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Molecular QCA timing: simulation and analysis of charge time evolution

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"It would be possible to describe everything
scientifically, but it would make no sense;
it would be without meaning, as if you
described a Beethoven symphony as
a variation of wave pressure."

Albert Einstein

Summary

The main goal of the thesis work is to demonstrate that an evaluation of switching time in MQCA molecules is possible exploiting molecular dynamic (MD) simulations, as reported in some works in literature, where molecule charges are investigate in time domain under the action of an external electric field. The switching process consists of the re-arrangement of internal local charge after a change of the surrounding conditions, such as electric field and/or neighbouring QCA cells, and it is characterized by the idea of switching time, t_{ST}. The switching time is the time required by charges to tunnel, inside the molecule, from one dot to the other one through molecular bonds, when the external electric field is changed. Moreover, during the design process of the QCA molecule, it is possible to estimate the corresponding frequency switching and in an ideal case it is in THz range.

In order to perform MD simulations and obtain time charge evolution a molecular dynamics simulator is used. It is widely used in the advanced research, especially in materials science and chemistry, to understand and to predict some phenomena and properties related to the atomic structures of a system. In particular, the simulator used is classified as quantum mechanical method that allows to study and to evaluate the electronic and energetics structures of molecules (organic or inorganic), surfaces and solids. It is based on DFT calculation and it is also one of the fastest methods for molecular calculation. The simulation module is characterized by an high accuracy of the results and a relative low computational cost with respect to a standard *ab-initio* method. Since simulations can be launched from command line,parameters are defined.

The main results concern the oscillation of DOTs charges an *ad-hoc* software, using *Python* language, has been developed in order to handle simulations in automatic all simulation data. It is composed by GUI through which all simulation in decatriene molecule under the action of electric fields. In particular, it is investigate the role of two electric fields: one along DOT-axis (switching field) and another one along vertical direction (clock field). From simulation data, a coherent behaviour of the DOTs charges are obtained according to field considered. At the end, a switching process is performed and an estimation of switching frequency is done, computing the switching time, and it is in the range of THz.

A possible future scenario is the analysis of other MQCA molecules, such as bisferrocene. The developed software can be easily adapted to other molecule, changing only the *.txt* file related to the initial geometry.

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List of Acronyms

MDS Molecular Dynamics Simulator

MD Molecular Dynamic

DFT Density Functional Theory

HF Hartree-Fock

LCAO Linear Combination of Atomic Orbitals

LDA Local Functionals

GGA Gradient-Corrected Functionals

DNP Double Numerical plus Polarization

HOMO Highest Occupied Molecular Orbital

LUMO Lowest Unoccupied Molecular Orbital

QCA Quantum Cellular Automata

MQCA Molecular Quantum Cellular Automata

SCF Self-Consistent Field

MUL Mulliken

ESP Electro-Static Potential

MM Molecular Mechanics

QM Quantum Mechanics

GUI Graphical User Interface

SPE Single-Point Energy

MVC Model-View-Controller

SW Switching Field

CK Clock Field

Chapter 1

Introduction

The development of the electronic technology is mainly based on silicon technology, which guarantee a good trade-off between performances and production costs. This technological development is well described by the *Moore's Law* that guided for years the trend of scaling. The reducing of device sizes allows to obtain fast devices, reduction of power dissipation and a greater density on chip. However, beyond a certain dimension (gate length below 0.1 μm), some problems arise related mainly to quantum effects that become predominant in the nano-scale range and it will be impossible to satisfy *Moore's Law* only by reducing dimensions. A possible solution to keep growth in device density is to change from the FET-based paradigm to others based on nanostructures. This kind of approach is called *More Than Moore* and it bases on the development of new technologies in which device functions are performed without physical current flowing in metal devices. In the last decades, many solution have been proposed to design new alternative devices (e.g. based on electron spin or on magnetic properties) in the *Emerging Research Devices* (ERD) section of the *International Technology Roadmap for Semiconductors* [6].
Among all new proposals, the so called *Field coupled nano-computing* (FCN), a new family for binary operations based on nanodevices, seems to be one of the most promising to overcome CMOS technology and it includes Quantum-dot Cellular Automata (QCA).

1.1 QCA principles

In 1993, a new approach has been proposed by C. S. Lent and his co-worker [7]. The new paradigm is demonstrated in [8, 9, 10] at earl '90s. According to it a new digital devices could be design bases on a cellular automata cell which consists of couple quantum dots and a cluster of free charges. The nanostructure used by

QCA paradigm are quantum dots that are structure in which electrons (free charges) remain confined until sufficient energy is provided to change their position in the cell.

The ideal QCA device is constituted by a square cell and inside it there are two free charges and six quantum dots: four dots in the corner (called *working dots* or *active dots*) and the last two in the middle. Due to quantum mechanic and the Coulomb interaction, a charge confinement of the two free charges is obtained to minimize total energy and free charges are confinement along one of the diagonal of the square. A logic information can be memorized according to diagonal occupied, as illustrated in figure 1.1.

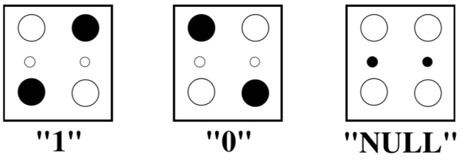
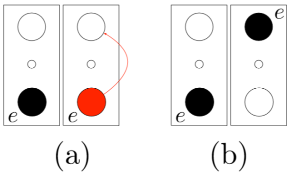


Figure 1.1: Ideal QCA device: basic cell and possible logic state [1]

The "NULL" configuration is useful for the clock system, explained in section 1.3. Notice that due to confining potential and coupling mechanisms, the free charges can tunnel among dots inside the square cell, but they cannot leave the cell.

To better explain the coupling mechanism, let's consider half QCA cell composed only by two active dots and one free charge (figure 1.2) with another one next to it to build a QCA cell. The free charge (electrons in the sketch) of the first half QCA cell (black spot), due to Coulomb interaction, forces the second electron (red spot) in the opposite dot in order to minimize repulsion and then a stable configuration is reached (case b)).



(a) (b)

Figure 1.2: Re-arrangement process of the charges; a) initial condition; b) final condition after re-arrangement; [2]

1.2 How informations travel

Once behaviour of single cell has been explained, the communication between near cells are described. The interaction is purely electrostatic, this means that information propagation does not require charge transport as in silicon or metal devices and then the energy dissipation is significantly reduced. The key point is the distance among cells and the ideal one (called d) between two near-neighbour cells is equal to the width of the single cell and since cell is squared it is also the distance between two corner quantum dots, as reported in figure 1.3. In this layout, the free charge arrangement at the edge of two consecutive cells interact (electrostatically) each others and free charges in the next cell, at the end, are disposed to minimize the electrostatic repulsion among the free charges at the cell edges.

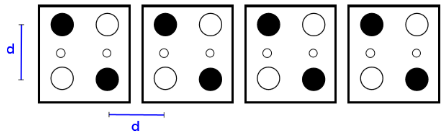
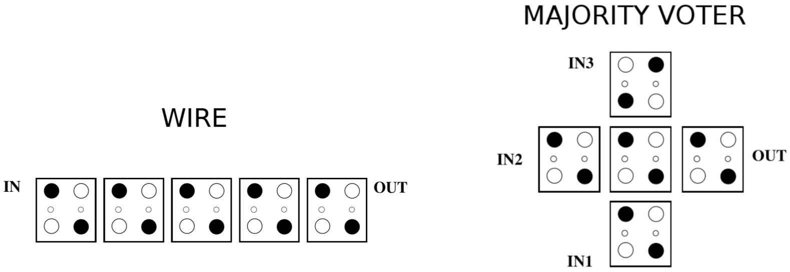


Figure 1.3: Interaction between QCA cells; [1]

By arranging different QCA cells in a specific layout, it is possible to implement many logic devices such as wires, majority voters or adders [11]. The simplest device is a wire (displayed in figure 1.4 a)).



(a) QCA Wire

(b) QCA Majority Voter

Figure 1.4: Example of QCA logic devices [1]

Up to now, devices and communication are considered ideal, but in real case some issues arise related to influences among cells. First consideration is the interaction between driver (first cell) to others becomes weaker due to its electrostatic nature (depends on distance) and its influence on the next cells is ruined. This degradation could be lead to a non complete switching of next cells and then losses part of the signal. Other consideration, more complex, concerns the influence of surrounding cells on a single cell. In other words, a single cell is not influenced only by the previous and the next cell, but by all other molecules in the device. For these reason a clock system and an additional quantum dot have been required to allow a good signal propagation.

1.3 Clock system

In order to avoid instability problems related to the degradation of the signal during its propagation, an external electric field (called *Clock* field) is required. If clock signal is abrupt, many problems arise related to metastability [12]. The clock signal allow to change potential barriers inside cells to hinder or to facilitate charge rearrangements. According to Lent and co-worker studies [13, 14], a possible solution to overcome these issues is to change the way in which clock is applied: *adiabatic switching*. In particular, adiabatic switching consists on different consecutive phases of clock field, reported in figure 1.5, in order to avoid abrupt switching of clock field.

To implement the adiabatic switching, the QCA circuit requires to be divided into *clock regions*, where in each zones a different clock can be applied. The four consecutive phases of clock are:

1. *Switch phase:* inter-dot potential barrier is reduced and free charges can move along one of the two diagonal encoding the binary information according the surrounding (other cells and/or external electric field). In this phase cell pass from NULL state to one of the two logical states: ”0” or ”1”;

2. *Hold phase:* potential barrier is increased to fix the binary information encoded in the previous phase (no more switching) that will influence the next cell where a switch phase of the clock is applied. Clock field is positive and then (positive) charges are pushed towards the logical DOTs;

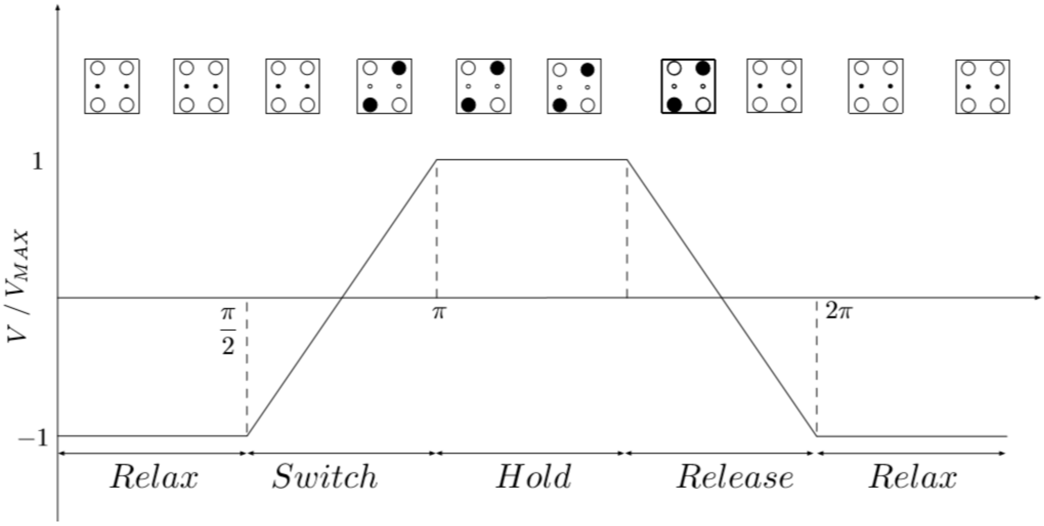


Figure 1.5: Clock phases; [2]

3. *Release phase:* potential barrier is lowered and free charges can return in the NULL state (initial state). Clock field is slowly reduced;

4. *Relax phase:* potential barrier is increased to maintain free charges in the NULL state. Clock field is negative and then (positive) charges are pushed towards the NULL dot;

1.4 Possible implementations

The new QCA paradigm may be implemented in different ways and many solutions were proposed and implemented in the last two decades, in which information is not encoded exploiting charge flows or voltages as in standard electronic devices, but using other properties such as charge distribution or spin. Some examples are:

- *Metal-dot solution:* structure bases on metal (Al) islands over a silicon oxide (SiO_2) substrate. Disadvantages: metal islands are very large, no nanodevice but microdevice, temperature limitations (works only for temperature in the mK range, no realistic) and maximum operation frequency is in the MHz range;

- *Semiconductor-dot solution:* alternative solution of metal-dot one where it is exploited the semiconductors technologies to build structures with some dots where the free charges are stored. Same disadvantages of metal-dot solution;
- *Magnetic solution:* the first successful implementation and still adopted, where informations is encoded exploiting the two directions of nano-magnets. Clock signal in this case is a magnetic field able to erase the magnetization encoded. Advantages: nanodevice, low power dissipation and possible implementation at room temperature. Disadvantages: due to magnetism, the speed is not very high.
- *Molecular Solution:* the most promising implementation and since it is the subject of this thesis, it is well explained in the next chapter;

Chapter 2

Molecular QCA

Among all the possible implementations of QCA technology, the Molecular Quantum-dot Cellular Automata (MQCA) is the most promising and for this reason the thesis work is focused on it.

The QCA cell consists of a molecular system, usually two molecules positioned one close to the other. Molecules used generally are characterized by at least two redox centres, which act as quantum dots to confine charges. In particular a redox centre is a cluster of atoms that change their oxidation number, in order to gain or lose electrons. In other words, they are particular molecule sites in which free charges can be aggregated. Moreover, the two/three redox centres are linked through a tunnelling path, provided by molecular bonds, that allows electrons (the free charges) to move from one dot to the other one. The informations in MQCA cell is encoded exploiting the charge confinement in one of the two/three dots (the third dot is required to perform a good transmission, *adiabatic switching* explained in section 1.3).

An important aspect related to its molecular nature is that molecule can be used in its neutral form, where its total charge is zero, or in oxidized/reduced form in which an electron is removed/added and the total charge is not more zero. Using oxidized or reduced molecule, it is observed an enhancement of the QCA performances. Both two configurations can be realized during synthesis of the molecule.

As already mentioned, a complete QCA cell is obtained joining together two molecules and the most used MQCA molecules are characterized by two or three redox centres, then a single cell is composed by four or six dots. Figure 2.1 shows an example of MQCA molecule characterized by three redox centres.

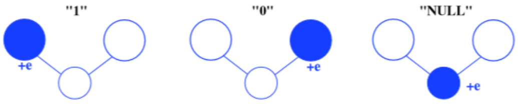


Figure 2.1: Example of encoding for 3-Dots molecule; [1]

2.1 Advantages

MQCA technology, since it is the most promising solution, is characterized by several advantages:

- *Small size:* QCA cell is scaled up to molecular dimensions, about tens of $\mathring{A}$;
- *High density:* as a consequence of small size, density is of the order of $10^{11}-10^{14}$ cm^{-2};
- *Room operation temperature:* due to small dimensions the Coulomb interaction increases with respect other solution and then cryogenic temperature are not required;
- *Cells are the same size:* since molecules are all the same size, no problems related to uniform mass production of nanodivices;
- *High speed:* switching speed is ideally in the range of THz;

2.2 Possible Candidates

An important effort has been done in the study of the emerging MQCA paradigm and it consists on the study of possible candidate molecules to build MQCA cells. Most of molecules are ideal because they have been never synthesized, this means that they has been studied only by simulations and never by physical implementation. Moreover, another limitation is that most molecule may be used only in gas phase or in solution because they do not have a binding element for their deposition on a substrate. In the following, the only three molecule are described.

2.2.1 Diallyl-butane molecule

Diallyl-butane is the first molecule proposed for QCA application and it is very ideal molecule. It is reported in figure 2.2 and it is characterized by two allyl groups, which represent active DOTs: *DOT1* and *DOT2*, connected by a butane bridge. The free charges are able to move from one dot to the other through the butane bridge.

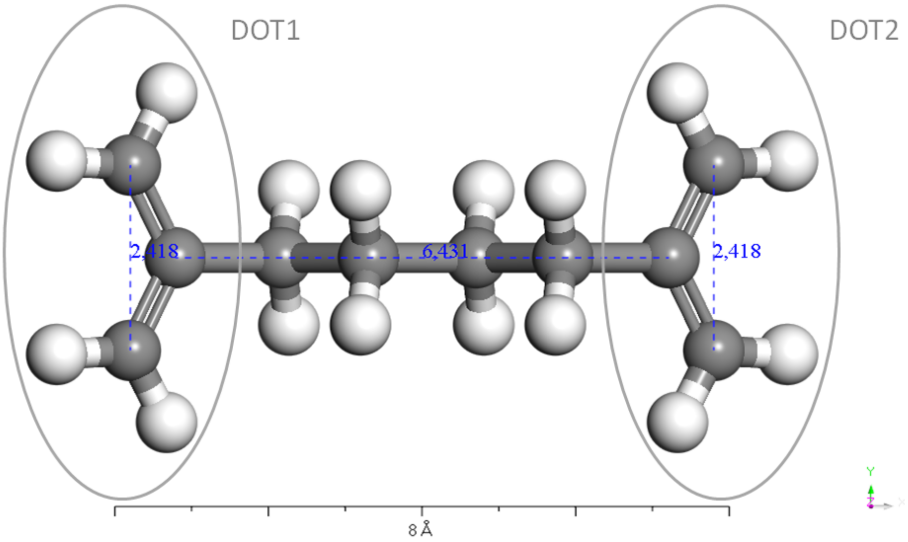


Figure 2.2: Diallyl-butane molecule

Of course, diallyl-butane constitutes only half QCA cell and then a whole QCA device can be obtained positioning two molecules one close to the other in order to form a squared structure. It presents a good capability to confinement charges but it is not useful in real application because lacks both the DOT3, required to add NULL state for adiabatic switching and the binding element to link it to a substrate.

2.2.2 Decatriene molecules

A possible solution to overcome limitations of Diallyl-butane molecule is the use of decatriene molecule as possible candidate for MQCA applications. It is a three dots molecule, where each quantum dots is composed of ethylene group (circled in figure 2.3).

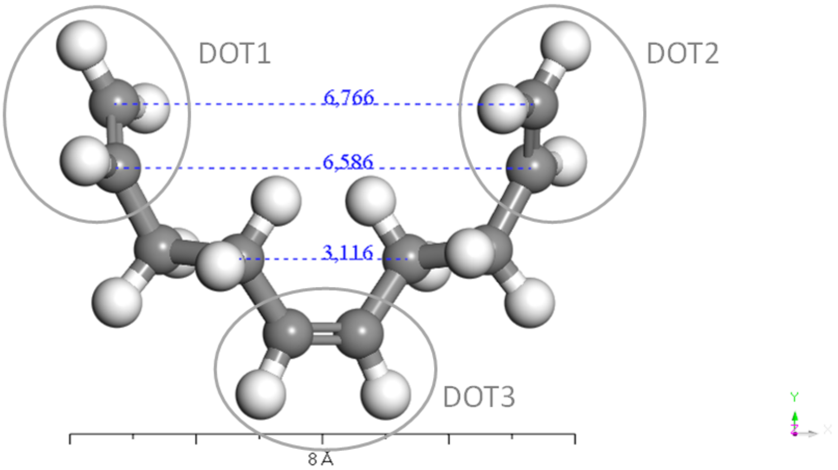


Figure 2.3: Decatriene molecule

As in diallyl-butane molecule, decatriene one is only half QCA cell and two molecules are required to build QCA device. The three dots allow to use decatriene molecule performing adiabatic switching and considering orbitals it is possible to recognize the three allowed configurations: "0", "1" and "NULL".

Figure 2.4: Logical state encoding HOMO visualization

The decatriene molecule is studied in this thesis work because it is quite more realistic than diallyl-butane molecule and it is smaller than bis-ferrocene molecule, less number of atoms, which means reasonable time required to simulated it.

2.2.3 Bis-ferrocene molecule

Continuously research of the best candidate for MQCA applications lead to the definition of the most promising candidate: the bis-ferrocene molecule, shown in figure 2.5. It is composed by two ferrocene, acting as active dots (*DOT1* and *DOT2*) and a carbazole bridge that is the DOT3, fundamental for the definition of the "NULL" state. Notice that also bis-ferrocene molecule is half QCA cell and its inter-dot distance is about 10 Å, this means that edge of the ideal complete QCA cell is about 1 nm. The bis-ferrocene molecule may present a binding bridge made by an alkyl chain that guarantees the attachment to a gold surface.

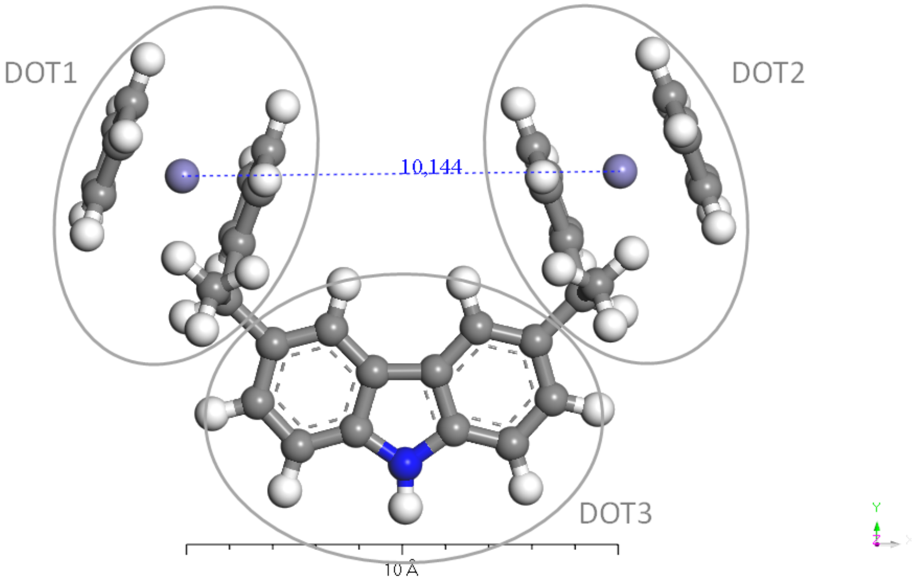


Figure 2.5: Bis-ferrocene molecule

Moreover, it has been synthesized of the chemistry department at the University of Bologna, in a collaboration between the University of Bologna and Politecnico di Torino.

2.3 Switching

One of the most interesting advantages of MQCA technology is its high speed to perform switching. In this work an estimation of the speed velocity is proposed exploiting molecular dynamic simulations. In particular, the switching of decatriene molecule is studied but the procedure used can be easily extended to other molecules as bis-ferrocene molecule. The switching process consists of in the re-arrangement of internal local charge after a change of the surrounding conditions, such as electric field and/or neighbouring cells, and it is characterized by the idea of switching time, t_{SW}, and switching velocity.

The switching time is defined as the time required to charges to tunnel from one dot to the other one through molecular bonds, when external electric field is changed. Moreover, during the design process of the molecule, it is possible to estimate the corresponding frequency switching and in ideal case it is in THz range.

The idea of switching time is illustrated in figure 2.6. The t_{SW} is defined as time to complete charge inversion and it is considered completed when *DOT1* (in figure Q1) charge becomes almost equal to *DOT2* (in figure Q2) at time zero (t=0) and, to analogy, when *DOT2* becomes almost same to *DOT1* at time zero [3].

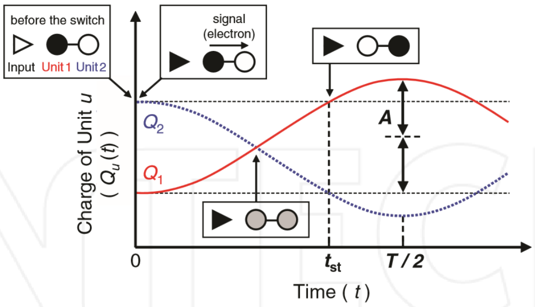


Figure 2.6: Schematic view of switching time [3]

At time $t = 0$, field is inverted (switching of the field) and DOTs charges move according to field polarity up to reach a situation where they are almost equal in magnitude to initial charges but are located in the opposite DOTs, respect to initial condition.

In figure 2.7, charge evolution for Double-Cage Fluorinated Fullerenes [4] is displayed and the switching time is evaluated. In particular, at $t = 0 fs$ electric field is inverted and then DOTs charges start to move following the field. The switching time is about $2.5 fs$.

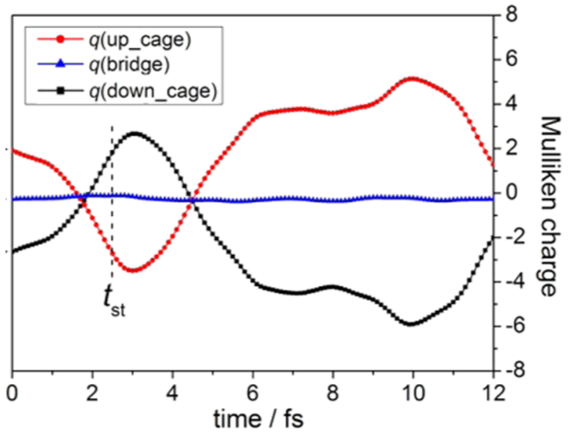


Figure 2.7: Evaluation of switching time in Double-Cage Fluorinated Fullerenes [4]

Chapter 3

Tool for MQCA simulation

3.1 Computational Chemistry

With the development of efficient computer technology, the computational chemistry is significantly developed. It is an important branch of chemistry that uses powerful calculators to solve chemical problems in order to evaluate the properties and structures of a given physical system, such as molecules or solids. Using a mix of chemically, physically and mathematically notions, this new approach has made possible to solve, in an efficient way, the quantum many-body problems (system composed by several interacting particles), and in some cases to predict chemical phenomena before observing them. For these reasons it is widely used in the investigation of new materials or molecules. Moreover, the computational chemistry is able to study physical systems both in static and in dynamic regime. Some properties that could be calculated are: geometries of the molecules (expected atom positions and velocities), electronic structures, absolute and interaction energies and mechanical properties.

Several approaches are possible to perform this kind of calculation and the main difference is related to the physical principles adopted in the calculation:

- **Molecular Mechanics (MM) approach** uses the principles of classical physics (Newtonian mechanics) to model the system. It is based on so-called *forcefields* that are a set of parameters used to analyse the molecular system and they are mainly derived from experiment.
  Usually it is used to simulate very large system (like enzyme) in a reasonable time with a quite good result. Possible applications are geometry optimization and dynamic simulation.

- **Quantum Mechanics (QM) approach** relies on quantum physics in which objects have both particle-like and wave-like behaviour (wave-particle duality) and energy, momentum and other quantities are quantized (discrete values). In this approach, molecular structure and other properties are computed starting from quantum principles, without any experimental data. This kind of approach is called *ab-initio* method. It allows to study molecules in a very precisely way, but it is rather computationally expensive and so it is applicable to only small system composed by tens of atoms.

3.1.1 Quantum Mechanics

A generic quantum system (such as a molecule) is described by the Schrödinger equation (eq. 3.1) and its solution describes the state of the system:

$$i\hbar\frac{\partial\Psi(\vec{r},t)}{\partial t} = \hat{H}\Psi(\vec{r},t) \tag{3.1}$$

where $\Psi(\vec{r},t)$ is the wavefunction that depends on the position $\vec{r}$ and time t and describes te probability to find an electron in the position $\vec{r}$ at a specific time t; $\hbar$ is the reduced Planck constant; $\hat{H}$ is the so-called Hamiltonian operator related to the total energy of the system. The total energy is not simple to determine and it is linked to kinetic and potential energies of the whole system:

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r},t) = \hat{T}_e + \hat{T}_N + \hat{V}_{ee} + \hat{V}_{NN} + \hat{V}_{eN} \tag{3.2}$$

where $\hat{T} = -\frac{\hbar^2}{2m}\nabla^2$ is the kinetic energy operator related to electrons e and nuclei N; $\hat{V}$ is the potential energy operator that includes electron-electron ee, nuclei-nuclei NN and electron-nuclei eN interactions.

Since the Schrödinger equation (eq. 3.1) can be solved only for the hydrogen atom and for all other systems it is cannot be solved exactly, some approximations are required. Usually, the assumptions to simplify the problem are:

1. **Born-Oppenheimer approximation:** nuclei of atoms can be considered fixed with respect to the motion of electrons. This assumption is justify because nuclei are heavier than electrons.

2. **Linear Combination of Atomic Orbitals (LCAO):** molecular orbitals can be computed as result of a linear combination of the starting atomic orbitals.

According to the desired level of accuracy, three main classes of methods are distinguished in quantum mechanics:

- **Semi-empirical method:** it uses the Hartree-Fock (HF) formalism in a simplified version, where some parameters are obtained from empirical data. Usually, it is important to treat large number of atoms with a reasonable accuracy, otherwise the exact HF method is too computational expensive.
- ***Ab-initio* method:** it relies on the solution of the Schrödinger equation (eq. 3.1) to extract useful informations and quantities of the system (such as electron densities and energies). The calculations start from quantum principles and fundamental physical constants, without any information from experiments. For these reasons, this method is highly accurate and, inevitably, also high computation expensive.
- **Density Functional Theory (DFT) method:** it bases on functionals and, in particular, on the idea that all the ground-state properties of a system are uniquely determined by an electron density, which depends only on three spatial coordinates. In this method the electron correlation is included, instead in the HF formalism it is not taking into account. The electron correlation is a measure of the influence on an electron of the surrounding electrons. Computational cost is relatively low with respect to the traditional *ab-initio* method and the result could be very accurate. So, this method is widely used in computational chemistry.

Notice that any computational method is characterized by a theoretical procedure (or *method*) such as Hartree-Fock or post-HF, and a *basis set* that is a set of functions used to describe (mathematically) electronic wave functions, exploiting the LCAO approximation. Basis set could influences the accuracy of calculation because a large basis set means good approximation of the molecular orbitals but, at same time, requires more computational cost.

In order to treat a physical system using the quantum mechanics approach and to solve the Schrödinger equation, many ad-hoc softwares have been developed. These programs are generally called also *ab-initio* simulators. Some example of these kind of simulators used in literature are: Gaussian 09, GAMESS US and Materials Studio (MDS). The latter simulator is used in this work and in the following sections is examined.

3.2 Molecular Dynamics Simulator Package

Since the aim of this thesis is the characterization in time domain of the molecules explained in the section 2.2, a computational chemistry software has been required and a molecular dynamics simulator (MDS) package has been selected. The choice to use it coming from the necessity to investigate dynamic behaviour of molecules, since the more common simulators (such as Gaussian) are not able to perform this task. Moreover, searching in literature as confirm of its capability, an interesting work [4] has been found where a molecule is studied in the time domain and, in particular, its atomic charges evolution.

Molecular Dynamics Simulator package is a modelling and simulation environment and it is composed by several simulation and visualization tools. It is widely used in the advanced research, especially in materials science and chemistry, to understand and to predict some phenomena and properties related to the atomic structures of a system. Thanks to the large number of simulation tools inside it, various materials could be simulated and investigated from a periodic bulk materials to surfaces and from polymers to single molecules. Moreover, its graphical interface allows to construct and manipulate the geometry of our system.

3.2.1 Briefly introduction

In this part a briefly introduction of MDS software is explained.

In the figure 3.1, the graphical user interface of MDS is reported with a simply water molecule. The interface is composed in three main parts: in the upper part are reported the shortcuts of visualization and simulation tools, at the left part is visualized the working directory and at the center-right part the XYZ space to visualize the system under test.

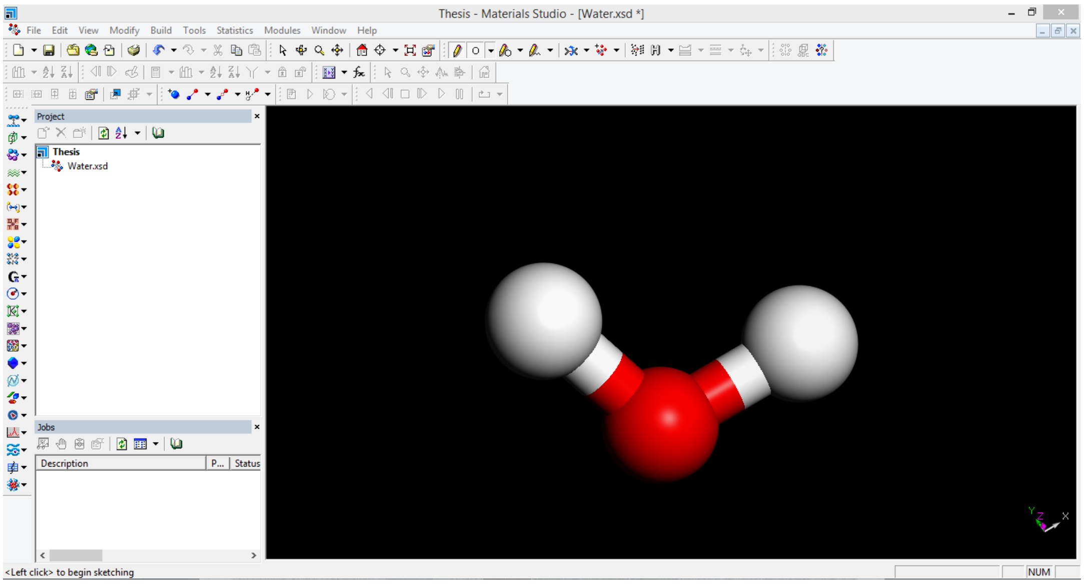


Figure 3.1: An example of MDS interface

Firstly, it is necessary to create a new MDS project, otherwise it does not start. Secondly, to define the geometry of our system a geometry file (3D Atomistic Document, *.xsd*) must be created, where all informations related to the geometries are conserved. Then to define the system, in our case a water molecule, the sketch tool can be used and it allows to directly draw atoms in the desired position in the XYZ plane. Moreover, using other drawing tool in the *Build* menu, user is able to build different structure: crystal, polymer, surface and nanostructure.

Once the system geometry is defined, MDS can performs several kind of simulation according to the chosen tool. All available tools are reported in the *Modules* menu or in the shortcuts part, in the upper region of the interface. Naturally, modules included in MDS package are a restricted version of standard simulation program. Some example of modules are:

- **CASTEP:** a DFT method based on a plane wave basis set for the simulation of solid-state materials. Useful to predict structural, optical and electronic properties;
- **DMol^3:** a DFT quantum mechanical module that can simulate periodic and non periodic structures, like molecules, in gas phase and solid environments;
- **Forcite:** a set of molecular mechanics tools able to simulate a wide range of systems, where the potential energies on which atomic nuclei move are based on forcefields;
- **Gaussian:** a restricted version of Gaussian that employs Hartree-Fock and DFT methods to study molecular systems in static condition, allowing predictions on structural, electronic and thermodynamic properties.

Among all the modules available on MDS, the most attractive for the aim of this thesis is certainly the DMol^3. In fact, it allow to simulate one single molecule in the static and dynamic regime investigating mainly its geometry and electronic properties.

3.3 Simulation module

In the following, the selected module in MDS is analysed first from the theoretical point of view and then from executive one.

This modulus is classified as quantum mechanical method that allows user to study and to evaluate the electronic and energetics structures of molecules (organic or inorganic), surfaces and solids. It is based on DFT calculation and it is also one of the fastest methods for molecular DFT calculation. The simulation module is characterized by an high accuracy of the results and a relative low computational cost with respect to a standard *ab-initio* method. Notice that it is considered a quantum mechanical *ab-initio* method, even thought for some functionals it uses parameters based on experiment data or more complex calculations, like in molecular

mechanics.
The simulation tool in MDS can currently perform different tasks and the more interesting ones are:

- *Energy:* it performs a single-point energy (SPE) calculation, in which the wavefunction, charge density and energy are calculated for a given arrangement of the atoms;

- *Geometry optimization:* it searches the minimum energy of a given structure, in order to bring the system in a stable geometry. It is an iterative method in which atoms positions are adjusted up to obtain a stationary configuration;

- *Dynamics:* it performs a molecular dynamics

Since the latter task is the fundamental part of this thesis, it will be better explained in the next paragraph.

Moreover, the simulation tool requires a set of different input files, mainly text files, to define all parameters of the simulation and produces as result many output files, *.txt* and not. For this reason, each simulation generates a subfolder in the working directory, with the same name of the simulation, that contains all simulation files. Input files will be explained in paragraph 3.3.4, while the output ones in paragraph 3.3.5.

3.3.1 Dynamic simulation theory

This task in the simulation module allow user to perform a molecular dynamics (MD) simulation and so to understand how the atoms in a structure will move in time under the influences of some external/internal forces. Usually, the MD exploits the stepwise integration of Newton's equation (eq. 3.3) of motion modified, in appropriate way, to consider the effects of temperature. The simplest expression for the classical equation of motion for a single particle is:

$$\sum \vec{F} = m\vec{a} \tag{3.3}$$

The main difference of MD performed by the simulation module with respect to the conventional (forcefield-based) MD is that the atomic forces are computed exploiting DFT calculation rather than from experimental potentials and interatomic interaction. For this reason it is considered an *ab-initio* MD, but the drawback of the calculation is inevitably the increasing of the computational cost because forces and energies are computed starting from first principles. The main contribute in the speed of the MD simulation is relative to DFT calculation. At the end, the trajectories of atoms are computed integrating the equation of motion following the Verlet algorithm.

In order to perform the integration other parameters are needed:

- *Thermodynamic ensemble: NVE or NVT.* The adiabatic or micro-canonical ensemble (NVE) is when a system does not exchange energy E and not change its volume V. Instead, the isotermal or canonical ensemble (NVT) is a system in which the temperature T is maintained constant thanks to an heat exchange with an external thermostat and also the volume V is kept constant;

- *Time step:* it is an important parameter in the integration algorithm, because for a good dynamic it should be quite large, but if too large the simulation fails due to the large energy difference between steps (instability);

- *Geometrical constraints:* they are applicable in MD simulation and are divided in internal and individual constraints. The internal are related to the distances and angles between atoms. Instead, the individual ones consist of the fixing atomic positions along X, Y and Z directions;

3.3.2 Charge distribution theory

Since the analysis of the charge distribution is a fundamental aspect for this thesis work, a briefly considerations on models to evaluate molecular charge must be done. Usually in a physical systems, nuclei are considered as fixed charges, while electrons as mobile charge and they are described by probability functions. Due to the non localization of electrons charges, statistical models are required to model charge.

In a molecule, the total charge is defined as the sum of all the charge contributions given by nuclei and electrons and each atom has its charge. Therefore, if the molecule is neutral the total charge must be zero because the number of electrons is equal to the protons number. Instead, if the molecule is oxidized or reduced the total charge is expected to be different to zero. Notice that, in any case, the local charge inside the molecule could be different to zero due to the delocalization of electrons inside it and the evaluation of these local charges is extremely important in the characterization of molecules for MQCA applications.

The simulation tool makes available three different models to evaluate the charge: Hirshfeld charge, Mulliken population (MUL) and ESP charge.

The *Hirshfeld analysis* is based on the deformation density ρ_d that is simply the difference between the molecular and the unrelaxed atomic charge densities:

$$\rho_d(\vec{r}) = \rho(\vec{r}) - \sum \rho_\alpha(\vec{r} - R_{\alpha)} \tag{3.4}$$

where $\rho(\vec{r})$ is the molecular density and $\rho_\alpha(\vec{r} - R_\alpha)$ is the density of the free atom α positioned at coordinates R_α. From the deformation density the effective atomic charge q_α is computed exploiting the following formula:

$$q_\alpha = Z_\alpha - \int \rho_d(\vec{r}) W_\alpha(\vec{r}) d\vec{r} \tag{3.5}$$

where Z_α is the charge on nucleus α and $W_\alpha(\vec{r})$ is a weight function defined for atomic density for atom α at coordinate $\vec{r}$.
This kind of analysis has several disadvantages as reported in [15] and the main drawback is that this approach underestimates the atomic charges.

The *Mulliken analysis* is one of the most used model for the evaluation of atomic charge. As explained in Remacle and Levine works [16] and [17] and also in Tokunaga papers [3] and [18], the Mulliken charge of atom α is defined as:

$$Q_\alpha = Z_\alpha - \sum_{\nu}^{Basis} (P \cdot S)_{\nu\nu} \tag{3.6}$$

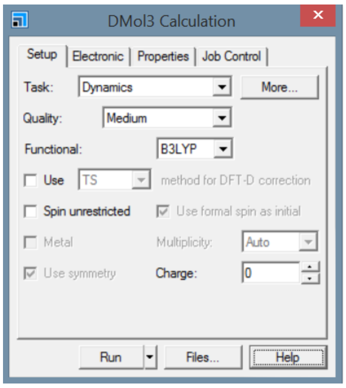
where Z_α is the nuclear charge of atom α; P is the density or population matrix and S is the overlap matrix. Both matrices depend significantly on the basis set used in the calculation.

The Mulliken charge analysis is simpler, but it strongly depends on the basis set considered.

The *ESP analysis* is an electro-static potential (ESP) fitting method useful to determine the net charge of each atoms. This method can be applied only for small molecules and not for large molecules and bulk systems, otherwise the fitting fails. The main idea is to fit the electro-static potential with a set of charges. The first step is the evaluation, using DFT calculation or HF approach, of the electrostatic potential outside the molecule. This potential is given by a nuclei and an electron contributions. Once the potential is evaluated, a set of charges in the atom positions are fitted, using the least square method, in order to reproduce the computed potential with the potential given by effective charges.
This approach is rather simple, as Mulliken analysis, but it is much less sensitive to the basis set used in the calculation and, generally, it provides more accurate results.

3.3.3 Simulation setting

Once the geometry of the system is defined as reported in paragraph 3.2.1, a simulation can be launched from the graphical interface of MDS. Choosing the simulation module from *Modules* menu, a setting window (reported in figure 3.2) is opened and it allow user to choose all the simulation parameters, from DFT calculation to properties of the system that will be calculated.



Task: Dynamics
Quality: Medium
Functional: B3LYP
☐ Use TS method for DFT-D correction
☐ Spin unrestricted
☑ Use formal spin as initial
☐ Metal
Multiplicity: Auto
☑ Use symmetry
Charge: 0

Figure 3.2: Setting window for simulation module

The configuration window (figure 3.2) is divided in several tabs: *setup*, *electronic*, *properties* and *job control*.

Setup Tab

Calculation window shows as first the *Setup* tab, which allow user to set fundamental parameters of the simulation, such as:

- *Task:* to define the simulation typology (see paragraph 3.3);
- *Quality:* it is the accuracy of simulation and the DFT method;
- *Functional:* defines the the DFT exchange-correlation potential to be used. Four classes are available: local functionals (LDA), gradient-corrected functionals (GGA), B3LYP (an hybrid functionals) and meta-GGA functionals;
- *Spin unrestricted:* when checked, the calculation is done using different orbitals for different spins; otherwise, if not checked a restricted calculation is performed (same orbitals for α and β spins);
- *Charge:* sets the total charge of the molecule or unit cell, in large system;

A fundamental choice is this tab is the functional for the DFT calculation. Reasonable functionals are *blyp* [19], which belongs to GGA group, and the most used *B3LYP* (Becke, three-parameter, Lee-Yang-Parr) functional, that is an hybrid functional where it is takes into account the exact exchange term from HF and the exchange-correlation energy from other theories or experiments.

Notice that there are additional options to set in this tab (*More...* button), but they are considered and explained later (paragraph 4.2.2).

Electronic Tab

The second tab shows in the calculation interface is the *Electronic* one that allow user to set the parameters related to the electronic Hamiltonian. The main parameters are:

- *Integration accuracy:* to determine the precision in the integration of the Hamiltonian. Coarse, medium and fine quality are available and in medium are used about 1000 points for the integration. It is defined automatic according to the quality chosen in the *Setup* tab, but it can be changed;

- *SCF tolerance:* defines the threshold to determine when SCF calculation has converged. As the previous parameter, the values are defined automatically from quality imposed in the *Setup* tab, but it can be personalized;
- *Basis Set:* to set the atomic orbitals basis set and its version;
- *Orbital cutoff quality:* specifies the range of the cutoff of the basis set. Choosing the quality, user determine the size of the cutoff range, this means the distance (from the atomic centre) at which the atomic orbitals are zero. It is expressed in Å. As for the previous quality, it is defined according to the simulation quality imposed and it can be customized;
- *Max SCF cycles:* determines the maximum number of SCF iterations permitted in the energy calculation; if the simulation requires more cycles, the calculation fails.

Certainly, the choice of the basis set is crucial because together with functional, it models the system under analysis and all results depend on them. A bad choice of functional or basis set could produce a completely wrong results. According to [19] and reading the manual of MDS, a possible good basis set is *DNP* version *4.4*, which is optimize for H, C and Si atoms. It is characterized by an high accuracy and high computational cost. Moreover, a better version of *DNP* is *DNP+*, which requires a very large cutoff ranges meaning more computational expensive than classic *DNP*.

Properties Tab

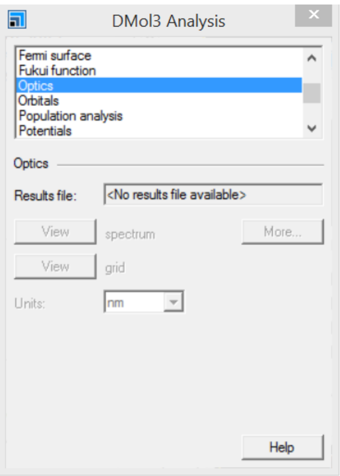
The third tab is related to what user wants to investigate of system under analysis. In fact, it is simply a list of all properties that the simulator is able to compute. In the following, all properties useful for the thesis work is explained:

- *Electron density:* to compute the total or deformation charge density and the result is stored in a *.grd* file;
- *Electrostatic:* to evaluate all the properties related to the electrostatic of the system under analysis. In particular, the *Electrostatic potential* and *Electrostatic moments* (computes the dipole moment) are checked;

- *Orbitals:* when checked, the molecular orbitals are computed and stored in a a *.grd* file. The HOMO and LUMO are computed and can be visualized in 3D plot.

- *Population analysis:* allows user to calculate the atomic charges on the input structure. The evaluation can be done exploiting Hirshfeld, Mulliken and ESP analysis (discussed in paragraph 3.3.2), the desired model must be checked in the tab.

Notice that the 3D properties are stored in a *.grd* file and MDS allow user to plot them in the 3D space, superposing 3D feature on molecule. In order to do this, user must exploit the *Analysis* tool (shown in figure 3.3) available on *Modules* menu, such as *Calculation* window.



Results file: <No results file available>

Units: nm

Figure 3.3: Analysis window for simulation module

Job Control

In this last tab of the *Calculation* window allow user to control some aspect of the simulation to perform. The main parameter is the *Run in parallel on*, which establish the number of computer cores to be used in parallel. Other parameters can be setted, such as the use of memory in the simulation or time after that the structure is updated.

3.3.4 Input files

As already mentioned, the simulation tool requires a set of input files to define all the simulation settings. Two files are fundamental, one related to the parameters that will be used in calculation and the other one contains all geometric informations of the system. Moreover, other files are required, but they are automatically created starting from the definition of the two previous files but they can be personalized opening them as test file. These last group of input files are hidden files type in the simulation subdirectory and then they are not displayed in the working directory on MDS interface (left part of the interface). User can visualize hidden files opening the working directory using the filesystem, bypassing the MDS interface.

The file related to the parameters setted, through the *Calculation* windows (see paragraph 3.3.3), is a *.input* file and it can be edited using any text editor. In the following, an extract of it is reported and its relevant parts are explained, a complete *.input* file used in MD simulation is reported in appendix A.1 and well discussed in the paragraph 4.2.2.

```
# Task parameters
Calculate                     optimize
[...]
Max_memory                    2048
File_usage                    smart
Scf_density_convergence       1.000000e-006
Scf_iterations                50

# Cartesian constraints
MD_Fixed_Coordinate
1   Y

# Electronic parameters
Spin_polarization             unrestricted
Charge                        0
Basis                         dnp
basis_version                 basfile_v4.4
```

```
Pseudopotential              none
Functional                   b3lyp umesh=xcoarse minu=-3
Aux_density                  octupole
Integration_grid             fine
Occupation                   fermi
Cutoff_Global                3.7000 angstrom

# Calculated properties
[...]
Electrostatic_moments        on
Mulliken_analysis            charge
Hirshfeld_analysis           charge
Esp_fit                      on
[...]
electric_field               0.004 0.0 0.0
```

The *.input* file divided in many sections: *Task parameters*, *Cartesian constraints*, *Electronic parameters* and *Calculated properties*. It is just a series of lines, where each line begins with a *keyword* followed by values. Keywords are a sort of command related to all the simulation parameters and its value represents the magnitude of the parameter. All keywords are well documented in the MDS manual. Generally, the first section is characterized by the `Calculate` keyword and its value expresses the type of calculation will be performed (possible value: energy, optimize, molecular_dynamics and so on). In the task parameters part are reported other keyword relative to the specific task chosen and also the quality of calculation, i.e. `Scf_density_convergence` and `Scf_iterations`. Notice that the last values are determined the simulation quality, as explained in paragraph 3.3.3. The second part is related to geometric constraints and, in this case, user has fixed the Y coordinate of the atom 1. Instead, the third section is defined according to values setted in the electronic tab (section 3.3.3), where total charge (`Charge`), type of basis set (`Basis` and `basis_version`), functional (`Functional`) and cutoff range for basis set (`Cutoff_Global`) are defined. In the last part, quantities selected in the properties tab are declared. In the example reported, dipole moment

(`Electrostatic_moments`) and population analysis are performed exploiting all the three available models (`Mulliken_analysis`, `Hirshfeld_analysis` and `Esp_fit`).

An important aspect of the *.input* file is that it can be created either through simulator interface, as discussed in paragraph 3.3.3, or directly writing right keywords using an text editor. As a consequence of the last method is that user can modify or add keywords in order to improve the simulation setting. For example, due to the aim of this thesis, a fundamental keyword has been considered and it is `electric_field` keyword to add a constant electric field in XYZ space (expressed in *a.u.*).

Once all the simulation parameters are well defined, the last aspect to consider is the geometric one. As already explained in section 3.2.1, geometry is defined by user through sketch tools, available in MDS package, creating a *.xsd* file. This last type of file is a peculiar file type of MDS and it is used to visualize and draw 3D structure exploiting the visualization tool. Moreover, it contains also information about atomic charges. Parallel to *.xsd* file, MDS creates another file containing the same structural informations but in a format that can be visualize using a text editor. This file is a *.car* file and belongs to the hidden files in the working directory. For completeness, a third file should be consider to complete the geometrical description of the system and it is the *.mdf* file, but if it is not defined it is created starting from the *.car* file.

To summarize, a simulation requires two files: *.input* file to define all simulation parameters and *.car* file containing structure of the system (coordinate, charge, bonds and so on)

3.3.5 Output files

Once simulation is finished results are stored in many files, according to the simulation typology. The main files, for a static simulations, are certainly: *.outmol* file, *.grd* files and the *.car* file. Instead, in the dynamic simulations also other file must be considered: the *.arc* file. Among all the output data, according to the aim of this work, the more significant values are related to the charge population, simulation temperature, geometrical features (i.e. coordinates and velocities) and energies.

The *.outmol* file

Certainly, the most important file is the *.outmol* file, where all intermediate states and values of the simulation are stored, such as intermediate coordinates or energies. In the following a generic example of dynamic simulation output will be analysed in the significant sections and the complete version of the file is reported in appendix A.2. Starting from the beginning, a check part is reported in which the initial atomic coordinates and *.input* file are displayed. After preliminary part, there is a sort of initialization (shown below), according to the chosen task and to calculate the SCF energy of the initial point and the atomic coordinates and velocities.

```
MD initialization

degrees of freedom =                            2
number of fixed cartesian coordinates =         1
number of constrained internal coordinates =    0

setup virgin md run
Warning: molecule has been put into center of mass coordinate system
translated by    0.01138985848348    0.63990975857391    0.00000000000000
user defined velocities

dq          ATOMIC  VELOCITIES (bohr/atu)
x          y          z
dq    O    -0.000836   0.000000   0.000000
dq    H     0.015384  -0.016090   0.000000
dq    H     0.018916   0.008189   0.000000
Message: Generating Coulomb integrals
Peak memory usage               2 M

Total Energy           Binding E       Cnvgnce     Time   Iter
Ef           -80.846886Ha        -4.9695527Ha      3.08E-01     0.0m       1
Ef           -80.830726Ha        -4.9533926Ha      1.68E-01     0.0m       2
[...]
```

```
Ef          -80.402986Ha        -4.5256530Ha      2.26E-05     0.0m     23
Ef          -80.402986Ha        -4.5256528Ha      2.03E-05     0.0m     24
Ef          -80.402986Ha        -4.5256527Ha      6.67E-07     0.0m     25
Message: SCF converged

Energy of Highest Occupied Molecular Orbital:  -0.31101Ha    -8.463eV
Energy of Lowest Unoccupied Molecular Orbital:   0.06747Ha     1.836eV

HOMO is orbital number    10
LUMO is orbital number    11

df              ATOMIC  COORDINATES (au)                    DERIVATIVES (au)
df            x          y          z            x          y          z
df    O    -0.004102   0.516002   0.000000    -0.018822   0.003768   0.000000
df    H     1.560053   1.481112   0.000000     0.008648   0.005755  -0.000000
df    H    -1.291348   1.765626   0.000000     0.010174  -0.009524  -0.000000
df  binding energy      -4.5256526Ha      -123.14933eV      -2839.947kcal/mol


Energy components:
Sum of atomic energies =      -75.8773334Ha
Kinetic =       -1.5116292Ha
Electrostatic =       -0.5458759Ha
Exchange-correlation =        0.1688324Ha
Nonlocal-exchange =        1.7825704Ha
Spin polarization =       -4.4195503Ha

Total Energy           Binding E                   Time   Iter
Ef          -80.402986Ha        -4.5256526Ha                   0.0m     26

Step   Kin.+Pot. Energy        Pot. Energy Temperature
MD       0     -80.4025166 Ha     -80.4029860 Ha    148.24 K
```

Once the initial step is defined, the MD starts evolving the system for a time equal to the *simulation step* setted, this means to apply the Verlet algorithm to evaluate the atomic coordinates. After that another SCF calculation is done to compute the total energy and then the final atomic velocities, simulation temperature and system energy are shown. This section is reported in the following:

```
Progress: 0

+++ Entering MD/SA Stage Number    1 +++

Performing NVE MD using velocity Verlet propagator
with       1 steps in this stage


write car file with the new structure

update arc file with the new structure
Message: Generating Coulomb integrals
Peak memory usage                2 M

Total Energy           Binding E       Cnvgnce     Time   Iter
Ef          -80.752505Ha        -4.8751718Ha      1.22E-02     0.0m      1
Ef          -80.821155Ha        -4.9438218Ha      8.43E-03     0.0m      2
[...]
Ef          -80.402936Ha        -4.5256031Ha      2.03E-05     0.0m     17
Ef          -80.402936Ha        -4.5256030Ha      6.72E-07     0.0m     18
Message: SCF converged

Energy of Highest Occupied Molecular Orbital:  -0.31102Ha    -8.463eV
Energy of Lowest Unoccupied Molecular Orbital:   0.06751Ha     1.837eV

HOMO is orbital number    10
LUMO is orbital number    11
```

```
df              ATOMIC  COORDINATES (au)                 DERIVATIVES (au)
df             x           y           z            x           y           z
df    O    -0.004369   0.516002   0.000000    -0.020385   0.004528  -0.000000
df    H     1.566496   1.472652   0.000000     0.009288   0.006038  -0.000000
df    H    -1.283372   1.770699   0.000000     0.011097  -0.010566   0.000000
df  binding energy      -4.5256030Ha      -123.14798eV       -2839.915kcal/mol


Energy components:
Sum of atomic energies =      -75.8773334Ha
Kinetic =       -1.5120021Ha
Electrostatic =       -0.5455897Ha
Exchange-correlation =        0.1689052Ha
Nonlocal-exchange =        1.7826338Ha
Spin polarization =       -4.4195503Ha

Total Energy           Binding E                  Time   Iter
Ef          -80.402936Ha        -4.5256030Ha                  0.0m     19

write car file with the new structure

update arc file with the new structure

Progress: 100

dq          ATOMIC  VELOCITIES (bohr/atu)       ACCELERATIONS (bohr/atu**2)
dq             x           y           z            x           y           z
dq    O    -0.000243   0.000000   0.000000     0.001274  -0.000283   0.000000
dq    H     0.011076  -0.018923   0.000000    -0.009215  -0.005991   0.000000
dq    H     0.013807   0.013014   0.000000    -0.011010   0.010483   0.000000

Step      System Energy        Pot. Energy   Temperature
MD       1     -80.4025122 Ha     -80.4029364 Ha    133.94 K
```

```
System Energy is a sum of:
Potential  =     -80.4029364Ha
Kinetic    =       0.0004242Ha
Thermostat =       0.0000000Ha
```

At the end, after calculation sections, there is the properties part that is related to properties chosen from properties tab. Here there are all informations about charge population computed followed the three methods. In this output example, section properties shows as first result the Hirshfeld analysis, as second the dipole moment, as third the Mulliken analysis and as last the ESP charges.

```
 +++ Entering Properties Section +++

Charge partitioning by Hirshfeld method: (  0.0004    0.0000)
O     1 charge   spin                 -0.2954    0.0000
H     2 charge   spin                  0.1481   -0.0000
H     3 charge   spin                  0.1478   -0.0000

Dipole moment vectors (au):
x                y                z
electronic:        0.003996        -6.685506         0.091338
nuclear:           0.080663         7.408336        -0.011434
net:               0.084658         0.722830         0.079904
dipole magnitude:     0.73214 au        1.8609 debye

Dipole moment vectors in initial coordinates (au):
x                y                z
net:               0.084658         0.722830         0.079904

Mulliken Population analysis
[...]
summarized population analysis
```

```
spin up    down    charge    spin
O (  1) 10     1.001   1.001     2.001  -0.000
O (  1) 20     0.919   0.919     1.839  -0.000
O (  1) 21     2.328   2.328     4.655   0.000
O (  1) 32     0.011   0.011     0.022   0.000
H (  2) 10     0.313   0.313     0.626   0.000
H (  2) 21     0.063   0.063     0.126   0.000
H (  3) 10     0.304   0.304     0.608   0.000
H (  3) 21     0.061   0.061     0.122   0.000

Mulliken atomic charges:
charge    spin
O (  1)  -0.517  -0.000
H (  2)   0.248   0.000
H (  3)   0.269   0.000

Fermi energy:   -0.316817   -0.316817   -0.316817
[...]
grid specifications: I_dim, Origin, n_intervals to corner:
3   -5.6692   -4.7243   -6.6140   29   -5.6692   -4.7243    7.0865
26   -5.6692    7.5589   -6.6140   25    6.1416   -4.7243   -6.6140

Limits of the ESP box:
-6.632398 -5.879429 -6.988568
6.595685  7.348654  7.184378
Solution:
-6.7517E-01  3.3805E-01  3.3712E-01  1.1818E-01
======================================

Summary of ESP fitting calculations
Number of points         :       2460
Total integration weight :     784.71
Spacing between          :       0.50 Ang
```

```
Sigma                     : 0.2311E-02
RMDS of V(exact)           : 0.1626E-01
RRMDS fit                  :      14.22 %

ESP-fitted charges         :
n Elem    chg   vdW(in)  vdW(ex)
1  O     -0.675   1.72   3.22
2  H      0.338   1.30   2.80
3  H      0.337   1.30   2.80
======================================
```

The *.grd* files

Molecular dynamics simulator visualization tool allows user 3D visualization of some properties, such as electron density, HOMO and LUMO orbitals and electrostatic potential. The *.grd* files contains volumetric data to describe a particular property and they can be imported into MDS. Thanks to the *Analysis* tool (available in the *Modulus* menu) is possible to import and visualize volumetric data superposing them on the simulated system. An example is reported in figure 3.4, where a electron density is displayed on a water molecule under the action of an electric field from left to right and it is possible to observe a slightly enlargement of the electron cloud on the left hydrogen. These kind of file can be visualized only through MDS interface.

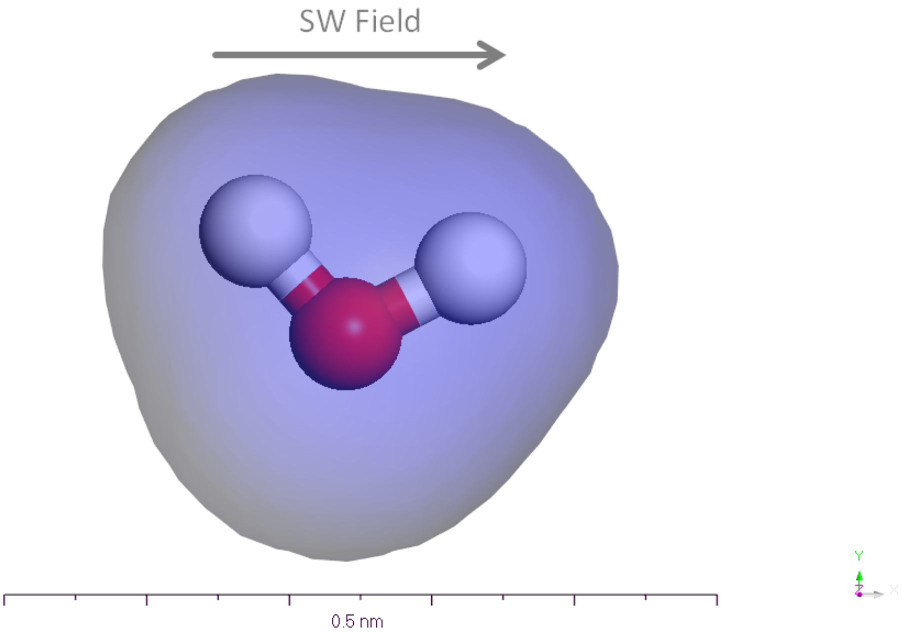


Figure 3.4: Example of electron density visualization

The *.car* and *.arc* files

If a dynamic simulation is performed, output structural informations are fundamental and these data are stored in the *.car* and *.arc* files. As already explained, the *.car* file contains informations about atomic positions in a single frame, this means a single atomic configuration. Instead, the *.arc* file, is a trajectory file that describes the evolution of the system at each frame of the simulation, fundamental in the dynamic output. This file contains the same structural information of *.car* for each frame of the trajectory, it is a sort of a set of *.car* file. MDS interface allow to display content of *.arc* file showing an animation of the system evolution. After importing *.arc* file in MDS, a *.xtd* file is created, and exploiting *Animation* tool[1] of MDS, the animation can be launched.

---

[1] It must be enable from *View* menu → *Toolbars*

Chapter 4

Dynamic simulations

The aim of this thesis is the characterization of possible candidate molecules for MQCA applications, therefore molecular dynamic (MD) simulations are fundamental tools to investigate such molecules in time under the action of an external electric field. Using the simulator, molecules can be also simulated in its neutral, oxidized or reduced form. Moreover, thanks to MD, it is possible to observe the switching of the molecule, key point for QCA theory.

This chapter deals with all the aspects to perform a dynamic simulations using the simulator in MDS package. It is organized in such way that user can replicate dynamic analysis following steps explained in the following. In particular, the first section concerns how dynamic analysis has been faced and organized, the second one is related to the setting of simulation parameters and the third is about initial conditions to be imposed, which have a very important impact on the evolution of the system and the last two explaine operative steps to perform a MD simulation.

4.1 Methodology

The final purpose of this work is the evaluation of the local charges of the molecule as a function of time, under specific conditions. Exploiting the simulator, the charge evolution can be observed, this means that, at the end, dots charges are displayed as a function of time. First of all, an important aspect of the simulations must be highlighted. The dynamic simulation computes all selected properties only at the end, in other words it provides properties calculated only for final frame of the simulation. Therefore, all informations related to charge, dipole moment, electron density and so on, are not saved frame by frame. Instead, total energy and simulation temperature are shown in intermediate states. Naturally, geometric data (coordinates and velocities) are also stored frame by frame in a specific file, *.arc* file (reported in paragraph 3.3.5).

To explain better the last concept, if user want to compute charge evolution (charge vs time plot) for a MD simulation $2fs$ long, it is not sufficient to launch a single simulation $2fs$ long because, in this way, the simulator computes charge only for the last structure, this means only for time equal $2fs$ and not for intermediate points. In conclusion, to produce plot where charge is reported as function of time, it is necessary to launch several MD simulations in order to obtain also the charge values for intermediate points.

Considering this sort of limitation in MD simulation, two different approaches are adapted in this work, one very simple but longer and the other one quite difficult but reasonable fast, especially for large molecule and long simulation time.

4.1.1 Approach A: *SameInit*

An immediate and simple solution, to overcome problem of lose of the intermediate charge values, is to perform different MD simulations, in which initial configuration is the same and the simulation time is progressive increased, up to desired value. The idea is schematic in the figure 4.1:

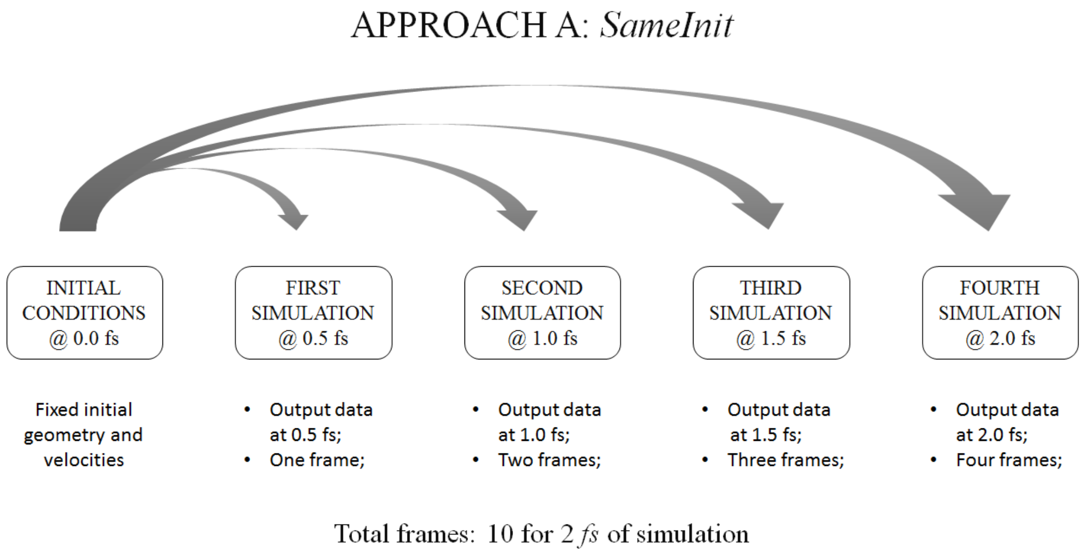


Figure 4.1: Scheme of *SameInit* approach

It is the first approach due to its simplicity, but it is evident that time required for obtain a long MD simulation is considerably increased. For small molecule, as water, it is still applicable, but with the increasing of molecule size and so of the time required to perform DFT calculation, this method becomes impossible to apply.

4.1.2 Approach B: *Cascade*

The second possible approach has been required due to the limitation of the *SameInit* approach, where is too time consuming in large molecule case. It is quite complicate, but it allows to perform very long MD simulation in more reasonable time. Following this approach, MD simulation is composed by a cascade of many sub-MD simulations. To better explain, a schematic view is displayed in figure 4.2:

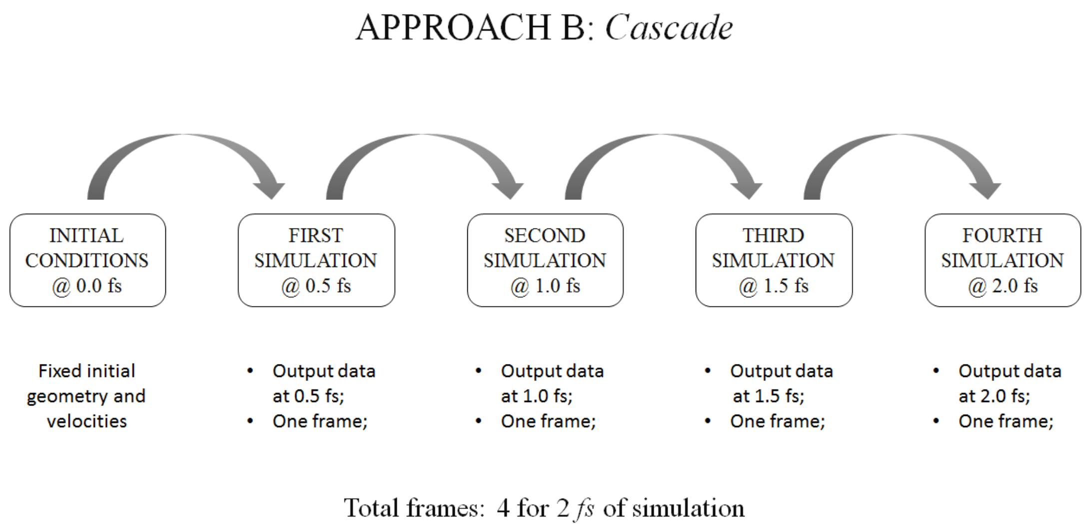


Figure 4.2: Scheme of *Cascade* approach

The starting idea is relative simple, in order to obtain intermediate charge values of a MD simulation, the whole dynamic is divided in many sub-MD simulations.
For example, a simulation $2fs$ long with a time step equal to $0.5fs$ (this means that dynamic simulation is composed by 4 frames), to not lose intermediate values, is subdivided in 4 MD simulations and each one is $0.5fs$ long. In this way, for a $2fs$ long simulation, four short ($0.5fs$ long) simulations are required, but output values can be saved. At the end, following this procedure, a charge evolution plot

is obtained sampling with 4 points the $2fs$ dynamic simulation. A critical aspect of this method is defining a continuity link between two consecutive simulations. The link is provided by geometries informations, such as structure geometry and velocities, and temperature of the system. To create this link, input data of a sub-simulation are provided by output data of previous one.

This approach is applicable using MDS interface, but it is not convenient because manipulation of *.txt* files are needed and so an *ad-hoc* software is developed to perform it. This software is described in chapter 5.

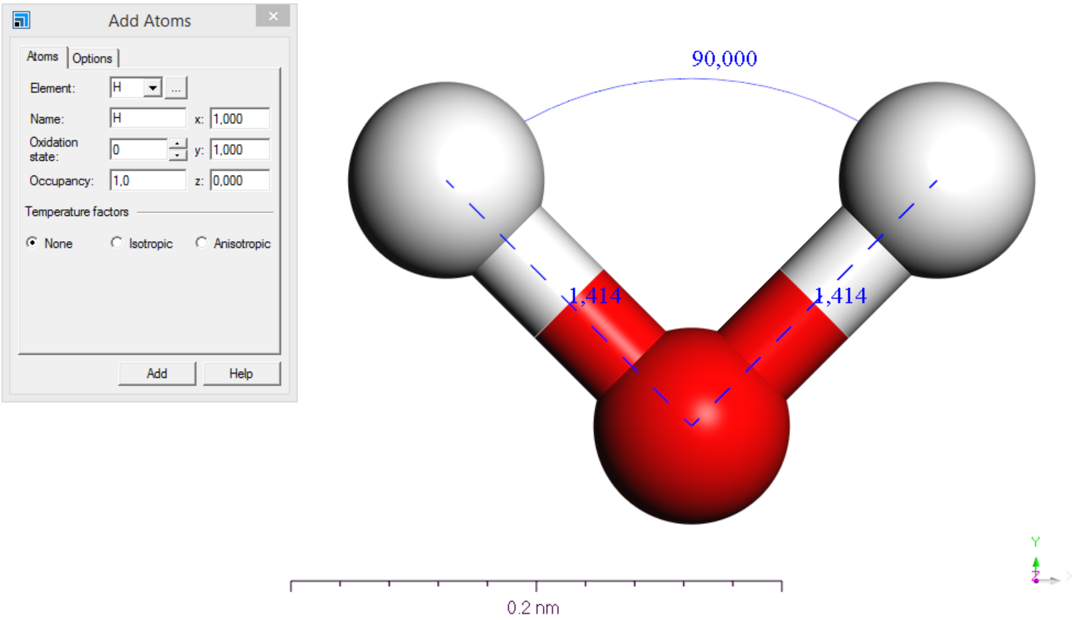
4.2 Dynamic Simulaiton Setup

Since input of a dynamic simulation consists of geometric and computational informations (as explained in paragraph 3.3.4), the dynamic procedure setup is divided in two parts: one relative to the structure definition and second one to the calculation. Notice that all considerations are done considering water simulation, but naturally they can be extended to other molecules, such as decatriene.

4.2.1 Structure definition and *.car* file

First consideration of MD simulation is how molecule can be defined and, in particular, the position in the XYZ space. The MQCA molecule can undergo the action of a switching (SW) along DOT-axis and a clock (CK) field, that are orthogonal to each other. All simulations are performed considering SW field along X axis and CK field along Y direction. For this reason, molecule is drawn in such way the DOT-axis is parallel to SW field. In water case, this means Y and Z coordinates of H atoms (DOT1 and DOT2) are equal. A simple way to positioned atoms in a specific position is using the *Add Atom* tool, available from *Build* menu → *Add Atom*. In this simply tool, user can chose atom type and its position specifying the X, Y and Z coordinates, then bonds are created simply linking atoms. In figure 4.3 is shown the procedure done using *Add Atom* tool.

In the figure 4.3, the water molecule has a stranger structure, this means unusual angle and bond lengths. In fact, the molecule has been created only positioning atoms, therefore an optimization simulation is required to obtain the exact structure,



Element: H
Name: H
x: 1,000
Oxidation state: 0
y: 1,000
Occupancy: 1,0
z: 0,000
Temperature factors
● None ○ Isotropic ○ Anisotropic

Figure 4.3: Draw of water molecule using *Add Atom* tool

oriented in the right way along fields direction. Optimized structure is represented in figure 4.4, in which angle and bonds lengths are reasonable values for a water molecule.

The procedure explained up to now is good for small molecule as water, because molecule are formed atom by atom. Instead, in more large molecule case, like decatriene, structure is created by *.car* file using a text editor, writing directly atom type and coordinates. After importing the *.car* file in MS, the 3D visualization is obtained though *.xsd* file. As in the previous procedure, before performing MD simulation an optimization calculation is required. In figure 4.5 an example of optimized decatriene molecule is illustrated.

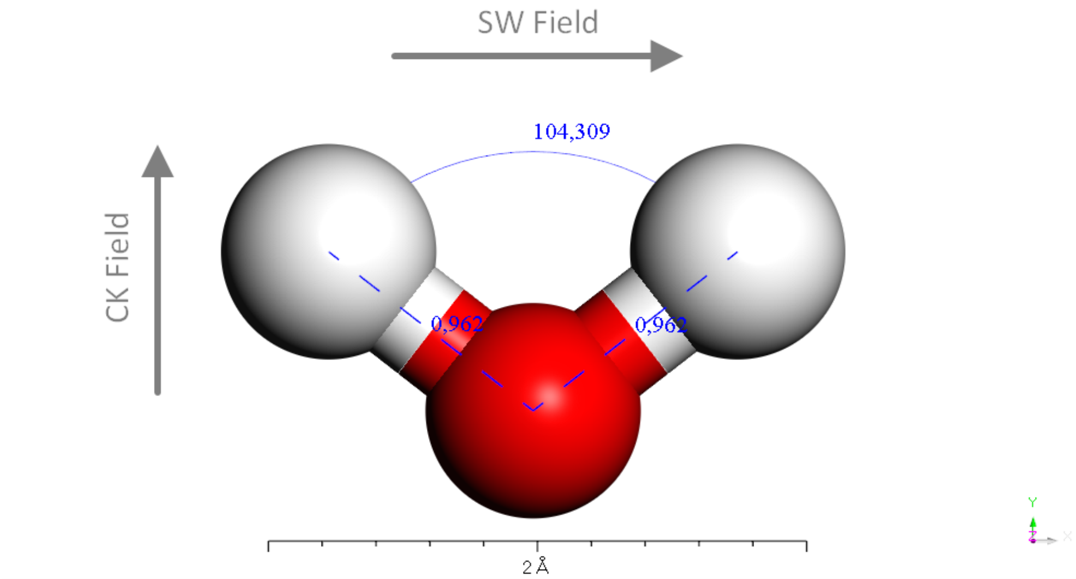


Figure 4.4: Switching and Clock fields for an optimized water molecule

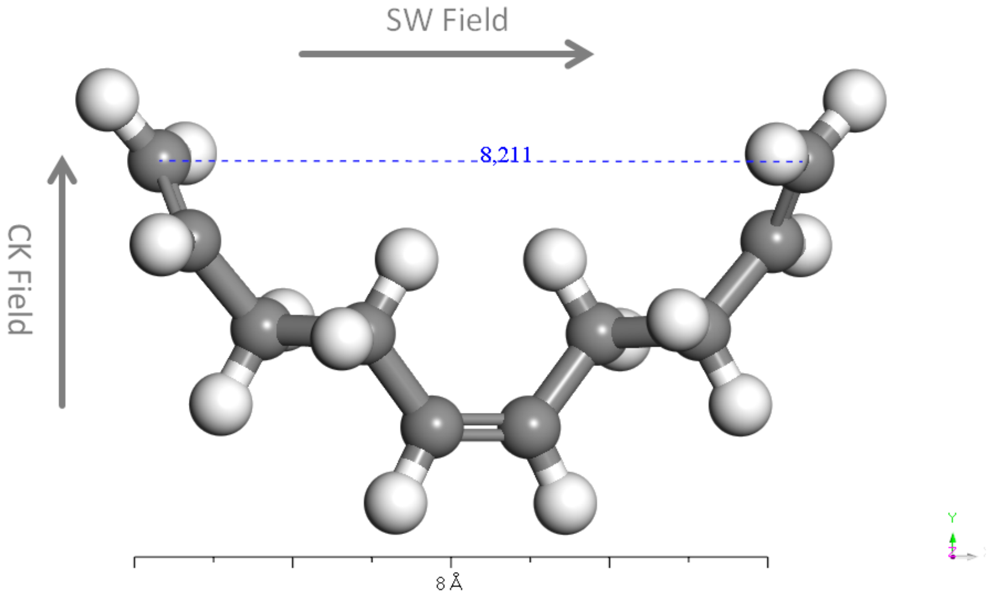


Figure 4.5: Switching and Clock fields for an optimize decatriene molecule

4.2.2 Simulation parameters and *.input* file

The second element required to launch a simulation is the *.input* file (discussed in paragraph 3.3.4) that contains all parameters to perform calculations. In this section *.input* file for a dynamic simulation is well explained section by section and therefore all setted parameters are discussed. In particular, each section will be reported and analysed. Recall that all the following settings can be also defined using *Calculation* window (explained in section 3.3.3) and *.input* file is automatically created. An example of complete *.input* file is reported in appendix A.1.

The first lines contains informations on typology of task to compute (value of `Calculate` keyword) and the enabling of data saving for what concern trajectory data (`Write_HIS_File`, writing *.his* file) and coordinate data (`Write_ARC_File`, *.car* file).

```
Calculate                     molecular_dynamics
Write_HIS_File                on
Write_ARC_File                on
```

The next section is fundamental in MD simulations and, in particular, if they are performed using *Cascade* approach (section 4.1.2):

```
MD_Velocity                   user_defined
1      1.000000000     -0.001859  -0.007638    0.00000
2      1.000000000      0.02223   -0.005826    0.00000
3      1.000000000      0.028283   0.005826    0.00000

MD_Time_Step                  1.0000
MD_Simann_panel
2 MD_NVE     300.0000
```

The keyword `MD_Velocity` allow to set initial velocities of the simulation and it has two possible values: `random`, where initial velocities are setted random by the simulator and `user_defined` to set arbitrary values. As reported in MDS manual, `user_defined` has an own syntax:

```
atom speed v_x v_y v_z
```

where `atom` is the atom number, `speed` is the total speed and `v_x v_y v_z` defines velocities component. Notice that all values are reported in atomic unit (*a.u.*) and the blank line at the end is required to terminate velocity section. Moreover, if after `user_defined` no velocity specifications, all atoms will have zero velocities.
After velocities section, a dynamic one is present where the time step used in MD is defined in fs through `MD_Time_Step`. The other keyword `MD_Simann_panel`, according to its syntax, allow to define the number of frames to perform (first value), the ensemble used (NVE or NVT) and the simulation temperature. In this case, a $2fs$ long simulation with $1fs$ steps at $300K$ using NVE ensemble.

Moreover, a geometric section is available to force structural constraints through the keyword `MD_Fixed_Coordinate` (to fix atomic coordinates) or `MD_Constraint` (to fix angles or distances in the molecule).

```
# Cartesian constraints
MD_Fixed_Coordinate
1   YZ
```

where, in this example, Y and Z coordinates of the first atom is fixed during MD simulations.

According to complete MD *.input* file in the appendix A.1, there is an important section related to calculation settings:

```
Symmetry                        off
Max_memory                      2048
File_usage                      smart
Scf_density_convergence         1.000000e-006
Scf_charge_mixing               2.000000e-001
Scf_spin_mixing                 5.000000e-001
Scf_diis                        6 pulay
Scf_iterations                  50

# Electronic parameters
Spin_polarization               unrestricted
Charge                          0
Basis                           dnp
```

```
basis_version                 basfile_v4.4
Pseudopotential               none
Functional                    b3lyp umesh=xcoarse minu=-3
Aux_density                   octupole
Integration_grid              fine
Occupation                    fermi
Cutoff_Global                 3.3000 angstrom
```

Among the first lines of this block, the main keywords are: `Scf_density_convergence`, its value is defined by the quality chosen for the simulation and in this case quality is setted to fine and `Scf_iterations` that its value fixes the maximum allowed cycles in SCF calculation and value of 50 is reasonable, because generally SCF computation converges in some tens of cycles and, then, if it requires more than 50 means that the calculation diverges. Other values are defined automatically and it is not convenient to change them. While, the second group of keywords is mainly related to electronic calculation:

- `Spin_polarization` to set type of spin-wavefunction restricted or unrestricted;
- `Charge` defines the total charge of the molecule;
- `Basis` its values indicates basis set used;
- `basis_version` indicates version of basis set, it is not always available, depends on basis set selected;
- `Functional` to set functional used in DFT calculation;
- `Integration_grid` selects the quantity of mesh points to perform numerical integration;
- `Occupation` determines orbital occupations used in SCF calculation;
- `Cutoff_Global` defines the range of cutoff in the basis set, its recommended value is reported for each type of atoms in MS manual;

The choice of basis set and functional is not trivial, because from them depends the quality of the final results. A good trade-off between quality [19] and time consuming

is *DNP* version 4.4 as basis set and *B3LYP* (Becke, three-parameter, Lee-Yang-Parr) as functional, that is an hybrid functional where it is takes into account the exact exchange term from HF and the exchange-correlation energy from other theories or experiments. Notice that a more accurate basis set is available and it is *DNP+*, but it is much more time consuming than *DNP* and the results are not significantly different. For this reason *DNP* has been selected.
The last section of MD *.input* file concerns properties that must be computed in the simulation:

```
# Calculated properties
Print_eigval_window           -1.d9
Plot                          homo
Plot                          lumo
Plot                          density
Plot                          potential
Electrostatic_moments         on
Mulliken_analysis             charge
Hirshfeld_analysis            charge
Esp_fit                       on
Grid                          msbox  3 0.2500 0.2500 0.2500 3.0000
plot_dos                      on

electric_field   0.002 0.0 0.0
```

The first five keywords are related to compute orbitals (HOMO and LUMO), electron density and electrostatic potential and results are stored in *.grd* files (explained in section 3.3.5). Instead, others properties such as dipole moment (`Electrostatic_moments`) and charge analysis, using all the three method (`Mulliken_analysis`, `Esp_fit` and `Hirshfeld_analysis`), are reported in the *.outmol* file (see paragraph 3.3.5).

To complete the MD *.input* file analysis, the keyword `electric_field` is added at the end though text editor in order to simulate system under the action of an electric field. Its value is a triplet that represents the three coordinate and so its components. Naturally also in this case, its is expressed in atomic units *a.u.*, where $0.002 a.u. \simeq 1 V/nm$. Notice that it is not possible to add electric field from simulator *Calculation* window, user can add it directly writing on *.input* file the keyword `electric_field`.

4.3 Different initial configurations

An important role in MD simulations is certainly played by initial conditions of our molecule and this section explains all possible initial configurations and their influence on dynamic evolution. Since the starting geometries is usually the optimized one, different initial configurations are possible only changing some quantities in the *.input* file because the other file required to launch simulation (*.car* file) is fixed by optimized geometry.

According to the detailed description in the previous section (paragraph 4.2.2), different initial conditions are obtained playing with (considering initial geometry always optimized):

- **Initial velocities**: random or user defined;
- **Geometric constraints**: fix atomic positions mainly;
- **Ensemble**: NVE or NVT;
- **Simulation temperature**
- **Total charge**: neutral, oxidized or reduced molecule;
- **Electric field**: switching and/or clocking field;

Among all the possible variables in the initial configuration, velocity one is the most significant because it has a directly, immediate effect on simulation. To explain better, defining a set of initial velocities, atoms move instantaneously at imposing velocities without any transitory time, as in the case of electric field where molecule undergoes field but it responds with a certain time. In addition, initial velocities defines also the simulation temperature in some cases, but it will be well explained in section 6.3. For these reasons, the setting of initial velocities is not trivial and it must be done carefully. Moreover, geometric constraints are useful in the dynamic and they can be used to model molecule anchored to a substrate or to limited its motion. For example, in water molecule case it is convenient to fix oxygen atom both to simulate bond with a substrate and to limit the rotation due to the influence of electric field.

To conclude, mixing all these simulation parameters it is possible to analysed molecule in many significant cases and combining it in right way, switching of the molecule can be observed demonstrating the QCA principle.

4.4 Commutation time

One of the most important result in this thesis is the demonstration that candidate QCA molecules are able to perform a *switching*, which is a fundamental in MQCA applications. This kind of analysis is made possible exploiting dynamic simulations.

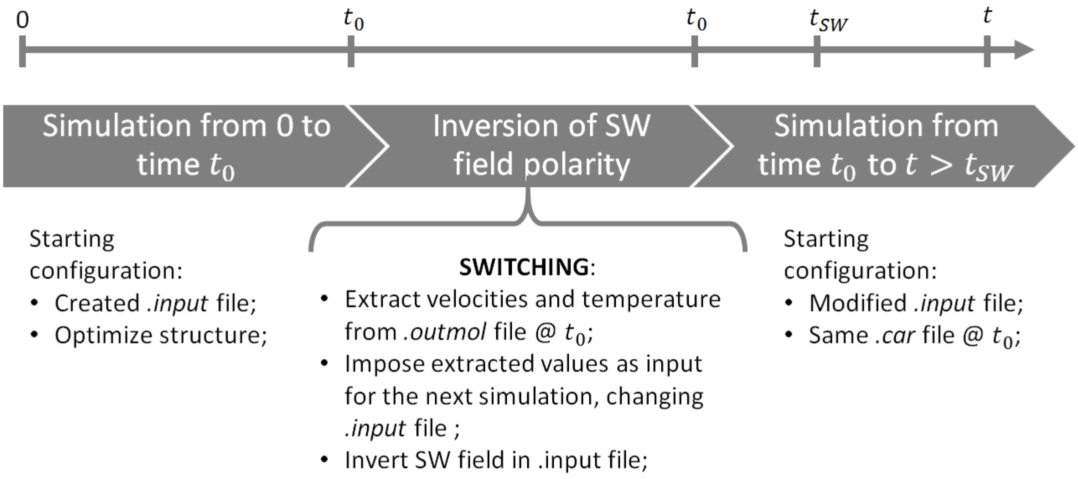
As already explain in paragraph 2.3, the switching process consists of inversion of dots charges (generally *DOT1* and *DOT2*) as response of the inversion of the electric field polarity applied along DOT-axis, the switching (SW) field. Due to the changing of the sign of SW field, the electron cloud tends to follow this variation redistributing it in the molecule, producing a variation in the local charges. Naturally, this process of the inversion does not occur in instantaneously way, but it requires a certain time to rearrangement of the charge inside the molecule. According to Wang work on Double-Cage Fluorinated Fullerenes [4] and Tokunaga one [3], in order to characterize switching process, for a given molecule, a sort of time to switch (t_{SW}) is defined and its evaluation is possible only through MD simulations.

From operative point of view, to perform a MD simulation to evaluate switching time, it is enough to play with keyword `electric_field` inverting its value related to X-component. To explain better, the operating steps required to obtain a time-evolution of charge performing a switch are:

1. Start simulation up to desired time t_0, where user want to perform switching;
2. Extract values from t_0 *.outmol* file (i.e. final velocities, temperature and SW field) and set them as initial value for the next simulation (starting configuration corresponds to t_0), where only the sign of electric field along X-axis is changed (for right switching, field must be inverted only);

3. Perform MD simulation starting from t_0 to time $t > t_{SW}$, where t_0 conditions are well defined;

A schematic representation is shown in figure 4.6.



Starting configuration:
- Created *.input* file;
- Optimize structure;

SWITCHING:
- Extract velocities and temperature from *.outmol* file @ t_0;
- Impose extracted values as input for the next simulation, changing *.input* file ;
- Invert SW field in .input file;

Starting configuration:
- Modified *.input* file;
- Same *.car* file @ t_0;

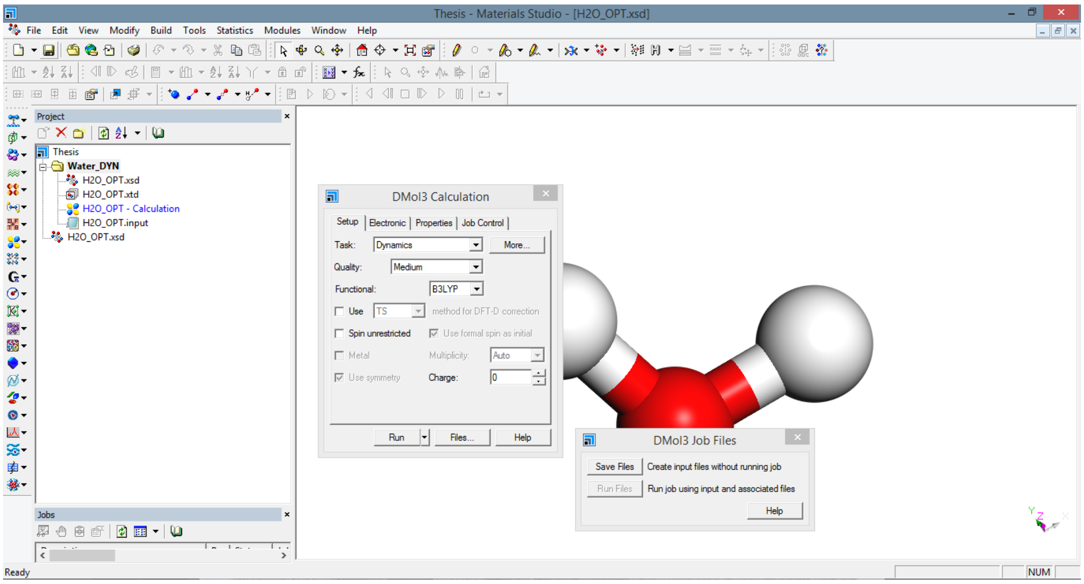
Figure 4.6: Schematic procedure to perform a MD simulation with switching

Of course, this procedure bases mainly on editing of *.input* files, especially at time t_0 where MD simulation must be interrupt to invert electric field value. As already explained, the continuity link is guaranteed by geometric information and velocities. This procedure can be performed easily following the *Cascade* approach and using the developed software, instead the MDS interface.

4.5 Launch dynamic simulation

Once all the aspects related to the MD simulation setup, such as input geometry and calculation parameters, are well discussed, a detailed procedure step by step to launch a dynamic simulation (using MDS interface), in case of water molecule, is reported in this section.

First of all, geometry of the molecule is defined following instructions explained in paragraph 4.2.1 either through MDS interface or directly writing on *.car* file. Once geometry file are saved, a recommended method for the *.input* file must be done in order to save all possible files. This procedure consists of:



Task: Dynamics

Quality: Medium

Functional: B3LYP

☐ Use TS method for DFT-D correction

☐ Spin unrestricted ☑ Use formal spin as initial

☐ Metal Multiplicity: Auto

☑ Use symmetry Charge: 0

Save Files Create input files without running job

Run Files Run job using input and associated files

Figure 4.7: Procedure to save input files in a subdirectory

1. Open *.xsd* file that allow to visualize the 3D structure;
2. Open *Calculation* window, reported in figure 3.2;
3. Set all calculation parameters in each tab and desired properties to calculate, as explained in section 3.3.3;
4. Click on *Files...* button to open simulator *Job Files* window;

5. Press *Save Files* button to generate a new subfolder where all geometric files and automatically generated *.input* file are stored;

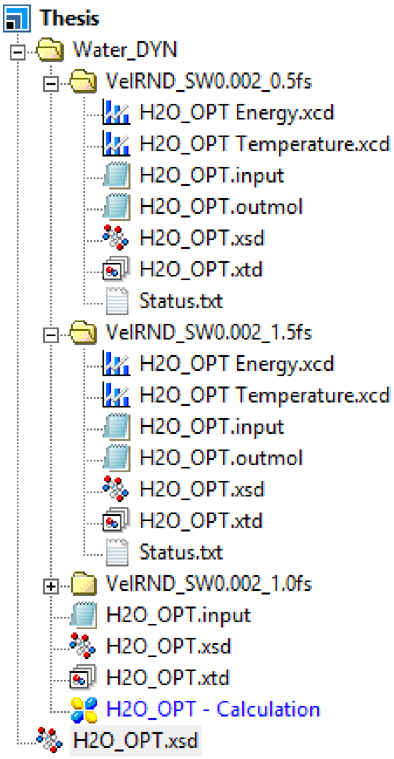
At the end, a set of input files are available in a subfolder (called *Water_DYN* in figure 4.7 or 4.8) and they will be used to launch the simulation. Notice that all these files can be modified as user want and it is the advantage of this procedure. In fact, the *.input* file can be edited for any reason, for example to switch-on or modify electric field adding the keyword `electric_field` with its value or to modify time step (`MD_Time_Step`) or number of frames (`MD_Simann_panel`).

At this point, all input files, modified in according to simulation to be performed, are defined in the subfolder and in order to launch a simulation based on them, the following steps are required:

1. Open the modified *.input* file in subfolder;
2. Open *Job Files* window;
3. Press *Run Files* to launch simulation based on files in the subdirectory;

Notice that result files will be stored in an automatically created subfolder contained in the folder where simulation has been launched.

Following this method all possible MD simulations can be performed playing with the initial conditions available. For example, using *SameInit* approach, saving at the beginning all input files, it is possible to perform simulation with different dynamic range, changing only the number of frames in the *.input* file, starting always from same geometry. To better explain, in figure 4.8 is reported an example where initial geometry and *.input* file are stored in *Water_DYN* subdirectory and then several MD simulations are launched from the same starting condition, changing only the number of frames in the *.input* file in *Water_DYN* directory. As reported in the figure, each simulation creates own subfolder, where output data will be stored (i.e. *VelRND_SW0.002_Xfs*).



- Thesis
  - Water_DYN
    - VelRND_SW0.002_0.5fs
      - H2O_OPT Energy.xcd
      - H2O_OPT Temperature.xcd
      - H2O_OPT.input
      - H2O_OPT.outmol
      - H2O_OPT.xsd
      - H2O_OPT.xtd
      - Status.txt
    - VelRND_SW0.002_1.5fs
      - H2O_OPT Energy.xcd
      - H2O_OPT Temperature.xcd
      - H2O_OPT.input
      - H2O_OPT.outmol
      - H2O_OPT.xsd
      - H2O_OPT.xtd
      - Status.txt
    - VelRND_SW0.002_1.0fs
    - H2O_OPT.input
    - H2O_OPT.xsd
    - H2O_OPT.xtd
    - H2O_OPT - Calculation
  - H2O_OPT.xsd

Figure 4.8: Automatically generated folder tree in MDS package

Chapter 5

Developed Software

A significant part of this thesis work has been the development of *ad-hoc* software to perform in the optimum way all dynamic simulations required to characterized MQCA molecule. The idea was to create a code able to handle in automatic way all simulated data, i.e. input and output files, and to optimize simulation time.

The software development was made possible thanks to *standalone* mode allowed in the simulator tool. It consists in overcoming MDS interface to launch simulation using only a set of input files (explained in paragraph 3.3.4) and an executable file provided by the simualtor. This file is a *.bat* file (in Windows environment) and generally it is stored in bin directory of installation simulator path. Of course, this command is characterized by own syntax and it is well documented in MDS manual.

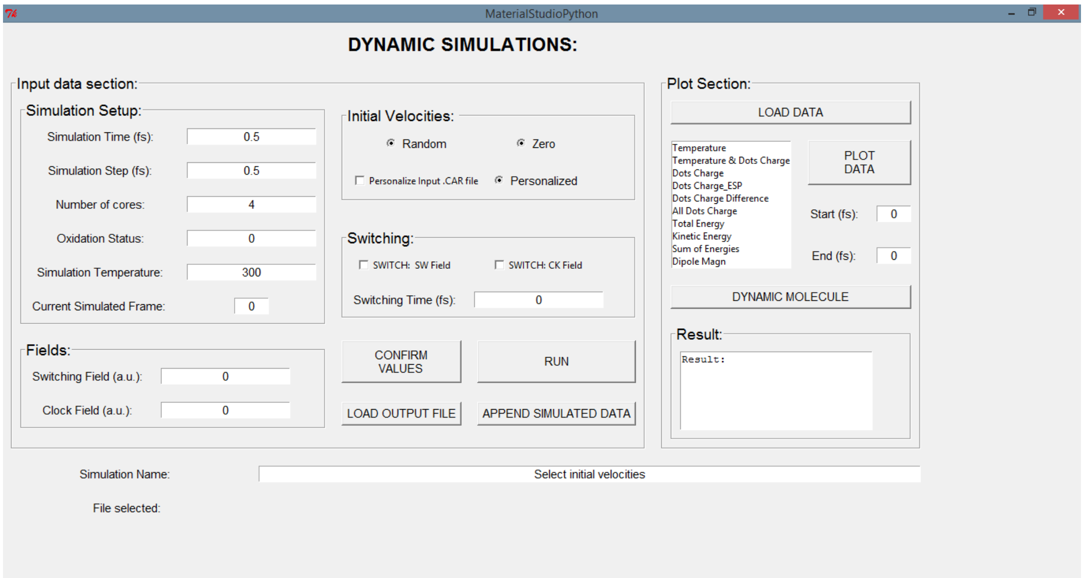
Moreover, it is chosen to use *Python* as programming language to develop software because it allows to program using object-oriented approach and it is able to run both on Windows or on Linux environments. Another advantage to use *Python* is the possibility to realize graphical user interfaces (GUIs) in simple way exploiting several libraries (e.g. *Tkinter*).

At the end, a very elaborate code has been developed able to handle autonomously MD simulations and it is based on a GUI, through which it is possible to set all significant initial parameters of dynamic simulation. Furthermore exploiting GUI, user can visualize output results, i.e. dots charge, energies, dipole moment, dynamic of the molecule and so on.

In this chapter, the developed software is examined: the first section is related to GUI description, intermediate paragraphs explains all logic and architecture of the code and in the last section is reported a step by step procedure to perform a simulation and to visualize results.

5.1 GUI

In this section the developed GUI is described and its functions are explained. As mentioned in the introduction part, it is developed exploiting *Tkinter* package. The GUI is reported in figure 5.1.



Simulation Time (fs): 0.5
Simulation Step (fs): 0.5
Number of cores: 4
Oxidation Status: 0
Simulation Temperature: 300
Current Simulated Frame: 0
Switching Field (a.u.): 0
Clock Field (a.u.): 0
Switching Time (fs): 0
Start (fs): 0
End (fs): 0
Result:
Simulation Name: Select initial velocities
File selected:

Figure 5.1: GUI of the developed software

The interface is divided in two main parts, according to its tasks: one related to input data and to the launch of MD simulation and the other one refers to visualization of the output data.

5.1.1 Simulation Tool

Starting from *Input data section*, on the left side, user can define in the *Simulated Setup* part:

- *Simulation Time:* time length of dynamic simulation;
- *Simulation Step:* time length of each frame of MD simulation;
- *Number of cores:* number of cores used by *.bat* file;

- *Oxidation Status:* total charge of the molecule (0: neutral, 1: oxidized, -1: reduced);
- *Simulation Temperature:* temperature at which simulation is performed;
- *Current Simulated Frame:* useful when initial condition is not at time zero, for example it is used to continue a simulation;
- *Switching Field (a.u.):* electric field along X-direction;
- *Clock Field (a.u.):* electric field along Y-direction;

In the central part, in the *Initial Velocities* section user can:

- impose initial geometrical structure checking or not *Personalized Input .CAR file*. When it is checked a personalized *.car* file is used and when not the optimize one is adapted.
- select initial velocities and allowed values are: *Random* means that they are defined randomly by program according to simulation temperature, *Zero* or *Personalized* when a set of arbitrary velocities are setted by user.

Instead in the last part in the centre, the *Switching* one, it is possible to select which field must be switched and also at which time. Notice that in *Switching Time (fs)* field, a set of times can be introduced, for example if user want to perform switching at $10fs$ and $20fs$, it will write $10; 20$.

To conclude the part related to the simulation tool, there are some buttons:

- *CONFIRM VALUES* button confirms all values introduced in fields in *Simulation Setup* and creating, from them, *simulation name* (section 5.2);
- *RUN* button launches simulation after parameters confirming;
- *LOAD OUTPUT FILE* button opens filesystem window to allow user to select a desired *.outmol* file imposing the corresponding configuration (i.e. geometry, velocities, fields...) as initial condition for a new simulation that can be launch using *RUN* button;

5.1.2 Visualization Tool

As already mentioned, developed software returns as output of a MD simulation some files in which all computed properties are stored. In particular, it produces six different files (explained in 5.4) related to atomic and DOTs charges, energies, coordinates, velocities and dipole moment. The visualization tool, on the right side of interface, allows user to decide which quantities must be visualized as function of time.

In order to plot a specific quantity, user must choose it among all available ones in the box and then click on *LOAD DATA* button to chose which file, related to the selected quantity, must be loaded. This button opens a filesystem window, filtering all *.txt* files, showing only files that contain selected quantity, but related to different MD simulations. Once corrected file is loaded, user can plot it, selecting the initial and final time, clicking on *PLOT DATA*.

Moreover, this tool is able to visualize a sort of animation of the dynamic simulation, considering coordinates *.txt* file, clicking on *DYNAMIC MOLECULE* button. The latter button opens a new window, where XY- and XZ-plane dynamic are visualized frame by frame.

5.2 Simulation name

Starting from parameters inserted through GUI, the software defines automatically a name that summarizes all features of the simulation, following a defined syntax. For example, `Decatriene_0_OX_NVE_T300.0K_VelRND_SW0.004_CK0.0_0step_` is a simulation of oxidized decatriene molecule in *NVE* ensemble at 300 *K*, in which initial velocities are random and switching field is equal to 0.004 *a.u.*. This name will be used to characterized each set of *.txt* results files and to name subdirectories in which simulation files will be stored.

5.3 Logic of dynamic simulation

In order to perform a simulation in a reasonable time, a good idea is to use *Cascade* approach (explained in 4.1.2) and the developed code exploit it to minimize the time consuming. Moreover, this approach bases on manipulation of text files, a *Python* code is very convenient to edit them in a simple way. In figure 5.2, a scheme of procedure used is displayed.

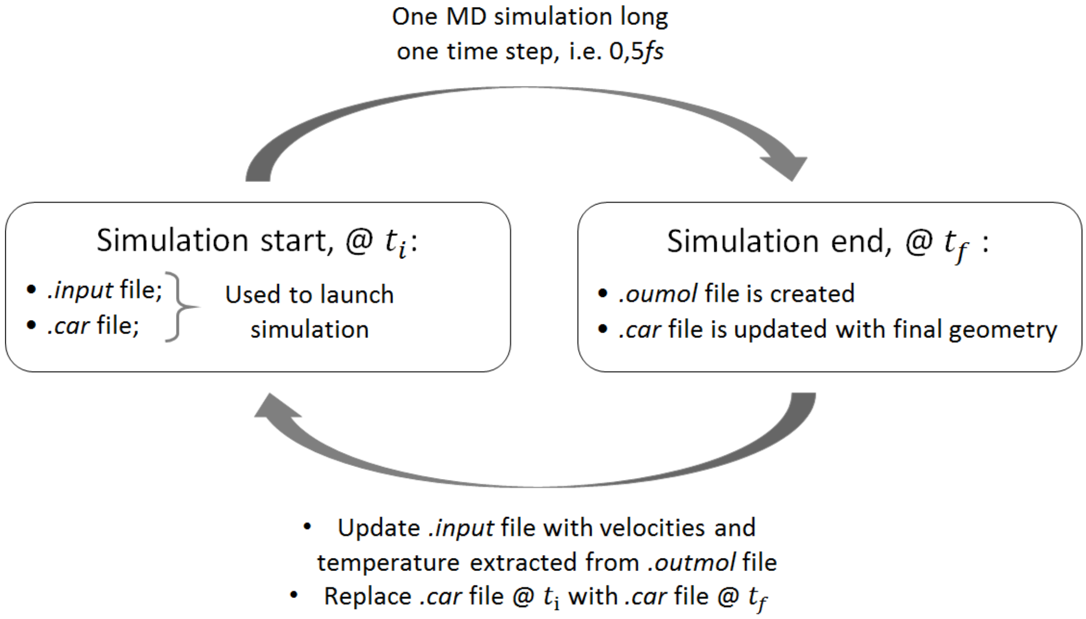


Figure 5.2: Logic scheme of *Cascade* approach used in the developed software

when t_f is equal to *Simulation Time* imposted by GUI, the cycle is interrupt and MD simulation is over. For each cycle, *.txt* result files are update in order to save properties computed at each frame.

More in detailed, the working space (called *Standalone* directory) of the code is subdivided in three different fundamental directories, each one contains a set of files to perform a specific task:

1. **Refernce Files** folder contains all geometric and *.input* files used as reference;
2. **RUN** folder where file *.bat* is located and in which simulation is performed;
3. **Results** folder in which all partial and final results are saved;

In particular, *Reference Files* contains *.input* file as described exactly in section 4.2.2 and all reference geometries (*.car* files), optimized or not, of molecules, such as water and decatriene. Instead, considering *Results* directory, an aspect to highlight is that each simulation produces in the *RUN* folder a set of files. These simulation files are stored creating a new subdirectory in *Result* and its name will be *SimulataionName_X* (explained in section 5.2), where *X* represent number of simulated frame.

To better understand the logic of the code, a scheme of procedure used to perform and to save data is illustrated in figure 5.3. Firstly, according to initial conditions

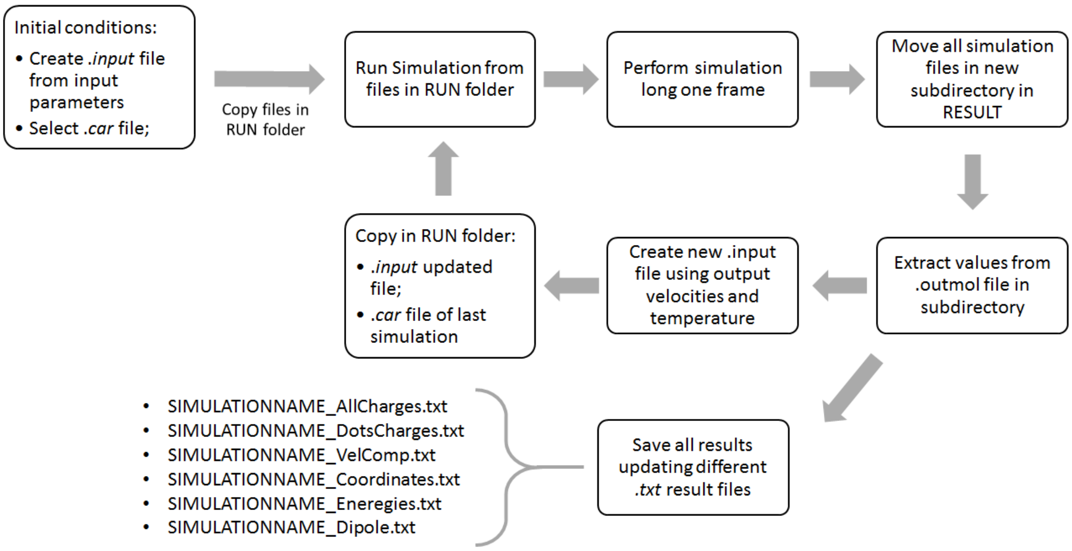


Figure 5.3: A schematic view of code logic

setted in the GUI, a specific geometry *.car* file and *.input* file are created and copied into *RUN* directory. In particular, *.input* file is defined starting from *.input* file in *Reference Files* directory and changing only parts related to velocities, ensemble, total molecule charge and fields inserted by GUI. Then, a MD simulation is performed and its duration is equal to one time step (only one frame is simulated). Simulation produces a set of files that are moved in the new directory, created in *Result* folder, named by its simulation name and number of simulated frame. After, from the last *.outmol* file all important quantities are read. Velocities and temperature are extracted to create a new *.input* file, following always file contained in the *Reference Files*, for the next simulation (*Cascade* approach). Instead, data related to charges, energies, coordinates, velocities and dipole moment are extracted and stored in *.txt* files (explained in paragraph 5.4), where they are reported frame by frame. Once simulation data are saved, the updated *.input* file and *.car* file of the last simulation are copied in *RUN* directory and another cycle is performed. The simulation finishes when required number of frame is reached.

5.4 Result files

As already explained, the developed software provides a group of *.txt* result files in which desired properties are stored frame by frame, in order to plot a certain properties as a function of time exploiting the visualization tool (paragraph 5.1.2). The developed software is able to save informations related to DOTs charges, atomic charges, energies, geometric coordinates, atomic velocities and dipole moment. In this section, the text formatting in each file are explained.

All *.txt* files are named by *SimulationName_ContainedProperty.txt*, where *ContainedProperties*, according to possible calculated properties, can be: *_DotsCharges*, *_AllCharge*, *_Energies*, *_Coordinates*, *_VelComp* and *_Dipole*. All these six files are characterized by the same first four columns that represent: number of frame, temperature, SW field and CK field. Other columns depend on typology of contained properties:

- *_DotsCharges* contains values of DOTs charge computed using Mulliken approach and ESP fit. Syntax is:

...	DOT1_MUL	DOT2_MUL	DOT3_MUL	DOT1_ESP	DOT2_ESP	DOT3_ESP

- *_AllCharge* contains values of all atomic charges computed using Mulliken approach and ESP fit. Syntax is:

...	Atm1_MUL	Atm2_MUL	...	Atm1_ESP	Atm2_ESP	...

- *_Energies* contains values of energies, in particular:

...	TotalEN	PotentialEN	KineticEN

- *_Coordinates* contains space coordinates of each atom:

...	Atm1_X	Atm1_Y	Atm1_Z	Atm2_X	Atm2_Y	Atm2_Z	...

- *_VelComp* contains velocities components for each atom:

... | Vel1_X | Vel1_Y | Vel1_Z | Vel2_X | Vel2_Y | Vel2_Z | ...

An example of some lines of *_DotsCharges* file, in water case, is reported in the following:

```
1 218.73 0.002 0.0 0.265 0.277 -0.541 0.352 0.361 -0.712
2 192.17 0.002 0.0 0.263 0.278 -0.541 0.352 0.36 -0.712
3 162.29 0.002 0.0 0.261 0.28 -0.54 0.353 0.36 -0.712
4 147.69 0.002 0.0 0.26 0.28 -0.54 0.353 0.359 -0.712
5 158.79 0.002 0.0 0.261 0.28 -0.541 0.353 0.359 -0.712
```

where, for the first line: 1 is frame number, 218.73 temperature, 0.002 SW field, 0.0 CK field, [0.265, 0.277, -0.541] Mulliken charges and [0.352, 0.361 -0.712] ESP charges for DOT1, DOT2 and DOT3.

5.5 Structure of code

Considering complexity of the software, due to implementation of a GUI and several operation on files, it is required to well organize the code structure. In particular, in code development the Model-View-Controller (MVC) pattern has been used. It is an architectural pattern very useful for software based on GUI, where the main idea is to divide code in three main parts: *Model*, *View* and *Controller*.

As reported in figure 5.4, each block has a specific function and, in particular:

- *Model* block is a sort of storage, where all variables of the system are saved and each function or operation in the code acts on the variable saved in this module. It does not contain functions, only values of variables. This is an ordered way to store variables and to not risk to have different variables that refer to same quantity;
- *View* block consists of all functions and/or operations performed by GUI. In fact, it contains all structure definitions of the GUI layout and functions called when a button is clicked;

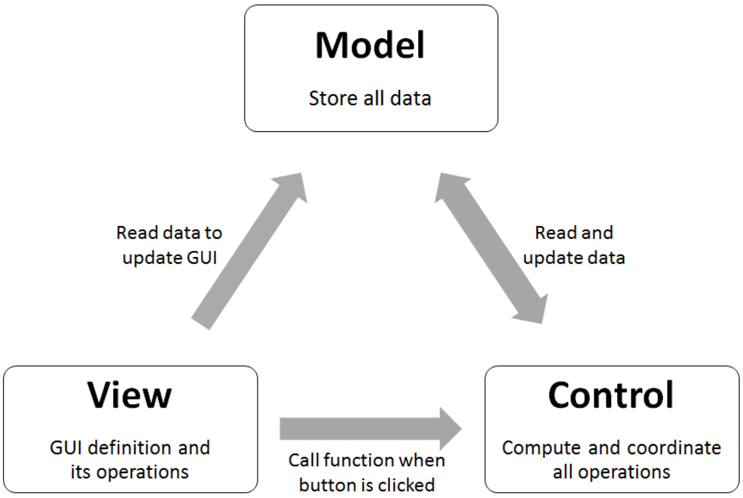


Figure 5.4: A Model-View-Controller logic implemented in the code

- *Control* block, as explain by its name, is the core of the code. It contains and performs all functions, such as simulation launching, copying files, extracting value from file and so on;

This pattern is very useful in complex code because each module has its specific function and all variables are stored only in a specific path, always accessible. In this way, if user want to change layout, it must modify only *View* module or if want to modify some calculation (e.g. computation of aggregate charges), it must work only on *Model* module.

To better explain the logic of MVC pattern, for example to confirm values inserted by GUI, user clicks on *CONFIRM VALUES* button and the code works as in the following:

1. Click on button calls a function in *Control* that updates variables in *Model* with inserted values;
2. A function in *Control* generates the *SimulationName* and updates it in *Model*;
3. A GUI updating function is called and it, checking variables values in *Model*, updates GUI, i.e. update the field related to the simulation name with the name created by input parameters;

Notice that, each function, in *Control* module, reads variable values only from *Model*, performs some operations and then update its value in *Model*, in this way each successive operation can read the updated values of the variable in a simple way.

In specific, the developed code is divided, according to MVC pattern, in different files: `MyModel.py` (as *Model* module), `MyView.py` (as *View* module) and `MyFunctions` and `MyControl.py` (as *Control* module). Moreover, another fundamental file is defined and it is called `MyPath.py`. It contains all paths of the directory used in the software, such as *RUN* and *Results* folders. Changing PC where software works, it is sufficient to change values in this file that means redefine path of directories. In figure 5.5, a scheme of code organization through subdivision in modules is displayed:

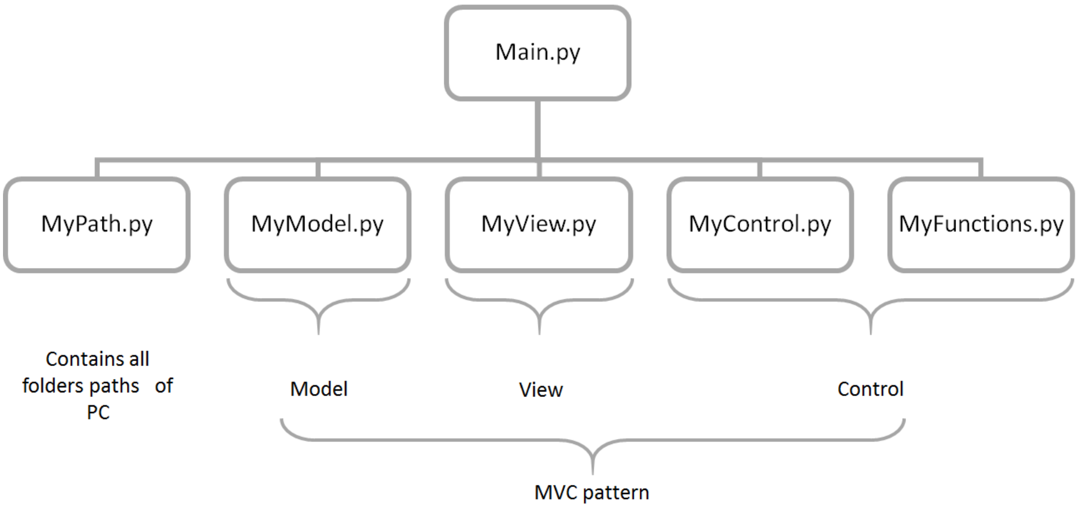


Figure 5.5: Representation of the code modules

To complete the code description, to launch the developed software it is sufficient to execute the main file, called `Main.py`, that opens GUI and all the operations described above are possible.

5.6 Example of simulation

Once all more significant aspects of the developed software are discussed, in this section a procedure step by step is explained.

Firstly, user must choose which molecule want to simulate because from this choice depends some input files of simulation. Selecting molecule, it is defined the total number of atoms in molecule and this number must be inserted manually in `Model.py`, updating the `TotNumAtoms` variable, which is used to initialize a lot of variables. After fix the value of total atoms number in the system to simulate, following procedure can be followed:

1. Launch `Main.py` from a windows command prompt to open GUI;
2. Insert all input parameters, such us simulation time, fields, initial velocities, switching time and so on;
3. Confirm input parameters through *CONFIRM VALUES* button, creating ;
4. Simulation name is created and displayed in the corresponding field in the GUI and user can modified it;
5. Run simulation using *RUN* button

At the end, a set of *.txt* result files and several subdirectory, each one related at simulated frame, are obtained in *Result* folder.

Instead, in order to visualize output data contained in *.txt* result files, user can perform these step:

1. Select from box in *Plot Section* the properties that user wants to visualize;
2. Load the corresponding *.txt* file through *LOAD DATA* button;
3. If user want, it can choose a certain temporal range in which plots selected property;
4. Plot data using *PLOT DATA* button and a new window is open to display the plot;

Chapter 6

Procedure of Analysis

After explaining all simulation tools in the previous chapters, this one deals the adopted procedure and considerations to perform a dynamic analysis of the local charges in molecules.

At first approach, it was chosen to study the water molecule in order to become familiar with molecular simulator and with MD simulations. It has been choice the water molecule mainly due to its simplicity and because its geometry is similar to a possible candidate molecules for MQCA applications. In fact, the three atoms that component water molecule can be seen as a sort of three DOTs of a QCA molecule. In particular, the two hydrogen atoms are associated to DOT1 and DOT2, instead oxygen atom has the role of DOT3.

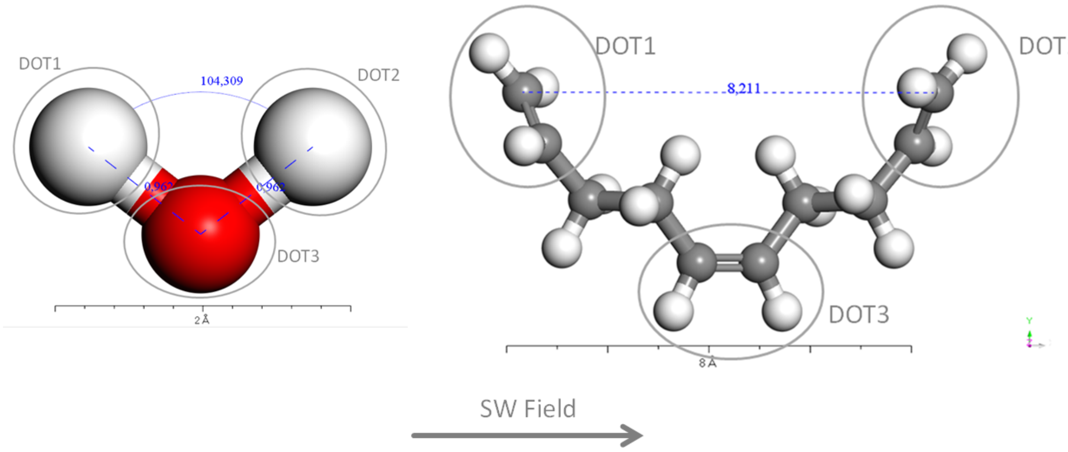


Figure 6.1: Definition of DOTs charges in water molecule

Another reason to start with water molecule is related to time required for MD simulation. Increasing the atoms number in the system, time to perform a simulation is significant increased. For example to simulate water molecule for 15 fs is required few minutes, instead to simulate decatriene molecule about 8 hours, for the same dynamic range and calculation parameters.

Considering the previous motivations, the dynamic analysis has been carried out on water molecule understanding as much as possible the influence of the initial conditions (discussed in 4.3) in a MD simulation and then the study was extended on decatriene molecule. The following sections explain consideration done, in order to reach reasonable results for the time evolution of local charges. Notice that all the results are obtained using the developed software (described in chapter 5) bypassing the MDS package, if not specified.

An important consideration is that the aim of this thesis work is the investigation mainly of the charge evolution and not mechanical dynamic, even if it is not neglected in the simulations.

6.1 Optimization step

A fundamental step to ensure a good result is the use of the optimized structure as initial configuration, means as initial *.car* file. Optimization calculation is required, especially, in MD simulation, because if structure is not at equilibrium the internal force could be too large to lead to failure of Verlet algorithm (integration of motion equations, explained in section 3.3.1).

The optimization is done using the simulator interface, because the developed software is configured to perform only dynamic simulations. Starting from not optimized structure, defined in *.xsd* file to 3D representation in MDS environment, user launches optimization simulation and as result it produces, among all output results, the *.xsd* file, in which 3D visualization structure is contained. Parallel to *.xsd* file, the simulator creates an hidden *.car* file that contains the same information of *.xsd* file, but in text form. This last file is the most important because it will be the initial and reference structure (stored in *Reference Files* folder, see section 5.3) that will use in the developed software.

Once the optimize *.car* file of molecule under analysis is created, different MD simulations can be done using the developed code changing initial parameters in *.input* file.

6.2 Constraints

Since thesis is interested to evaluate the time evolution of charges minimizing mechanical deformations, because during simulation they deform atomic positions and then the structure of molecule leading to a not good alignment between DOT- and Y-axis. In order to limit the deformation, especially in long time MD simulations, a reasonable solution is to use dynamic constraints. In particular, constrains related to atomic positions are used.

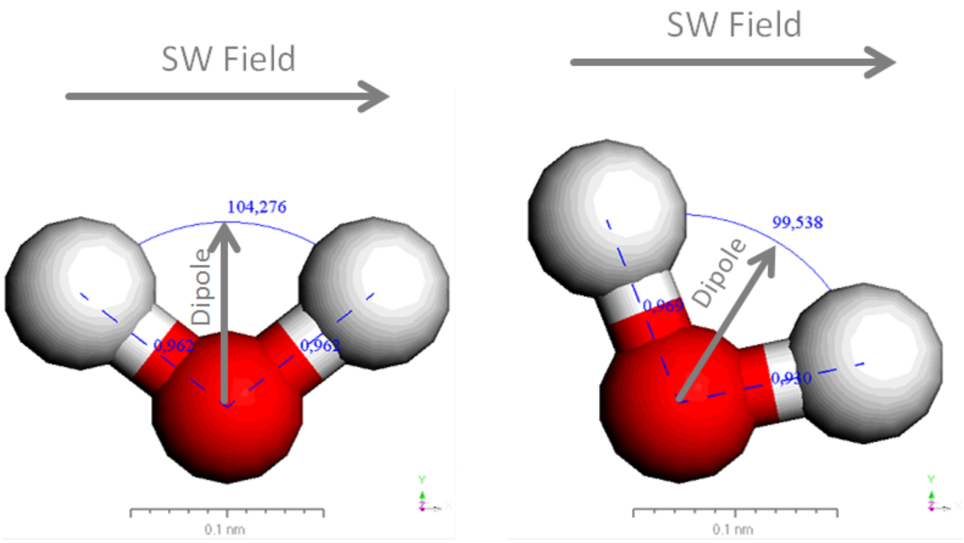
For example, under the action of electric field, especially along Y-direction (SW field), small molecule could start to rotate according to field in order to align its dipole moment along field direction, as reported in figure 6.2. A good idea to limit this rotation is to fix oxygen atom through constraints.

6.3 Velocity and Temperature impact

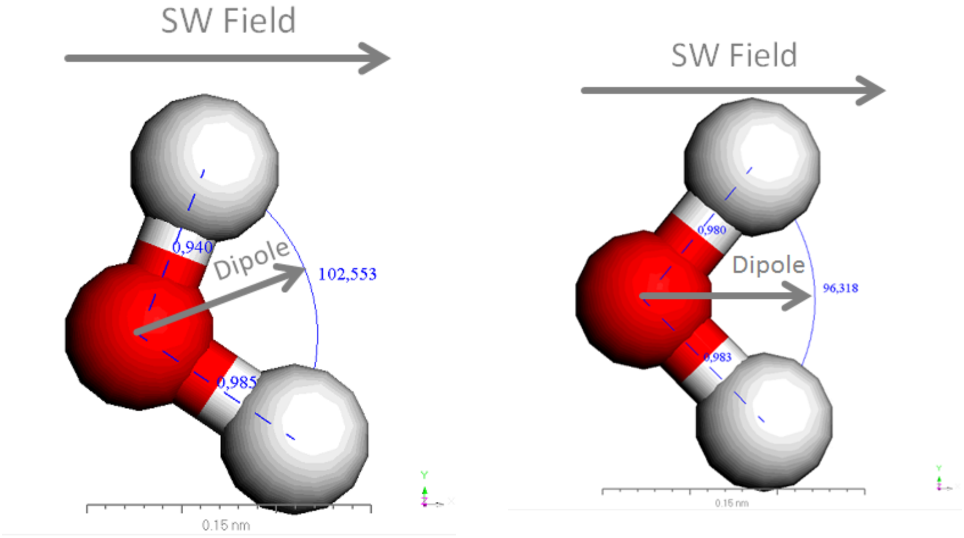
After initial geometrical structure, the main important input parameters are the initial velocities and initial temperature. They are fundamental because define the initial energy of the system that influences motion of molecule. Of course, high energy means that atoms are more excited and their vibrations and motion are significant. For this reason, the impact of initial velocities on time evolution of charge is analysed.

An aspect to highlight is that the simulator defines simulation temperature starting always from velocities. This means that simulation temperature in each frame is defined by values of input velocities of the corresponding frame. Then, if user defines a certain set of initial velocities, automatically defines also the initial temperature. Instead, if user sets random initial velocities, the initial temperature has an important role because the simulator defines a random set of atomic initial velocities such that it guarantees the imposed simulation temperature.

To summarize, initial temperature influences initial configuration of a MD simulation only if initial velocities are setted in random way, while if user defines a certain set of initial velocities, temperature has not role in the definition of the initial configuration. Of course, temperature affects dynamic evolution according to ensemble setted, especially in NVT case.



(a) Frame A (b) Frame B



(c) Frame C (d) Frame D

Figure 6.2: Evolution of water molecule under the action of SW field

6.4 Fields impact

Considering the QCA theory, the effects of two fields must be analysed and one is the switching field (SW field) oriented along DOT-axis and so X-axis and the other one is the clock field (CK field) oriented along Y-direction. For what concern SW field, if it is zero the mean DOTs charge split should be almost zero, while if its magnitude increases the mean split of DOTs charges should also increase. Instead considering CK field, if it is positive (means oriented from the bottom to the top) the charge available to the split in DOT1 and DOT2 is increased and then also the mean DOTs charge split is enhanced [20].

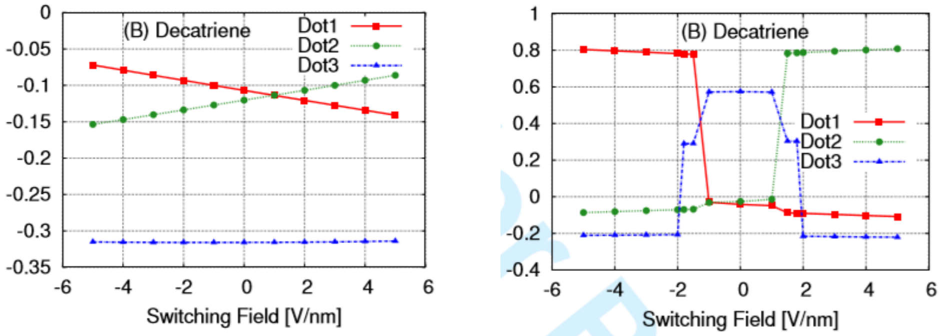
Another effect of fields, as already explained, is that they cause a deformation in the molecule structure and, in particular, in small molecule fields can induce a rotation to align its dipole moment to the field direction, as illustrated in figure 6.2

6.5 Ensemble impact

Another relevant aspect is the ensemble adopted in the dynamic simulation, because it has an impact on the evolution of the system. For this reason, the two allowed ensembles are used in order to evaluate their influences. In particular, using *NVE* ensemble system are isolated and it will not dissipate its energy, while using *NVT* one system can exchange energy with external world to maintain its temperature almost constant. As consequence, the simulation temperature in each frame depends on velocities which in turn depend on type of ensemble selected that define the dynamic evolution.

6.6 Total charge effect

As reported in work [5], the molecule response to the applied fields depends on its total charge. In fact, according to its oxidation status, it is observed a different behaviour under the action of electric field. In particular, the difference of the DOTs charges values (mainly DOT1 and DOT2) is depends strongly on molecule total charge. As displayed in plot in figure 6.3, oxidized molecule is more reactive than the corresponding neutral, this is true for the main molecule candidates for QCA applications.



(a) Neutral decatriene molecule (b) Oxidized decatriene molecule

Figure 6.3: DOTs charge split in neutral and oxidized molecule [5]

6.7 Switching

Since the aim of this thesis work is the analysis of time evolution of local charges, the last important considerations are related to how observe switching of the molecule. The operative procedure adopted is explained in paragraph 4.4.

In order to perform a reasonable evaluation of the switching time, user must evaluate it in the worst case this means in the case where it is maximized. Considering what explained in paragraph 2.3, where its evaluation is described, user must perform switching of field in the configuration in which the DOTs charge split is maximum and the values of DOTs charges are coherent with SW field. It is the worst configuration because it is maximized the charge to move.

To better explain, two possible choices are reported in figure 6.4, where time evolution of absolute DOTs charges is displayed under the action of SW field applied from DOT1 to DOT2 (from left to right):

Relying on figure 6.1, where molecule position and applied SW field are shown, and according to simple electrostatic, DOT2 should have a charge more positive than DOT1 because electric field pushes electron cloud (negative charges) in opposite way to its direction. Then, in this example, the DOTs charge split (defined as $DOT2 - DOT1$), due to internal charges oscillations, varies in time and it is mainly positive, but in some cases it becomes negative (when $DOT2 < DOT1$). In order to evaluate the maximum switching time, the charge to move from one DOT to the other (as response to the field switching) must be maximized. From figure 6.4, it

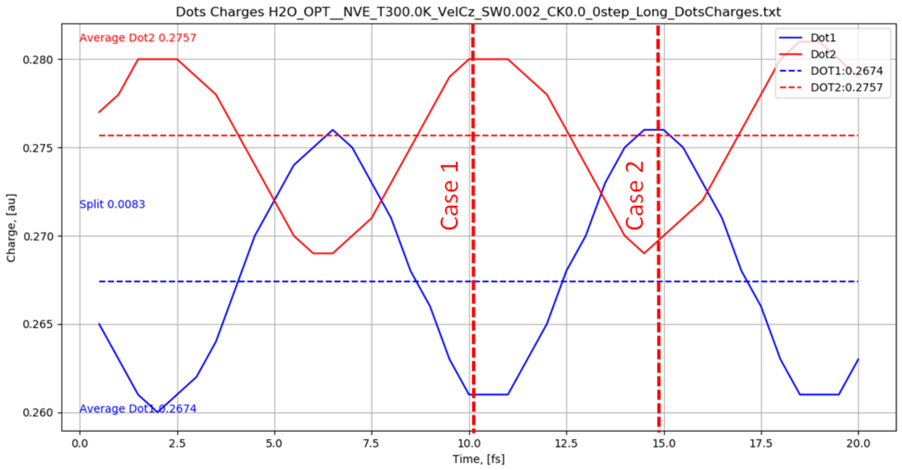


Figure 6.4: Comparison between two possible choices where perform switching

is possible to see that *Case 1* is where switching must be performed (worst case), instead *Case 2* is not a good time for switching because the charge to move is less and the split is even negative, means no coherent with the field direction. The last concept of the coherence with the applied field is related to the fact that due to charge oscillation, the DOTs charges can assume values not as expected considering the direction of the field. In this example, in *Case 2* $DOT2 < DOT1$ and it is not expected because electric field is oriented from DOT1 to DOT2 and so DOT2 should have always charge more positive than DOT1.

Chapter 7

Water Molecule Results

The work of this thesis is mainly centred on the analysis of the time evolution of charge in molecule, especially in MQCA molecules such as decatriene one. In particular, the final goal of this thesis is the demonstration that MQCA molecules are able to perform a switching process (described in paragraph 2.3) under the action of an electric field. This capability is possible to verify only through MD simulations, because a temporal analysis is required.

Notice that all MD simulations are performed using the developed software (explained in chapter 5) and calculation parameters discussed in paragraph 4.2.2.

The analysis of time evolution of the charge, main task of this thesis work, is done evaluating atomic charge using Mulliken model, according also to Wang work on Double-Cage Fluorinated Fullerenes [4] and Tokunaga one [3]. Even though this evaluation highly depends on selected basis set, but in all reported simulations the basis set is the same: *DNP* version *4.4* (see paragraph 4.2.2).

In this chapter results of dynamic simulations for water molecule are discussed up to demonstrate the switching capability. The analysis (following procedure in chapter 6) starts from water molecule to become familiar with MD simulations and then it ends with temporal analysis of decatriene molecule, in chapter 8.

7.1 Starting considerations

Exploiting similarity of the water molecule with MQCA molecules and its small size that means, in term of dynamic simulation, short simulation time, it was possible to carry out a significant temporal analysis on it. Both its charge time evolution but also its geometry are studied. All considerations introduced in chapter 6 are well investigated and in the following results are discussed.

Firstly, optimization of the structure is performed and figure 7.1 shows the reference structure for all water simulations.

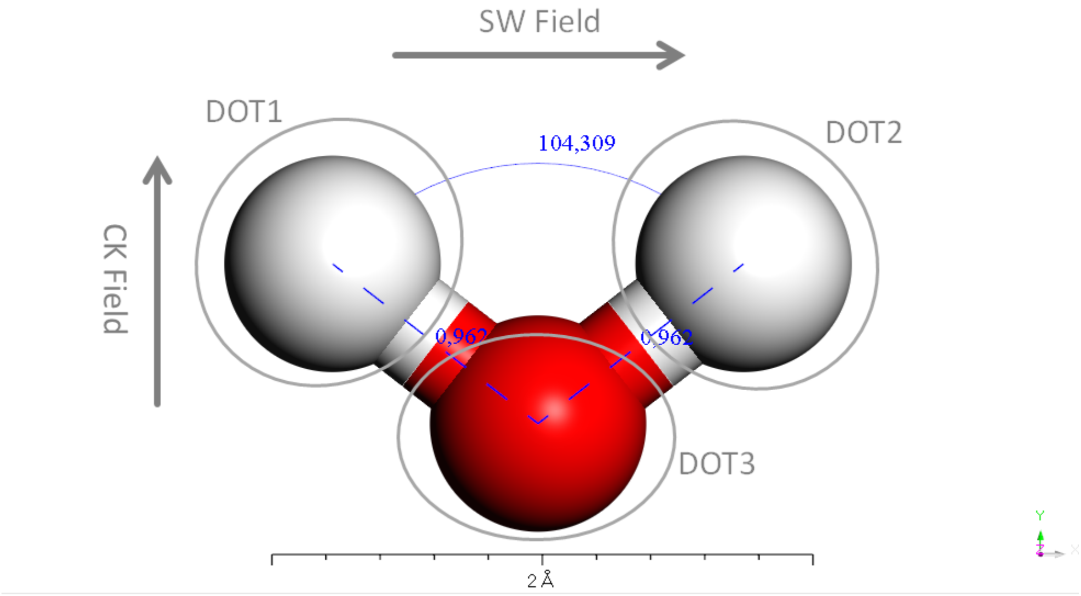


Figure 7.1: Optimized water molecule used as reference

where CK field is along Y-direction and SW field along X-axis and also DOTs-axis.

7.2 Charge Evolution

In this section all relevant plots, where (DOTs) charges are reported as a function of time, are discussed. In particular, following procedure in chapter 6, it is investigated the influence on charge evolution of: initial velocities, initial temperature and fields. Moreover, water molecule is simulated in *NVE* ensemble that means as an isolate system (no dissipation).

Notice that for the rest of the chapter, considering optimized structure (figure 7.1): *DOT1* is the left hydrogen (*H1*), *DOT2* the right hydrogen (*H2*) and *DOT3* the oxygen.

7.2.1 Constraints

As first approach, a water molecule is simulated setting random initial velocities at 300 K with zero fields and due to its initial velocities molecule starts to rotate according to the sign of the velocities. As explained in paragraph 6.2, molecule must be fixed as much as possible to maintain the alignment between DOTs- and Y-axis (SW field). A reasonable choice is to fix only the Y coordinate of *DOT3*, in this way MD simulation has sufficient degrees of freedom to evolve and the clockwise and counter-clockwise rotations are limited. Then, in all water simulations the previous constraint is used.

7.2.2 Initial velocities

Once all aspects related to molecule structure are faced, the impact of the initial velocities is studied focusing mainly on DOTs charge oscillations and less on mechanical dynamic, because for what concern MQCA theory electron cloud changes is more significant than geometric deformations (it should be minimized).

Firstly, the simplest simulation setup is one in which it is setted random velocities and temperature at 300 K and several of these simulations are performed in order to investigate the role of the random initial velocities on charge time evolution. Moreover, to understand mechanic behaviour, means how atoms move in time, quite long simulations has been performed, up to 60 fs. In the following, two significant plots (figure 7.2 and 7.3) are shown, where DOTs charge oscillations are plotted as a function of time. Both MD simulations have the same calculation parameters and initial conditions, excluding initial velocities that are random and so each simulations have different set of initial velocities: *RND_1* and *RND_2*. These velocities sets are expressed component by component in table 7.4.

Considering works [4] and [3], the charge oscillations should be in anti-phase, this means that charge in *DOT1* must have its maximum value at the same time when *DOT2* has its minimum value and vice-versa and not in phase where instant of maximum charge coincides in both DOTs. This last condition is achievable modifying initial velocity, in fact, *VelRND_2* is a good choice instead *VelRND_1* no because in this configuration oscillations are in phase. In conclusion, after several simulations, in order to observe an anti-phase oscillation, the initial velocities of the

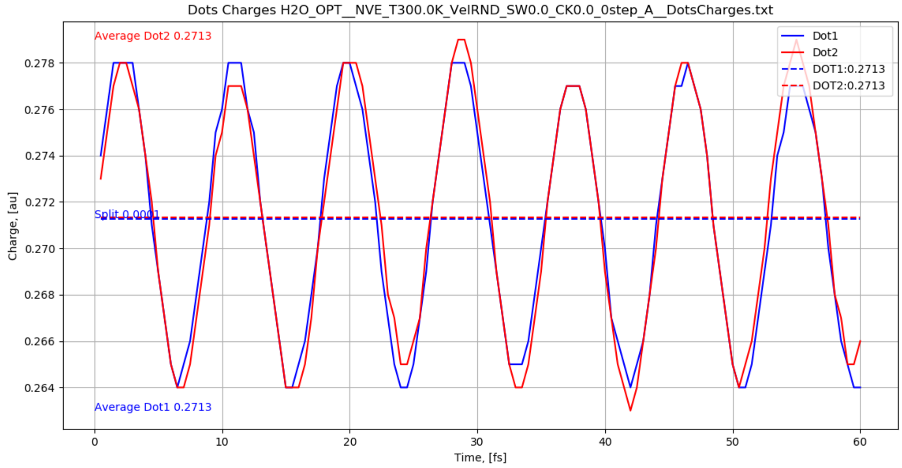


Figure 7.2: Charge evolution of water molecule; NVE, VelRND_1, 300 K and 60 fs

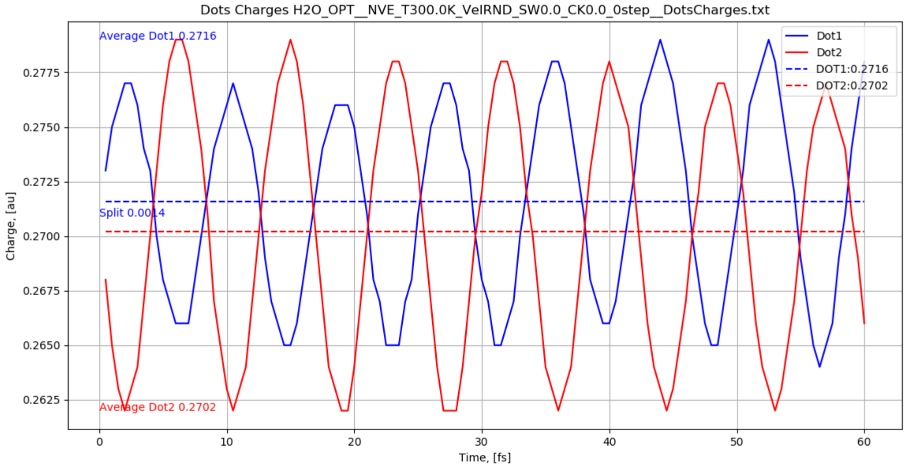


Figure 7.3: Charge evolution of water molecule; NVE, VelRND_2, 300 K and 60 fs

two hydrogen atoms must be similar and have the same sign, opposite of oxygen atom sign, are shown in table 7.4

In light of the consideration above, different set of arbitrary initial velocities are simulated to evaluate their impact on oscillations. The two initial velocities groups considered (called *Vel005* and *Vel01*) are reported in table b in 7.5. The values setted are nearly unreal (especially *Vel01* because produce a simulation temperature

DOTs	**Vel_X**	**Vel_Y**	**Vel_Z**
DOT1	-0.016321	0.005535	0.005048
DOT2	0.022333	-0.005535	-0.031025
DOT3	-0.000379	-0.001278	0.001636

(a) *VelRND_1* → No good

DOTs	**Vel_X**	**Vel_Y**	**Vel_Z**
DOT1	-0.010023	0.010441	0.021697
DOT2	-0.017504	-0.010441	-0.011532
DOT3	0.001734	-0.006160	-0.000640

(b) *VelRND_2* → Good

Figure 7.4: Different velocity RND used in the two simulations at 300K

DOTs	**Vel_X**	**Vel_Y**	**Vel_Z**
DOT1	0.005000	0.000000	0.000000
DOT2	0.005000	0.000000	0.000000
DOT3	-0.010000	0.000000	0.000000

(a) *Vel005* → T = 260.57 *K*

DOTs	**Vel_X**	**Vel_Y**	**Vel_Z**
DOT1	0.010000	0.000000	0.000000
DOT2	0.010000	0.000000	0.000000
DOT3	-0.020000	0.000000	0.000000

(b) *Vel01* → T = 1020.31 *K*

Figure 7.5: Two arbitrary initial velocities sets used in the two simulations at 300K

about one thousand of Kelvin), but they are imposed to emphasize the role of initial velocities mainly in the Y-direction that is also the SW field direction. In fact, from plot 7.6 and 7.7 observing their maximum values, it is possible to understand that high initial velocities produce a wider oscillation than small ones. This is justified considering that high atomic velocities means high energy and then atoms are more energetic and excited. Moreover, the oscillations are symmetric due to velocities of two hydrogen atoms are the same, really unreal configurations.

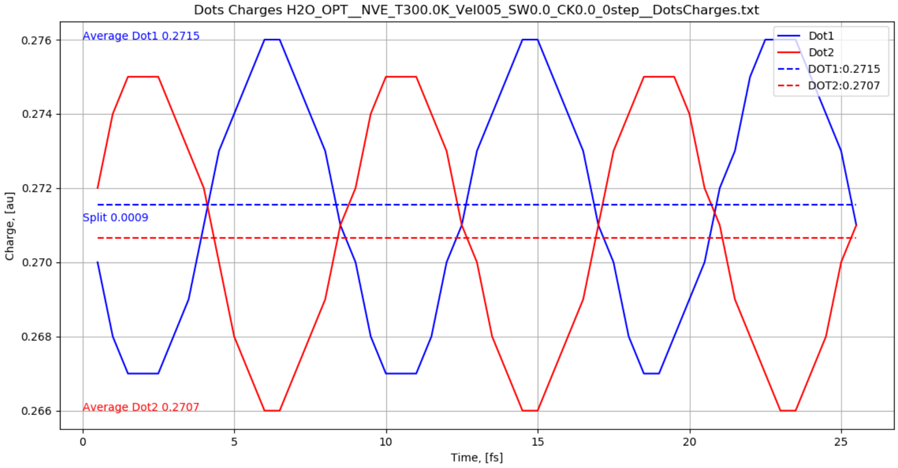


Figure 7.6: Charge evolution of water molecule; NVE, *Vel005*, 300 K and 25.5 fs

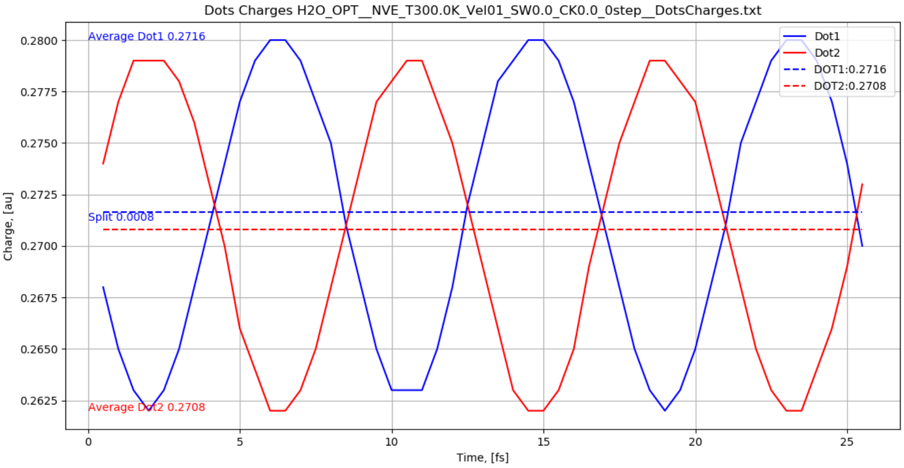


Figure 7.7: Charge evolution of water molecule; NVE, *Vel01*, 300 K and 25.5 fs

Since the last two configurations are too non-physical, a new set of initial velocities (called *VelA*, table 7.8) is derived starting from velocities values extracted from a simulation frame, in which simulation temperature is about 300 K. The extracted set *VelA* produces a charge evolution reported in figure 7.9.

DOTs	**Vel_X**	**Vel_Y**	**Vel_Z**
DOT1	0.028283	0.005826	0.001801
DOT2	0.012230	-0.005826	-0.005561
DOT3	-0.001859	-0.007638	0.000237

(a) *VelA* → T = 323.58 K

Figure 7.8: Extracted velocities set, *VelA*

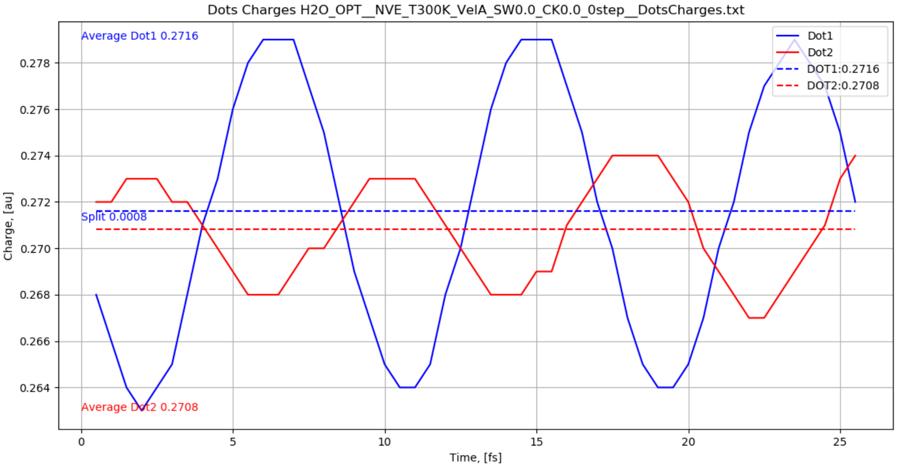


Figure 7.9: Charge evolution of water molecule; NVE, *VelA*, 323.58 K and 25.5 fs

The last consideration done on initial velocity is related to the symmetry of oscillations of *DOT1* and *DOT2*, as it is possible to see in figure 7.9, *DOT2* oscillation has small amplitude. In order to make the oscillations symmetric, a last set of initial velocities are defined, starting from *VelA*, and it is called *VelCz* configuration, reported in table 7.10.

DOTs	**Vel_X**	**Vel_Y**	**Vel_Z**
DOT1	0.028283	0.005826	0.000000
DOT2	0.022230	-0.005826	0.000000
DOT3	-0.001859	-0.007638	0.000000

(a) *VelCz* → T = 372.84 K

Figure 7.10: Optimal set of initial velocities, *VelCz*

Notice that all Z-components are fixed to zero in order to eliminate the rotation in the XZ-plane, because this rotation produces a sort of noise in the oscillations. It is more relevant when fields are applied. The optimal group of initial velocities produce a charge time evolution plot (reported in figure 7.11) much more similar to those reported in [4] and in [3].

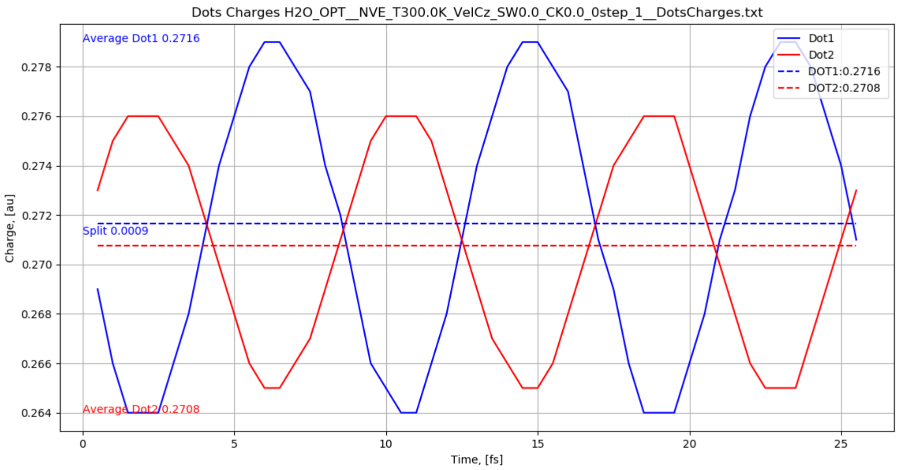


Figure 7.11: Charge evolution of water molecule; NVE, $VelCz$, 372.84 K and 25.5 fs

7.3 Fields Influence

Once the optimal configuration for what concern geometry and initial velocity are defined in the last two paragraphs, in this section it is analysed the impact of the electric fields, both switching (SW) field and clocking (CK) field. All the following simulations are performed using $VelCz$ as input velocities, at 300 K and in NVE ensemble. The more interesting effect is related to the SW-field (oriented along Y-axis) and in figure 7.12 is shown the charge evolution under the action of a SW field of magnitude 0.002 $a.u. \simeq 1V/nm$ for a long dynamic, up to 100 fs.

Observing plot 7.12, charge oscillations do not have always the same shape and magnitude, especially in the last half of the dynamic, after 40 fs. In particular, after 30 fs they are not more in anti-phase. This apparent strange behaviour is due

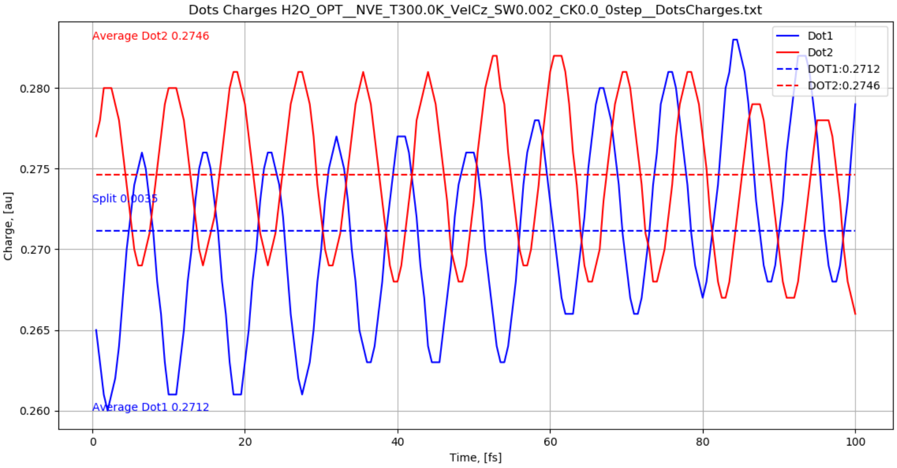
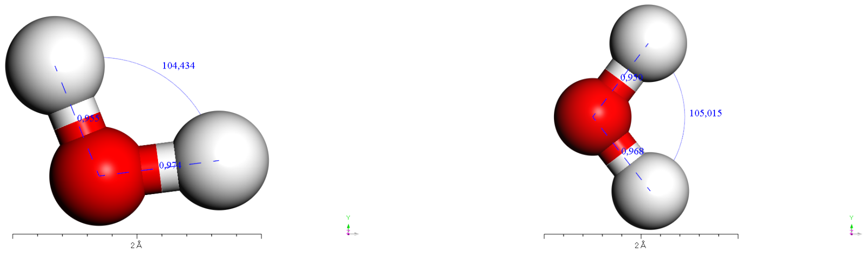


Figure 7.12: Charge evolution of water molecule; NVE, *VelCz*, 372.84 K, SW $=$ 0.002 $a.u.$ and 100 fs

to the rotation of the molecule to orient its dipole to the field direction, as explained in section 6.2. In figure 7.13, water molecule is displayed in two different frames of the previous simulation and in these frames it is possible to observe rotation due to the SW field.



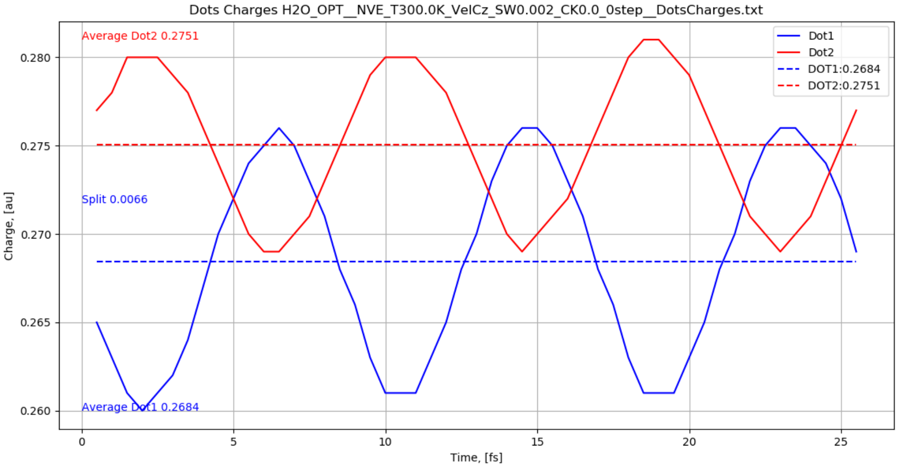
(a) Water molecule at 35 fs;

(b) Water molecule at 80 fs;

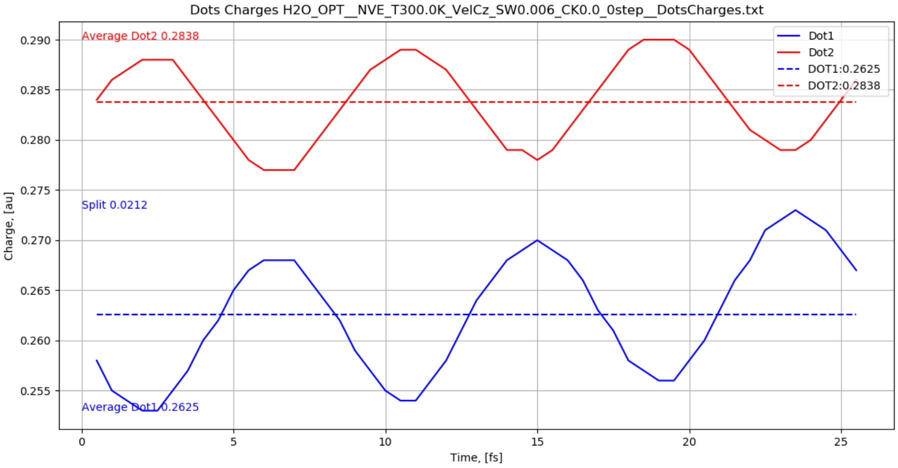
Figure 7.13: Two frames of simulation: NVE, *VelCz*, 372.84 K, SW $=$ 0.002 $a.u.$

From the last observation, the dynamic range can be reduced because from MQCA point of view it is not interesting to analyse molecule when it DOT-axis is not aligned with SW field direction. For this reason, in the following it will reported simulations with only 25.5 fs of dynamic.

As already said in section 6.4, increasing the SW field the average split of DOTs charges (defined as $DOT2 - DOT1$) should be increased. To verify it, different simulations are performed, always in the previous conditions, where only SW field varies:



(a) SW field = 0.002 $a.u.$;



(b) SW field = 0.006 $a.u.$;

Figure 7.14: Water charge evolution comparison varying SW field; NVE, *VelCz*, 372.84 K, CK = 0.0 $a.u.$, 25.5 fs

Figure 7.14 shows coherent results because the average DOTs charge split is increased from 0.0066 *a.u.* to 0.0212 *a.u.*, more accurate and quantitative analysis is done in paragraph 7.5. The last two values are obtained making the difference of the average DOTs charges, computed by averaging over all simulation time.

To complete the influence of the field, it is investigate also the role of the CK field and, as in the previous, two simulations are reported as confirm of what mentioned in section 6.4.

Also in this case, the predict impact of CK field is confirmed. In fact, the average values of DOTs charge is higher in positive CK field case than negative one. For example, average *DOT1* charge is 0.2749 *a.u.* with positive CK, instead is 0.2684 *a.u.* with negative CK.

A more accurate (quantitative) analysis is done in paragraph 7.5, since concept of period of oscillation must be introduced.

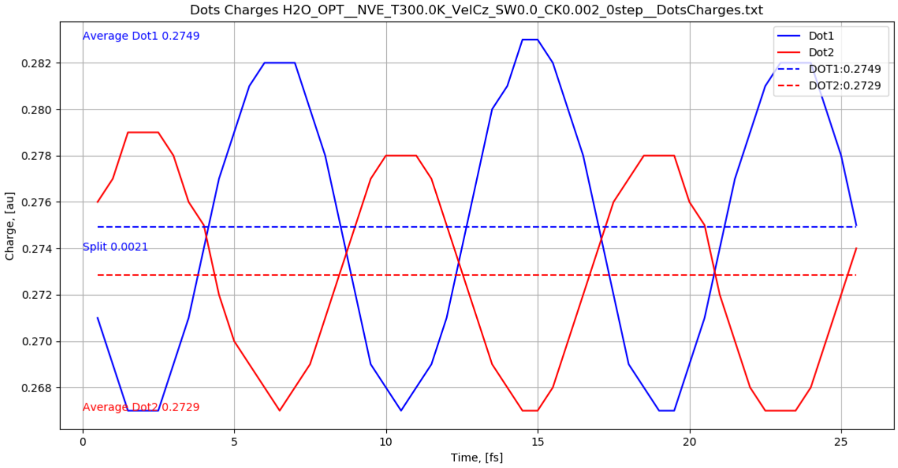
7.4 Period of charge oscillation

In all previous plots, a common feature comes out and it is related to the charge oscillations: the oscillation period. This quantity is defined as the time necessary to complete an oscillation of the charge in each dot. Observing oscillation period in all simulations, it is possible to affirm that it is always the same and then it is a characteristic of the molecule. For water molecule, the period of charge oscillation is about 8.5 fs in any cases. In fact, from an accurate analysis, it is found that it does not depend on initial condition and/or fields. To conclude, in figure 7.16 a generic simulation is reported and independently on initial velocity and oscillation amplitude, the period of charge oscillation is always about 8.5 fs.

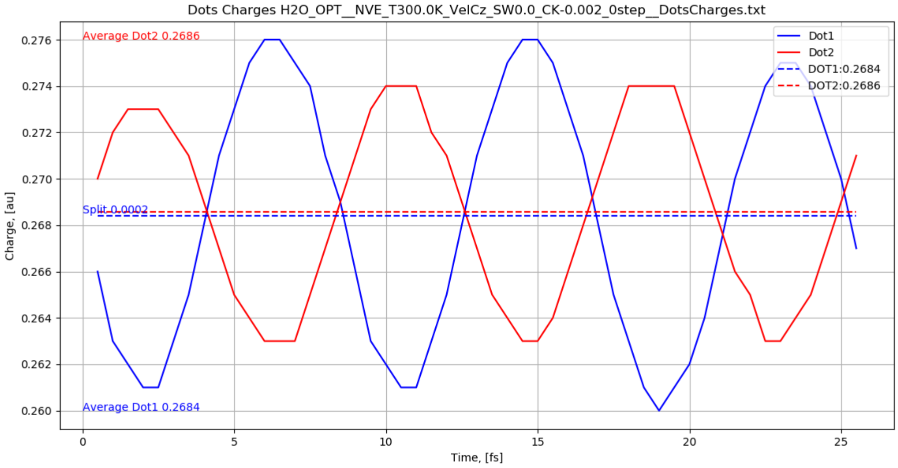
7.5 Consideration on the average trend

Exploiting the low required time to simulate water molecule, it has been possible to perform a very large number of simulations to quantify the role and influences of initial velocity and mainly of fields, both SW and CK ones.

The main idea to carry out a quantitative analysis is based on consider the mean values of DOTs charges, since these quantities are oscillating in time. Therefore, it



(a) CK field = 0.002 $a.u.$;



(b) CK field = -0.002 $a.u.$;

Figure 7.15: Water charge evolution comparison varying CK field; NVE, *VelCz*, 372.84 K, SW = 0.0 $a.u.$, 25.5 fs

was necessary to consider a right interval over which compute average values and the choice was to consider exactly the period of charge oscillation, explain in the previous paragraph.

The analysis is carried out considering different:

- *velocities* and then also different energy and temperature. Values considered

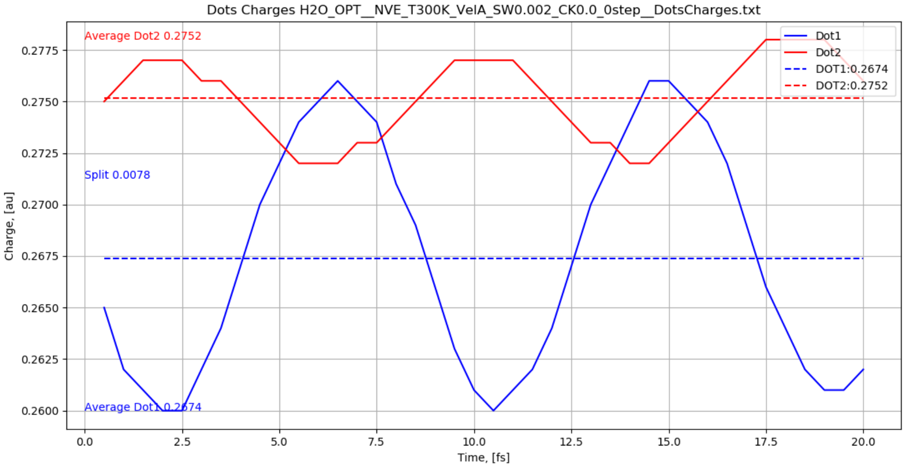


Figure 7.16: Charge evolution of water molecule; NVE, *VelA*, 323.58 K, SW = 0.002 $a.u.$ and 25.5 fs

are: *VelA*, *VelC* and *VelRND*;

- *SW fields* from -0.004 $a.u.$ to 0.01 $a.u.$;
- *CK fields* from -0.01 $a.u.$ to 0.01 $a.u.$;

and the computed quantities are: average DOTs charge, average split and average simulation temperature, which provides an idea of system energy. Each of these quantities are averaged on time of 8.5 fs. To better explain, an simulation example is displayed in figure 7.17, which is characterized by NVE, *VelCz*, 300 K and SW = 0.002 $a.u.$

The dashed lines in the figure represents average DOTs charge values. A table to summarize average values is reported in table 7.1.

As it is expected, with positive SW field, the DOTs charges split is positive because charge in $DOT2 > DOT1$.

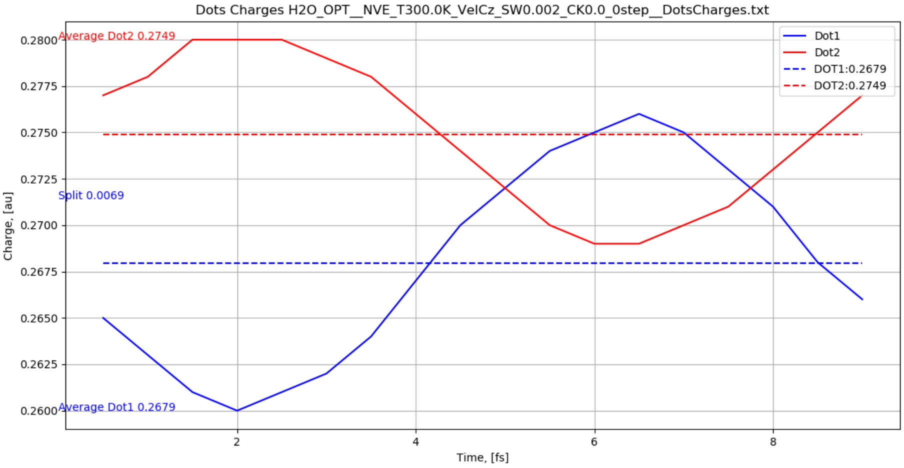


Figure 7.17: Charge evolution of water molecule; NVE, *VelCz*, 372.84 K, SW $=$ 0.002 $a.u.$ and 8.5 fs

DOTs	**Average Value ($a.u.$)**	**Average Split ($a.u.$)**
DOT1	0.267944	0.006944
DOT2	0.274889	

Table 7.1: Average values of DOTs charges of water molecule; NVE, *VelCz*, 372.84 K, SW $=$ 0.002 $a.u.$, 8.5 fs

7.5.1 Switching field effect

In the following three tables all average values are reported related to simulation where SW field varies and initial velocities are: *VelA* (table 7.2) , *VelC* (table 7.3) and *VelRND* (table 7.4). An important aspect must be highlighted and it is related to *VelRND* configuration, for each SW field it has been performed three different simulations, where only random velocities are changed (because they are setted randomly by software). In this way, a sort of statistic has been considered and the final average values are obtained averaging firstly over time for each simulation and secondly over three simulations.

VelA

Average values for several simulation in which only SW field varies; same initial geometry, same initial velocity *VelA* and same initial temperature.

SW field $[a.u.]$	**CK field** $[a.u.]$	**Temp** [K]	**DOT1** $[a.u.]$	**DOT2** $[a.u.]$	**Split** $[a.u.]$
-0.004	0.0	103.11	0.278889	0.262778	-0.016111
-0.002	0.0	119.69	0.275222	0.266889	-0.008333
0.0	0.0	139.50	0.271444	0.270722	-0.000722
0.001	0.0	150.62	0.269722	0.272667	0.002944
0.002	0.0	162.55	0.267944	0.274611	0.006667
0.004	0.0	188.81	0.264222	0.278611	0.014389
0.006	0.0	218.27	0.260667	0.282611	0.021944
0.008	0.0	250.87	0.256944	0.286556	0.029611
0.01	0.0	286.62	0.253333	0.290556	0.037222

Table 7.2: Average values of temperature, DOTs charges and average split of water molecule; NVE, *VelA*, 323.58 K, SW fields, 8.5 fs

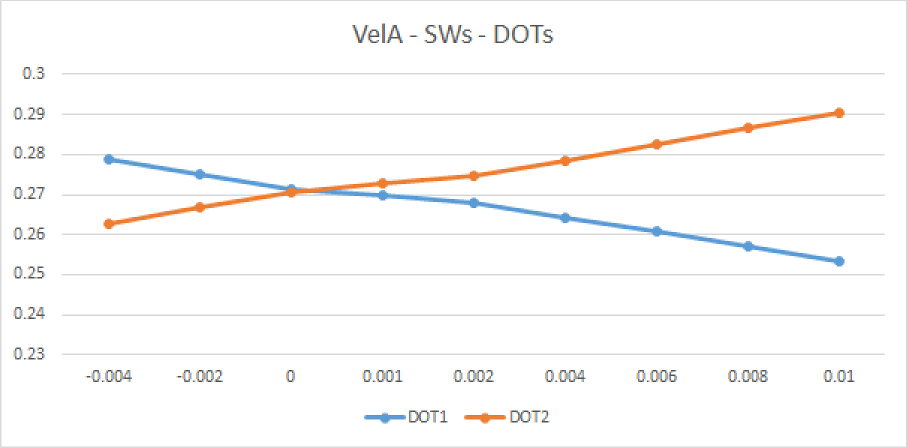


Figure 7.18: Charge evolution of water molecule; NVE, *VelA*, 323.58 K, SW fields, 8.5 fs

VelCz

Average values for several simulation in which only SW field varies; same initial geometry, same initial velocity *VelC* and same initial temperature.

SW field $[a.u.]$	**CK field** $[a.u.]$	**Temp** [K]	**DOT1** $[a.u.]$	**DOT2** $[a.u.]$	**Split** $[a.u.]$
-0.004	0.0	136.88	0.278944	0.262722	-0.016222
-0.002	0.0	157.02	0.275278	0.266944	-0.008333
0.0	0.0	180.39	0.271556	0.270944	-0.000611
0.001	0.0	193.27	0.269722	0.272889	0.003167
0.002	0.0	206.97	0.267944	0.274889	0.006944
0.004	0.0	236.76	0.264333	0.278778	0.014444
0.006	0.0	269.70	0.260778	0.282778	0.022000
0.008	0.0	305.81	0.257167	0.286778	0.029611
0.01	0.0	345.03	0.253500	0.290889	0.037389

Table 7.3: Average values of temperature, DOTs charges and average split of water molecule; NVE, *VelCz*, 372.84 K, SW fields, 8.5 fs

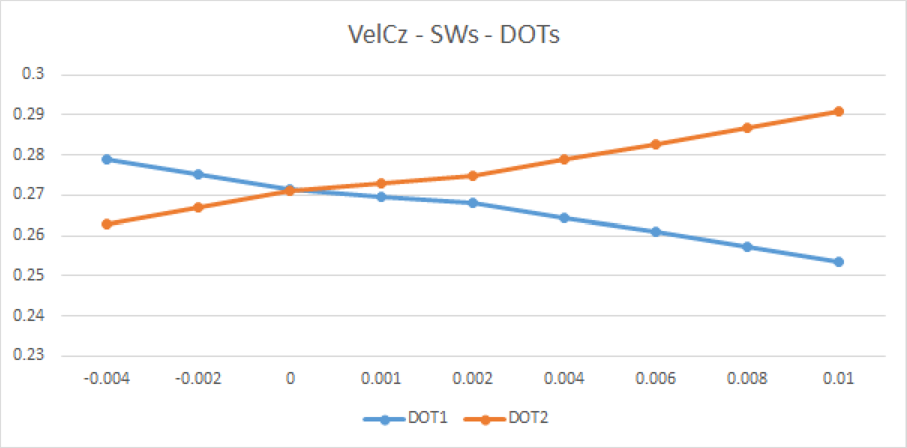


Figure 7.19: Charge evolution of water molecule; NVE, *VelCz*, 372.84 K, SW fields, 8.5 fs

VelRND

Average values for several simulation in which only SW field varies and initial velocities are randomly setted by software. As already mentioned, for each SW field value three simulations are performed and the average values are mediated firstly over simulation time of each simulation and secondly over the three simulations.

SW field [$a.u.$]	**CK field** [$a.u.$]	**Temp** [K]	**DOT1** [$a.u.$]	**DOT2** [$a.u.$]	**Split** [$a.u.$]
-0.004	0.0	0.2789445	0.263278	-0.015667	
-0.002	0.0	0.2750000	0.266944	-0.008056	
0.0	0.0	0.2712780	0.270945	-0.000333	
0.001	0.0	0.2694025	0.272709	0.003306	
0.002	0.0	0.2679444	0.274589	0.006644	
0.004	0.0	0.2639813	0.278574	0.014593	
0.006	0.0	0.2600367	0.282241	0.022204	
0.008	0.0	0.2561483	0.286000	0.029852	
0.01	0.0	0.2526110	0.290074	0.037463	

Table 7.4: Average values of temperature, DOTs charges and average split of water molecule; NVE, *VelRND*, 300.0 K, SW fields, 8.5 fs

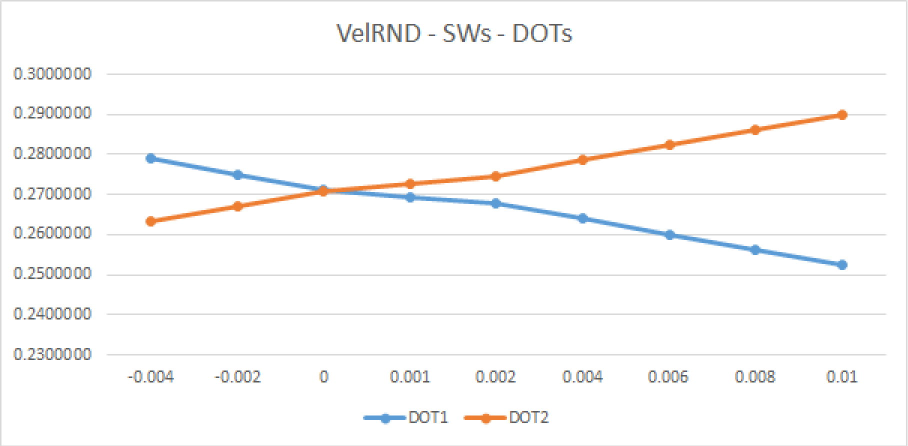


Figure 7.20: Charge evolution of water molecule; NVE, *VelRND*, 300.0 K, SW fields, 8.5 fs

Considerations

From all the previous data, it is possible to observe that independently on initial velocity, the behaviour of the average values of DOTs charges are almost the same at fixed SW field. It is an interesting result because means that initial velocities do not impact on the mean values of the charge, but, as explained in previous section, they influence only on amplitude of the charge oscillations, high value means high energy and charge oscillations are wider.

The second important consideration is related to the DOTs charges split (defined as $DOT2 - DOT1$). In fact, from data and in figure 7.21, it is possible to affirm that increasing the magnitude of SW field, the split increases according to direction of field, means that for positive SW field it is more positive, while for negative SW field it becomes more negative.

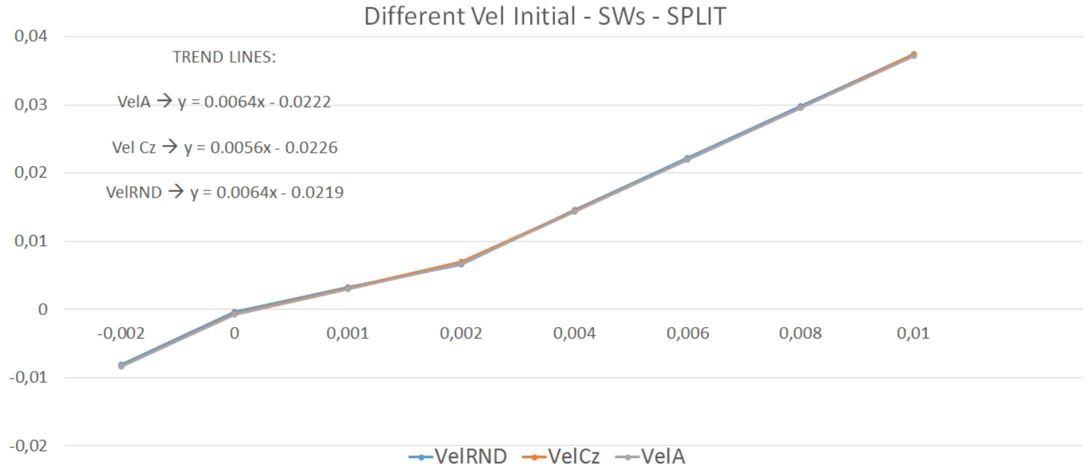


Figure 7.21: DOTs charges split behaviour of water molecule as a function of SW fields;

In this last plot (figure 7.21), DOTs charges split behaviour is reported for all three velocities: *VelA*, *VelC* and *VelRND*. As further confirm, the three behaviours are piratically the same, lines are overlapped and also their trend line are very similar.

7.5.2 Clock field effect

In order to investigate the CK field influence on water molecule dynamic, a new analysis following the same procedure done for SW field. Considering only simulations where initial velocities corresponds to *VelCz* configuration and a SW field of 0.002 $a.u.$ is applied, the following behaviour is found:

SW field [$a.u.$]	**CK field** [$a.u.$]	**DOT1** [$a.u.$]	**DOT2** [$a.u.$]	**Split** [$a.u.$]
0.002	-0.01	0.252833	0.262278	0.009444
0.002	-0.008	0.255889	0.264722	0.008833
0.002	-0.006	0.258889	0.267333	0.008444
0.002	-0.004	0.261778	0.269944	0.008167
0.002	-0.002	0.264833	0.272389	0.007556
0.002	0.0	0.267944	0.274889	0.006944
0.002	0.002	0.271000	0.277389	0.006389
0.002	0.004	0.274000	0.279944	0.005944
0.002	0.006	0.277000	0.282667	0.005667
0.002	0.008	0.280000	0.285056	0.005056
0.002	0.01	0.283000	0.287667	0.004667

Table 7.5: Average values of temperature, DOTs charges and average split of water molecule; NVE, *VelCz*, 372.84 K, SW = 0.002 $a.u.$, CKs, 8.5 fs

Considerations

As it is possible to observe in figure 7.22, an unexpected behaviour is found, because increasing CK field the DOTs charges split is reduced. Completely opposite with respect to what is expected in MQCA molecules, as explained in section 6.4. This strange behaviour could be justify considering the fact that water molecule has very few electrons with respect to a complex MQCA molecule and then a positive CK field pushes down the few electrons and the mobile charge available is reduced. In fact from data (table 7.5), for positive CK field the split is reduced. While, with negative CK field mobile charges are in the upper part of the molecule (*DOT1* and *DOT2*) and, in this way, the split is increased.

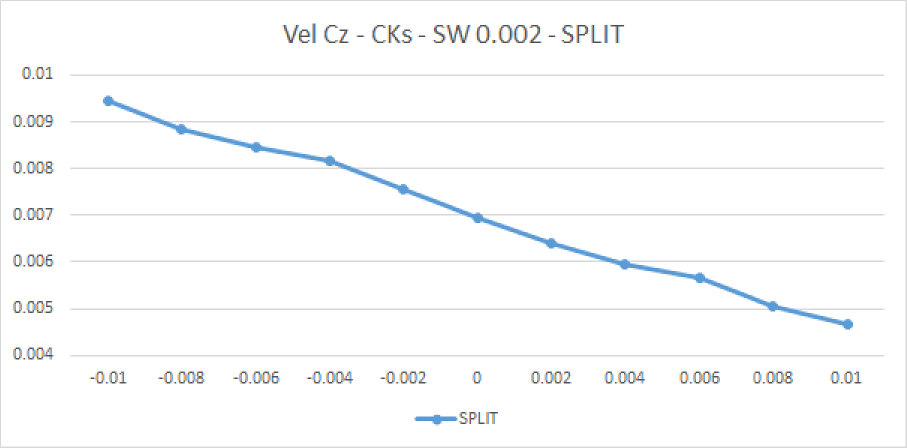


Figure 7.22: DOTs charges split behaviour of water molecule as a function of CK fields; NVE, *VelCz*, 372.84 K, SW = 0.002 $a.u.$, CKs, 8.5 fs

7.6 Switching

Once all possible considerations are discussed in the previous, switching process (described in paragraph 2.3) is faced and interesting results are obtained up to estimate the switching time t_{SW}. It is a characteristic quantity of water molecule that indicates time required by molecule to complete switching as response of a variation of electric field. All simulations are performed using optimized structure and initial velocities *VelCz*, if not specified.

First of all, a consideration related to time in which perform switching must be done. As explained in section 6.7, in order to estimate the maximum value of switching time it is required to evaluate it in the worst case, where charge to move is maximized.

Two cases must be considered, according to sign of the initial field: one with positive SW field and the other one with negative one. This is needed to optimize point in which invert SW field, because DOTs charge oscillations must be coherent with the field and, at the same time, its split must be maximized. Then for positive SW field case optimized time to perform switching is 10.5 fs and for negative one is 14.5 fs. The worst cases are individuated from figures 7.23 and 7.24.

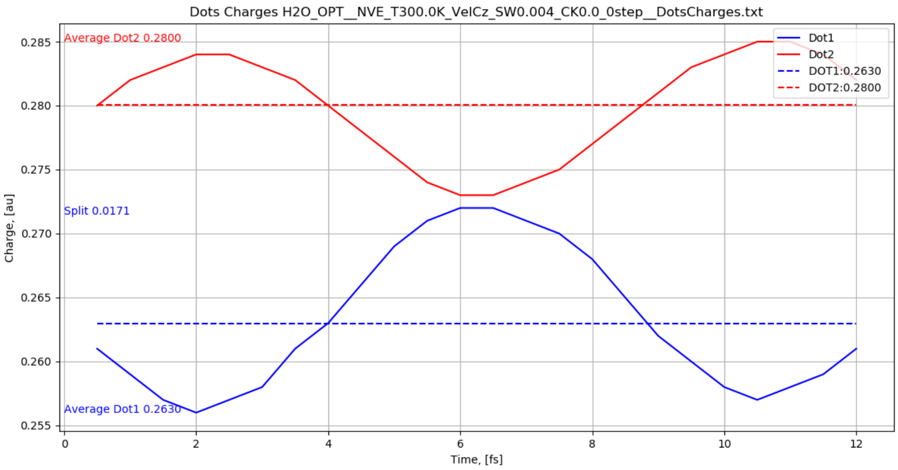


Figure 7.23: Switching: charge evolution of water molecule; NVE, *VelCz*, 372.84 K, SW = 0.004 $a.u.$, CKs, 12.0 fs

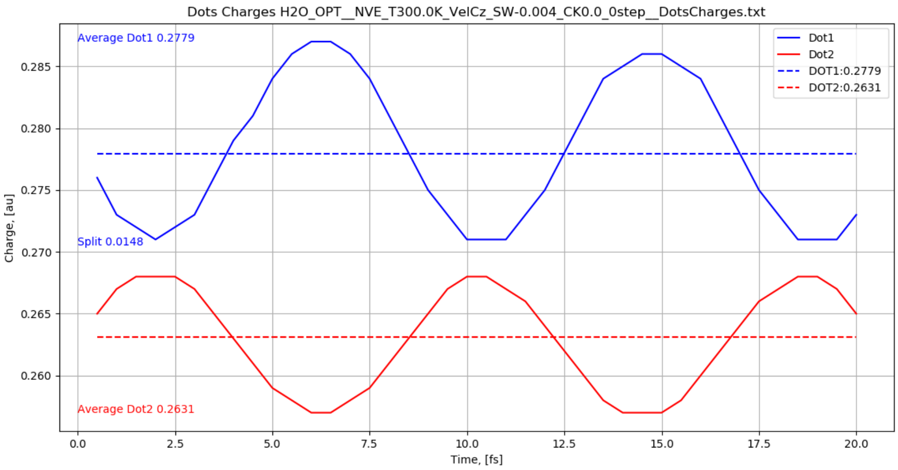


Figure 7.24: Switching: charge evolution of water molecule; NVE, *VelCz*, 372.84 K, SW = -0.004 $a.u.$, CKs, 20.0 fs

In the following some significant plots are displayed where only the magnitude of SW field changes and switching is performed at optimize instant and SW field is inverted, same amplitude.

Positive initial SW field

Here is shown plots related to switching with different SW fileds: 0.002 $a.u.$ (figure 7.25) and 0.006 $a.u.$ (figure 7.26).

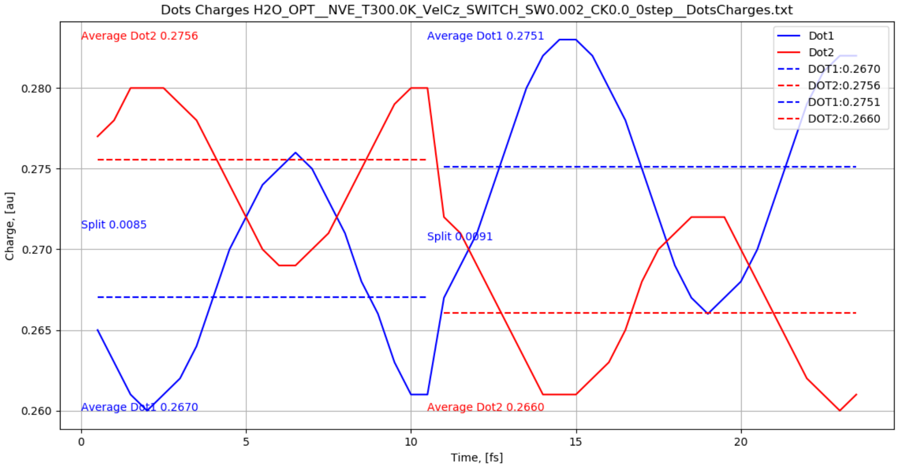


Figure 7.25: Switching: charge evolution of water molecule; NVE, $VelCz$, 372.84 K, SW = 0.002 $a.u.$, CKs, 23.5 fs

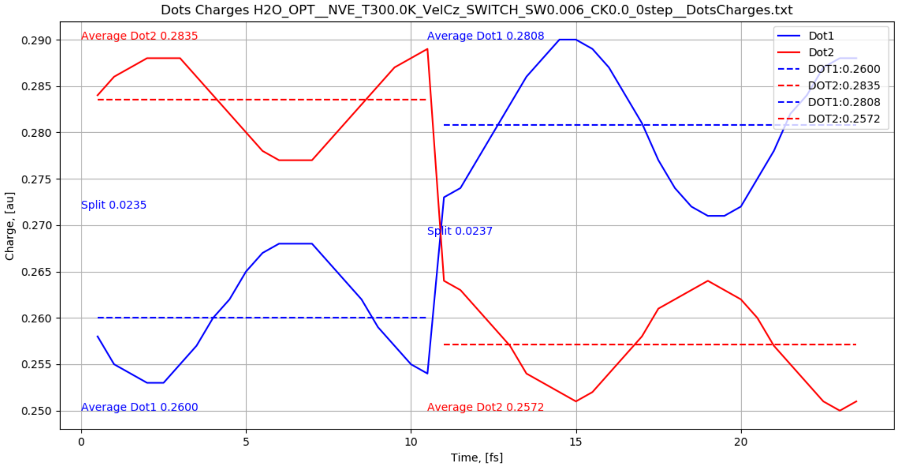


Figure 7.26: Switching: charge evolution of water molecule; NVE, $VelCz$, 372.84 K, SW = 0.006 $a.u.$, CKs, 23.5 fs

The estimation of switching time is performed graphically and its values is between 3.5 and 4.0 fs, as it is possible to see in the following plot (figure 7.27), where a zoom is reported.

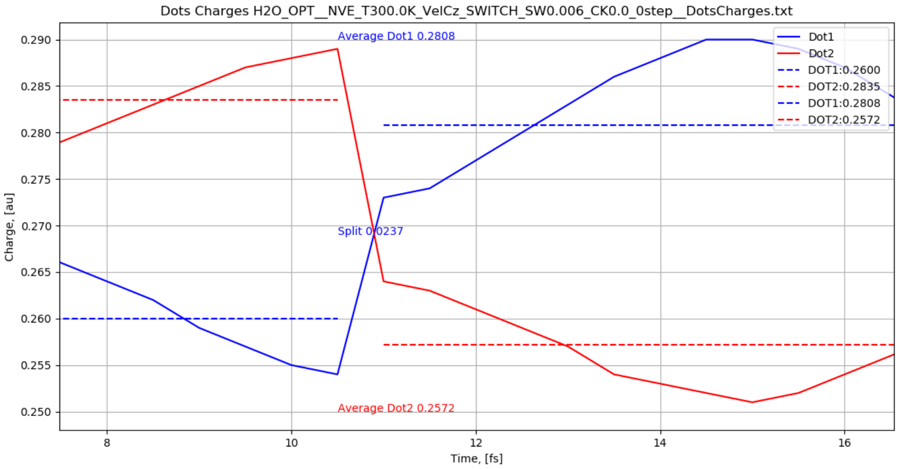


Figure 7.27: Switching zoom: charge evolution of water molecule; NVE, *VelCz*, 372.84 K, SW = 0.006 $a.u.$, CKs, 23.5 fs

Negative initial SW field

For negative case, in this section is reported only switching with SW field equals to -0.002 $a.u.$ (figure 7.28)

The estimation of switching time is performed graphically and its values, as in the positive initial field case, is between 3.5 and 4.0 fs (figure 7.29).

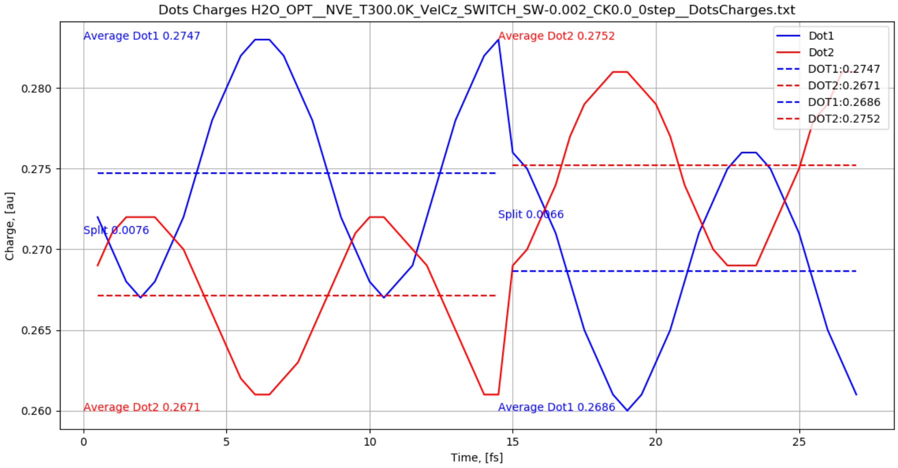


Figure 7.28: Switching: charge evolution of water molecule; NVE, *VelCz*, 372.84 K, SW = -0.002 $a.u.$, CKs, 27.0 fs

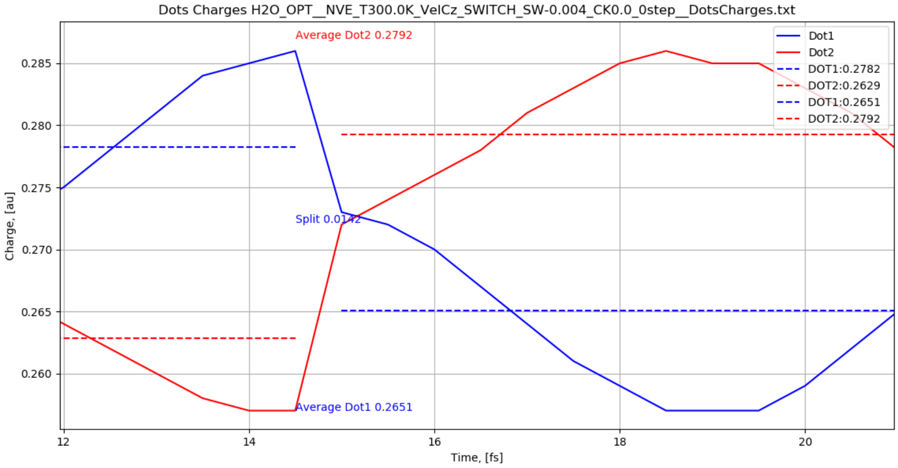


Figure 7.29: Switching zoom: charge evolution of water molecule; NVE, *VelCz*, 372.84 K, SW = 0.006 $a.u.$, CKs, 27.0 fs

Chapter 8

Decatriene Molecule Results

Once analysis of water molecule is finished, considering all significant roles of simulation parameters, a dynamic analysis is performed on decatriene molecule. The idea of the analysis is to reproduce water molecule study using decatriene one, following procedure in chapter 6.

The main goal of this thesis work is the analysis of time evolution of the charge in the decatriene molecule, it is done evaluating atomic charge using Mulliken model, according also to Wang work on Double-Cage Fluorinated Fullerenes [4] and Tokunaga one [3]. Even though this evaluation highly depends on selected basis set, but in all reported simulations the basis set is the same: *DNP* version *4.4* (see paragraph 4.2.2). Notice that all MD simulations are performed in *NVE* ensemble using the developed software (explained in chapter 5) and calculation parameters discussed in paragraph 4.2.2.

An important consideration must be done and it is related to simulation time. The decatriene simulations are very time consuming with respect to water ones due to its large structure, it is composed by 26 atoms. In addition, since decatriene molecule is more robust of water one, it is necessary to simulate it for a much longer time in order to study the influences of the fields. For these reasons, a reduced number of simulations has been performed. For example, each frame, which is long 0.5 fs required about twenty minutes and to simulate molecule for 16 fs is needed about 8 hours.

In this chapter results of dynamic simulations of decatriene molecule are presented, starting from simple dynamic with no field up to demonstrate the role of electric fields and, at the end, the switching capability of the molecule.

8.1 Starting considerations

First of all, molecule structure must be optimized through an optimization simulation done using simulator interface, because the developed software is not configured for an optimization task. After, the output structure produced by simulation (file *.car* and *.xsd*, see paragraph 5.3) are used to launch simulation exploiting the developed structure.
The optimized structure is reported in figure 8.1: where CK field is along Y-direction and SW field along X-axis and also DOTs-axis.

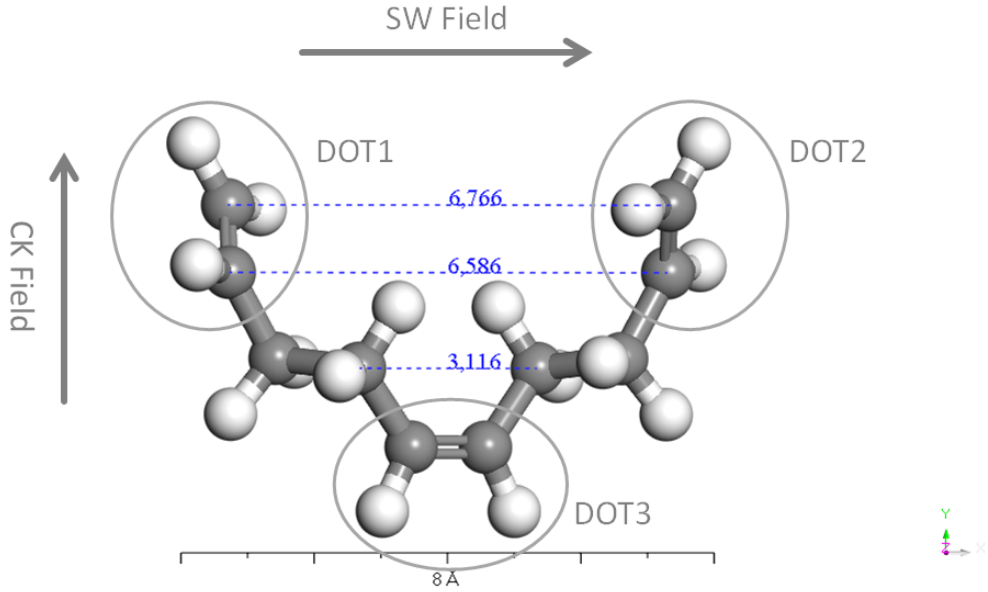


Figure 8.1: Optimized decatriene molecule used as reference

8.2 Neutral and Oxidized molecule

As first approach, it is investigate the impact of total charge of the molecule on charge time evolution. It has been simulated both neutral (net charge is zero) and oxidized (net charge is one) decatriene molecule. Simulations are performed with a SW field equals to 0.004 *a.u.* at 300 *K* in *NVE* ensemble setting initial random velocities. Charge evolution of neutral molecule is reported in figure 8.2, while in figure 8.3 for oxidized case.

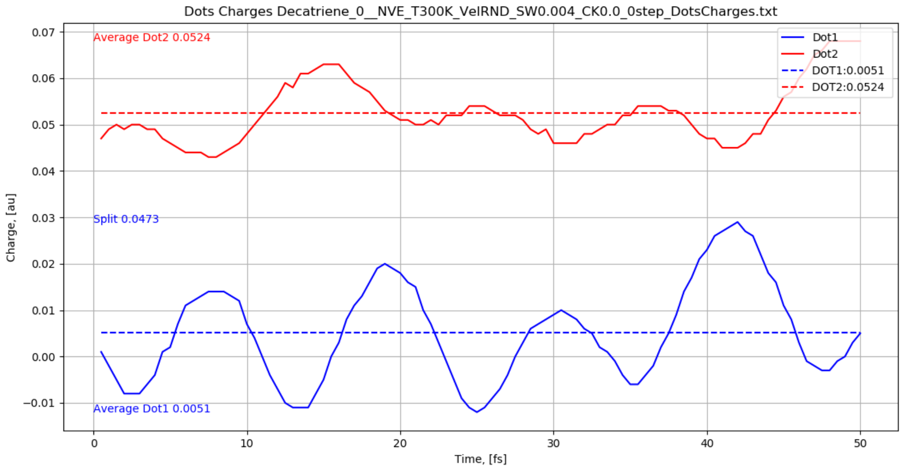


Figure 8.2: Charge evolution of neutral decatriene molecule; NVE, *VelRND*, 300 K, SW Field 0.004 $a.u.$ and 50.0 fs

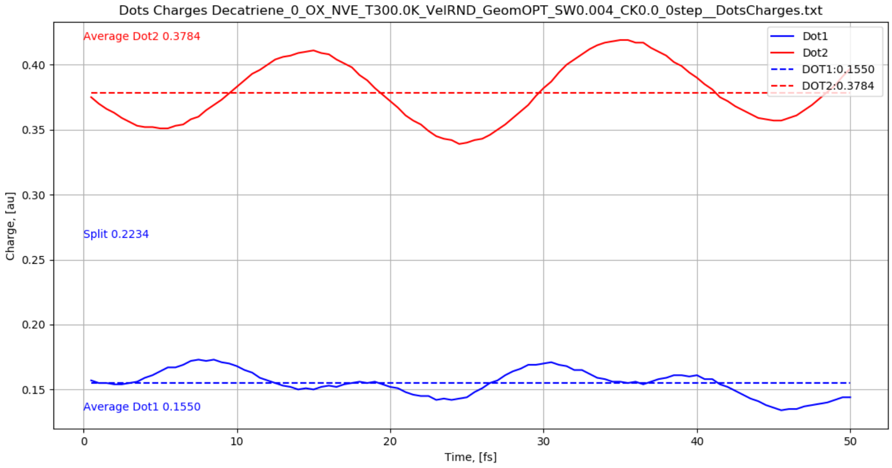


Figure 8.3: Charge evolution of oxidized decatriene molecule; NVE, *VelRND*, 300 K, SW Field 0.004 $a.u.$ and 50.0 fs

To better evaluate the impact, average values of DOTs charges are reported in table 8.1. The following mean values are obtained averaging over all dynamic range, which is 50.0 *fs* for both cases.

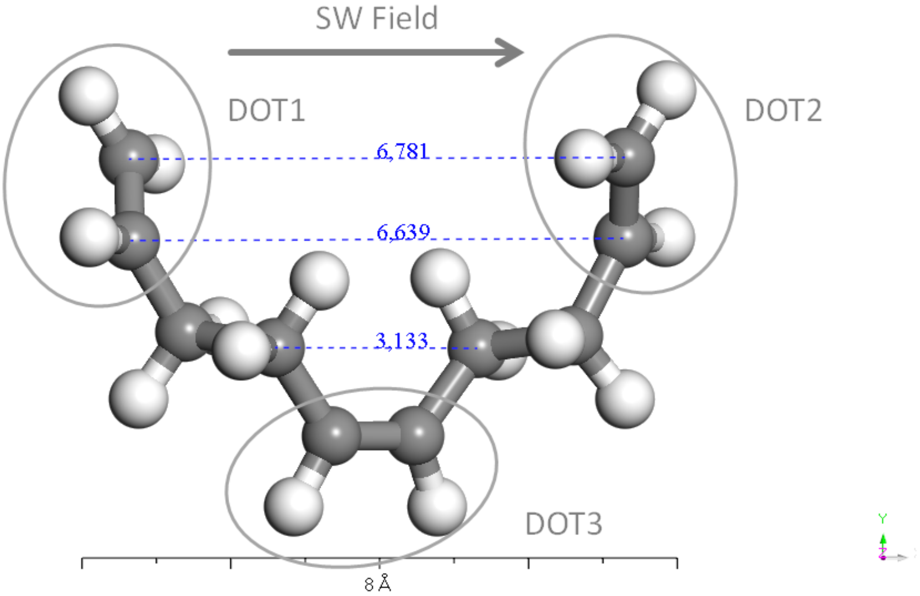
Oxidation status	**SW Field [*a.u.*]**	**DOT1 [*a.u.*]**	**DOT2 [*a.u.*]**	**Split [*a.u.*]**
Neutral	0.004	0.0051	0.0524	0.0473
Oxidized	0.004	0.1550	0.3784	0.2234

Table 8.1: Average values of DOTs charges of decatriene molecule; NVE, *VelRND*, 300 *K*, SW Field 0.004 *a.u.* and 50.0 *fs*

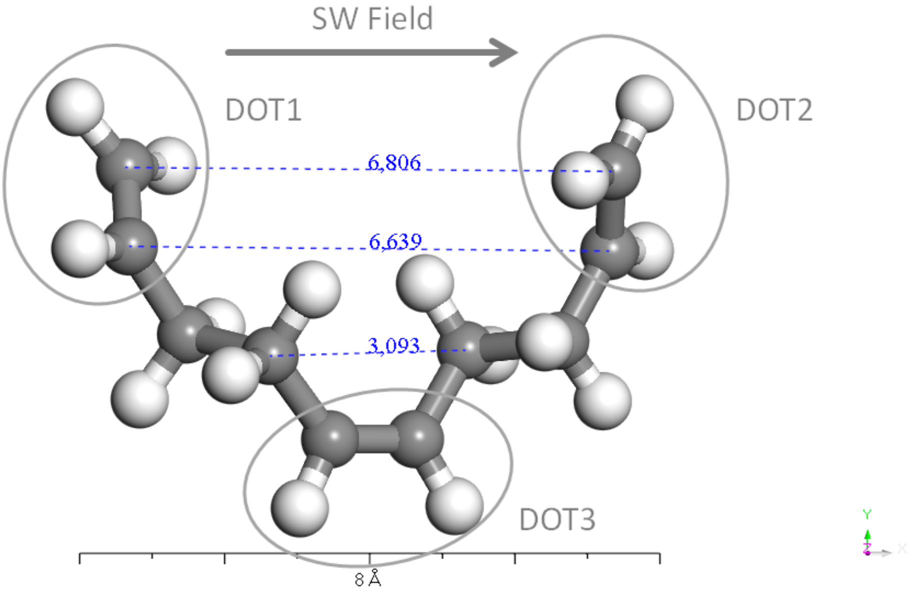
Data in the table 8.1 confirm that oxidized molecule has better QCA performances than neutral one, as explained in section 6.6. The free charges in oxidized molecule are more reactive. Considering this behaviour, in this work it is preferred to investigate only oxidized molecule due to the long simulation time.

8.3 Constraints

Since decatriene molecule is large molecule with respect to water, in MD simulations it not necessary to force constraints in the molecule. Performing a very long simulation (about 60 *fs* long) under the action of a SW field equals to 0.004 *a.u.*, the decatriene molecule does not rotate or move in the direction of the field, as water case. In particular, its atoms vibrate and the mean DOTs positions are kept constant. Of course, if the time under the action of the field is increased, molecule will be distorted and this will be also an impact on average DOTs charge values. In figure 8.4, two frames of the same simulation are reported where SW field is applied and the initial structure is one shown in figure 8.1. No structure deformation is observed, only a slightly variation of intermolecular distances.



(a) Time: 30 fs;



(b) Time: 56 fs;

Figure 8.4: Mechanical evolution of oxidized decatriene molecule; NVE, *VelRND*, 300 K, SW Field 0.004 $a.u.$ and 56.0 fs

8.4 Period of charge oscillation

A common characteristic among all simulations of oxidized decatriene arises and it is related, as for water molecule, to the charge oscillations that is defined as the time necessary to complete an oscillation of the charge in a dot. This quantities is almost the same for each configuration of fields and initial velocities. Its value can be estimated around 20-21 fs, much longer than water period and it is justify considering the size of the molecule. As shown in figure 8.3.

8.5 Fields Influence

In this section, the influences of applied fields is investigated, both SW and CK field, according to the procedure of analysis in chapter 6.

8.5.1 Switching field effect

The field along DOTs-axis may be increase the difference of DOTs charge and in order to verify it two simulation are performed where initial geometry is always the optimized one, same initial velocities (*Vel1*) and SW field varies from 0.004 $a.u.$ to 0.008 $a.u.$. The dashed lines individuate the mean values (reported in tab 8.2) and they are computed averaging DOT charges over 20 fs, a single oscillation period.

SW Field $[a.u.]$	**DOT1** $[a.u.]$	**DOT2** $[a.u.]$	**Split** $[a.u.]$
0.004	0.1591	0.3799	0.2208
0.008	0.0791	0.4909	0.4118

Table 8.2: Average values of DOTs charges of oxidized decatriene molecule; NVE, *VelRND*, 300 K, SW Fields and 20.0 fs

Data of table 8.2 show a coherent behaviour of the molecule under the action of SW filed. In fact, if magnitude of the field is doubled also the DOTs charges split doubles, more or less.

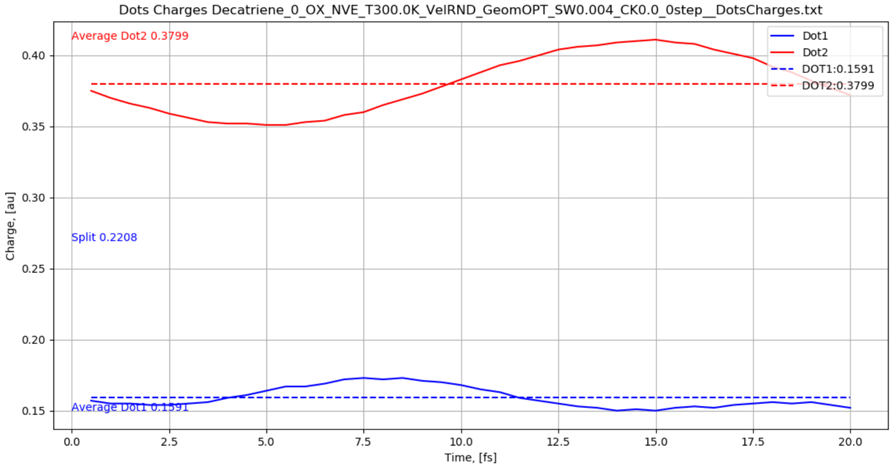


Figure 8.5: Charge evolution of oxidized decatriene molecule; NVE, *Vel1*, 300 K, SW Field 0.004 $a.u.$ and 20.0 fs

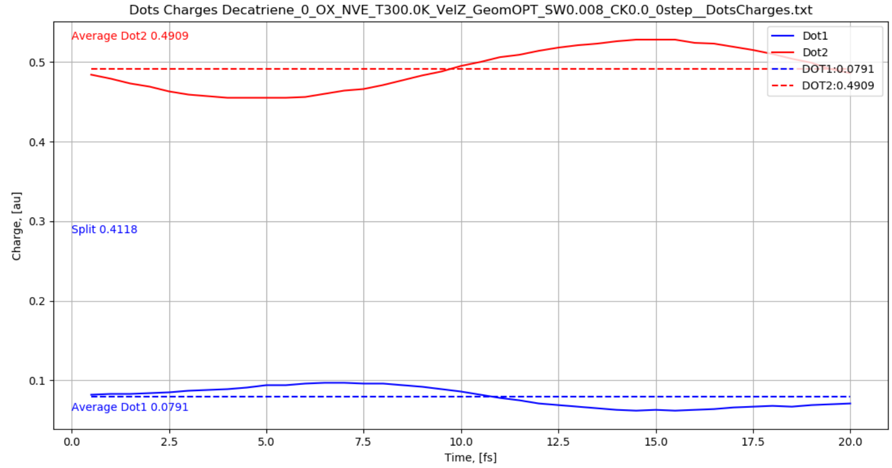


Figure 8.6: Charge evolution of oxidized decatriene molecule; NVE, *Vel1*, 300 K, SW Field 0.008 $a.u.$ and 20.0 fs

8.5.2 Clock field effect

In order to verify the impact of the clock field on decatriene molecule, the same analysis done for SW field, in the previous section is repeated. The simulations performed clock action are characterized by same initial velocities (equals also to the SW field simulations, *Vel1*), optimized structure, SW field equals to 0.004 $a.u.$ and CK field varies from 0.004 $a.u.$ (figure 8.8) and -0.004 $a.u.$ (figure 8.7).

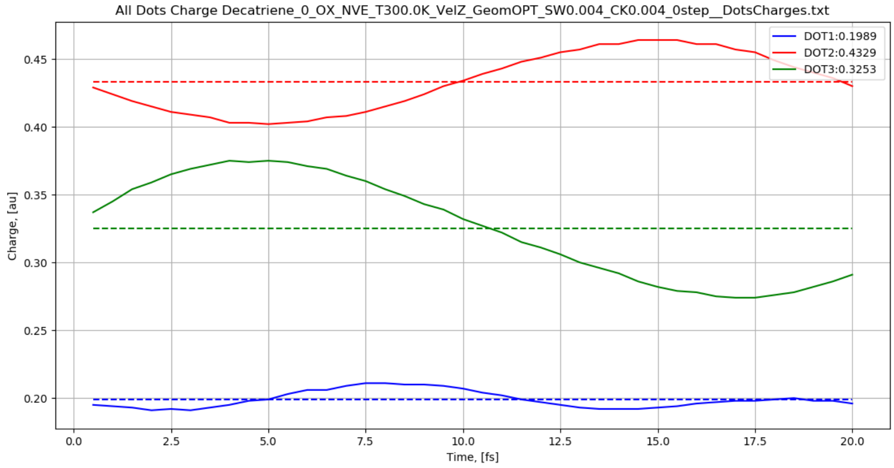


Figure 8.7: Charge evolution of oxidized decatriene molecule; NVE, *Vel1*, 300 K, SW Field 0.004 $a.u.$, CK Field 0.004 $a.u.$ and 20.0 fs

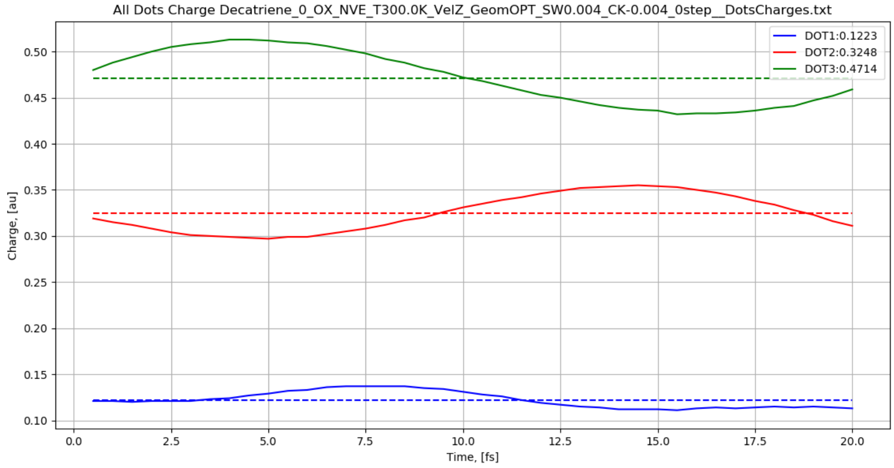


Figure 8.8: Charge evolution of oxidized decatriene molecule; NVE, *Vel1*, 300 K, SW Field 0.004 $a.u.$, CK Field -0.004 $a.u.$ and 20.0 fs

The dashed lines individuate the mean values (reported in tab 8.3) and they are computed averaging DOT charges over 20 fs, a single oscillation period.

SW Field $[a.u.]$	**CK Field** $[a.u.]$	**DOT1** $[a.u.]$	**DOT2** $[a.u.]$	**Split** $[a.u.]$	**DOT3** $[a.u.]$
0.004	-0.004	0.1223	0.3248	0.2026	0.4714
0.004	0.000	0.1591	0.3799	0.2208	0.3982
0.004	0.004	0.1989	0.4329	0.2340	0.3253

Table 8.3: Average values of DOTs charges of oxidized decatriene molecule; NVE, *VelRND*, 300 K, SW Field 0.004 $a.u.$, CKs and 20.0 fs

Observing data in table 8.3, the action of clock is coherent with what explained in the clock system (section 1.3) and with idea of adiabatic switching. In particular, negative CK field case the mean dots charges values are lowered and this means that free charges are pushed down in the molecule, in the third dot ("NULL" state), instead in positive CK case free charges are forced in the upper part of the molecule (in *DOT1* and *DOT2*). The DOT3 charge values is a confirm of this trend, indeed, it decrease from negative to positive clock.
Moreover a slightly increasing in the charge split is observed from negative to positive clock, this is consistent because increasing the charge available in the upper part (positive CK case) SW field can split more charges, at fixed SW field magnitude.

8.6 Switching

The main result of thesis work is discussed in this section and it concerns the ability of the decatriene molecule to perform switching process (explained in paragraph 2.3). This analysis lead to interesting results up to estimation of the switching time t_{SW} of decatriene. It is a characteristic quantity of molecule that describes time required by molecule to complete switching as response of a variation of electric field. All simulations are performed using oxidized molecule, optimized structure and initial velocities *Vel1* at 300 K in *NVE* ensemble.

First of all, a consideration related to time in which perform switching must be done. As explained in section 6.7, in order to estimate the maximum value of switching time it is needed to evaluate it in the worst case, where local free charges to move are maximized. Considering the time charge evolution with SW field equal to 0.004 *a.u.*, reported in figure 8.3, a good choice where perform switching of the field is around 15 *fs* because the charge split is maximum and then also the free charges to move. Taking into account this last consideration, a switching process is simulated where the initial SW field is equal to 0.004 *a.u.* and after switching point at 15*fs*, SW field is inverted and it becomes equal to -0.004 *a.u.*. The corresponding time charge evolution of this switching simulation is shown in figure 8.9, while the charge evolution of the all three dots are reported in the appendix

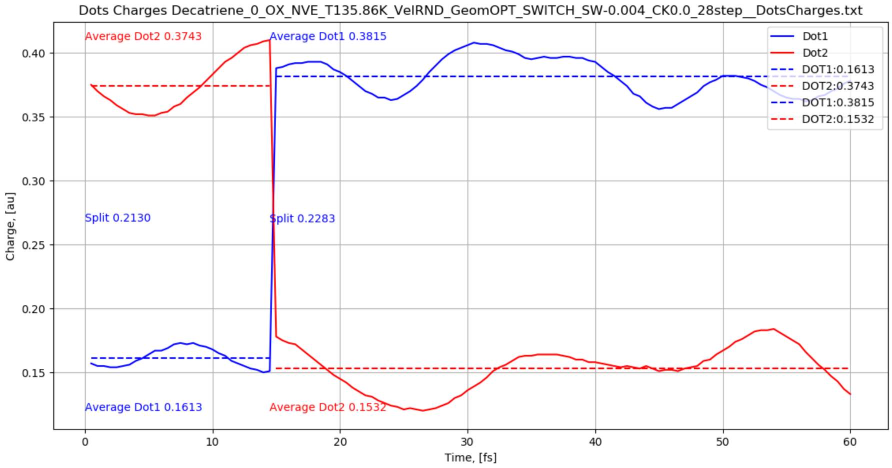


Figure 8.9: Switching: charge evolution of decatriene molecule;; NVE, *Vel1*, 300 *K*, SW Field from 0.004 *a.u.* to 0.004 *a.u.* and 20.0 *fs*

The estimation of the switching time is performed graphically form the previous plot and it is evaluated around 15 *fs*. It is time required by the most charged DOT to switch, in our case *DOT1* because after switching the SW field is oriented from right to left and then *DOT1* should be the more positive DOT.

Notice that charge oscillations are not symmetric because velocities are defined randomly by program and then the DOTs velocities are not equal, in section 7.2.2 is explained.

Chapter 9

Conclusions and future perspectives

The main goal of this thesis work is the demonstration that an evaluation of switching time in a MQCA molecule is possible exploiting molecular dynamic (MD) simulators. Starting from the study molecular dynamic of water molecule, since it is very similar to a molecular QCA candidate, it was possible to understand how perform reasonable MD simulations up to simulate a switching process in decatriene molecule.

The final and most significant results are related to estimation of switching time both for water and decatriene molecule, reported in the last paragraph of the chapters 7 and 8. From MD simulations, the switching times are 3.5-4 fs and 15 fs for water and for decatriene molecule, respectively. These two values correspond to switching frequencies equals to [250, 286] THz for water molecule and about 66.7 THz, which are coherent with the prediction of the THz range. In this way, it was demonstrated one of the advantages of the MQCA technology: its very elevate switching speed. Notice that the switching frequencies are ideal, means that they are computed in the optimum case, where molecules are optimized and perfect alignment between DOTs-axis and SW field. They represent a sort of upper limits, the real ones are certainly lowered. Considering the optimized structures, it is not take into account that molecules (especially, small one) can be distorted under a long action of an external electric field, both SW and CK field.

Other possible studies could be, extending the developed software at other possible candidates for MQCA applications, such as diallyl-butane and bis-ferrocene molecule, in order to estimate their switching time, following exactly the procedure adopted for decatriene analysis.

Other scenarios are: dynamic analysis of two or more molecules (i.e. a wire) and study of possibility to perform adiabatic switching in one or more molecules. The latter scenario can be performed, in quite simple way, using the developed software, in which it is possible to define an arbitrary value of the field (in this case CK field) in each simulation frame. The adiabatic switching can be simulated setting values of CK field that describe a smooth function with a certain slope.

Appendix A

Simulation Files

A.1 Complete *.input* file

In the following a complete *.input* file is reported for a generic dynamic simulation characterized by fine quality of calculation:

```
# Task parameters
Calculate                     molecular_dynamics
Write_HIS_File                on
Write_ARC_File                on
MD_Velocity                   user_defined
1     1.000000000    -0.001859  -0.007638   0.0000
2     1.000000000    0.02223  -0.005826   0.00000
3     1.000000000     0.028283   0.005826   0.00000

MD_Time_Step                  0.5000
MD_Simann_panel
1  MD_NVE     300.0000
#

# Cartesian constraints
MD_Fixed_Coordinate
1   Y

Symmetry                      off
Max_memory                    2048
File_usage                    smart
```

```
Scf_density_convergence       1.000000e-006
Scf_charge_mixing             2.000000e-001
Scf_spin_mixing               5.000000e-001
Scf_diis                      6 pulay
Scf_iterations                50

# Electronic parameters
Spin_polarization             unrestricted
Charge                        0
Basis                         all
basis_version                 basfile_v4.4
Pseudopotential               none
Functional                    b3lyp umesh=xcoarse minu=-3
Aux_density                   octupole
Integration_grid              fine
Occupation                    fermi
Cutoff_Global                 3.3000 angstrom

# Calculated properties
Print_eigval_window           -1.d9
Plot                          homo
Plot                          lumo
Plot                          density
Plot                          potential
Plot                          fukuip
Plot                          fukuim
Plot                          fukui0
Electrostatic_moments         on
Mulliken_analysis             charge
Hirshfeld_analysis            charge
Esp_fit                       on
Grid                          msbox  3 0.2500 0.2500 0.2500 3.0000
plot_dos                      on
```

```
empty_bands                   12
electric_field               0.002   0.0   0.0
```

A.2 Complete *.outmol* file

In the following a complete *.output* file is reported for a generic dynamic simulation of a single step and charcterized by fine quality of calculation:

```
===============================================================
Materials Studio DMol^3 version 8.0
compiled on Dec  4 2014 21:29:06
===============================================================

===============================================================
Density Functional Theory Electronic Structure Program
Copyright (c) 2014, Accelrys Inc. All rights reserved.
Cite work using this program as:
B. Delley, J. Chem. Phys. 92,  508  (1990).
B. Delley, J. Chem. Phys. 113, 7756 (2000).
DMol^3 is available as part of Materials Studio.
===============================================================


DATE:     May 18 18:22:04 2018

Job started on host VLSI_WINDOWS

This run uses    8 processors

Message: License checkout of MS_dmol successful

Message:  Using user-supplied basis set file: basfile_v4.4
```

```
Basis set is read from file:
C:\PROGRA~2\Accelrys\MATERI~1.0\share\Resources\Quantum\DMol3\basfile_v4.4


parallel run with   8 processors

no INCOOR file: try ZMAT
no ZMAT file: try CAR

Geometry is read from file: H2O_OPT.car

INCOOR, atomic coordinates in au (for archive):
______________________________________________________________________>8

$coordinates
O            -0.00410245179818    0.51600150465134    0.00000000000000
H             1.56005264805708    1.48111207550890    0.00000000000000
H            -1.29134806838511    1.76562649889533    0.00000000000000
$end
______________________________________________________________________>8


N_atoms =    3     N_atom_types =  2


INPUT_DMOL keywords (for archive):
______________________________________________________________________>8

<--
# Task parameters
Calculate                     molecular_dynamics
Write_HIS_File                on
Write_ARC_File                on
```

```
MD_Velocity                   user_defined
1     1.000000000    -0.000836000     0.000000000     0.000000000<--
2     1.000000000     0.015384000    -0.016090000     0.000000000<--
3     1.000000000     0.018916000     0.008189000     0.000000000<--
MD_Time_Step                  0.5000
MD_Simann_panel
1 md_nve 148.24                                                        <--
<--
# Cartesian constraints
MD_Fixed_Coordinate
1   y                                                                  <--
Symmetry                      off
Max_memory                    2048
File_usage                    smart
Scf_density_convergence       1.000000e-006
Scf_charge_mixing             2.000000e-001
Scf_spin_mixing               5.000000e-001
Scf_diis                      6 pulay
Scf_iterations                50
<--
# Electronic parameters
Spin_polarization             unrestricted
Charge 0
Basis                         dnp
basis_version                 basfile_v4.4
Pseudopotential               none
Functional                    b3lyp umesh=xcoarse minu=-3
Aux_density                   octupole
Integration_grid              fine
Occupation                    fermi
Cutoff_Global                 3.3000 angstrom
<--
# Calculated properties
```

```
Print_eigval_window           -1.d9
Plot                          homo
Plot                          lumo
Plot                          density
Plot                          potential
Plot                          fukuip
Plot                          fukuim
Plot                          fukui0
Electrostatic_moments         on
Mulliken_analysis             charge
Hirshfeld_analysis            charge
Esp_fit                       on
Grid                          msbox  3 0.2500 0.2500 0.2500 3.0000
plot_dos                     on
empty_bands                  12
electric_field 0.0 0.0 0.0
---------------------------------------------------------------------->8


Publications of specific relevance to this calculation:

Density functional:
Nonlocal B3LYP functional:
A.D. Becke, J.Chem.Phys. 98 (1993) 5648-5652
C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785-789
S.H. Vosko, L. Wilk, M. Nusair, Can. J. Phys. 58 (1980) 1200-1211
P.J. Stephens, et al., J.Phys.Chem. 98 (1994) 11623-11627

Spin unrestricted calculation


Massive thermostatting in isothermal density functional molecular dynamics simulations
Windiks Delley: J. Chem. Phys. 119, 2481 (2003)
```

```
Parallel eigenvalue solution:
Parallel solution of partial symmetric eigenvalue problems from electronic struc
Auckenthaler, Blum, Bungartz, et al.: Parallel Computing 37, 783 (2011)

Message: No orbital symmetry used in B3LYP calculation.



Calculation is Spin_unrestricted



Warning: no SYM file, no symmetry used in vibrational analysis
Warning: at least C1 SYM file should be there for optgeom
Hydrogen     nbas=  1, z=   1, nrfn=  5, rcut=  6.24, e_ref= -0.039054 Ha
rcore=  0.00  zval=   1.00   1.00
n=1  L=0  occ= 1.00 e=      -0.221510Ha        -6.0276eV
n=1  L=0  occ= 0.00 e=      -0.844683Ha       -22.9850eV
n=2  L=1  occ= 0.00 e=      -1.999949Ha       -54.4214eV
n=1  L=0  occ= 0.00 e=      -0.092490Ha        -2.5168eV  eliminated
n=2  L=1  occ= 0.00 e=      -0.058675Ha        -1.5966eV  eliminated
Oxygen       nbas=  2, z=   8, nrfn=  9, rcut=  6.24, e_ref=  4.497658 Ha
rcore=  0.00  zval=   8.00   8.00
n=1  L=0  occ= 2.00 e=     -18.862785Ha      -513.2827eV
n=2  L=0  occ= 2.00 e=      -0.862375Ha       -23.4664eV
n=2  L=1  occ= 4.00 e=      -0.322345Ha        -8.7714eV
n=2  L=0  occ= 0.00 e=      -2.133181Ha       -58.0468eV
n=2  L=1  occ= 0.00 e=      -1.589454Ha       -43.2513eV
n=3  L=2  occ= 0.00 e=      -1.999440Ha       -54.4076eV
n=1  L=0  occ= 0.00 e=      -0.092490Ha        -2.5168eV  eliminated
n=2  L=1  occ= 0.00 e=      -0.058675Ha        -1.5966eV  eliminated
n=3  L=2  occ= 0.00 e=      -0.441118Ha       -12.0034eV  eliminated

Symmetry orbitals C1
```

```
n  norb    representation
1    24        a
total number of valence orbitals:     24

Orbitals: valence   6 core:   1 aux:  17

molecule charge=      0.0   active electron number=      10.0
(without charge=            10.0)


real array elements, matrices vectors etc:       0.9 MB
integer arrays                           :       0.0 MB
min recommended for all-incl workspace   :       1.4 MB
Total memory allocated for arrays         :       3.1 MB
Memory for temporary file storage on disk :       0.8 MB
Total memory allocated                    :       3.8 MB
Max memory requested                      :    2048.0 MB
Default spin density on atom O (  1), L= 1 was used on start: M_s=  2.0
1  2.000 start spin density on O (   1), L= 1 M_s=  2.0


Electric field components (a.u.) as read from input:
0.0000000   0.0000000   0.0000000

There is   1 MD simulated annealing stage

MD initialization

degrees of freedom =                          2
number of fixed cartesian coordinates =       1
number of constrained internal coordinates =    0

setup virgin md run
```

```
Warning: molecule has been put into center of mass coordinate system
translated by    0.01138985848348    0.63990975857391    0.00000000000000
user defined velocities

dq          ATOMIC  VELOCITIES (bohr/atu)
x          y          z
dq    O    -0.000836   0.000000   0.000000
dq    H     0.015384  -0.016090   0.000000
dq    H     0.018916   0.008189   0.000000
Message: Generating Coulomb integrals
Peak memory usage                2 M

Total Energy           Binding E       Cnvgnce     Time   Iter
Ef           -80.846886Ha        -4.9695527Ha      3.08E-01     0.0m       1
Ef           -80.830726Ha        -4.9533926Ha      1.68E-01     0.0m       2
Ef           -80.821807Ha        -4.9444735Ha      9.94E-02     0.0m       3
Ef           -80.823873Ha        -4.9465393Ha      7.40E-02     0.0m       4
Ef           -80.821167Ha        -4.9438337Ha      2.98E-02     0.0m       5
Ef           -80.821119Ha        -4.9437858Ha      1.66E-02     0.0m       6
Ef           -80.821218Ha        -4.9438851Ha      9.28E-03     0.0m       7
Ef           -80.821239Ha        -4.9439053Ha      5.13E-03     0.0m       8
Ef           -80.821252Ha        -4.9439186Ha      3.14E-03     0.0m       9
Ef           -80.821264Ha        -4.9439305Ha      1.54E-04     0.0m      10
Ef           -80.821264Ha        -4.9439310Ha      7.49E-05     0.0m      11
Ef           -80.821265Ha        -4.9439312Ha      3.03E-05     0.0m      12
Ef           -80.821265Ha        -4.9439312Ha      1.59E-05     0.0m      13
Ef           -80.821265Ha        -4.9439312Ha      8.41E-06     0.0m      14
Ef           -80.821265Ha        -4.9439312Ha      3.82E-06     0.0m      15
Ef           -80.821265Ha        -4.9439312Ha      1.18E-06     0.0m      16
local part converged switching to nonlocal functional
Ef           -80.821265Ha        -4.9439312Ha      1.00E-03     0.0m      17
Ef           -80.471762Ha        -4.5944283Ha      5.20E+00     0.0m      18
Ef           -80.403045Ha        -4.5257116Ha      3.08E-03     0.0m      19
```

```
Ef          -80.403051Ha        -4.5257174Ha      3.44E-03     0.0m     20
Ef          -80.402976Ha        -4.5256426Ha      1.03E-03     0.0m     21
Ef          -80.402988Ha        -4.5256545Ha      1.53E-04     0.0m     22
Ef          -80.402986Ha        -4.5256530Ha      2.26E-05     0.0m     23
Ef          -80.402986Ha        -4.5256528Ha      2.03E-05     0.0m     24
Ef          -80.402986Ha        -4.5256527Ha      6.67E-07     0.0m     25
Message: SCF converged


Energy of Highest Occupied Molecular Orbital:  -0.31101Ha    -8.463eV
Energy of Lowest Unoccupied Molecular Orbital:   0.06747Ha     1.836eV

HOMO is orbital number    10
LUMO is orbital number    11

df              ATOMIC  COORDINATES (au)                  DERIVATIVES (au)
df            x          y          z            x          y          z
df    O    -0.004102   0.516002   0.000000    -0.018822   0.003768   0.000000
df    H     1.560053   1.481112   0.000000     0.008648   0.005755  -0.000000
df    H    -1.291348   1.765626   0.000000     0.010174  -0.009524  -0.000000
df  binding energy      -4.5256526Ha      -123.14933eV       -2839.947kcal/mol


Energy components:
Sum of atomic energies =      -75.8773334Ha
Kinetic =       -1.5116292Ha
Electrostatic =       -0.5458759Ha
Exchange-correlation =        0.1688324Ha
Nonlocal-exchange =        1.7825704Ha
Spin polarization =       -4.4195503Ha

Total Energy           Binding E                   Time   Iter
Ef          -80.402986Ha        -4.5256526Ha                   0.0m     26
```

```
Step   Kin.+Pot. Energy        Pot. Energy Temperature
MD       0     -80.4025166 Ha     -80.4029860 Ha    148.24 K

Warning: fixed atoms
atom  x  y  z
1  0  1  0

Progress: 0

+++ Entering MD/SA Stage Number    1 +++

Performing NVE MD using velocity Verlet propagator
with       1 steps in this stage


write car file with the new structure

update arc file with the new structure
Message: Generating Coulomb integrals
Peak memory usage                2 M

Total Energy           Binding E       Cnvgnce     Time   Iter
Ef          -80.752505Ha        -4.8751718Ha      1.22E-02     0.0m      1
Ef          -80.821155Ha        -4.9438218Ha      8.43E-03     0.0m      2
Ef          -80.821199Ha        -4.9438653Ha      5.27E-03     0.0m      3
Ef          -80.821204Ha        -4.9438707Ha      1.02E-03     0.0m      4
Ef          -80.821206Ha        -4.9438730Ha      1.69E-04     0.0m      5
Ef          -80.821206Ha        -4.9438722Ha      6.06E-05     0.0m      6
Ef          -80.821206Ha        -4.9438725Ha      2.39E-05     0.0m      7
Ef          -80.821206Ha        -4.9438724Ha      2.43E-06     0.0m      8
Ef          -80.821206Ha        -4.9438724Ha      1.70E-06     0.0m      9
local part converged switching to nonlocal functional
```

```
Ef          -80.821206Ha        -4.9438724Ha      1.00E-03     0.0m     10
Ef          -80.471713Ha        -4.5943794Ha      4.70E-03     0.0m     11
Ef          -80.402995Ha        -4.5256619Ha      3.08E-03     0.0m     12
Ef          -80.403001Ha        -4.5256677Ha      3.44E-03     0.0m     13
Ef          -80.402926Ha        -4.5255929Ha      1.03E-03     0.0m     14
Ef          -80.402938Ha        -4.5256049Ha      1.53E-04     0.0m     15
Ef          -80.402937Ha        -4.5256033Ha      2.25E-05     0.0m     16
Ef          -80.402936Ha        -4.5256031Ha      2.03E-05     0.0m     17
Ef          -80.402936Ha        -4.5256030Ha      6.72E-07     0.0m     18
Message: SCF converged


Energy of Highest Occupied Molecular Orbital:  -0.31102Ha    -8.463eV
Energy of Lowest Unoccupied Molecular Orbital:   0.06751Ha     1.837eV

HOMO is orbital number    10
LUMO is orbital number    11

df              ATOMIC  COORDINATES (au)                 DERIVATIVES (au)
df             x          y          z           x          y          z
df     O    -0.004369   0.516002   0.000000    -0.020385   0.004528  -0.000000
df     H     1.566496   1.472652   0.000000     0.009288   0.006038  -0.000000
df     H    -1.283372   1.770699   0.000000     0.011097  -0.010566   0.000000
df   binding energy      -4.5256030Ha      -123.14798eV       -2839.915kcal/mol


Energy components:
Sum of atomic energies =      -75.8773334Ha
Kinetic =       -1.5120021Ha
Electrostatic =       -0.5455897Ha
Exchange-correlation =        0.1689052Ha
Nonlocal-exchange =        1.7826338Ha
Spin polarization =       -4.4195503Ha
```

```
Total Energy           Binding E                  Time   Iter
Ef          -80.402936Ha        -4.5256030Ha                 0.0m     19

write car file with the new structure

update arc file with the new structure

Progress: 100

dq          ATOMIC  VELOCITIES (bohr/atu)       ACCELERATIONS (bohr/atu**2)
dq             x          y          z           x          y          z
dq    O    -0.000243   0.000000   0.000000    0.001274  -0.000283   0.000000
dq    H     0.011076  -0.018923   0.000000   -0.009215  -0.005991   0.000000
dq    H     0.013807   0.013014   0.000000   -0.011010   0.010483   0.000000

Step      System Energy        Pot. Energy   Temperature
MD       1     -80.4025122 Ha     -80.4029364 Ha    133.94 K


System Energy is a sum of:
Potential  =     -80.4029364Ha
Kinetic    =       0.0004242Ha
Thermostat =       0.0000000Ha

+++ Entering Properties Section +++



Charge partitioning by Hirshfeld method: (  0.0004   -0.0000)
O     1 charge   spin                     -0.3067   -0.0000
H     2 charge   spin                      0.1558    0.0000
H     3 charge   spin                      0.1514    0.0000
```

```
Dipole moment vectors (au):
x               y               z
electronic:       -0.153778        -6.615429         0.000000
nuclear:           0.248168         7.371363         0.000000
net:               0.094390         0.755934         0.000000
dipole magnitude:     0.76180 au        1.9363 debye

Dipole moment vectors in initial coordinates (au):
x               y               z
net:               0.094390         0.755934         0.000000

Mulliken Population analysis

Population analysis for representation  1    a
spin up    down    charge    spin
O (  1) 10 0   1.000   1.000     2.000   0.000
O (  1) 20 0   0.867   0.867     1.734   0.000
O (  1) 20 0  -0.009  -0.009    -0.018   0.000
O (  1) 21-1   0.787   0.787     1.574  -0.000
O (  1) 21-1  -0.001  -0.001    -0.002  -0.000
O (  1) 21 0   0.974   0.974     1.948   0.000
O (  1) 21 0   0.003   0.003     0.006   0.000
O (  1) 21 1   0.643   0.643     1.286  -0.000
O (  1) 21 1  -0.008  -0.008    -0.017   0.000
O (  1) 32-2   0.009   0.009     0.018   0.000
O (  1) 32-1   0.002   0.002     0.004  -0.000
O (  1) 32 0   0.003   0.003     0.005  -0.000
O (  1) 32 1   0.000   0.000     0.000  -0.000
O (  1) 32 2   0.001   0.001     0.002   0.000
H (  2) 10 0   0.295   0.295     0.590  -0.000
H (  2) 10 0   0.035   0.035     0.070   0.000
H (  2) 21-1   0.009   0.009     0.019  -0.000
```

```
H (  2) 21 0   0.010   0.010     0.020   0.000
H (  2) 21 1   0.012   0.012     0.025  -0.000
H (  3) 10 0   0.296   0.296     0.591  -0.000
H (  3) 10 0   0.039   0.039     0.077   0.000
H (  3) 21-1   0.012   0.012     0.024   0.000
H (  3) 21 0   0.011   0.011     0.022   0.000
H (  3) 21 1   0.011   0.011     0.022   0.000


summarized population analysis
spin up    down    charge    spin
O (  1) 10     1.000   1.000     2.000   0.000
O (  1) 20     0.858   0.858     1.716   0.000
O (  1) 21     2.397   2.397     4.795  -0.000
O (  1) 32     0.015   0.015     0.029  -0.000
H (  2) 10     0.330   0.330     0.660  -0.000
H (  2) 21     0.032   0.032     0.064  -0.000
H (  3) 10     0.334   0.334     0.668  -0.000
H (  3) 21     0.034   0.034     0.068   0.000

Mulliken atomic charges:
charge    spin
O (  1)  -0.540  -0.000
H (  2)   0.276  -0.000
H (  3)   0.264  -0.000

Fermi energy:   -0.311023   -0.311023   -0.311023


Plotting output:
property:                                                file name:
DMol3 total electron density                             H2O_OPT_density.grd
DMol3 electrostatic potential Ha*electron(-1)            H2O_OPT_potential.grd
```

```
orbital   10   5 -a     -0.3110  1.00   H2O_OPT_homo.grd
orbital   11   6 +a      0.0675  0.00   H2O_OPT_lumo.grd

grid specifications: I_dim, Origin, n_intervals to corner:
3   -6.6140   -4.7243   -5.1967   23   -6.6140   -4.7243    5.6692
26   -6.6140    7.5589   -5.1967   30    7.5589   -4.7243   -5.1967

Limits of the ESP box:
-6.944911 -5.867534 -6.614041
7.228035  7.360549  6.614041
Solution:
-7.1282E-01  3.5445E-01  3.5837E-01  9.7714E-02
======================================

Summary of ESP fitting calculations
Number of points         :       2473
Total integration weight :     790.06
Spacing between          :       0.50 Ang
Sigma                    : 0.2322E-02
RMS of V(exact)          : 0.1695E-01
RRMS fit                 :      13.70 %

ESP-fitted charges        :
n Elem    chg   vdW(in)  vdW(ex)
1  O     -0.713   1.72   3.22
2  H      0.354   1.30   2.80
3  H      0.358   1.30   2.80
======================================


Starting finite difference SCF calculation for Fukui(-) function
Using a charge of  0.10
```

```
molecule charge=      0.1   active electron number=       9.9
(without charge=            10.0)

Message: Generating Coulomb integrals
Peak memory usage               2 M

Total Energy           Binding E       Cnvgnce     Time   Iter
Ef           -80.217338Ha        -4.3400047Ha      2.43E-02     0.0m       1
Ef           -80.284872Ha        -4.4075385Ha      1.39E-02     0.0m       2
Ef           -80.284155Ha        -4.4068217Ha      9.64E-03     0.0m       3
Ef           -80.283622Ha        -4.4062883Ha      2.64E-03     0.0m       4
Ef           -80.283621Ha        -4.4062877Ha      6.80E-04     0.0m       5
Ef           -80.283618Ha        -4.4062845Ha      1.20E-04     0.0m       6
Ef           -80.283618Ha        -4.4062845Ha      6.47E-05     0.0m       7
Ef           -80.283618Ha        -4.4062843Ha      5.18E-06     0.0m       8
Ef           -80.283618Ha        -4.4062843Ha      3.77E-06     0.0m       9
Ef           -80.283618Ha        -4.4062843Ha      2.00E-06     0.0m      10
local part converged switching to nonlocal functional
Ef           -80.283618Ha        -4.4062843Ha      1.00E-03     0.0m      11
Ef           -80.438783Ha        -4.5614496Ha      1.36E-02     0.1m      12
Ef           -80.370297Ha        -4.4929637Ha      3.21E-03     0.1m      13
Ef           -80.370304Ha        -4.4929711Ha      3.66E-03     0.1m      14
Ef           -80.370225Ha        -4.4928917Ha      1.30E-03     0.1m      15
Ef           -80.370238Ha        -4.4929047Ha      1.37E-04     0.1m      16
Ef           -80.370237Ha        -4.4929036Ha      2.37E-05     0.1m      17
Ef           -80.370237Ha        -4.4929033Ha      2.08E-05     0.1m      18
Ef           -80.370237Ha        -4.4929032Ha      7.59E-07     0.1m      19
Message: SCF converged


Energy of Highest Occupied Molecular Orbital:  -0.35417Ha    -9.637eV
Energy of Lowest Unoccupied Molecular Orbital:   0.03578Ha     0.974eV
```

```
HOMO is orbital number    10
LUMO is orbital number    11

Energy components:
Sum of atomic energies =      -75.8773334Ha
Kinetic =       -1.9441366Ha
Electrostatic =       -0.0582935Ha
Exchange-correlation =        0.1591762Ha
Nonlocal-exchange =        1.7699010Ha
Spin polarization =       -4.4195503Ha
Ef          -80.370237Ha        -4.4929032Ha      7.59E-07     0.1m     20

df  binding energy      -4.4929032Ha        -122.25817eV       -2819.396kcal/mol


Charge partitioning by Hirshfeld method: (  0.1004    0.0000)
O     1 charge   spin                   -0.2428    0.0000
H     2 charge   spin                    0.1740    0.0000
H     3 charge   spin                    0.1692   -0.0000

Mulliken Population analysis

Population analysis for representation  1    a
spin up    down    charge    spin
O (  1) 10 0   1.000   1.000     2.000  -0.000
O (  1) 20 0   0.868   0.868     1.737   0.000
O (  1) 20 0  -0.009  -0.009    -0.017   0.000
O (  1) 21-1   0.791   0.791     1.582   0.000
O (  1) 21-1  -0.002  -0.002    -0.003   0.000
O (  1) 21 0   0.926   0.926     1.852  -0.000
O (  1) 21 0   0.002   0.002     0.004  -0.000
O (  1) 21 1   0.651   0.651     1.301  -0.000
```

```
O (  1) 21 1  -0.008  -0.008    -0.016  -0.000
O (  1) 32-2   0.009   0.009     0.019  -0.000
O (  1) 32-1   0.002   0.002     0.004   0.000
O (  1) 32 0   0.003   0.003     0.005  -0.000
O (  1) 32 1   0.000   0.000     0.000   0.000
O (  1) 32 2   0.001   0.001     0.002  -0.000
H (  2) 10 0   0.286   0.286     0.572   0.000
H (  2) 10 0   0.037   0.037     0.073  -0.000
H (  2) 21-1   0.009   0.009     0.019  -0.000
H (  2) 21 0   0.010   0.010     0.019  -0.000
H (  2) 21 1   0.013   0.013     0.025   0.000
H (  3) 10 0   0.287   0.287     0.574   0.000
H (  3) 10 0   0.040   0.040     0.080  -0.000
H (  3) 21-1   0.012   0.012     0.024   0.000
H (  3) 21 0   0.010   0.010     0.021  -0.000
H (  3) 21 1   0.011   0.011     0.022   0.000


summarized population analysis
spin up    down    charge    spin
O (  1) 10     1.000   1.000     2.000  -0.000
O (  1) 20     0.860   0.860     1.720   0.000
O (  1) 21     2.360   2.360     4.721   0.000
O (  1) 32     0.015   0.015     0.029  -0.000
H (  2) 10     0.322   0.322     0.645   0.000
H (  2) 21     0.032   0.032     0.063  -0.000
H (  3) 10     0.327   0.327     0.654  -0.000
H (  3) 21     0.034   0.034     0.067   0.000

Mulliken atomic charges:
charge    spin
O (  1)  -0.470   0.000
H (  2)   0.292   0.000
```

```
H (  3)   0.279   0.000



Plotting output:
property:                             file name:
DMol3 fukui function                                              H2O_OPT_fukui.grd

grid specifications: I_dim, origin, n_intervals to corner:
3   -6.6140   -4.7243   -5.1967   23   -6.6140   -4.7243    5.6692
26   -6.6140    7.5589   -5.1967   30    7.5589   -4.7243   -5.1967



Fukui Indices for Electrophilic Attack (Fukui(-))
atom   Mulliken  Hirshfeld
O (  1)   0.698       0.639
H (  2)   0.157       0.183
H (  3)   0.145       0.178



Starting finite difference SCF calculation for Fukui(+) function
Using a charge of -0.10



molecule charge=     -0.1   active electron number=      10.1
(without charge=             10.0)

Message: Generating Coulomb integrals
Peak memory usage                2 M

Total Energy           Binding E       Cnvgnce     Time   Iter
Ef          -80.237928Ha        -4.3605947Ha      1.25E-02     0.1m      1
Ef          -80.306868Ha        -4.4295348Ha      9.46E-03     0.1m      2
Ef          -80.306104Ha        -4.4287703Ha      4.58E-03     0.1m      3
```

```
Ef          -80.305898Ha        -4.4285649Ha      1.44E-03     0.1m      4
Ef          -80.305891Ha        -4.4285579Ha      1.67E-04     0.1m      5
Ef          -80.305891Ha        -4.4285580Ha      1.21E-04     0.1m      6
Ef          -80.305892Ha        -4.4285583Ha      1.93E-05     0.1m      7
Ef          -80.305892Ha        -4.4285583Ha      5.48E-06     0.1m      8
Ef          -80.305892Ha        -4.4285583Ha      3.41E-06     0.1m      9
Ef          -80.305892Ha        -4.4285583Ha      1.33E-06     0.1m     10
local part converged switching to nonlocal functional
Ef          -80.305892Ha        -4.4285583Ha      1.00E-03     0.1m     11
Ef          -80.464243Ha        -4.5869095Ha      5.18E+00     0.1m     12
Ef          -80.395095Ha        -4.5177617Ha      3.17E-03     0.1m     13
Ef          -80.395098Ha        -4.5177650Ha      3.45E-03     0.1m     14
Ef          -80.395047Ha        -4.5177141Ha      1.22E-03     0.1m     15
Ef          -80.395057Ha        -4.5177241Ha      1.25E-04     0.1m     16
Ef          -80.395057Ha        -4.5177232Ha      2.66E-05     0.1m     17
Ef          -80.395056Ha        -4.5177231Ha      2.03E-05     0.1m     18
Ef          -80.395056Ha        -4.5177229Ha      7.63E-07     0.1m     19
Message: SCF converged


Energy of Highest Occupied Molecular Orbital:  -0.27958Ha    -7.608eV
Energy of Lowest Unoccupied Molecular Orbital:   0.08882Ha     2.417eV

HOMO is orbital number    10
LUMO is orbital number    11

Energy components:
Sum of atomic energies =      -75.8773334Ha
Kinetic =       -1.1809738Ha
Electrostatic =       -0.8746270Ha
Exchange-correlation =        0.1738783Ha
Nonlocal-exchange =        1.7835500Ha
Spin polarization =       -4.4195503Ha
```

```
Ef          -80.395056Ha        -4.5177229Ha      7.63E-07     0.1m     20

df  binding energy      -4.5177229Ha        -122.93355eV       -2834.971kcal/mol


Charge partitioning by Hirshfeld method: ( -0.0996    0.0000)
O     1 charge   spin                   -0.3357    0.0000
H     2 charge   spin                    0.1170    0.0000
H     3 charge   spin                    0.1192    0.0000

Mulliken Population analysis

Population analysis for representation  1    a
spin up    down    charge    spin
O (  1) 10 0   1.000   1.000     2.000  -0.000
O (  1) 20 0   0.868   0.868     1.737   0.000
O (  1) 20 0  -0.023  -0.023    -0.046  -0.000
O (  1) 21-1   0.791   0.791     1.582  -0.000
O (  1) 21-1  -0.004  -0.004    -0.008  -0.000
O (  1) 21 0   0.974   0.974     1.948   0.000
O (  1) 21 0   0.003   0.003     0.007   0.000
O (  1) 21 1   0.642   0.642     1.283  -0.000
O (  1) 21 1  -0.009  -0.009    -0.017  -0.000
O (  1) 32-2   0.009   0.009     0.018  -0.000
O (  1) 32-1   0.002   0.002     0.004   0.000
O (  1) 32 0   0.002   0.002     0.005  -0.000
O (  1) 32 1   0.000   0.000     0.000  -0.000
O (  1) 32 2   0.001   0.001     0.002  -0.000
H (  2) 10 0   0.325   0.325     0.650   0.000
H (  2) 10 0   0.040   0.040     0.080  -0.000
H (  2) 21-1   0.009   0.009     0.019  -0.000
H (  2) 21 0   0.010   0.010     0.020  -0.000
H (  2) 21 1   0.012   0.012     0.025   0.000
```

```
H (  3) 10 0   0.320   0.320     0.640   0.000
H (  3) 10 0   0.043   0.043     0.086  -0.000
H (  3) 21-1   0.012   0.012     0.024   0.000
H (  3) 21 0   0.011   0.011     0.022  -0.000
H (  3) 21 1   0.011   0.011     0.022  -0.000



summarized population analysis
spin up    down    charge    spin
O (  1) 10     1.000   1.000     2.000  -0.000
O (  1) 20     0.846   0.846     1.691   0.000
O (  1) 21     2.397   2.397     4.795  -0.000
O (  1) 32     0.014   0.014     0.028  -0.000
H (  2) 10     0.365   0.365     0.730   0.000
H (  2) 21     0.032   0.032     0.063  -0.000
H (  3) 10     0.363   0.363     0.725   0.000
H (  3) 21     0.034   0.034     0.067  -0.000

Mulliken atomic charges:
charge    spin
O (  1)  -0.514  -0.000
H (  2)   0.207   0.000
H (  3)   0.207   0.000



Plotting output:
property:                            file name:
DMol3 fukui function                                                H2O_OPT_fukui.

grid specifications: I_dim, origin, n_intervals to corner:
3   -6.6140   -4.7243   -5.1967   23   -6.6140   -4.7243    5.6692
26   -6.6140    7.5589   -5.1967   30    7.5589   -4.7243   -5.1967
```

```
Fukui Indices for Nucleophilic Attack (Fukui(+))
atom   Mulliken  Hirshfeld
O (  1)  -0.261       0.290
H (  2)   0.695       0.388
H (  3)   0.566       0.322


Fukui Indices for Radical Attack (Fukui(0))
atom   Mulliken  Hirshfeld
O (  1)   0.218       0.464
H (  2)   0.426       0.285
H (  3)   0.356       0.250


molecule charge=      0.0   active electron number=      10.0
(without charge=             10.0)

Message: License checkin of MS_dmol successful

Message: DMol3 job finished successfully

time all done       0.08m        4.58s

DMol3.pl message: DMol3 job finished in 0 hr 0 min 8 sec.
```

A.3 Optimized water molecule file

The *.car* used in simulation is reported and it contains the geometry structure of the water molecule:

```
!BIOSYM archive 3
PBC=OFF
Materials Studio Generated CAR File
!DATE Mon Mar 19 16:41:28 2018
O1         0.000001728     0.273056237     0.000000000 XXXX 1
xx        O   −0.542
H1         0.759909860     0.863469959     0.000000000 XXXX 1
xx        H    0.271
H2        −0.759911588     0.863473805     0.000000000 XXXX 1
xx        H    0.271
end
end
```

A.4 Optimized decatriene molecule file

The *.car* used in simulation is reported and it contains the geometry structure of the decatriene molecule

```
!BIOSYM archive 3
PBC=OFF

!DATE      Jul 05 13:16:29 2018
C1         1.331034790   −0.572000453   −0.806956215 XXXX 1
xx      C    0.000
C2        −1.334075485   −0.568326017    0.808092499 XXXX 1
xx      C    0.000
C3         2.597632649   −0.424297120    0.071320296 XXXX 1
xx      C    0.000
C4        −2.600322353   −0.419040122   −0.070335150 XXXX 1
xx      C    0.000
C5         0.554599358   −1.751941651   −0.367818408 XXXX 1
xx      C    0.000
C6        −0.560193968   −1.750146392    0.369904331 XXXX 1
xx      C    0.000
C7         3.287450558    0.861507705   −0.193890811 XXXX 1
xx      C    0.000
C8        −3.287578178    0.868232492    0.194254899 XXXX 1
xx      C    0.000
C9         3.317877836    1.871936480    0.673413567 XXXX 1
xx      C    0.000
C10       −3.312953374    1.879560761   −0.672147158 XXXX 1
xx      C    0.000
H11        1.631284358   −0.689814362   −1.848156450 XXXX 1
xx      H    0.000
H12        0.747523584    0.342642166   −0.744194052 XXXX 1
xx      H    0.000
```

```
H13     -1.634080628   -0.683999664    1.849649299  XXXX  1
xx      H    0.000
H14     -0.748707111    0.345020726    0.743821975  XXXX  1
xx      H    0.000
H15      2.313898682   -0.481816552    1.120594742  XXXX  1
xx      H    0.000
H16      3.264597969   -1.263438858   -0.129945870  XXXX  1
xx      H    0.000
H17     -2.316087583   -0.477123477   -1.119450214  XXXX  1
xx      H    0.000
H18     -3.268916118   -1.256966681    0.130671944  XXXX  1
xx      H    0.000
H19      0.986207157   -2.712259271   -0.606893226  XXXX  1
xx      H    0.000
H20     -0.991390324   -2.709277437    0.614088396  XXXX  1
xx      H    0.000
H21      3.771680315    0.971517589   -1.156253573  XXXX  1
xx      H    0.000
H22     -3.774376880    0.978443704    1.155309243  XXXX  1
xx      H    0.000
H23      3.834105809    2.792522031    0.452103393  XXXX  1
xx      H    0.000
H24      2.834427195    1.802030883    1.637539957  XXXX  1
xx      H    0.000
H25     -3.829361815    2.800435771   -0.452472165  XXXX  1
xx      H    0.000
H26     -2.827263404    1.809080728   -1.635100809  XXXX  1
xx      H    0.000
end
end
```

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