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Molecular properties of energetic materials and the use of quantumchemical methods for their determination

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Summary

Energetic materials find countless applications of relevance to the defence sector, as typical classes of energetic materials are propellants, explosives and fuels. To ensure safe handling of such materials, obtaining knowledge about their sensitivity to impact is crucial. In this report, quantum chemical methods are utilized to consider the problem of sensitivity from different angles. Such computational methods might complement – and even replace – practical experiments in some cases. Included topics are determination of transition states, machine learning as a quantum chemistry tool, and the desensitizing effect of amino groups in nitro-containing explosives. For the latter, two ethene derivatives as well as their anionic counterparts are explored and compared. The Gaussian 09 software is employed for density functional theory (DFT) calculations, and the parameters of interest are the dissociation energies of different C–NO₂ cleavage reactions, bond lengths, and partial charges. The results point towards Z-1-amino-2-nitroethene being less sensitive than nitroethene, due to increased conjugation by amino electron donation and perhaps increased hydrogen bonding. From the computational results related to the anions, detonation is expected to occur at lower temperatures in the cases where electric sparks may occur. The transition state geometry for nitrobenzene proposed in the literature was confirmed through a frequency calculation. Neural networks and SchNetPack (a deep learning toolbox for atomistic systems) are topics of discussion, but further work is needed in order to produce useful results.

Sammendrag

Energetiske materialer har svært mange bruksområder med relevans for forsvarssektoren, etter som både drivstoff og eksplosiver faller innenfor denne kategorien. For å sikre trygg håndtering av slike materialer er det essensielt å vite hvor sensitive de er for ulike typer påvirkning, som for eksempel slag eller temperaturforandringer. I denne rapporten blir sensitivetsproblemet sett på fra ulike vinkler ved hjelp av kvantekjemiske metoder, som kan komplettere og til en viss grad erstatte laboratorieforsøk. Viktige temaer inkluderer bestemmelse av overgangstilstander, maskinlæring som et kvantekjemisk verktøy, og aminogruppens dempende effekt på sensitiviteten til nitrobaserte eksplosiver. I sammenheng med sistnevnte ble to etenderivater, samt deres korresponderende anioner, undersøkt og sammenliknet. Programvaren Gaussian 09 benyttes for tetthetsfunksjonalteoretiske beregninger på C–NO₂-dissosiasjonsenergier, bindingslengder og partialladninger. Resultatene indikerer at Z-1-amino-2-nitroeten er mindre sensitiv enn nitroeten, grunnet økt grad av konjugasjon i systemet – og muligens hydrogenbindinger. Ut fra beregningsresultatene knyttet til anionene forventes det at detonasjon vil skje ved lavere temperaturer i de tilfellene der elektriske gnister kan forekomme. Geometrien til en overgangstilstand for nitrobenzen, identifisert i litteraturen, blir bekreftet gjennom en frekvensberegning. Nevrale nettverk og SchNetPack (en programpakke for å kunne anvende dyplæring på atomistiske systemer) blir diskutert, men videre arbeid med dette behøves for å få fram nyttige resultater

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Preface

This report provides an overview of the focus areas of my work at the Norwegian Defence Research Establishment (FFI) during the summer of 2020. The main objective of my summer internship was to get to know the work, people, and methods of the establishment in general and the energetic materials group in particular, in order to build a solid foundation for the upcoming cooperative project that will be my Master's thesis. For this reason, no concrete or isolated project was defined. The focus has rather been on exploring different options, trying different things and getting to know some of the relevant literature. This focus will be reflected in the report through its different sections and varying topics.

I would like to direct thanks to Erik Unneberg for all his help, support and understanding, to Dennis Christensen for sharing his knowledge about mathematics and machine learning and for helping out with program code that would not obey and finally to Tomas Lunde Jensen for providing relevant literature and examples and for his chemical insight. Lastly, I would like to thank the entire group of energetic materials and my office mates Jon and Emilie, for making me feel welcome and supported throughout the summer and thus making these first months at FFI an exciting and pleasurable experience.

Kjeller, 7 August 2020
Kristine Wiik

1 Introduction

Energetic materials, *i.e.* materials with high amounts of stored chemical energy that can be released [1], find countless applications of relevance to the defence sector, as typical classes of energetic materials are propellants, explosives and fuels. To ensure the safe handling of such materials, it is crucial to possess knowledge about their sensitivity to different types of impact. There exist experimental methods, *e.g.* the fallhammer test [2], designed for just this purpose. However, due to the great advancement of computer hardware and software, as well as that of quantum chemical methods like density functional theory, it is now possible to obtain a wide range of chemical information without ever stepping foot inside a laboratory. This is useful in many situations, which includes but is not limited to cases where experimental results are difficult or dangerous to obtain and cases where one would like to explore the feasibility of a new energetic material before actually attempting to synthesize it.

However widely employed, the theoretical framework of energetic materials is quite sparse, particularly when it comes to sensitivity. The detonation of an energetic material appears to be a complex, many-step process [3], depending on factors like crystal defects and local temperature. Discovering possible correlations between the impact sensitivity of an energetic material and its chemical properties, like the activation energy of a bond breaking reaction or the heat of detonation, is a work in progress. In 2020, Jensen *et al.* [4] proposed several models for the impact sensitivity, based on chemical properties like the bond dissociation energy (BDE) of the weakest molecular bond and the heat of detonation. Although some correlations were observed, more research is needed in order to achieve models with high predictive power for all relevant classes of molecules.

It is desirable to produce energetic materials with high amounts of releasable energy that are also insensitive to impact, so-called Insensitive High-Energy Explosives (IHEs). Since high energy and low sensitivity are typically contradicting concepts, this is a challenging task in practice, and it is therefore of great interest to further investigate the phenomena governing the sensitivity of this class of materials. In this report, several ways of approaching this challenge is described and somewhat explored. First, the reader will be guided through the basics of quantum chemistry. For the remaining sections, the 2020 paper by Jensen *et al.* [4] serves as a starting point and inspiration for the topics and methods described.

2 Quantum Chemistry

Although Newton's laws of motion have contributed greatly to science since they were first formulated in 1687 [5], it soon became clear that they did not tell the whole story of gravity. While the laws describe the physics of our macroscopic day-to-day activities with great accuracy,

they cease to be useful when we wish to describe microscopic systems such as molecules, atoms and elementary particles. At the atomic scale, nature is not deterministic, and classical notions like trajectories and velocities are no longer meaningful [6]. For a while, this was a mystery to physicists, and great efforts were made to build a theory, which could fill this void. This led to the birth of quantum mechanics, a theory that has proved to be astonishingly accurate and to hold high predictive power. The terms quantum mechanics, quantum physics and quantum theory are used interchangeably within the field, while quantum chemistry refers to molecular quantum mechanics. In the latter, the quantum mechanical framework is applied to problems that are chemical in nature, such as bonding in molecules, chemical reactions, formation enthalpies, and so on.

Quantum theory is, in contrast to classical physics, probabilistic in nature. Classical concepts like trajectories and velocities are discarded in favor of the more fundamental quantum state Ψ . The quantum state is a mathematical concept from which all observable information about a molecular system can be derived. This includes but is not restricted to its energy, charge distribution, dipole moment, vibrational frequencies and response to external electric or magnetic fields. Its evolution in time is described by the time-dependent Schrödinger equation,

$$\hat{H}\Psi(x, t) = i\hbar \frac{\partial \Psi}{\partial t}, \quad (2.1)$$

where \hat{H} is the energy operator (which for historical reasons is termed the Hamiltonian), \hbar is the reduced Planck's constant, and i is the imaginary unit $i^2 = -1$. Knowing that all observable information about any system can be derived from Ψ , it is perhaps not surprising that the entire field of quantum chemistry is devoted to finding ever more accurate solutions to the Schrödinger equation [6].

As for any fundamental physical theory, quantum mechanics must rely on postulates. In fact, we have already stated two of them: The first says that any system is completely specified by its quantum state Ψ , while another postulate states that Ψ 's evolution in time is described by the Schrödinger equation. A third postulate of quantum mechanics is the one-to-one correspondence of observable quantities A and linear operators \hat{A} . An example of this is the Hamiltonian \hat{H} of the Schrödinger equation, which is the operator corresponding to the energy observable. By inspection of Equation 2.1, we note that the evolution in time of Ψ is uniquely determined by \hat{H} .

Mathematically, quantum states are elements in a finite or infinite dimensional complex vector space \mathbf{H} equipped with a Hermitian inner product, which we denote as $\langle u | v \rangle$ for $u, v \in \mathbf{H}$.¹ Usually, the inner product is given by

$$\langle \Psi | \Phi \rangle = \int_{\mathcal{R}^3} \Psi \bar{\Phi} dx$$

which allows for the understanding of $\|\Psi\|^2 = \langle \Psi | \Psi \rangle$ as a probability density for square-integrable states Ψ . Since any particle must, at any point in time, be somewhere in space,

¹ We require further that \mathbf{H} must be a complete Hilbert space, meaning that (a) there exists a countable topologically dense subset of \mathbf{H} and (b) every Cauchy sequence in \mathbf{H} converges in \mathbf{H} .

integration of the probability density function for the particle's position over all space must yield unity. In fact, if a particle finds itself in the state $\Psi(x, t)$, a measurement of its position at time t will yield the value x with a probability density of $|\Psi(x, t)|^2$. The Born rule of quantum theory [7] then tells us that

$$\int_{\mathcal{R}^3} |\Psi(x, t)|^2 = 1 < \infty.$$

Now imagine an electron in some quantum state. After some time, a scientist makes a measurement of the electron's position, and the result of the measurement is the position vector x^* . Astonishingly, if the scientist repeats the measurement process for this system (after first finding x^*) one, two, or even a hundred times, the result of every measurement on this system will yield x^* . The probabilistic nature of the quantum state has simply vanished, and the Schrödinger equation no longer holds. This puzzling, and to this day poorly understood, phenomenon is known as the collapse of the wave function². Prior to the measurement, the electron could be found anywhere in its available space with some probability, and that after the measurement, this is no longer true. Unfortunately, we have no mathematical description of what happens in the moment that the measurement is made and the wave function collapse occurs. This goes to show that even though quantum theory is powerful in its ability to predict various phenomena, there are still missing pieces in our understanding of the quantum universe.

The mass of the proton is 1836 times larger than the mass of the electron [8]. As a result, the electrons move much faster than the atomic core they surround. The velocity difference is indeed so large that in the viewpoint of electrons, the nuclei are fixed. This is the basis for the Born-Oppenheimer [8] approximation, where it is assumed that the state of the electrons can be determined at fixed nuclear coordinates. When the time dependency of the quantum state is solely provided through a phase factor, which is the case for time independent Hamiltonians [9], the Born-Oppenheimer approximation reduces the Schrödinger equation to the eigenvalue equation

$$\hat{H}\psi_n(\mathbf{r}) = E_n\psi_n(\mathbf{r}), \quad (2.2)$$

where \mathbf{r} denotes the collection of electron coordinates, and ψ_n only differs from Ψ_n by omitting the phase factor. To highlight the fact that the wave function ψ_n depends parametrically on the nuclear coordinates \mathbf{R} , we may write Equation 2.2 as $\hat{H}\psi_n(\mathbf{r}; \mathbf{R}) = E_n(\mathbf{R})\psi_n(\mathbf{r}; \mathbf{R})$. This dependence clarifies [6] the term potential energy surface (PES) given to the electronic energies $E_n(\mathbf{R})$. Let us take the hydrogen molecule, H_2 , as an example. The geometry of this diatomic molecule can be described by a single quantity: the bond length R . By calculating the energy of the molecule at different values of R , one may plot the energy versus R in a one-dimensional graph, so in this case the PES is one-dimensional. For larger molecules, there are several geometric parameters, giving the PES higher dimension which makes it harder to visualize. However, the PES is often thought about as a landscape, with its associated hills and valleys [10]. The geometries at which a molecule is stable corresponds to the minima of its PES, and are called equilibrium geometries.

² Several equivalent formulations exist for quantum mechanics. First came Heisenberg's formulation, in which vectors represent quantum states and operators are represented by matrices. Later came Schrödinger's version, where the quantum states are represented as mathematical functions called wave functions.

In geometry optimization processes, such minima are located through minimization of the energy with respect to the nuclear coordinates.

Equation 2.2 is known as the time independent Schrödinger equation, and is solved for a fixed set of nuclear coordinates \mathbf{R} . The wave functions ψ_n correspond to the states available to the system defined by the Hamiltonian \hat{H} having fixed energy E_n .

In quantum chemistry, we are concerned with the properties of molecules, chemical bonds and reactions. Since a molecule consists of several atoms, which again contain several quantum particles like protons and electrons, the wave function of a molecule describes a many-body system. As it turns out, increasing the number of electrons of our system make calculations drastically more complex. Many-body quantum theory is anything but trivial, and a great number of simplifications are needed in order to find an approximation of the wave function, from which molecular properties may be determined.

Electrons are in principle indistinguishable. This means that for a system containing two electrons, there is no difference between (a) electron 1 in ψ_1 , electron 2 in ψ_2 and (b) electron 1 in ψ_2 , electron 2 in ψ_1 . Consequently, the two systems have the same probability of detection, such that $|\psi(\mathbf{r}_1, \mathbf{r}_2)|^2 = |\psi(\mathbf{r}_2, \mathbf{r}_1)|^2$, where \mathbf{r}_1 and \mathbf{r}_2 represent the coordinates of electrons 1 and 2, respectively, and the first and second position of the parameters refer to ψ_1 and ψ_2 , respectively. This concept expands to systems of larger number of electrons – any permutation of electrons will yield the same probability of detection – and we say that the probability of detection is invariant under permutation of particles.

It is well known that electrons obey the Pauli principle, which dictates that at any moment in time, two electrons of equal spin cannot occupy the same spatial state. In fact, all half-spin particles, known as fermions, possess this quality, while integer-spin particles, bosons, do not. The fact that two electrons cannot occupy the same state at the same time, such that they in some sense avoid each other, is termed Pauli repulsion. It is, however, important to note that this is purely a quantum effect and it has nothing to do with Coulombic repulsion. As a consequence of the Pauli principle, the wave function of an electronic system must change sign when two electrons are swapped. In other words, the total wave function of any electronic system must be antisymmetric.

To a large extent, modern quantum chemistry owes its success to the impressive accuracy of Hartree-Fock theory. In this framework, the antisymmetry of the electronic wave function is achieved using a so-called Slater determinant:

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \bar{\varphi}_1(\mathbf{r}_1) & \bar{\varphi}_1(\mathbf{r}_2) & \cdots & \bar{\varphi}_1(\mathbf{r}_N) \\ \bar{\varphi}_2(\mathbf{r}_1) & \bar{\varphi}_2(\mathbf{r}_2) & \cdots & \bar{\varphi}_2(\mathbf{r}_N) \\ \vdots & \ddots & \ddots & \vdots \\ \bar{\varphi}_N(\mathbf{r}_1) & \bar{\varphi}_N(\mathbf{r}_2) & \cdots & \bar{\varphi}_N(\mathbf{r}_N) \end{vmatrix} \quad (2.3)$$

In the above, $\bar{\varphi}_i(\mathbf{r})$ are *spinorbitals* defined by

$$\bar{\varphi}_i(\mathbf{r}) = \varphi_i(\mathbf{x})\sigma(s) \quad (2.4)$$

where $\varphi_i(\mathbf{x})$ is the molecular orbital (spatial function) and $\sigma(s)$ is the spin function. The molecular orbitals are expanded in a set of atomic orbitals,

$$\varphi_i(\mathbf{x}) = \sum_{\mu} c_{\mu i} \chi_{\mu}(\mathbf{x}) \quad (2.5)$$

where the atomic orbitals χ_{μ} are known functions that are normalized but not necessarily orthogonal. The expansion coefficients $c_{\mu i}$ are determined according to the variational principle. The variational theorem tells us that for any approximate wave function ψ^{trial} the expectation value for its energy satisfies

$$\inf(\xi) \leq \frac{\langle \psi^{trial} | \hat{H} | \psi^{trial} \rangle}{\langle \psi^{trial} | \psi^{trial} \rangle} \leq \sup(\xi) \quad (2.6)$$

where ξ is the energy spectrum of the true wave function ψ , *i.e.* it is the set of energy eigenvalues satisfying Equation 2.2 for some molecular geometry. The denominator of Equation 2.6 is a normalization factor, which equals unity in the case of a normalized trial function. In Equation 2.6 the terms “inf” and “sup” refers to the minimum and maximum value of the eigenvalue set, respectively. The most important implication of the variational theorem is that, when we are concerned with finding the energy of a system’s ground state, our computational results are upper bounds of the true energy. In other words, we have a way of comparing different ground state trial wave function: Whichever gives the lowest energy is the best choice.

Minimization under the constraints that both the total wave function ψ and the molecular orbitals φ should be normalized yields a set of implicit equations which must be solved iteratively. The solution is termed the Hartree-Fock wave function and is the lowest energy Slater determinant we can possibly construct with our choice of basis.

Beginning with a set of M spinorbitals φ_i , where $i = 1, 2, \dots, N, \dots, M$, we may construct all possible N -electron Slater determinants of the form of Equation 2.3. The span of these determinants forms a subspace of \mathbf{H} called the *Fock space*. Over the years, several wave function methods have descended from the Hartree-Fock theory. In these methods, approximations of the Schrödinger equation are solved by expanding the wave function ψ in terms of certain subsets of the Fock space. Examples of this can be found in the impressively accurate, but expensive, hierarchy of coupled cluster theories [11, 12].

A great deal of the *ab initio* methods of quantum chemistry are so-called post-Hartree-Fock methods. These are methods in which the Hartree-Fock wave function is calculated, followed by a series of steps to improve the solution by adding the effects of *electron correlation*. Electron correlation was defined by Löwdin in 1959 [13], somewhat arbitrarily, as “what is not covered by Hartree-Fock”, such that

$$E_{corr} = E - E_{HF} \quad (2.7)$$

where E_{corr} is the electron correlation energy, E is the true energy and E_{HF} is the Hartree-Fock energy. We may note that E_{corr} is a negative quantity, since $E_{HF} > E$ according to the variational principle. Hartree-Fock theory is what we call a mean field theory, meaning that any one electron only interacts with the mean electrostatic field provided by the other electrons. In reality, each pair of electrons interact and instantaneously adjust to each other, meaning that their motion is correlated. As previously mentioned, a Slater determinant contains what we may refer to as Pauli repulsion, exchange correlation or Fermi correlation (a dear child has many names) that describe the correlation of electrons of the same spin that is preventing them from occupying the same spatial orbital. This type of interaction is therefore, by Löwdin's definition, not electron correlation. Now, electrons of any spin will repel each other due to the fact that they all have the same charge, via the Coulomb repulsion. Since the Hartree-Fock method does not take this into account, the Hartree-Fock wave function reflects a situation where the electrons are – on average – too close to each other. This in turns lead to energies that are too high (ref. the variational principle). Thus, the aim of post-Hartree-Fock methods is to lower E_{HF} by accounting for electron correlation in various ways. An example of such a method is perturbation theory.

Although many of the *ab initio* methods can provide extremely accurate results for small systems, they can quickly become infeasible when the system size in-creases. It should be mentioned that the progress of computer science and the methods themselves have improved the situation a whole lot. However, it is definitely still relevant for systems above a certain size. Optimally, one would like to combine great accuracy with low computational cost. This was probably the greatest motivation for the construction of density functional theory (DFT) where the complicated many-electron wave function is substituted by the much simpler electron density $\rho(\mathbf{r})$. It was truly a remarkable discovery that the wave function is, in a certain sense, redundant - it tells you more than you need to know. Although attempts to use the electron density instead of the wave function for obtaining molecular information date all the way back to the works of Thomas and Fermi in 1927 [14], DFT as we know it today was born in 1964 by the efforts of Hohenberg and Kohn [13]. The first and second Hohenberg-Kohn theorems state that

1. the electron density $\rho(\mathbf{r})$ uniquely determines the Hamiltonian and thus all properties of the system.
2. the variational theorem also holds for functionals of the electron density. In other words, the functional that delivers the ground state energy of the system, delivers the lowest energy if and only if the input density is the true ground state density, ρ_0 [13].

The term functional refers to a function that takes another function as its input and returns a scalar as its output. In the context of DFT, the input function is always some electron density $\rho(\mathbf{r})$. The pursuit of the unknown - but undoubtedly existent, according to the first Hohenberg-Kohn theorem - functional relationship $E = E[\rho(\mathbf{r})]$ is the main objective in DFT. Everything we could possibly wish to know about our system may be derived from this relation, analogous to the Schrödinger equation in wave function theory.

To a first approximation, we can write $E = E[\rho(\mathbf{r})]$ as the sum

$$E[\rho(\mathbf{r})] = T[\rho(\mathbf{r})] + \bar{V}_{e-n}[\rho(\mathbf{r})] + \bar{V}_{e-e}[\rho(\mathbf{r})], \quad (2.8)$$

where T is the kinetic energy of hypothetical non-interacting electrons, \bar{V}_{e-n} is the average interaction of the electrons and the nuclei, and \bar{V}_{e-e} is the average interaction of electrons with other electrons. All of these terms are obtained without difficulty, and it seems that whatever is not covered by Equation 2.8 must be small. Note that, due to the fact that the only electron-electron interaction present in Equation 2.8 is the average interaction \bar{V}_{e-e} , it is fair to assume that electron correlation effects are missing. In fact, in contrast to the Hartree-Fock theory, the antisymmetry of the electronic quantum state is not readily taken care of in the first approximation above, meaning that the exchange energy is also missing. Consequently, the remaining part of $E[\rho(\mathbf{r})]$ has been termed the exchange-correlation functional and is denoted $E_{xc}[\rho(\mathbf{r})]$.

It turns out that while proving the existence of the exact exchange-correlation functional is a relatively easy task, finding its form is not. In fact, with no agreed upon or systematic procedure to identify this functional, a great number of approximations have been proposed. Their accuracies are often quite dependent on the class of molecules on which they are employed. It is worth mentioning that, since the functionals of Equation 2.8 are easily obtained, they are not too interesting to us, and it is therefore customary to simply refer to the approximative exchange-correlation functionals as functionals. For simplicity, the term functional will be used exclusively in this way in the remainder of this report.

Most functionals are so-called local density approximations (LDAs) or generalized gradient approximations (GGAs) [15], where

$$\begin{aligned} E_{xc}^{LDA}[\rho(\mathbf{r})] &= \int f[\rho(\mathbf{r})] d\mathbf{r} \\ E_{xc}^{GGA}[\rho(\mathbf{r})] &= \int f[\rho(\mathbf{r}), \nabla\rho(\mathbf{r})] d\mathbf{r} \end{aligned} \quad (2.9)$$

In addition, there are hybrid functionals, which are linear combinations of other functionals. These hybrids are constructed by mixing in a fraction of exact HartreeFock exchange with conventional DFT exchange-correlation functionals [16]. A popular example is the B3LYP [17,18] functional, which combines Hartree-Fock exchange with an LDA and two GGAs [19].

In order to employ the electron density $\rho(\mathbf{r})$ for calculations, we must determine its form. This is typically achieved through the approach of Kohn and Sham [20], who wrote $\rho(\mathbf{r})$ as

$$\rho_{KS}(\mathbf{r}) = \sum_i |\varphi_i(\mathbf{r})|^2, \quad (2.10)$$

i.e. as the density of a single Slater determinant. From this, the ground state energy is minimized by varying the spinorbitals $\varphi_i(\mathbf{r})$. The resulting equations are termed the *Kohn-Sham equations*, and are solved iteratively for the electron density [10,21].

Recalling the discussion on the Born-Oppenheimer approximation, the reader has probably noted that we have yet to discuss the part of the wave function describing the nuclei. Mathematically, the decoupling of electronic motion from that of the nuclei is understood in terms of the product-form wave function $\psi(\mathbf{r}, \mathbf{R}) = \psi_{nuc}(\mathbf{R})\psi_{el}(\mathbf{r}, \mathbf{R})$. At any temperature above absolute zero, the nuclei takes on three different types of motion as they vibrate, rotate and translate in three-dimensional space. To a first approximation, these modes of motion are taken to be independent. This results in a further decoupling, such that

$$\psi_{nuc}(\mathbf{R}) = \psi_{trans}(\mathbf{R}_{cm})\psi_{rot}(\alpha, \beta, \gamma)\psi_{vib}(Q_1, \dots, Q_{3N-6}), \quad (2.11)$$

where \mathbf{R}_{cm} is the coordinate of the center of mass, α , β and γ are the angles describing the molecule's orientation, and Q_1, \dots, Q_{3N-6} are so-called normal mode coordinates. Note that variation of a single normal mode corresponds to a vibration of the entire molecule. In quantum chemical frequency calculations the frequency of the normal modes are determined, as well as their intensities. A truly remarkable quantum effect is that, even at zero temperature, molecules vibrate. The energy corresponding to this motion is termed the zero point energy.

3 Determination of Transition States

In the context of chemistry, a transition state corresponds to a local or global maximum of the PES, which connects two equilibrium structures through a reaction path. Such states or structures are highly unstable. In other words, one would not find a molecule in one of its transition states for an extended period of time. Rather, the molecule would follow the reaction path, along one direction or the other, until it stabilizes at one of the two equilibrium structures that the transition state connects.

Transition states and activation energies are two closely connected concepts. The activation energy E_a of a chemical reaction is defined as the difference between the transition state energy and the energy of the reactant(s),

$$E_a = E(\text{Transition state}) - E(\text{Reactants}), \quad (3.1)$$

and therefore represents the energy barrier the reactants must overcome to form the products. This transition includes the breaking of at least one molecular bond, and sometimes also the creation of new molecular bonds. Transition states must not be confused with intermediates, which are stable states corresponding to local minima on the potential energy surface.

Since transition states correspond to stationary points on the potential energy surface, such states can be located by the use of the optimization feature in Gaussian [22]. Since transition states are

characterized by exactly one imaginary frequency, a frequency job on the optimized geometry provides a simple way to confirm that the optimization has indeed converged to a transition state.

It is important to note that even in the case of a successful transition state optimization, one needs to make sure that the calculation has converged to the desired transition state, *i.e.* that which connects the reactants and products of interest. One might begin the investigation by examining the normal mode corresponding to the imaginary frequency, and from this determine whether or not the motion tends to deform the transition structure as expected. If this is too hard to tell for certain (which is often the case), one can dig deeper into the problem by running an intrinsic reaction coordinate (IRC) calculation. Such a calculation starts at the saddle point and proceeds by following the reaction path in both directions, optimizing the geometry of the system at each point along the path [22]. Even though the IRC calculation usually will not proceed all the way to the reactant and product states, one can usually tell what kind of structure the system *tends to* in both ends, and from this determine whether or not the obtained transition structure was the desired one.

No matter how straightforward it might sound, finding a desired transition structure directly by specifying a reasonable guess for its geometry can be challenging in many cases. In the following, an example of such a case will be discussed.

Initially, the intention of my work was to locate as many transition states as the time frame would allow for the bond breaking processes described by Jensen *et al.* [4]. The main objective of this task was to obtain the activation energies for the C–NO₂ homolytic cleavage reaction for the molecules and investigate whether this would improve the correlations described in [4]. However, this proved to be a challenging task. Even after some good hours of struggling to find a good enough starting geometry, the molecule would simply bounce back to an equilibrium structure. Solace was found in the 2019 paper by Nikolaeva *et al.* [23]. By performing a great amount of DFT calculations on nitrobenzene, they discovered that at the B3LYP level of theory using the 6-31G(d,p) basis set, a minimum of the electronic energy with respect to the C–NO₂ bond length could simply not be found. They were, however, able to locate the transition state of the C–NO₂ homolytic cleavage reaction by a method utilizing the Gibbs energy.

To confirm the findings of Nikolaeva *et al.* [23], a frequency calculation was performed for their reported molecular geometry of the transition state. The calculation was performed using B3LYP with the 6-311G(d,p) basis set, and exactly one imaginary frequency was found, showing that the proposed structure indeed corresponds to a transition state. Due to the short time frame and the complexity of the problem, a decision was made to let the transition state search related to the Jensen *et al.* paper [4] rest for a while, in favor of other projects.

4 Amino Group Desensitization of Nitro Based Explosives

4.1 Introduction

In the field of explosives, it is desired to create substances of high energy density that is simultaneously insensitive to various types of impact. Such materials are termed insensitive high explosives (IHEs).

Since there is usually a contradiction between increasing energy densities and reducing sensitivity, creating new IHEs is in practice a challenging task. The computational results of Cao *et al.* [24] indicate that amino groups are conditionally advantageous to IHEs in the sense that the presence of amino groups can lower the sensitivity of certain types of nitro based explosives, while for other types it offers no improvement. In particular, amino groups were found to be advantageous in nitroaromatic explosives, as well as for conjugated systems like nitro derivatives of ethene and ethyne. However, for unconjugated systems, they found no improvement on detonation performance or sensitivity by the introduction of amino groups. In fact, some of the molecules turned out to be less stable after the amino enrichment.

Due to the importance of safety and control in the context of high-energy explosives and the resulting strong desire to create new IHEs, it is of great interest to investigate the phenomenon of amino group desensitization in conjugated systems. In this section, two nitro derivatives of ethene will be explored and compared. The goal is not to produce high quality predictions of molecular properties, but rather to get a better qualitative understanding of the amino group's desensitizing effect in nitro explosives.

4.2 Theory and Methods

The Gaussian 09 software [25] is employed for DFT calculations. The chosen ethene derivatives are 1-amino-2-nitroethene (compound **1**) and nitroethene (compound **2**) as shown by their structural formulas in Figure 4.1.

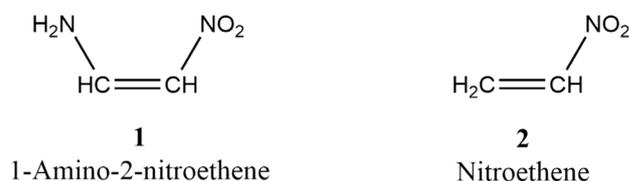


Figure 4.1 The chosen molecules for the exploration of amino group desensitization in nitro explosives. Compound **1**: Z-1-amino-2-nitroethene. Compound **2**: nitroethene.

Working with ethene derivatives, as opposed to nitroaromatics, keeps the computational cost low. Additionally, due to the molecules' similarity to the IHE 1,1-diamino-2,2-dinitroethene, also

known as FOX-7 [26] or DADNE [27], ethene derivatives are in themselves interesting in the context of IHEs. Nevertheless, the *cis* forms of the molecules were chosen to maximize the similarity to nitroaromatics. A small basis set, namely the correlation-consistent polarized basis set cc-pVDZ [28], was used for all calculations. As was DFT, with the Minnesota [29] global hybrid exchange-correlation functional M06-2X [30]. This functional contains 54 % Hartree-Fock exchange, and has been found to perform better [31–34] than the popular B3LYP functional for a range of organic molecules and reactions, as well as to yield results of similar accuracy to higher level methods in certain cases [35].

The sensitivity of each compound is assessed based on molecular stability. The properties of interest are the bond dissociation energies BDEs and bond lengths of the assumed weakest bond. This choice of sensitivity parameters is somewhat inspired by the work of Cao *et al.* [24]. Additionally, Zhang *et al.* [36] have showed a correlation between nitro group charges and impact sensitivities, and because of this, the partial atomic charges of the nitro groups will also be considered. The methodology of Zhang *et al.* will be followed, such that the nitro group net charge Q_{NO_2} will be calculated as

$$Q_{NO_2} = Q_N + Q_{O1} + Q_{O2} \quad (4.1)$$

where Q_i is the Mulliken charge of atom *i*. Additionally, a full natural bond orbital [37] (NBO) analysis will be performed to obtain the atomic charges since this method is known to be less basis set dependent than the Mulliken population analysis [38].

NBO analysis stresses the role intermolecular orbital interaction. The analysis is carried out by considering all possible interactions between filled donor and empty acceptor NBOs, and then estimating their energetic importance by second-order perturbation theory [39]. The interaction energy $E^{(2)}$ is calculated for each donor NBO *i* and acceptor NBO *j* as

$$E^{(2)} = q_i \frac{(F_{ij})^2}{\epsilon_j - \epsilon_i}, \quad (4.2)$$

where q_i is the orbital occupancy, ϵ_i and ϵ_j are diagonal elements of the Fock matrix, and F_{ij} is an off-diagonal element of the Fock matrix. The NBOs are classified as either core (Cor), valence (Val) or Rydberg (Ry) orbitals, and specified as either bonding (BD), antibonding (BD*) or lone pair (LP).

According to the trigger linkage hypothesis, the first step in the initiation of an energetic molecule is a bond cleavage [4]. For covalent nitro-containing compounds the X–NO₂ bond is usually the weakest bond in the molecule [3,36], and this particular bond will therefore be at the center of attention in this section.

Figures 4.2, 4.3 and 4.4 show the different bond breaking processes that will be considered. Compounds **3** and **4** are the anionic radical versions of compounds **1** and **2**, respectively, and are included due to the interesting findings by Pruitt and Goebbert [40]. Through spectroscopic measurements, they showed that the dissociation energies associated with nitrite removal from some anionic nitroaromatics were lower than those associated with the homolytic cleavage of the

C–NO₂ bond of the corresponding neutral molecules. Note that the term *bond dissociation energy* by definition refers to the homolytic cleavage reaction, and that the energies associated with the other bond breaking processes will go under the term dissociation energies (*D*s). The role of anions in decomposition reactions is assumed to be limited to special cases, such as in electric detonation, but it is still an interesting and perhaps less explored object of investigation.

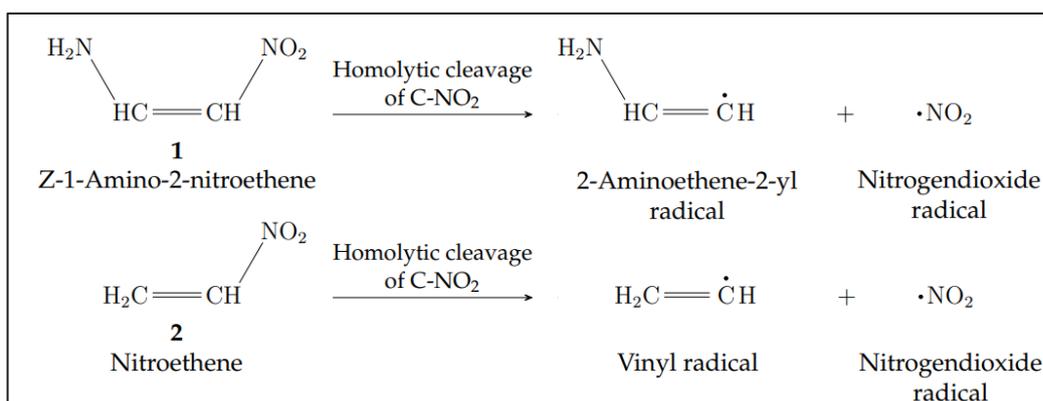


Figure 4.2 Homolytic cleavage of the C–NO₂ bond of compounds **1** and **2**.

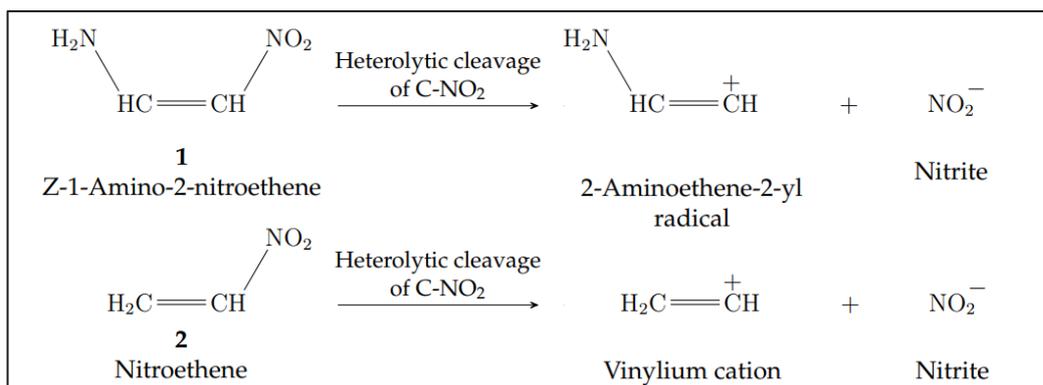


Figure 4.3 Heterolytic cleavage of the C–NO₂ bond of compounds **1** and **2**.

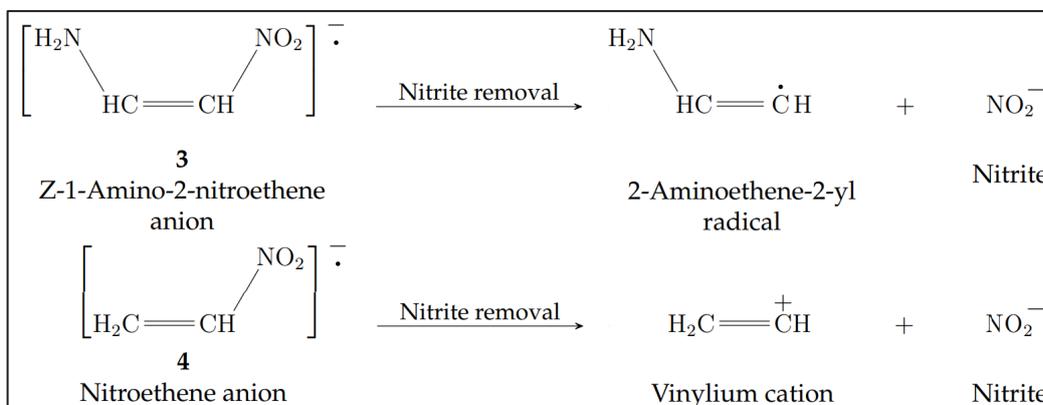


Figure 4.4 Removal of nitrite from compounds **3** and **4**.

The BDEs will be calculated according to the method in [22]. For the reaction $AB \rightarrow A + B$, the BDE is thus given by

$$BDE = E(A) + E(B) - E(AB), \quad (4.3)$$

where $E(i)$ is the ground state electronic energy of compound i at a given temperature, including the zero point energy and thermal corrections. The dissociation energies for the heterolytic cleavage reactions and the anionic nitrite removals will be determined in the same way.

4.3 Results and Discussion

4.3.1 Homolytic Cleavage of the C–NO₂ Bond

As can be observed in Table 4.1, the C–NO₂ BDE is found to be around 55 kJ mol⁻¹ larger for compound **1** than for compound **2** at both 0 and 298.15 K. This indicates a higher stability, and thus a lower sensitivity, for compound **1**. We may also observe that the BDE of the homolytic cleavage reaction decreases slightly as the temperature increases from 0 to 298.15 K.

Table 4.1 The C–NO₂ BDEs for Z-1-amino-2-nitroethene and nitroethene, calculated with Gaussian 09 using the M06-2X functional and the cc-pVDZ basis set at T = 298.15 K.

Compound	BDE(C–NO ₂) [kJ mol ⁻¹]	
	T = 0 K	T = 298.15 K
1	361.830657	356.663673
2	306.017778	301.916747

4.3.2 Heterolytic Cleavage of the C–NO₂ Bond

It is clear from Table 4.2 that the calculated dissociation energies for the heterolytic cleavage are significantly higher than the BDEs for the homolytic cleavage discussed above. Additionally, the dissociation energy associated with compound **2** is found to be significantly higher than that associated with compound **1**. In other words, it requires more energy to break the C–NO₂ bond of nitroethene heterolytically than to break the corresponding bond in Z-1-amino-2-nitroethene in this manner. We may also note that as the temperature increases, so do the dissociation energies.

Table 4.2 The C-NO₂ heterolytic dissociation energies for Z-1-amino-2-nitroethene and nitroethene, calculated with Gaussian 09 using the M06-2X functional and the cc-pVDZ basis set at T = 298.15 K.

Compound	D(C-NO ₂) [kJ mol ⁻¹]	
	T = 0 K	T = 298.15 K
1	779.374424	782.073438
2	994.8570855	999.769396

4.3.3 Removal of Nitrite from the Anionic Compounds

Table 4.3 shows the calculated dissociation energies associated with the removal of nitrite from the anionic compounds **3** and **4**. The results indicate that for this bond breaking process, as for the homolytic cleavage reaction, compound **1** appears to be the most stable. The dissociation energies are found to be smaller than for both of the previously discussed reactions. Consequently, under conditions at which the anionic compounds **3** and **4** may be created, e.g. the occurrence of an electric spark, one would expect the material to detonate at lower temperatures.

Table 4.3 The C-NO₂ dissociation energies for Z-1-amino-2-nitroethene anion and nitroethene anion, calculated with Gaussian 09 using the M06-2X functional and the cc-pVDZ basis set at T = 298.15 K.

Compound	D(C-NO ₂) [kJ mol ⁻¹]	
	T = 0 K	T = 298.15 K
3	221.274514	223.655843
4	213.096082	216.4645985

4.3.4 Bond Lengths

Table 4.4 displays the calculated length of the C-NO₂ bond for the compounds **1**, **2**, **3** and **4** in their optimized geometries. For the neutral compounds, we observe that compound **1** has the shortest C-NO₂ bond length. Given the hypothesis that the C-NO₂ bond is the weakest bond in each molecule, this indicates that compound **1** is more stable than compound **2**. In other words, the calculated bond lengths are in agreement with the BDE results.

Table 4.4 The C-NO₂ bond lengths of compounds **1**, **2**, **3** and **4**, calculated with Gaussian 09 using the M06-2X functional and the cc-pVDZ basis set.

Compound	C-NO ₂ bond length [Å]
1	1.42196
2	1.47080
3	1.37699
4	1.37702

For the anionic compounds, we observe the same trend, although the difference in bond lengths of compounds **3** and **4** is an order of magnitude smaller than that of compounds **1** and **2**. We also note that the bond lengths of the anions are shorter than those of their neutral counterparts.

4.3.5 Partial Atomic Charges

Using the Gaussian 09 software, a Mulliken population analysis as well as a full NBO population analysis was performed on compounds **1** and **2**. Tables 4.5 and 4.6 show the calculated Mulliken and NBO atomic charges, respectively. Both the atomic charges and net charge of the nitro groups are shown. Despite the procedural differences of the two methods, they seem to agree upon the net charge of the nitro groups of compounds **1** and **2**. The nitro groups are electron withdrawing and are therefore expected to constitute a negatively charged part of each of the compounds. Furthermore, the nitro group of compound **1** is found to have a more negative net charge than that of compound **2**. Zhang *et al.* found that the larger the value of $-Q_{NO_2}$, the less sensitivity the compound [36]. Compound **1** should therefore be the less sensitive of the two, coinciding with the interpretation of the dissociation energy results above.

Table 4.5 The Mulliken charges of the nitro group atoms and the total net charge of the nitro group for the compounds Z-1-amino-2-nitroethene and nitroethene. All quantities are given in atomic units.

Compound	Q_N^M	$Q_{O_1}^M$	$Q_{O_2}^M$	$Q_{NO_2}^M$
1	0.244	-0.342	-0.276	-0.378
2	0.234	-0.263	-0.254	-0.283

Table 4.6 The NBO charges of the nitro group atoms and the total net charge of the nitro group for the compounds Z-1-amino-2-nitroethene and nitroethene. All quantities are given in atomic units.

Compound	Q_N^{NBO}	$Q_{O_1}^{NBO}$	$Q_{O_2}^{NBO}$	$Q_{NO_2}^{NBO}$
1	0.517	-0.487	-0.404	-0.374
2	0.500	-0.409	-0.377	-0.286

In addition to providing partial atomic charges, the NBO can provide some understanding of how well the Lewis structure of a molecule coincides with the true structure. The term “true” in this sense refers to the approximate electronic structure found by the quantum chemical method one has chosen to employ. As explained above, the NBO procedure is based on localized orbitals, but through second order perturbation theory, interactions between the different orbitals are accounted for. Thus, the adjustments to the total energy are provided in form of $E^{(2)}$ values. The larger the $E^{(2)}$ values, the greater the delocalization of electrons, and thus the greater is also the stabilizing effect.

Table 4.7 shows the largest $E^{(2)}$ values for compounds **1** and **2** found by NBO analysis. The table is set up so that the interactions present in both compounds are found in the same row, so that half-filled rows indicate that the interaction is only present in one of the compounds. The interaction that is only present in compound **1** is the delocalization of electrons from the lone pair on the amino group’s nitrogen atom to the antibonding orbital of the carbon-carbon double bond. The $E^{(2)}$ value associated with this interaction is large. In fact, it is so large that it more than makes up for the energy difference of the strongest interaction between the two molecules, such that when we look at the sums of $E^{(2)}$ values for the two molecules, the largest is that of compound 1. Beside the two first rows of the table, the interaction energies do not differ by significant amounts in the two molecules.

Table 4.7 Results of the second order perturbation calculation performed in the NBO analysis. LP: lone pair orbital, BD: bonding orbital, BD*: antibonding orbital. Each row corresponds to a particular interaction, such that the half-filled row signifies an interaction only present in compound 1. N1 is the nitro group nitrogen and N2 is the amino group nitrogen. The energies are given in the unit kJ mol^{-1} .

Compound 1			Compound 2		
Donor	Acceptor	$E^{(2)}$	Donor	Acceptor	$E^{(2)}$
LP O1	BD* N1 - O2	731.3	LP O1	BD* N1 - O2	876.4
LP N2	BD* C1 - C2	335.64			
BD C1-C2	BD* N1-O2	132.80	BD C1-C2	BD* N1 - O2	94.81
LP O2	BD* N1 - O1	101.29	LP O2	BD* N1 - O1	98.16

The amino group NH_2 is electron donating, and this is reflected in the results discussed above. The delocalization brought on by the amino group increases the conjugation and promotes stability of compound 1, while compound 2 does not experience this stabilization. Based on the delocalization-conjugation-stabilization link mentioned above, one would expect compound 1 to be more stable than compound 2. However, one should probably tread carefully when it comes to drawing conclusions directly from results found through population analysis. One must recall that partial atomic charges cannot be measured and that all schemes made to assign such charges are essentially arbitrary. That said, in the literature, resonance is often used to explain stability. In their moderately comprehensive review of FOX-7, Trzciński and Belaada [27] stated “the stabilizing effect of hydrogen bonding and resonance effects cause FOX-7 to be one of the less sensitive explosives”. Although a thorough analysis on hydrogen bonding has not been included in this work, it is a fact that replacing a hydrogen atom with an amino group yields a molecule with both a) a larger number of hydrogen atoms, and b) hydrogen atoms that would be expected to have a larger positive partial charge due to differences in electro negativity. Thus, increased hydrogen bonding may also be a relevant stabilizing effect helping to make compound 1 more stable – and less sensitive – than compound 2.

4.4 Conclusions

Out of the compounds 1 and 2, the former was found to have the highest BDE and the shortest bond length for the C–NO₂ bond, as well as the most negatively charged nitro group. These results all point toward compound 1 being the most stable - and thus least sensitive - of the two. The NBO results suggest that the presence of the amino group leads to increased electron delocalization and thus a higher degree of conjugation in the system. Increased hydrogen bonding may be another important stabilizing effect. The calculated dissociation energies of the heterolytic cleavage of compounds 1 and 2 were found to be significantly higher than those of the homolytic

cleavage. Additionally, they seem to correlate positively with temperature, while the correlation is negative for the homolytic BDEs. This indicates that the hemolytic cleavage is the dominating reaction of the two at most temperatures. For the anionic compounds **3** and **4**, the dissociation energies were found to be lower than for both of the aforementioned processes. Thus, one would expect a lower detonation temperature for the cases where an electric spark occurs.

5 Machine Learning as a Quantum Chemistry Tool

Machine learning (ML) is a branch of artificial intelligence (AI) in which the computers learn the ability to find patterns in large data sets through the use of statistical methods. Arthur Samuel, who popularized the term machine learning in 1959 [41], defined it as field of study that gives computers the ability to learn without being explicitly programmed. The usefulness of ML cannot be overstated, and its applications stretch over a wide range of fields, affecting both our personal and professional lives.

Typically, a computer learns patterns from existing data and is then supplied with new data from which it makes predictions. The learning procedure is often referred to as training [42]. However useful ML has been since its birth in the 1950s, it was only applied to the quantum/computational chemistry field in the early 2010s [43–47]. The problem with scaling of quantum chemical methods has been a long-standing challenge. As the systems of interest grow in size and complexity, the computational cost increases drastically, and expensive supercomputers must often be employed in order to get reasonably accurate results in a reasonable amount of time. During the last couple of years, the possible applications of ML to molecular systems have gained traction. Once a predictive ML model is trained, it can make instantaneous predictions. Thus, if the training data set is, by some measure, good enough, the computational cost of predicting molecular properties could be lowered drastically.

In 2017, Schütt *et al.* [48] presented a deep-trained neural network (DTNN) capable of predicting the molecular energies of a substantial number of organic compounds. As an example of chemical relevance, they reported the predicted energies of several aromatic compounds and linked this to the relative ring stability. The mean absolute error of the DTNN was 1.0 kcal mol⁻¹, for both data sets for which the model was trained. In other words, this was a much promising result with regard to the challenge of reducing computational cost. Schütt *et al.* also showed that their DTNN could also provide an accurate molecular mechanics trajectory for toluene.

Building upon the principles of the previously described DTNN, the artificial neural network SchNet was proposed in 2018 as an improved neural network architecture for learning representations for materials and molecules [49]. SchNet is a continuous-filter convolutional neural network. It is available for download and use through the SchNetPack Python library [50], and offers several trained models ready for use as well as the tools needed to train new ones.

Amongst other utilities, SchNet can be employed to predict the energies, dipole moments and polarizabilities of different molecules, to create molecular dynamics trajectories and to create plots of local chemical potential.

The original plan for this section was to devote it to the discussions of local chemical potential isosurface plots produced using SchNetPack. Unfortunately, due to the limited time frame and my lack of experience within this field, producing such plots was not possible. However, I hope that it can serve as a great supplementary tool for the research establishment in the future. Even though more work is needed in order to obtain the aforementioned desired results, I believe that the time invested in experimentation, testing and error handling over this summer will pay off in terms of increased knowledge and experience.

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About FFI

The Norwegian Defence Research Establishment (FFI) was founded 11th of April 1946. It is organised as an administrative agency subordinate to the Ministry of Defence.

FFI's mission

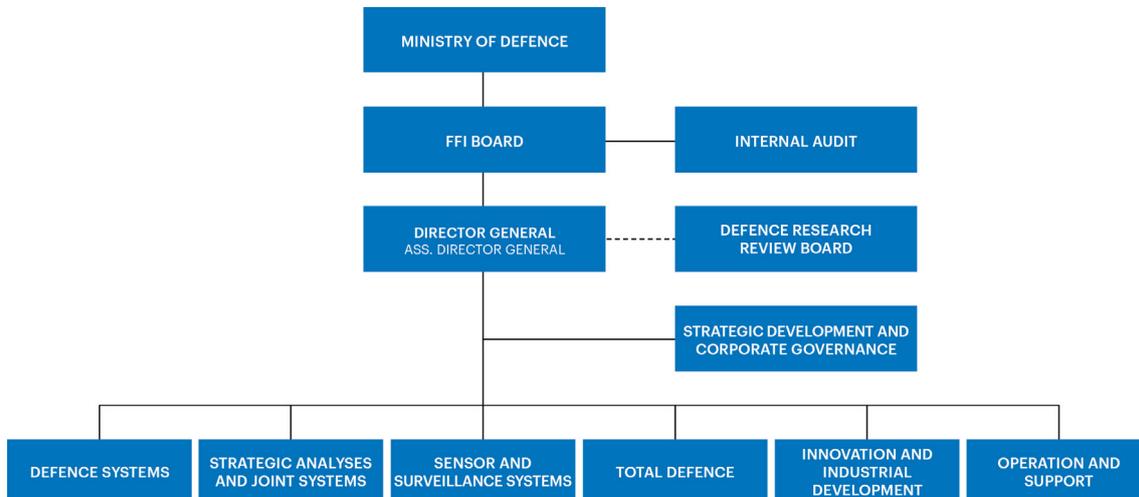
FFI is the prime institution responsible for defence related research in Norway. Its principal mission is to carry out research and development to meet the requirements of the Armed Forces. FFI has the role of chief adviser to the political and military leadership. In particular, the institute shall focus on aspects of the development in science and technology that can influence our security policy or defence planning.

FFI's vision

FFI turns knowledge and ideas into an efficient defence.

FFI's characteristics

Creative, daring, broad-minded and responsible.



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