Reactivity of Condensed Energetic Systems from an Atomistic Perspective

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"Doctor of Philosophy"

By

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"...throw off the bowlines. Sail away from the safe harbor. Catch the trade winds in your sails. Explore. Dream. Discover. "

Mark Twain

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Abstract

In this thesis we explore chemical reactivity of energetic materials from an atomistic viewpoint. Despite decades of research, some prominent open questions in the fundamental chemistry of materials under extreme conditions are yet to be resolved. Continuum theories neglect the discreteness of matter and so are approaching their limits. Experimental techniques are limited in their resolution under the extreme conditions that prevail during energetic materials decomposition. Thus, it is our aim to reveal, using atomistic computational methods, the interplay between molecular structure and material performance.

We develop new descriptions of chemical reactivity in the form of reactive force fields based on quantum chemical calculations, and use them in molecular dynamics simulations. The simulations are applied to several kinds of complex, condensed phase systems to explain key unsettled phenomena. Specifically, (I) in Chapter 3 we study the effects of the molecular environment on the initiation of explosion in nitro aromatic solid explosives; In addition, a parallel study concentrates on the liquid phase (Appendix A); (II) in Chapter 4 we employ novel simulation methods to predict how the decomposition of an emerging improvised explosive - Erythritol tetranitrate, is affected by nanometre-scale crystal imperfections. We arrive at the complete decomposition mechanism in the neat crystal phase and in the defected crystal. The defects substantially enhance the reactivity of the explosive through mechanochemical routes. Further calculations and experimental measurements did verify parts our work (Appendix B); (III) in Chapter 5 we propose a theoretical model, based on reactive molecular dynamics simulations, to explain major experimental findings of a recently developed laser based mass-spectrometry technique. The model links between the laser and analyte parameters and allows to tune the experimental parameters to achieve better performance; (IV) in Chapter 6 we develop a new reactive force field for a liquid explosive – Hydrazoic acid, and use it to characterize its decomposition sequence. Excellent agreement is reached between our model and significantly more costly, tight-binding DFT model; (V) lastly, in Chapter 7 we develop an enhanced particle swarm optimization algorithm by augmenting the equations of motion with isotropic Gaussian mutation operators. The new method shows superior performance compared to several global optimization algorithms with respect

to non-linear, multimodal benchmark functions. The algorithm is implemented in a standalone C++ numerical package and can be used to effectively train ReaxFF reactive force fields.

A Letter of Contribution

All of the work on this PhD thesis was done by David Furman as the main contributor, under the supervision of Prof. Ronnie Kosloff and Prof. Yehuda Zeiri. In particular, the following holds:

1. The study introduced in chapter 3, *Decomposition of condensed phase energetic materials – interplay of uni and bimolecular processes*, was performed in collaboration with Faina Dubnikova, Sergey Zybin, William Goddard, Naomi Rom and Barak Hirshberg. Nevertheless, David Furman is the main contributor and author of this work, under the supervision of Prof. Ronnie Kosloff and Prof. Yehuda Zeiri.

2. The study introduced in chapter 4, *Effects of nanoscale heterogeneities on the reactivity of shocked Erythritol Tetranitrate*, was performed by David Furman, under the supervision of Prof. Ronnie Kosloff and Prof. Yehuda Zeiri.

3. The study introduced in chapter 5, *Mechanism of intact adsorbed molecules ejection using high-intensity laser pulses*, was performed by David Furman, under the supervision of Prof. Ronnie Kosloff and Prof. Yehuda Zeiri.

4. The study introduced in chapter 6, *Reactive force field for liquid Hydrazoic acid with applications to detonation chemistry*, was performed in collaboration with Faina Dubnikova and Adri van Duin. Nevertheless, David Furman is the main contributor and author of this work, under the supervision of Prof. Ronnie Kosloff and Prof. Yehuda Zeiri.

5. The study introduced in chapter 7, *Enhanced particle swarm optimization algorithm: efficient training of ReaxFF reactive force fields*, was performed in collaboration with Benny Carmeli. Nevertheless, David Furman is the main contributor and author of this work, under the supervision of Prof. Ronnie Kosloff and Prof. Yehuda Zeiri.

Contents

Chapter 1

Introduction and outline

In the fleeting moment of a high-explosive's detonation, the resulting detonation wave produces a pressure 500,000 times that of the Earth's atmosphere, it travels as fast as 10 kilometers per second, and the internal temperatures of shocked material could reach up to 5000K. The traditional theoretical description of detonation propagation is provided within the Chapman-Jouguet (CJ) theory, based on the assumption of an instantaneous transformation of explosives into decomposition products in the detonation wave front. The prevailing theory of Zel'dovich-von Neumann-Döring (ZND) appeared as an extension to the over simplified CJ model. In the ZND model, the transformation mechanism of parent explosive material into decomposition products proceeds by a combustion of a layer of finite thickness of shock-compressed explosive behind the shock front with the velocity of the front. However, some experimental findings turned out to be inconsistent with the theory. The independence of the width of the reaction zone on the detailed structure of an explosive (i.e. particle size, single crystal or cast, type of filler materials, and states of matter) is a prominent example.

Under the extreme conditions present during a detonation, continuum theories, such as CJ and ZND models, are limited in their predictive power, since they ignore the essential discrete nature of matter. An especially fundamental challenge of hydrodynamic theory emerges where the theory approaches its limits, namely on the scale where continuum concepts break down. Local thermodynamic equilibrium assumes that the macroscopic fluid variables do not change much over molecular length and time scales, a clearly oversimplifying assumption. The chemical reactions and material microstructure is of considerable importance in understanding processes that these materials experience under impact and detonation conditions. The generation of hot-spots[1], crystal orientational sensitivity anisotropy[2], and the coupling of shocks with molecular systems[3] are only a few examples where basic understanding is missing and continuum models are mainly phenomenological and largely questionable[4-6]. The structure and dynamics of every explosive molecule is fully determined by its electronic structure and

specific arrangement inside the crystal. The necessity to account for the finer scales is now evident, however hydrodynamic theory alone fails at this quest. Hence, a fundamental understanding that is based on molecular level processes underpinning continuum phenomena is highly desirable.

Advances in the experimental and theoretical understanding of chemical kinetics at high pressures and temperatures extended the basic theory of ZND. Dlott et al.[7, 8], have developed a model describing the flow of energy in a shocked solid consisting of large molecules. They used it to gain fundamental understanding of secondary explosives chemical initiation mechanisms under shock strengths characteristic of accidents. Tarver[9], in his qualitative extension to the hydrodynamic theory accounted for vibrational excitation processes that precede, control the rates of, and follow the chemical reaction sequence in a detonation. Smirnov and Dremin[10] studied the influence of energy transfer mechanisms to internal degrees of freedom in detonation waves. They showed, using molecular dynamics simulations that the shock and detonation structure depends strongly on the vibrational spectra and normal modes of the molecules.

Current understanding of detonation at the molecular level remains mainly qualitative and no molecular theory of detonation has been put forward[11]. Just before detonation is initiated, burning fronts travel at a velocity of several hundred meters per second, while at the same time, the respective time-scales of atomic vibrations in decomposing molecules are on the order of $\sim 10^{-16}$s. Although first-principles theoretical methods can accurately predict ground and excited state properties of an explosive molecule, they are typically limited to $<$1ps simulation time for small isolated systems. So a central question is whether a theoretical method can reliably account for several important time and length scales? And precisely, what are the requirements for an accurate molecular description of the chemistry that governs an explosive's material response towards thermal, mechanical or electromagnetic stimuli? In this thesis, we attempt to answer these questions by developing and validating reactive descriptions of chemical dynamics in extreme conditions at atomic resolution. ReaxFF reactive molecular dynamics simulations provide, to date, the only access to chemical reactions in the bulk. We note that the simulations make no approximations other than the ones implied in the interatomic potentials and the fact that the dynamics of the atoms is purely classical. For example, no approximation is made as to what type of chemical reaction can or cannot occur; complex phenomena such as pressure effects, multi-molecular reactions and relaxation processes.

Thus, it is our aim to unravel, at the molecular level, the initiation mechanisms, detailed decomposition pathways, kinetic rates at high-pressure and temperature and the strong links between materials microstructure and

chemical reactivity. Specifically, we develop first-principles based reactive force fields in ReaxFF formalism and optimize them to reproduce extensive sets of accurate density functional theory (DFT) calculations. The training datasets include key molecular configurations and energy barriers pertaining to both ambient and possible high-energy conditions. Remarkably, with a balanced training set of DFT data together with a proper fitting of all relevant force field parameters, a near quantum chemical accuracy is achieved in simulating systems with over 10^6 atoms and for long durations (>100ps). In addition, a new method for efficient global optimization of reactive force fields and general multidimensional, highly nonlinear problems is proposed and validated.

The methods developed in this thesis are employed to tackle some challenging open questions concerning the behavior of bulk chemical systems under extreme conditions. It is our aim to contribute to the development of a fundamental understanding of hydrodynamic phenomena from atomistic-scale simulations to bridge the time- and length-scale gaps of *ab initio* methods. Specifically, we devoted our efforts to (I) elucidate prominent experimental contradictions in the decomposition sequence of aromatic high-explosives (Chapter 3); (II) study the effects of nm-size spherical voids in crystalline home-made explosives on the chemical reactivity (Chapter 4); (III) offer a novel theoretical model to reveal the physical mechanism that governs a recently developed experimental technique of laser-assisted mass spectrometry (Chapter 5); and (IV) predict the kinetics and thermodynamics of detonating liquid explosive (Chapter 6). Finally, we have developed an efficient algorithm for global optimization of reactive force fields based on swarm intelligence (Chapter 7).

Chapter 2

Theoretical background

"Given for one instant an intelligence which could comprehend all the forces by which nature is animated and the respective positions of the beings which compose it, if moreover this intelligence were vast enough to submit these data to analysis, it would embrace in the same formula both the movements of the largest bodies in the universe and those of the lightest atom; to it nothing would be uncertain, and the future as the past would be present to its eye." Pierre Laplace, 1812

2.1 Molecular dynamics simulations

2.1.1 Introduction

Computer simulation methods have become a very powerful tool to solve the N-body problem in physics and chemistry. The traditional numerical methods for these systems can be divided into two classes of stochastic and deterministic simulations, which are largely covered by the Monte Carlo (MC) method and the molecular dynamics (MD) method, respectively. MD methods are governed by the system's Hamiltonian and consequently Hamilton's equations of motion (Eq. 1) are integrated to move particles to new positions and to get new velocities at these new positions.

$$\dot{p}_i = -\frac{\partial \mathcal{H}}{\partial q_i} \quad , \quad \dot{q}_i = \frac{\partial \mathcal{H}}{\partial p_i} \tag{1}$$

This is an advantage of MD simulations with respect to MC, since not only is the configuration space probed but the whole phase space which gives additional information about the dynamics of the system. Both methods are complementary in nature but they lead to the same averages of static quantities, given that the system under consideration is ergodic and the same statistical ensemble is used. MD simulations always require a model for the interaction between system constituents. This model has to be tested against experimental results, i.e., it should reproduce or approximate experimental findings like

distribution functions or phase diagrams, and theoretical constraints, i.e. it should obey fundamental laws like energy conservation. Modern interaction models, popularly called "force fields", are established from approximate *ab initio* treatments using more accurate methods like DFT and post-HF methods and are expected to reproduce them to some desired accuracy.

The ingredients of an MD simulation are threefold: (I) a model for the interaction between system constituents (atoms and molecules) is needed. Often, it is assumed that particles interact only pair-wise, which is exact e.g. for particles with fixed partial charges; (II) an integrator is needed, which propagates particle positions and velocities from time t to $t+\mathrm{d}t$. It is a finite difference scheme which moves trajectories discretely in time. The time step, $\mathrm{d}t$, has to be properly chosen to guarantee stability of the integrator, i.e. there should be no drift in the system's total energy; (III) a statistical ensemble has to be chosen, where thermodynamic quantities like pressure, temperature or the number of particles are controlled. The natural choice of an ensemble in MD simulations is the microcanonical ensemble (NVE), since the system's Hamiltonian without external potentials is a conserved quantity. Nevertheless, there are extensions to the Hamiltonian which also allow to simulate different statistical ensembles.

An important issue of a simulation is the accessible time- and length-scale coverable by microscopic simulations. It is clear that the more detailed a simulation technique operates, the smaller is the accessibility of long times and large length-scales. Classical molecular dynamics approximates electronic distributions in a rather coarse-grained fashion by putting either fixed partial charges on interactions sites or by adding an approximate model for polarization effects. In both cases, the time-scale of the system is not dominated by the motion of electrons, but the time of intermolecular collision events, rotational motions or intramolecular vibrations, which are orders of magnitude slower than those of electron motions. Consequently, the time step of integration is larger and trajectory lengths are of order 10^{-9}s and accessible lengths of order 10^{1}-10^{2}A.

Classical molecular dynamics methods are nowadays applied to a huge class of problems, e.g. properties of liquids, defects in solids, fracture, surface properties, molecular clusters, energetic materials and biomolecules. Due to the large area of applicability, simulation codes for molecular dynamics were developed by many groups. Among them, which are partly available free of charge, are CHARMM[12], NAMD[13], NWCHEM[14] and LAMMPS[15]. The MD results presented in this thesis were carried out with the freely available LAMMPS package.

2.1.2 Fundamentals of molecular dynamics simulation

The time evolution of an atomic system is typically determined and described by Newtonian equations of motion. This constitutes a set of 3N second-order, nonlinear, coupled partial differential equations for the coordinates of all of the atoms. Apart from conserving total energy and linear and angular momentum, the equations are time reversible.

Statistical ensembles:

The time evolution can likewise be thought of as a trajectory through phase space of 6N dimensions in which there is an axis for every position and every conjugate momentum. For classical systems, the energy is conserved and the phase space trajectory adheres to a surface of constant energy. Systems that are ergodic and able to reach equilibrium are able to fully explore all parts of phase space that have the same energy as the constant total. That is, the trajectory of an ergodic system will visit all points in phase space on the constant energy hypersurface with equal probability. Technically, in an MD simulation, it is impossible to explore exhaustively all accessible regions of phase space. However, we can explore a subset of the accessible regions that are statistically identical or that are representative. In this sense, the simulation can be ergodic and reach equilibrium. The succession of states generated in MD simulation are in accordance with the distribution function for the microcanonical ensemble (NVE). If we wish to study other ensembles, i.e. systems at constant pressure or temperature, it is possible to invent a kind of equation of motion, i.e. a means of generating, from one state point, a succeeding state point (will be described in sections 1.1.3-1.1.4). Such an equation should satisfy three conditions: (I) the probability density for the ensemble of interest should not change as the system evolves; (II) any reasonable starting distribution should tend to this stationary solution as simulation proceeds; (III) we should be able to argue that ergodicity holds. If these conditions are met, we should be able to generate a succession of state points which, in the long term, are sampled in accordance with the desired probability density (constant NVT, NPT, etc.). In these circumstances, the *ensemble* average will be equal to the *time* average of the property under consideration.

Time integration:

To generate dynamics, a time integration scheme is used to update the atomic positions and velocities in a discretized form of Newton's equations using a small enough time step. Consider a Taylor expansion of the position vector in time increments δt:

$$r(t+\delta t) = r(t) + \frac{dr(t)}{dt}\delta t + \frac{d^2r(t)}{2dt^2}\delta t^2 + \frac{d^3r(t)}{6dt^3}\delta t^3 + O(\delta t^4)$$
$$= r(t) + v(t)\delta t + \frac{f(t)}{2m}\delta t^2 + \frac{d^3r(t)}{6dt^3}\delta t^3 + O(\delta t^4) \quad (2)$$

Similarly,

$$r(t-\delta t) = r(t) - v(t)\delta t + \frac{f(t)}{2m}\delta t^2 - \frac{d^3r(t)}{6dt^3}\delta t^3 + O(\delta t^4) \quad (3)$$

Adding these two equations together and moving the $r(t-\delta t)$ term to the RHS yields:

$$r(t+\delta t) = 2r(t) - r(t-\delta t) + \frac{f(t)}{m}\delta t^2 + O(\delta t^4) \quad (4)$$

This last equation forms the basis of the *Verlet* algorithm for molecular dynamics. The system is propagated forward in time by a time step δt. To do so, we use the positions at the previous two time steps as well as the forces at the current time step. To get the forces, we use the gradient of the potential energy function (i.e. force field):

$$f(t) = -\frac{dU(r(t)}{dr} \quad (5)$$

The accuracy of this equation is of order $O(\delta t^4)$. Alternatively, we could use the velocity to determine the position at the next step. We can approximate the velocities using:

$$v(t) = \frac{r(t+\delta t) - r(t-\delta t)}{2\delta t} + O(\delta t^3) \quad (6)$$

One disadvantage of the Verlet algorithm is that it requires us to store in memory two sets of positions, $r(t+\delta t)$ and $r(t)$. An alternative is the so-called *velocity Verlet* algorithm, which is a reformulation of the original algorithm that uses the velocity directly:

$$r(t+\delta t) = r(t) + v(t)\delta t + \frac{f(t)}{2m}\delta t^2 \quad (7)$$

$$v(t+\delta t) = v(t) + \frac{f(t+\delta t) + f(t)}{2m}\delta t$$

This integration algorithm is one of the most frequently used in molecular simulations because of its ease of implementation.

Periodic boundary conditions:

Enforcing periodic boundary conditions (PBC) means that the particles interact over the boundaries of the simulation volume. This will create a repetition of the simulation volume in all directions, which approximates an infinite system (i.e. bulk of a material) typically used to describe crystals. Using PBC just requires to keep track of the particles inside of the simulation volume. Any particle position in one of the replicas can be calculated by using the information about the real particle position. A particle position in one of the replicas, $\boldsymbol{r}_{replica}$, can be easily calculated by

$$\boldsymbol{r}_{replica} = \boldsymbol{r}_{real} + \boldsymbol{n}L \tag{8}$$

where $\boldsymbol{r}_{real}$ is the particle position in the simulation volume, L the length of the side of the simulation voume, which for simplicity is assumed to be cubic, and $\boldsymbol{n}$ is a three dimensional vector with integer components corresponding to in which replica of the simulation volume that $\boldsymbol{r}_{replica}$ is in.

A general form of PBC would be that each particle in the simulation volume interacts with all other particles in the simulation volume and all the particles in the replicas, including the particle's own replica. This general case is not possible in practice. A summation of all particle interactions would be an infinite sum, making the above approach impossible to implement. Also, the fact that particles interact with their own replicas will give rise to correlations. In MD simulations, most of the interactions are short ranged, meaning that most of the interaction energy arises from interactions with neighboring particles inside of a cutoff distance, r_C. A special case of interest is when $r_C < L/2$, leading to that particles just interact with the nearest replica of the other particles and never with it's own replica. Long range interactions need special treatment and how this is done depends on the system. Another important fact about PBC is that the simulation volume can be defined to be anywhere in the system of replicas, without the result of the simulation being changed, but it must have the same shape and orientation. This is an effect that the infinite system is periodic over the distance L in the direction of the boundaries.

2.1.3 Controlling the temperature in MD simulation

Different methods were proposed to fix the temperature to a fixed value during a simulation without allowing temperature fluctuations. In the first method[16], the velocities are scaled according to $\boldsymbol{p}_i \rightarrow \sqrt{T_0/T}\,\boldsymbol{p}_i$, where T_0 is the reference temperature and T the actual temperature, calculated from the velocity of the particles. This method, called, *velocity re-scaling*, often leads to discontinuities in the momentum of the phase space trajectory due to the rescaling procedure. In a second method, a proportional thermostat tries to correct deviations of the

actual temperature T from the prescribed one T_0 by multiplying the velocities by a certain factor λ in order to move the system dynamics towards one corresponding to T_0. The difference with respect to the previous method is that the method allows for fluctuations of the temperature, thereby not fixing it to a constant value. In each integration step, it is insured that the T is corrected to a value more close to T_0. A thermostat of this type is called a *Berendsen* thermostat[17]. In the third method, additional degrees of freedom are introduced into the system's Hamiltonian for which equations of motion can be derived. They are integrated in line with the equations for the spatial coordinates and momenta. The idea of the method invented by Nosé[18] is to reduce the effect of an external system acting as heat reservoir to keep the temperature of the system constant, to one additional degree of freedom. The thermal interactions between a heat reservoir and the system result in a change of the kinetic energy, i.e. the velocity of the particles in the system. Formally it may therefore be expressed as scaling of the velocities. Nosé introduced two sets of variables: real and so called virtual ones. The virtual variables are consistently derived from a Sundman transformation[19] $d\tau/dt = s$, where τ is a virtual time and s is a resulting scaling factor, which is treated as dynamical variable. The transformation from virtual to real variables is then performed as (Eq. 4):

$$\boldsymbol{p}_i = \boldsymbol{\pi}_i s \quad , \quad \boldsymbol{q}_i = \boldsymbol{\rho}_i \tag{4}$$

The introduction of the effective mass, Ms, connects also a momentum to the additional degree of freedom, π_s. The resulting Hamiltonian, expressed in virtual coordinates reads (Eq. 5):

$$\mathcal{H}^* = \sum_{i=1}^{N} \frac{\boldsymbol{\pi}_i^2}{2m_i s^2} + U(\boldsymbol{\rho}) + \frac{\boldsymbol{\pi}_s^2}{2M_s} + g k_B T \ln s \tag{5}$$

where g = 3N + 1 is the number of degrees of freedom in a system of N free particles. The Hamiltonian in Eq. 5 was shown to lead to a probability density in phase space, corresponding to the canonical ensemble. The equations of motion drawn from this Hamiltonian are:

$$\frac{\partial \boldsymbol{\rho}_i}{\partial \tau} = \frac{\boldsymbol{\pi}_i}{s^2} \tag{6}$$

$$\frac{\partial \boldsymbol{\pi}_i}{\partial \tau} = -\frac{\partial U(\boldsymbol{\rho})}{\partial \boldsymbol{\rho}_i} \tag{7}$$

$$\frac{\partial s}{\partial \tau} = \frac{\pi_s}{M_s}$$

(8)

$$\frac{\partial \pi_s}{\partial \tau} = \frac{1}{s^3}\sum_{i=1}^{N}\frac{\boldsymbol{\pi}_i^2}{m_i} - \frac{g k_B T}{s}$$

(9)

If one transforms these equations back into real variables, it is found[20] that they can be simplified by introducing the new variable $\xi = \partial s/\partial t = s\, p_s/M_s$ (p_s is real momentum connected to the heat bath)

$$\frac{\partial \mathbf{q}_i}{\partial t} = \frac{\mathbf{p}_i}{\mathrm{m}_i}$$

(10)

$$\frac{\partial \mathbf{p}_i}{\partial t} = -\frac{\partial U(\mathbf{q})}{\partial \mathbf{q}_i} - \xi \mathbf{p}_i$$

(11)

$$\frac{\partial \ln s}{\partial t} = \xi$$

(12)

$$\frac{\partial \xi}{\partial t} = \frac{1}{M_s}\left(\sum_{i=1}^{N}\frac{\mathbf{p}_i^2}{m_i} - g k_B T\right)$$

(13)

These equations describe the so called Nosé-Hoover thermostat. Several stochastic methods[21, 22] also exist to control the temperature and pressure in MD simulations, however these will not be elaborated here.

2.1.4 Controlling the pressure in MD simulation

In order to control the pressure in an MD simulation cell, it is necessary to allow for volume variations. A simple picture for a constant pressure system is a box the walls of which are coupled to a piston which controls the pressure. In contrast to the case where the temperature is controlled, no coupling to the dynamics of the particles is performed but the length scales of the system will be modified. In addition, the conserved quantity will not be the system's energy, since there will be an energy transfer to or from the *external* system (piston etc.), but the enthalpy H will be constant. The *Berendsen* barostat acts on a volume change, which may be expressed in a scaling of particles' positions[17]:

$$\frac{\partial \mathbf{q}_i}{\partial t} = \frac{\mathbf{p}_i}{\mathrm{m}_i} + \alpha \mathbf{q}_i$$

(14)

while a change in volume is postulated as

$$\dot{V} = 3\alpha V$$

(15)

A change in pressure is related to the isothermal compressibility κ_T

$$\dot{P} = -\frac{1}{\kappa_T V}\frac{\partial V}{\partial t} = -\frac{3\alpha}{\kappa_T} \tag{15}$$

which is approximated as

$$\frac{(P_0 - P)}{\tau_P} = -\frac{3\alpha}{\kappa_T} \tag{16}$$

and therefore Eq. 14 can be written as

$$\frac{\partial \mathbf{q}_i}{\partial t} = \frac{\mathbf{p}_i}{\mathrm{m}_i} - \frac{\kappa_T}{3\tau_P}(P_0 - P) \tag{17}$$

which corresponds to a scaling of the box length and coordinates $\mathbf{q} \to \mathbf{sq}$ and $L \to \mathrm{s}L$, where

$$s = 1 - \frac{\kappa_T \delta t}{3\tau_P}(P_0 - P) \tag{18}$$

The time constant τ_P was introduced into Eq. 16 as a characteristic timescale on which the system pressure will approach the desired pressure P_0. It also controls the strength of the coupling to the barostat and therefore the strength of the volume/pressure fluctuations. If the isothermal compressibility, κ_T, is not known for the system, the constant $\acute{\tau}_P = \tau_P/\kappa_T$ may be considered as a phenomenological coupling time which can be adjusted to the system under consideration. A drawback for this method is that the statistical ensemble is not known. In analogy to the thermostat, it may be assumed to interpolate between the microcanonical and the constant-pressure ensemble, depending on the coupling constant τ_P. A second method to control the pressure during MD simulation is analogous to the Nosé-Hoover thermostat, i.e. one can introduce a new degree of freedom into the system's Hamiltonian which controls volume fluctuations. The idea is to include the volume as an additional degree of freedom and to write the Hamiltonian in a scaled form, where lengths are expressed in units of the box length $L = V^{1/3}$, i.e. $\mathbf{q}_i = L\boldsymbol{\rho}_i$ and $\mathbf{p}_i = L\boldsymbol{\pi}_i$. Since L is also a dynamical quantity, the momentum is not related to the simple time derivative of the coordinates but $\partial_t \mathbf{q}_i = L\partial_t \boldsymbol{\rho}_i + \boldsymbol{\rho}_i \partial_t L$. The extended system Hamiltonian is then written as

$$\mathcal{H}^* = \frac{1}{V^{2/3}}\sum_{i=1}^{N}\frac{\boldsymbol{\pi}_i}{2m_i} + U\left(V^{1/3}\boldsymbol{\rho}\right) + P_{ex}V + \frac{\boldsymbol{\pi}_V^2}{2M_V}$$

(19)

where P_{ex} is the prescribed external pressure and $\boldsymbol{\pi}_V$ and M_V are a momentum and a mass associated with the fluctuations of the volume. The equations of motion derived from this Hamiltonian in real variables then gives

$$\frac{\partial \mathbf{q}_i}{\partial t} = \frac{\mathbf{p}_i}{\mathrm{m}_i} + \frac{1}{3V}\frac{\partial V}{\partial t}\mathbf{q}_i \tag{20}$$

$$\frac{\partial \mathbf{p}_i}{\partial t} = -\frac{\partial U(\mathbf{q})}{\partial \mathbf{q}_i} - \frac{1}{3V}\frac{\partial V}{\partial t}\mathbf{p}_i \tag{21}$$

$$\frac{\partial V}{\partial t} = \frac{\boldsymbol{p}_V}{M_V} \tag{22}$$

$$\frac{\partial \boldsymbol{p}_V}{\partial t} = \frac{1}{3V}\left(\sum_{i=1}^{N}\frac{\mathbf{p}_i^2}{m_i} - \mathbf{q}_i\frac{\partial U(\mathbf{q})}{\partial \mathbf{q}_i}\right) - P_{ex} \tag{23}$$

In the last equation the term in brackets corresponds to the pressure, calculated from the virial theorem. The associated volume force, introducing fluctuations of the box volume is therefore controlled by the internal pressure, originating from the particle dynamics and the external pressure, P_{ex}.

2.1.6 Simulating shock waves in MD simulation

Several methods commonly used to simulate the passage of shock waves in a material were developed during the years. In reality, shocks are set up in solid media by either explosive means, or by accelerating a thin flat plate (flyer) to a high velocity prior to that flyer impacting upon the sample. In MD, it is possible to recreate the flyer plate experiment by superimposing an additional uniform velocity upon a subset of the atoms within the simulation[23, 24]. This method is attractive in that in enables a faithful representation of the experimental conditions. However, there is a severe drawback. Since, as in the experiment, a shock is set up at the flyer-sample interface, two shock fronts are observed; one travelling forward into the sample and another travelling back into the flyer. Now the shock travelling into the flyer reaches the free surface at the rear of the simulation and, as in the experiment, is reflected back into the material as a release wave. Since the release wave is moving into compressed material, the sound speed is high and this wave will catch up with the shock travelling forward into the sample, after which time the amplitude of that shock is eroded. Therefore, of one wishes to observe relaxation effects or chemical reactions which are much slower than shock traversal time, it will be necessary to include a large flyer. In an alternative method, the boundaries of the

simulation cell are utilized. Here a test is carried out on the motion of the atoms near to the boundary on one side of the cell. The test examines whether, during the time covered by that time step, any atom will pass across the boundary. For any atom where such a motion is predicted, then its position is not updated, and its velocity towards the wall is reversed, thus creating a *momentum mirror* on one side of the simulation cell. The entire set of atoms in the simulation is then given a superimposed additional velocity in the direction of the momentum mirror. This causes the atoms to compress up against that mirror, and a shock then propagates away from the mirror boundary. This method though has been found to cause peculiar effects of atoms reaching the boundary[25]. A better way to introduce a shock wave in a material uses a repulsive potential energy wall instead of the momentum mirror. In this way a piston is created which drives into the simulation cell and creates a stationary planar shock wave[24]. Nevertheless, this method cannot account for long time-scale phenomena behind the shock front since as soon as it reaches the boundary, a reflection wave is propagating backwards and will cause tension of the shock-compressed material. Thus, in order to observe chemical reactions for long enough periods of time, long after the passage of the shock, other methods of shock simulation are needed. In chapter 4 we present one such method that decouples the time scale of shock propagation and late chemical evolution in the shocked material.

2.1.5 Empirical potential energy surfaces

Due to the non-locality of interactions in quantum mechanics, the high accuracy of *ab initio* molecular dynamics methods comes at a high computational cost. Brute force approaches to such calculations suffer from the exponential growth of computational complexity with the number of electrons in the simulated system. Even with the approximations to reduce computational costs, *ab initio* methods do not scale well with the system size; N being the number of electrons, coupled cluster methods scale as N^7, perturbation methods as N^5 and some localized variants can bring the scaling factor down to N^3. On the other hand, density functional based methods typically scale as N^3. Hence, force field methods that treat the nuclei core together with orbital electrons as a single entity are more computationally attractive. Since electrons are not treated explicitly, their roles and effects are approximated by means of approximate functional forms and parameters.

However, while traditional atomistic force fields are successful in reproducing features of real systems to varying degrees, they are limited in many respects. Some of these limitations include: (I) due to specific parameterizations, these methods are not generic and cannot be used for arbitrary systems; (II) while this is true for any empirical force field, conventional methods start with the assumption of static bonds in their target system, therefore they cannot be used to model reactive systems; and (III) in most atomistic methods, charges are

kept fixed throughout the simulation. Although polarizable force fields were introduced almost two decades ago[26], they have only recently gained significant attention for modeling charge transfer in empirical force fields[27]. Polarization is achieved either by inducible point dipole methods, or by fluctuating charge models. Even though polarizable force fields are built upon their non-polarizable counter-parts, their development still requires considerable effort since charges are not assumed to be fixed in the target system. This requires most of the parameters to be re-parameterized.

To bridge the gap between quantum methods and classical MD methods, a number of models with empirical bond order potentials have been proposed. These techniques mimic quantum overlap of electronic wave functions through a bond order term that describes the bonds in the system dynamically based on the local neighborhoods of each atom. A widely used bond order potential has been the Reactive Empirical Bond Order (REBO) potential[28]. REBO is built on the Tersoff potential[29], which was inspired by Abell's work[30]. REBO was extended to describe interactions with Si, F and Pt. Like many other bond order potentials, REBO lacks long range interactions, which are important in modeling molecular systems. AIREBO was an attempt by Stuart et al.[31] to generalize REBO to include long range interactions. However, it retained the fundamental problems in the shapes of the dissociation and reactive potential curves of REBO. The ReaxFF developed by van Duin et al.[32], is the first reactive force field that contains dynamic bonds and polarization effects in its formulation. The flexibility and transferability of the force field allows ReaxFF to be easily extended for many systems of interest, including organic materials, semiconductors, ceramics, metal alloys and more.

2.1.6 ReaxFF Reactive Force Field

In classical molecular dynamics, atoms constitute molecules through static bonds, akin to a "balls and springs" model in which springs are statically attached. This approach cannot simulate chemical reactions, since reactions correspond to bond breaking and formation. In reactive molecular dynamics using the ReaxFF force field, each atom is treated as a separate entity, whose bond structure is updated at every time-step through the bond order for every pair of atoms in the system. This dynamic bonding scheme, together with charge redistribution (equilibration to minimize electrostatic energy) constitutes the core of ReaxFF. The number of energy terms included in ReaxFF is quite substantial, and only the bond order (BO) function and the bond energy where the BO function is employed will be described here. This demonstrates the use of the BO function and similar procedures are applied to all bonded interactions. A full description of the energy terms ReaxFF applies can be found in appendix X.

The BO between a pair of atoms, i and j, is the strength of the bond between the two atoms. In ReaxFF, bond order is modeled by a closed form (Eq. 24), which computes the BO in terms of the times of atoms i and j, and the distance between them:

$$BO_{ij}^{\alpha'} = exp\left[a_\alpha \left(\frac{r_{ij}}{r_{0\alpha}}\right)^{b_\alpha}\right] \tag{24}$$

where α corresponds to $\sigma\sigma$, $\sigma\pi$ or $\pi\pi$ bonds, a_α and b_α are parameters specific to the bond type, and $r_{0\alpha}$ is the optimal length for this bond type. The total bond order (BO'_{ij}) is computed as a summation of to $\sigma\sigma$, $\sigma\pi$ or $\pi\pi$ bonds as follows:

$$BO'_{ij} = BO_{ij}^{\sigma'} + BO_{ij}^{\pi'} + BO_{ij}^{\pi\pi'} \tag{25}$$

The use of pair-wise bond order potentials could sometimes lead to unsatisfactory description of complex bond structures. For this reason, it is essential to account for the total coordination number of each atom and 1-3 bond corrections in valence angles. For instance, the bond length and strength between O and H atoms in a hydroxyl group are different than those in a water molecule. Alternately, taking the example of H atoms in a water molecule, detach the two H atoms from the middle O atom and put them in vacuum while preserving the distance between them. Those two same H atoms between which we do not observe any bonding in a water molecule would then share a weak covalent bond. These examples suggest the necessity of aforementioned corrections, which are applied in ReaxFF using the following equation:

$$BO_{ij} = BO_{ij}^{\sigma'} \cdot f_1(\Delta'_i, \Delta'_j) \cdot f_4(\Delta'_i, BO'_{ij}) \cdot f_5(\Delta'_j, BO'_{ij}) \tag{26}$$

Here, Δ'_i is the deviation of atom i from its optimal coordination number, $f_1(\Delta'_i, \Delta'_j)$ enforces over-coordination correction, and $f_4(\Delta'_i, BO'_{ij})$ together with $f_5(\Delta'_j, BO'_{ij})$ account for 1-3 bond order corrections. Only corrected bond orders are used in energy and force computations in ReaxFF. Once bond orders are calculated, the simulation process resembles classical MD. Indeed, in ReaxFF the total energy of the system is comprised of partial energy contributions as follows

$$\begin{aligned} E_{ReaxFF} = E_{bond} + E_{system} + E_{lp} + E_{over} + E_{under} + E_{val} + E_{pen} + E_{3-conj} \\ + E_{tors} + E_{4-conj} + E_{H-bond} + E_{vdW} + E_{Coulomb} \end{aligned} \tag{27}$$

In Eq. 27, most of the terms are similar to classical MD methods. However, due to the dynamic bonding scheme of ReaxFF, these potentials must be modified

to ensure smooth potential energy curves as bonds form or break. For example, the bond energy is related to the bond order as follows

$$E_{bond} = -D_e^{\sigma} \cdot BO_{ij}^{\sigma} \cdot exp\left[p_{be1}\left(1 - \left(BO_{ij}^{\sigma}\right)^{p_{be2}}\right)\right] - D_e^{\pi} \cdot BO_{ij}^{\pi} - D_e^{\pi\pi} \cdot BO_{ij}^{\pi\pi} \tag{28}$$

As can be seen from Eq. 28, in ReaxFF the effects of neighboring bonds are taken into consideration by computing the energy incident on a bond from all bond order constituents. The higher the bond order, the lower the energy and the stronger the force associated with the bond. In addition, the function ensures that the energy and force due to a bond smoothly go to zero as the bond breaks (i.e. bond order is 0).

2.1.7 Training ReaxFF reactive force fields

Determination of parameters is vital for ensuring the accuracy of any empirical model. In order for a mathematical model of a molecular system to have relevance to experimentally observable systems, the parameters governing their interactions must be chosen such that the model is a reasonably accurate representation of the reference system. Parameters can be chosen by solving the constrained optimization problem:

$$\min_{p \in P} f(p) \tag{29}$$

where P is the parameter space to be explored, p is a point in the parameter space and f is a cost function which measures the discrepancy between model predictions and target data[33]. The parameter space P may be bounded or unbounded. In the case of bounded optimization, limits are placed on parameter values, including limits on complex functions of parameter values. If a maximum value optimizes the model, the problem can be solved by minimizing $-f$.

The general problem of optimization arises in many different fields from physical sciences and engineering to social sciences and finance. Different models and methods for determining the suitability of models lead to a wide variety of optimization problems. Because of the substantial differences in the computation costs of the comparison, the size of the parameter space, and the characteristics of the target function in optimization problems, there are many methods for obtaining solutions. Target functions for molecular models typically have certain properties which make the optimization procedure a significant challenge. The computational cost of a target function evaluation is often very high. For the specific case of molecular models, the target function is very rarely a closed, analytic function. Rather, evaluation of the target function involves simulations of the model followed by comparison of model observations with those of either experiment or a more fundamental model (such as *ab initio*

quantum mechanics in the case of atomistic molecular dynamics or atomistic models in the case of coarse-grained molecular dynamics). The comparison of simulation results can be inexpensive, if only single point calculations (e.g. partial charges, bond orders, energy) are used for tuning.

Unfortunately, gradient-based minimization schemes require that the derivatives be computed at each iteration step; therefore these methods are not suitable when the derivative function is not known, may be computationally expensive to obtain or for which the derivative of the cost function is not defined at a particular point[34]. The Downhill Simplex method is a heuristic method that improves on the gradient method in that it does not require the calculation of the derivatives[35]. Unfortunately, both the gradient-based and Downhill Simplex method can only go downhill and thus find only nearby minimum in parameter space. They are unlikely to find the global minimum in a multidimensional parameter space as is often encountered in molecular force fields where the number of dimensions be as high as 100 per chemical element. Recent approaches to molecular model parameter optimization have included the usage of gradients of observables with respect to potential parameters[36]. This typically involves the usage of second- and third-order fluctuations of MD observables in the optimization procedure, which is difficult to determine precisely. The successive one-parameter search algorithm[26] is another method that is extensively used to optimize the ReaxFF reactive force field. According to this method, one particular parameter $\mathbf{s}$ in the force field is chosen at a time, and then a parabolic fit is made between three values of the cost function against three values for that parameter; one being the initial value, and the other two being small perturbations δs in both directions, $s \pm \delta s$. The optimum value for this parameter $\mathbf{s}$ is then calculated by minimizing this parabola. The procedure is then repeated by choosing a different parameter and is continued until the error no longer decreases. There are several problems with this algorithm from the point of view of global optimization. Cost functions of high dimensionality are rarely separable and thus exhibit high degrees of correlation between parameters. Thus, the procedure has to be repeated along several rounds over all the parameters to get a converged force field and might require prohibitively long optimization cycles. Another drawback lies in the fact that the procedure transforms a global optimization problem into a consecutive set of local optimization tasks. This means the algorithm can only find a local minimum in parameter space and that a very good initial guess for the parameters is necessary, otherwise the resulting force field will behave unexpectedly. For new systems of interest that have no adequate previous parameterizations to serve as an initial guess, this could be a formidable task.

In chapter 7, we attempt to overcome the above listed limitations and present an efficient approach to search for global minima of highly nonlinear,

multidimensional optimization problems. In addition, we apply it to train the ReaxFF reactive force field for an improved description of long range dispersion forces in organic explosive crystals.

2.2 Density functional theory

2.2.1 Introduction

In 1964, the work of Hohenberg and Kohn set the foundations of modern quantum chemistry methods by three theorems[37]. The first theorem states that the ground-state electron density uniquely determines the electronic wave function and hence all ground-state properties of the system. The second one establishes that the energy of an electron distribution can be described as a functional of the electron density, while the third one indicates this functional minimizes the ground state density. This, the problem of solving the many-body Schrödinger equation is transformed to minimize a density functional. Because of this complexity reduction, DFT has become increasingly useful for the understanding and calculation of the ground state density and energy of molecules, clusters, and solids – any system consisting of nuclei and electrons – with or without applied static perturbations. Whereas Thomas-Fermi and Hartree-Fock (HF) theories are intrinsically approximate, their successor, DFT, is in principle exact.

Wave function methods are ordinarily preferable when dealing with few-atom systems ($N \lesssim 5-10$) and when high accuracy is required. DFT is preferable when larger molecular systems are of interest and a more modest accuracy is acceptable. The key building blocks of traditional methods are single-electron orbitals ψ_j and many-electron wave functions Ψ, constructed from them. The key element of DFT is the electron density and, in the Kohn-Sham formulation, the fictitious single-particle orbitals. An intrinsic limitation of DFT is that it depends on the adequate knowledge of the exchange correlation energy functional, and although more and more accurate forms are constantly being developed[38-40], there is not a systematic way to achieve arbitrarily high accuracy. Nevertheless, it remains the method of choice to compute the energies, geometries, vibrational spectra and reaction barriers of many-electron systems in chemistry.

2.2.2 Fundamentals of DFT

A system of N nonrelativistic, interacting electrons in a nonmagnetic state is described with the Hamiltonian

$$H \equiv T + V + U \tag{30}$$

where the above terms are defined as follows (in atomic units)

$$T \equiv -\frac{1}{2}\sum_j \nabla_j^2\,, \quad V \equiv \sum_j v(r_j)\,, \quad U = \frac{1}{2}\sum_{i\neq j}\frac{1}{|r_i - r_j|} \tag{31}$$

In the above definition, a broad class of Hamiltonians with electrons moving in an arbitrary external potential $v(r_j)$ is considered.

The starting point of DFT is the rigorous, lemma of Hohenberg and Kohn: The specification of the ground state density, $n(r)$, determines the external potential $v(r_j)$ uniquely,

$$n(r) \to v(r) \tag{31}$$

Since $n(r)$ also determines the number of electrons N by integration, it determins the full Hamiltonian H and hence, implicitly all properties determined by it: full N-particle ground state wave function, electrical polarizability, nth excitation energy, vibrational force constants and potential energy surfaces for chemical reactions.

With the help of this lemma, a variational principle for the energy as functional of $n(r)$ can be derived[37]. For given $v(r)$ one defines the following energy functional of $n(r)$:

$$E_{v(r)}[n(r)] \equiv \int v(r)n(r)\mathrm{d}r + F[n(r)] \tag{32}$$

where

$$F[n(r)] \equiv \min\left(\Psi_{n(r)}, (T+V)\Psi_{n(r)}\right) \tag{33}$$

and the minimum is from among all antisymmetric wave functions $\Psi_{n(r)}$ with density $n(r)$.[Levy, M. PNAS, 1979, 76, 6062] The variational principle holds:

$$E_{v(r)}[n(r)] \geq E_{v(r)}[n_0(r)] \equiv \mathrm{E} \tag{34}$$

where $n_0(r)$ and E are the density and energy of the ground state. The equality in Eq. 34 holds only if $n(r) = n_0(r)$.

By making approximations for $F[n(r)]$, one can easily retrieve the Thomas-Fermi approximation. However, for most purposes a different approach has proved to be more useful[41]. We extract from $F[n]$ its largest and elementary contributions, by writing

$$F[n(r)] = T_s[n(r)] + \frac{1}{2}\int \frac{n(r)n(\acute{r})}{|r-\acute{r}|}\mathrm{d}r\mathrm{d}r + E_{xc}[n(r)]$$

(35)

where $T_s[n(r)]$ is the kinetic energy of a *non-interacting* system with density $n(r)$, and the next term is the classical expression for the interaction energy. The remaining E_{xc}, the so-called exchange correlation energy, is defined by Eq. 35.

If E_{xc} is ignored, the physical content of the theory becomes identical to that of the Hartree approximation. It is then no surprise that the Euler-Lagrange equation associated with the stationarity of $E_v[n]$ can be transformed into a new set of self-consistent (so-called Kohn-Sham) equations:

$$\left(-\frac{1}{2}\nabla^2 + v(r) + \int \frac{n(\acute{r})}{|r-\acute{r}|}\mathrm{d}\acute{r} + v_{xc}(r) - \epsilon_j\right)\varphi_j(r) = 0$$

$$n(r) = \sum_{j=1}^{N}\left|\phi_j(r)\right|^2 \ , \quad v_{xc}(r) = \delta E_{xc}[n(r)]/\delta n(r)$$

(35)

which differ from the Hartree equations only by the inclusion of the exchange correlation potential $v_{xc}(r)$. The *local* equations (Eq. 35) must be solved self-consistently, like the Hartree equations, calculating v_{xc} in each cycle with an appropriate approximation for $E_{xc}[n(r)]$. It is noteworthy that in spite of the appearance of simple, single particle orbitals, the Kohn-Sham equations are in principle *exact* provided that the exact $E_{xc}[n(r)]$ is used In other words, the only error in the theory is due to approximations of the exchange correlation functional. The ground state energy is given by

$$E = \sum_{1}^{v}\epsilon_j - \frac{1}{2}\int\frac{n(r)n(\acute{r})}{|r-\acute{r}|}\mathrm{d}r\mathrm{d}\acute{r} - \int v_{xc}(r)n(r)\mathrm{d}r + E_{xc}[n(r)]$$

(36)

where the ϵ_j and n are the self-consistent quantities.

The individual eigenfunctions and eigenvalues, φ_j and ϵ_j, have no strict physical significant, with one exception: For isolated systems with $v(\infty) = 0$, the highest eigenvalue, ϵ_N, is the negative of the exact, many-body, ionization potential. To put this theory into practical use, good approximations for E_{xc} are needed.

2.2.3 Exchange-Correlation functionals

Numerous approximations to the exchange-correlation (xc) energy, $E_{xc}[n(r)]$, have been developed. In this section, we will describe some prominent versions that were used in this work. A more general exposition can be found in Refs. [42, 43].

It is common to split the xc functional into an exchange term and a correlation term, namely

$$E_{xc} = E_x + E_x \tag{37}$$

The xc functionals may depend on several variables, for example, the electron density, its gradient, or other differential forms constructed from the Kohn-Sham orbitals

$$E_{xc} = E_{xc}[\rho, \nabla\rho, \phi] \tag{38}$$

The density and orbital variables are often separated into two variables, one for each type of electron spin, α and β (i.e. $\rho \to \rho_\alpha, \rho_\beta$). Depending on which variables are contained in the xc functional, the functionals are separated into different classes. The local density approximation (LDA) is dependent only on the electron density ρ. The generalized approximations (GGA) are also dependent on the density gradient $\nabla\rho$. In this class some known functionals include the BLYP and PBE forms. The hybrid functionals include a proportion of HF exchange

$$E_{xc} = \sum_{ij} \iint \frac{\phi_i^*(\mathbf{r})\phi_i(\mathbf{r}')\phi_j(\mathbf{r})\phi_j^*(\mathbf{r}')}{|\mathbf{r}' - \boldsymbol{r}|} \tag{39}$$

using the well-known HF exchange energy expression. Functionals of this type include the B3LYP, PBE0 and CAM-B3LYP forms. A set of relevant functionals described in the next section.

BLYP: The BLYP functional is a GGA functional dependent on both the electron density and its gradient. BLYP consists of the Becke functional[44] for exchange and the Lee-Yang-Parr functional[45, 46] for correlation. The exchange functional has the correct asymptotic behavior of the exchange potential for large distances and contains one empirical parameter fitted to exact energies of noble gas atoms from HF calculations. The LYP correlation functional is based on the expression for the correlation energy developed by Colle and Salvetti[45] which has been reformulated into a functional dependent on the electron density and its second-order gradient.

PBE: The Perdew-Burke-Ernzerhof functional is a GGA functional for both exchange and correlation[47]. The main idea behind the functional development is to satisfy exact conditions on the exchange and correlation functionals important for the energy evaluation rather than fitting parameters to empirical data. The functional contains no empirical parameters except the LDA correlation parameters of VWN[48].

B3LYP: The popular Becke-3-parameter-Lee-Yang-Parr functional is an admixture of the LDA, BLYP exchange-correlation and HF exchange energy and it contains three empirical parameters[49]. The inclusion of 20% HF exchange energy makes it a hybrid functional. In the original paper by Becke, the PW01 correlation functional[50] was used in the expression

$$E_{xc}^{\mathrm{B3PW91}} = E_{xc}^{\mathrm{LDA}} + a_0(E_x^{\mathrm{HF}} - E_x^{\mathrm{LDA}}) + a_X \Delta E_x^B + a_C \Delta E_C^{PW91} \tag{40}$$

The parameters $a_0 = 0.20$, $a_X = 0.72$ and $a_C = 0.81$ were fitted to thermochemical data. Later, Stephens et al.[51] found a slightly better performance when replacing PW91 with LYP, and the resulting functional is B3LYP.

The accuracy of this functional has been reported to give an average deviation in the energy prediction of 3.11kcal/mol on the 148-molecules test set G2-2[52] by comparing to experimental energies. This deviation is much higher than the deviation obtained by using G2-theory[52] which gives an average energy deviation of 1.58kcal/mol. Parts of this set have been used to parameterize the B3LYP functional[49], thus a comparison using a bigger test set will give a more systematic estimate for the accuracy. Such a comparison has been performed by Curtiss et al. who reported an average energy deviation of 4.14kcal/mol. The B3LYP functional also seems to describe well radical reactions as Bernardi et al.[53] report that the unrestricted B3LYP functional gives errors between 9-18% on reaction barriers for open-shell systems consisting of small hydrocarbon radicals and is superior to unrestricted HF and MP2 methods.

PBE0: The PBE0 functional[54, 55] is a hybrid functional based on the PBE formalism, that contains 25% HF exchange energy,

$$E_{xc}^{\mathrm{PBE0}} = E_{xc}^{\mathrm{PBE}} + \frac{1}{4}(E_x^{\mathrm{HF}} - E_x^{\mathrm{PBE}}) \tag{41}$$

It is claimed to contain no empirical parameters as the factor 1/4 in Eq. 41 can be determined from perturbation theory[56].

CAM-B3LYP: The CAM-B3LYP functional[57] belongs to the class of range-separated functionals, meaning that the exchange interaction is described by different mechanisms for short and long inter-electron distances. It is possible to write $\frac{1}{r_{12}}$ as

$$\frac{1}{r_{12}} = \frac{[\alpha + \beta \mathrm{erf}(\mu r_{12})]}{r_{12}} + \frac{1 - [\alpha + \beta \mathrm{erf}(\mu r_{12})]}{r_{12}} \tag{42}$$

where α , β and μ are parameters and erf is the error function. The parameterization allows the partitioning of two different exchange energy expressions E_{xc}^{LR} and E_{xc}^{SR}, both dependent on $\frac{1}{r_{12}}$

$$E_x(r_{12}) = E_{xc}^{\mathrm{LR}}\left(\frac{\alpha + \beta\,\mathrm{erf}(\mu r_{12})}{r_{12}}\right) + E_{xc}^{\mathrm{SR}}\left(\frac{1 - [\alpha + \beta\mathrm{erf}(\mu r_{12})]}{r_{12}}\right) \tag{43}$$

where E_{xc}^{LR} is the exchange functional whose importance increases at long range and E_{xc}^{SR} is the exchange functional whose importance increases at short range when α, β and $\alpha + \beta$ take values between 0 and 1. In CAM-B3LYP, the long range E_{xc}^{LR} is the exact HF exchange energy and the short range E_{xc}^{SR} is the Becke 1988 functional. The correlation energy in CAM-B3LYP is described by the B3LYP correlation contribution. The fitted parameters are $\alpha = 0.19$, $\beta = 0.46$ and $\mu = 0.33a_0^{-1}$, with a_0 being the Bohr radius. The sum $\alpha + \beta$ determines the amount of HF exchange at long range which should be equal to 1 for the correct asymptotic behavior of the exchange potential.

2.2.4 Basis sets

One can coarsely separate basis sets into two types: Slater type orbitals (STO's) and Gaussian type orbitals (GTO's) which are used to define the wave function. Using GTO's is a more common practice, which are of the form

$$f(x, y, z) = Nx^{l_x}y^{l_y}z^{l_z}e^{-ar^2} \tag{44}$$

where the l_i's are integers, instead of the exponential dependence used in STO's[58]. To approximate the functional form of the STO's (which have the shape of non-interacting one-electron orbitals), a linear combination of a certain number of GTO's is carried out, often called a "contraction". A typical set of such STO-like orbitals are the STO-nG basis sets[59], where a STO has been approximated by n GTO's. Another common approach is to separate valence orbitals and core orbitals (i.e. "split-valence"), as the valence orbitals describe most of the chemical properties of a molecule. Usually, the orbitals are centered on the nuclei, as this is the case for the one-electron systems without external fields. Here we note some characteristics of the most common basis sets used in this thesis.

6-311 basis sets: These basis sets[60, 61] describe the core orbitals as one contraction of 6 GTO's, and the valence orbitals as one contraction of 3GTO's and 2 uncontracted GTO's, thus the name 6-311. More specifically, for 1st row atoms, the core 1s-orbital is given as one contraction of 6 GTO's, the valence 2s-orbital and the 3 2p-orbitals are given as linear combinations of 3, 1 and 1 contracted GTO's. The 1s orbital of hydrogen is also described as a linear combination of 3, 1 and 1 contracted GTO's.

This set of contracted orbitals is optimized to describe the proper orbitals. However, some effects are not described properly. The contracted set is not flexible enough to polarize properly, and we therefore often add such flexibility by adding another GTO for each atom. The "(d,p)" in 6-311++G(d,p) means that 5 d-type GTO's (1 per d-orbital direction) have been added to the heavy atoms, while 3 p-type GTO's (1 per p-orbital direction) have been added to hydrogen. Another problem with the contracted basis sets is that the constructed wave function approaches zero earlier than the true wave function for long distances from the atomic center. In particular anions[62], lone pair electrons and weakly bounded systems such as hydrogen-bond systems[63] suffer from this poor description. A correction for describing such systems properly is then included by adding a flat and broad s-type GTO, also called a "diffuse" function. Such a function can be added only to the heavy atoms (signified by one +, e.g. 6-311+G(d,p)) or also to hydrogens (signified by two +'s, e.g. 6-311++G(d,p)).

Dunning's correlation consistent basis sets: These basis sets were specially designed for post-HF calculations, in which correlation is better taken into account than at the HF level[64]. Because they are intended, ideally, to give with such calculations improved results in step with (correlated with) their increasing size, they are called "correlation-consistent" (cc) basis sets. Ideally, they systematically improve results with increasing basis set size, and permit extrapolation to the infinite basis set limit. The cc-sets are designated cc-pVXZ, where p stands for polarization functions, V for valence, X for the number of shells the valence functions are split into, and Z for zeta (split valence). Thus, we have cc-pVDZ (cc polarized valence doubly-split zeta), cc-pVTZ (cc polarized valence triply-split zeta), cc-pVQZ (cc polarized valence quadruply-split zeta), and cc-pV5Z (cc polarized valence five-fold-split zeta). These basis sets can be augmented with diffuse and extra polarization functions, giving aug-cc-pVXZ sets. The cc-pVDZ is roughly comparable in size to the 6-31G(d); the other cc sets are much bigger. Correlation-consistent basis sets sometimes[65] but do not necessarily[66] give results superior to those with 6-31G basis sets that require about the same computational time.