_{AB}$ and $R_{BC}$ and the angle $\theta_{ABC}$ shows the PES. In theoretical chemistry, performing the electronic energy calculations for different sets of nuclear coordinates, gives a full-dimensional PES. From that surface it is possible to extract the barrier for any chemical reaction.

Using the transition state theory (TST), one can calculate the rate constant of a reaction,

$$k = \kappa \frac{k_B T}{h} e^{-\frac{\Delta^G}{RT}},$$

(2.2)

where $\Delta^G$ is the relative free energy of the TS and $\kappa$ is a unitless constant that takes into account e.g., tunneling effects and recrossings. This equation shows how the rate of a chemical reaction can be computed using theoretical chemistry.

2.2 Excited State Reactivity

Another class of chemical reactions is excited state reactions, most of them involve light. These processes are more complicated to study than the ground state reactions, since more PESs are taken into account. As an example, one can consider chemi- or bioluminescence process. Chemiluminescence (CL) is a process where an excited state of a molecule is formed by a chemical reaction, this excited molecule releases the excitation energy by light emission.

Bioluminescence (BL) is a CL process taking place in living organisms. Nature provides us with impressive examples of such chemical phenomena, e.g., jellyfish, stoplight loosejaws, firefly beetles and glowworms. Out of these organisms the firefly beetle is the most well-known. In the BL process, an oxidation of a substrate, so-called luciferin, in the active site of an enzyme, luciferase, is the responsible for the emission of light. It has been believed, that this reaction leads to a key peroxide intermediate, which is the actual light emitter. Therefore, a detailed study on small CL models including peroxide compounds can lead us to characterize the chemiluminophore properties, such as the ability to transfer the system from ground to excited state.

In order to characterize chemiluminescence we first need to put it in relation to well-known photophysical and photochemical processes. These phenomena occur through interactions between PESs, see Figure 2.1. Photophysics refers to radiative and non-radiative processes in the absence of any chemical reaction. The term photochemistry can be used for photoinduced processes that involve the formation or breakage of a bond. The aim of photochemistry is to determine the reaction path that follows the light absorption; when the excited state is populated, it either comes back to the previous structure, which is called photostability or produces new compounds, which refers to a photoin-
duced process. Figure 2.2 illustrates the basic differences of photophysics and photochemistry on a PES. The adiabatic photochemistry term in the Figure 2.2 refers to the evolution of changing geometries which takes place only through one PES. In contrast to adiabatic processes, non-adiabatic process refers to evolutions involving at least two PESs.

Looking at the molecular light absorbtion in more detail, the photon energy causes excitation of an electron from the initial occupied orbital to an unoccupied higher energy orbital. This typically creates two singly occupied orbitals. Depending on whether the spin of these electrons are antiparallel or parallel, a state can be noted as singlet or triplet, respectively. Throughout this chapter, we focus on the following notations to describe the most crucial states; the ground singlet state ($S_0$), the lowest-lying excited singlet state ($S_1$) and lowest-lying excited triplet state ($T_1$).

As we specified above, photophysical and photochemical processes refer to transitions between states (ground state to excited state and vice versa). Such phenomena are classified as radiative and radiationless events, cf., Figure 2.3. The most common radiative processes are as follows:

1- **Spin-forbidden** absorption. These processes are singlet-triplet absorptions ($S_0 \rightarrow T_1$).

2- **Spin-forbidden** triplet-singlet emission ($T_1 \rightarrow S_0$). Such radiative transitions are called phosphorescence, and occur very slowly.

3- **Spin-allowed** singlet-singlet absorption ($S_0 \rightarrow S_1$).
Figure 2.2. Schematic representation of ground state and excited state surfaces. The figure depicts three different parts: (I) the molecule can come back to the GS through a decay. The decay of the molecule occurs through a CIx or singlet-triplet crossing (STC), this decay does not radiate light, thus it is called radiationless decay; (II) there is absorption and light emission with no chemical reaction, the system comes back to the original structure; (III) there is a production of new species which is far from the first reactant.

4- **Spin-allowed** singlet-singlet emission ($S_1 \rightarrow S_0$). These light emissions which occur from one state to another of the same spin is called fluorescence. The most common radiationless processes are:

1- **Spin-allowed** transitions between two surfaces with the same spins ($S_1 \rightarrow S_0$). These transitions are multidimensional space in which two surfaces are almost degenerated along all the integral degrees of freedom. These spin-allowed transitions or internal conversion (conical intersections (CIx)) are very important to understand non-adiabatic processes.

2- **Spin-forbidden** transitions between one state to another state of different spin ($S_1 \rightarrow T_1$). These radiationless decays are known as intersystem crossings (ISC). The rate of intersystem crossing from the lowest-lying singlet to triplet manifold is relatively large if a radiationless transition involves a change of orbital configuration, this selection rule is known as the El-Sayed rule. In other words, El-Sayed’s rule declares that when two spin surfaces are close in
energy there must be a large amount of spin-orbit interactions for an ISC to occur efficiently.

These transitions can be classified not only by spin states, but also by orbitals involved. An excitation from a $\sigma$ bonding to the $\sigma^{*}$ antibonding orbital is referred to as a $\sigma\sigma^{*}$ excitation. In the same way, an excitation from a $\pi$ bonding to a $\pi^{*}$ antibonding corresponds to a $\pi\pi^{*}$ excitation. Finally, the excitations from a lone pair to a $\pi^{*}$ antibonding is labelled as a $n\pi^{*}$ excitations.

The main difference between CL and photochemistry is that in photochemistry, the absorbed light is used to produce a chemical reaction, whereas the CL is production of excited state and consequently light emission by a chemical reaction. The difference between a photophysical transformation and a CL process is how the excited state is formed. The formation of an excited state by light absorption refers to a photophysical transformation, and the formation of an excited state by chemical reaction corresponds to a CL process.

In order to form an electronically excited state, with enough energy to emit visible light (wavelength of 400–700 nm), the chemical transformation has to be highly exothermic. With almost no exception, oxygen is indispensable reactant in chemi- and bioluminescence processes. So far, there have been three observed types of CL reactions; peroxide decompositions, electron-transfer reactions and formation of excited oxygen. In this thesis we focus on the study of peroxide decompositions. Figure 2.4 is a schematic representation of how the PES of a CL process looks like. In fact there is no general explanation

Figure 2.3. A scheme of the main photophysical and photochemical molecular processes.
of why the O–O cleavage is the main responsible of light emission in such chemical reactions. However, one reason can be the formation of carbonyl compounds. The carbonyl compounds contain two important characteristics. First, the carbon-oxygen double bond is very stable and can cause a highly exothermic reaction which leads to form an electronically excited state. Second, the product includes a chromophore which can be formed in the excited state.

To be able to explain the mechanism of a chemical reaction, a detailed description of the PES is required. The PES illustrates how the excited state is populated, whether the transformation is spin-allowed or spin-forbidden, etc. Using theoretical chemistry, one can, in principle, compute the chemical properties of any system in any state. In this branch of study, the short-lived excited states can be treated at the same level as the ground states. That is why theoretical chemistry is a unique tool to understand the mechanism of chemical processes at the molecular level.

To understand the mechanism we seek a high-resolution description of the PES. To obtain that, accurate calculations of the relative energies of ground and excited states are required. Therefore, to get the right answers and to demonstrate the relation to the experimental observations, one needs to apply the correct methodology for each specific system. In Chapter 3 we show how
to choose the proper methodologies and how to apply them, which will allow us to ask the right questions.
3. Theory

“We all want progress. [...] If you are on the wrong road, progress means doing an about-turn and walking back to the right road; and in that case, the man who turns back soonest is the most progressive man.”

C. S. Lewis

Before starting on the applications, we give a brief explanation about some concepts of computational chemistry of importance to the present thesis. The Born-Oppenheimer (BO) approximation leads to the concept of potential energy surface on which local minima correspond to stable molecules, and the minimum energy pathways between minima describe reaction mechanisms. Once the PES is calculated using electronic structure methods, different mechanisms can be easily described. However, the accuracy of the PES depends on the methodologies applied on specific systems. Our explanations give insights into different levels of theory and make it easy to employ the correct methodologies.

3.1 The Born-Oppenheimer Approximation

The BO approximation is the most crucial approximation in quantum chemistry and chemical physics. According to the BO approximation one can consider the movements of the electrons to be in the field of the fixed nuclei, since the electrons are much lighter than the nuclei, hence they move faster.\[10\] Considering the complete non-relativistic molecular Hamiltonian:

$$\hat{H} \simeq T_e + V_{ee} + T_N + V_{NN} + V_{eN}$$  \hspace{1cm} (3.1)

which includes kinetic energy of the nuclei ($T_N$), kinetic energy of the electrons ($T_e$), electron-nuclear attractive Coulomb potential ($V_{eN}$), electron-electron repulsive Coulomb potential ($V_{ee}$) and nuclear-nuclear repulsive Coulomb potential ($V_{NN}$). The Schrödinger equation is:

$$\hat{H}\Psi(r, R) = E\Psi(r, R).$$  \hspace{1cm} (3.2)
According to the BO approximation one can assume the wave function $\Psi$ to be separated into a product of electronic and nuclear part:

$$\Psi(r, R) = \psi(r; R) \chi(R)$$

(3.3)

where $\psi$ is a wave function as a solution of the electronic part of the Schrödinger equation in the field of fixed nuclear coordinates, and $\chi$ is a wave function associated with nuclear motion. When solving the electronic Schrödinger equation, the nuclei kinetic energy can be neglected from the Hamiltonian of the system, which depends only on the electronic coordinates, and (3.3) will be written as:

$$(T_e + V_{NN} + V_eN + V_{ee})\psi = E_{el}(R)\psi$$

(3.4)

where the energy $E_{el}$ is the electronic energy as a parametric function of the nuclear coordinates $R$ and $V_{NN}$ is just a constant. Inserting (3.4) and (3.3) into (3.2), we obtain:

$$(T_N + E_{el})\psi\chi = E_{tot}\psi\chi.$$  

(3.5)

Since $T_N\psi\chi = \psi T_N\chi$ according to the BO approximation, $\psi$ can be integrated out from the both sides of (3.5), giving the nuclear Schrödinger equation:

$$(T_N + V)\chi = E_{tot}\chi$$

(3.6)

in which

$$V = V_{NN} + E_{el}$$

(3.7)

is the electronic potential energy surface.

The BO approximation is generally a good approximation, however in the case of crossings in which two solutions to the electronic Schrödinger equation become too close, cf., Figure 3.1, it breaks down. As an example one can consider the photoinduced molecular processes like non-adiabatic photochemical reactions in which one part of the reaction takes place on the excited state and after a surface crossing continues on the ground state. These cases and their applications are explained in Chapter 2 in detail.

### 3.2 Foundations of Electronic Structure Theory

Solutions to the electronic Schrödinger equation can be computed by electronic structure theory. Two different types of methods can be applied for determining the PES, electron wave function based methods and electron density based methods. This section contains a general description of these methods, starting with principles that are common in both.
Figure 3.1. Three different examples in which the BO approximation breaks down.

3.2.1 The Variational Method

A way to determine approximate solutions to the Schrödinger equation in quantum mechanics is to find the lowest energy eigenstate or ground state. The variational method consists of a trial wave function for which, by definition, the expectation value of the energy is higher than the exact energy. This method is often specified as in the following equation:

$$E_{\text{trial}} = \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle} \geq E_0 \quad (3.8)$$

where $E_0$ is the exact ground state energy value and $\psi$ is normalized. The function $\psi$ is called a “trial variation energy function” and the integral is well-known as the “variational integral”. Expanding $\psi$ in terms of the exact eigenfunctions of $\hat{H}$ with energy eigenvalues, $E_n$, we denote $\psi$ as:

$$\psi = \sum_n C_n \chi_n \quad (3.9)$$

Then:

$$\sum_n (E_n - E_0) |C_n|^2 \geq 0 \quad (3.10)$$

The theorem is proved, since the value of $(E_n - E_0)$ is inevitably non-negative but positive or zero. According to the variation theory, the obtained energy value can only be equal to $E_0$, if $\psi$ equals to the wave function of the ground state of the considered system, otherwise it is greater than $E_0$. The variational theorem accurately enables us to determine which trial wave function gives the lowest possible energy, and this wave function is the one closest to the correct solution.
3.2.2 Basis Sets

A basis set is a set of functions, so-called basis functions $\chi_j$, from which the molecular orbitals of the trial wave function can be constructed:

$$\phi_i = \sum_j C_{i,j} \chi_j$$

(3.11)

where $M$ is the number of basis functions. In variational methods the basis set coefficients are optimized to get the best molecular orbitals of the trial wave function.

In order to represent all of the occupied orbitals of the molecule, a minimum number of basis functions is required. By increasing the number of basis functions, the molecular orbitals of the trial wave function will be closer to the exact solution. However, using a large number of basis functions increases the cost of the optimization procedure.

As it is mainly the valence electrons that take part in bonding, the valence orbitals are often represented by more than one basis function. To indicate the number of basis functions used for each type of atomic orbital, the basis sets are labeled as double, triple, quadruple-zeta $\zeta$, etc. There are two types of split-valence basis sets used in this thesis, Pople basis sets and correlation-consistent basis sets.

The correlation-consistent basis set notation for the first and second row atoms is cc-pVXZ in which X=D,T,Q,5,... (D for double, T for triple, etc., $\zeta$). In that notation “cc-p” means correlation-consistent polarized and “V” implies that the specification for the basis set size (X) only applies to the valence. [11] Augmented versions of these basis sets indicate that diffuse functions are added. The basis set coefficients in correlation-consistent basis sets are optimized at coupled-cluster level.

So far, we explained the segmented contraction basis sets, in which each primitive Gaussian function contributes to only one or a few contracted functions. Another type of basis set used in this thesis is general contraction of which atomic natural orbitals (ANO) basis set is an example. In ANO basis sets all primitive Gaussian functions contribute to all contracted functions. The LCAO coefficients of this type of basis sets are computed based on complete active space (CAS) methods.

3.3 Electronic Wave Function - Single-Configurational

*Ab Initio* Methods

3.3.1 Hartree-Fock Approximation

In dealing with a problem in quantum chemistry, the standard approach is to solve the electronic Schrödinger equation. However, exact solutions to the
Schrödinger equation are only possible for very small simple systems. Therefore, one can only apply approximate solutions for the many-body problems. The Hartree-Fock (HF) approach provides us with an approximate solution to the electronic Schrödinger equation. The first simplification introduced in the HF method is the orbital approximation, in which the $N$-electron problem is decomposed into $N$ one-electron problems. Therefore, the total many-electron wave function is constructed from a set of one-electron functions called orbitals. According to the Pauli principle the wave function has to be antisymmetric, to guarantee this the total electronic wave function is described by a Slater determinant instead of a single product of molecular orbitals.

A spatial orbital, $\phi(r)$, is a function of position $r$ of an specific electron, through the probability, $|\phi|^2$, of the electron distribution in space. However, finding a complete description of the electron entails to specify the state of the electron spin, which can be represented by $\alpha(\omega)$ and $\beta(\omega)$ spin wave functions, for spin up and spin down, respectively and $\omega$ is the spin coordinate. In order to describe both spatial distribution and the spin state of the electron, one requires the spin orbital, $\phi(r, \omega)$. The occupation of two electrons of different spins can be illustrated by spin restricted Hartree-Fock (RHF) and spin unrestricted Hartree-Fock (UHF). In the RHF scheme, each spatial orbitals $\phi_k(r)$ can be occupied by two different spins like a pair of degenerated spin orbitals $\phi_k(r)\alpha(\omega)$ or $\phi_k(r)\beta(\omega)$. In contrast, in the UHF scheme, two sets of spatial functions are devoted to describe the $\alpha$ and $\beta$ electrons, $[\phi_k^\alpha(r)]$ and $[\phi_k^\beta(r)]$, respectively.

The electronic energy, which is a function of the occupied spin orbitals can be simplified as:

$$E^{el} = E_{HF} = \sum_k h_{kk} + \frac{1}{2} \sum_{k,j} [J_{kj} - K_{kj}], \quad (3.12)$$

where $h_{kk}$, $J_{kj}$ and $K_{kj}$ are the one-electron core integrals, the two-electron Coulomb and exchange integrals, respectively.

Since the HF equations:

$$\hat{f}\phi_k = \varepsilon_k \phi_k \quad (3.13)$$

are defined to be nonlinear and have to be solved iteratively, it is called the self-consistent field (SCF) procedure. The Fock operator depends on the shape of all the occupied MOs. In this formalism each electron feels only the average field of the other electrons. This means that HF does not include the electron correlation.

The HF approximation includes electron exchange, i.e., the correlation between electrons with parallel spin through the Pauli principle. However, the Coulomb correlation which describes the correlation between the spatial position of electrons due to their Coulomb repulsion, has not been defined within the HF method. Comparing the exact solution of the non-relativistic
Schrödinger equation with the HF solution using a complete basis, gives a difference of energy called correlation energy.\[12\]

\[
E_{\text{corr}} = E_{\text{exact}} - E_{\text{HF}}
\] \hspace{2cm} (3.14)

Neglecting electron correlation can cause large deviations from experimental results. This is the most important weakness of HF method. Electron correlation can be divided into two parts: non-dynamical (static) correlation and dynamical correlation. In order to include electron correlation to the multi-electron wave function, different approaches called beyond or post-Hartree-Fock methods have been devised. Static correlation is well described by the use of multi-configurational wave function methods. Dynamical correlation can be described with the configuration interaction (CI), coupled-cluster (CC), Møller-Plesset perturbation theory (MP), etc., which are addressed later on in this chapter, and also under electron correlation dynamics.

3.3.2 Configuration Interaction

Configuration interaction (CI) is a variational method for solving the non-relativistic Schrödinger equation within the BO approximation. It is also a beyond or post-Hartree-Fock method. CI includes electron correlation in molecular calculations. The CI wave function is defined by a sum of many Slater determinants, in which the coefficients of the Slater determinant summation are variationally optimized:

\[
\psi = \sum_i c_i D_i
\] \hspace{2cm} (3.15)

where the determinants \(D_i\) are obtained by the excitation of one or more electron(s) from occupied orbitals of the HF ground state to unoccupied orbitals. The determinants are labeled by the number of excited electrons. For instance, single excitations refer to the determinants in which one electron is excited. In the same way, if only single and double excitations are included it is called singles-doubles CI (CISD).

One problem with CI is that it is not size-consistent. For a method that is not size-consistent, the energy of two specific molecules at a large distance is not equal to twice the energy of a single molecule. Quadratic configuration interaction (QCI) is an extension of CI in order to correct the size-consistency errors. This method, developed by Pople,\[13\] has been used in the PES calculations mentioned in Chapter 3. It normally gives very similar results to coupled-cluster. A CI expansion in which all possible excitations are included is called “full CI” (FCI), which gives the exact answer within the chosen basis.
### 3.3.3 Coupled-Cluster

Coupled-cluster (CC) is a method for describing electron correlation in many-body systems. CC uses a wave function that is derived from the HF wave function ($\psi_0$) and constructs multi-electron wave function employing the exponential cluster operator for electron correlation.

$$\psi_{CC} = e^{\hat{T}} \psi_0$$  \hspace{1cm} (3.16)

The exponential of $\hat{T}$ can be written as:

$$e^{\hat{T}} = 1 + \hat{T} + \frac{1}{2!} \hat{T}^2 + \frac{1}{3!} \hat{T}^3 + \ldots = \sum_{k=0}^{\infty} \frac{1}{k!} \hat{T}^k.$$  \hspace{1cm} (3.17)

In the operator $\hat{T}$:

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \ldots$$  \hspace{1cm} (3.18)

$T_1$ represents single excitations, $T_2$ double, $T_3$ triple, and so forth. The advantage of this form of wave function is to include higher order excitations through the disconnected (e.g., $\hat{T}_2^2$) terms. Thus, it is capable to describe more of the correlation energy than CI methods. The Schrödinger equation using the coupled-cluster wave function will then be:

$$\hat{H} e^{\hat{T}} \psi_0 = E_{cc} e^{\hat{T}} \psi_0.$$  \hspace{1cm} (3.19)

The commonly used version of CC is the one including single and double excitations (CCSD) in the $\hat{T}$ operator. To further improve the result the effects of triple excitations can be included using perturbative approach giving the CCSD(T) method which has been employed for the calculations of both $S_N/2$ reactions in this thesis.

The electron correlation methods are significantly more time consuming to perform, compared to HF calculations. In addition they also require large basis sets to give converged results. The basis set sensitivity of coupled-cluster methods comes from the CC operators:

$$\hat{T}_1 = \sum_{a,i} t_{a,i} \hat{E}_{a,i}$$  \hspace{1cm} (3.20)

$$\hat{T}_2 = \sum_{a,b,i,j} i_{a,i}^{b,j} \hat{E}_{b,j} \hat{E}_{a,i}$$  \hspace{1cm} (3.21)

in which $t_{a,i}$ are the amplitudes and $\hat{E}_{a,i}$ are annihilation and creation operators. The indices $i$ and $j$ are used for the occupied orbitals and in the same way, $a$ and $b$ are used for the virtual orbitals. The operator $\hat{E}_{a,i}$ annihilates an electron from orbital $i$ and creates an electron in $a$, so that it depends on the number and the shape of the virtual orbitals, which are specified by the basis set. This causes the method to be very sensitive to the change in size of the basis set.
3.3.4 Time-Independent Perturbation Theory

Perturbation theory uses mathematical methods to find approximate solutions, by the use of the exact solutions of a related problem. The Hamiltonian, $\hat{H}$, is expressed as a sum of the zeroth-order term $\hat{H}_0$, for which there is an exact solution, and a time-independent perturbation $\hat{V}$:

$$\hat{H} = \hat{H}_0 + \lambda \hat{V}$$  \hspace{1cm} (3.22)

in which $\lambda$ is a parameter that determines the strength of the perturbation. The eigenfunctions of $\hat{H}_0$ are $\phi_n$ with the eigenvalue $E_n$. In order to develop the full Schrödinger equation, we use the following expansion for the wave function.

$$\psi = \psi_0 + \lambda \psi_1 + \lambda^2 \psi_2 + ...$$  \hspace{1cm} (3.23)

Because $\phi_0$ and $\phi_1$ are both eigenfunctions to the $\hat{H}_0$ operator, $\langle \phi_0 | \phi_1 \rangle = 0$. Thus:

$$E^{(1)} = \langle \phi_0 | \hat{V} | \phi_0 \rangle.$$  \hspace{1cm} (3.24)

For the higher-order terms, the energy of wave function can be developed in a similar way:

$$E^{(2)} = \sum_{i \neq 0} \frac{\langle \phi_0 | \hat{V} | \phi_i \rangle \langle \phi_i | \hat{V} | \phi_0 \rangle}{E_0 - E_i}.$$  \hspace{1cm} (3.25)

Up to now the theory has been completely general and to get a specific electronic structure method, $\hat{H}_0$ and $\hat{V}$ have to be defined. In the Møller-Plesset second order perturbation theory (MP2), which is another beyond or post-HF method, $\hat{H}_0$ is the sum over the Fock operators. Because the $\hat{H}_0$ counts the average electron-electron interaction ($\langle \hat{V}_{ee} \rangle$) twice, the perturbation $V$ has to be the exact $\langle \hat{V}_{ee} \rangle$ operator minus twice the average $\langle \hat{V}_{ee} \rangle$ operator.

In second order perturbation theory (MP2), the Equation (3.25) implies that two electrons are excited with respect to the ground state configuration. MP2 accounts for almost 80–90% of the correlation energy and it is an economical method to include significant amounts of the dynamical correlation.

3.4 Electronic Wave Function - Multiconfigurational Ab Initio Methods

So far, we have discussed the single-configurational methods in which the wave function is derived from the HF wave function. The HF wave function, represents the lowest possible energy for a single determinantal wave function, which in many cases is a good approximation to the exact wave function. However, there are some cases where the HF wave function even qualitatively
fails to describe the correct behavior. As an example, one can consider the cases with homolytic bond breakage where a single reference wave function cannot express the dissociation limit. Other cases, are the degenerate systems, e.g., two or more degenerated orbitals for which there are fewer electrons than the number of orbitals. In such instances, the degenerate orbitals should be equally treated. Whereas, the HF wave function would optimize only the orbitals that are occupied. In this case, including the determinants where the other orbitals are occupied would still not give back the correct degenerate wave function. These problems appear in, e.g., dissociation limits for chemical bonds, molecules with unfilled valences in ground electronic state (ozone molecule for instance), molecules containing atoms with low-lying excited states (Li, Be, transition metals, etc.) and finally, photochemical reactions which are more likely to have the unpaired electrons in degenerate orbitals.

To solve these dilemmas, an application of a multiconfiguration wave function is required to correct the reference state of the system. The key to get the right orbitals, is also to include coefficients of the basis functions, shown in Eq. (3.11), in the optimization. This is different than in the CI expansion of the HF in which only a set of coefficients of configuration determinants is optimized, see Eq. (3.15). Such a wave function is known as multiconfigurational self-consistent field (MCSCF). The MCSCF includes the static correlation, and gives a correct set of degenerate molecular orbitals. An important difference compared to the CI expansion is that even in cases where the coefficient of the HF configuration is rather small, MCSCF is a good description.

The most used multiconfigurational \textit{ab initio} method is known as complete active space self-consistent field (CASSCF) method which implies the selection of a space of active electrons and orbitals. The CASSCF method implies that the active orbitals are optimized at FCI level of theory whereas the inactive and virtual orbitals are optimized at HF. The CASSCF wave function covers the static correlation and some dynamical correlation. This approach has been proved to be accurate to describe the molecular properties, however, the size of the CAS CI expansions increases dramatically with the number of active orbitals. The calculations can be performed with a large number of orbitals, if and only if the number of active electrons or holes is small.[14]

Moreover, the CASSCF calculation is not very accurate for energy values, due to the lack of significant parts of the dynamical correlation. An example is the dissociation of an O—O bond where the dissociation limit is correctly described using the CASSCF wave function, whereas the stability of the equilibrium geometry is underestimated. To solve this, a more useful and practical approach is multiconfigurational second-order perturbation theory (CASPT2) applied to a CASSCF reference wave function.

The CASPT2 approach is not only capable to take static correlation into account, but also to compute dynamical correlation quantitatively. Therefore, the CASPT2 approach can be considered as a standard for many multiconfigurational problems. However, CASPT2 is not free of problems. The main
limitation of this approach is the cost, especially for the CASSCF reference wave function with a large active space.

There are some well-defined problems of the standard Hamiltonian of the CASPT2 ($\hat{H}_0$). As CASPT2 is a perturbational approach, the size of the perturbation should be small, which means that the weight of reference wave function must be as large as possible. In addition, the weight variation of the reference wave function for a set of calculations, e.g., for several states or while probing of PES, should be rather small. In the cases that the variation is large, there is normally a manifestation of an intruder state. There is a technique, called imaginary level shift, which keeps the weight variation of the reference wave function small.[15]

The state specific (SS) CASPT2 first-order wave functions are non-orthogonal, whereas the state average (SA) CASSCF wave function is orthogonal itself. To recover the non-orthogonality of the CASPT2 model, one can couple several electronic states through an effective Hamiltonian, multi-state CASPT2 approach (MS-CASPT2).[16] Taking a system with two states as an example, the Hamiltonian of the MS-CASPT2 can be written as:

$$\hat{H} = \begin{pmatrix} \hat{H}_{11} & \hat{H}_{12} \\ \hat{H}_{21} & \hat{H}_{22} \end{pmatrix} \approx \begin{pmatrix} E_1 & \frac{\hat{H}_{12} + \hat{H}_{21}}{2} \\ \frac{\hat{H}_{12} + \hat{H}_{21}}{2} & E_2 \end{pmatrix} = \begin{pmatrix} E_1 & \Delta \\ \Delta & E_2 \end{pmatrix},$$  \tag{3.26}

Although this method has been shown to be effective, e.g., for valence-Ryderb mixings and crossing regions, employing MS-CASPT2 approach one must be aware of the off-diagonal elements. In the cases that the off-diagonal elements, $\hat{H}_{12}$ and $\hat{H}_{21}$, are similar and rather small, the MS-CASPT2 can be considered reliable and good. In case that the off-diagonal elements are large or very different, the MS-CASPT2 could be unreliable. A solution to this problem is to enlarge the active space and redo the calculations until small and similar values are obtained. If this is not affordable, one can estimate that the right solution is somewhere between SS-CASPT2 and MS-CASPT2.

### 3.5 Electron Density Methods

So far the beyond or post-HF methods have been described that can treat electron correlation. However, to get accurate result requires sophisticated time-demanding computations which cannot be applied to large molecules. Therefore, one needs a method to solve the ground state electronic structure problems with less computer time. During the last two decades density functional theory (DFT) has been developed sufficiently to give good agreement with experimental data for a large number of chemical systems. The disadvantage of DFT however is that there is no direction to improve except changing the parametrized potential, while improving the wave function and basis sets can systematically improve an $ab\ initio$ method.
The basis of DFT is to determine the ground state electronic energy by using the electron density $\rho$. The electronic density $\rho(r)$ shows the probability of finding any electron in a volume $d^3r$ around $r$, by defining $\rho(r)d^3r$. The ground state energy in DFT is written as a functional of $\rho(r)$ without referring to any wave function $\psi$. A functional is a mathematical object that produces a value from a function, i.e., a function of another function. On the other hand, a function takes a number and returns a number. Although the first concept of DFT originally had been proposed by Thomas and Fermi, it was put into firm theoretical ground by the two Hohenberg-Kohn (HK) theorems that proved that all system properties, among those also the total energy, are determined by the electron density $\rho(r)$.

In terms of the functional, $E[\rho]$ can be written as:

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

(3.27)

where $T[\rho]$ is the electronic kinetic energy, $V_{ee}[\rho]$ is the electron-electron interaction energy. In order to calculate the kinetic energy to good accuracy, Kohn and Sham introduced a system of non-interacting electrons in molecular orbitals. In this system the kinetic energy $T_s[\rho]$ can be calculated exactly and it turned out to be a good approximation to the real kinetic energy $T[\rho]$. Writing Eq. (3.27), in terms of contributions that can be calculated exactly gives the following expression for the functional.

$$E[\rho] = V_{ne}[\rho] + T_s[\rho] + J[\rho] + (T[\rho] - T_s[\rho] + V_{ee}[\rho] - J[\rho])$$

(3.28)

where $J[\rho]$ is the classical Hartree (Coulomb) repulsion of the density. Collecting the terms in the parenthesis of the Eq. (3.28) into a single exchange correlation functional $E_{XC}[\rho]$ gives:

$$E_{XC}[\rho] = T[\rho] - T_s[\rho] + V_{ee}[\rho] - J[\rho]$$

(3.29)

Now the $E_{XC}[\rho]$ is a minor part of the total energy and finding the right expression for this functional should in principle give the exact energy value. However the form of this functional is not known and lots of efforts have been put into finding good approximations. Early attempts to find a good expression for $E_{XC}$ used a theoretical model, the uniform electron gas, for which essentially exact values of exchange and correlation could be obtained by local density approximation (LDA). However when applied to molecules there were large errors in binding energies.

Generalized gradient approximation (GGA) introduces information about the density gradient which is an improvement over LDA that assumes constant electron density. GGA exchange energies usually are very close to exact exchange energies for atoms, but is also a good approximation for molecules. A prominent exchange functional is the Becke88 (B88) which uses a correction to the LDA exchange energy with the correct behavior of the energy density for large distances. GGA correlation functionals are mainly designed
to model dynamical correlation. One example is the LYP functional which has been fitted to describe the correlation in the helium atom. The complete exchange correlation functional $E_{XC}$ is typically the sum over individual exchange and correlation functionals, e.g., BLYP. There are two well-known approaches to design functional: derivation from theoretical arguments giving, e.g., PW91, PBE or derivation from a semi-empirical fit, e.g., BLYP, OLYP and HCTH. In both cases, atomization energies, bond lengths, local excitations and other energy quantities are quite reasonable.

The third approach to design functionals is the hybrid approach.

$$E_{XC}^{\text{hyb}}[\rho] = \alpha(E_{X}^{\text{HF}} - E_{X}^{\text{GGA}}) + E_{XC}^{\text{GGA}} \quad (3.30)$$

which replaces part of the GGA exchange with contributions from exact (HF exchange) and where $\alpha$ describes the amount of HF exchange that is included. Atomization energies bond lengths and other energy quantities are an improvement over the GGA results. Further extensions to the functionals is to include also the kinetic energy density which gives the meta-GGA functionals. Combined with HF exchange this gives the hybrid meta-GGA functionals. The results of both these classes of functionals are generally in good agreement with experimental data.

Here we describe the basic ideas behind the construction of the functionals used in the studies of the reactions described in this thesis, i.e., the hybrid B3LYP and hybrid meta-GGA M06-2X functionals.

**B3LYP**
The most commonly applied hybrid functional is B3LYP, developed from the GGA functional BLYP.[23–25] The exchange correlation functional of B3LYP can be written as:[26]

$$E_{XC}^{\text{B3LYP}} = E_{XC}^{\text{LDA}} + \alpha_0(E_{X}^{\text{HF}} - E_{X}^{\text{LDA}}) + \alpha_X(E_{X}^{\text{GGA}} - E_{X}^{\text{LDA}}) + \alpha_C(E_{C}^{\text{GGA}} - E_{C}^{\text{LDA}}), \quad (3.31)$$

where $\alpha_0$, $\alpha_X$, $\alpha_C$ are universal parameters fitted to experimental data with values of 0.20, 0.72 and 0.81, respectively.

**M06-2X**
M06-2X is part of a set of four meta-GGA DFT functionals. The “2X” suffix indicates twice amount of exact exchange (HF) compared to the M06 functional (54%). This functional has been specifically designed to describe chemical kinetics. It is also proposed as a good functional for studying non-covalent interactions.[27]
3.6 Composite Methods, Gaussian-4 Theory

Increasing the size of basis sets and improving correlation is the way to improve the accuracy of the results, although the computational cost prevents obtaining the exact answer even for small systems. Based on additivity of basis set and level of theory improvements, one can develop composite methods that combine the results of several calculations to reach a high level of accuracy. Approximate additivity avoids direct calculation of high level of theory using large basis sets. Gaussian-4 (G4) theory was introduced by Curtiss et al., in 2007.[28] The combining calculation rungs of G4 theory are described below.

First of all, the geometry optimization to obtain the equilibrium structure has been implemented at the B3LYP/6-31G(2df,p) level. In the next rung, the HF energy limit is computed using the following equation:

\[ E_{\text{HF/\text{aug-cc-pVnZ}}} = E_{\text{HF/\text{limit}}} + B \exp(-\alpha n) \]  

(3.32)

where \( n \) and \( \alpha \) indicate the number of basis set constructions in the valence shell and adjustable parameter, respectively. In the fourth step, a series of single point correlation energy calculations is performed at MP4/6-31G(d), MP4/6-31+G(d), MP4/6-31G(2df,p), CCSD(T)/6-31G(d) and MP2(full)/G3LargeXP. Next, the four correlation corrections obtained from previous rung, are combined with the correction for HF limit and a spin-orbit correction. Then, an additive of Higher-Level Correction (HLC) term is included in the energy calculation. After that, the B3LYP/6-31G(2df,p) equilibrium structure is applied to calculate the harmonic frequencies. Harmonic frequencies are scaled by a factor of 0.9854.[29] They give the zero-point energies \( E(\text{ZPE}) \). Finally, the total energy at 0 K is achieved by using the following expression:

\[ E_0(G4) = E_\pi(G4) + E(\text{ZPE}) \]  

(3.33)

3.7 Accuracy of Different Levels of Theory

In order to describe chemical reactivity, taking the energy differences into account is the most important thing rather than the total energies. In this section we discuss the accuracy and deficiencies of widely used levels of theory when it comes to the calculations of relative energies. Generally, we seek to calculate the rate constant of a reaction as well as the equilibrium constant. Using the TST, one can estimate the rate constant of a reaction only by knowing the TS barrier, see Eq. (2.2). As it is explained in Eq. (3.14), the HF wave function lacks electron correlation, which leads to a dramatic error in the relative energy values. For a database of 76 barriers, Zhao et al., reported a mean absolute deviation of 10.3 kcal/mol,[30] cf., Table 3.1. The errors for 233 heats of formation are larger than 100 kcal/mol.[31] Including
Table 3.1. Accuracy of different levels of theory

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<tr>
<td>HF</td>
<td>Low</td>
<td>10.3(^a) kcal/mol</td>
<td>[30]</td>
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<tr>
<td>MP2</td>
<td>Medium</td>
<td>5.5(^a) kcal/mol</td>
<td>[30]</td>
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<tr>
<td>Coupled-Cluster</td>
<td>Very High</td>
<td>0.8 kcal/mol</td>
<td>[32]</td>
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<td>Very High</td>
<td>1.0(^a) kcal/mol</td>
<td>[30]</td>
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<td>DFT</td>
<td>Low</td>
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<td>[33]</td>
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<tr>
<td>Gaussian-4</td>
<td>Medium</td>
<td>0.9–3.0 kcal/mol</td>
<td>[28]</td>
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<tr>
<td>CIS</td>
<td>Low</td>
<td>10 eV</td>
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<tr>
<td>Coupled-Cluster (SACCI, CC2, CC3)</td>
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<td>0.2–0.3(^c) eV</td>
<td>[34]</td>
</tr>
<tr>
<td>TDDFT</td>
<td>Low</td>
<td>0.6–6.0 eV</td>
<td>[35]</td>
</tr>
<tr>
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<td>[36]</td>
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<tr>
<td>CASPT2</td>
<td>High</td>
<td>0.0–0.2 eV</td>
<td>[37]</td>
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</table>

\(^a\)The weighted average from 76 TS barriers, \(^b\)Depending on which functional is used, the MAD can be varied, \(^c\)Deviations in excitation energies of singlet and triplet states of 28 benchmark molecules with respect to CASPT2/TZVP.

the dynamic correlation at MP2 level decreases these errors to 7.4 and 10.6 kcal/mol, respectively.[30, 31] Even better results are achieved using higher levels of theory, e.g., CCSD and QCISD with errors in barrier height of only 1 kcal/mol.[30, 32] The electron wave function based methods, e.g., MP2, QCISD and CCSD, generally require large basis sets to give converged result due to the electron correlation.

The B3LYP hybrid functional is the main responsible for DFT becoming the most popular tool in theoretical chemistry. In a comparison of atomization energies, the error for the B3LYP functional is 6.1 kcal/mol.[31] For most reactions the barriers are underestimated and errors of 4.55 kcal/mol are shown.[33]

The M06-2X hybrid meta-GGA functional has excellent results for main group chemistry. It has better performance (2.3 kcal/mol) than B3LYP (6.1 kcal/mol) with respect to the 223 heats of formation.[38] For the same database of 76 barriers, M06-2X has a mean absolute deviation of 1.26 kcal/mol, which is mainly due to overestimation of the barriers.[33] This overestimation is because of the large amount of HF exchange (54\%) that is included in M06-2X.

In a comparison of 270 enthalpies of formation, the mean absolute deviation for the G4 method is 0.80 kcal/mol. The G4 energy barriers for hydrogen transfer reactions show a mean deviation of 0.91 kcal/mol. However it gives large errors, greater than 3 kcal/mol for some reactions including fluorine, while none of the deviations for hydrogen transfer is greater than 3 kcal/mol.
These large errors are mainly due to the use of B3LYP/6-31G(2df,p) geometries for the transition states.[39]

The PES computation is a much harder assignment for excited states than for the ground state. In this part, we discuss the methods used for such problems. The configuration interaction-singles (CIS), which is basically a single-reference method that uses the HF solution as reference wave function, overestimates excitation energies due to the lack of correlation energy effects. The size-extensive CC based on single-reference wave function is the most accurate quantum chemical approach for ground state systems. For excited states, the main problem of this method is that it employs the HF zeroth-order reference, which is in fact poor to describe these states. To obtain accurate excitation energies, the single-configuration CC method requires the inclusion of high excitation levels to compensate both the poor reference wave function and the multiconfigurational character of the excited states.[40] Therefore, it is in many cases more efficient to directly apply a multiconfigurational approach for excited states.

The CASPT2 method applied on a CASSCF reference wave function treats the dynamical correlation and is so far the most applicable method to compute all types of excited states.[40] An error of 0.0–0.2 eV is typical in excitation energies[37] and CASPT2 is often used as a reference to benchmark other methods.[34, 41]

The time-dependent density functional theory (TDDFT) approach is on the other hand becoming popular due to its simplicity and perhaps black-box behavior. Despite of its disadvantages, the mean deviation of 0.4 eV in the calculation (B3LYP) of the excited states of 21 different molecules speaks for the popularity of TDDFT.[42]

3.8 Exploring The Potential Energy Surface

Performing the calculations of the electronic energy for different sets of nuclear coordinates gives the PES. For any nonlinear system, consisting of $N$ atoms, $3N - 6$ independent coordinates (degrees of freedom) defines the PES. Using computational chemistry calculations a full-dimensional PES can be calculated. The path of least potential energies is the most feasible pathway. The highest point along these pathways are the transition states (TS) and using the transition state theory (TST), one can calculate the rate constant of the reaction, cf., Eq. (2.2), a unitless constant that takes into account, e.g., tunneling effects and recrossings, but cannot be obtained only from the electronic structure calculations.
Computational Strategies to Probe PESs

An efficient exploration of the PES is the first step of such approach. Once we explored the PES, one needs systematic computational strategies to connect the PES’s stationary point for having a good theoretical description about the mechanism of chemical reactions. Three different approaches to connect PES’s stationary points have been used in this thesis: changing one/a few internal coordinate(s) manually; constrained optimizations; intrinsic reaction coordinates (IRC).[43, 44]

Stretching a chemical bond, bending an angle or adjusting a torsion angle manually can be useful if there is only one mode connecting reactants and products. When there are more than one mode, it is better to apply constrained optimizations in which the system is optimized using one specific mode as a constraint. While employing constrained optimization, one has to be aware of forcing the system to those points on the PES which are chemically irrelevant. For instance, applying constrained optimization to scan the PES of 1,2-dioxetane using the dihedral angle as the constraint clearly shows a twisting instead of torsion which is basically far from what we expect in the thermal decomposition mechanism. Finally, the most reliable strategy is the IRC calculations in which the reaction coordinate is defined as a curve passing through the transition points and orthogonal to energy contour surfaces. Following the mentioned strategies, one must be aware of the shape and barrierless characters of the paths throughout the PES. The shape of the pathways is sensitive to the level of electron correlation and the size of basis set used.

In order to pursue all possible pathways, the artificial force induced reaction (AFIR) method has been used. AFIR is a code developed by Maeda and Morokuma which automatically and systematically discovers unexpected reaction paths.[2] This method is implemented in a local development version of the Global Reaction Route Mapping (GRRM) program. In AFIR the reactants are pressed to each other by a constant force, and its exploration of a potential energy surface includes several steps.[45] Assume that we have a collinear diatomic reaction of A and B single atoms, a constant force between A and B can be defined as a linear function of distance:

\[ F(r_{AB}) = E(r_{AB}) + \alpha r_{AB} \quad (3.34) \]

where \( E(r_{AB}) \) and \( \alpha \) are the potential energy function and the parameter of the strength of the force, respectively. The linear force function should be unique at all geometries, differentiable up to the second order and finally a sum of isotropic functions at each atom. Therefore, Eq. (3.34) for a system with multiple degrees of freedom can be written as:

\[ F(Q) = E(Q) + \alpha \sum_{i \in A} \sum_{j \in B} \frac{[R_i + R_j]}{r_{ij}} p r_{ij} \sum_{i \in A} \sum_{j \in B} \frac{[R_i + R_j]}{r_{ij}} p \quad (3.35) \]
where $E(Q)$ is the PES on the coordinates $Q$, and $p$ is a parameter of weight. Minimizing the force gives an approximate geometry of the stationary points that can be used as initial guesses for full optimizations without the artificial force.

However, there are pieces of information that cannot be obtained only by studying the stationary points of the PES, e.g., resonance and tunneling effects. This information can be taken into account by applying molecular quantum dynamics. Generating a full-dimensional PES is in practice very difficult except for small systems. To treat this dilemma a reduced dimensionality modeling approach, including the most important degrees of freedom, has been used. With only one or two dimensions, this reduced dimensionality PES can be visualized in a diagram which depicts the potential energy versus relevant coordinates. Figure 3.2 shows the reaction mechanism of the $S_{N2}$ at phosphorus center using two molecular coordinates.

### 3.9 Molecular Reaction Dynamics

The quantum mechanical study of changing observables over time is called quantum dynamics, and describes the motion of the atoms under the influence of a force or potential. The aim is to provide insight into the reactions at a microscopic level, e.g., rate laws and rate constants. The $S_{N2}$ reaction at phosphorus has been studied to determine the rate constant of the reaction using quantum dynamics.

#### 3.9.1 Time-Dependent Schrödinger Equation

To describe the motion on the atomic scale, quantum mechanics must be used. The Newton equations of motion are not valid. The equation of
motion for non-relativistic quantum mechanics, is called the time-dependent Schrödinger equation.

The Schrödinger equation for the nuclei can be solved by different numerical methods. Both basis functions and grid discretization can be used for solving the nuclear Schrödinger equation. Grid discretization has been employed in the study of $S_N^2$ at phosphorus center.[46] However, a full-dimensional quantum dynamics simulation would require the handling of $10^{3N-6}$ dimensional wave function, assuming 10 grid points per dimension. This leads to a significant increase in the computational cost for the quantum dynamics. To minimize the cost of the calculations, a reduced-dimensional PES can be used for the dynamics simulation.

In this thesis, the PES for the reaction of $\text{PH}_2\text{Cl} + \text{Cl}^-$, with the form of a deep well with a transition complex (TC), has been investigated. One- and two-dimensional models are compared with respect to the quantum dynamics simulations. Finally, the rate constant which is a function of the cumulative reaction probability $N(E)$, has been computed and discussed.

3.9.2 Rate Constant and State-to-State Reaction Probabilities

Understanding the mechanism of any reaction is an important conundrum for chemists. One way of understanding the mechanism is to describe the rate constant and hence the reaction rate. From a fully quantum aspect, the reaction rate can be computed as a function of the cumulative reaction probability $N(E)$, and a Boltzmann average over the total energy.

$$k(T) = (2\pi\hbar Q_r(T))^{-1} \int_0^\infty dE e^{-E/kT} N(E), \quad (3.36)$$

The cumulative reaction probability (CRP), gives the total reaction probability. The CRP converges fast and is not very sensitive to the modeling parameters. It can be obtained from a flux operator function:[47]

$$N(E) = (2\pi\hbar)^{-1} \text{Tr} [\hat{F} \delta(E-H)\hat{F} \delta(E-H)]$$

$$= (2\pi\hbar)^{-1} \text{Tr} [P(E)] \quad (3.37)$$

in which $\hat{F}$ and $H$ are the flux operator and the Hamiltonian of the system, respectively. The CRP is Hermitian and can be simplified as an operator called the reaction probability operator $\hat{P}$. By computing the sum of the eigenvalues of $\hat{P}$, the probability for a reaction can be obtained (between zero and one). More information about the reaction rate, which is the first property to be calculated for a complex system, can be obtained from the state-to-state reaction probability $P_{n_p,n_r}(E) = |S_{n_p,n_r}(E)|^2$, where $S$ is the scattering matrix, $n_r$ and $n_p$ are defined vibrational and rotational quantum states of the reactant and the product, respectively. State-to-state reaction probabilities are very sensitive to system parameters in order to converge. They also require more computational effort than the total reaction rate.

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4. Haloalkane Reactions with Cyano Radicals

“There is an infinite number of wrong ways to get the right answer.”

A.D. McLean

Haloalkanes play important roles in the degradation of the ozone layer and for the greenhouse effect. To better understand the long term effects of these molecules, it is critical to model their reactions with other atmospheric species. Haloalkanes are stable molecules, therefore they mainly interact with reactive species like atmospheric radicals. One important radical species is the cyano radical, formed either in combustion reactions or photoreactions.[48, 49] To systematically investigate the details of how cyano radicals affect the stability of haloalkanes, the PESs of the reactions \( \text{CX}_3\text{Y}^+ \cdot \cdot \cdot \text{CN} \) (\( X=\text{H}, \text{F} \); \( Y=\text{Cl}, \text{Br} \)) have been explored using theoretical chemistry methods.

Since the mechanism of reactions of this type is largely unknown, the aim of this project is to give a general description of all the feasible pathways. The exploration of the PES has been accomplished by the use of the AFIR algorithm which is able to automatically locate the stationary points on the PES. In previous studies this algorithm has been able to find a large number of pathways that had not been considered in manual explorations of the PES.[50] As a first approximation, the obtained barrier heights can be used to distinguish between all alternative reaction mechanisms.

The reactions between cyano radicals and saturated hydrocarbons are barrierless, except for methane which has a small energy barrier. The proposed mechanism for these reactions is hydrogen abstraction.[51, 52] In halomethanes, a number of new reaction pathways can be assumed, e.g., halogen abstraction by cyano radicals.

This chapter is structured as follows: First the exploration of the PES is discussed. After that the reactivity of the \( \text{CH}_3\text{Cl} \), which is the most abundant organohalogen in the atmosphere, is explained. Then, the effects of fluorine substitution to chloromethane is analyzed. Finally the role of bromine substitution to \( \text{CH}_3\text{Cl} \) and \( \text{CF}_3\text{Cl} \) is discussed.

4.1 Potential Energy Surface Exploration of \( \text{CX}_3\text{Y}^+ \cdot \cdot \cdot \text{CN} \)

Using the AFIR method, the stationary points of \( \text{CX}_3\text{Y}^+ \cdot \cdot \cdot \text{CN} \) (\( X=\text{H}, \text{F} \) and \( Y=\text{Cl}, \text{Br} \)) were obtained. The PES exploration was carried out with the
B3LYP hybrid functional using the GTBas3 basis set, which is equal to 6-31G(2df,p) for H, C, N, F and Cl, and 6-31G(2fg) for Br. The reason for employing this level of theory is that the composite G4 method uses the same method to optimize the equilibrium structures.

A complete AFIR exploration of stationary points was made for CH$_3$Cl which led to 36 TS structures and 35 local minima. For CF$_3$Cl, the algorithm was terminated after locating all possible reaction pathways, due to the very high barrier of all except one feasible path, therefore only 13 TS structures and 18 local minima were obtained. Substituting Br with Cl can be assumed to lead to the corresponding reaction energy diagrams of CH$_3$Br and CF$_3$Br. Therefore the geometry of the stationary points of the chlorine systems were used as starting points to explore the PES of the bromine-containing counterparts.

After locating the stationary points, energies were calculated with the G4 method. Single-point calculations were also performed at CCSD(T) and the DFT functionals B3LYP and M06-2X levels with the augmented correlation-consistent triple-$\zeta$ basis set (aug-cc-pVTZ). Relative energies were calculated using the separated CX$_3$Y and ·CN reactants as a reference. The large deviation of the barrier height of reactions including fluorine with the G4 method, due to the errors in the B3LYP geometry optimization,[39] motivated us to employ QCISD level of theory to optimize the lowest-energy transition states. The reported energies for all stationary points include free-energy corrections using the same method as in the geometry optimization.

4.2 Reactivity of CH$_3$Cl

The separated fragments of ·CN and CH$_3$Cl are followed by three local minima on the electronic energy surface: Min3, Min4 and Min8; see Figure 4.1. These structures are different in the relative orientation of the reactants. The positive free-energies for these three structures are caused by the loss of entropy and imply that they are not stable species.

Following the three reactant complexes, one can find eight different TSs for the reaction between CH$_3$Cl and ·CN, see Figure 4.2. The lowest barrier of 6.9 kcal/mol belongs to hydrogen abstraction by the carbon of the cyan radical (TS8). Chlorine abstraction by the carbon of the cyano radical has the second lowest barrier of 12.2 kcal/mol (TS3). The corresponding barriers of hydrogen and chlorine abstraction by the nitrogen of cyano radical give higher energies of 15.0 kcal/mol (TS0) and 36.9 kcal/mol (TS1), respectively. Two direct S$_N$2 TSs with chlorine radical as the leaving group, one with carbon as nucleophile (TS17) and the other one with nitrogen (TS23) have barriers of 23.1 and 36.7 kcal/mol. There are also two TSs for hydrogen elimination, one for carbon attack (TS4) at 42.6 kcal/mol. and the other for nitrogen attack of cyano radical (TS2) at 58.7 kcal/mol.
The high energy barriers of direct $S_N2$ pathways compared to hydrogen and chlorine abstraction clearly show that the direct $S_N2$ pathways are not favorable mechanisms. The hydrogen abstraction pathway has the lowest barrier and the difference between the barrier heights for hydrogen and chlorine abstraction is large, 5.3 kcal/mol. Taking the maximum deviation of 2.3 kcal/mol of the G4 method for hydrogen transfer barriers into account, hydrogen abstraction by the carbon of cyano radical is the most probable mechanism for the reaction. This is also in agreement with experimental data, which show a barrier in the entrance channel and a large deuterium kinetic isotope effect (KIE). This implies that hydrogen abstraction is the dominant mechanism also for chlorinated methanes.[53]

This TS forms a hydrogen cyanide (HCN) and a chloromethyl (-CH$_2$Cl) radical (Min20) that either dissociate to separated fragments or lead to formation of CH$_2$ClCHN (Min24). From Min24 there are two pathways, but the high reaction barriers along these paths prevent further reactions. This means that the formation of chlorine radical is not possible through this specific pathway.
Figure 4.2. TS structures of CH₃Cl + ·CN optimized at B3LYP/GTBas3 functional, except TS0, TS3 and TS8 which are optimized at QCISD/GTBas3. Relative free-energy values (in kcal/mol) are obtained at G4 composite method (green for CH₃Cl and red for the corresponding reaction with CH₃Br).

4.3 Effects of Fluorine Substitution

In CH₃Cl, the hydrogen abstraction mechanism is the most viable pathway. However, in fluorinated haloalkanes this channel is blocked. Therefore, a new exploration of the PES was performed for CF₃Cl. The PESs of CH₃Cl and CF₃Cl are significantly different. From the separated fragments seven different local minima on the electronic energy surface have been located. The positive free-energies for these structures indicate that none of them is a stable species, although the energy difference is lower than 1 kcal/mol for the most stable ones.

The reactant complexes are followed by twelve different TSs. However most of the TSs have high barriers and do not represent viable reaction pathways. Rather, only those transition states that can be compared to the corresponding CH₃Cl TSs, are selected, see Figure 4.3. The lowest barrier height, 16.4 kcal/mol, belongs to the chlorine abstraction by the carbon of the cyano radical, (TS1), while the reaction with the nitrogen of the cyano radical (TS0) has significantly higher barrier. The barrier heights for fluorine abstraction in
Figure 4.3. TS structures of CF$_3$Cl + ·CN optimized at B3LYP/GTBas3 functional, except TS1 which is optimized at QCISD/GTBas3. Relative free-energy values (in kcal/mol) are obtained at G4 composite method (Green for CH$_3$Cl and red for the corresponding reaction with CF$_3$Br).

CF$_3$Cl are 52.4 with carbon (TS2) and 90.9 kcal/mol with nitrogen (TS7) of the cyano radical. This is caused by the largely inert nature of the C–F bonds. Even though the hydrogen (fluorine) abstraction channel has been blocked for this system, still direct S$_N$2 mechanisms are not viable pathways with barriers of 78.8 kcal/mol (TS8) and 70.7 kcal/mol (TS10) for carbon and nitrogen attack, respectively. The higher inversion barrier of the trifluoromethyl radical compared to the methyl radical in direct S$_N$2 mechanisms causes significant increase in barrier height of CF$_3$Cl relative to CH$_3$Cl.

The high barriers of fluorine abstraction and the direct S$_N$2 mechanisms clearly show that the chlorine abstraction is preferable. Chlorine abstraction leads to the formation of CICN and ·CF$_3$ that either dissociate to the separated fragments or lead to CF$_3$CClN. Compared to this intermediate, the acetonitrile and chlorine radical product is located 5.7 kcal/mol higher in energy. With an increase of the barrier in the entrance channel from 6.9 kcal/mol in CH$_3$Cl to 16.4 kcal/mol in CF$_3$Cl, the calculations clearly shows that fluorine substitution not only leads to a change in reaction mechanism but also leads to a significant decrease in the reactivity of the system.

4.4 Effects of Bromine Substitution

Considering halogen abstraction as the most viable pathway for CF$_3$Cl leads us to compare the reactivity of chlorine and bromine containing haloalkanes. The same stationary points as for CX$_3$Cl could be located for
the bromine reactions. For CH$_3$Br, hydrogen abstraction by the carbon of the cyano radical (TS8) has a barrier at 4.9 kcal/mol, while this value with the nitrogen (TS0) is significantly higher, 15.0 kcal/mol, see Figure 4.2. Large effects on the barrier heights for bromine abstraction compared to chlorine abstraction have been observed. The barrier height is 5.0 kcal/mol with the cyano carbon (TS3) and 25.2 kcal/mol with the nitrogen (TS1), a decrease of 7.2 and 11.6 kcal/mol compared to the CH$_3$Cl. The similarity of the barrier heights for hydrogen and bromine abstractions makes it difficult to determine the dominant mechanism.

In CF$_3$Br, halogen abstraction is the only viable pathway. The barrier decreases from 16.4 kcal/mol for chlorine to 7.6 kcal/mol for bromine, see Figure 4.3. Bromine abstraction leads to the bromine radical product without having to surmount any high energy obstacle, unless the system dissociates already at the BrCN and ·CF$_3$ intermediate.

The barrier for bromine abstraction is lower than for chlorine abstraction for both, CH$_3$Br and CF$_3$Br. In addition to the change in reaction barriers, for CH$_3$Br there is also a change in the reaction mechanism as halogen abstraction becomes competitive with hydrogen abstraction. Comparing the hydrogen compounds, it can be seen that the difference in reactivity between CH$_3$Br and CH$_3$Cl is relatively small because hydrogen abstraction is among the dominant mechanisms for both. However, the results for fluorine compounds clearly show that the reactivity of bromine compared to chlorine is high because only halogen abstraction is available.

4.5 Analyzing Chemical Trends

Despite the considerable complexity of the complete potential energy surfaces, it is clear that the most feasible reaction pathways belong to hydrogen and halogen abstractions by the carbon of the cyano radical. Most of the observations follow chemical intuition, but the differences in rate constants have not been previously quantified, for example the similar barriers for bromine and hydrogen abstraction. Theoretical chemistry also provides a tool to rationalize the relative rates of different reactions. The direct S$_{N}$2 reaction is disfavored because the cyano radical, due to the hole in the low-lying σ orbital, is a very poor nucleophile. The higher reactivity of the cyano carbon compared to the cyano nitrogen can be attributed to the predominant carbon character of the frontier orbital, and that nitrogen attack products, e.g., hydrogen isocyanide, are less stable than those formed after carbon attack, e.g., hydrogen cyanide.

The effects of substitutions on the rates can be explained using terms from valence bond theory; the energy gap in the reactant, related to the bond dissociation energy, the reaction energy, and the resonance energy in the TS.[54, 55] Fluorine substitution leads to significantly lower reactivity, primarily because the hydrogen abstraction routes are blocked, but also because the rate constants...
for halogen abstraction increase significantly. Part of this increase can be attributed to the increase in the carbon-halogen bond strength by 4–6 kcal/mol, while the changes in reaction energies are smaller (0–2 kcal/mol). Fluorination also leads to a lower resonance energy in the TS. In the fluorinated system, the fluorine 2p orbitals contribute strongly to the frontier orbital. These contributions decrease the electron donor capability of the system. At the same time, the halogen contribution decreases, which decreases the overlap with the CN during the halogen abstraction reaction, and therefore the resonance energy. The results highlight the potential of this approach to analyze and rationalize complex chemical reactions and motivate future studies of other radical species.
5. Nucleophilic Substitution at Phosphorus Centers

"If quantum mechanics hasn’t profoundly shocked you, you haven’t understood it yet.”

Niels Bohr

After exploring the PES, one can describe the dynamics of a reaction in order to get a complete and highly accurate description of its reactivity. As an example of this approach, the seemingly simple symmetric reaction between Cl⁻ and PH₂Cl has been studied. This reaction is a prototype for the SN₂ reactions at phosphorus centers (SN2@P), which play a key role in organic and biological processes. To understand in detail how the shape of the PES affects the rate constant, the dynamical effects on the reaction rate are outlined by computing the quantum reaction probability for both one- and two-dimensional PESs.

5.1 Generating the Potential Energy Surface

In this section we discuss our calculations of the PES of the Cl⁻ + PH₂Cl → ClPH₂ + Cl⁻ reaction in detail. This reaction is proposed to have a transition complex well,[6] with symmetric P–Cl distances. This system was modeled, using reduced dimensionality modeling, employing only the most important degrees of freedom. The main important advantage of this approach is that the results can be improved by increasing the dimensionality of the model, since the error stems from the low dimensionality of the modeling.

The Møller-Plesset second order perturbation level of theory (MP2) was employed for the geometry optimization using the 6-31++G(d,p) basis set. The well depth of the discovered TC is 21.6 kcal/mol. The P–Cl distances are 2.42 Å and the angle Cl – P – Cl is 168.7 degrees, i.e., the reaction is not collinear.

The PES was probed using P–Cl distances from 0.1 Å to 9.0 Å with a step size of 0.05 Å, see Figure 5.1. The Cl – P – Cl angle was kept fixed at 168.7 degrees in all calculations. The sum of the energy of the two non-interacting fragments, Cl⁻ + PH₂Cl, was used as a reference energy.
Figure 5.1. The two-dimensional potential energy surface using symmetric coordinates \( q_1 = \frac{1}{2} (R_1 + R_2) \) and \( q_2 = R_1 - R_2 \) where \( R_1 \) and \( R_2 \) are the two Cl–P bond distances.

To test the sensitivity of the calculated PES with regard to the choice of electronic structure method, the energy of the TC was compared to the G4 composite method. The G4 energy value of 24.9 kcal/mol shows that MP2/6-31++G(d,p) underestimates the well depth by 3.3 kcal/mol. Also the basis set convergence at the MP2 level was benchmarked by using basis sets from double- to quadruple-\( \zeta \). Increasing the size of the basis set increases the depth of the well. The MP2 energy is converged at triple-\( \zeta \) basis set level. However, this level overestimates the well depth by 2.4 kcal/mol compared to G4 method.

Applying a more accurate level of theory would improve the accuracy of the well depth. However, as will be shown later, a deviation in the well depth will not significantly change the quantum dynamics calculations for this system. Therefore, the MP2/6-31++G(d,p) level of theory is sufficient to describe the reaction dynamics and hence the rate constant of this system.
5.2 Dynamics on the One-dimensional PES

The one-dimensional potential energy profile was constructed from the minimum energy path from reactants to products. The deep transition complex well can be described to first order by an inverted Eckart potential:

$$ V = \frac{-V_0}{\cosh(q/\alpha)} $$

(5.1)

where $V_0$ is the depth, $\alpha$ the width of the potential and $q$ the reaction coordinate. The MP2 result of the minimum energy path shows that even at very long distances, e.g., 9.0 Å, the energy is lower than the separated fragments. This is caused by the electrostatic interaction between the Cl anion and the PH$_2$Cl dipole. To solve this, and have a better fit to the computed PES, the inverted potential was fitted according to the equation, see Figure 5.2:

$$ V = \begin{cases} 
-\frac{V_0}{\cosh^2(q/\alpha)}, & -q_c < q < q_c \\
\sum_k \frac{c_k}{|q|^k}, & \text{otherwise},
\end{cases} $$

(5.2)

giving $V_0 = 20.81$ kcal/mol, $\alpha = 2.275$ Å and $q_c = 2.51$ Å.

Numerical calculations of the transmission probability, $T(E)$, using the potential in Equation (5.2) yield a similar result to the analytical solution of the Eckart potential (5.1). Therefore the analytical solution of the transmission probability, Equation (5.3), can be used to rationalize the effects of the changes in well depth. The equation is;

$$ T(E) = \frac{\sinh^2(k\alpha/\hbar)}{\sinh^2(k\alpha/\hbar) + \cos^2(\pi z)}, $$

(5.3)

where $k = \sqrt{2\mu E}$, $E$ is the collision energy and $z = \frac{1}{2} \sqrt{8\mu V_0 \alpha^2 / \hbar^2 \pi^2 + 1}$. Now the question is whether the accuracy of the computed well depth using MP2 affects the transmission probability for this model. The answer is that the well depth enters only in the $\cos^2(\pi z)$ term of the transmission probability, Equation (5.1), where $\cos^2(\pi z)$ is a small term compared to $\sinh^2(k\alpha/\hbar)$ for all relevant energies. Therefore, the transmission probability is essentially unity for all energies independent of the well depth.

These calculations thus give an essentially exact description of the one-dimensional problem. The next step to improve the modeling of the reaction is to include at least one more dimension in the reaction dynamics. This will be discussed in the next section.
5.3 Dynamics on the Two-dimensional PES

A two-dimensional potential energy surface was constructed by scanning the P–Cl distances, as described in section 4.1. An analytical PES was constructed by fitting the MP2 energy values to the analytical form of:

\[
V(R_1, R_2) = V_0 + \sum_{k,l=1}^{4} c_{kl} V_1^k V_2^l
\]

\[
V_i(R_i) = 1 - e^{-\beta(R_i - R_e)}, \quad i = 1, 2
\]

in which \( R_e = 2.07 \text{ Å} \) and \( \beta = 1.70 \text{ Å}^{-1} \). This equation gives the correct asymptotic limit for large P–Cl distances. In order to model the reaction on the two-dimensional PES and perform the numerical calculations, an evenly spaced grid in the \( R_i \) coordinates was created for the system and sincDVR was used for the kinetic energy operator. The reaction probability, Equation (3.37), is completely different from the transmission probability of the one-dimensional model, with a quite involved resonance structure. As is shown in the Figure 5.3, the reaction probability increases around 2 kcal/mol and reaches a local maximum at 5 kcal/mol. The reaction probability is also very

Figure 5.2. The computed minimum energy path (red line) compared to an inverted Eckart potential (black line) and the combination of Eckart and polynomial potentials (blue line).
small, between 8 and 12 kcal/mol. This is probably due to elastic scattering. Above 15 kcal/mol the probability increases steadily, although the complicated resonance structure remains. The shape of $N(E)$ implies that there might be incoming wave packets that stay for a very long time at the transition complex geometry before going to products or back to the reactant geometry.

To systematically peruse the reaction probabilities, we have also computed the state-to-state reaction probabilities. The first vibrationally excited reactant state also gives considerable contributions to the vibrational ground state of the products, although the reaction probabilities ($P_{1,0}$) are consistently lower than for the ground state to ground state reaction ($P_{0,0}$). Already the second vibrationally excited reactant state shows very low probability of reaching the ground state of the product, and higher vibrationally excited states should have even lower contributions to the product ground state.

5.4 Comparison of the Dimensionality

In Figure 5.4 we compared the rate constant from one- and two-dimensional models, see Equation (3.36), with respect to $2\pi\hbar Q_r(T)k(T)$ where $Q_r$ is the
Figure 5.4. Arrhenius plot of the thermal rate constant $k(T)$ times the partition function $2\pi\hbar Q_r(T)$ as a function of the inverse temperature $(1/T)$. The sensitivity to the accuracy of the computed PES is illustrated by comparing the result with rate constants computed with a potential depth that is changed $\pm 10\%$. Included is also a comparison with the one-dimensional model, i.e., with $N(E) = 1$.

The result clearly shows that the difference between one- and two-dimensional model is almost two orders of magnitude at room temperature, black and blue solid lines, respectively. The higher probability (black solid line) is for the one-dimensional model, thus the complexity of the resonance structures in the two-dimensional model leads to a lower reaction probability at the same temperature.

On the other hand, a change of the depth of the well by 10%, which is the same range as the deviation between the MP2 and the benchmark G4 result, affects the rate constant by only a factor of 2. This is similar to the one-dimensional rate constant which is basically independent of the depth of the well. Thus, our results indicate that increasing the dimensionality of the modeling is more important than increasing the accuracy of the used level of theory, see Figure 5.4. The situation would be different for reactions with energy barriers where a change in barrier height of $\pm 2$ kcal/mol would affect the rate by a factor of 50 according to the transition state theory, Equation (2.2).
An extension of this two-dimensional model would be to further increase the dimensionality in the quantum dynamics simulation. For this system there are seven additional degrees of freedom, and the question is whether including any of them would have a critical effect on the calculated reaction rates. The most obvious change of the dimensionality in this specific system is to include the angle of \( \text{Cl} \rightarrow \hat{P} \rightarrow \text{Cl} \). However, the angle of acceptance of phosphorus is large and the energy is rather insensitive to changes in the angle. The expected effect is therefore less significant than the excitations of the \( P \rightarrow \text{Cl} \) stretch that are included in the two-dimensional model.
6. Thermal Dissociation and Chemiluminescence Mechanisms of 1,2-Dioxetane

“She come real stars to fill the upper skies,  
And here on earth come emulating flies, 
That though they never equal stars in size,  
(And they were never really stars at heart)  
Achieve at times a very star-like start. 
Only, of course, they can’t sustain the part.”  
Robert Frost

So far, we have considered multiple pathways on a ground state potential energy surface. In the next part of the thesis, various feasible pathways in multiple surfaces have been investigated. A very fascinating phenomenon is chemiluminescence, the phenomenon in which a chemical reaction that initially proceeds on a ground state generates a light-emitting product. These processes are more complicated to study than the ground state reactions, since more PESs are taken into account. A complicated ground- and excited-state decomposition mechanism of another simple system, 1,2-dioxetane, has been studied. This four-membered ring peroxy compound has been proved to play a key role in chemi- and bioluminescence processes.

As we mentioned in Chapter 2, chemiluminescence is a chemical reaction which generates an emissive product. The same phenomenon happening in living organisms is referred to as bioluminescence. Nature provides us with lots of examples of such chemical processes of which the firefly beetle is the most famed. It has been shown that the bioluminescence involves a substrate, luciferin, and an enzyme named luciferase which catalyzes the reaction. A 1,2-dioxetane moiety is the product of luciferin’s oxidation. Understanding the thermal decomposition of isolated 1,2-dioxetane, as the simplest example of chemi- and bioluminescence, at the molecular level is the key to a detailed description of the chemistry of such phenomena.

6.1 Suggested Mechanisms and Channels

According to more than 20 years of significant theoretical and experimental efforts, three different mechanisms for the decomposition of 1,2-dioxetane
have been proposed; the concerted, merged and biradical mechanisms, see Figure 6.1. The concerted mechanism is a single-step process in which the O–O’ and C–C’ bonds dissociate simultaneously. The merged mechanism indicates that while the O–O’ rupture is not fully completed, the C–C’ breakage comes into action. Finally, the two-step biradical mechanism implies that the C–C’ cleavage occurs after the complete O–O’ bond breaking.

It has been shown that three channels compete in the decomposition of 1,2-dioxetane to two formaldehyde fragments. From the two formaldehyde fragments, one fragment is generated in the excited state, from which the system emits light and returns to the ground state. Depending on the feasibility of singlet and triplet paths, fluorescence and phosphorescence emissions can therefore be produced, respectively. The first decomposition channel is thermal decomposition in which the molecule is thermally dissociated into two formaldehyde products without radiation emission. The other decomposition channel is the dissociation along the lowest-lying triplet manifold which causes phosphorescence emission. Finally, the dissociation along the lowest-lying singlet excited state, which leads the system to fluorescence emission, see Figure 6.1.

Although a series of studies gives support to the merged mechanism on the basis of highly efficient chemiexcitation, and argue that a biradical mechanism would result in formation of only ground state products, there is still no strong proof in favor of either the merged or the biradical mechanism.[8, 56] Moreover, Adam and Baader reported the same activation energy of thermal dissociation and chemiluminescence. These authors illustrated that triplet generation is more favorable than the singlet by a factor of 1000.[8] In this chapter we rationalize most of the past decade’s significant studies. Also, we clarify the large triplet/singlet ratio of chemiluminescence emission.
6.2 Generating the Potential Energy Surface

In this section we discuss our calculation of the PESs of the decomposition of 1,2-dioxetane giving rise to two formaldehyde fragments. This reaction was previously proposed by De Vico et al., to have several stationary points including two TSs, the TS involving O−O’ rupture (TS$_{S0}$) and the TS involving C−C’ cleavage.[57] In the present study, the PESs were also modeled using reduced dimensionality modeling, employing only the most important degrees of freedom, C−C’ and O−O’.

6.2.1 One-dimensional Modeling of the PES

The structures which are relevant for the mechanism of thermally activated light emission of the 1,2-dioxetane molecule are as follows: the starting geometry, Reac; the TS on the ground state related to the O−O bond cleavage, TS$_{S0}$; the singlet and triplet biradical minima with O−C−C’−O’ dihedral angle of 70°, Min$_{S1}(70)$ and Min$_{T1}(70)$; and 180°, Min$_{S1}(180)$ and Min$_{T1}(180)$; the singlet and triplet TSs involving C−C’ bond breaking with dihedral angle of 70°, TS$_{S1}(70)$ and TS$_{T1}(70)$; and 180°, TS$_{S1}(180)$ and TS$_{T1}(180)$; and finally the products on the excited singlet and excited triplet states, Prod$_{S1}$ and Prod$_{T1}$, respectively.

Regarding the active space selection in CASPT2 calculations, the most relevant orbitals in this molecule and the chemiluminescence process were used, this is 12 electrons distributed in 10 orbitals. These correspond to C−C’, C−O, C’−O’ O−O’ σ bonding and σ* antibonding orbitals, as well as two oxygen lone-pair orbitals.

First of all, the CASSCF and CASPT2 methods in conjunction with the atomic natural orbital basis set (ANO-RCC), using a triple-ζ contraction, were employed for geometry optimizations of the stationary points. Additional CASPT2 energy computations in conjunction with quadruple-ζ basis set (ANO-RCC-VQZP) were also performed to test the accuracy of our method. Energies of the four singlet (S$_0$, S$_1$, S$_2$ and S$_3$) and four triplet (T$_1$, T$_2$, T$_3$ and T$_4$) lowest-lying states were computed. Although the CASSCF method itself was accurate enough for the geometry optimization of the 1,2-dioxetane, energy values are dramatically affected by dynamical correlation which is included in the CASPT2 approach. The multistate (MS) approach of the CASPT2 was also used throughout to maintain the consistency with Ref.[57]. The comparison of the MS and state specific (SS) CASPT2 clearly shows that the MS approach lowers the energies around 2-3 kcal/mol in all the cases.

Further improvements to the energetics come from the zero-point vibrational energy (ZPVE) and Gibbs free energy corrections that were calculated numerically at the CASSCF/ANO-RCC-VTZP level. The findings obtained by including the ZPVE clearly illustrate that each bond breakage implies a de-
crease of around 2 kcal/mol of the corresponding TSs. Therefore the inclusion of ZPVE corrections stabilizes TS$_{S_{0}}$, TS$_{S_{1}/T_{1},70}$ and TS$_{S_{1}/T_{1},180}$ by 1.8, 4.8 and 4.5 kcal/mol, respectively, with respect to the reactant. Taking into account the Gibbs free energy corrections; bond dissociation changes the entropy, stabilizes the open structures and causes an energy decrease. The stabilizations of the TS$_{S_{0}}$, TS$_{S_{1}/T_{1},70}$ and TS$_{S_{1}/T_{1},180}$ are 2.1, 5.9 and 5.5 kcal/mol at 300 K, respectively. Figure 7.2 shows the relative energies of the stationary points computed at different levels of theory.

The spin-orbit coupling (SOC) terms between singlet and triplet states were also computed at the CASPT2/ANO-RCC-VQZP level. A strong SOC of 49 cm$^{-1}$ for the biradical structures (degeneracy region) was computed for the chemiluminescence mechanism of 1,2-dioxetane.

These findings demonstrate that at 300 K the activation energies of the decomposition of 1,2-dioxetane are 23.0, 23.9 and 29.2 kcal/mol for the O–O’ rupture on the $S_{0}$ surface, the C–C’ cleavage on the $T_{1}$ manifold and finally C–C’ cleavage on the $S_{1}$ manifold, respectively. Therefore, the eligible total energy to dissociate the O–O’ bond seems to be enough to access TS$_{T_{1}}$, which is basically in good agreement with the experimental activation energy (22.7 ± 0.8 kcal/mol), while the C–C’ dissociation on the $S_{1}$ state needs a significant amount of extra energy with respect to the level of TS$_{S_{0}}$. The fact that the triplet TSs (TS$_{T_{1}(70)}$ and TS$_{T_{1}(180)}$) are close in energy to TS$_{S_{0}}$ is consistent with the observed ratio of triplet/singlet formation.

6.2.2 Two-dimensional Modeling of the PES

In the next step, in order to verify the proposed mechanisms for the chemiluminescence of 1,2-dioxetane, a reduced two-dimensional PES was probed at MS-CASPT2/CASSCF(12in10)/ANO-RCC-VTZP by means of the constrained optimization technique, using C–C’ and O–O’ distances in the range of 1.42–2.02 and 1.48–3.08 Å, respectively, with a step size of 0.1 Å. The other considered possibility was to use C–C’ bond and O–C–C’–O’ dihedral angle where the range of values were 1.42–2.02 Å with step size of 0.1 Å for C–C’ and 0°–180° with different step sizes for O–C–C’–O’. However, the selection of C–C’ bond and O–C–C’–O’ dihedral angle as constraints forced the system to points on the PES that are chemically irrelevant and the structure does not twist properly, as it was already mentioned in Chapter 3. Therefore, in doing the constrained optimization, one must be aware of such behavior and compare with the MEPs paths.

The mapped PES using O–O’ and C–C’ bonds explicitly shows that the concerted mechanism can be discarded because it implies larger energy barriers and there is no state degeneracy in the C–C’ axis. The results indicate that the most feasible pathway to the excited formaldehyde is the formation of the biradical structure which must surmount a second barrier, on the triplet
manifold, that has more or less the same energy barrier as the first TS. Hence, the idea of a merged mechanism can also be discarded.

### 6.3 *Ab Initio* Molecular Dynamics (AIMD)

Since a quantum dynamical simulation of such reaction (including excited states) is in practice very difficult, *ab initio* molecular dynamics (on-the-fly) simulations were performed. Meanwhile, the statistic behavior of canonical ensemble (NVT) at which the temperature is constant was generated throughout, because most of the chemical experiments are accomplished at constant temperature.

A set of 300 trajectories at a constant temperature of 300 K on the ground state (S₀) starting from the TSₘ₀ without considering the transfer of population to the other states was run using the CASSCF(6in6)/ANO-RCC-VDZP approach in order to simulate the dynamical behavior in the so-called entropic trapping volume of the phase space in which the molecule splits the population among the lowest four singlet and four triplet states. The MS-CASPT2 energies of the lowest-lying states (S₀, S₁, S₂, S₃, T₁, T₂, T₃ and T₄) were also computed at each integration step.

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**Figure 6.2.** Relative energies of the stationary points of 1,2-dioxetane.
The C–C’ bond dissociation occurs in all dynamics simulations within the limit time of 1 ps. Also, a torsion of the O–C–C’–O’ dihedral angle was shown in the biradical region in which the lowest four singlet and triplet states are degenerated. This degeneracy disappears as soon as the C–C’ bond breaks. The half-life time obtained from our simulations is 613 fs which is quite a long time and allows the system crossings and recrossings among the four singlet and four triplet degenerate states.

These findings confirm the following step-wise mechanism for 1,2-dioxetane; first of all, the O–O’ bond is dissociated and the molecule enters into a region of biradical character, in which four singlet and triplet states are degenerated. The half-life time spent in this region is 613 fs. The spin-forbidden triplet population is also largely probable in the biradical region, according to the SOC calculations. To produce the chemiluminescence product, a second barrier corresponding to C–C’ rupture has to be surmounted in either the first singlet or triplet excited states. The activation energy of the triplet state is not only lower than the singlet one, but also degenerated with the first TS on the ground state related to the O–O’ rupture. These results are in good agreement with the experiments.
7. Chemiluminescence of the Dewar Dioxetane

“The day science begins to study non-physical phenomena, it will make more progress in one decade than in all the previous centuries of its existence.”

Nikola Tesla

After understanding the thermal decomposition of 1,2-dioxetane in detail, one can consider more complicated reaction mechanisms involving peroxide compounds, such as the 1,2-dioxetane moiety attached to terminal carbon atoms of 1,3-butadiene (hereafter, Dewar dioxetane). This molecule was first presented by McCapra in the study of the thermal decomposition of Dewar benzene.[9] Light emission was observed in this process and it was shown to depend on the presence of oxygen. Thus, the Dewar dioxetane was suggested to be formed in this process and to be responsible of the luminescence.

According to the study of 1,2-dioxetane we have the following scenario; the system dissociates through a two-step reaction mechanism of biradical character. First, the O–O’ bond dissociates and the molecule enters a biradical region in which all the lowest-lying singlet and triplet states are degenerated. After that, the C–C’ rupture comes into action. The TS corresponding to C–C’ breakage on the triplet manifold has more or less the same amount of energy as the first TS which corresponds to the O–O’ bond breaking, while the TS on the singlet excited state surface is about 5 kcal/mol higher in energy. Therefore, from the two possible excited-state dissociation channels, dissociation on the T1 and the S1 manifolds, dissociation on the T1 excited state is dominant due to the lower energy barrier compared to the singlet excited state.[58] In this chapter we discuss our understanding of the thermal decomposition of Dewar dioxetane into 2,4-hexadienial using the mentioned 1,2-dioxetane’s scenario.

7.1 Generating the PES and Stationary Points

Following the study of 1,2-dioxetane, we obtained a similar process of a two-step biradical mechanism: an initial O-O’ bond breaking and subsequent C–C’ cleavage. Also, the three different channels: thermal dissociation, dissociation on the T1 manifold and dissociation on the S1 manifold are followed
Figure 7.1. Optimized geometries of the stationary points for the chemiluminescence mechanism of Dewar dioxetane.

by the study of 1,2-dioxetane. Several relevant structures characterize the mechanism between the reactant and products: the TS related to the O₁−O’₁ cleavage on the singlet ground state manifold (TS_{S₀, O₁−O’₁}) in which the four singlet and four triplet excited states become degenerate with S₀, the singlet and triplet biradical minima (Min_{S₁} and Min_{T₁}), the triplet TS related to the C₂−C’₂ bond rupture (TS_{T₁}), and the corresponding TS of C₂−C’₂ cleavage on the singlet excited state (TS_{S₁}). The TS related to the C₂−C’₂ cleavage on the ground-state manifold is quite shallow and therefore difficult to compute. Since the aim of the present study is to comprehend the excited state dissociation (chemiluminescence) of Dewar dioxetane, finding the second TS related to C₂−C’₂ on the ground state has been excluded. Regarding the product of the reaction, the 2,4-hexadienedial is obtained. This molecule has two conjugated C−C double bonds, C₃−C₄ and C’₃−C’₄, which provide the system with Z/E isomerism at each double bond. Additionally, these bonds are weaker and longer in the excited state than in the ground state. Thus, several conformations might be possible. In particular, six different isomers and conformers of the product in the singlet (¹C₆H₆O₂) and triplet (³C₆H₆O₂) states are found, see Figure 7.1.

The CASSCF method in conjunction with the atomic natural orbital, double-ζ, basis set (ANO-RCC-VDZP) was employed for geometry optimization of the stationary points. Then, additional CASPT2 energy calculations were performed using the triple-ζ (ANO-RCC-VTZP) basis set. Energies of
the lowest-lying four singlet (S₀, S₁, S₂ and S₃) and four triplet (T₁, T₂, T₃ and T₄) states were computed. A comparison of the state specific (SS) and MS-CASPT2 was performed to be sure whether the results of these approaches are consistent and our CASPT2 calculations are accurate enough to describe the PES.

The results reveal some differences of the geometrical parameters for the stationary points in the chemiluminescence mechanism of Dewar dioxetane compared to 1,2-dioxetane. The differences are due to conjugation and steric hindrance. For instance, the optimized dihedral angle of biradical minima (on first singlet or triplet excited state surface) and their corresponding TSs are 45°, in contrast to 1,2-dioxetane in which it was almost 70 degrees. Nevertheless, the calculations imply that at 300 K the activation energies of the decomposition of Dewar dioxetane are 24.1, 24.6 and 27.4 kcal/mol for the O–O’ rupture on the S₀ surface, the C–C’ cleavage on the T₁ manifold and finally C–C’ cleavage on the S₁ manifold, respectively (with inclusion of the ZPVE and Gibbs free energy corrections). Therefore, the total energy to dissociate the C–C’ bond seems to be enough to access TSₜ₁, while the C–C’ dissociation on the S₁ state needs a 3 kcal/mol of extra energy with respect to the level of the TSₜ₀.

Figure 7.2. Chemiluminescence mechanism and MEPs of Dewar dioxetane.
7.2 Chemiluminescence Mechanism

McCapra reported a light emission from the heating of Dewar benzene, although the nature of the light was not specified in that study.[9] According to the CASPT2/ANO-RCC-VTZP//CASSCF/ANO-RCC-VDZP findings, an activation energy of 25.2 kcal/mol related to the O–O' bond breaking is required to reach the biradical intermediate in which an energy degeneracy exists between the lowest-lying four singlet and triplet states of the molecule. In the mentioned region the population can be transferred to the singlet excited state through a non-adiabatic process or to the triplet excited state, taking into account the strong spin-orbit coupling (20 cm\(^{-1}\)). A second energy barrier corresponding to the C–C' breakage is needed to dissociate the molecule in the excited state surface, with a slightly lower activation energy on the triplet manifold. According to the computed Gibbs free energies, the most probable dissociation mechanism on the excited state at low temperature corresponds to the bond breaking via the triplet surface. However, a radiationless decay from the triplet structure of E,Z-2,4-hexadienedial\(_T\) isomer to the ground state speaks contrary to McCapra’s light observation. The radiationless decay is predicted for this evolution via a singlet-triplet crossing (STC) crossing of biradical character of the E,Z-2,4-hexadienedial\(_T\).

Although, the activation energy of the S\(_1\) manifold is a bit higher than T\(_1\), the emission of light observed by McCapra could be assigned to the singlet channel, since it does not require the singlet to triplet population transfer in the biradical region prior to the C–C' transition state and would therefore be favored. In the case where the difference between activation energies of S\(_1\) and T\(_1\) is greater than our computed one, a non-emissive channel is highly expected and no light would be observed. In contrast to 1,2-dioxetane, where both singlet and triplet channels give rise to emissive species, in the decomposition of Dewar dioxetane, all emission is predicted to come from the singlet.
8. Conclusion

“In the race for quality, there is no finish line.”

David T. Kearns

The complete picture of a chemical reaction can be obtained by a systematic theoretical study. Theoretical chemistry is a unique tool to describe chemical reactivity at the molecular level. To exemplify how this tool can be applied to understand ground and excited state reactivities, four different chemical reactions have been modeled. To begin with, all feasible pathways to break down halomethanes through ground state reactions with cyano radical have been efficiently explored using the AFIR method. Accurate calculations on reaction barriers make it possible to distinguish between hydrogen and halogen abstraction, direct S_N2 reaction and hydrogen elimination. The relative reactivity trends can be rationalized taking into account reaction energy, bond strength and resonance energy in the TS. This approach can be used for a large number of bimolecular reactions.

After finding the most feasible mechanism, an accurate calculation of the rate constant can be done using quantum dynamics. Since performing full-dimensional quantum dynamics simulations is in practice very difficult, a reduced-dimensional surface can be calculated using the most relevant degrees of freedom. Quantum dynamics simulations on the reduced-dimensional PES of the Cl^- + PH2Cl system revealed complex resonance structures in the reaction probability, which had a large effect on the reaction rate. The results clearly indicate that for barrierless reactions, increasing the number of dimensions is more important than applying a more accurate level of theory. Together, these two steps, PES exploration and quantum dynamics, give an efficient description about the details of a ground state chemical reaction.

In the next part of the thesis, various feasible pathways on multiple surfaces have been investigated. As an example of these excited state reactions, the thermal decomposition of a four-membered ring peroxide compound, called 1,2-dioxetane, has been studied as the simplest model of chemi- and bioluminescence. The results imply a two-step biradical mechanism and rationalize the high ratio of triplet to singlet dissociation products that was experimentally observed. Finally, the study on thermal decomposition of Dewar dioxetane allows us to understand the effect of conjugated double bonds adjacent to the dioxetane moiety in the chemiluminescence mechanism of dioxetane. These
accurate calculations on the simplest model give rise to a level of understand-
ing of excited state reactivity that cannot be obtained from any other method.

For excited state systems, an automatic exploration of the reaction pathways would be even more useful than it is for ground state reactions. For these sys-
tems, it is significant to not only find the minima and transition states on mul-
tiple PESs, but also singlet-triplet crossing points and conical intersections. Therefore, an important step forward would be to combine AFIR-type algo-
rithms with the most efficient multiconfigurational quantum chemistry pack-
ages. Moreover, performing dynamics simulations is highly required for es-
timating the reaction rates and detailed product distributions. Compared to
ground state, the short time scale of excited state processes makes them much
easier to follow in real time simulation.
9. Summary in Swedish

Teoretiska studier av reaktioner i grund och exciterade tillstånd

En nyckel till att förstå världen är att förstå varför och hur snabbt kemiska reaktioner sker. Några exempel är de atmosfäriska reaktioner som påverkar luftens kvalitet, ozonlagret, och den globala uppvärmningen. Andra exempel är i biologiska system som utgör grunden för allt liv. Den här avhandlingen visar hur avancerade teoretiska modeller kan användas för att få unik kunskap om dessa kemiska reaktioner och de faktorer som bestämmer hur snabbt de sker.


De kemiska reaktionerna blir än mer komplicerade om de sker på mer än en potentialyta. Sådana reaktioner är vanliga inom fotokemin där absorptionen av...
ljus tar systemet från grundtillståndet till ett exciterat tillstånd där reaktiviteten kan vara mycket högre. Än mer fascinerande processer är kemiska reaktioner som i sig kan avge ljus utan att energi tillförs, så kallad luminiscens. Det sker i vissa kemiska reaktioner, kemiluminiscens, men också i olika biologiska system, då kallad bioluminiscens. För att förstå såpass avancerade processer behövs det utvecklas och tillämpas noggranna teoretiska modeller.

Ett första viktigt steg för att modellera en reaktion är att jämföra olika mekanismer. Ett exempel är reaktionen mellan halometaner och cyanoradikaler:

$$CX_3Y + CN\cdot \rightarrow CX_3CN + Y\cdot,$$  \hspace{1cm} (9.1)

där $X = F, H$ och $Y = Cl, Br$; har studerats. Stabiliteten hos fluorerade kolväten som CF$_3$Cl gör att de når ända upp till stratosfären där de ingår i reaktioner som bryter ner ozonlagret. Stabiliteten beror på att reagerar mycket långsamt med många vanliga atmosfäriska radikaler. Reaktiviteten skiljer sig dock mycket mellan olika radikaler. Cyanoradikalen ($\cdot CN$) är en viktig atmosfärisk radikal och bildas från HCN vid förbränning av biomassa. För att kunna studera alla möjliga reaktionsvägar har en ny metod använts, artificial force induced reaction, AFIR. Med hjälp av den metoden har upp till åtta olika reaktioner med sammanlagt 36 olika övergångstillstånd hittats och hastighetskonstanterna för de reaktionerna har uppskattats med relativt god noggrannhet.

För en mer exakt beräkning av hastighetskonstanter behövs en kvantdynamisk behandling av kärnorna. Effekten av en sådan behandling har beräknats för en nukleofil substitutionsreaktion ($S_N^2$) på ett fosforcenter. Den reaktionen spelar en nyckelroll i biologiska processer såsom DNA replikering och utgör ett möjligt mål för medicinska behandlingar. Modellreaktionen:

$$PH_2Cl + Cl^- \rightarrow ClPH_2 + Cl^-,$$  \hspace{1cm} (9.2)

är den reaktion i sin klass som har minst antal atomer. Reaktionen fortskrider genom bildandet av ett komplex istället för ett övergångstillstånd. Det ger upphov till långlivade tillstånd, vilka försvårar beskrivningen av systemets dynamik. Istället för att studera alla dimensioner av potentialytan så har kvantdynamiksimuleringen utförts på en och tvådimensionella potentialytor som inkluderar de bindingar som skapas och bryts under reaktionen. I de tvådimensionella simuleringarna så framgår tydligt effekten av resonansstrukturen och hastighetskonstanterna minskar hundrafalt jämfört med en klassisk beskrivning. Studien visar hur en exakt beskrivning av den molekylära kvantdynamiken kan ge betydelsefull förståelse för dynamiken i dessa elementära kemiska processer.

Komplexiteten ökar ytterligare när reaktionen sker på mer än en potentialyt. Ett fascinerande fenomen som sker på åtminstone två potentialytor, både grund och exciterade tillstånd, är bioluminiscens hos eldsflugor, lymmaskar och maneter. Reaktionen har även stort medicinskt intresse eftersom det ger
möjligheten att se hur ett läkemedel påverkar förhållanden i närheten av en cancertumör. Ett viktigt exemplet på en luminescensreaktion är termisk nedbrytning av 1,2-dioxetan, det förmodligen enklaste exemplet på en sådan reaktion:

\[ C_2H_4O_2 \rightarrow 2CH_2O + hv. \] (9.3)

En detaljerad beskrivning av sönderdelningen av 1,2-dioxetan på molekylnivå är en nyckel till att förstå kemin i större kemi- och bioluminescensreaktioner där 1,2-dioxetan är en gemensam funktionell grupp, från dioxetanon, dioxytandion till reaktionen i eldsflugans enzym luciferas.

För detta system har potentialytorna för grund och exciterade tillstånd karaktäriserats genom att hitta stabila tillstånd, övergångstillstånd samt vägarna mellan dessa tillstånd med lägst energi. Reaktionen börjar med att syresyren bindningen bryts i en tvåstegsmechanism där de två barriärerna motsvarar klyvning av O–O och C–C bindingarna. Efter det att O–O bindningen klyvs så bildas en biradikal där grund och exciterade tillstånd ligger nära vilket gör det enkelt att byta mellan olika tillstånd. Klyvning av C–C bindningen ger sedan upphov till två formaldehydfragmente där en liten andel produceras i ett exciterat tillstånd som kan återgå till grundtillståndet genom ljusemision. Den återstående delen av formaldehyden genereras utan någon emission av strålning. Reaktionens förlopp styrs bland annat av barriärhöjden för C–C klyvning på de olika potentialytorna. Dessa beräkningar visar hur det går att få en tydlig bild av olika mekanismer och kanaler i nedbrytningen av 1,2-dioxetan.

Den detaljerade bild som fås från den grundläggande luminiscensreaktionen kan nu användas för att tolka och förstå relaterade kemiska processer. Ett sådant exempel är Dewarbensen där ljus observerats efter uppvärmning. Förekomsten av ljus föreslogs vara beroende av syremolekyler och eftersom kemiluminescens sker genom syreklyvande processer, så kan det antas att peroxiden Dewardioxetan bildas som ett mellansteg och är den molekyl som avger ljus:

\[ C_6H_6O_2 \rightarrow C_6H_6O_2 + hv. \] (9.4)

Termisk nedbrytning av Dewar-dioxetan, som är en sammansättning av 1,2-dioxetan och butadien, kan då analyseras med hjälp av tidigare kunskaper från isolerad 1,2-dioxetan. De studierna visar att den stora skillnaden mellan 1,2-dioxetan och Dewardioxetan är att det konjugerade systemet i butadiendelen öppnar en väg tillbaka till grundtillståndet, vilket gör molekylen betydligt mindre effektivt som luminescent system.

Tillsammans visar beräkningarna i denna avhandling hur teoretisk kemi kan användas för att få en unik insikt i kemiska reaktivitet. Genom en effektiv utforskning av potentialytan så går det att bestämma de viktigaste reaktionsmekanismerna och hur snabbt olika reaktioner sker. Det går att förklara hur olika typer av modifiering av molekylerna påverkar hastigheten, eller hur i vissa fall systemet helt styrs om så att nya kanaler tar över.
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L. Wittgenstein

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