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Theoretical Studies of Seemingly Simple Chemical Reactions

by

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“Logic will get you from A to B.  
Imagination will take you everywhere.”

Albert Einstein
To fully understand the details of chemical phenomena encountered in our daily life, requires a systematic theoretical approach. Two different steps in such an approach have been used in this thesis; an efficient exploration of the potential energy surface followed by accurate quantum dynamics with reduced dimensionality. To exemplify how such detailed knowledge can be achieved, two seemingly simple chemical reactions have been modeled. As an example of the first step the potential energy surfaces of the reactions between haloalkanes (CX₃Y) and cyano radicals (CN⁻) have been explored using the artificial force induced reaction algorithm. The large number of feasible pathways for reactions of this type, up to eleven, shows that even seemingly simple reactions can be quite complex. The effects of quantum dynamics have been considered for the Cl⁻ + PH₂Cl reaction. 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. The two examples in this thesis illustrate how a systematic approach can be applied to understand the details of chemical reactions.
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List of Publications

1. Breakdown of Halomethanes by Reactions with Cyano Radicals
   Pooria Farahani, Satoshi Maeda, Joseph S. Francisco and Marcus Lundberg (Manuscript)

2. Ab initio Quantum Mechanical Calculation of the Reaction Probability for the \( Cl^- + PH_2Cl \rightarrow ClPH_2 + Cl^- \) Reaction

Additional Publications not Included in This Thesis

3. Revisiting the Non-Adiabatic Process in 1,2-Dioxetane

4. Hierarchical Approach to Electron Correlation in Multiconfigurational Perturbation Theory

5. 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
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The Author’s Contribution to the Papers in This Thesis

1. From the stationary points computed by the AFIR algorithm, carried out the energy calculations, analyzed and compared the data at different levels of theory.

2. Performed the electronic structure calculations and computed the two-dimensional potential energy surface.
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<td>AFIR</td>
<td>Artificial Force Induced Reaction</td>
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<tr>
<td>CRP</td>
<td>Cumulative Reaction Probability</td>
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<tr>
<td>KIE</td>
<td>Kinetic Isotope Effect</td>
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<tr>
<td>HLC</td>
<td>Higher Level of Correction</td>
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To those unexpected events without whose existence this thesis would have been completed four months earlier;

and

to you who are not here to see this.
Chapter 1

Introduction

The aim of this thesis is to explore how theoretical chemistry can be used to describe and understand chemical phenomena encountered in our daily life. Atmospheric chemistry, which is of importance because of its interaction with living organisms, is one example. Acid rain, ozone depletion and global warming[1] are some important problems in atmospheric chemistry that can be addressed. Another type of phenomena of interest is biological and subsequently medical processes. These chemical reactions can be very complicated. Therefore, having a good theoretical description about the mechanism of the mentioned processes can be very useful.

An approach to systematically investigate and comprehend the details of chemical reactions is required. Theoretical chemistry uses both quantum and classical mechanics to give a good account of chemical observations. The quantum theory is based on both the time-independent and the time-dependent Schrödinger equations. The nuclei are considered to be moving on a potential energy surface (PES) constructed from the solution of the electronic Schrödinger equation, which can be calculated using different electronic structure methods. 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 proton transfer, tunneling, 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. The solutions to these equations, give a level of detail into the chemical processes that cannot be obtained from other methods.

To exemplify how such detailed level of understanding can be accomplished, seemingly simple nucleophilic substitution (SN2) reactions have been investigated. The SN2 reactions are considered as one of the simplest examples of chemical reactions. This one-step reaction mostly occurs with a halide atom, an electronegative stable leaving group (X),
which is attached to an aliphatic sp\(^3\) carbon (C-X). Nucleophilic attack on the halide carbon leads to the transition state (TS). At the same time as the C-Nu bond is formed, the halide atom leaves the system. The proposed TS of such reaction is the direct pentacoordinate transition state as it is shown in Figure 1.1.

In spite of assuming the S\(_N\)2 as a simple reaction, there are some evidences that indicate that the mechanism of such systems can be quite complex. One system that has been extensively studied, both theoretically and experimentally, is F\(^-\) + CH\(_3\)I. For instance, Hase et al.[2] proposed a "roundabout" mechanism including a hydrogen-bonded F\(^-\)...HCH\(_2\)I minimum and a [F...HCH\(_2\)...I]\(^-\) TS. In this reaction, the direct one step mechanism does not exist, instead, a rotation of CH\(_3\) about the massive I atom leads to the S\(_N\)2 product.

In order to simplify the investigation and understanding of the complexity of a chemical process, two systematic approaches have been used in this thesis, an efficient exploration of the potential energy surface followed by accurate quantum dynamics on a reduced-dimensionality PES. As an example of an efficient exploration of the PESs, reactions including a haloalkane and a cyano radical, which are potentially S\(_N\)2 reactions:

\[
CX_3Y + CN^- \rightarrow CX_3CN + Y^-;
\]  

(1.1)

where X = F, H and Y = Cl, Br; have been studied. The cyano radical (.C≡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.

In this project, various feasible pathways for the reaction between CX\(_3\)Y and the cyanide radical have been compared with respect to relative energies of the rate-determining transition states. To be able to explore the large number of different pathways, a special computational algorithm, the artificial force induced reaction (AFIR) has been employed.[3]

Among the eight discovered pathways, two correspond to hydrogen abstraction similar to what was suggested by Hase et al.[2] This illustrates how complex a seemingly simple
S_N2 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 just by the PES.

The next step to the systematic approach is to study the quantum dynamics of the nuclei. The reaction under study, a S_N2 at phosphorus center, plays a key role in organic and biological processes such as the DNA replications,[4, 5] as well as in medical treatments.[6] The dynamics of these types of reactions can be quite complex.[7, 8] The nucleophilic substitution between a halide anion and a halophosphine, is valence isoelectronic with S_N2 at carbon center, although the central electrophilic atom in such cases is tricoordinate. As a prototype of the S_N2 reaction at phosphorus we studied the symmetric substitution reaction:

\[
PH_2Cl + Cl^- \rightarrow ClPH_2 + Cl^-, \tag{1.2}
\]

which is the reaction in its class with the least number of atoms. The reaction proceeds through a transition complex well instead of a transition state barrier.[9] 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.

The articles presented in this thesis deal with the application of computational quantum chemistry and quantum molecular dynamics. The electronic structure calculations are used to study the entire PESs. Also quantum dynamics on important parts of the PES are studied. In the next chapter a brief account is given about the theoretical foundations of the methods used. In chapter 3, the exploration of the PES of the reaction between haloalkanes and cyano radical is discussed, and the reactivity of different haloalkanes with 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 4. Finally, a summary of the complexity of these chemical reactions is given in the last chapter.
Chapter 2

Theory

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 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 potential energy surface is calculated using electronic structure methods, different pathways can be efficiently explored by using an advanced optimization algorithm. The details about the reaction mechanisms can be further explored by the use of molecular dynamics on multi-dimensional potential energy surfaces, giving reaction rates and state-to-state reaction probabilities.

2.1 Born-Oppenheimer Approximation

The Born-Oppenheimer approximation is the most crucial approximation in quantum chemistry and chemical physics. According to the Born-Oppenheimer (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;

\[ H \equiv T_e + V_{ee} + T_N + V_{NN} + V_{eN} \]  

(2.1)

which includes kinetic energy of the nuclei \( (T_N) \), kinetic energy of the electron \( (T_e) \), electron-nuclear attractive Coulomb potential \( (V_{eN}) \), electron-electron repulsion Coulomb potential \( (V_{ee}) \) and nuclear-nuclear repulsion Coulomb potential \( (V_{NN}) \), and the Schrödinger
equation is;

\[ \hat{H}\Psi(r, R) = E\Psi(r, R). \]  \hfill (2.2)

According to the BO approximation one can assume the wave function \( \Psi \) to be separated into a product of electronic and the nuclear parts;

\[ \Psi(r, R) = \psi(r; R)\chi(R) \]  \hfill (2.3)

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 (2.3) will be written as;

\[ (T_e + V_{NN} + V_{eN} + V_{ee})\psi = E_{el}(R)\psi \]  \hfill (2.4)

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 the (2.4) and (2.3) into (2.2), we obtain;

\[ (T_N + E_{el})\psi\chi = E_{tot}\psi\chi. \]  \hfill (2.5)

Since \( T_N\psi\chi = \psi T_N\chi \) according to the BO approximation, \( \psi \) can be integrated out from the both sides of (2.5), giving the nuclear Schrödinger equation;

\[ (T_N + V)\chi = E_{tot}\chi \]  \hfill (2.6)

in which

\[ V = V_{NN} + E_{el} \]  \hfill (2.7)

is the electronic potential energy surface.

### 2.2 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.
2.2.1 Variational Method

A way to determine approximate solution 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 the expectation value of the energy is higher than the exact energy. This method is often specified as in the following equation;

\[ E_{\text{trial}} = \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle} \geq E_0 \]  \hspace{1cm} (2.8)

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

\[ \psi = \sum_n C_n \chi_n \]  \hspace{1cm} (2.9)

Then;

\[ \sum_n (E_n - E_0)|C_n|^2 \geq 0 \]  \hspace{1cm} (2.10)

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 \( E_0 \) of the Hamiltonian of the system. 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.

2.2.2 Basis set

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;

\[ \phi_i = \sum_j C_{i,j} \chi_j \]  \hspace{1cm} (2.11)

where \( M \) is the number of basis function. 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 function, 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 represent the number of basis functions used for each type of atomic orbital, the basis sets are labeled as double, triple, quadruple-zeta ζ 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 are cc-pVXZ in which X=D,T,Q,5,...(D for double, T for triple, etc., ζ). In that notation "cc-p" depicts 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 the diffuse functions are added.

2.3 Electron Wave Function Methods

2.3.1 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 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 the Slater determinant instead of a single product of molecular orbitals.

A spatial orbital, φ(r), is a function of position r of an specific electron, through the probability, |φ|^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 α(ω) and β(ω) spin wave functions, for spin up and spin down, respectively and ω is the spin coordinate. In order to describe both spatial distribution and the spin state of the electron, one requires the spin orbital, φ(r,ω). 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 φ_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:

\[
E_{\text{el}} = E_{\text{HF}} = \sum_k^{\text{occ}} h_{kk} + \frac{1}{2} \sum_{k,j}^{\text{occ}} [J_{kj} - K_{kj}],
\]

(2.12)

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:

\[
f \phi_k = \epsilon_k \phi_k
\]

(2.13)

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 the 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.

\[
E_{\text{corr}} = E_{\text{exact}} - E_{\text{HF}}
\]

(2.14)

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.
2.3.2 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;

\[ \psi = \sum_i c_i D_i \]  

(2.15)

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 with 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.

2.3.3 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.

\[ \psi_{CC} = e^{\hat{T}} \psi_0 \]  

(2.16)

The exponential of \( \hat{T} \) can be written as;

\[ e^{\hat{T}} = 1 + \hat{T} + \frac{1}{2} \hat{T}^2 + \frac{1}{6} \hat{T}^3 + ... = \sum_{k=0}^{\infty} \frac{1}{k!} \hat{T}^k. \]  

(2.17)
In the operator $\hat{T}$:

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + ...$$  \hfill (2.18)

$T_1$ represents single excitation, $T_2$ 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:

$$He^{\hat{T}}\Psi_0 = E_{cc}e^{\hat{T}}\Psi_0.$$  \hfill (2.19)

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 the both 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:

$$\hat{T}_1 = \sum_{a,i} t_{a,i} \hat{E}_{a,i}$$  \hfill (2.20)

$$\hat{T}_2 = \sum_{a,b,i,j} t_{b,j,a,i} \hat{E}_{b,j} \hat{E}_{a,i}$$  \hfill (2.21)

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 $\hat{E}$ annihilates an electron from orbital $a$ and creates an electron in $b$, 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.

### 2.3.4 Time-Independent Perturbation Theory

Perturbation theory consists of mathematical methods which are employed for problems which needs to be treated approximately. Since solving the electronic Schrödinger
equation is too complicated to do exactly, one is to develop the Hamiltonian as a sum of the zeroth-order $H_0$ for which there is an exact solution, and a time-independent perturbation $V$, as;

$$H = H_0 + \lambda V$$

(2.22)

in which $\lambda$ is a parameter that determines the strength of the perturbation. The eigenfunctions of $H_0$ are $\phi_n^0$, and the eigenvalues are $E_n^{(0)}$. In order to develop the full Schrödinger equation, we use the following expansion for the wave function.

$$\psi_n = \phi_n^{(0)} + \lambda \phi_n^{(1)} + \lambda^2 \phi_n^{(2)} + ...$$

(2.23)

Because $\phi_n^{(0)}$ and $\phi_n^{(1)}$ are both eigenfunctions to the $\hat{H}_0$ operator, $\langle \phi_n^{(0)}|\phi_n^{(1)} \rangle = 0$. Thus;

$$E_n^{(1)} = \langle \phi_n^{(0)}|V|\phi_n^{(1)} \rangle.$$

(2.24)

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

$$E_n^{(2)} = \sum_{k \neq n} \frac{\langle \phi_n^{(0)}|V|\phi_k^{(0)} \rangle \langle \phi_k^{(0)}|V|\phi_n^{(0)} \rangle}{E_n^{(0)} - E_k^{(0)}}.$$ 

(2.25)

Up to now theory has been completely general and to get specific electronic structure method, $H_0$ and $V$ have to be defined. In the Møller-Plesset second order perturbation theory (MP2), which is another beyond or post-HF method, $H_0$ is the sum over the Fock operators. Because the $H_0$ counts the average electron-electron interaction ($<V_{ee}>$) twice, the perturbation $V$ has to be the exact $<\hat{V}_{ee}>$ operator minus twice the average $<\hat{V}_{ee}>$ operator.

In second order perturbation theory (MP2), the Equation 2.25 implies that two electrons are excited with regards to the ground state configuration. MP2 accounts for almost 80-90% of the correlation energy and it is the most economical method to include significant amounts of the dynamical correlation. MP2 is fairly inexpensive, since the perturbation only includes two occupied and two virtual MOs.

### 2.4 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 basis of DFT is to determine the ground state electronic energy by using the electron
density $\rho$.[14] 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[15] and Fermi[16], it
was put into firm theoretical ground by the two Hohenberg-Kohn (H-K) theorems[17]
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;

$$E[\rho] = V_{ne}[\rho] + T[\rho] + V_{ee}[\rho]$$  \hspace{1cm} (2.26)

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 intro-
duced a system of non-interacting electrons in molecular orbitals.[18] In this system the
kinetic energy $T_s[\rho]$ can be calculated exactly and it turned out to be a good approxi-
mation to the real kinetic energy $T[\rho]$. Writing Equation 2.26, in terms of contributions
that can be calculated exactly gives the following expression for the functional.

$$E[\rho] = V_{ne}[\rho] + T_s[\rho] + J[\rho] + (T[\rho] - T_s[\rho] + V_{ee}[\rho] - J[\rho])$$  \hspace{1cm} (2.27)

where $J[\rho]$ is the classical Hartree (Coulomb) repulsion of the density. Collecting the
terms in the parenthesis of the Equation 2.27 into a single exchange correlation functional
$E_{XC}[\rho]$ gives;

$$E_{XC}[\rho] = T[\rho] - T_s[\rho] + V_{ee}[\rho] - J[\rho]$$  \hspace{1cm} (2.28)

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)\cite{19} 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 functionals $E_{XC}$ is typically the sum over individual exchange and correlation functionals \textit{e.g.}, BLYP. There are two well-known approaches to design functionals; derivation from theoretical arguments giving \textit{e.g.}, PW91, PBE or derivation from a semi-empirical fit \textit{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.

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

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 the 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 \textit{i.e.}, the hybrid B3LYP and hybrid meta-GGA M06-2X functionals.

**B3LYP**

The most common applied hybrid functional is B3LYP, developed from the GGA functional BLYP.\cite{20, 21, 22} The exchange correlation functional of B3LYP can be written as:\cite{23}

$$E_{XC}^{\text{B3LYP}} = E_{XC}^{\text{LDA}} + \alpha_0(E_X^{HF} - E_X^{\text{LDA}}) + \alpha_X(E_X^{\text{GGA}} - E_X^{\text{LDA}}) + \alpha_C(E_C^{\text{GGA}} - E_C^{\text{LDA}}),$$

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.[24]

2.5 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 has been introduced by Curtiss et al., in 2007.[25] 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.

$$E_{HF/aug-cc-pVnZ} = E_{HF/limit} + B \exp(-\alpha n)$$  \hspace{1cm} (2.31)

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(2df,p), CCSD(T)/6−31G(d) and MP2(full)/G3LargeXP. Next, the four correlation corrections obtained from previous rungs, are combined with the 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.[26] They give the zero-point energies $E(ZPE)$ to gain $E_0$. Finally, the total energy at 0 K is achieved by using the following expression:

$$E_0(G4) = E_c(G4) + E(ZPE)$$  \hspace{1cm} (2.32)
2.6 Accuracy of Different Levels of Theory

In this section we discuss the accuracy and deficiencies of widely used levels of theory. The electron wave function based methods, e.g., QCISD, CCSD and MP2, generally require large basis sets to give converged result due to the electron correlation. MP2 theory accounts for dynamical correlation. However MP2 may produce inaccurate result when the static correlation must be taken to account.

The B3LYP hybrid functional is the main responsible for DFT becoming the most popular tool in theoretical chemistry. In a comparison of 223 heats of formation, the average absolute deviation for the B3LYP functional is 6.1 kcal/mol, while this value for MP2 is 10.6 kcal/mol.[27] For a database of 76 barriers, Zhao et al., reported a mean absolute deviation of 4.55 kcal/mol for B3LYP, and for most reactions the barriers are underestimated. [28]

The M06-2X hybrid meta 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.[27] 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.[28] 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.[29]

2.7 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) exposes the PES. Using computational chemistry calculations a full-dimensional PES can be calculated. Local minima correspond to stable molecules, and the minimum energy pathways connecting minima describe reaction mechanisms. 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, Equation (2.33);

\[ k = \kappa \frac{k_BT}{h} e^{-\frac{\Delta G^\ddagger}{RT}}. \]  

(2.33)

where \( \Delta G^\ddagger \) is the relative free energy of the TS and \( \kappa \) is a unitless constant that takes into account \( e.g. \), tunneling effects and recrossings, but cannot be obtained only from the electronic structure calculations.

In order to pursue all possible pathways, the artificial force induced reaction has been used. AFIR is a code developed by Maeda and Morokuma which automatically and systematically discovers unexpected reaction paths.\[3\] 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.\[30\] 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;

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

(2.34)

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, the Equation (2.34) for a system with multiple degrees of freedom can be written as;

\[ F(Q) = E(Q) + \alpha \frac{\sum_{i \in A} \sum_{j \in B} \left[ \frac{R_i + R_j}{r_{ij}} \right]^p r_{ij}}{\sum_{i \in A} \sum_{j \in B} \left[ \frac{R_i + R_j}{r_{ij}} \right]^p} \]  

(2.35)

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 to 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 \textit{versus} relevant coordinates. Figure 2.1 shows the reaction mechanism of the \( S_N2 \) at phosphorus center using two molecular coordinates.
2.8 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 $S_N2$ at phosphorus has been studied to determine the rate constant of the reaction using quantum dynamics.

2.8.1 Time-Dependent Schrödinger Equation

To describe the motion on the atomic scale, quantum mechanics must be used. The Newton equation of motions 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 $S_N2$ at phosphorus center. One of the most useful methods to describe unknown values within the range of a discrete set of points is sincDVR in which the grid spacing is assumed to be equidistant. The energy quantum of the grid equals to $\frac{\hbar}{(2m\Delta x^2)}$, where $\Delta x$ is the grid spacing.[31] 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. Therefore, 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.

### 2.8.2 Rate Constant and State-to-State Reaction Probabilities

Understanding the mechanism of any reaction is an important dilemma 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.

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

(2.36)

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

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

(2.37)

in which \( F \) and \( H \) are the flux operator and the Hamiltonian of the system, respectively. The CPR 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 systems, 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 state 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.
Chapter 3

Haloalkane Reactions with Cyano Radicals

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.\[33, 34\] To systematically investigate the details of how cyano radicals affect the stability of haloalkanes, the PESs of the reactions CX\(_3\)Y + CN\(^-\) (X=H,F; Y=Cl, Br) have been explored using theoretical chemistry methods.

Since the mechanism of reactions of this type are 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 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.\[35\] 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.\[36, 37\] In halomethanes, a number of new reaction pathways can be assumed \textit{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 CH\(_3\)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 CH$_3$Cl and CF$_3$Cl is pursued.

### 3.1 Potential Energy Surface Exploration of CX$_3$Y + CN

Using the AFIR method, the stationary points of CX$_3$Y + CN (X= H, F and Y= Cl, 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 lead 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-$\zeta$ (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, 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.

### 3.2 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, see Figure 3.1. 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 implies 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 3.2. The lowest barrier of 6.9 kcal/mol belongs to
hydrogen abstraction by the carbon of the cyano 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 $S_N2$ 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.[38]

This TS forms a hydrogen cyanide (HCN) and a chloromethyl (CH₂Cl) radical (Min20) that either dissociate to separated fragments or lead to formation of CH₂ClCHN (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.

### 3.3 Effects of Fluorine Substitution

In CH₃Cl, the hydrogen abstraction mechanism is the most viable pathway. However, in a 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 CH$_3$Cl TSs, are selected, see Figure 3.3. 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 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 abstraction channel has been blocked for this system, still direct S$_N$2 mechanisms are not viable pathways with barriers of 78.8 kcal/mol (TS8) and 70.7 kcal/mol (TS10) for carbon and nitrogen attack, respectively. The higher inversion barrier of the trifluoromethyl radical compare to the methyl radical in direct S$_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$2 mechanisms clearly show that the chlorine abstraction is preferable. The chlorine abstraction leads to the formation of CICN and CF$_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.
3.4 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 localized 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 3.2. Large effects on the barrier heights for bromine abstraction to compare with 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 3.3. The 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 to compare with chlorine is high because only halogen abstraction is available.
Chapter 4

Nucleophilic Substitution at Phosphorus Centers

After exploring the PES, one can describe the dynamics of a reaction in order to get the complete and highly accurate description of reactivity. As an example of this approach, the seemingly simple symmetric reaction between $\text{Cl}^- + \text{PH}_2\text{Cl}$ has been studied. This reaction is a prototype for the $\text{S}_\text{N}2$ reactions at phosphorus centers ($\text{S}_\text{N}2@\text{P}$), which plays 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 is outlined by computing the quantum reaction probability for both one and two-dimensional PESs.

4.1 Generating the Potential Energy Surface

In this section we discuss our calculations of the PES of the $\text{Cl}^- + \text{PH}_2\text{Cl} \rightarrow \text{ClPH}_2 + \text{Cl}^-$ reaction in detail. This reaction is proposed to have a transition complex well,[9] 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 refers to 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 between $\text{Cl}^- - \text{PH}_2 - \text{Cl}$ 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 the step size of 0.05 Å, see Figure 4.1. The $\text{Cl}^- - \text{PH}_2 - \text{Cl}$ angle was kept fixed at 168.7 degrees in all
Figure 4.1: 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–PH\(_2\) bond distance.

calculations. The sum of the energy of the two non-interacting fragments, Cl\(^-\) + PH\(_2\)Cl, were used as a reference energy.

To test the sensitivity of the calculated PES with regards 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-\(\zeta\) (zeta). Increasing the size of the basis set increases the depth of the well. The MP2 energy is converged at triple-\(\zeta\) (zeta) basis set level. However, this level overestimates the well depth by 2.4 kcal/mol.

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.
4.2 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;

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

(4.1)

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 \( e.g., 9.0 \ \text{Å} \), 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 4.2;

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

(4.2)

giving \( V_0 = 20.81 \ \text{kcal/mol}, \alpha = 2.275 \ \text{Å} \) and \( q_c = 2.51 \ \text{Å} \).

The numerical calculations of the transmission probability, \( T(E) \), using the potential in Equation 4.2 is similar to the results from analytical solution of the Eckart potential 4.1. Therefore the analytical solution of the transmission probability, Equation 4.3, can be used to rationalize the the effects of the changes in well depth. The equation is;

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

(4.3)

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 that 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 (4.1) where \( \cos^2(\pi z) \) is a small term to compare with \( \sinh^2(k\alpha/\hbar) \) 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.
4.3 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:

\[
V(R_1, R_2) = V_0 + \sum_{k,l=1}^{4} c_{kl} V_k^1 V_l^2 \tag{4.4}
\]

\[
V_i(R_i) = 1 - e^{-\beta(R_i - R_e)} \quad i = 1, 2 \tag{4.5}
\]

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 2.37, is completely different from the transmission probability of the one-dimensional model with a quite involved resonance structure. As is shown in the Figure 4.3, the reaction probability increases around 2 kcal/mol and reaches a local maximum at 5 kcal/mol. The reaction probability is also very 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.

### 4.4 Comparison of the Dimensionality

In Figure 4.4 we compared the rate constant from one and two-dimensional models, see Equation 2.36, with respect to the $2\pi\hbar Q_r(T)k(T)$ where $Q_r$ is the molecular partition function. The result clearly shows that the difference between one and two-dimensional model is almost two order 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 the lower reaction probability at the same temperature.
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Figure 4.4: 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 ±10%. Included is also a comparison with the one dimensional model, i.e. with $N(E) = 1$.

On the other hand, the 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 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 4.4. The situation would be different for reactions with energy barriers where a change in barrier height of ±2 kcal/mol would affect the rate by a factor of 50 according to the transition state theory, Equation 2.33.

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 Cl-PH$_2$-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-Cl stretch that are included in the two-dimensional model.
Chapter 5

Conclusion

The complete picture of a chemical reaction requires the simulation of the full-dimensional quantum dynamics. However, with the exception of very small molecules, the large number of degrees of freedom prevents a full description of the dynamics of the system. Instead, an efficient exploration of the PES can give all the possible reaction pathways. As it is explained for the haloalkane reactions, this makes it possible to distinguish between hydrogen and halogen abstraction, direct $S_N2$ reaction and hydrogen elimination. After finding the most feasible mechanism, the reduced dimensional surface can be calculated using the most relevant degrees of freedom. In the next rung, quantum dynamics simulations can be accomplished on the reduced dimensional PES. The quantum dynamics on the $\text{Cl}^- + \text{PH}_2\text{Cl}$ system revealed complex resonance structures in the reaction probability, which had a large effect on the reaction rate. Together, these two steps, PES exploration and quantum dynamics, give an efficient description about the details of chemical reactions.

Potential targets for the approach described above are the mechanisms of even more complicated processes such as chemi- and bioluminescence reactions. For these excited state systems, it is significant to not only find the minima and transition states, but also intersystem crossings and conical intersections. For such systems, the short time scale also makes it possible to perform dynamics simulations that cover the real time of the reaction.
Bibliography


