Theoretical study of the reaction
$\text{PH}_3 + \text{H} \rightarrow \text{TS}^\dagger \rightarrow \text{PH}_2 + \text{H}_2$

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This Bachelor Thesis is dedicated to Rock'n'Roll music

*For those about to rock, we salute you* — Song made famous by AC/DC

**Abstract:** In this bachelor thesis a theoretical study is performed for the reaction:

\[
\text{PH}_3 + \text{H} \rightarrow \text{TS}^+ \rightarrow \text{PH}_2 + \text{H}_2.
\]

In the first part of the study the geometry of the molecules are optimized using the methods: AM1, PM3, HF/6-311++G(d,p), B3LYP/6-311++G(d,p), B3PW91/6-311++G(d,p) and QCISD/6-311++G(d,p). The various methods are compared, and the conclusion is that methods with a longer computational time tend to give results closer to experimental values. After that the geometry of the transition state and its imaginary vibration frequency are calculated.

In the second part of the study a potential energy surface is calculated with the QCISD/6-311++G(d,p) method. The two dimensional surface gives quantum mechanical information about the reaction dynamics for the system, for instance molecular vibrations are described. At last the reaction probability is calculated, which can describe the quantum mechanical tunneling effect.
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Chapter 1

Introduction

During my three years at the university of Uppsala I have studied chemistry, physics, mathematics and computational science. In this project I will have use from the knowledge I have received from the various courses I have read. The field I am interested in is known as “Quantum Chemistry” which is a combination of the four subjects mentioned above.

Many problems in chemistry need theoretical studies to be understood since some properties cannot be measured experimentally. In other cases experiments are too expensive or time-consuming, in those cases a theoretical study can be a good complement.

To understand the structure of molecules and how molecules interact with other particles one needs to understand how the electrons interact and move around the nuclei. Quantum mechanics, which is built on a foundation of mathematical formulations, is needed to describe the motion of the electrons.

To make the calculations even possible one needs to use computers. There is a bunch of methods to choose among, all with their own benefits and disadvantages. Usually, the more accurate methods need more calculation time.

From the quantum chemical calculations one can get information for example about molecular structures, energies, vibration frequencies and transition states. This information is then used to understand the dynamics, thermodynamics and kinetics of reactions.

The goals of the project are the following:

1. To theoretically analyze the reaction \( PH_3 + H \rightarrow TS' \rightarrow PH_2 + H_2 \).

2. To learn how to use modern computational programs (in this case Gaussian09) for electron structure calculations.

3. To use one and two dimensional models to describe the reaction dynamics.
Chapter 2

Theoretical background

2.1 Reaction dynamics and kinetics

A simple chemical reaction could for example be written as $A + B \rightarrow C + D$.
The reaction goes from the reactants $A$ and $B$ to the products $C$ and $D$. That is a
simplified explanation of the reaction. In reality the reactants often need to form a
transition state (TS) which is the structure with the highest energy the reactants $A$ and $B$
can form along the reaction path [1], [2].

A better way to explain the reaction formula would be $A + B \rightarrow AB^\ast \rightarrow C + D$ where $AB^\ast$
is the transition state, this is displayed in figure 2.1.

![Energy diagram showing reactants, transition state, and products]

**Figure 2.1** – Diagram showing the energy of reactants, the TS and the products [3].
The reaction formula $A + B \rightarrow C + D$ only describes the thermodynamics while the reaction formula $A + B \rightarrow AB^\dagger \rightarrow C + D$ also considers the kinetics of the reaction [1], [2], [3], this can be seen in figure 2.2.

![Diagram showing the kinetics and thermodynamics of a reaction](image)

**Figure 2.2** – Diagram showing the kinetics and thermodynamics of a reaction [3].

There are two kinds of reactions. Either unimolecular or bimolecular. In the unimolecular case there is only one reactant involved and in the bimolecular case there are two reactants involved. In a bimolecular reaction two reactants need to collide with each other both from the right direction and with the right energy [1].

Single step reactions with three reactants or more are extremely rare since it is very unlikely for three reactants to collide all together at the same time. Reactions where three reactants or more are needed are almost always going in many steps [2].
2.1.1 Rate coefficients

Let us consider the reaction between the species $A$ and $B$. The reaction is bimolecular and the rate of the reaction is proportional to the concentrations of the reactants. The proportionality constant is called the rate coefficient $k(T)$ and is defined by the rate law:

$$-\frac{d[A]}{dt} = k(T)[A][B]. \quad (2.1)$$

The rate coefficient depends on many factors but the most important one is the temperature [1]. Arrhenius proposed the following empirical equation for $k(T)$:

$$k(T) = Ae^{-E_{a} / RT}. \quad (2.2)$$

$A$ is the pre-exponential factor, $E_{a}$ is the activation energy, $R$ is the gas constant and $T$ is the temperature of the system. The activation energy $E_{a}$ is defined as the energy needed for a chemical reaction to occur [4].

2.1.2 Reaction cross-sections

In the simple collision theory it is assumed that reactants are hard spheres and that reactions take place via collisions [1]. The rate coefficient for a bimolecular reaction is defined as:

$$k(T) = Z_{AB}^{0} e^{-\epsilon_{0} / k_{B}T}. \quad (2.3)$$

$k_{B}$ is Boltzmann's constant and $\epsilon_{0}$ is the energy of the reaction barrier, which is the energy needed for a reaction to occur. $Z_{AB}^{0}$ is the collision frequency factor and is defined as:

$$Z_{AB}^{0} = \left( \frac{8 k_{B} T}{\pi \mu} \right)^{1/2} \sigma_{c}. \quad (2.4)$$

The first factor is the average relative speed of the reactants, where $k_{B}$ is the Boltzmann's constant, $T$ is the temperature and $\mu = m_{A}m_{B} / m_{AB}$, where $m_{AB} = m_{A} + m_{B}$. $m_{A}$ is the mass of reactant $A$ and $m_{B}$ is the mass of reactant $B$. The second factor $\sigma_{c}$ is the collision cross-section. The factor $\sigma_{c}$ represents the area within which reactants $A$ and $B$ must approach one another for collisions to take place [1].

In other words, a reactant has to collide at the right part of the other reactant for a reaction to take place. The reactants also need the right speed (energy) for a reaction to happen [1].
2.1.3 Differential cross-section

After the collision of two reactants the products are scattered in a variety of directions with different scattering angles. The angular dependence of the reaction cross-section is known as the *differential cross-section* $d\sigma$, being related to the *total cross-section* $\sigma_r$ according to:

$$\sigma_r = \frac{2\pi}{\omega} \int_0^\infty \int_0^\pi d\sigma_r \sin \theta \, d\theta \, d\phi. \quad (2.5)$$

Where $\omega$ is the solid angle while $\theta$ and $\phi$ are the scattering angles. Note that the total cross-section $\sigma_r$ does not depend on the angles, which the differential cross-section $d\sigma_r$ does. The differential cross-section is of interest since it is among the easiest properties to measure, and can thereafter be compared with theoretical results [1].

2.1.4 Reaction probability

Say one got a reaction between the reactants $A$ and $B$. The two molecules can either collide “head-on” or with “a glancing blow” (Fig. 2.3). The collision is described by the impact parameter $b$ [1].

When $b = 0$ the collision occurs head-on. When $b > 0$ the collision occurs with a glancing blow.

![Figure 2.3 – Picture of the impact parameter $b$ [1].](image)

It is impossible to measure the magnitude of the impact parameter experimentally since one cannot control at which angle a collision occurs [1]. This problem is solved by considering the reaction cross-section as an average of all possible collisions:

$$\sigma_r = \int_0^{b_{\text{max}}} P(b) 2\pi b \, db. \quad (2.6)$$

$P(b)$ is the probability for a reaction to take place at a specified impact parameter, and is known as the *opacity function*. The upper limit $b_{\text{max}}$ implies there is a finite range of impact parameters that leads to a reaction [1].
Reaction probability and cross-section do depend not only on the total energy of the reactants, but also on the degrees of freedom (translation, rotation and vibration) in which the energy is initially stored. For example vibrational energy is needed to break a bond. Depending on the rotational and vibrational state of the reactants the reaction probability is influenced. The reactants approach in their initial quantum states and the products depart in specific final states [1].

2.1.5 From cross-sections to rate coefficients

The thermal rate coefficient must reflect the average outcome of all the collision encountered at a certain temperature. At a given temperature states of the reactant molecules are populated according to the Boltzmann law [1], [2].

The thermal rate coefficient is better explained as a function of reaction probabilities rather than in terms of reaction cross-sections (equation 2.3):

\[
k(T) = \frac{1}{h q_r} \int_0^\infty N(\epsilon) e^{-\epsilon/k_B T} d\epsilon. \quad (2.7)
\]

\(h\) is Planck's constant and \(q_r\) is the total reactant molecular partition function, which is based on the energy levels of the reactants translational, rotational and vibrational states. \(\epsilon\) is the sum of the total energy of the reactants. \(k_B\) is once again Boltzmann's constant. \(T\) is the temperature. \(N(\epsilon)\) is the cumulative reaction probability [1], [5].

Equation 2.7 is much simpler than equation 2.3 since it only depends on the dimensionless factor \(N(\epsilon)\) instead of the much more complicated factor \(Z_{AB}^0\).

2.1.6 Cumulative reaction probability

The cumulative reaction probability \(N(\epsilon)\) is defined as the sum of reaction probabilities \(P_m(\epsilon)\) (lying between 0 and 1) over all initial reactant states \(m\):

\[
N(\epsilon) = \sum_{n=1}^{m} P_n(\epsilon). \quad (2.8)
\]

\(\epsilon\) is the energy of the system. A reactant state is purely reactive if \(P_n(\epsilon) = 1\) and purely unreactive if \(P_n(\epsilon) = 0\) [1].
2.2 Potential energy surfaces (PES)

A potential energy surface (PES) is a graph where the energy of the system or molecule is a function of one or more nuclear coordinates. Examples of parameters are bond lengths and bond angles [1].

The one and two dimensional cases are the most useful ones since they are possible to visualize, although for some problems it is necessary to use more than two parameters. A multidimensional problem is sometimes visualized using a one dimensional curve where the energy is plotted along the reaction path.

The one dimensional PES is often used to visualize the zero point energy, which is the energy of the most stable molecular configuration for a molecule. The two dimensional PES is often used to visualize the minimum energy path (MEP), which is the reaction path with the lowest energy [1].

2.2.1 One dimensional PES

The one dimensional case gives rise to a curve with energy on the y-axis and the nuclear coordinate on the x-axis (Fig. 2.4). The graph can give information about the basic kinetics and thermodynamics for a reaction if the energy of the reactants, transition state and products are compared with each other (see Fig. 2.2) [1]. The energy minimum represents the most stable structure and corresponds to a first derivative equal to zero.

Figure 2.4 – A one dimensional PES showing the energy of a diatomic molecule. $R_e$ is the equilibrium bond distance where the molecule is the most stable. This graph is commonly known as the The Morse potential [3].
2.2.2 Two dimensional PES

In the two dimensional case one gets a surface instead of a curve. There is one molecular parameter on the x-axis and another on the y-axis. Examples of parameters are bond lengths and bond angles. The energy of the system is on the z-axis.

The two dimensional PES provides more information than the one dimensional PES since one can see how the minimum energy path (MEP) is going from reactants to products via one or many transition states. Depending on how complex the reaction is one can get many different transition states and energy paths (Fig. 2.5) [1], [6].

![Two dimensional PES diagram](https://via.placeholder.com/150)

**Figure 2.5** – Picture of a two dimensional PES showing one reactant and two products, A and B. One can also see two transition states, one for each product. The purple line is the minimum energy path [6].
2.3 Quantum chemistry methods

Quantum chemistry is for example used to predict molecular structures, electronic spectra and to model chemical reaction mechanisms. Many times a computational method works as a complement for an experimental method where measurements take a long time and require a high precision.

For fast reactions it is difficult to perform accurate measurements, it is especially difficult to analyze the reaction dynamics and the transition state. If a theoretical method is to be valid for chemistry the cost has to be low and the results need to be reliable.

There are a lot of various computational methods to choose among, all with their own benefits and disadvantages. Depending on which system one is analyzing some methods give more accurate results compared to experimental values than others. If one wants more accurate results one often needs to use a method with a longer computational time.

For large systems one might have to choose a method based on classical physics instead of quantum mechanics, such a system would for example be DNA or large proteins. In some cases different methods are combined to increase the accuracy.

In this study all computational methods are based on quantum mechanics, the difference is the parametrizations or approximations they use.

In this report, the sources to the theoretical part containing quantum chemistry methods can be found here: [2], [7], [8], [9], [10].
2.3.1 The Hartree-Fock method (HF)

The molecular systems involved in this study is described by the time-independent Schrödinger equation:

\[ \hat{H} \psi = E \psi. \]  \hspace{1cm} (2.9)

The Hamiltonian \( \hat{H} \) is an operator corresponding to the energy of the system and is a sum of the kinetic energy operator \( \hat{T} \) and the potential energy operator \( \hat{V} \):

\[ \hat{H} = \hat{T} + \hat{V}. \]  \hspace{1cm} (2.10)

The total kinetic energy operator \( \hat{T} \) consists of the kinetic energy of the nuclei \( (T_n) \) and the kinetic energy of the electrons \( (T_e) \). The total potential energy operator \( \hat{V} \) consists of the attraction between electrons and the nuclei \( (V_{n,e}) \), the repulsion between the nuclei \( (V_{n,n}) \) and the repulsion between the electrons \( (V_{e,e}) \). The Hamiltonian \( \hat{H} \) is then:

\[ \hat{H} = T_n + T_e + V_{n,n} + V_{e,e} + V_{n,e}. \]  \hspace{1cm} (2.11)

To simplify the Schrödinger equation the Born-Oppenheimer approximation is used where one separates the motions of the electrons from the nuclei. Since the nuclei are much heavier than the electrons they move much more slowly, the nuclei is therefore approximated to be completely still.

In the Born-Oppenheimer approximation the kinetic energy of the nuclei \( T_n \) is considered to be zero and the term for repulsion between the nuclei \( (V_{n,n}) \) can be seen as a constant. The Hamiltonian \( \hat{H} \) is then written:

\[ \hat{H} = T_e + V_{e,e} + V_{n,e}. \]  \hspace{1cm} (2.12)

The Schrödinger equation for a molecular system cannot be solved analytically due to the electron-electron repulsion term \( V_{e,e} \).

The energy for the system is a functional of one-electron orbitals and is optimized using the variation principle, where one first suggests a trial wave-function \( \psi^{\text{trial}} \). The expectation value obtained by this wave-function never lies below the exact value of the ground state energy.

\[ E_{\text{expectation}} = \frac{\langle \psi^{\text{trial}} | H | \psi^{\text{trial}} \rangle}{\langle \psi^{\text{trial}} | \psi^{\text{trial}} \rangle} \geq E_{\text{exact}}. \]  \hspace{1cm} (2.13)
To satisfy the Pauli principle which states that the wave-function must change sign under the permutation of any pair of electrons one writes the wave-function $\psi$ as a sum of all possible permutations with the appropriate sign. The entire sum can be written as a Slater determinant:

$$
\psi = \frac{1}{\sqrt{N!}} \begin{vmatrix}
\chi_1(1) & \chi_2(1) & \cdots & \chi_N(1) \\
\chi_1(2) & \chi_2(2) & \cdots & \chi_N(2) \\
\vdots & \vdots & \ddots & \vdots \\
\chi_1(N) & \chi_2(N) & \cdots & \chi_N(N)
\end{vmatrix}.
$$

(2.14)

$N$ is the total number of electrons and $\chi$ is a spin-orbital which is a product of a spatial orbital and an electron spin eigenfunction.

The energy of the ground state wave-function is written:

$$
E = \langle \psi | H | \psi \rangle.
$$

(2.15)

After introducing the Slater determinant the energy of the system becomes:

$$
E = \sum_{k=1}^{\text{occ}} 2h_{kk} + \sum_{k=1}^{\text{occ}} \sum_{j=1}^{\text{occ}} (2J_{kj} - K_{kj}).
$$

(2.16)

The sums run over all occupied orbitals (occ). $h_{kk}$ are the one-electron core integrals, $J_{kj}$ are the Coulomb integrals and $K_{kj}$ are the exchange integrals. The integrals are defined as:

$$
h_{kk} = \int \chi_k^*(1) \hat{h}(1) \chi_k(1) d\tau_1, \quad (2.17)
$$

$$
J_{kj} = \iint \chi_k^*(1) \chi_j^*(1) \frac{1}{r_{12}} \chi_j^*(2) \chi_k(2) d\tau_1 d\tau_2, \quad (2.18)
$$

$$
K_{kj} = \iint \chi_k^*(1) \chi_j^*(1) \frac{1}{r_{12}} \chi_j^*(2) \chi_k(2) d\tau_1 d\tau_2. \quad (2.19)
$$

$r_{12}$ is the distance between the electrons. $\hat{h}(1)$ is the one-electron core Hamiltonian which contains the kinetic energy of the electrons ($T_e$) and the potential energy for the attraction between the nuclei and the electrons ($V_{n,e}$).
The best set of orbitals that correspond to a minimum value of the energy are obtained by solving the Hartree-Fock equations:

\[
\hat{f} \chi_k = \varepsilon_k \chi_k. \quad (2.20)
\]

The Fock operator \( \hat{f} \) is an effective one-electron Hamiltonian which is defined as:

\[
\hat{f}(1) = \hat{h}(1) + \sum_{j=1}^{\text{occ}} [\hat{J}_j(1) - \hat{K}_j(1)]. \quad (2.21)
\]

The sums run over all occupied orbitals \( \text{occ} \). \( \hat{J}_j \) is the Coulomb operator and \( \hat{K}_j \) is the exchange operator. The two operators are defined as:

\[
\hat{J}_j \chi_k(1) = \left[ \int \frac{1}{r_{12}} \chi_j^*(2) \chi_j(2) d\tau \right] \chi_k(1), \quad (2.22)
\]

\[
\hat{K}_j \chi_k(1) = \left[ \int \frac{1}{r_{12}} \chi_j^*(2) \chi_k(2) d\tau \right] \chi_j(1). \quad (2.23)
\]

\( r_{12} \) is the distance between the electrons.
The next step is to write the Hartree-Fock equations for molecular orbitals by integration of the spin functions of the spin-orbitals. As mentioned previously, a spin-orbital \( \chi \) is a product of a spatial orbital \( \psi \) and an electron spin eigenfunction which can be \( \alpha \) or \( \beta \). This can be done using a restricted Hartree-Fock (RHF) or an unrestricted Hartree-Fock (UHF) scheme, as displayed in Fig. 2.7.

In RHF the \( \alpha \)- and \( \beta \)-electrons are constrained to occupy the same spatial orbital, while they occupy different spatial orbitals in UHF:

\[
\psi_{RHF}^\alpha = \psi_{RHF}^\beta , \quad \psi_{UHF}^\alpha \neq \psi_{UHF}^\beta . \tag{2.24}
\]

**Figure 2.6** – The RHF and UHF spatial orbital energies [9].

A single electron has spin \( \frac{1}{2} \) and a molecule with a single unpaired electron is in a doublet state. A molecule with no unpaired electrons is in a singlet state, a molecule with two unpaired electrons is in a triplet state and so on. Systems with unpaired electrons are generally called radicals.

The UHF wave-function is not an eigenfunction of the spin operator but contains an artificial mixing of other electronic spin-states. This is called spin contamination. If the spin contamination is high, the properties calculated with UHF for a radical are inaccurate. Therefore, in a calculation involving radicals the spin contamination must be eliminated.
The Hartree-Fock equations are further written for atomic orbitals by introducing the *linear combination of atomic orbitals* (LCAO) approximation into the formalism. This will allow to obtain the solution in form of analytical functions, with contributions from the different atoms in the system, instead of the series of numbers obtained in the numerical solution.

In the LCAO approximation each molecular orbital \( \psi_k \) of the molecular system is a linear combination of all the atomic orbitals \( \{ \phi_i \} \) of the atoms present in the system:

\[
\psi_k = \sum_{i=1}^{n} \phi_i c_{ik}.
\] (2.25)

The \( \{ c_{ik} \} \) are the LCAO-coefficients and \( n \) is the size of the basis set \( \{ \phi_i \} \). The larger the LCAO expansion is the higher the accuracy of the result. There are many different basis sets to choose among, an example is the valence basis sets where only valence-shell orbitals are included for each atom.

Before starting a calculation one has to choose which basis set one wants to use, depending on the level of accuracy desired.

The two most common types of atomic orbitals used are the *Slater type orbitals* (STOs) and the Gaussian type orbitals (GTOs). STOs are approximations to the rigorous hydrogenic atomic orbitals which are the exact solution of the Schrödinger equation for the hydrogen atom. Therefore the STOs constitute a good approximation for the atomic orbitals. On the other hand, the GTOs are also approximate orbitals which have been proposed to reduce the mathematical complexity of the calculations. However, a GTO does not have the correct physical behavior neither close to the nucleus nor at large distances. This is illustrated in the following:

\[
\phi_{n,l,m}^{\text{STO}} = N_{\text{STO}} r^{n-1} e^{-\zeta r} Y_l^m(\theta, \phi), \quad (2.26)
\]

\[
\phi_{n,l,m}^{\text{GTO}} = N_{\text{GTO}} r^{n-1} e^{-\zeta r} Y_l^m(\theta, \phi). \quad (2.27)
\]

\( n \) is the principle quantum number, \( N_{\text{STO}} \) and \( N_{\text{GTO}} \) are normalization constants, \( r \) is the distance between the electron and the atomic nucleus, \( \zeta \) is the effective charge of the nucleus and \( Y_l^m \) are the spherical harmonics which are the eigenfunctions of the angular orbital momentum.
A simple picture of the behavior of an STO \( y = e^{-x} \) and a GTO \( y = e^{-x^2} \) is displayed in Fig. 2.7.

![STO vs. GTO graph](image)

**Figure. 2.7** – Simple picture showing the radial part of the STO (in red), and the GTO (in blue). The plot was made by the author using the program Matlab [11].

As can be seen in Fig. 2.7, the Gaussian function goes to zero too quickly at large distances and furthermore it does not have a cusp at the origin. In contrast, the exponential function has got the correct asymptotic behavior of an atomic orbital both at the origin and at large distances. Therefore, while only one STO is needed to represent an atomic orbital, many GTOs will be needed for a good description of the atomic orbital.

Using the LCAO approximation in the Hartree-Fock method results in the *Roothaan equations*:

\[
F c = S c \varepsilon. \quad (2.28)
\]

Where \( F \) is a matrix formed from the Fock operator, \( S \) is the matrix of overlap integrals, \( c \) is a matrix corresponding to the orbital coefficients and \( \varepsilon \) is a matrix containing the molecular orbital energies.
Since the Fock operator (equation 2.21) depends on its eigenfunctions it is said to be non-linear, and because of this the Hartree-Fock equations have to be solved iteratively.

The molecular structures are optimized with a method called the self-consistent field (SCF) procedure. When the SCF calculation has converged the minimum energy and the equilibrium geometry of the molecular system studied are obtained. From this, various properties such as the dipole moment and ionization energy are computed.

Another important property obtained is the vibration frequencies. From the PES the potential for the various nuclear coordinates are obtained. By writing the potential as a Taylor expansion series at the equilibrium (a local energy minimum) one can determine the frequencies. From the first derivatives one gets the forces acting on the atoms and from the second derivatives one gets the vibration frequencies.

The force constant matrix only consists of positive eigenvalues at a potential minimum. Outside the equilibrium the force constant matrix consists of one or more negative numbers. Because the vibration frequencies are proportional to the square root of the force constants, only real vibration frequencies are obtained for a minimum. In contrast if one and only one imaginary frequency is obtained, this corresponds to a saddle-point or transition state on the potential surface.
2.3.2 Semi-empirical methods

For large molecules the calculation time for the Hartree-Fock method is way too long. To solve this problem the semi-empirical methods were introduced which include additional approximations. For example one can consider explicitly in the calculations only the valence electrons of the molecular system at hand, as these are the ones responsible for the chemical bonding. Furthermore in semi-empirical models some of the terms in the Roothaan formalism are neglected while other terms are fitted to experimental parameters.

The semi-empirical methods used in this study are based on the neglect of diatomic differential overlap (NDDO) approximation [10], where for example the overlap matrix $S$ (equation 2.27) is replaced by the unit matrix.

One method based on the NDDO approximation is the Modified Neglect of Diatomic Overlap (MNDO) [12]. However, this method tends to overestimate core repulsion between two atoms at van der Waals distances. For this reason, two other semi-empirical models were developed: the Austin Method 1 (AM1) [13] and the Parametrization Method 3 (PM3) methods [13].

The PM3 method is similar to the AM1 method, the difference is the parametrization procedure used. One advantage with the semi-empirical methods is that they use experimental data that include electron correlation effects. However, if data is missing to construct parameters from, the calculations for unusual types of molecules is often inaccurate.
2.3.3 Density Functional Theory (DFT)

One of the most used techniques to calculate molecular structures is the density functional theory (DFT). It demands less computational effort and computer time since the only variables needed are the three space coordinates, no matter how many atoms are involved. For the ab initio methods the number of variables needed depends on the number of atoms multiplied with three. The reason for this is that the DFT methods uses the electron density $\rho$ instead of the wave-function $\psi$ [2].

For the DFT methods the energy of the molecules is a function of the electron density, $E(\rho)$, and electron density is itself a function of position, $\rho(r)$. In mathematics a function of a function is called a functional, and from this comes the “functional” part in the name of DFT [2].

The equation for electron density is defined as:

$$\rho(r) = \sum_{m} |\psi_m(r)|^2. \quad (2.29)$$

$\psi_m$ is calculated from the Kohn-Sham (KS) equations which are similar to the Hartree-Fock equations in that sense that both are solved iteratively and self-consistently. The exception is the term $V_{XC}$ called the exchange-correlation potential. The Kohn-Sham equations are defined as:

$$[\hat{h}(1) + \int_{r_{12}} \rho(2) d\tau_{z} + V_{XC}(1)]\psi_m(1) = \varepsilon_m \psi_m(1). \quad (2.30)$$

The difficulty for the DFT methods is to construct the exchange-correlation potential $V_{XC}$. There are many different density functional theory functionals to choose among.

This study will use the B3LYP [14] and the B3PW91 [14] functionals.
2.3.4 The QCISD method

The QCISD method is a method developed chronologically after the Hartree-Fock method, and is based on the quadratic configuration interaction (QCI) method that is an extension of the configuration interaction (CI) method. Instead of a single determinant (as in the HF method) the CI method uses a linear combination of determinants [15], due to this fact the CI method is more accurate compared to the HF method, to the cost that it requires more CPU time.

The determinental wave-functions are derived from the initial wave-function by substitution of occupied spin orbitals by virtual spin orbitals [15]. The operators for the singly, doubly and triply substituted determinant are defined as:

\[ T_1 = \sum_{ia} A_i^a \hat{t}_i^a, \quad T_2 = \frac{1}{4} \sum_{ijab} A_{ij}^{ab} \hat{t}_{ij}^{ab}, \quad T_3 = \frac{1}{36} \sum_{ijkabc} A_{ijk}^{abc} \hat{t}_{ijk}^{abc}. \] (2.31)

A is a matrix containing coefficients. The symbols \( a, b \) and \( c \) are occupied spin orbitals, while \( i, j \) and \( k \) are virtual spin orbitals. \( \hat{t} \) are the elementary substitution operators [15].

The wave-functions for some configuration interaction (CI) methods are expressed:

\[ \psi_{CID} = (1 + T_2) \psi_0, \quad (2.32) \]
\[ \psi_{CISD} = (1 + T_1 + T_2) \psi_0. \quad (2.33) \]

The letters \( S \) and \( D \) indicates if a singly or doubly substituted determinant is added to the wave-function. The operators \( T_1 \) and \( T_2 \) are defined in equation 2.31. The QCI method add quadratic terms to the wave-function [15] and the QCISD method is expressed:

\[ \psi_{QCISD} = (1 + T_1 + T_2 + \frac{1}{2} T_2^2) \psi_0. \quad (2.34) \]

In this project the QCI method will be used using both the singly and doubly substituted determinants, but without using any triply substituted determinants. In other words the QCISD method will be used in this study.
2.4 Gaussian 09 and GaussView 4.1

The program used to perform the computational quantum chemical calculations is Gaussian 09 [16] together with its interface GaussView 4.1. With Gaussian 09 a computer can perform geometry optimizations, calculate molecular energies, study vibrations among many of other things [17].

First one must create a molecule in GaussView and after that calculation type (for example geometry optimization or vibration frequency calculation) and method (for example the AM1, PM3, HF or QCISD method) are chosen. The molecule is then saved as an input file. For many methods it is also possible to choose which approximations to be used and the size and type of the basis set [17].

After the calculations are finished they will be saved in an output file that can be read in either GaussView or a text program.

One of the most useful things Gaussian has to offer is the scan function. By scanning a coordinate one can for example change a bond length or angle in smaller steps and the program will calculate the energy optimized structure in each point [17].

---

**Figure 2.8** – Window in GaussView where various methods can be chosen [17].
Chapter 3

Optimizing the geometry of the molecules and finding the transition state

The reaction to be analyzed is $PH_3+H\rightarrow TS\rightarrow PH_2+H_2$.

Gaussian 09 (see section 2.4) is used to optimize the geometries of the molecules. The methods used are HF, AM1, PM3, B3LYP, B3PW91 and QCISD. For the HF method, the two DFT methods (B3LYP and B3PW91) and the QCISD method the *split-valence basis set 6-311++G(d,p)* [18] is used.

The number 6-311 in the name “6-311++G(d,p)” indicates that the core orbital basis function is built up by six primitive Gaussian functions. The valence orbitals are composed of three basis functions each, the first one composed of a linear combination of three primitive Gaussian functions and the other two are composed of a single primitive Gaussian function [18], [19].

The plus signs indicate that diffuse functions are added, the first plus sign if they are added only for heavier atoms and the second if they are added for the hydrogen atoms too. Diffuse functions are added to describe the orbital part far away from the core, without them the electron repulsion is overestimated, especially for anions [14], [18], [20]. (d,p) indicates that polarization functions have been added for both heavier atoms and the hydrogen atoms. [18].

The results of this study will be compared with experimental data [21], [22]. The results computed will also be compared with a similar theoretical study in which the same reaction was studied with the method *QCISD/6-311+G(d,p)* [23].

From the calculations one gets information for example about the geometry and energy of the molecules as well as vibration frequencies and CPU time.

From a method known as *QST2* the geometry of the transition state is calculated. QST2 is a method in the program Gaussian09 where one starts with the structure of the reactants in one window and the structure of the products in another window [17], the program will then calculate the transition state's geometry and the result is obtained in a new window.


3.1 Geometry of the optimized molecules

In the following pages the results of the geometry optimization calculations are reported. Properties such as bond lengths, angles and CPU time are reported. Results from various methods are compared with experimental results and theoretical studies [23].

As mentioned previously the methods AM1, PM3, HF/6-311++G(d,p), B3LYP/6-311++G(d,p), B3PW91/6-311++G(d,p) and QCISD/6-311++G(d,p) are used.

3.1.1 The PH\textsubscript{3} molecule

![Figure 3.1 – Structure of the PH\textsubscript{3} molecule. Taken from [23].](image)

<table>
<thead>
<tr>
<th>Method</th>
<th>P-H (Å)</th>
<th>Angle θ (degrees)</th>
<th>CPU time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment [21]</td>
<td>1,419</td>
<td>93,5</td>
<td>-</td>
</tr>
<tr>
<td>QCISD/6-311+G(d,p) [23]</td>
<td>1,415</td>
<td>94,08</td>
<td>-</td>
</tr>
<tr>
<td>AM1</td>
<td>1,362</td>
<td>96,48</td>
<td>2,8</td>
</tr>
<tr>
<td>PM3</td>
<td>1,323</td>
<td>97,06</td>
<td>2,6</td>
</tr>
<tr>
<td>HF/6-311++G(d,p)</td>
<td>1,408</td>
<td>95,67</td>
<td>8,1</td>
</tr>
<tr>
<td>B3LYP/6-311++G(d,p)</td>
<td>1,423</td>
<td>93,59</td>
<td>16,7</td>
</tr>
<tr>
<td>B3PW91/6-311++G(d,p)</td>
<td>1,424</td>
<td>93,30</td>
<td>16,4</td>
</tr>
<tr>
<td>QCISD/6-311++G(d,p)</td>
<td>1,413</td>
<td>94,21</td>
<td>167,6</td>
</tr>
</tbody>
</table>

Table 3.1 – Properties of the PH\textsubscript{3} molecule.

The semi-empirical methods AM1 and PM3 calculate the geometry of the molecule inaccurate compared to the experimental value. All the other methods perform geometry optimization well. Especially the two functionals for the DFT method give values close to the experimentally value. The values for the DFT methods and the QCISD/6-311++G(d,p) method are similar, but the QCISD method needs a lot more calculation time than the DFT methods. There is just a small difference between the two QCISD basis sets, although in this case the one without diffuse functions for the hydrogen atoms give values closer to the experimentally value.
### 3.1.2 The PH$_2$ molecule

![Structure of the PH$_2$ molecule. Taken from [23].](image)

**Figure 3.2** – Structure of the PH$_2$ molecule. Taken from [23].

<table>
<thead>
<tr>
<th>Method</th>
<th>P-H (Å)</th>
<th>Angle θ (degrees)</th>
<th>CPU time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UQCISD/6-311+G(d,p) [23]</td>
<td>1,418</td>
<td>91,92</td>
<td>-</td>
</tr>
<tr>
<td>AM1</td>
<td>1,358</td>
<td>97,09</td>
<td>2,9</td>
</tr>
<tr>
<td>PM3</td>
<td>1,334</td>
<td>96,77</td>
<td>2,7</td>
</tr>
<tr>
<td>UHF/6-311++G(d,p)</td>
<td>1,411</td>
<td>93,68</td>
<td>8,9</td>
</tr>
<tr>
<td>UB3LYP/6-311++G(d,p)</td>
<td>1,428</td>
<td>91,67</td>
<td>14,0</td>
</tr>
<tr>
<td>UB3PW91/6-311++G(d,p)</td>
<td>1,428</td>
<td>91,47</td>
<td>14,4</td>
</tr>
<tr>
<td>UQCISD/6-311++G(d,p)</td>
<td>1,417</td>
<td>91,92</td>
<td>100,3</td>
</tr>
</tbody>
</table>

**Table 3.2** – Properties of the PH$_2$ molecule.

All methods except the AM1 and PM3 method give similar values. The UQCISD/6-311++G(d,p) method needs significant more CPU time than all the other methods, this is because the QCISD method uses less approximations than the other methods, and therefore perform more calculations. The difference between the two DFT functionals is only for the angle, while the bond length is the same. The difference between the two UQCISD basis sets is almost none. No experimental values were found to compare the results with.
3.1.3 The H₂ molecule

![Structure of the H₂ molecule](image)

Figure 3.3 – Structure of the H₂ molecule.

<table>
<thead>
<tr>
<th>Method</th>
<th>H-H (Å)</th>
<th>CPU time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment [22]</td>
<td>0.741</td>
<td>-</td>
</tr>
<tr>
<td>QCISD/6-311+G(d,p) [23]</td>
<td>0.744</td>
<td>-</td>
</tr>
<tr>
<td>AM1</td>
<td>0.677</td>
<td>3</td>
</tr>
<tr>
<td>PM3</td>
<td>0.699</td>
<td>2.7</td>
</tr>
<tr>
<td>HF/6-311++G(d,p)</td>
<td>0.735</td>
<td>5.4</td>
</tr>
<tr>
<td>B3LYP/6-311++G(d,p)</td>
<td>0.744</td>
<td>4.2</td>
</tr>
<tr>
<td>B3PW91/6-311++G(d,p)</td>
<td>0.745</td>
<td>15.1</td>
</tr>
<tr>
<td>QCISD/6-311++G(d,p)</td>
<td>0.743</td>
<td>21.5</td>
</tr>
</tbody>
</table>

Table 3.3 – Properties of the H₂ molecule.

The bond length from AM1 and PM3 calculations are too short compared to the experimental value. The value from the HF method is a little bit short and the values from the two DFT methods is a little bit too long compared to the experimentally value. The bond length from the QCISD/6-311++G(d,p) calculation is closest to the experimentally value.
3.2 Geometry of the transition state

The QST2 method (see beginning of Chapter 3) in Gaussian09 (see section 2.4) was used to calculate the transition state (Fig. 3.4). Since it is almost impossible to analyze the transition state experimentally one has got no value to compare the theoretical methods with. It was not possible to perform the TS calculation with the B3LYP method as Gaussian09 only gave error messages for the QST2 method with this method.

![Figure 3.4 – Structure of the transition state. Taken from [23].](image)

<table>
<thead>
<tr>
<th>Method</th>
<th>P-H$^{(3,4)}$</th>
<th>P-H$^{(2)}$</th>
<th>H$^{(2)}$-H$^{(5)}$</th>
<th>Angle $\alpha$</th>
<th>Angle $\beta$</th>
<th>CPU time</th>
</tr>
</thead>
<tbody>
<tr>
<td>UQCISD/6-311+G(d,p) [23]</td>
<td>1,415</td>
<td>1,485</td>
<td>1,259</td>
<td>92.92</td>
<td>170.61</td>
<td>-</td>
</tr>
<tr>
<td>AM1</td>
<td>1,363</td>
<td>1,391</td>
<td>1,343</td>
<td>98.15</td>
<td>83.89</td>
<td>2.7</td>
</tr>
<tr>
<td>PM3</td>
<td>1,321</td>
<td>1,415</td>
<td>1,169</td>
<td>99.33</td>
<td>78.44</td>
<td>3.1</td>
</tr>
<tr>
<td>UHF/6-311++G(d,p)</td>
<td>1,409</td>
<td>1,548</td>
<td>1,117</td>
<td>93.47</td>
<td>171.23</td>
<td>17.4</td>
</tr>
<tr>
<td>UB3PW91/6-311++G(d,p)</td>
<td>1,424</td>
<td>1,448</td>
<td>1,591</td>
<td>92.92</td>
<td>170.46</td>
<td>64.8</td>
</tr>
<tr>
<td>UQCISD-FC/6-311++G(d,p)</td>
<td>1,415</td>
<td>1,484</td>
<td>1,262</td>
<td>93.21</td>
<td>168.36</td>
<td>1485</td>
</tr>
</tbody>
</table>

Table 3.4 – Properties of the TS. Distances in Ångströms, angles in degrees and time in seconds.

The semi-empirical methods AM1 and PM3 give incorrect values, especially the angle $\beta$ is much smaller compared to the other methods. The HF method gives a too long bond length for P-H$^{(2)}$, while the B3PW91 method gives a too long bond length for H$^{(2)}$-H$^{(5)}$.

The QCISD method values are very similar to the ones from the article [23], which is because this study uses the same method with the same basis set, while also adding diffuse functions for the hydrogen atoms. The bond lengths are not changed much by adding diffuse functions, however, the bond angles changes a little.

One can also note the calculation time for the QCISD method is much longer than for the other methods. For more complex molecules the CPU time of the QCISD method is often way to long.
3.3 The imaginary vibration frequency for the transition state

Gaussian09 (see section 2.4) calculates all vibrations for the transition state. The table below shows the single imaginary frequency which is the stretching vibration where the bond H\(^{(2)}\)-H\(^{(5)}\) forms and breaks. The table below is showing the vibration frequency for the stretching vibration taking place at the H\(^{(2)}\)-H\(^{(5)}\) bond. See figure 3.4 for the molecular structure of the transition state.

<table>
<thead>
<tr>
<th>Method</th>
<th>Vibration frequency (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>QCISD/6-311+G(d,p) [7]</td>
<td>1182i</td>
</tr>
<tr>
<td>AM1</td>
<td>1010i</td>
</tr>
<tr>
<td>PM3</td>
<td>1075i</td>
</tr>
<tr>
<td>UHF/6-311++G(d,p)</td>
<td>2059i</td>
</tr>
<tr>
<td>UB3PW91/6-311++G(d,p)</td>
<td>398i</td>
</tr>
</tbody>
</table>

Table 3.5 – The imaginary vibration frequency for the TS.

The vibration frequency for the HF method is almost twice as large compared to the other methods, while the value from the DFT method is less than half the size of the values from the methods AM1 and PM3. The frequencies for the semi-empirical methods are somewhat close to the one obtained from other studies [23]. If the values from AM1 and PM3 are trustworthy is another question, the structure of the transition state for those two methods are far away from the other methods (see section 3.2), and it is therefore very unlikely that the frequency obtained represents the right reaction path.

As can be seen in table 3.5 a high frequency is related to a small H\(^{(2)}\)-H\(^{(5)}\) bond (see table 3.4), while a low frequency means there is a relatively long bond. The vibration frequency also varies a lot between the different methods.
Chapter 4

Reaction dynamics and reaction probability

In the following section the reaction dynamics and reaction probability for the reaction $PH_3 + H \rightarrow TS \rightarrow PH_2 + H_2$ is studied. The QCISD/6-311++G(d,p) method is used since it gave the most accurate geometry optimized structures (see sections 3.1 and 3.2).

Gaussian09 and its scan function (explained in section 2.4) are used. The two parameters used are the $R_1$ and $R_2$ bond lengths (Fig. 4.1). The energy of 439 different molecular configurations were calculated. More configurations were calculated near the transition state and along the minimum energy path (MEP) since those areas are of great importance for the reaction dynamics (Fig. 4.2).

![Figure 4.1 – The transition state with the bond distances $R_1$ and $R_2$.](image)

![Figure 4.2 – All the 439 configurations with $R_1$ (Å) on the x-axis and $R_2$ (Å) on the y-axis. In each point the energy for the molecular configuration was calculated.](image)
4.1 The two dimensional potential energy surface

From the energy of the 439 different molecular structures (Figure 4.2) a 3D-interpolation of the points (Figure 4.3) was made with Matlab [11]. Visualizations of the results were also made with Matlab.

![Interpolation plot of the two dimensional scan](image)

Figure 4.3 – Interpolation plot of the two dimensional scan. On the x-axis is \( R_1 \) (Å) and on the y-axis is \( R_2 \) (Å). On the z-axis is the energy (Hartree) of the system. Blue and red colors correspond to low and high energy, respectively.

The energy is reported in the unit Hartree (Ha). One Ha is defined as \( 2R_\infty hc \), where \( R_\infty \) is Rydberg's constant, \( h \) is the Plack's constant and \( c \) is the speed of light.

\[ 1 \text{ Ha} \approx 4.360 \times 10^{-18} \text{ J}. \]
**Figure 4.4** – An interpolation plot without the scan points. On the x-axis is $R_1$ (Å) and on the y-axis is $R_2$ (Å). On the z-axis is the energy (Hartree) of the system. Blue and red colors correspond to low and high energy, respectively.

From the plot in Fig. 4.4 one can see that the energy of the products is lower than that for the reactants. There also seems to be a small barrier for the transition state. The energy curve has the shape of an “U-shaped ditch” and one could say that the molecules are at the bottom of the ditch and do not like to climb on the sides of the ditch.
Figure 4.5 – Contour plot with $R_1$ (Å) on the x-axis and $R_2$ (Å) on the y-axis. Red represents high energy and blue represents low.

By using a contour PES as can be seen in Fig. 4.5, the reaction path is seen better. The plot was made using the program Matlab [11].

The reactants exist when $R_1$ is somewhere around 1,5 Å and $R_2$ is larger than 2,5 Å. The products exist when $R_1$ is larger than 2,75 Å and $R_2$ is around 0,75 Å. The transition state is somewhere around $R_1 \approx 1,5$ Å and $R_2 \approx 1,25$ Å.

In other words the reaction goes from the blue area up to the left to the dark blue area down to the right.

Two areas have been marked with a black ring. These areas do not look as smooth as expected. This indicates that more molecular configurations need to be calculated in those areas for a more accurate result.

The reason for the strange shapes might be that the computational program Gaussian09 approximates that for large distances there is no interaction between two species, this assumption sometimes leads to computational errors [17].
Figure 4.6 – Contour plot with the minimum energy path (MEP) drawn as a black line. On the x-axis is $R_1$ (Å) and on the y-axis is $R_2$ (Å). Red color represents high energy and blue represents low. The plot was made using Matlabs `imagesc` commando [24].

The reactants area is turquoise while the products area is dark blue (Fig. 4.6). The color for the area between the reactants and products (area of the transition state) is a little more yellowish than for the area of the reactants. Red color represents high energy and blue represents low energy. The picture above confirms that the reaction is going from higher to lower energy.

The minimum energy path illustrates the reaction path in one dimension. The two dimensional PES in Fig. 4.6 shows that there is a possibility to move orthogonal to the MEP. This corresponds to a vibration motion and both of the two bonds $R_1$ and $R_2$ vibrate along the minimum energy path.
4.2 The minimum energy path (MEP)

From the energy values of the 439 molecular structures (see Fig. 4.2) an interpolation surface was made (Fig. 4.3) from which the minimum energy path (Fig. 4.6) was extracted by following the interpolation surface orthogonally to the MEP and examine the first derivative when it was equals to zero. The MEP was then plotted as a first dimensional potential energy surface (Fig. 4.7). This was all done with the program Matlab [11].

![Figure 4.7](image)

The minimum energy path. The reaction path goes from reactants to the transition state to products. The energy on the y-axis is the relative energy with the products energy set as 0 eV. The relative energy for the reactants is 0.929 eV and for the TS it is 1.112 eV.

The relative energy for the products is much lower than for the reactants and the transition state. The reaction barrier is rather low compared to the the reactants, the structure of the transition state is therefore “reactant like”.

From section 3.1.1-3.1.3 and 3.2 one can note that the P-H\(^{(2)}\) bond (see Fig. 4.1) is 5.02\% longer for the TS than for the PH\(_{3}\) molecule while the H\(^{(2)}\)-H\(^{(5)}\) bond is 69.9\% longer for the TS than the H\(_{2}\) molecule. This confirms that the transition state is reactant like [23] and Fig. 4.7 probably represents the minimum energy path in a good way.

The curve is however not as smooth as expected. This is probably due to errors in the two dimensional PES. For a more accurate result more energies from different molecular configurations (see Fig 4.2) are needed.
4.3 Cumulative reaction probability

The cumulative reaction probability (Fig. 4.8) was calculated using the flux auto-correlation formalism [5] and implement in Matlab [25].

![Graph for the cumulative reaction probability.](image)

In classic mechanics the reaction probability only depends on the height of the reaction barrier and is either zero or one.

As can be seen from Figure 4.8 the reaction probability for the reaction $PH_3 + H \rightarrow TS' \rightarrow PH_2 + H_2$ is zero when the energy is far below the barrier and one when the collision energy is much higher than the height of the transition state.

In between there is a smooth transition from zero to one, due to the possibility to tunnel through the barrier, i.e. even if the energy is lower than the height of the barrier there is a chance that the reaction occur. This can be viewed as a consequence of the quantum mechanical wave-particle duality.
Chapter 5

Conclusions

All three goals set in Chapter 1 have been reached during this project.

The first goal was to theoretically analyze the exchange reaction. Literature studies were done to understand the basics of reaction dynamics and computational chemistry. In Chapter 3 geometries for the reactants and products were calculated with various methods. Also the transition state with its vibration frequency was studied. In Chapter 4 the dynamics and probability of the reaction were examined.

The second goal was to learn how to use modern computational programs for electron structure calculations. This was done both theoretically and practically. Information about quantum chemistry methods were written in Chapter 2.

In Chapter 3 geometry optimizations were performed and methods were compared. One could clearly see that methods with a longer computational time tend to give more accurate results compared to experimental values. During this project the computational programs Gaussian09 with its interface GaussView 4.1 were used to perform electron structure calculations.

The third goal was to use one and two dimensional models to describe the reaction dynamics. This was done in Chapter 4 where several diagrams, contour- and 3D-plots were created.

The knowledge obtained in this work could be used further to for example examine rate constants, spectroscopic, electronic and magnetic data for the reaction $PH_3 + H \rightarrow TS^* \rightarrow PH_2 + H_2$.

Personally this study has gained me the knowledge how to use Gaussian09 and GaussView 4.1 to perform computational chemistry. I have also gained a lot of theoretical knowledge about reaction dynamics and molecular quantum mechanics that I will have use from.

In the future I will be able to study even more complicated systems than the one examined in this project thanks to what I have learned during my months at the Department of Theoretical Chemistry at the university of Uppsala.
Acknowledgment

Först och främst vill jag tacka Nessima Salhi och Hans Karlsson. Stort tack för att jag har fått göra mitt examensarbete med er, ni har båda varit till enorm hjälp. Dem här tre månaderna har studiemässigt varit bland dem mest lärorika under hela min utbildning.

Jag vill även tacka alla på avdelningen i teoretisk kemi som hjälpt mig under projektet.

Tack till alla bra lärare jag haft under min studietid.

Ett stort tack till mina fantastiska vänner, såväl alla nya jag träffat i Uppsala till mina gamla barndomsvänner hemma i Sala (inga namn nämnda, inga glömda).

Tack till alla släktingar nere i Småland.

Tack farmor och farfar för alla trevliga samtal och god mat.

Tack mamma, pappa, Patrik och Moses, jag älskar er av hela mitt hjärta.

Tre år har gått och jag är nu klar med mitt kandidat-examensarbete i kemi. Det känns inte alls länge sen som jag slutade gymnasiyet (den där svinkalla sommardagen år 2009). När jag så började universitetet senare samma höst hade jag målet inställt:

“Jag ska plöja igenom kandidat- och masterprogrammet på fem år för att sedan direkt gå och bli doktorand, hela mitt liv kommer ägnas åt forskning och jag kommer garanterat bli professor”.

Första året ägnade jag all tid åt min utbildning och fick bara fyror och femmor i betyg, men under mitt andra år förändrades saker och ting. Jag upptäckte en liten plats kallad livet och insåg att allt inte bara är studier. Allt är inte bara meriter på ett papper eller en titel på sitt visitkort.

Det enda av verkligt värde här i livet är hur vi mår själdligen och existentiellt. Det enda av verkligt värde är hur vi förhåller oss till dem som verklig betyder något, dem vi älskar, vår familj och våra vänner.


I slutändan måste vi ändå fråga oss, spelar det verkliga någon roll vart livet leder oss?

_Det viktiga här i livet är inte våra mål. Det viktigaste är resan dit._
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[25] H. Karlsson, Department of Theoretical Chemistry at the University of Uppsala, private communication.