Hydrogen bonds in water clusters from an ELF perspective

Victoria Castor Villegas

Máster en Química Teórica y Modelización Computacional

MÁSTERES
DE LA UAM
2021-2022

Facultad de Ciencias

Universidad Autónoma
de Madrid

Master Erasmus Mundus in

Theoretical Chemistry and Computational Modelling

Hydrogen bonds in water clusters from an ELF perspective

Victoria Castor Villegas

Director: Dra. Julia Contreras-García
Codirector: Dra. M. Merced Montero-Campillo
Place where the project was carried out: Laboratoire de Chimie Théorique of Sorbonne Université

Master Thesis. Course 2021-2022

Universidad Autónoma de Madrid

Tutora (Sorbonne University)	Dra. Julia Contreras-García
Cotutora (Autonomous University of Madrid)	Dra. M. Merced Montero-Campillo
Jury Members	
Chair	Ismanuel Rabadán
Secretary	Cristina Sanz
	Paula Pla
	Sandra Rodríguez
	Felipe Zapata

Dra. Julia Contreras-García
Director

Dra. M. Merced Montero-Campillo
Codirector

Victoria Castor Villegas
Student

This work was done at LCT at Sorbonne University Campus Pierre et Marie Curie. Paris, Île de France, République française.

Acknowledgements

Mis más sinceros agradecimientos a todas aquellas personas que de una u otra forma han hecho que haya llegado al punto en donde me encuentro hoy.

A la Unión Europea, a través del programa Erasmus Mundus+ que me ha provisto de lo necesario para realizar mis estudios de máster. Estudios realizados en las universidades: i) Universidad Autónoma de Madrid, ii) Université Toulouse III Paul Sabatier y iii) Sorbonne Université Campus Pierre et Marie Curie. TFM escrito principalmente en ésta última, bajo la supervisión de dos excelentes asesoras, Julia Contreras-García y Merche Montero-Campillo.

A través de mis 24 años de edad he tenido el apoyo de mi núcleo familiar, con los que me he formado como persona y siendo un pilar importante para llegar a ser quien soy. Libia Villegas Morales (madre), Victor Castor Arenas (padre) y Ana Karen Castor Villegas (hermAna).

Expreso mi gratitud a las amistades que he logrado tener a través del tiempo. Jenifer Wences, por tu larga amistad. Pau LC, gracias por ser parte del Manateam🦕. *Andrea FL, hail Ciencias. Angy, por ser de las mejores entrenadoras Pokémon.*

Durante el tiempo vivido en Madrid tuve la grandiosa oportunidad de estar con los mejores compañeros de piso. Danny, Víctor, José, (Mauri et Ana as honorific members). Pasar el tiempo con ustedes fue de las mejores cosas que me pudieron haber pasado en este Erasmus. Desde Filomena con nieve en la cocina, hasta los 40 °C *en pleno verano, pasando por cocinar pancakes los findes.*

非常感谢，高晗。*You smell like a biscuit.*

Compañeros del programa TCCM. El tiempo en Aspet, París, Toulouse y en Madrid no hubiera sido nada parecido sin ustedes. Intentar esquiar, ir al Louvre, caminar por calles occitanas, las tarde noches de terraza... gracias. Sin olvidar a la camarada no inscrita en este máster, pero presente en casi todo grupo de investigación científica, Алекса́ндра Элбакя́н.

A mis compañeros de investigación: Trinidad, Julen, Bruno y Andrea. A pasar de hablar distintos dialectos el "aquario hispanoparlante" era la mejor oficina del LCT po'.

Si al final no me la he pasado tan mal.

-Ginebras.

CONTENTS

NOTATION

G Gravitational constant.

Ψ Wavefunction.

$\hbar$ Reduced Plank's constant, ${}^{h}\!/_{2\pi}$.

$|\Psi\rangle$ Ket of wavefunction, braket notation also called Dirac notation.

∇^2 Laplace operator, $\nabla \cdot \nabla$.

π number π.

$\widehat{H}$ Hamiltonian operator.

c Speed of light in the vacuum.

i Imaginary unit, square root of -1, $\sqrt{-1}$.

k_B Boltzmann constant.

$n-\mathrm{mer}$ aggregate of n molecules.

ACRONYMS

BCP Bond Critical Points.

CCP Cage Critical Points.

CFA Central Field Approximation.

CP Critical Points.

DFT Density Functional Theory.

ELF Electron Localization Function.

GGA Generalized-Gradient Approximation.

HB Hydrogen Bond.

HF Hartree-Fock.

HK Hohenberg-Kohn.

IQA Interacting Quantum Atoms.

IUPAC International Union of Pure and Applied Chemistry.

KS Kohn-Sham.

LCAO	Linear Combination of Atomic Orbitals.
LSDA	Local-Spin Density Approximation.
MP2	Møller–Plesset at second order.
NCP	Nuclear Critical Points.
QTAIM	Quantum Theory of Atoms In Molecules.
RCP	Ring Critical Points.
RDG	Reduced Density Gradient.
SCF	Self Consistent Field.
TDDFT	Time-Dependent Density Functional Theory.

CHAPTER 1

INTRODUCTION

Hydrogen Bonding (HB) is one of the most important non-covalent chemical interactions, in this thesis we will work around that interaction, through the use of Quantum Chemistry tools such as Electron Localization Function (ELF) and Interacting Quantum Atoms (IQA) our systems have been analysed, and as shown in Munárriz et al. [1], with those tools simple correlations have been found, and can be explained with elementary models such as the homogeneous electron gas.

Published papers as Guevara-Vela et al. [2] and Castor-Villegas et al. [3] have analysed topology in water cluster, where the IQA partition was done through electron density analysis by Quantum Theory of Atoms In Molecules. In this thesis we will approach the IQA partition using the ELF, with the help of PROMELF [4] code.

To approach the problem of HB in water clusters, we studied different clusters not only modifying the size of the clusters, but also with multiple arrangements for the same cluster size. The clusters were treated by DFT calculations to obtain the energy and wavefunction, with these results we made the ELF analysis, which allows us to compute the IQA electronic energy partition.

1.1 Water

In ancient times water was considered as an element, it was not until 1781 Henry Cavendish (1731-1810) postulated that water is a combination of simpler elements and the first proof provided that water is made by two volumes of H for every volume of O was developed by Gay-Lussac in 1804 [5]. Nowadays it is well known that the water molecule is composed of two hydrogen atoms interacting by a single bond with a central oxygen atom that has two lone electron-pairs.

The lone electron-pairs are know to play an indispensable role in describing not only structures but also reactivity of molecules. Classically, a lone pair is defined as a valence electron pair, bound to a nucleus, not utilized in chemical bonding [6]. However, author as Kumar et al. [7] brought together various quantum mechanical perspectives to describe the lone electron-pairs, along Bonding Theories, Molecular Electrostatic Potential, and Scalar Fields as QTAIM. And as we will discuss in Section 3.7 they are also related with the ELF.

Work as the published by Gallivan and Dougherty [8] even approach if the electron pairs in water can have a binding interaction with a π system such as the π that lies in hexafluorobenzene, concluding with an affirmative answer to the presence of an attractive interaction. Remarking the importance of those lone electron-pairs.

The electron pairs mentioned above confer particular properties to water [9]. Some of those properties are: *i*) water has an autoprotolysis equilibrium [10], *ii*) the ionic mobility of the hydronium ion in water is high due to the migration mechanism [11], *iii*) water has a high surface tension value ($72.88\,\mathrm{mN\,m^{-1}}$ at $20\,^{\circ}\mathrm{C}$) due to the strong cohesion of its molecules [12], *iv*) water has high melting and boiling points, compared to other hydrogen chalcogenides [13], *v*) water has a negative melting volume change, so the density of the liquid state is greater than that of the solid state [14], *vi*) the value of the fusion enthalpy of water is unusually large, $333.6\,\mathrm{J\,g^{-1}}$ a $0\,^{\circ}\mathrm{C}$ [15]. The above properties, among many others, make water a molecule worthy of several theoretical and experimental studies.

1.2 Hydrogen Bond

Several of the water particular properties are mostly explained by an special non-covalent interaction, the Hydrogen Bond (HB). The Figure 1.1 shows a cluster of five water molecules interacting by HBs. The total number of HB interactions for a cluster that is as large as Avogadro constant (N_A) is $2N_A$. This HB lattice gives the system a cohesion that is unusual for hydrogen chalcogenides [16].

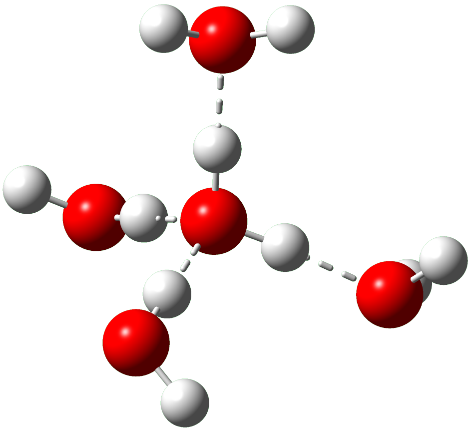


Figure 1.1: The central water molecule is accepting two hydrogen bonds and giving other two, then it can be said that the molecule has 4 HB, two of these as an acceptor and two as donor.

The HB was discovered more than one hundred years ago and it is not possible to attribute this finding to a single author. Moreover, there is no published paper that can be consider as the beginning of the term. Scientific papers about HB start to appear at the end of XIX century, in particular in English and German literature. However, the HB relevance was not enough recognized and almost completely ignored [17, 18].

> *... there are several interesting ideas in this paper, but there is one you'll never get chemists to believe: the idea that a hydrogen atom can be bonded to two other atoms at the same time...*
>
> Hildebrand [19]

Later studies developed around 1920 [17] tried to explain certain phenomena already known (the vapor phase density of hydrogen fluoride, anomalous freezing points or vapor density curves of various liquid mixtures [18]), but with a new perspective. "*The idea of a hydrogen kernel held between two atoms as a theory in regard to certain organic compounds*" [20], "*it seems that the hydrogen nuclei instead of forming duplets with electrons in the same atom, form duplets in which the two electrons are in different atoms*" [21].

At that time only two research groups (Thomas Lowry of Cambridge University and Nevil Sidgwick at Oxford) and Huggins (in two papers [22, 23]) use the concept of Hydrogen Bond, despite not using the term, in contrast they use terms as “coordination of hydrogen” [24]. In those works the H atom is bonded to two atoms.

The first one who used the term Hydrogen Bond was Pauling in 1931 [25]. At the end of 1930 the HB was explained in terms of classic electrostatic phenomena, it was approached in those terms since the examples found at that time were only weak interactions. Currently, the cases where the HB has a higher interaction energy are known, where the non-classic contribution cannot be neglected, besides the very weak ones that are mostly van der Waals.

The Hydrogen Bond interaction is classified as medium range interaction (typically from 5 to 30 $\mathrm{kJ\,mol^{-1}}$), in view of the fact that: *i*) the phenomenon appears over larger distances than covalent bonds and is weaker than covalent bonds, *ii*) the conventional HB are not enough weak to be classified as a dispersion force [26].

Steiner [17] proposed the following definition for HB:

> An X-H$\cdots$A interaction is called a “Hydrogen Bond” if *i*) it constitutes a local bond, and *ii*) X-H acts as proton donor to A.

This way of describing the HB is flexible enough to include a wide range of phenomena, in which a non-covalent interaction around an H atom is involved. The Steiner definition is valid from the simplest HB cases in which the donor X has just one H able to interact with an acceptor A which has only an electron-pair free to make the bond [27]; and also for more complex interactions as the HBs involved at proteins folding.

The IUPAC defines the HB as follows:

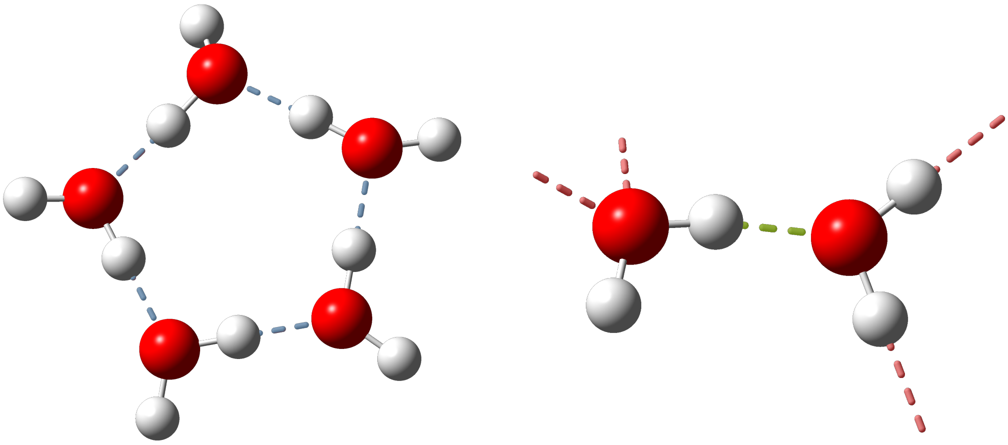
> The hydrogen bond is an attractive interaction between a hydrogen atom from a molecule or a molecular fragment X–H in which X is more electronegative than H, and an atom or a group of atoms in the same or a different molecule, in which there is evidence of bond formation [28].

This definition goes far beyond the traditional HB definition usually found in common textbooks, in which ones where HBs are more closed to interactions of H with F, N or O.

The IUPAC also provides a list of criteria used to characterize hydrogen bonds, the list of criteria is based in theoretical and experimental knowledge and evidence. Some of those criteria are [28]:

1. The forces involved in the formation of a hydrogen bond include those of an electrostatic origin, those arising from charge transfer between the donor and acceptor leading to partial covalent bond formation between H and Y, and those originating from dispersion.
2. The $X–H \cdots Y$ angle is usually linear (180°) and the closer the angle is to 180°, the stronger is the hydrogen bond and the shorter is the $H \cdots Y$ distance.
3. The Gibbs energy of formation for the hydrogen bond should be greater than the thermal energy of the system for the hydrogen bond to be detected experimentally.

1.3 Cooperativity and Anticooperativity of HB



(a) Homodromic case. **(b)** Cooperative and anticooperative effects.

Figure 1.2: Cooperative and anticooperative effects. In green the strongest HB (cooperative), in blue the homodromic interactions and in red the weakest interactions (anticooperative).

The complexity of the HB lattice in water clusters comes from: *i*) the water capacity to be donor and acceptor (even at the same time), *ii*) the HBs encompass a broad distribution of forces and directions. Then, in the three-dimensional real lattice there lie a big variety of angles and distances for HB interactions [29, 16].

The cooperative and anticooperative effects found in water clusters are one of the main phenomena characterizing HBs, which can be found inside interaction lattices, as is shown in Figure 1.2.

Cooperative effects can be qualitatively rationalized in terms of the acid-base behavior of each monomer, since the donor acid character increases when the oxygen becomes protonated while its basic character increase when the OH group gives its proton away [30].

In Figure 1.2a a cyclic homodromic pentamer is shown *i. e.*, all the water molecules are accepting and giving a proton. While cooperative and anticooperative effects are shown in in Figure 1.2b, for the cooperative case we need to note how *i*) the HB donor (left molecule) is accepting two HBs, having a charge bereft, charge that can be recover by donating a HB, and *ii*) the HB acceptor (right molecule) is donating two HB, being overcharged, charge that can be easily transferred by accepting a HB.

In contrast, in the same system we will see also anticooperative effects, for that we should thought the last two points trough the other four HB interactions that the system has, where there are *i*) a HB donor that is doubly charge deprived and *ii*) a HB acceptor being doubly overcharged. These effects at the same time results in an anticooperative phenomenon for the red highlighted HB in Figure 1.2b, not forgetting that the green one is the interaction that exhibits the cooperative phenomenon. Therefore, in a same system we can have both phenomena depending which HB is being analysed.

Work such as the ones carried out by Mó et al. [30] show how Pople basis sets as 6-31G* overestimate the cooperative effects at HF level, whereas the 6-311+G(d,p) basis yields values closer to those obtained with much larger basis. As we will see in our work we also use a triple-ζ basis set but Dunning instead of Pople, mainly because Dunning basis sets were developed for post Hartree Fock methods [31].

The capability to act as a donor or acceptor in water molecules also depends on the coordination of the molecule as shown in Guevara-Vela et al. [2], Castor-Villegas et al. [3] where the tricoordinated (double donor, acceptor) water molecule is the best acceptor and the tricoordinated (double acceptor, donor) is the best donor. Particularly, those two cases are in our water clusters, thus, we intend to forecast the same trend, a match between the ELF and electronic density topologies.

The above ideas are intended to be the cornerstone for this thesis, and through a quick overview of the theory behind the quantum mechanical tools that we use, we pretend to know how we will deal the problems that arise in the realization of this thesis.

CHAPTER 2

OBJECTIVES

Several researches of HB in water clusters have been proposed, one of those is the description of the HB interactions between water molecules by the ELF.

The principal objective of this thesis is the study of HB interaction through an IQA analysis of the ELF, with the particularity hypothesis that the ELF can give us enough information necessary to understand the HB in water clusters. In particular, to improve on previous knowledge published in the scientific literature on IQA partitioning of ELF and water clusters, the next points are searched

1. Describe the HB by an ELF analysis and if possible in different ways.
2. Analyse the non-covalent interactions and how those interactions are related with the ELF.
3. Analyse how the exchange-correlation and classical contributions are in HB interactions.
4. A computational goal is to compute all systems with PROMELF code [4], since researchers how have already used the code have had problems with "big" number (more than 300) of Gaussian primitive functions.

CHAPTER 3

METHODS

In this chapter we will concentrate on the main theoretical bases needed for the computation of physical chemistry methods used on this work. Starting with the Variational Principle and ending with ELF and IQA, going through DFT and Hartree-Fock.

Also, with this chapter we purport to have a general idea about the theory and postulates taken into account for the results and conclusions in this thesis. Additionally, we will also give details of computational details.

3.1 Quantum Mechanics Foundations

> "*I think I can safely say that nobody understands quantum mechanics*".
>
> -Richard Feynman

One of the cornerstones of the current physics and one of the biggest (maybe the biggest until now) paradigm shift for science is Quantum Mechanics. Some sources say that William Thomson, 1st Baron Kelvin, never said "There is nothing new to be discovered in physics now. All that remains is more and more precise measurement", and that is just a misattributed quote. Whether that quote was said by Kelvin or not, fortunately the point of the quote is not true.

Now we know that even the most powerful mathematical model of universe that we have, the Standard Model of Particle Physics, cannot predict all the phenomena that mankind has measured. And paradoxically, for people outside of science, the things we cannot predict are what is really interesting for science.

The scientific community thought that Newton made a mistake in describing light as a particle, since Young's interference experiment showed the wave nature of light. However, Einstein came with Plank's ideas [32] to say that they both had the correct answer at the same time. Nowadays we know that is not exactly a duality between waves and particles, but that idea is really helpful since our brains cannot understand quantum events at all, we can only imagine them with classic mechanics.

One of the first steps of Quantum Mechanics (as a new theory with its own mathematical model) was the Schrödinger Equation (Equation 3.1), postulated by Erwin Schrödinger in 1925, and published one year after Schrödinger [33]. It was reformulated two years after by Dirac for massive particles with $^1/_2$ spin, taking into consideration relativistic effects (Equation 3.2) [34], being one of the scant bridges between Quantum Physics and Relativity [35].

$$i\hbar\frac{\partial}{\partial t}|\Psi\rangle = \left[\frac{-\hbar^2}{2m}\nabla^2 + V(\mathbf{r},t)\right]|\Psi\rangle = \widehat{H}|\Psi\rangle \tag{3.1}$$

$$i\hbar\gamma^\mu\partial_\mu\psi - mc\psi = 0 \tag{3.2}$$

Where $i = \sqrt{-1}$, $\hbar$ is the reduced Plank's constant, γ^μ is the μ^{th} gamma matrix, and ∂_μ is the derivative over time and space as $\left(c^{-1}\frac{\partial}{\partial t}, \vec{\nabla}\right)$.

Another bridge between Quantum Physics and Relativity was given by Stephen Hawking [36], with his work about the radiation that occurs at the event horizon of black holes. This is because this phenomena involves the Heisenberg's uncertainty principle with the space-time singularities.

Since the mathematical formulation about the Hawking radiation other mathematical expressions have been developed, but it was the first expression with constants from Quantum and Relativity, equation expressed as:

$$T_H = \frac{\hbar c^3}{8\pi G M k_B} \tag{3.3}$$

Nevertheless, in Chemistry we are more interested in the Quantum Mechanics that does not depend on space-time singularities and for our case, the one that does not depend on time. That is why the Time-Independent Schrödinger Equation is actually useful, Equation 3.4:

$$\widehat{H}\Psi = E\Psi \tag{3.4}$$

where Ψ is the wavefunction of the system, a mathematical tool that does not have any physical meaning. However, it is really useful because Ψ is involved in the majority of Quantum Mechanics development.

That last equation can be solved analytically just for the hydrogen atom. Nevertheless, since it is an eigenvalue problem, there are several approaches developed for the resolution of the Schrödinger Equation.

3.1.1 Variational Method

As was described above, the Schrödinger Equation is an eigenvalue problem, then it is possible to use approaches created for eigenvalue problems, as the variational method. This method can give an approximate solution for eigenvalues for general form: $\widehat{O}\varphi = \omega\varphi$. It is common to use this method to compute the energy for atomic and molecular systems with N electrons.

Let $\widehat{A}$ be an hermitian operator, and suppose that there exists a finite set of exact solutions of the eigenvalue equation such that:

$$\widehat{A}|\phi_\alpha\rangle = \epsilon_\alpha|\phi_\alpha\rangle \qquad with: \ \epsilon_0 \leq \epsilon_1 \leq \ldots \leq \epsilon_\alpha \leq \ldots \tag{3.5}$$

If we suppose that the set ϵ_α is a set of discrete values, the eigenfunctions are orthonormal and if we apply $\langle\phi_\beta|$ by the left in Equation 3.5 we have:

$$\langle\phi_\beta|\widehat{A}|\phi_\alpha\rangle = \epsilon_\alpha\delta_{\alpha\beta} \tag{3.6}$$

Since the eigenfunctions of $\widehat{A}$ form a complete set, any function φ is a linear combination of ϕ_α if and only if φ satisfies the boundary conditions of the system [37],

$$|\varphi\rangle = \sum_\alpha |\phi_\alpha\rangle c_\alpha = \sum_\alpha |\phi_\alpha\rangle\langle\phi_\alpha|\varphi\rangle, \tag{3.7}$$

and

$$\langle\varphi| = \sum_\alpha c^\star_\alpha\langle\phi_\alpha| = \sum_\alpha\langle\varphi|\phi_\alpha\rangle\langle\phi_\alpha \tag{3.8}$$

The variational theorem enunciates that if in a system that *i*) has a time independent Hamiltonian, *ii*) the ground state eigenvalue is ε_0 and *iii*) the normalized function φ satisfies the boundary conditions, then:

$$\langle\varphi|\widehat{H}|\varphi\rangle \geq \varepsilon_0 \tag{3.9}$$

The minimization of the electronic energy from a wavefunction is the starting point of the variational method. Optimizing the coefficients of the expansion, we obtain the ground wavefunction.

3.1.2 Hartree-Fock Formalism

One of the first ideas developed to obtain an approached solution for Quantum Mechanics problems of many electrons was worked out independently by Douglas Hartree and Vladimir Fock. The first main assumption in the approach is that every electron interacts with all the other electrons, as if it were interacting with an electronic density, and not as a sum of contributions of two-body interactions. Under this assumption, the equation does not depend anymore on $3(N-1)$ spacial coordinates of the rest of electrons, but only on the distance r. The idea is called Central Field Approximation, taking a spherical average, it can be expressed as:

$$V_1(r_1) = \frac{1}{4\pi}\int_0^{2\pi}\int_0^{\pi} V_1(\vec{r}_1)\sin\theta \mathrm{d}\theta \mathrm{d}\varphi \tag{3.10}$$

To approximate a polyelectronic system as a function of monoelectronic systems, it is necessary to take an orbital approximation (Hartree product), as shown in Equation 3.11. To guarantee the antisymmetry principle, we use a Slater determinant as described in Equation 3.12, and most commonly written in its compact form (Equation 3.13).

$$\Psi = \prod_{i=1}^{n} \chi_i(\vec{r_i}), \tag{3.11}$$

$$|\Psi_0\rangle = \frac{1}{\sqrt{N!}}\begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) & \cdots & \chi_N(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) & \cdots & \chi_N(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\mathbf{x}_N) & \chi_2(\mathbf{x}_N) & \cdots & \chi_N(\mathbf{x}_N) \end{vmatrix}, \tag{3.12}$$

$$|\Psi_0\rangle = |\chi_1\chi_2\cdots\chi_N\rangle, \tag{3.13}$$

where χ_n and $\mathbf{x}_\mathrm{n}$ represent a spin-orbital and spatial coordinates of each electron, respectively, $\frac{1}{\sqrt{N!}}$ is the normalization constant.

The energy of the HF system is expressed by Equation 3.14, and through the variational principle it is possible to get a better wavefunction, since it is the one that provides the lowest energy, but it depends on the selection of the spin-orbitals.

$$E_0 = \langle\Psi_0|\widehat{H}|\Psi_0\rangle \tag{3.14}$$

The minimization of the energy in Equation 3.14 in addition to the restriction of the spin-orbitals orthonormalized $\langle\phi_i|\phi_j\rangle = \delta_{ij}$ gives rise to the Hartree-Fock Equation,

$$\widehat{F}\chi_i(\mathbf{x}_i) = \varepsilon_i\chi_i(\mathbf{x}_i), \tag{3.15}$$

where $\widehat{F}$ is the Fock operator and ε_i is the energy of the i^{th} spin-orbital χ_i. The electronic repulsion inside of the Fock operator is treated as an average, expressed as:

$$\widehat{F}(i) = \widehat{h}(i) + \sum_{b=1}^{Ne}[\hat{J}_b(i) - \hat{K}_b(i)], \tag{3.16}$$

where $\widehat{h}(i)$ is the sum of the operators for the kinetic energy and the attraction due to nuclei, the operators $\hat{J}_b$ and $\hat{K}_b$ are the Coulomb operator (electrostatic) and the exchange operator (without classic interpretation, since it is an antisymmetry consequence), respectively,

$$\widehat{h}(i) = -\frac{1}{2}\nabla_i^2 - \sum_{A=1}^{N}\frac{Z_A}{r_{iA}}, \quad \hat{J}_b(1) = \langle\phi_b(2)|r_{12}^{-1}|\phi_b(2)\rangle, \quad \hat{K}_b(1) = \langle\phi_b(2)|r_{12}^{-1}|\phi_a(2)\rangle, \tag{3.17}$$

The operators $\hat{J}$ and $\hat{K}$ are part of the bi-electronic term and are usually used also as the Coulomb and Exchange integrals, as follows:

$$J_{ij} \equiv \int \frac{\phi_i^\star(i)\phi_j^\star(j)\phi_i(i)\phi_j(j)}{r_{ij}} d^3\tau_i d^3\tau_j = \int \frac{\rho_i(i)\rho_j(j)}{r_{ij}} d^3\tau_i d^3\tau_j, \tag{3.18}$$

$$K_{ij} \equiv \int \frac{\phi_i^\star(i)\phi_j^\star(j)\phi_i(j)\phi_j(i)}{r_{ij}} d^3\tau_i d^3\tau_j, \tag{3.19}$$

also written as:

$$J_{ij} = \langle ij|ij\rangle = (ii|jj) \tag{3.20}$$

$$K_{ij} = \langle ij|ji\rangle = (ij|ji) \tag{3.21}$$

With this it is possible to rewrite the Fock Equation as in Equation 3.22, and it should be solved as a self-consistent problem, *i. e.* the solutions of the Fock Equation are obtained by an iterative process. Hence, it is necessary to start from an initial spin-orbital set, from which the Fock operator is built and determine the eigenfunctions of $\widehat{F}$, with which the Fock operator is rebuilt until the functions with which $\widehat{F}$ is constructed and its eigenfunctions are as close to the predetermined threshold as wanted. Equation written as:

$$\left(\widehat{h}(i) + \sum_{b}^{N_{occ}} [\hat{J}_b(i) - \hat{K}_b(i)]\right) \chi_a(i) = \varepsilon_a \chi_a(i) \qquad \forall a \in (1, N) \tag{3.22}$$

where N_{occ} means about the occupied spin-orbitals and N all spin-orbitals in the system (occupied and virtual).

This approach is important for chemical systems, not only because it provides the energy and the wavefunction of the system, but also because it is a very good starting point for post-HF approaches.

The Hartree-Fock Equations are not linear, they are also integro-differential equations so it is complicated to solve them. Thus, other methods are used, as proposed by Roothaan in 1951 [38] where the HF orbitals are linear combinations of known functions, basis functions [39]. This approximation is known as the SCF method (Self Consistent Field). It is based on using a set of basis functions to represent the searched spin-orbitals, where the basis is normalized, but not necessarily orthogonal. Therefore, it is possible to obtain a Linear Combination of Atomic Orbitals (LCAO) with k known basis functions as shown in the following equation:

$$\psi_i = \sum_{\nu}^{k} C_{\nu i} \phi_\nu, \tag{3.23}$$

where ϕ_ν represent the basis set functions, and $C_{\nu i}$ are the coefficients of each spin orbital. For a complete set of functions we would reach the exact solution.

But how good is Hartree-Fock? Comparing the values of a system that has an analytical solution and how far it is from the value obtained by HF approximation, we can have an idea to answer that question, as Moshinsky shows in 40. The problem of two particles with spin 1/2 in an harmonic oscillator common potential interacting through harmonic oscillator forces (in atomic units) is represented by the following Hamiltonian:

$$\widehat{H} = \frac{1}{2}[p_1^2 + r_1^2] + \frac{1}{2}[p_2^2 + r_2^2] + \kappa \left[\frac{1}{\sqrt{2}(r_1 - r_2)} \right]^2 \tag{3.24}$$

where r_1, r_2 are the coordinates of the two particles and p_1, p_2 their corresponding momenta. The strength of the interaction is given by the parameter κ. Thus, the energy expressions of the system analytically and at HF level are:

$$E = \frac{3}{2}\left[1 + \sqrt{1 + 2\kappa}\right] \qquad E_{HF} = 3\sqrt{1 + \kappa} \tag{3.25}$$

with the wavefunctions, respectively:

$$\psi = \pi^{-3/2}(2\kappa + 1)^{3/8} e^{-\frac{1}{2}R^2} e^{-\frac{1}{2}(2\kappa+1)^{1/2} r^2} \tag{3.26}$$

$$\psi_{HF} = \pi^{-3/2}(\kappa + 1)^{3/4} e^{-1/2(\kappa+1)^{1/2}(r^2+R^2)}$$

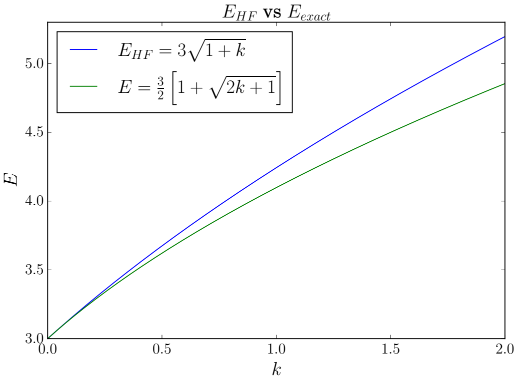


Figure 3.1: Graphical comparison between the energy computed by HF and the analytic solution for the same system [40].

In Figure 3.1 it is possible to see how the analytic solution and the Hartree Fock approach are close at small κ values. For the energy it is possible obtain 95 % of the exact energy, but just the 65 % for the overlap. In Figure 3.2 it is possible to see how the HF wavefunction moves away from the exact solution as κ increases.

Therefore, using HF for quantum chemistry can be a cheap and meaningful way in computational terms, functional for small systems with low correlation, as it is shown with small κ values in the previous system, *e. g.* the optimization of the equilibrium distance for H_2 or CH_4 [41].

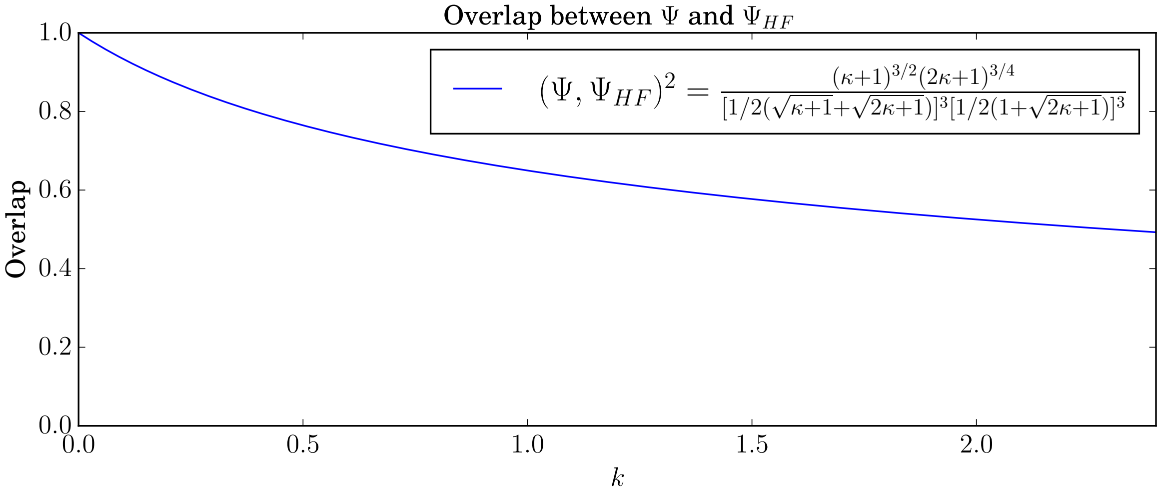


Figure 3.2: Overlap as a function of parameter k.

In contrast, HF fails for dissociation processes where the total spin value is not conserved as the nuclear coordinates change [42]. Some other problems that HF has are: *i*) it does not respect the Pauli's exclusion postulate, *ii*) in Central Field Approximation (CFA) the spherical harmonics are not necessary eigenfunctions of the monoelectronic equation, *iii*) there is not an obvious way to improve the orbital approach, and *iv*) it does not consider correlation effects, which are not necessarily despicable in all cases.

3.2 Electronic Density

One of the most important terms to define in theoretical chemical physics is the electronic density $\rho(\vec{r})$, which for a system of two electrons with spin-spatial coordinates $\vec{x}_1$ and $\vec{x}_2$, is defined as: $|\Psi(\vec{x}_1, \vec{x}_2)|^2$ [43]. To compute the probability to find simultaneously the electron 1 in $d\vec{x}_1$ and 2 in $d\vec{x}_2$, it is necessary to integrate the density function over $d\omega_1 d\vec{x}_2$, where: $d\vec{x}_n = d\vec{r}_n d\omega_n$,

$$P(\vec{r}_1) = \int |\Psi(\vec{x}_1, \vec{x}_2)|^2 d\omega_1 d\vec{x}_2, \tag{3.27}$$

and, since the electrons are indistinguishable, we obtain the following expression:

$$\rho(\vec{r}) = 2\int |\Psi(\vec{x}_1, \vec{x}_2)|^2 d\omega_1 d\vec{x}_2, \tag{3.28}$$

Then, for a system with N electrons, the electronic density can be generalized as follows:

$$\rho(\vec{r}) = N\int |\Psi(\vec{x}_1, \vec{x}_2, \ldots, \vec{x}_N)|^2 d\omega_1 d\vec{x}_2 \ldots d\vec{x}_N, \tag{3.29}$$

such that:

$$\int \rho(\vec{r}) d\vec{r} = N, \tag{3.30}$$

In the case of a Slater Determinant (Hartree-Fock), it is possible to write the electronic density for a closed shell with spacial orbitals ψ_a as:

$$\rho(\vec{r}) = 2\sum_{a=1}^{N/2} |\psi_a(\vec{r})|^2 \tag{3.31}$$

For a system with N particles, it is possible to write an operator for the density $\hat{\rho}$ and then, get the expected value for the system wavefunction,

$$\hat{\rho} = \sum_{i}^{N} \delta(\hat{r}_i - \vec{r}_0), \tag{3.32}$$

then $\rho(\vec{r})$ is a expected value of a quantum mechanics operator, which can be written as:

$$\rho(\vec{r}) = \int \Psi^\star(\vec{x}_1, \ldots, \vec{x}_N) \sum_{i}^{N} \delta(\hat{r}_i - \vec{r}_0) \Psi(\vec{x}_1, \ldots, \vec{x}_N) d\vec{x}_1 \ldots d\vec{x}_N \tag{3.33}$$

The value of the electronic density is very important, since it is a value that can be obtained from experimental data. The experiments from which we can obtain $\rho(\vec{r})$ information are the X-Ray diffraction or neutron diffraction [44, 45]. Thus, we can compare the theoretical values with experimental data, and have an idea of how good are the theoretical considerations for the computation.

However, it is also possible to establish a density function for an electron couple, also called pair density, such that:

$$\rho_2(\vec{r_1}, \vec{r_2}) = N(N-1) \int |\Psi(\vec{x}_1, \vec{x}_2, \ldots, \vec{x}_N)|^2 d\omega_1 d\omega_2 d\vec{x}_3 \ldots d\vec{x}_N, \tag{3.34}$$

where $\rho_2(\vec{r}_1, \vec{r}_2)N^{-1}(N-1)^{-1}$ determines the probability of simultaneously finding two electrons per volume centered at positions $\vec{r_1}$ and $\vec{r_2}$, commonly expressed by a sum which involves independent pairs terms and correlations, $\rho_2(\vec{r}_1, \vec{r}_2) = \rho(\vec{r}_1)\rho(\vec{r}_2) + \rho_2^{xc}(\vec{r}_2, \vec{r}_1)$.

The relevance of the electron and the pair densities (Equations 3.29 and 3.34, respectively) comes from the fact that the energy of the system within the Born-Oppenheimer approximation and in the absence of external fields can be expressed in terms of these two densities:

$$\begin{aligned} E = &-\frac{1}{2}\int \nabla^2 \rho_1(\vec{r}_1, \vec{r}_1')\Big|_{\vec{r}_1' \to \vec{r}_1} d\vec{r}_1 - \sum_A \int \frac{Z_A \rho_1(\vec{r}_1)}{r_{1A}} d\vec{r}_1 + \sum_{A \neq B} \frac{Z_A Z_B}{r_{AB}} \\ &+ \frac{1}{2}\int\int \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 - \frac{1}{2}\int\int \frac{\rho_2^{xc}(\vec{r}_1, \vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 \\ &= T + V_{ne} + V_{nn} + V_{ee} + V_{xc} \end{aligned} \tag{3.35}$$

where the first term is the kinetic energy, the second and the third terms are the nucleus-electron and nucleus-nucleus energy from Born-Oppenheimer approximation. Then the electron-electron repulsion is computed by the product of densities. Finally, the last term, the pair density, it is used to compute the exchange-correlation phenomenon. Subtracting the product between $\rho(\vec{r_1})$ and $\rho(\vec{r_2})$ from the pair density we have the information of the exchange-correlation phenomenon, since this term contains all the information about the indistinguishability of electrons and how one of the electrons is conditioned by the other one.

In practice, Equation 3.35 for a electronic structure method requires to express the density distribution as a function of the molecular orbital basis, ϕ_i,

$$\rho_1(\vec{r}) = \sum_{ij} D_{ij}\phi_i(\vec{r})\phi_j(\vec{r}), \tag{3.36}$$

$$\rho_2(\vec{r}_1, \vec{r}_2) = \sum_{ijkl} d_{ijkl}\phi_i(\vec{r}_1)\phi_j(\vec{r}_1)\phi_k(\vec{r}_2)\phi_l(\vec{r}_2), \tag{3.37}$$

where D_{ij} and d_{ijkl} are the matrix elements of the first and second order density matrix.

3.2.1 Density matrix

We know that the expected value for any operator can be obtained as:

$$\begin{aligned}\langle\widehat{Q}\rangle &= \int \Psi^\star(x_1, x_2, \ldots, x_n)\widehat{Q}\Psi(x_1, x_2, \ldots, x_n)dx_1 \ldots dx_n \\ &= \int \widehat{Q}\Psi(x_1, x_2, \ldots, x_n)\Psi^\star(x'_1, x'_2, \ldots, x'_n)dx_1 \ldots dx_n,\end{aligned} \tag{3.38}$$

with emphasis on the fact that the operator does not act for the primed variables.

If we have an operator that involves m variables, with $m \leq n$, we can write:

$$\begin{aligned}\langle\widehat{Q}\rangle &= \int \widehat{Q}\Psi(x_1, \ldots, x_m, x_{m+1}, \ldots, x_n)\Psi^\star(x_1, \ldots, x_m, x_{m+1}, \ldots, x_n)dx_1 \ldots dx_n \\ &= \int dx_1 \ldots dx_m\widehat{Q} \int \Psi(x_1, \ldots, x_m, x_{m+1}, \ldots, x_n)\Psi^\star(x_1, \ldots, x_m, x_{m+1}, \ldots, x_n)dx_{m+1} \ldots dx_n \\ &= \int dx_1 \ldots dx_m\widehat{Q}(x_1, \ldots, x_m)F_m(x_1, \ldots, x_m; x'_1, \ldots, x'_m),\end{aligned} \tag{3.39}$$

with:

$$F_m(x_1, \ldots, x_m; x'_1, \ldots, x'_m) = \int dx_{m+1} \ldots dx_n\Psi(x_1, \ldots, x_m, x_{m+1}, \ldots, x_n)\Psi^\star(x'_1, \ldots, x'_m, x'_{m+1}, \ldots, x'_n) \tag{3.40}$$

The F function can be related to the density matrix Γ at order m defined by:

$$\Gamma_m(x_1, \ldots, x_m; x'_1, \ldots, x'_m) = \binom{n}{m} \int dx_{m+1}dx_n\Psi^\star(x'_1, \ldots, x'_m, x'_{m+1}, \ldots, x'_n)\Psi(x_1, \ldots, x_n), \tag{3.41}$$

where $\binom{n}{m}$ are the combinations of n elements taken in m

$$\binom{n}{m} = \frac{n!}{m!(n-m)!} \tag{3.42}$$

There is a hierarchy between the density matrix according to their order,

$$\begin{aligned}\Gamma_m(x_1,\ldots,x_m;x_1',\ldots,x_m') &= \frac{\binom{n}{m}}{\binom{n}{m+1}}\int dx_{m+1}\Gamma_{m+1}(1,\ldots,m,m+1;1',\ldots,m',(m+1)')\\ &= \frac{m+1}{n-m}\int dx_{m+1}\Gamma_{m+1}(1,\ldots,m,m+1;1',\ldots,m',(m+1)')\end{aligned} \tag{3.43}$$

Since in quantum chemistry the operators are mono- or bi-electronic, the density matrices with useful information are the first and second order density matrices. There are two normalization criteria, $\frac{n(n-1)}{2}$ or $n(n-1)$, exposed by Löwdin and McWeeny respectively [46, 47],

$$\Gamma_1(x_1;x_1') = n\int \Psi^\star(1',2',\ldots,n')\Psi(1,2,\ldots,n)dx_2\ldots dx_n \tag{3.44}$$

$$\Gamma_2(x_1,x_2;x_1',x_2') = \frac{n(n-1)}{2}\int \Psi^\star(1',2',\ldots,n')\Psi(1,2,\ldots,n)dx_3\ldots dx_n \tag{3.45}$$

For many applications it is convenient to work with the first order density matrix, also called Fock-Dirac (Equation 3.44), and when it is integrated with respect to the spin coordinate it gives the first order reduced matrix,

$$\rho_1(r_1,r_1') = \int \Gamma_1(x_1;x_1') \tag{3.46}$$

Unlike the density functions, the matrix elements have no physical meaning, except for the diagonal ones, which in the case of the first order reduced matrix coincides with the electronic density.

It is important to highlight that the sum of the elements of the first order density matrix, which is an integral because of the continuous nature of the matrix indices, is equal to the total number of the electrons of the system.

Hence, many properties of the polyelectronic systems, and particularly the energy, can be expressed as a function of the first order density matrix and bi-electronic density.

3.3 Density Functional Theory

Before starting with the Density Functional Theory,it would be helpful to know about functionals, a term that has many definitions. For theoretical physics and chemistry the functionals are really useful, the main idea is that the functional does not depend on a scalar, vector, matrix or tensor at any order, but on a function; and it renders a number.

This idea is very useful to explore concepts such as the functional derivative, useful in Lagrange mechanics, or the functional integrals which are the central idea behind the path integrals exposed by Richard Feynman.

The three most common definitions used to describe a functional are [48]:

- In linear algebra, it makes reference to a linear mapping from a vector space V into its field of scalars, that is, an element of the dual space V^*.
- In functional analysis and related fields, it refers more generally to a mapping from a space X into the real or complex numbers. In functional analysis, the term linear functional is a synonym of linear form; that is, it is a scalar-valued linear map. Depending on the author, such mappings may or may not be assumed to be linear, or to be defined on the whole space.
- In computer science, it is synonymous of higher-order functions, that is, functions that take functions as arguments or return them.

Clarified the functional term, we can start with a brief summary of Density Functional Theory, which is one of the most important theories used in theoretical physical chemistry. Where the Hohenberg and Kohn [49] and Kohn and Sham [50] papers are among the most cited papers until now, which will be covered in Sections 3.3.1 and 3.3.2.

It is worth noting that it is a variational method where the functional of the electronic energy is minimized with respect of the electronic density. This is a really important step, because we are not using anymore the wavefunction *per se*, which leads to some computational benefits to solve big systems.

The electronic density is a scalar magnitude easier to compute because it depends just on three spacial variables, unlike the wavefunction which depends on $3N$ variables. However, except for the easiest cases, DFT has the inconvenience that although although there exists an exact functional that provides the exact energy of the system, its form is unknown.

This way of understanding the Quantum Mechanics is a clear exhibition of the Copenhagen interpretation. One of the principal drawbacks of DFT is that even being a exact theory, it can be only applied approximately, because of this there is not a systematic way of knowing how close the result is to the exact value.

Additionally, the exchange interaction is not correctly treated, thus the exchange-correlation energy can be very different depending of how the calculation is approached.

Due to the above and some other perspectives, there is a scientific community division, between defenders and detractors. On the one hand, defenders claim that the results are really good for the computational cost and it is a good way to approach big systems; on the other hand, the detractors argue that the results are not as reliable as a classical *ab initio* treatment.

Historically, the first approaches to obtain information of a system using the electronic density started in 1927 with Llewellyn Hilleth Thomas and Enrico Fermi works [51, 52]. The main idea is to take the kinetic energy in terms of the nucleus-electron and electron-electron contributions, purely treated as classical interactions, in a uniform electronic gas. Let a fictitious system be with a constant electronic density:

$$T_{\mathrm{TF}}[\rho(\vec{r})] = \frac{3}{10}(3\pi^2)^{(2/3)} \int \rho^{(5/3)}(\vec{r}) d\vec{r} \tag{3.47}$$

Combining T_{HF} with the above mentioned contributions, we obtain an expression for the Thomas-Fermi atomic energy. This approximation, shown in Equation 3.48, works quite well for alkaline metals and moderately well for alkaline-earth metals:

$$E_{\mathrm{TF}}[\rho(\vec{r})] = \frac{3}{10}(3\pi^2)^{(2/3)} \int \rho^{(5/3)}(\vec{r}) d\vec{r} - Z \int \frac{\rho(\vec{r})}{r} d\vec{r} + \frac{1}{2} \int \int \frac{\rho(\vec{r_1})\rho(\vec{r_2})}{r_{12}} d\vec{r_1} d\vec{r_2} \tag{3.48}$$

This way of approaching quantum mechanical problems became significantly important in 1964 when Hohenberg and Kohn published their theorems [49]. More specifically *i*) the energy is a functional of the density and *ii*) the density of a system minimizes the functional.

Another big step in DFT was published by Kohn and Sham one year after [50], and it says that it is possible to write an equation for orbitals of a particle, from which the density can be obtained.

Nowadays, this method is widely used; however, in the early days it was used more in solid physics, since it was not considered a method accurate enough to be applied to chemistry. Although if originally DFT did not contemplate temporal dependency, it was introduced using relativistic quantum mechanics, being denoted as TDDFT (Time-dependent Density Functional Theory).

In 1984, a generalization of the Hohenberg-Kohn theorems was published, carried out by Runge and Gross for the case of the time dependency. It states that there is a one-to-one relationship between the time dependent density $\rho(\vec{r}, t)$ and the external potential of a body $v_{ext}(\vec{r}, t)$ to an initial state [53]. Unlike DFT, there is not a general minimization principle in time dependent quantum mechanics, therefore its proof is more complicated.

3.3.1 Hohenberg-Kohn Theorems

Theorem 1 [49]

The energy, and therefore, the rest of the system properties, are unequivocally determined by the electronic density. If two systems with N particles are in external fields $v_1(\vec{r})$ and $v_2(\vec{r})$, with the same electronic density at the ground state $\rho(\vec{r})$, the difference between $v_1(\vec{r})$ and $v_2(\vec{r})$ is necessarily a constant. Therefore, there cannot be two potentials to describe the same ground state.

Corollary: the potential and all system properties are uniquely determined through the density of the fundamental state, including the many-body wavefunction of the state. Particularly, the HK functional is defined as $F[\rho] = T[\rho] + U[\rho]$ (universal density functional), which does not strictly depend on an external potential.

The value of the ground state of any observable is a unique function of the exact electronic density of the ground state given by:

$$\langle \psi | \widehat{A} | \psi \rangle = A[\rho_0(r)] \tag{3.49}$$

Theorem 2

The functional that gives the ground state energy gives the lowest energy, if and only if, the density that gives the functional is the true density of the ground state. *i. e.,* the energy obtained from the Hamiltonian is the absolute minimum when the electron density of the ground state is used.

For any potential $v_{ext}(\vec{r})$ and natural N, the density function $F[\rho]$ exists as:

$$E_{v,N}[\rho] = F[\rho] + \int v_{ext}(\vec{r})\rho(\vec{r})d^3r, \tag{3.50}$$

and the minimum value is obtained in the ground state density for N electrons with the potential $v_{ext}(\vec{r})$. The minimum value of $E_{v,N}[\rho]$ is then the energy of the ground state of the system.

The second theorem establishes that the exact value of the energy is a minimum value of the functional, *i. e.*, we have an inferior limit for the calculation. Thus, there is a variational principle for the energy,

$$E_0 \leq E[\rho] = T[\rho] + V_{Ne}[\rho] + V_{ee}[\rho] \tag{3.51}$$

3.3.2 Kohn-Sham Approximation

Kohn and Sham proposed a new approximation to solve the problem of many electrons based on the HK theorems. The total energy of the external potential functional $v_{ext}(\vec{r})$ can be described by:

$$E[\rho(\vec{r})] = T[\rho(\vec{r})] + \int v_{ext}(\vec{r})\rho(\vec{r})d^3r + V_{ee}[\rho(\vec{r})] \tag{3.52}$$

with:

$$V_{ee}[\rho(\vec{r})] = \frac{1}{2}\int\int \frac{\rho(\vec{r})\rho(\acute{r})}{|\vec{r}-\acute{r}|}d^3rd^3\acute{r} + E_{xc}[\rho(\vec{r})] \tag{3.53}$$

The first term of Equation 3.52 is the kinetic energy $T[\rho(\vec{r})]$, the second one is the external potential given by the nuclei arrangement, and the last one is the classic and non-classical contributions (exchange correlation behind of the mean field theory of electron-electron interaction). To solve the Kohn-Sham equations it is necessary to assume a reference system with non-interacting particles with the same density as the ground state interacting system. Thus, we can write the next equation for the system:

$$\left[-\sum_i \frac{1}{2}\nabla_i^2 + v_{eff}[\rho(\vec{r})]\right]|\psi_i\rangle = \epsilon_i|\psi_i\rangle, \tag{3.54}$$

where the subscript eff means effective, hence v_{eff} means effective potential in the non-interacting system. We thus have an expression for the kinetic energy of the non-interacting system:

$$T_{eff}[\rho(\vec{r})] = \sum_i \epsilon_i - V_{eff}[\rho(\vec{r})] \tag{3.55}$$

The new pseudo-kinetic-energy is used to compute the exchange-correlation functional of the energy $E_{xc}[\rho(\vec{r})]$ which is expressed as:

$$E_{xc}[\rho(\vec{r})] = T[\rho(\vec{r})] - T_{eff}[\rho(\vec{r})] + V_{ee}[\rho(\vec{r})] - J[\rho(\vec{r})] \tag{3.56}$$

Using *i*) the new exchange-correlation functional of the total energy of the system, *ii*) differentiating the new total non-interactive energy and the effective potential with respect to the electronic density $\rho(\vec{r})$, and *iii*) the Schrödinger Equation for an electron moving in a potential v_{eff}:

$$\left[-\frac{1}{2}\nabla^2 + v_{eff}[\rho(\vec{r})]\right]\psi_i(\vec{r}) = \epsilon_i\psi_i(\vec{r}) \tag{3.57}$$

We have the energy of the interacting system:

$$E[\rho] = \sum_i \epsilon_i - \frac{1}{2}\int\int \frac{\rho(\vec{r})\rho(\acute{r})}{|\vec{r}-\acute{r}|}d^3r d^3\acute{r} + E_{xc}[\rho(\vec{r})] - \int \frac{\delta E_{xc}[\rho(\vec{r})]}{\delta\rho(\vec{r})}\rho(\vec{r})d^3r \tag{3.58}$$

3.3.3 Exchange-Correlation Functionals

There are many types of functionals for exchange-correlation inside DFT and it is possible to classify them by the approximations that are used in their construction:

- **Local Density Approximation (LDA)**. In LDA the density is shaped as a local homogeneous electronic gas, with electronic density ρ. In this system, the electrons move in a distribution of positive charges, additionally, the gas is electrically neutral and with an infinite volume which contains an infinite number of non-interacting electrons [54].

  $E_{xc}^{LDA}[\rho] = \int \rho(r)\varepsilon_{xc}(\rho(r))dr$

  Taking the functional derivative of E_{xc}^{LDA} we obtain:

  $v_{xc}^{LDA} = \frac{\delta E_{xc}^{LDA}}{\delta\rho} = \varepsilon_{xc}(\rho(r)) + \rho\frac{\partial\varepsilon_{xc}(\rho(r))}{\partial\rho}$

  where ε_{xc} can be decomposed in the contributions of exchange and correlation, with the expression for ε_x as:

  $\varepsilon_x = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}\rho^{1/3}$

  Functionals developed in LDA approach have different ways to improve the results. The X$_\alpha$ method [55] has an empiric value α, The Local Spin Density Approximation (LSDA) [55] is used to spin polarized system through the employment two spin-densities (ρ_α, ρ_β).

  Unfortunately, there is no known analytical expression for the correlation energy (ε_{cor}). Nevertheless, some studies was developed with Quantum Monte-Carlo by Vosko, Wilk and Nussar, as published in the functional VWN [56]. Another way to approach the correlation problem was done by Perdew and Zunger, they used the values from Ceperley and Alder [57] to adjust an expression that fulfill the conditions at low and high densities in their functional PL [58].

- **Generalized-Gradient Approximation (GGA)**. In GGA approximation is aim to correct the density constant introducing the density gradient.

  $E_{xc}^{GGA}[\rho] = \int \rho(r) v_{xc}(\rho(r), \nabla\rho(r)) dr$

  As in LDA case, the energy E_{xc}^{GGA} can be decomposed in the exchange and correlation contributions.

  There are many ideas to insert the gradient, one of those was proposed by Becke, incorporating the concept of correlation hole for its formulation, Becke published sundry functionals, but one of the most famous is B88 [59]. While other GGA functionals were developed as an improvement of an previous GGA functional, as the mPW functional [60], where is improved the long-range behavior.

  The functional B88 is frequently accompanied by the correlation functional LYP [61], which is a correlation functional that considers the term of Weizsacker kinetic energy [62] to transform the Colle and Salvetti functional [63] (correlation for closed shells).

  Another popular functional in GGA approach is P86 developed with the idea of the natural separation between exchange and correlation, thus the density-gradient expansion of each is recovered in the slowly varying limit. Also the uniform-gas and inhomogeneity effects beyond the random phase approximation are built in [64]. The gradient dependent term is neglected for uniform densities, therefore, the functional recover the local form for uniform electron gases.

- **Meta-Generalized Gradient Approximation (meta-GGA)**. In meta-GGA the Laplacian of the density is also included, $\nabla^2\rho(r)$. This allows to obtain a better description of the system. In practice the kinetic energy density is used, where the sum is over the KS occupied orbitals.

  $\tau(r) = \sum_i^N \frac{1}{2} |\nabla\psi_i(r)|^2$

  $E_{xc}^{MGGA}[\rho] = \int \rho(r) v_{xc}(\rho(r), \nabla\rho(r), \tau(r)) dr$

  The kinetic energy density and the Laplacian are related by the external potential:

  $\tau(r) = \sum_i^N \frac{1}{2} \varepsilon_i |\psi_i(r)|^2 - v(r)\rho(r) + \frac{1}{2}\nabla^2\rho(r)$

The use of the Laplacian is computationally expensive, and for a long time the performance was not much improved. Some new functionals (*e. g.* SCAN [65]) have shown nevertheless an important improve over GGAs.

Two popular meta-GGA functionals are: *i*) the VSXC functional [66] which approach the meta-GGA through the density matrix expansion, and *ii*) the KCIS functional [67] which propose an accurate self-interaction-corrected correlation with a gap on the electron gas.

- **Hybrid Functionals**. These functionals include one part of the exact exchange energy at Hartree-Fock level, which is computed with the Kohn-Sham orbitals.
  $$E_x^{HF}[\theta_i] = -\sum_{i=1}^{N/2}\sum_{j=1}^{N/2}\frac{\theta_i^\star(r_1)\theta_j^\star(r_1)\theta_i(r_2)\theta_j(r_2)}{r_{12}}dr_1dr_2$$
  The most popular hybrid functional is B3LYP, it was built for the first time in 1994, combining Becke's three-parameter hybrid functional [68] with correlation functional LYP [61]. Following the next equation:
  $$E_{xc}^{B3LYP} = aE_x^{Slater} + (1-a)E_x^{HF} + bE_x^{Becke88} + cE_c^{LYP} + (1-c)E_c^{VWN},$$
  where a=0.80, b=0.72 and c=0.81 are empirical parameters adjusted to the ionization, enthalpy of atomization, proton affinity and atomic energies.

  Other examples of hybrid functionals are PBEh1PBE [69] and M06-2X [70].

In this work the M06-2X functional is used in the majority of calculations, which is a Hybrid Functional belonging to the functional series developed by Zhao and Truhlar at the University of Minnesota [70]. These functionals were developed taking empirical parameters, but still thinking in the free electron gas model.

The functional is a hybrid meta-GGA with high delocalization, containing 54 % of Hartree Fock exchange. Also it depends on three variables which are *i*) the spin density, *ii*) the reduced gradient of the density,

$$x_\sigma = \frac{|\nabla\rho_\sigma|}{\rho_\sigma^{4/3}},\ \sigma = \alpha, \beta, \tag{3.59}$$

and *iii*) the spin kinetic energy τ_σ.

The functional M062X includes terms based on the functional VSXC [66], which contains the variable z_σ and the functions γ and h, as well as an empiric constant C_F, defined as:

$$\begin{aligned} z_\sigma &= \frac{2\tau_\sigma}{\rho_\sigma^{5/3}} - C_F \\ C_F &= \frac{3}{5}\left(6\pi^2\right)^{2/3} \\ \gamma(x_\sigma, z_\sigma) &= 1 + \alpha(x_\sigma^2 + z_\sigma) \\ h(x_\sigma, z_\sigma) &= \left(\frac{d_0}{\gamma(x_\sigma, z_\sigma)} + \frac{d_1 x\sigma^2 + d_2 z_\sigma}{\gamma^2(x_\sigma, z_\sigma)} + \frac{d_3 x_\sigma^4 + d_4 x_\sigma^2 z_\sigma + d_5 z_\sigma^2}{\gamma^3(x_\sigma, z_\sigma)}\right) \end{aligned} \tag{3.60}$$

where α, $d_i (i = 0, ..., 5)$ are parameters adjusted to experimental data.

The exchange part of M062X came from a linear combination between M05 and VSXC [70].

$$E_X^{DFT} = \sum_\sigma \int \left(F_{X_\sigma}^{PBE}(\rho_\sigma, \nabla\rho_\sigma) f(w_\sigma) + \varepsilon_{X_\sigma}^{LSDA} h_X(x_\sigma, z_\sigma)\right) d\mathbf{r}, \tag{3.61}$$

where $F_{X_\sigma}^{PBE}(\rho_\sigma, \nabla\rho_\sigma)$ is the exchange energy density from PBE [70], $\varepsilon_{X_\sigma}^{LSDA}$ is the exchange energy per particle in the LSDA approximation, $f(w_\sigma)$ is a correction factor of the density of spin kinetic energy, and $h(x_\sigma, z_\sigma)$ was already defined in Equation 3.60. That last term is peculiar in M062X, since M062X takes the exchange part from M05, $h_X(x_\sigma, z_\sigma) = 0$ [70, 71].

The correlation part is composed of two terms, one with opposite spins $E_C^{\alpha\beta}$ and another one with parallel spins ($E_C^{\sigma\sigma}$), in where $h(x_\sigma, z_\sigma)$ is not zero as in the exchange part:

$$E_C^{\alpha\beta} = \int \varepsilon_{\alpha\beta}^{\text{GEH}} \left[g_{\alpha\beta}(x_\alpha, x_\beta) + h(x_{\alpha\beta}, z_{\alpha\beta})\right] d\mathbf{r} \tag{3.62}$$

$$E_C^{\sigma\sigma} = \int \varepsilon_{\sigma\sigma}^{\text{GEH}} \left[g_{\sigma\sigma}(x_\sigma) + h(x_\sigma, z_\sigma)\right] d\mathbf{r} \tag{3.63}$$

The functions $g_{\alpha\beta}$ and $g_{\sigma\sigma}$ in Equation 3.63 include empirical parameters, $h(x_{\alpha\beta}, z_{\alpha\beta})$ and $h(x_{\sigma}, z_{\sigma})$ are defined in Equation 3.60, D_{σ} is a auto-interaction correction factor, and $\varepsilon_{\alpha\beta}^{\mathrm{GEH}}$ and $\varepsilon_{\sigma\sigma}^{\mathrm{GEH}}$ are the correlation energies that depend on spin.

The total correlation energy in M062X is given by:

$$E_C^{DFT} = E_C^{\alpha\beta} + E_C^{\alpha\alpha} + E_C^{\beta\beta} \tag{3.64}$$

As mentioned before, M062X incorporates 54 % of Hartree-Fock exchange, therefore, the final expression for exchange-correlation energy at M062X is:

$$E_C^{\mathrm{M062X}} = \frac{54}{100} E_X^{\mathrm{HF}} + \left(1 - \frac{54}{100}\right) E_X^{DFT} + E_C^{DFT} \tag{3.65}$$

3.4 Topology

Before continuing with the theoretical background of this thesis, it is necessary to take a short mathematical parentheses on topology, since following topics are based on topology.

One of the awesome steps that the mathematicians made in the XIX century was the division of "*geometriam situs*" from geometry, giving rise to topology as a new branch of math.

Euler was the first to approach a geometry problem in which structural properties and not metrics were the key to find the solution [72]. Euler called that new branch as *geometriam situs*, nowadays called topology, name given by Johann Benedict Listing (Gauss's student) to mark the autonomy of topology from geometry [73].

Many applications of topology were developed with time. Graph theory can give optimized trajectories for flights, and is used in the version-control system git developed by Linus Torvalds. Knot theory provides a way to relate the knots at DNA and the knots in a rope. Hairy ball theorem in algebraic topology gives as a corollary that there will always be a windless place in any planet.

Currently, topology has a variety of results. One of them is the four colour theorem, which is a good story because it was one of the first times that the use of computers went beyond doing jobs like a huge calculator. The theorem says that any map with continuous regions can be coloured with the maximum of four colours avoiding any adjacent regions with the same colour [74]. We illustrate an example in Figure 3.3.

(a) Australia map coloured with four colours. **(b)** Australia map with its corresponding graph. **(c)** Graphic corresponding of the Australia map.

Figure 3.3: Example of the four colours theorem.

In 1976 Kenneth Appel and Wolfgang Haken proved the theorem by making 1936 maps that are part of any counterexample to the theorem, the work to obtain the 1936 maps was hard. However, the real problem was to prove that all that 1936 counterexamples could be coloured with four colours. That work was done by a IBM 370 [75] with about 1 000 computing hours. Of course at that time the proof had a lot of criticism because the computers "*have not mathematical rigor*".

Topology has applications not only in abstract mathematics. In 1874 Carl Schorlemmer [75] found the relationship between the number of isomers and the topological trees. Since isomers are different ways of arranging the same number of atoms, the number of isomers equals the number of trees with the number of vertices equal to the number of atoms.

Other applications of topology in science are:

- Quantum Hall Effect
- Topological Insulators
- Topological States

3.5 Quantum Theory of Atoms In Molecules

The Quantum Theory of Atoms In Molecules (QTAIM) gives useful information on molecular systems. This theory is based on the analysis of the topological properties of the electron density [76]. QTAIM offers several insights of covalent and non-covalent interaction nature, as the Hydrogen Bonding. This theory provides an approach that recovers important concepts borned in chemistry on which chemistry is based. As for example the definition of an atom inside a molecule, and moreover, functional groups, the fragment of a molecule or a molecule in a cluster can also be defined.

With QTAIM it is possible to define an atom in a molecule using the electron density, $\rho(\vec{r})$, which is a scalar field as we noted in Section 3.2, which can be obtained experimentally. Also, the chemical behaviour of many systems can be described through the electronic density [76, 77].

3.5.1 Topological properties of the electronic density

Topological properties of electron density can be examined in terms of critical points, as for example the saddle points in between maxima [76, 78, 77].

The critical points of any scalar field are given by the positions where the gradient is equal to $\vec{0}$:

$$\nabla\rho(\mathbf{r}_c) = \frac{\partial\rho(\mathbf{r_c})}{\partial x}\mathbf{i} + \frac{\partial\rho(\mathbf{r_c})}{\partial y}\mathbf{j} + \frac{\partial\rho(\mathbf{r_c})}{\partial z}\mathbf{k} = \mathbf{0}. \tag{3.66}$$

Given a critical point $(\mathbf{r_c})$ of a scalar field $\rho(\vec{r})$, the way to know if it is a local minimum, local maximum or a saddle point is via the second derivatives of the scalar field evaluated at the critical point. There are nine second derivatives of $\rho(\vec{r})$. Each one of the second derivatives can be fixed on a matrix arrangement, called Hessian matrix, when it is evaluated at a critical point is written as:

$$\mathbf{A}(\mathbf{r_c}) = \begin{pmatrix} \frac{\partial^2\rho(\mathbf{r})}{\partial x^2} & \frac{\partial^2\rho(\mathbf{r})}{\partial x\partial y} & \frac{\partial^2\rho(\mathbf{r})}{\partial x\partial z} \\ \frac{\partial^2\rho(\mathbf{r})}{\partial y\partial x} & \frac{\partial^2\rho(\mathbf{r})}{\partial y^2} & \frac{\partial^2\rho(\mathbf{r})}{\partial y\partial z} \\ \frac{\partial^2\rho(\mathbf{r})}{\partial z\partial x} & \frac{\partial^2\rho(\mathbf{r})}{\partial z\partial y} & \frac{\partial^2\rho(\mathbf{r})}{\partial z^2} \end{pmatrix}_{\mathbf{r}=\mathbf{r_c}} \tag{3.67}$$

The Hessian matrix is real and symmetric, thus it is diagonalizable. This diagonalization is equivalent to rotating the system, $(x, y, z) \rightarrow (x', y', z')$, taking as new axes the primed system, which corresponds to the principal axes of the curvature at the critical point, denoting the new matrix as $\mathbf{\Lambda}(\mathbf{r_c})$,

$$\mathbf{\Lambda}(\mathbf{r_c}) = \begin{pmatrix} \frac{\partial^2\rho(\mathbf{r}')}{\partial x'^2} & 0 & 0 \\ 0 & \frac{\partial^2\rho(\mathbf{r}')}{\partial y'^2} & 0 \\ 0 & 0 & \frac{\partial^2\rho(\mathbf{r}')}{\partial z'^2} \end{pmatrix}_{\mathbf{r}'=\mathbf{r_c}} = \begin{pmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_3 \end{pmatrix}_{\mathbf{r}'=\mathbf{r_c}} \tag{3.68}$$

where λ_1, λ_2 and λ_3 are the eigenvalues of the Hessian matrix and correspond to the curvature of the density with respect to the primed axes.

The principal characteristics of the resulting critical points of the Hessian matrix analysis are summarized in Table 3.1.

Table 3.1: Topological description of the critical points (CP) more used at the analysis of the $\rho(\mathbf{r})$ topology. The range (ω) represents the number of nonzero eigenvalues and the signature (σ) the algebraic sum of the eigenvalues signs.

(ω, σ)	**CP**	**Description**	**Interpretation**
(3, −3)	NCP	All the curvatures are negatives and $\mathbf{r}_c$ is a local maximum of $\rho(\mathbf{r})$.	Nuclear position.
(3, −1)	BCP	Two negative curvatures and one positives.	In between two atoms attached by a bond.
(3, 1)	RCP	Two curvatures positives and one negative.	Within an atom cluster attached making a ring.
(3, 3)	CCP	All the curvatures are positives and $\mathbf{r}_c$ is a local minimum of $\rho(\mathbf{r})$.	Inside an atom cluster making a cage.

The definition of an atom inside a molecule in QTAIM is marked by the behaviour of the vector field $\nabla\rho(\vec{r})$ and particularly with its flux lines. The flux lines of $\nabla\rho(\vec{r})$ are trajectories $\sigma(t)$ given by the equation:

$$\sigma'(t) = \nabla\rho\left(\sigma(t)\right) \tag{3.69}$$

The nuclei, because of its charge, act as attractors for the flux lines $\sigma(t)$. The space region where all flux lines converges to a nucleus is known as atomic basin and corresponds to the chemical concept of an atom [76]. The atoms in QTAIM, or Bader atoms, are delimited by their flux lines of the vector field gradient of the electronic density that fulfill the zero flux condition:

$$\nabla\rho(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) = 0 \qquad \forall \mathbf{r} \in S(\Omega), \tag{3.70}$$

where Ω refers to the atomic basin, S refers to the surface that bounding Ω, and $\mathbf{n}(\mathbf{r})$ to the normal vector of the interatomic surface. Therefore, in QTAIM an atom can be understood as the union of a nucleus with its associated basin.

Summarizing, the spatial partition in disjoint Bader regions [76] is based on the gradient of the electronic density, $\nabla\rho(\mathbf{r})$, which leads to a vector field $\mathbf{F} : \mathbb{R}^n \to \mathbb{R}^n$ that can be characterized by flux lines, which are trajectories $\sigma(t) : \mathbb{R} \to \mathbb{R}^n$, defined by the equation 3.69.

As shown in Figure 3.4, the borders of the space regions known as atoms satisfy the zero condition flux 3.70 and in general, an analysis of maximum and minimum electronic density can be done with the values in Table 3.1.

3.5.2 Atom properties in molecules

The regions Ω defined in QTAIM are identified as atoms in chemistry, and it is provable that the postulates of quantum mechanics are fulfilled within these atomic basins [76]. Taking the zero flux condition, for an atom inside a molecule, we come to a variational definition of the properties that the subsystem has [80]. Starting from the borders, iden-

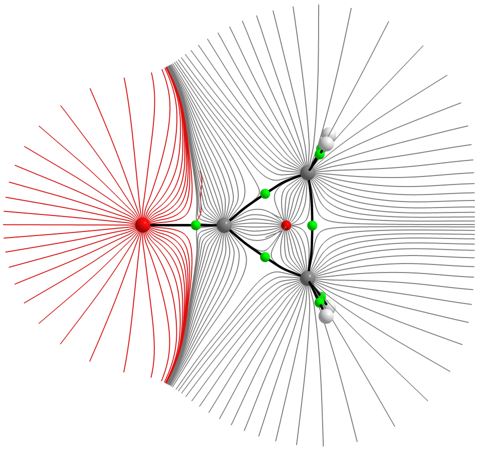


Figure 3.4: Flux lines $\nabla\rho(\mathbf{r})$ of the cyclopropanone molecule (C_3H_4O). These trajectories delimit regions that can be identified as atoms [79].

tified as interatomic surfaces, and the molecular structure, the molecular properties are defined as the addition of all atomic properties:

$$A = \sum_{\Omega} a_{\Omega}, \tag{3.71}$$

where A is the molecular property and a_{Ω} is the same property inside the basin Ω. This is based on the atomic variational principle, which states that if $\hat{A}$ is an operator equivalent to a sum of monoelectronic operators, $\hat{A} = \sum \hat{a}$, the its expected value is given by:

$$A(\Omega) \equiv \langle \widehat{A} \rangle_{\Omega} = \int_{\Omega} \int \cdots \int \int \cdots \int \left[\frac{N}{2} \Psi_{el}^{\star} \hat{a} \Psi_{el} + (\hat{a}\Psi_{el})^{\star} \Psi_{el} \right] d\omega_1 \ldots d\omega_N d\mathbf{r_2} \ldots d\mathbf{r}_N d\mathbf{r}_1. \tag{3.72}$$

This implies that an atomic property is determined across the integration of an associated operator density associated with that property,

$$\rho_A(\mathbf{r}) = \frac{N}{2} \int \cdots \int \int \cdots \int [\Psi_{el}^{\star} \hat{a} \Psi_{el} + (\hat{a}\Psi_{el})^{\star} \Psi_{el}] d\omega_1 d\omega_2 \ldots d\omega_N d\mathbf{r_2} \ldots d\mathbf{r}_N, \tag{3.73}$$

and

$$A(\Omega) = \int_{\Omega} \rho_A(\mathbf{r}) \mathrm{d}\mathbf{r}. \tag{3.74}$$

3.6 Interacting Quantum Atoms

Interacting Quantum Atoms, IQA, allows the electronic energy partition, using mainly the density matrix [81, 47]. The first order reduced matrix $\rho_1(\mathbf{r}_1;\mathbf{r}_1')$ and the pair-density $\rho_2(\mathbf{r}_1,\mathbf{r}_2)$ allow compute the non-relativistic electronic energy within the Born-Oppenheimer approximation, as was shown in Equation 3.35,

$$E_{\text{elec}} = \frac{1}{2}\sum_{A\neq B}\frac{Z_A Z_B}{r_{AB}} + \int \widehat{h}\rho_1(\mathbf{r}_1;\mathbf{r}_1')\mathrm{d}\mathbf{r}_1 + \frac{1}{2}\int\int\frac{\rho_2(\mathbf{r}_1,\mathbf{r}_2)}{r_{12}}\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2, \tag{3.75}$$

$$E_{\text{elec}} = V_{\text{nn}} + \langle\widehat{T} + \widehat{V}_{\text{ne}}\rangle + \langle\widehat{V}_{\text{ee}}\rangle. \tag{3.76}$$

The monoelectronic energy is a sum of the kinetic energy and the nucleus-electron attraction, *i. e.*, $\widehat{h} = \widehat{T} + \widehat{V}_{\text{ne}}$, the other three terms Z_X, $\widehat{V}_{\text{nn}}$ and $\widehat{V}_{\text{ee}}$ mean *i*)the atomic number of X, *ii*) the internuclear repulsion and *iii*) the electron-electron repulsion, respectively.

After a partition of the real space, as Bader proposed, and discussed in previous sections, in where every space region is delimited by the zero flux condition (Equation 3.70) contains only one nucleus, *i. e.*, the system has no non-nuclear attractor, then it is possible to rewrite the Equation 3.75 as:

$$\begin{aligned}
E_{\text{elec}} &= \frac{1}{2}\sum_{A\neq B}\frac{Z_A Z_B}{r_{AB}} - \frac{1}{2}\int\nabla^2\rho_1(\mathbf{r}_1;\mathbf{r}_1')\mathrm{d}\mathbf{r}_1 - \sum_A\int\frac{Z_A\rho(\mathbf{r}_1)}{r_{1A}}\mathrm{d}\mathbf{r}_1 + \frac{1}{2}\int\int\frac{\rho_2(\mathbf{r}_1,\mathbf{r}_2)}{r_{12}}\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2 \\
&= \frac{1}{2}\sum_{A\neq B}\frac{Z_A Z_B}{r_{AB}} - \frac{1}{2}\sum_A\int_A\nabla^2\rho_1(\mathbf{r}_1;\mathbf{r}_1')\mathrm{d}\mathbf{r}_1 - \sum_{AB}\int_B\frac{Z_A\rho(\mathbf{r}_1)}{r_{1A}}\mathrm{d}\mathbf{r}_1 + \frac{1}{2}\sum_{AB}\int_A\int_B\frac{\rho_2(\mathbf{r}_1,\mathbf{r}_2)}{r_{12}}\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2 \\
&= \frac{1}{2}\sum_{A\neq B}V_{\text{nn}}^{AB} + \sum_A T_A + \sum_A V_{\text{ne}}^{AA} + \sum_{A\neq B}V_{\text{ne}}^{AB} + \sum_A V_{\text{ee}}^{AA} + \frac{1}{2}\sum_{A\neq B}V_{\text{ee}}^{AB},
\end{aligned} \tag{3.77}$$

where the terms are given by:

$$V_{\text{nn}}^{AB} = \frac{Z_A Z_B}{r_{AB}}, \tag{3.78}$$

$$T_A = -\frac{1}{2}\int_A\nabla^2\rho_1(\mathbf{r}_1;\mathbf{r}_1')\mathrm{d}\mathbf{r}_1, \tag{3.79}$$

$$V_{\text{ne}}^{AB} = -Z_A\int_B\frac{\rho(\mathbf{r}_1)}{r_{1A}}\mathrm{d}\mathbf{r}_1, \tag{3.80}$$

$$V_{\text{ee}}^{AB} = \frac{2-\delta_{AB}}{2}\int_A\int_B\frac{\rho_2(\mathbf{r}_1,\mathbf{r}_2)}{r_{12}}\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2 \tag{3.81}$$

The IQA partition divides electronic energy into two main components: *i*) intra-atomic energy, which results from regrouping the terms:

$$E_{\text{net}}^{A} = T^{A} + V_{\text{ne}}^{AA} + V_{\text{ee}}^{AA}, \tag{3.82}$$

and *ii*) the interaction between atom-pairs energy, which can be obtained grouping the following terms:

$$E_{\text{int}}^{AB} = V_{\text{nn}}^{AB} + V_{\text{ne}}^{AB} + V_{\text{ne}}^{BA} + V_{\text{ee}}^{AB} \tag{3.83}$$

The addition of these two contributions (Equations 3.82 and 3.83), will result strictly in the total energy of the system,

$$E_{\text{elec}} = \sum_{A} E_{\text{net}}^{A} + \frac{1}{2}\sum_{A \neq B} E_{\text{int}}^{AB} \tag{3.84}$$

In the Equation 3.84 we can interpret E_{elec} as the addition of intra- and inter-atomic contributions. Additionally to the partition of electronic energy that IQA proposes, the definition of the internal energy of a fragment, or group of atoms, is of utmost importance for the development of this work, since the definition of the inner energy of a fragment, group of atoms, $\mathscr{G}$ is given by:

$$E_{\text{net}}^{\mathscr{G}} = \sum_{A \in \mathscr{G}} E_{\text{net}}^{A} + \frac{1}{2}\sum_{A \in \mathscr{G}} \sum_{\substack{B \in \mathscr{G} \\ B \neq A}} E_{\text{int}}^{AB} \tag{3.85}$$

Then the interaction energy between two groups is defined as:

$$E_{\text{int}}^{\mathscr{G}\mathscr{H}} = \sum_{A \in \mathscr{G}} \sum_{B \in \mathscr{H}} E_{\text{int}}^{AB} \tag{3.86}$$

It is possible to have an expression for the energy analogous to the Equation 3.84, since we are making groups of atoms, but in this case as a energy function of the groups that form the system and the interaction energies between them.

$$E_{\text{elec}} = \sum_{\mathscr{G}} E_{\text{net}}^{\mathscr{G}} + \frac{1}{2}\sum_{\mathscr{G} \neq \mathscr{H}} E_{\text{int}}^{\mathscr{G}\mathscr{H}} \tag{3.87}$$

The selection of atoms, and their interactions, which are in a fragment $\mathscr{G}$ as the atoms which make a molecule inside a molecular cluster give us a way to study the intermolecular interaction energy. And in that way, it allows a direct comparison with the non-covalent interaction and the changes that occur in the interactions when the fragment/molecule is in presence of another molecule/environment.

3.7 Electron Localization Function

The Electron Localization Function (ELF) kernel, χ_σ, can be interpreted as a measure of the surplus of local kinetic energy due to the Pauli Principle, in connection to the homogeneous electron gas kinetic energy density [82]. The ELF, $\eta(\vec{r})$, is mapped through a Lorentzian function 3.88, to a scale ranging from 0 (when $\chi_\sigma \to \infty$) to 1 (when $\chi_\sigma \to 0$).

$$\eta(\vec{r}) = \frac{1}{1+\chi_\sigma^2} \tag{3.88}$$

The gradient of this function, $\boldsymbol{\nabla}\eta$, is used to induce a topological partition which divides the space into non-overlapping regions (basins). Their properties can be determined by integrating the appropriate densities over their associated volume. Hence, if one is interested in, for example, in lone pairs populations, it suffices to integrate the electron density, ρ, over the corresponding region associated to the lone pair maximum [1].

The energies of the different topological basins can be computed with Interacting Quantum Atoms (IQA) energy decomposition scheme [81]. This approach provides a set of unique and rigorous energetic terms that additively recover the exact energy of the system. Unlike many topological analyses, this method is not only suitable for stationary points (*e.g.* equilibrium geometries), such as with virial related energy partitions, but also for non-equilibrium geometries. This feature was crucial for evaluating the energy terms along bond elongations in geometry scans. The energy terms are calculated by partitioning the first- and second-order density matrices with respect to the real space partitions, usually the QTAIM atomic basins, as in the Equation 3.84, rewritten as:

$$\begin{aligned} E &= \sum_A (T_A + V_{ee}^{AA} + V_{en}^{AA}) + \sum_{A>B} (V_{en}^{AB} + V_{ne}^{AB} + V_{nn}^{AB} + V_{ee}^{AB}) \\ &= \sum_A E_{\text{intra}}^A + \sum_{A>B} E_{\text{inter}}^{AB} \end{aligned} \tag{3.89}$$

In this thesis we will apply IQA to ELF partitions. When considering bonding basins (and valence in general) within the IQA partition, the nuclear terms presented in the previous equations become null ($V_{en}^{BB} = 0$, $V_{nn}^{AB} = 0$, $V_{en}^{AB} = 0$). Therefore, for a bonding basin, which interacts with the core basin that represents an atom A, the energy terms can be expressed as shown in Equations 3.90 and 3.91,

$$E_{\text{intra}}^{bond} = T^{bond} + V_{\text{cou}}^{bond} \tag{3.90}$$

$$E_{\text{inter}}^{A-bond} = V_{\text{cou}}^{A-bond} + V_{\text{XC}}^{A-bond} \tag{3.91}$$

This was the selected approach since we are interested in developing an energy model accounting for interactions between electron pairs. Its is possible to calculate interactions between atoms and “bonds”, as well as interactions between two “bonds” and “bonds” with “lone pairs”. For this purpose, the original code was modified so as to perform integration tasks over ELF basins [83].

The IQA-ELF approach provides and accurate reference that can be used to analyze the behaviour of the energy terms and to construct energy potentials that take into account classical and non-classical terms.

The original IQA implementation could only deal with a HF wavefunction. However, recent developments provide support for DFT-derived ones [84].

3.8 Non-Covalent Interactions

Most chemical interactions are dominated by non-covalent interactions, *e. g.* folding of proteins, self-assembly of nanomaterials, or catalyst and its substrate [85]. This class of interactions cover many interactions, such as London dispersion, dipole-dipole interaction, hydrogen bond, π-π interactions, not leaving out repulsive interactions [86].

The non-covalent interaction index is based on the density and its derivatives, which since as mentioned in Section 3.2, has the advantage over molecular orbital descriptors because it is an experimentally accessible scalar field, also supported by the HK theorem [49].

Moreover, NCI simultaneously allows an analysis and a visualization of all non-covalent interaction types as real-space surfaces. Thus, it is an important tool to analyze chemical systems [87, 88].

The mathematical core of NCI is the reduced density gradient $s(\rho)$, (RDG) it is a quantity from DFT used to describe how far away the system lies from an homogeneous electron distribution.

$$s(\rho) = C_F^{-1} \frac{|\nabla \rho|}{\rho^{4/3}} \tag{3.92}$$

where C_F^{-1} is the Fermi constant $(2(3\pi)^{1/3})$.

Using the above definition (Equation 3.92) we can exemplify an easy case, a single atomic orbital $\psi = e^{-\alpha r}$, thus the density is $\rho = e^{-2\alpha r}$ and the gradient is $\nabla \rho = -2\alpha\rho$, such that

$$s(\rho) = C_F^{-1} \frac{2\alpha\rho}{\rho^{4/3}} = \frac{2\alpha}{C_F} \rho^{-1/3} \tag{3.93}$$

The reduced density gradient assumes large values in the exponentially-decaying density tails far from the nuclei. Small $s(\rho)$ values occur close to the nuclei, due to the combination of large densities and small density gradients. The lower bound on the reduced density gradient is zero [89].

Analyzing $s(\rho)$ versus ρ shows a new feature, one or more spikes in low-density, low-gradient region are the signature of non-covalent interactions. This is the basis of NCI. When there is overlap between atomic orbital, a peak appears on the $s(\rho)$ diagram, the points that form this peak can identify the interaction when mapped the real space. Particularly, NCI interaction index allows an analysis and a visualization of non-covalent interactions types as real-space surface [89].

The $s(\rho)$ isovalue determines which features will appear in the NCI plot. Choosing large values would disclose atomic tails of the density. However, low values might miss some of the interactions of interest [90].

3.9 Computational Details

The geometries were taken from Force Field data bases. A single point calculation was carried out in order to obtain the wavefunction for the ELF/QTAIM analysis. The single point was carried out at the M06-2X/aug-cc-pVTZ [91, 92, 93] theory level, using the suite of GAUSSIAN16 [94]. The choice of the functional and the orbital basis was based on Jiménez Gravalos et al. work 95 in which it is shown the behaviour about the HB is well described for the water cluster with moderate computational time.

Later on, using the electronic densities computed via DFT we proceeded to analyse the topological properties of Electron Localization Function. Using the TopMod, NCI plot and PROMELF programs for these purposes [96, 97, 4]. The visualization of our results was carried out with the help of the GAUSVIEW [94], VMD [98] and VESTA [99] codes.

The PROMELF program analyzes first order real space and momentum molecular densities for a polyatomic molecule within basis set of GTO's function, it can make a topological analysis for real space densities. The program was developed in 2002 by A. Martín Pendás at University of Oviedo.

In PROMELF code for the topology analysis all the 3D and 1D scalars, not only their magnitudes, but also their first and second derivatives (gradients and hessians) are computed analytically. This allows us to make automatic topological analyses of them. A Morse consistency check is done on all topologies, and paths connecting (3,-1) to (3,-3) points are traced and studied [4].

CHAPTER 4

RESULTS

As proposed in the objectives, the most important results on the analysis of the ELF, ρ and NCI in water clusters are shown in this chapter.

4.1 Systems

All systems used in this work were taken from the literature [100]. In particular, there are divided in 3 groups of systems. Set 1 contains global minimal clusters, increasing the number of water molecules (from dimer to pentamer) and a pentamer that is a local minimum. Set 2 contains several dimers with different configurations. Set 3 contains different local minima from dimer to hexamer. All systems are plotted in the Figures 4.1, 4.2 and 4.3, the three sets mentioned above.

The first group was used as the assessment group for computational processing, choosing the best parameters and methods of integration (topic discussed in Section 4.2). Once all calculations were completed with good accuracy for Set 1, we started to compute Sets 2 and 3 with the help of some scripts (Supporting Information A.2).

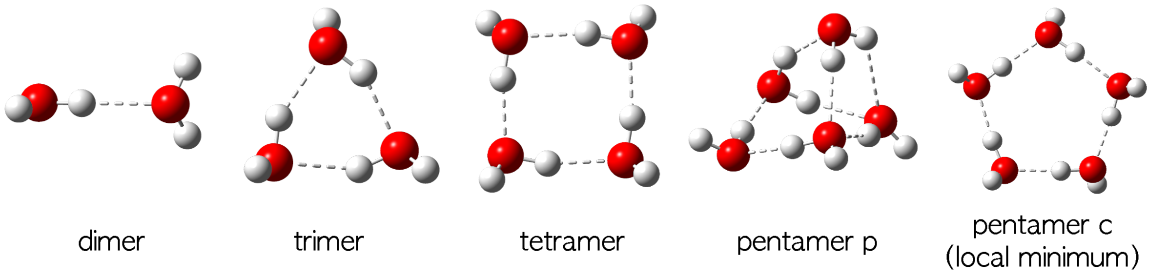
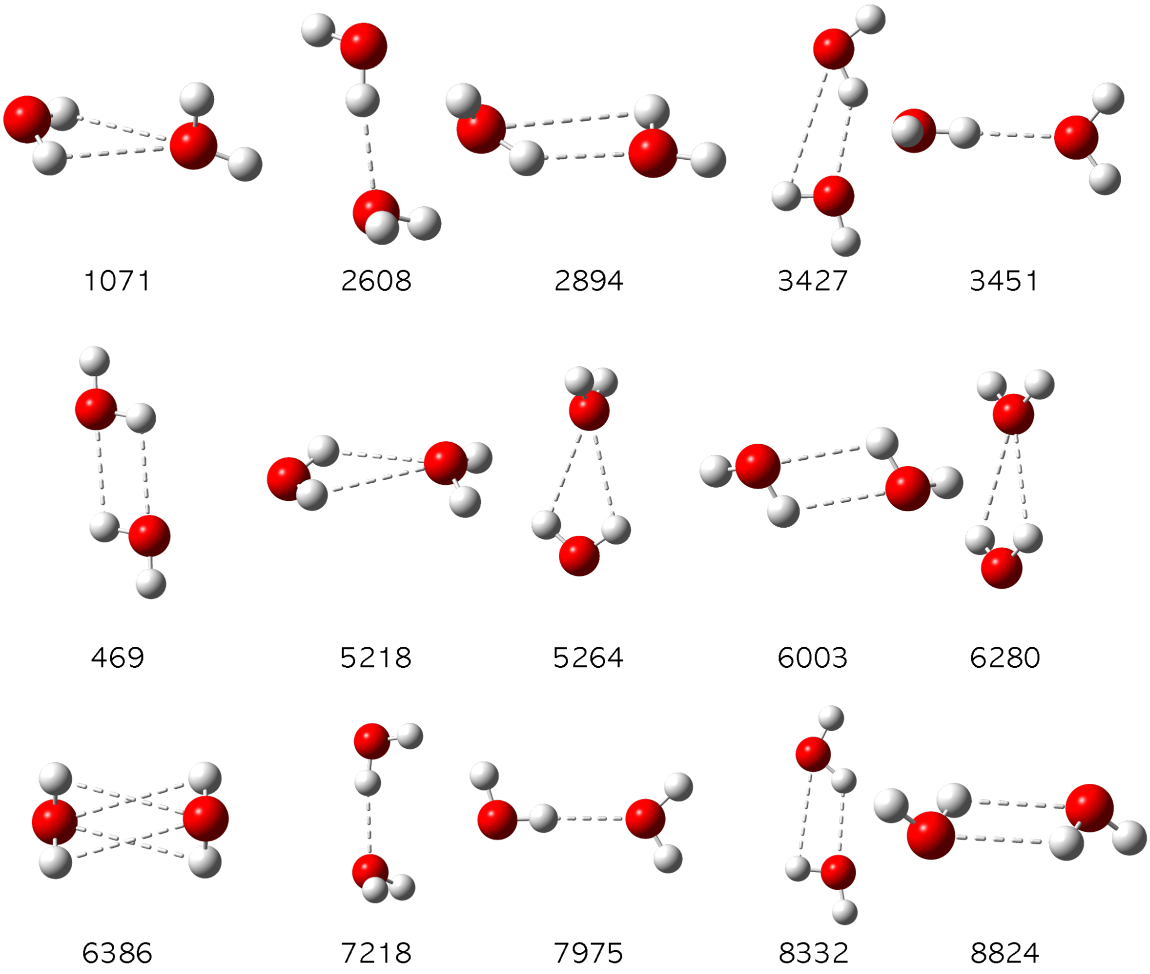

dimer trimer tetramer pentamer p pentamer c (local minimum)

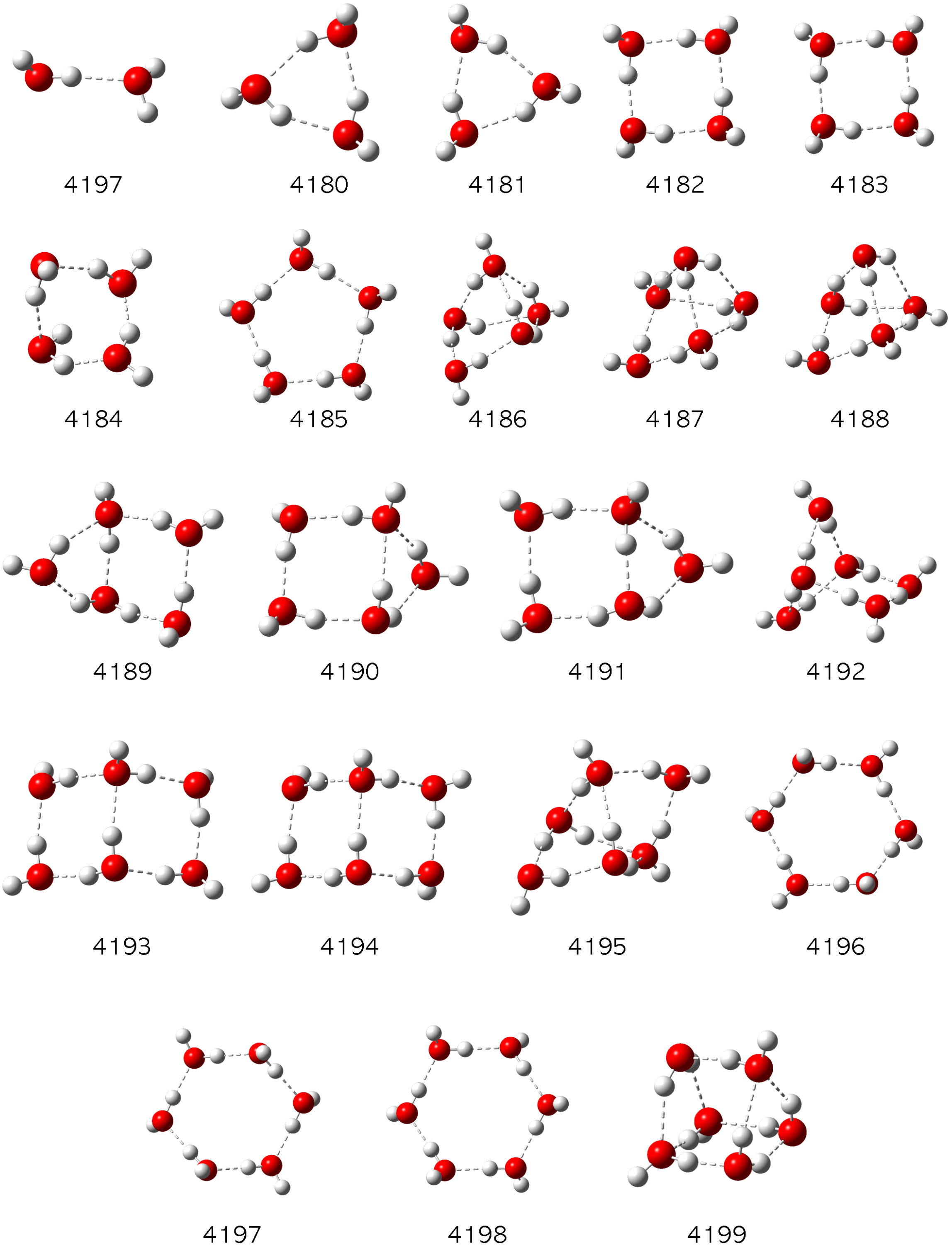
Figure 4.1: Set 1 of water clusters (global minima).


1071 2608 2894 3427 3451

469 5218 5264 6003 6280

6386 7218 7975 8332 8824

Figure 4.2: Set 2 of water clusters. Local minima of dimer clusters. Clusters are named by the file name where the coordinates were taken.



4197 4180 4181 4182 4183

4184 4185 4186 4187 4188

4189 4190 4191 4192

4193 4194 4195 4196

4197 4198 4199

Figure 4.3: Set 3 of water clusters. Local minima taken from Temelso et al. [100]. Clusters are named by the file name where the coordinates were taken.

4.2 Theory level, method election

The choice of the M06-2X/6-311++G(d,p) theory level is justified by the combination of the exchange-correlation functional with triple-zeta quality basis sets which adequately reproduce the cooperative and anti-cooperative behavior. This methodology allows an accurate description at a moderate computational cost, as shown in the work of Jiménez Gravalos et al 95.

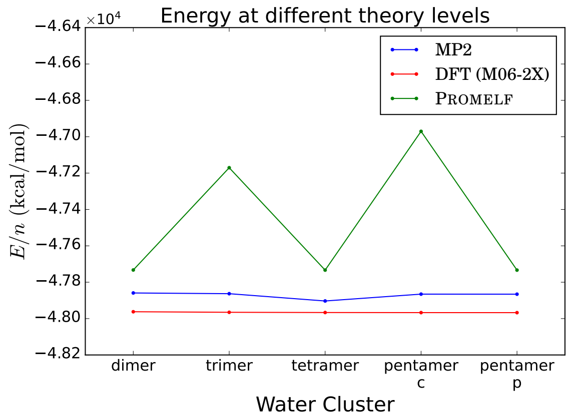


Figure 4.4: Energy divided by the cluster size in MP2, DFT and PROMELF, Set 1.

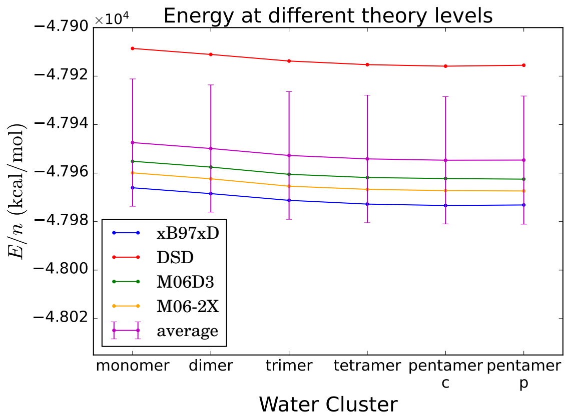


Figure 4.5: Energy divided by the cluster size in wB97XD, DSD, M06-2X and M06D3 functionals.

We also tried an *ab initio* method, Møller–Plesset at second order, getting good results for the energy, but having numerical problems with the PROMELF program (problems that will be described later on). Then the use of a DFT method was thought as a good solution, minimizing most of the numerical issues with PROMELF and also providing similar values for the energy, as we can see in the Figure 4.4, where even if the energy variation is bigger for PROMELF vs DFT than the difference between MP2 and DFT, the variation per water molecule is still in the same magnitude order.

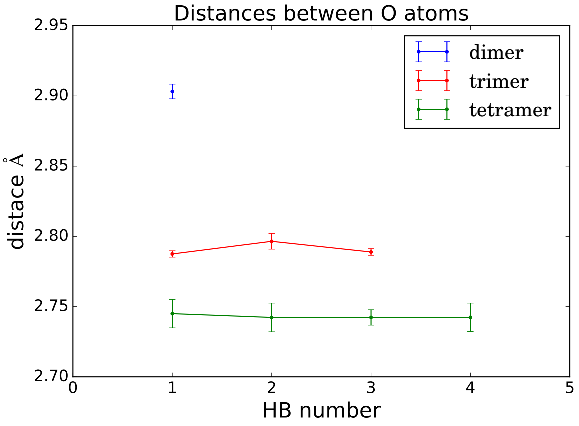


Figure 4.6: Distances between water molecules taking the oxygen atoms as a reference.

Once we known that we would use DFT, we also decided to compare different functionals, analyzing not only the energy at the same geometry, but also doing a geometry optimization at each level, looking at how the distances change. See Figures 4.5 and 4.6, where in case of the energies the differences are around tens of kcal mol^{-1}, and no any oxygen-oxygen distance change enough large to lend ambiguity between the different cases of $n-$mer[1] distances.

Later one, when M062X was chosen as the functional that we would use, we did a systematic analysis of the basis set dependency, through variations within Truhlar's calendar [101] we had an idea of the basis set dependency (see Figure 4.7). Particularly, the numerical value of the correlation energy limit is computable as plotted in Figure 4.8. In both previous figures we can see that the energy values do not change significantly after the use of aug-pVTZ, the above added to the fact that using a quadruple zeta basis set increase significantly the computing time. These observations, together with the previous assessment carried out by Jiménez Gravalos et al 95, justify our selection of the M06-2X/aug-cc-pVTZ level of theory.

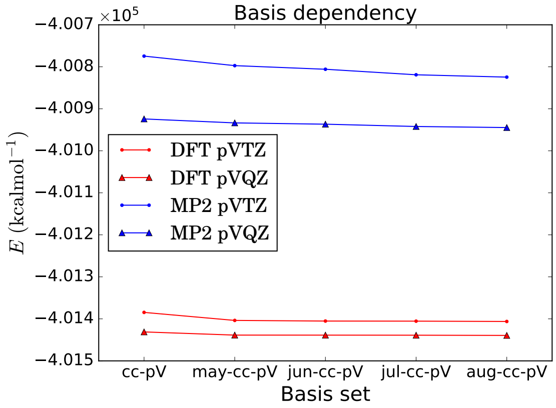


Figure 4.7: Energy in different basis set in water dimer system.

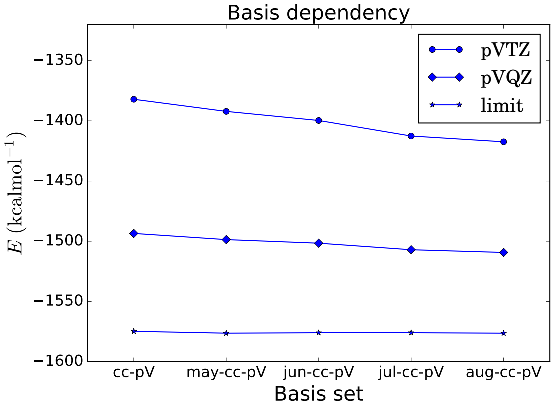


Figure 4.8: Limit for E_{corr} in water dimer system.

The wavefunctions obtained at the M06-2X/aug-cc-pVTZ level were analyzed by means of ELF thanks to the PROMELF program. However, some numerical problems appeared: *i*) the energy showed a considerable difference between the one obtained with GAUSSIAN16 and the PROMELF output (around 8 E$_h$), *ii*) the charge sum of all centers

---

[1] n-mer = aggregate of n molecules.

was not equal to the molecule charge value (zero in those cases), where PROMELF gave around 5 atomic units of charge in worst cases.

Those were the reasons why we guessed that the problems came from the numerical integration method and its accuracy, particularly with the solid angle grid. Because, if a numerical value is affected by *i*) the solid angle *ii*) the radial coordinate, and those values are (numerically, computationally) zero, the whole `DO for loop` that computes the integral is summing zero in all steps.

We tried many different setups for the calculation. Fortunately, the problems were fixed by modifying: *i*) the radial coordinate, that specifies the largest value of the radial coordinate in the integration, by default is 10.0, and we changed it to 6.0; *ii*) the default value used for points in the radial grid outside B-spheres is 100, we changed to 512; *iii*) the way to define the mapping function $r(u)$ $(-1 \leqslant u \leqslant +1)$ outside the B-spheres, the way we use is $r(u) = r_b \frac{1+u}{1-u+\eta} + r_0$ where r_b is a measure of the atomic radius (these radii are taken as the Slater-Bragg radii).

All these alterations of the default values were already available in the code. We also did attempts modifying the radial quadrature used in the integration within the B-spheres. However, the trapezoidal method (the easiest one), with the previous changes gives similar values than those given by more sophisticated methods, with the advantage that the trapezoidal method is the cheapest method in computational time.

4.3 Electronic Localization Function Analysis

The first two systems computed to know how the ELF behaves in water clusters were the water molecule and the dimer, that because in the first one we have the isolated molecule and in the second one the system has only one acceptor and one donor, where each molecule has no other interaction(s). Thus, they constituted good references.

All plots were made using the same isosurface value for all systems in this section, isovalue = 0.9. Thus, we can compare the systems just by mere visual plot inspection.

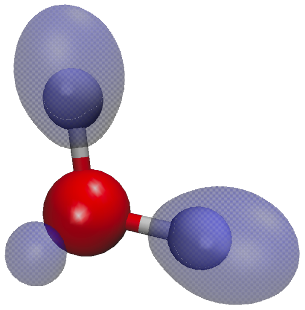


Figure 4.9: ELF in water molecule (isovalue = 0.9).

In the Figure 4.9 we can see how the basins have the same volume for a given ELF value for both H atoms, and also for lone electron pairs. Then, one of the easiest things to see in the water dimer (Figure 4.10) is how the ELF changes in the H atoms and in the lone pairs, since the chemical situation changes for those ELF maxima.

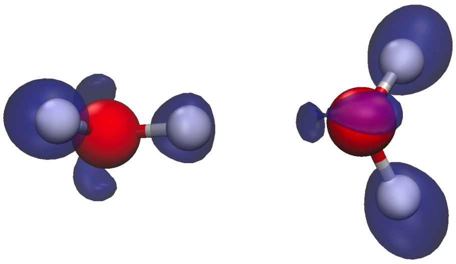


Figure 4.10: ELF in water dimer.

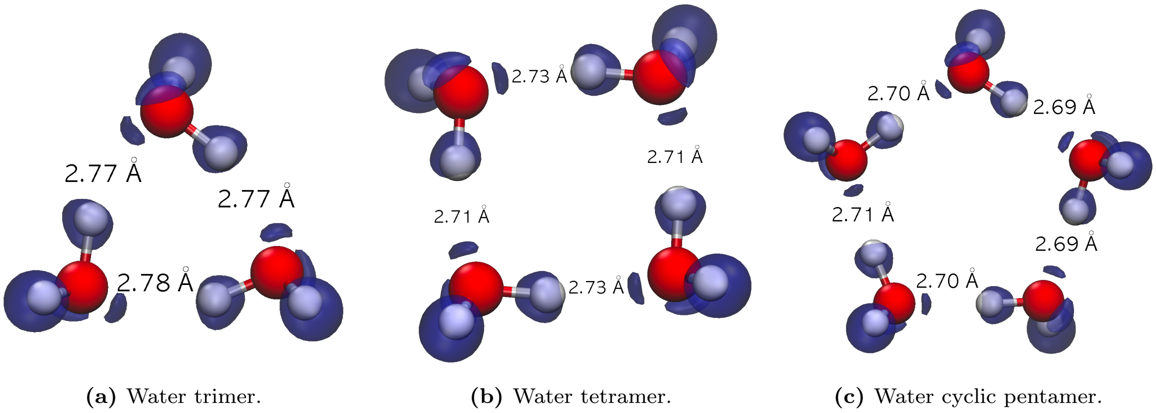
The ELF in the H atom that is involved in the HB is less diffused than the other H atoms that are not in a HB, we can see that in Figure 4.10 as a more compressed volume for the H in the HB. The same behavior occurs for lone pairs, the lone pair that is in the HB has a smaller volume than the other lone pairs that are not in a HB.

When a water molecule is acting only as acceptor of HB the ELF in H atoms are basically equal for both H, the difference lies in lone electron pairs, where the lone pair is more localized (compressed volume) for lone pairs those are in a HB than the lone pairs that are not in a HB.

There are homodromic cases for clusters of three, four and five water molecules, plotted with its respective ELF isosurface in Figure 4.28. Where it is easy to see the differences between the ELF for lone pairs that are involved in HBs and those that are not. This behavior is also observed for H atoms involved in HBs, particularly because the H that are not in a HB are pointing outside the ring.

As shown in Figure 4.28 for the three homodromic n-mers, all hydrogen atoms pointing outside the ring present larger basin volumes than those involved in hydrogen bonds. For electron pairs is more complicated see all the cases, but since the homodromic systems are symmetric, seeing some of them is enough to get the idea that the electron pairs that are in HB are more localized (smaller volume).

For homodromic clusters every molecule is acting as acceptor and as donor. All the density lost by the system as a donor is retrieved back as an acceptor. Also the distances in the cluster (see Figure 4.28) have a trend, every time we add a new water molecule in the system the distance between oxygen atoms is reduced, *i. e.*, the HB is stronger, thus we can see how the cooperativity is acting in the clusters.



(a) Water trimer. **(b)** Water tetramer. **(c)** Water cyclic pentamer.

Figure 4.11: Homodromic water clusters along with their corresponding hydrogen bond distances.

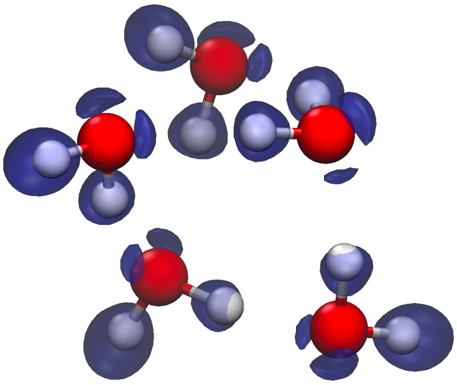


Figure 4.12: Polyhedric non-cyclic water pentamer (pentamer p).

Pentamer p is nonetheless an exception. Indeed, the system not only has bi-coordinated molecules, but also tri-coordinated ones. This happens in two cases: *i*) double donor, *ii*) double acceptor. These two sub-cases of tricoordinated water molecules make the ELF look more similar in H atoms when the water molecule is a double donor and similar for lone pairs when the water molecule is a double acceptor.

4.4 Non-Covalent Interactions

The usual colour values for NCI are shown in the Figure 4.13 where the attractive strongest interactions are shifted to blue and red, blue for attractive interactions and red for repulsive. For all our cases we have only strongly attractive interactions as expected since the HB is a strongly attractive non-covalent interaction.

Looking at the NCI in water clusters, the dimer presents a prominent feature, the only non-covalent interaction is the HB between the two water molecules, the well-known HB in water clusters. The same pattern appears in the trimer and tetramer with the addition of a small NCI region in the middle of the ring.

As we increase the number of water molecules in the cyclic clusters the NCI volume is smaller for HB, as well as the NCI that lies in the middle of the rings, this last type of NCI is enough small in the pentamer c (Figure 4.14d), that we changed the isosurface value to the plot, and therefore, see the NCI region, while the other plots has a isosurface value equals to 0.3, for the pentamer c is 0.5.

Pentamer p has the particularity that has different types of non-covalent interactions, as we can see in Figure 4.14e the system has four NCI within the rings and one NCI inside the cage. Moreover, we can see how even if the HBs are all blue coloured, they do not have the same volume, giving the idea that are not all same.

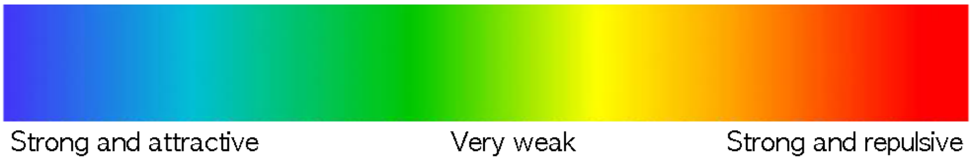
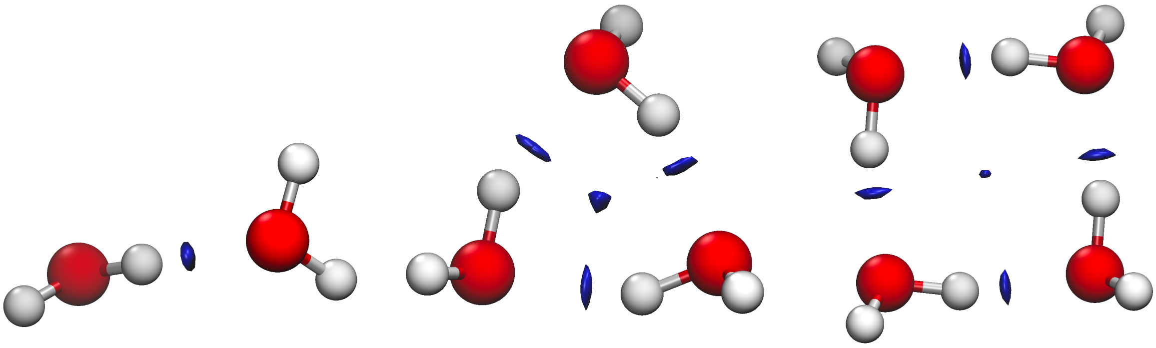
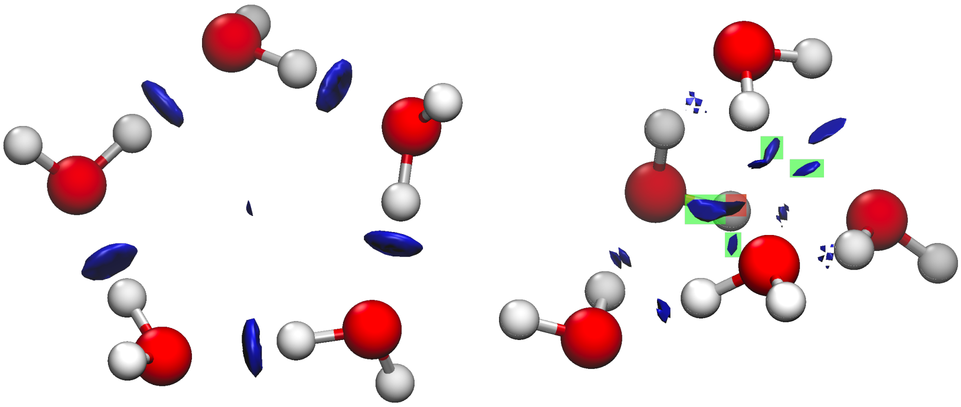


Figure 4.13: Usual colour scale for NCI.



(a) Water dimer. **(b)** Water trimer. **(c)** Water tetramer.



(d) Water cyclic pentamer (pentamer c). **(e)** Water non-cyclic polyhedric pentamer (pentamer p).

Figure 4.14: NCI method applied to Set 1 of water clusters. In Subfigures b, c and d the central isosurface is a RCP, while in Subfigure e the green highlight means a RCP, the red one is a CCP and the non highlighted interactions are HB.

4.5 PROMELF

The next ELF analysis was done about its topology, particularly how the HB interactions have their energy contributions as a function of their topology, the topology analysis was given by PROMELF.

After fixing the computational problems discussed in Section 4.2, we carried out a security check of how different is the energy given by PROMELF and the energy that GAUSSIAN16 [94] gives in the `*wfn` files. To compare the values we did a linear regression (see Figure 4.15). The slope is also near to one and the origin ordinate is close to zero, the slope and the origin ordinate have an uncertainties near to zero. Also the r^2 is really close to one. Hence, we can conclude that the basin integrals are recovering the full system.

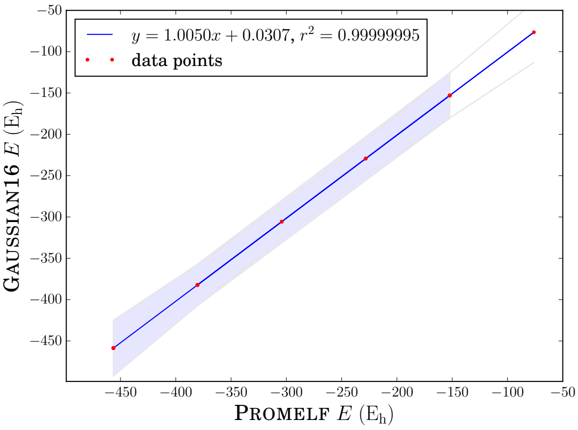


Figure 4.15: Linear Regression between energy by GAUSSIAN16 and PROMELF (atomic units).

The most interesting thing that we can see with the data is how far or close are the energy PROMELF values, and check their system-size dependency. Most of the time we are 0.487 % above the energy given by GAUSSIAN16 with a standard deviation of 0.014 %.

To know more about these fluctuations and the differences between PROMELF and GAUSSIAN16 we have also plotted the values of the energy divided per the number of water molecules that the system has.

As we can see in the Figure 4.16, GAUSSIAN16 energy always predicts a negative ΔE, while PROMELF predicts a positive one. Hence, the ΔE by PROMELF (and ΔG with GAUSSIAN16) cannot be used to predict if a system is energetically favorable for water clusters since the anharmonic contributions cannot be neglected and these contributions are not taken into account in the two software [102].

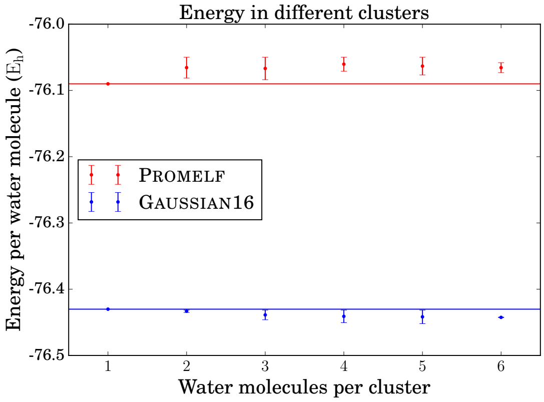


Figure 4.16: Energy of clusters divided by the number of water molecules [Sets 1, 2 and 3]. The two horizontal lines are the energy of one water molecule.

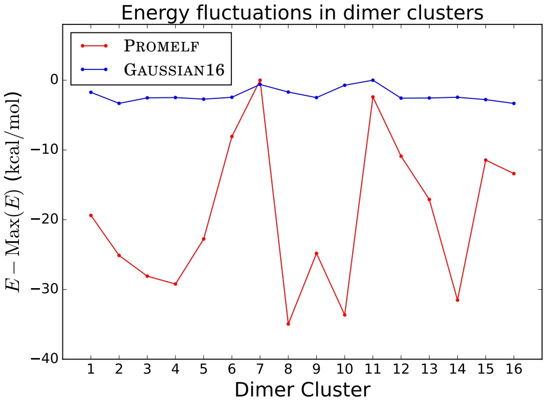


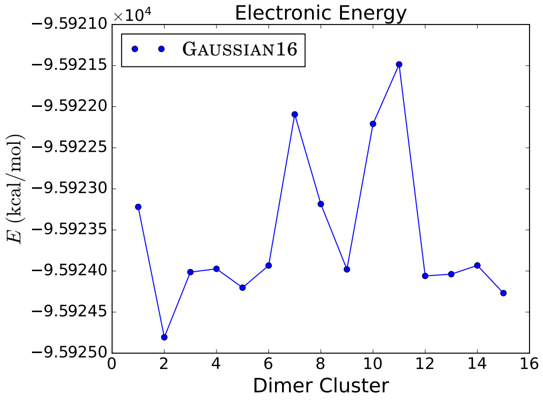
Figure 4.17: PROMELF and GAUSSIAN16 energy fluctuation of water dimers.

Figure 4.17 compares the energy fluctuation in dimers (Set 2) provided by PROMELF and GAUSSIAN16. This set allows a systematic assessment of the energy for a same system with different aggregate configurations. As evidence by the picture, the PROMELF line presents strong oscillations of several kcal mol^{-1}, in clear contrast with the results provided by GAUSSIAN16. Moreover, the minimum and the maximum do not correspond to the same systems.

One property that has the same behavior as the energy computed by GAUSSIAN16 is the exchange-correlation contribution in the HB interactions as we can see in the Figures 4.18 and 4.19, where particularly the minimum and maximum are the same systems in the two cases.

However, their relation is not 100 % correlated as we can see through a linear regression (Figure 4.20), having $r^2 = 0.84$ for the equation $y = 1.3335x + 203.8$.

As we said, the maximum and the minimum for the two cases are the same system. These two extreme cases correspond to the weakest and the strongest HB for any water dimer cluster computed. Therefore, the minimization/maximization of the energy are completely related with the exchange-correlation energy of HB. The two cases are shown in Figure 4.21, the difference of the two systems is 3.32 kcal mol^{-1} of the total electronic energy, and 5.05 kcal mol^{-1} for the exchange-correlation contribution.



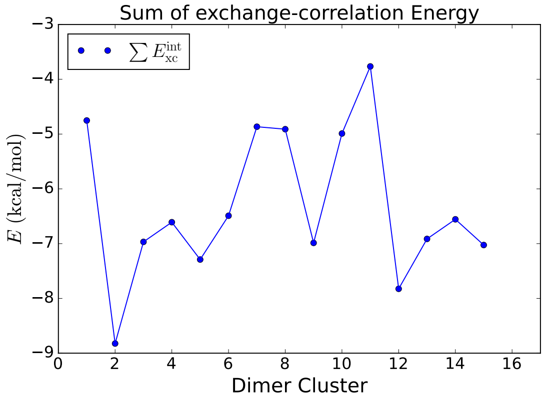
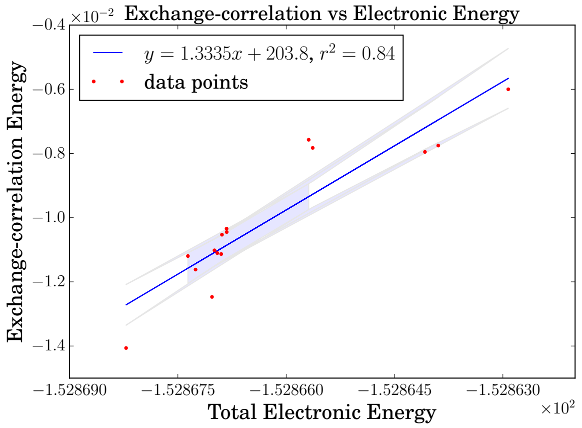


Figure 4.18: Electronic Energy for Dimer Clusters computed by GAUSSIAN16.

Figure 4.19: Exchange-correlation interaction energy for Dimer Clusters.



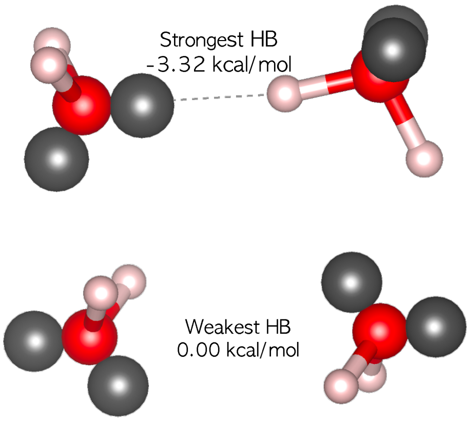


Figure 4.20: Linear regression between exchange-correlation contribution in interaction and electronic energy for whole system.

Figure 4.21: Strongest and weakest HB in water dimer clusters and their relative electronic energy.

To compute the exchange-correlation contribution, the various interactions between H and electron pairs were taken into account and not just the values coming from the classical HB (even if that was the largest contribution).

Looking for the population we did two analyses, one with the delocalization index (DI) and another one with the charge. The DI gives a quantitative idea of the number of electrons delocalized or shared between atoms and the charge is a measurement of how much the electrons are localized in the basins.

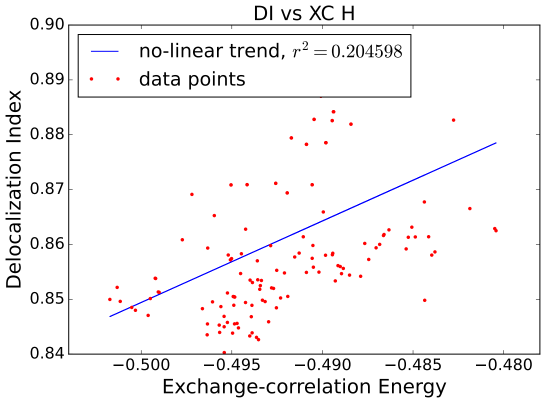


Figure 4.22: Linear regression between exchange-correlation energy and DI in H basin.

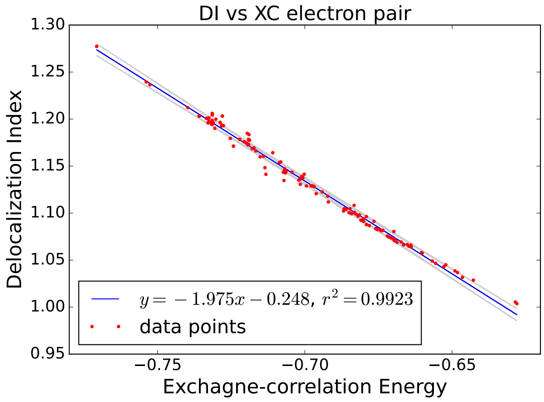


Figure 4.23: Linear regression between exchange-correlation energy and DI in lone pair electron basin.

With the delocalization index, we looked how the exchange-correlation energy is correlated with the the delocalized electrons. Having two different behavior cases. The first one, where the DI and the exchange-correlation energy are really well correlated with the ELF maximum basin associated to the lone electron pair in HB's, with a $r^2 = 0.9923$. However, there is not any correlation for the same phenomenon if we use the ELF maximum basin associated with the H atom ($r^2 = 0.204598$). These two correlations are shown in Figures 4.22 and 4.23.

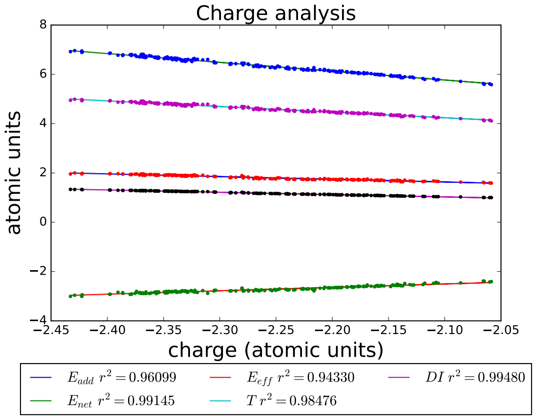


Figure 4.24: Linear regression about charge for lone pair electron basin.

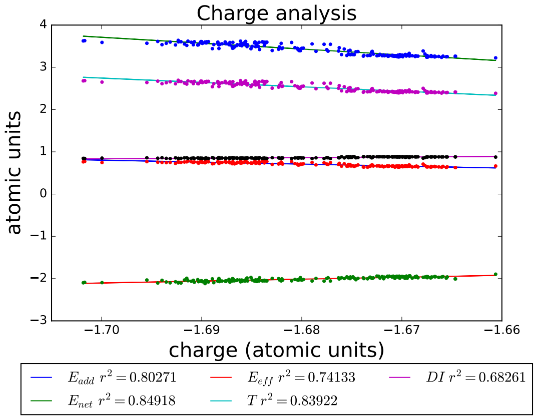


Figure 4.25: Linear regression about charge for H basin.

We also checked how the properties of the basins correlate within the same basin. For that in Figures 4.24 and 4.25 we plotted linear regressions of the charge versus: *i*) kinetic energy,*ii*) net energy E_{net}, as exposed by IQA partition in Section 3.6 (Equation 3.82), *iii*) effective energy $E_{\text{eff}}^{A} = E_{\text{net}}^{A} + \sum_{A\neq B} E_{\text{int}}^{AB}$, *iv*) additive energy $E_{\text{eff}}^{A} = E_{\text{net}}^{A} + \frac{1}{2}\sum_{A\neq B} E_{\text{int}}^{AB}$, and *v*) DI. The above for both the H basin and the electron pair basin. We can see once again, how the basins associated to lone pairs correlates with the charge and the other properties, while for H basins there is from little to no correlation (*e. g.* DI).

Looking at the dimer systems (Set 2) we did not find any correlation among the energy contributions of HB. However, we found the same trend over the addition of all HB contributions. For example, the exchange-correlation contributions sum for lone pairs has the same trend as the same contributions sum for H basin. The above for all dimers, as we can see in Figure 4.26. Even if the total energy does not follow any trend in the dimers, the exchange-correlation contribution follows a trend over the electron pair and H basins.

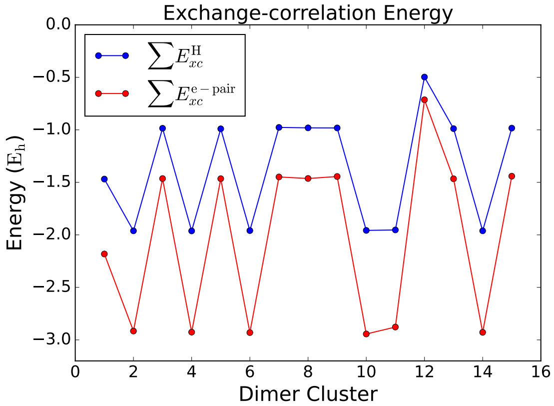


Figure 4.26: Trend of the sum of Exchange-Correlation Energy contribution for dimer systems.

Based on these results, we decided to check for all sets the sum over the kinetic, potential and exchange-correlation contributions to the total energy. A linear regression between the sum of each of these three energy contributions and the two ELF maxima (See Figure 4.27).

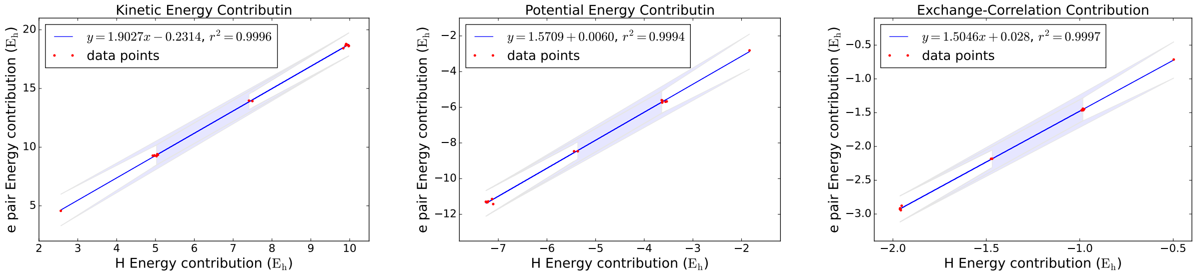


Figure 4.27: Linear Regressions between electron pair and H basins.

As was mentioned before, the homodromic clusters has a particular trend. The size does not really affect the ratio between the different energy contributions to the HB interaction (see Figure 4.28), *i. e.*, what does not change is the proportion between the different contributions to the interaction energy.

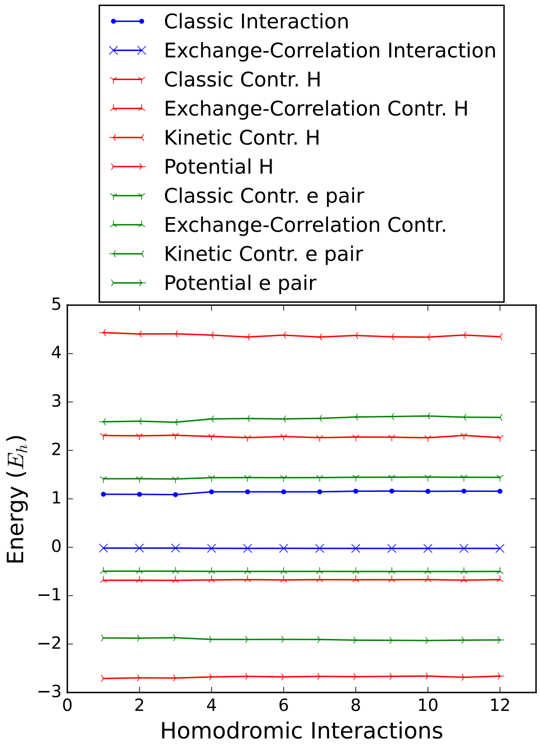


Figure 4.28: Contributions for HB in Homodromic Cases.

In Castor-Villegas et al. [3] work is shown that the strength of the HBs is related to the coordination between water molecules, paying attention to their roles as acceptors or donors. In our work, we have tried to reproduce these trends.

For the water clusters analyzed in this work, we have 6 types of the 10 that are reported in 3. The 6 types are plotted in the Figure 4.29.

Comparing the data obtained in this work and the reported in 3 we cannot claim that we predict exactly the same trend, since the dispersion data is too big to say whether it is the same trend or not. This dispersion could be due to three things, *i*) we do not have enough interactions to have a good statistic analysis, *ii*) the 3 work takes into account how the water molecules are affected since are not in theirs equilibrium geometry when their are not interacting with another chemical entity, that by the deformation energy, and *iii*) the topology for the ELF is more elaborated that the ρ topology (used in the 3 work) giving troubles for the computational integrals.

In particular, this last reason will be a future perspective, as computational problems around water clusters with PROMELF program arise once again while doing the topology calculations with ρ.

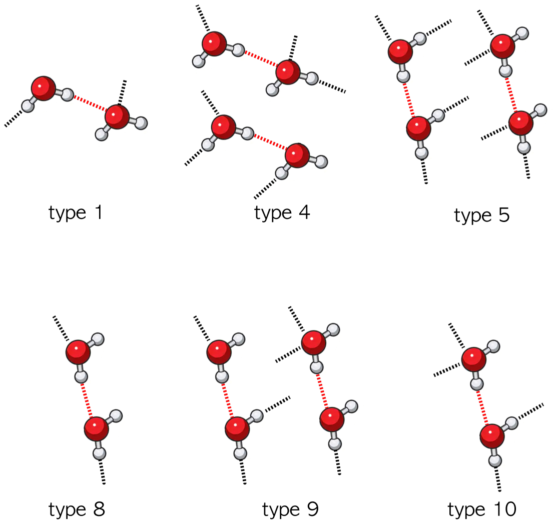


Figure 4.29: Types of HB in the analyzed water clusters.

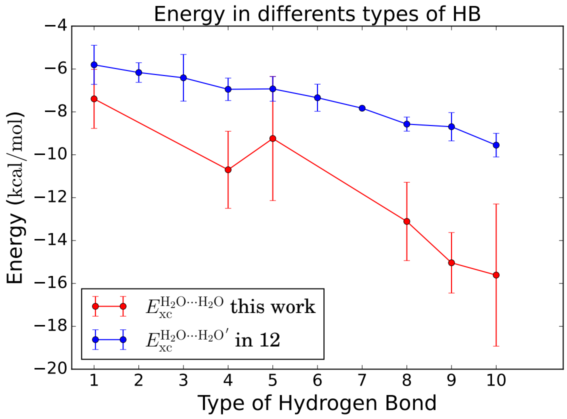


Figure 4.30: Comparison between the scale shown in 3 and this work.

The different types of HB as function of connectivity are shown in the Figure 4.29, and in the Figure 4.30 are the values obtained in this work and the computed in 3 are compared. We can see how the types 8, 9, 10 have the same trend in both works. However, the type 4 in the work 3 has basically the same value compared with the type 5, where in this work we have a significant difference and with the opposite trend that in 3, whereas the error bars are enough big to aim that the two topology perspectives predict different conclusions.

CHAPTER 5

CONCLUSIONS

We have used the IQA partition applied to the ELF topology to study the connectivity of small water cluster.

1. The use of M06-2X/aug-cc-pVTZ was a good way to predict the electronic energy and the wavefunction to compute a topology ELF analysis.

2. We have the best set up known to compute small water cluster ELF analysis with PROMELF code.

3. The results are in general consistent with topological studies on the electronic density in similar systems, as we compared with the result published [103, 2, 3].

4. The code written to compute the systems would be useful for future researchers having just one input file to do a NCI plot or TopMod work. As well to have a new `*.wfn` file with the ELF maxima.

5. As for now, the integration seem to be complicated, difficulting the analysis of general trends from IQA-ELF partition in water clusters.

APPENDIX A

SUPPORTING INFORMATION

A.1 Supporting tables

Energy for systems at different outputs hartree units

Cluster	MP2	DFT (M06-2X)	Promelf (M06-2X)
dimer	-152.539151959111	-152.868036441310	-152.13643137
trimer	-228.827663306177	-229.316617892800	-225.51627000
tetramer	-305.359223571261	-305.763780855504	-304.27701150
pentamer c	-381.398610398789	-382.208963954852	-374.26565610
pentamer p	-381.400573846193	-382.210068626837	-380.34641670

Energy for the system at wB97XD DSD and M06D3 functionals Hartree unit

Cluster	wB97XD	DSD	M06D3	average	σ
pentamer p	-382.256096	-381.796990	-382.171231	-382.07477	0.24428056
monomer	-76.439928	-76.348356	-76.422501	-76.403595	0.04862536
dimer	-152.887534	-152.704601	-152.852667	-152.81493	0.09712828
trimer	-229.344559	-229.069851	-229.293213	-229.23587	0.14605474
tetramer	-305.802591	-305.436006	-305.732757	-305.65712	0.19464603
pentamer c	-382.257905	-381.799987	-382.169303	-382.07573	0.24287605

Distance average between O atoms in optimized systems Å unit		
Bond	Average	σ
Dimer	2.9032	0.0052
Trimer (HB 1)	2.7875	0.0023
Trimer (HB 2)	2.7965	0.0056
Trimer (HB 3)	2.7889	0.0024
Tetramer (HB 1)	2.7450	0.0101
Tetramer (HB 2)	2.7423	0.0102
Tetramer (HB 3)	2.7423	0.0055
Tetramer (HB 4)	2.7424	0.0101

A.2 Scripts

All scripts written while we was working on this thesis are upload in a private GitHub repository (github.com/vcastor/TFMscripts). The code that not has an execution of PROMELF or use the LCT queue system is written down below.

Script to write a new wavefunction with the ELF maxima as atoms with charge zero for the nuclei:

```python
#!/opt/homebrew/bin/python3
# write a new wfn file with the coordiantes from a xyz in Atomic Units
import sys

xyz = sys.argv[1]
oldwfn = sys.argv[2]
newwfn = sys.argv[3]

a = []
x = []
y = []
z = []

archivo = open(xyz, 'r')
datacoor = archivo.readlines()
n = datacoor[0]
n = int(n)

for i in range(n):
    linen = datacoor[i+2]
    linen = linen.split()
    a.append(str(linen[0]))
    x.append(float(linen[1]))
    y.append(float(linen[2]))
    z.append(float(linen[3]))
archivo.close()

archivo = open(oldwfn, 'r')
dataold = archivo.readlines()
header = dataold[1]
header = header.split()
m = header[6]
m = int(m)

with open(newwfn, 'w') as f:
    sys.stdout = f
    print(dataold[0], end='')
```

```
    print(header[0], '{:>14}'.format(header[1]), *header[2:4], '{:>6}'.format(header[4]), header[5], '{:>8}'.format(m+n), header[7])
    for i in range(m):
        print(dataold[i+2], end='')
    for i in range(n):
        print(' ', a[i], ' ', '{:2d}'.format(m+i+1),'   (CENTRE', '{:2d}{}'.format(m+i+1,') '), f'{x[i]:+.8f}', f'{y[i]:+.8f}', f'{z[i]:+.8f}', ' CHARGE = 0.0')
    for i in range(len(dataold)-m-2):
        print(dataold[i+m+2], end='')
```

Where the first argument of the last script is the output of:

```
#!/opt/homebrew/bin/python3
import sys

coor = sys.argv[1]
xyz = sys.argv[2]

a = []
x = []
y = []
z = []

archivo = open(coor, 'r')
data = archivo.readlines()
n = data[0]
n = int(n)

for i in range(n):
    linen = data[i+1]
    linen = linen.split()
    a.append(str(linen[2]))
    if (a[i] == "(3,-3)"):
        x.append(float(linen[3]))
        y.append(float(linen[4]))
        z.append(float(linen[5]))
archivo.close()

with open(xyz, 'w') as f:
    sys.stdout = f
    print(len(y),'bohr\n')
    maxELF = True
    i = 0
    while (maxELF):
        if (a[i] == "(3,-3)"):#the xyz file WILL BE IN bohr not angstrom
            print('X', x[i], y[i], z[i])
            i+=1
```

```
        else:
            maxELF = False
```

The value integrals given by PROMELF were summarized in a smaller file with the following script:

```
#!/usr/bin/perl5.18 -w
#use strict;
#use warnings;

$outpromelf = $ARGV[0];
$integralsv = $ARGV[1];

my $line=`grep -ne "RELEVANT RESULTS FOR ALL THE ATOMS WITH LMAX = 10" $outpromelf | cut -f1 -d:`;
my $lineInicio=$line + 3;
my @line2=`grep -ne "------------------------------ TES PARTITION --------------------------------" $outpromelf | cut -f1 -d:`;
my $lineEnd=$line2[1] - 3;
my $d='$d';
system(`sed '1,${lineInicio}d;${lineEnd},$d' $outpromelf > tmp.1`);

my $nmax=`wc -l < tmp.1`;
$nmax=$nmax + 0;
system(`echo $nmax > $integralsv`);
system(`cat tmp.1 >> $integralsv`);
system(`rm tmp.1`)
```

And the interactions also given by PROMELF with the next one:

```
#!/opt/homebrew/bin/python3
#run as:
#./interactions.py *.put *.txt

import sys
import os
import numpy as np

pout  = sys.argv[1]
atoms = sys.argv[2]

couint      = []
xcint       = []
kinetic1    = []
kinetic2    = []
potential1  = []
potential2  = []
cou1        = []
```

```
cou2       = []
xc1        = []
xc2        = []
max1       = []
max2       = []
DI1        = []
DI2        = []

#################################
# How many interactions between ELF max's or nuclei
cmdcat = "cat " + str(atoms) +  " | sed '/^\\s*\$/d' | wc -l"
n = os.popen(cmdcat).read()
n = int(n)

archivo2 = open(atoms, 'r')
dataAtoms = archivo2.readlines()
for i in range(n):
    linen = dataAtoms[i]
    linen = linen.split()
    max1.append(int(linen[0]))
    max2.append(int(linen[1]))
archivo2.close()

#################################
# Contributions of Max1 et Max2
cmdgrep = "grep -ne 'Atomic Contributions for neq: ' "+ str(pout) +" | cut -f1 -d:"
outgrep = os.popen(cmdgrep).read()
outgrep = outgrep.split()

archivo1 = open(pout, 'r')
data = archivo1.readlines()
for i in range(n):                               #for max1
    dataT  = data[int(outgrep[max1[i]-1])+2] #kinetic
    dataV  = data[int(outgrep[max1[i]-1])+3] #potential
    dataC  = data[int(outgrep[max1[i]-1])+5] #Cou
    dataXC = data[int(outgrep[max1[i]-1])+6] #XC
    dataT  = dataT.split()
    dataV  = dataV.split()
    dataC  = dataC.split()
    dataXC = dataXC.split()
    kinetic1.append(float(dataT[3]))
    potential1.append(float(dataV[3]))
    cou1.append(float(dataC[2]))
    xc1.append(float(dataXC[2]))
    #                                        #for max2
    dataT  = data[int(outgrep[max2[i]-1])+2] #kinetic
    dataV  = data[int(outgrep[max2[i]-1])+3] #potential
```

```
    dataC  = data[int(outgrep[max2[i]-1])+5] #Cou
    dataXC = data[int(outgrep[max2[i]-1])+6] #XC
    dataT  = dataT.split()
    dataV  = dataV.split()
    dataC  = dataC.split()
    dataXC = dataXC.split()
    kinetic2.append(float(dataT[3]))
    potential2.append(float(dataV[3]))
    cou2.append(float(dataC[2]))
    xc2.append(float(dataXC[2]))
archivo1.close()

#################################
#Interaction between Max1 et Max2

cmdgrep = "grep -ne '===================  Interaction with atom:' "+ str(pout) +" | cut -f1 -d:"
outgrep = os.popen(cmdgrep).read()
outgrep = outgrep.split()

#x^2 -x -len(outgrep) = 0; 1+sqrt(1+4*len)/2
natoms = (1+np.sqrt(1+ 4*len(outgrep)))/2
natoms = int(natoms)

for i in range(n):
    if (max1[i] > max2[i]):
        a = outgrep[(max1[i]-1)*(natoms-1) + max2[i] - 1]
    else:
        a = outgrep[(max1[i]-1)*(natoms-1) + max2[i] - 2]
    a = int(a) + 1
    line = data[a]
    line = line.split()
    couint.append(line[4])
    xcint.append(line[5])

cmdcat = "cat " + pout +  " | sed '/^\\s*\$/d' | wc -l"
m = os.popen(cmdcat).read()
m = int(m)
m = m - natoms - 34

for i in range(n):
    dataDI1 = data[int(m+max1[i])-1]
    dataDI2 = data[int(m+max2[i])-1]
    dataDI1 = dataDI1.split()
    dataDI2 = dataDI2.split()
    DI1.append(float(dataDI1[6]))
    DI2.append(float(dataDI2[6]))
```

```python

for i in range(n):
  print(couint[i], xcint[i], cou1[i], xc1[i], kinetic1[i], potential1[i], DI1[i], cou2[i], xc2[i], kinetic2[i], potential2[i], DI2[i])
```

A wrapper was also written to run TopMod or NCI with the same input file.

```python
#!/opt/homebrew/bin/python3
#This wrapper launch TopMod and/or NCI with the same input
#I was written with a bash script lol

import sys
import os
from tqdm import tqdm

filein = sys.argv[1]
archivo = open(filein, 'r')
datalines = archivo.readlines()
cmdtop = "/Users/vcastor/Documents/Master_UAM/TFM/scripts/wrapper/topmod.exe "
cmdnci = "/Users/vcastor/Documents/Master_UAM/TFM/nci/nciplot-master/src_nciplot_4.0/nciplot "
cmdstc = "sbf_to_cube "
gridoption = ["fine\n", "ultrafine\n"]

# definimos los definible
def moving(cube):
        cubein = cube.replace(".wfn\n", "_elf.cube")
        cubeout = cube.replace(".wfn\n", "-elf.cube")
        cmd = "mv " + cubein + " " + cubeout
        os.system(cmd)
        cubein = cube.replace(".wfn\n", "_esyn.cube")
        cubeout = cube.replace(".wfn\n", "-esyn.cube")
        cmd = "mv " + cubein + " " + cubeout
        os.system(cmd)

def writetmp(inpf, wfn, inp):
        with open (inpf, 'w') as f:
                f.write(wfn)
                f.write(inp+"\n")
                f.write("1 1 1")

def stc(wfn):
        sbf = wfn.replace(".wfn\n", "_elf.sbf")
        esyn = wfn.replace(".wfn\n", "_esyn.sbf")
        inpsbf = wfn.replace(".wfn\n", ".tmp1")
        inpsyn = wfn.replace(".wfn\n", ".tmp2")
        outf = wfn.replace(".wfn\n", "-stc.out")
        writetmp(inpsbf, wfn, sbf)
```

```
        cmd = cmdstc + "< " + inpsbf + " >> " + outf
        os.system(cmd)
        writetmp(inpsyn, wfn, esyn)
        cmd = cmdstc + "< " + inpsyn + " >> " + outf
        os.system(cmd)
        moving(wfn)

def elf(wfn, gridtop):
        outf = wfn.replace(".wfn\n", "_topmodelf.out")
        wfntop = wfn.replace(".wfn\n", ".wfn ")
        cmd = cmdtop + wfntop + str(gridtop) + " &> " + outf
        os.system(cmd)
        stc(wfn)

def nci(wfnorxyz, gridnci):
        inpnci = wfnorxyz.replace(".wfn\n", ".nci")
        outf = wfnorxyz.replace(".wfn\n", "-nciplot.out")
        with open (inpnci, 'w') as f:
                f.write("1\n")
                f.write(wfnorxyz)
                f.write(gridnci)
        cmd = cmdnci + inpnci + " >> " + outf
        os.system(cmd)

def both(wfnorxyz, gridtop, gridnci):
        elf(wfnorxyz, gridtop)
        nci(wfnorxyz, gridnci)

def coffee(array):
        if len(array) > 5:
                c = "I'll take time, you can go for beer"
                c = '{:*^72}'.format(c)
                print(c)
        elif len(array) > 2:
                c = "I'll take time, you can go for coffee"
                c = '{:*^72}'.format(c)
                print(c)

#  Cute header
b = "holi, I hope I'll be useful"
b = '{:*^72}'.format(b)
a = '{:=^72}'.format('=')
print(a)
print(b)
#print(b) ABBA
print(a)

```

```
# Grid option, optional
gridtop = '7'        #defoult value
gridnci = ''         #defoult value
if (datalines[-1].lower() in gridoption):
        if datalines[-1].lower() == gridoption[0] : gridtop = '8'
        if datalines[-1].lower() == gridoption[1] : gridtop = '9'
        if datalines[-1].lower() == gridoption[0] : gridnci = datalines[-1].upper()
        if datalines[-1].lower() == gridoption[1] : gridnci = datalines[-1].upper()
        datalines = datalines[:-1]

#-----------------
# What will we do?
if (datalines[-2].lower() in {'elf\n', 'nci\n'}):            #launch both
        datalines = datalines[:-2]
        coffee(datalines)
        with tqdm(total=100) as pbar:
                for i in range(len(datalines)):
                        both(datalines[i], gridtop, gridnci)
                        pbar.update(100/len(datalines))
elif datalines[-1].lower() == 'elf\n':                       #launch ELF
        datalines = datalines[:-1]
        coffee(datalines)
        with tqdm(total=100) as pbar:
                for i in range(len(datalines)):
                        elf(datalines[i], gridtop)
                        pbar.update(100/len(datalines))
elif datalines[-1].lower() == 'nci\n':                       #launch NCI
        datalines = datalines[:-1]
        with tqdm(total=100) as pbar:
                for i in range(len(datalines)):
                        nci(datalines[i], gridnci)
                        pbar.update(100/len(datalines))

# A cerrar el chiringuito
d = 'Bueno, ADIOS'
d = '{:*^72}'.format(d)
print(a)
print(d)
print(a)


# Ahhhhh... delate temporal files
cmd = "rm -f *-stc.out *nci *res *tmp1 *tmp2"
os.system(cmd)
```

The wapper code can be written with a bash writer that install TopMod, NCI and even python3 if the computer does not have some of the software required.

```
#!/bin/bash
###########################################################################
# Bash wrapper writer. This code look around to know if your computer
# has everything ok to the correct wapper use.
#
#                                                          Victoria Castor
#                             Grupo de Investigación Julia Contreras-García
#                                Paris, Ile de France, Republique Francaise
###########################################################################
# Paperback Writer

OS=`uname`                                        # macOS or Linux flavour

# the wrapper was written for python3
# do we have it?
if ! ( command -v python3 &> /dev/null || command -v python &> /dev/null ); then
  if [ "$OS" = 'Darwin' ]; then
    if ! command -v brew &> /dev/null; then
      curl -fsSL https://raw.githubusercontent.com/Homebrew/install/HEAD/install.sh
    fi
    brew install python
  else
    sudo apt-get install python3.8
  fi
fi
# Ok, we have it, but where?
if command -v python3 &> /dev/null; then
    interpreter=( $(type python3) )
    firstline="#!${interpreter[2]}"
    pip3 install tqdm &> /dev/null
elif command -v python &> /dev/null; then
    interpreter=( $(type python) )
    firstline="#!${interpreter[2]}"
    pip install tqdm &> /dev/null
    echo "Be carfule with the python version that you're using"
fi

# One: don't pick up the phone
touch wrapper.py
echo $firstline > wrapper.py
sed -n 2,11p raw_code.txt >> wrapper.py

###########################################################################
# Is everything installed for proper wrapper operation?
```

```bash

# TopMod
if [[ ! -f "./topmod.exe" ]]; then
  if ! command -v gfortran &> /dev/null; then
    if [ "$OS" = 'Darwin' ]; then
      if ! command -v brew &> /dev/null; then
        curl -fsSL https://raw.githubusercontent.com/Homebrew/install/HEAD/install.sh
      fi
      brew install gcc
    else
      sudo apt-get install gfortran
    fi
  fi
  gfortran topmod.f90 -o topmod.exe
else
  if [ ! -x "./topmod.exe" ]; then chmod +x ./topmod; fi
fi
echo 'cmdtop = "'`pwd`'/topmod.exe "' >> wrapper.py

# NCI plot
if [[ ! -f "./nciplot" ]]; then
  if ! command -v git &> /dev/null; then
    if [ "$OS" = 'Darwin' ]; then
      if ! command -v brew &> /dev/null; then
        curl -fsSL https://raw.githubusercontent.com/Homebrew/install/HEAD/install.sh
      fi
      brew install git
    else
      sudo apt-get install git
    fi
  else
    git clone https://github.com/juliacontrerasgarcia/nciplot.git
    ( cd ./nciplot/src_nciplot_4.0 ; make mrproper; make )
    echo 'export NCIPLOT_HOME='`pwd`'/nciplot/' >> ~/.bash_profile
    echo 'cmdnci = "'`pwd`'/nciplot/src_nciplot_4.0/nciplot "' >> wrapper.py
  fi
else
  if [ ! -x "./nciplot" ]; then chmod +x ./nciplot; fi
  echo 'cmdnci = "'`pwd`'/nciplot "' >> wrapper.py
fi

# sbf_to_cube
if ! command -v sbf_to_cube &> /dev/null; then
  curl -O https://www.lct.jussieu.fr/pagesperso/silvi/topmod09.tar
  tar -xvf topmod09.tar
```

```
  if [ "$OS" = 'Darwin' ]; then
    ( cd ALL ; sed -i '' 's/ifort/gfortran/' 'Makefile' ; make all ; make install )
  else
    ( cd ALL ; sed -i 's/ifort/gfortran/' 'Makefile' ; make all ; make install )
  fi
fi
echo 'cmdstc = "sbf_to_cube "' >> wrapper.py

########################################################################
# c'est fini (about prerequisites)
sed -n '15,$p' raw_code.txt >> wrapper.py

# don't forget give executable permissions
chmod +x wrapper.py

# et voila; danke schon!
echo ""
echo "Everthing done, examples given in the directory: examples"
echo ""
echo "            Grupo de investigación Julia Contreras-García"
echo ""
echo "Read the README.md file to know the wapper limits"
echo ""
echo "Run as:"
echo "./wraper.py input1.inp"
```

A.3 Geometries of water clusters

Water clusters coordinates in Å, xyz format:

Set 1:

$(H_2O)_2$ dimer

```
6

 O                 -1.50717734   -0.01619638    0.11951854
 H                 -0.55462931   -0.00590939   -0.02463337
 H                 -1.85013806    0.10494076   -0.76562865
 O                  1.38293589    0.01487256   -0.11662184
 H                  1.71184985   -0.79058159    0.28742259
 H                  1.68684912    0.70214076    0.47966586
```

$(H_2O)_3$ trimer

```
9

O        -1.36001        -0.85106        -0.10182
O         1.42013        -0.73548        -0.08494
O        -0.06465         1.59564         0.11259
H         0.51728        -1.08942        -0.13293
H        -1.19423         0.10545        -0.06990
H         0.68178         0.97430         0.10814
H        -1.88445        -1.01261         0.68352
H         1.81248        -1.20503         0.65213
H         0.10337         2.15447        -0.64751
```

$(H_2O)_4$ tetramer

```
12

 O                  1.31666042    1.40884898   -0.10114327
 H                  1.47328619    0.44417348   -0.08491592
 H                  1.79749876    1.72180026    0.66627582
 O                 -1.41340625    1.30240188   -0.09052136
 O                 -1.31671813   -1.40889027    0.10125318
 H                 -0.45453416    1.48581031   -0.13146100
 H                 -1.72328997    1.84965743    0.63201522
 H                 -1.47310906   -0.44417044    0.08503586
 H                 -1.79738828   -1.72162437   -0.66636287
 O                  1.41342833   -1.30238915    0.09042744
 H                  1.72324141   -1.84954643   -0.63221482
 H                  0.45458012   -1.48587176    0.13149983
```

$(H_2O)_5$ pentamer c

```
15

 O                 -2.18682590    0.70240485   -0.11509339
 O                  0.00193252    2.28084187   -0.03021546
 O                  2.18219860    0.70806706    0.14906488
 O                  1.34929802   -1.83518722   -0.16063803
 O                 -1.33691158   -1.86386018    0.08983282
 H                 -2.75012938    1.09343667    0.55370746
 H                  0.20569627    2.79518292   -0.81257865
 H                  2.69347386    0.65837274    0.95760056
 H                  1.48372603   -2.28154279   -0.99761654
 H                 -1.70854960   -2.17468813    0.91603044
 H                 -1.40584413    1.29338678   -0.12471993
 H                  0.80956259    1.74235059    0.10033626
 H                  1.92106123   -0.22175430   -0.01423718
 H                  0.37965165   -1.87990920   -0.03152929
 H                 -1.70618177   -0.96296625   -0.01059971
```

$(H_2O)_5$ pentamer p

```
15

 O                 -1.51022296    0.13289323   -1.32180293
 O                 -1.31497666   -0.21222089    1.59611094
 O                  0.26111778   -1.78346738   -0.19132577
 O                  2.29342630   -0.00663568   -0.14127916
 O                  0.25609218    1.68441833    0.13141449
 H                  1.09927586    1.18101387    0.06492892
 H                  2.88255467   -0.25821138    0.57161957
 H                  1.67703015   -0.76748891   -0.21617951
 H                 -0.33022741   -1.41182666   -0.86016435
 H                 -0.20778080   -1.51593848    0.61453001
 H                 -1.98677753   -0.19744049    0.90761343
 H                 -1.80178626    0.42697033   -2.18516435
 H                 -0.92302221    0.83777012   -1.00349463
 H                 -0.80590129    0.57828396    1.37237998
 H                  0.51314155    2.60696678    0.14899027
```

Set 2:

$(H_2O)_2$ 1071

```
6

8   .1233790528   -.0083889420    .0070230942
1 -1.0603384215    .0689036426   1.3720856473
1  -.8981023766    .0642570990  -1.4835657889
8  4.5988798786   -.3047691677  -3.2937698911
1  3.9654964083  -1.6973561457  -2.3293613342
1  4.1591659475   1.1563325053  -2.3230018774
```

$(H_2O)_2$ 2608

```
6

8   .0960403007    .0462912807    .0630513033
1  -.9032609707    .8737269126  -1.1968313184
1  -.6212218236  -1.6085253290    .1959949374
8  5.1211401465   -.6893768837  -2.2655877418
1  6.4155699672    .0372942654  -1.2326514142
1  3.5862541454   -.3599668341  -1.3677175065
```

$(H_2O)_2$ 2894

```
6
8  -.0307428715   -.1191588926    .0140756184
1 -1.0552864605   1.3345475280    .3421077103
1  1.5432792960    .5569051250   -.5655351448
8  2.4677215526  -4.8224649724  -1.4698566665
1  1.7429721920  -5.4196569023  -3.0153847767
1  1.1265821987  -3.9198735278   -.6591588844
```

$(H_2O)_2$ 3427

```
6

8   .0236190360    .1152220795   -.0388342942
1  -.7787344622  -1.2199165880   -.9576327371
1   .4038208718   -.6090455917   1.5740636818
8  -.5415832182   3.5224573326  -4.4589440266
1  -.0287341444   5.2483463570  -4.6287965491
1  -.0465633375   3.0654193722  -2.7806625851
```

$(H_2O)_2$ 3451

```
6

8   .0969483060    .0427843661   -.0641296567
1  -.1172864297    .0149298264   1.7313882572
1 -1.4216094638   -.6940617061   -.7134347792
8  3.9511342861   3.1420071002  -3.0191190915
1  2.8815801145   1.9967248856  -2.1163790960
1  3.0550001719   4.7126724806  -2.9965162416
```

$(H_2O)_2$ 469

```
5

8   .1090805717   -.0558536666   -.0179968243
1 -1.5022829047   -.8331820034    .2462481005
1  -.2291928762   1.7197676673    .0394220683
8  -.8482815197  -5.2472278379    .1342524220
1  -.5100076705  -7.0228490927    .0768334454
1   .7630817791  -4.4698991243   -.1299924774
```

$(H_2O)_2$ 5218

```
6
1   .5121172060  -1.3918360158    .9012284817
1 -1.3288848525    .7940597088    .7843586751
8 -1.8867339535  -1.3107376492   5.2053244542
1 -2.4993812397    .0958088815   6.1628458046
1  -.6583791793  -2.0900868415   6.2797156128
```

$(H_2O)_2$ 5624

```
6

8   .0906718517    .0829379657    .0155562862
1 -1.1648789156   -.4225365146   1.2149914853
1  -.2743885250   -.8939681264  -1.4619221012
8  4.2122951076   3.8530059670    .7226903349
1  2.5353719068   4.1475287294    .1129839322
1  4.2686071652   2.0761026346   1.0543535317
```

$(H_2O)_2$ 6003

```
6

8  -.0744156896    .0989936649    .0021559987
1  1.2604112587   -.3076544216   1.1525608528
1  -.0791838209  -1.2637082017  -1.1867838080
8 -4.2330266362  -2.2376028826  -2.2389367138
1 -4.2241469143  -1.0498575712   -.8752141605
1 -5.5305246607  -3.4193728251  -1.8025015458
```

$(H_2O)_2$ 6280

```
6

8    .0885935293   -.0865536004   -.0013227583
1 -1.6924004590   -.3285073071    .1988666369
1    .2861229889   1.7024042404   -.1778700113
8 -4.1106552457   4.0160044923    .0613747216
1 -5.8916492339   3.7740507850    .2615641168
1 -3.9131257867   5.8049623333   -.1151725313
```

$(H_2O)_2$ 7218

```
6

8   -.0364056832   -.1179669287    .0100259082
1   -.5239947153   1.0879811635  -1.2463590293
1   1.1018754305    .7845510105   1.0872141239
8   2.3782834454  -4.6960848962  -2.2676442611
1   3.7553576153  -3.8942944477  -3.1228376798
1   1.4875960964  -3.3388971559  -1.4706031955
```

$(H_2O)_2$ 7975

```
6

8    .0744905069    .0989462039   -.0017035254
1    .5477750638  -1.6444796414   -.0855189567
1 -1.7301901045    .0738703847    .1125596377
8   4.2351854084   4.1508181672   -.1422359253
1   3.3878467786   5.7451677294   -.0391646082
1   2.9049909561   2.9265144010   -.0951192236
```

$(H_2O)_2$ 8332

```
6

8    .0236612951   -.1172133814   -.0322994613
1 -1.3829412185    .5067569279    .9177991642
1   1.0073568337   1.3538139147   -.4050980097
8 -4.4997302660  -1.6552649138   2.4810723139
1 -5.9986140613  -2.2479451939   3.3012152468
1 -3.7406091429  -3.1450611139   1.7920154374
```

$(H_2O)_2$ 8824

```
6

8    .0104519406   -.1220836016    .0181229144
1 -1.5063358121    .8396122268   -.1941340608
1   1.3404283394   1.0982654010   -.0935375832
8   4.2461948311    .4511089490   3.1653641179
1   5.7629825519   -.5105869297   3.3776210922
1   2.9162183940   -.7692400160   3.2770245721
```

Set 3:

$(H_2O)_2$ 4170

```
6

O         -1.62893        -0.04138         0.37137
H         -0.69803        -0.09168         0.09337
H         -2.06663        -0.73498        -0.13663
O          1.21457         0.03172        -0.27623
H          1.44927         0.91672        -0.58573
H          1.72977        -0.08038         0.53387
```

$(H_2O)_3$ 4180

```
9

O         -1.38183        -0.79188        -0.17297
H         -0.45433        -1.10048        -0.23187
H         -1.81183        -1.39808         0.44213
O          1.41257        -0.77648        -0.31737
H          1.22807         0.17372        -0.17317
H          1.93037        -1.04028         0.45363
O          0.01887         1.60382         0.21583
H         -0.73003         0.98002         0.13523
H         -0.21183         2.34962        -0.35147
```

$(H_2O)_3$ 4181

```
9

O         -1.13187        -1.11979        -0.35833
H         -1.76867        -1.58319         0.19837
H         -1.23847        -0.17309        -0.13963
O          1.56013        -0.35109        -0.32593
H          0.77843        -0.93769        -0.31313
H          2.23183        -0.81009         0.19197
O         -0.44827         1.56921         0.01767
H         -0.42977         2.22941         0.72047
H          0.44663         1.17631         0.00857
```

$(H_2O)_4$ 4182

```
12

O          -1.32019        -1.38034        -0.35874
H          -1.73839        -1.59494        -1.20154
H          -1.48339        -0.41684        -0.23524
O           1.40521        -1.34194        -0.00334
H           0.44761        -1.48074        -0.18804
H           1.61711        -1.97904         0.68986
O           1.30901         1.37056         0.43066
H           1.46721         0.40266         0.33856
H           1.95091         1.78236        -0.16074
O          -1.39399         1.35196        -0.06864
H          -0.43159         1.49496         0.08506
H          -1.82949         1.79136         0.67216
```

$(H_2O)_4$ 4183

```
12

O           1.39868        -1.34774        -0.12067
H           1.65578        -2.01444         0.52783
H           0.43717        -1.49494        -0.27167
O           1.31918         1.31006         0.57663
H           1.47618         0.36556         0.34493
H           1.99548         1.80066         0.09423
O          -1.39872         1.34796         0.12003
H          -0.43722         1.49516         0.27143
H          -1.65532         2.01416        -0.52907
O          -1.31942        -1.31014        -0.57607
H          -1.47632        -0.36564        -0.34467
H          -1.99542        -1.80064        -0.09297
```

$(H_2O)_4$ 4184

```
12

O           1.64293        -0.31429         0.72092
H           1.35033         0.42881         0.15752
H           2.59073        -0.18659         0.84522
O          -1.75747         0.21311         0.84372
H          -1.45837         0.23551         1.76222
H          -1.40477        -0.63249         0.49152
O           0.03963         1.28881        -0.91638
H          -0.70197         1.14211        -0.28528
H          -0.08137         2.17951        -1.26548
O          -0.36937        -1.72189        -0.70638
H          -0.33487        -1.03929        -1.39408
H           0.48453        -1.59329        -0.25348
```

$(H_2O)_5$ 4185

```
15

O          -1.25876        -1.92002        -0.34906
H          -1.63856        -1.06322        -0.04126
H          -1.79946        -2.17022        -1.10806
O          -2.21496         0.50378         0.45924
H          -1.49466         1.17408         0.52224
H          -2.69616         0.57528         1.29204
O          -0.10936         2.26268         0.56254
H           0.13574         2.70198         1.38584
H           0.71374         1.79938         0.27624
O           2.12914         0.90148        -0.20406
H           1.92084        -0.04832        -0.37116
H           2.57754         1.19728        -1.00576
O           1.43694        -1.69192        -0.67766
H           0.46344        -1.81652        -0.57636
H           1.83454        -2.40572        -0.16476
```

$(H_2O)_5$ 4186

```
15

O           0.05779        -1.97966        -0.32416
H          -0.05881        -1.77056         0.62374
H           0.01139        -2.94156        -0.38686
O          -0.15931        -0.34226         1.89564
H           0.60239         0.09544         1.43704
H           0.01219        -0.25346         2.84064
O           1.76089         0.46694         0.17584
H           1.64909        -0.35556        -0.32646
H           1.33679         1.14134        -0.39836
O           0.11909         2.12534        -1.35296
H          -0.66761         1.58174        -1.12326
H           0.11909         2.17434        -2.31656
O          -1.78931         0.29414        -0.48306
H          -1.64291         0.29974         0.47804
H          -1.35071        -0.53596        -0.73926
```

$(H_2O)_5$ 4187

```
15

O           1.84379        -0.11504        -0.12363
H           1.34249        -0.78144        -0.64713
H           2.76169        -0.20414        -0.40763
O           0.05569        -1.81254        -1.35843
H          -0.73261        -1.32314        -1.03713
H          -0.03131        -2.69024        -0.96553
O          -1.80581        -0.17524        -0.11693
H          -2.72801        -0.32044         0.12677
H          -1.31491        -0.06624         0.73537
O          -0.14231         0.44826         1.95117
H          -0.08431         1.33706         1.55037
H           0.69319         0.05536         1.64437
O           0.05559         2.25186        -0.28463
H          -0.70911         1.75366        -0.61393
H           0.79589         1.64226        -0.45313
```

$(H_2O)_5$ 4188

```
15

O           -0.10070      0.03763      2.15322
H            0.70500     -0.10157      1.62652
H           -0.31380      0.96103      1.94502
O            1.64720      0.06823     -0.22778
H            1.22860     -0.67177     -0.73528
H            2.56420      0.09893     -0.52618
O           -1.85160     -0.56057     -0.05818
H           -1.41190     -0.57577      0.81552
H           -1.74680      0.37533     -0.30138
O           -0.40190      1.98003     -0.09018
H           -0.31750      2.83123     -0.53658
H            0.41950      1.49033     -0.30038
O            0.12720     -1.78967     -1.48298
H           -0.69420     -1.42657     -1.06728
H            0.14670     -2.71677     -1.21408
```

$(H_2O)_5$ 4189

```
15

O            1.56145     -1.74294     -0.59077
H            0.59395     -1.91244     -0.57957
H            1.76525     -1.58834     -1.52187
O           -1.21465     -1.96274     -0.39767
H           -1.43345     -1.10404      0.01993
H           -1.52545     -2.62574      0.23163
O           -1.32745      0.56796      0.84243
H           -1.80735      0.79696      1.64793
H           -0.36505      0.53266      1.09613
O            1.34295      0.58056      0.97163
H            1.32735      1.26686      0.28053
H            1.58425     -0.23524      0.48163
O            0.12675      2.29596     -1.02307
H            0.01225      3.24316     -0.87467
H           -0.64075      1.88736     -0.58427
```

$(H_2O)_5$ 4190

```
15

O           -1.32243      0.59037      0.90663
H           -1.45523     -0.20793      0.33723
H           -2.04913      0.57577      1.54073
O           -1.39863     -1.63223     -0.64977
H           -0.44823     -1.89543     -0.67967
H           -1.64863     -1.52953     -1.57657
O            1.30577     -2.00243     -0.72337
H            1.80877     -2.69053     -0.27147
H            1.55767     -1.16063     -0.27377
O            1.60977      0.35717      0.62673
H            1.46147      1.16127      0.09423
H            0.78327      0.32217      1.13713
O            0.16347      2.58237     -0.45147
H            0.16867      3.44907     -0.02697
H           -0.53653      2.08057      0.01033
```

$(H_2O)_5$ 4191

```
15

O            1.43791     -1.95305     -0.15367
H            0.48771     -2.04965     -0.37587
H            1.64141     -2.72235      0.39203
O           -1.36189     -1.89445     -0.54687
H           -1.51469     -0.95345     -0.32147
H           -1.93019     -2.38015      0.06343
O           -1.35999      0.78675      0.35063
H           -1.92069      1.14825      1.04813
H           -0.45689      0.67515      0.75753
O            1.22651      0.59525      0.97853
H            1.41951      1.22695      0.26193
H            1.47001     -0.28235      0.61313
O            0.59981      2.41115     -1.17637
H            0.53181      3.34765     -0.95067
H           -0.27039      2.04425     -0.94037
```

$(H_2O)_6$ 4192

```
18

O           -0.74347      1.69528      0.24763
H            0.13813      1.65928     -0.21687
H           -1.01187      2.62118      0.19903
O           -0.11487     -2.03692      0.31843
H           -0.03377     -1.51552      1.13993
H           -0.92247     -1.66862     -0.08997
O            1.61483      1.44548     -0.98307
H            2.39553      1.68068     -0.46577
H            1.73543      0.48028     -1.17757
O            1.87853     -1.21202     -1.31017
H            1.78343     -1.65672     -2.16087
H            1.16953     -1.59782     -0.73297
O            0.01793     -0.02932      2.35453
H           -0.48047      0.02188      3.17893
H           -0.33587      0.68908      1.79423
O           -2.16277     -0.48102     -0.87327
H           -1.81777      0.36818     -0.53077
H           -3.10997     -0.46332     -0.69137
```

$(H_2O)_6$ 4193

```
18

O          -2.46557        -1.25995         0.27464
H          -3.10787        -1.76475        -0.23856
H          -1.59027        -1.44595        -0.15216
O          -0.06527        -1.42365        -0.94636
H           0.71813        -1.68105        -0.41606
H           0.09053        -0.48185        -1.13586
O           2.23433        -1.74905         0.62684
H           3.04253        -2.13085         0.26334
H           2.42133        -0.78865         0.70254
O           2.42443         1.02535         0.62684
H           1.62093         1.30875         0.14194
H           2.43163         1.55465         1.43334
O          -2.29767         1.43655         0.27944
H          -2.48167         0.46425         0.30834
H          -2.46007         1.74795         1.17814
O           0.13263         1.49825        -0.88316
H           0.10223         2.11595        -1.62406
H          -0.75027         1.57405        -0.43916
```

$(H_2O)_6$ 4194

```
18

O           2.17293         1.43957        -0.25833
H           3.06403         1.70497        -0.00013
H           2.26613         0.50357        -0.56873
O           2.20403        -1.18883        -0.87953
H           2.02413        -1.51613        -1.76923
H           1.42813        -1.48173        -0.33603
O           0.08583        -1.67893         0.73777
H           0.01783        -0.81293         1.17657
H          -0.75757        -1.74633         0.24217
O          -2.27177        -1.49033        -0.76793
H          -3.11417        -1.86223        -0.47933
H          -2.37237        -0.51963        -0.65483
O          -2.23077         1.23177        -0.24643
H          -2.11167         1.86957        -0.96103
H          -1.43427         1.33357         0.31637
O           0.04013         1.18147         1.37107
H           0.11733         1.65587         2.20767
H           0.87203         1.37677         0.86997
```

$(H_2O)_6$ 4195

```
18

O           0.74406        -1.20529        -1.33714
H           1.59616        -0.84469        -0.99614
H           0.98376        -1.81999        -2.04104
O          -0.86664         1.20781        -1.17484
H          -0.41784         0.41231        -1.51434
H          -1.71984         0.86171        -0.83984
O           0.62886         1.41881         1.03566
H           0.04506         1.48771         0.23006
H           0.56306         2.27261         1.48026
O          -0.62844        -1.24019         1.24126
H          -0.18474        -1.46479         0.40306
H          -0.19434        -0.40579         1.49326
O           2.78016         0.11211        -0.08904
H           2.16106         0.68411         0.41646
H           3.33216        -0.31169         0.57996
O          -2.91244        -0.00629         0.28756
H          -2.23494        -0.58619         0.70336
H          -3.67514        -0.57229         0.12156
```

$(H_2O)_6$ 4196

```
18

O           0.05762        -2.41498         1.07129
H           0.30222        -3.34768         1.08379
H           0.90642        -1.92818         0.94519
O           2.38772        -1.05478         0.69229
H           2.30672        -0.26788         0.10289
H           2.84922        -0.72518         1.47289
O           2.16842         1.11852        -0.93921
H           1.35912         1.66762        -0.81631
H           2.22172         0.95842        -1.88881
O          -2.17768        -1.44608        -0.15131
H          -2.22568        -1.83118        -1.03431
H          -1.36668        -1.83348         0.25319
O          -0.05838         2.60992        -0.44361
H          -0.31258         3.38922        -0.95161
H          -0.90338         2.13292        -0.26561
O          -2.38058         1.26722         0.03149
H          -2.30898         0.28582        -0.03631
H          -2.82518         1.41972         0.87409
```

$(H_2O)_6$ 4197

18

O	-2.23515	1.40378	0.82251
H	-2.34935	1.54538	1.77021
H	-2.25655	0.42508	0.71121
O	-2.18785	-1.30242	0.50051
H	-1.47275	-1.68642	-0.05879
H	-2.95655	-1.86462	0.35091
O	-0.15595	-2.36052	-0.98359
H	0.74085	-2.05742	-0.70449
H	-0.14335	-2.30032	-1.94619
O	-0.00845	2.54928	-0.25239
H	-0.26005	2.78758	-1.15259
H	-0.81925	2.14018	0.13421
O	2.31915	-1.49432	-0.23289
H	2.67645	-1.90722	0.56271
H	2.34295	-0.52742	-0.04459
O	2.28495	1.17828	0.30441
H	1.46825	1.68238	0.07941
H	3.01265	1.78878	0.13951

$(H_2O)_6$ 4197

18

O	-2.23515	1.40378	0.82251
H	-2.34935	1.54538	1.77021
H	-2.25655	0.42508	0.71121
O	-2.18785	-1.30242	0.50051
H	-1.47275	-1.68642	-0.05879
H	-2.95655	-1.86462	0.35091
O	-0.15595	-2.36052	-0.98359
H	0.74085	-2.05742	-0.70449
H	-0.14335	-2.30032	-1.94619
O	-0.00845	2.54928	-0.25239
H	-0.26005	2.78758	-1.15259
H	-0.81925	2.14018	0.13421
O	2.31915	-1.49432	-0.23289
H	2.67645	-1.90722	0.56271
H	2.34295	-0.52742	-0.04459
O	2.28495	1.17828	0.30441
H	1.46825	1.68238	0.07941
H	3.01265	1.78878	0.13951

$(H_2O)_6$ 4198

18

O	0.16151	2.68014	0.33887
H	0.15441	3.14764	1.18267
H	-0.71439	2.22824	0.29707
O	-2.37769	-1.25616	0.34227
H	-1.57149	-1.76056	0.08037
H	-2.68199	-1.68416	1.15147
O	2.37581	1.25514	-0.34393
H	2.68001	1.68134	-1.15413
H	1.57121	1.76164	-0.08123
O	-0.16139	-2.67826	-0.34043
H	0.71521	-2.22786	-0.29773
H	-0.15519	-3.14416	-1.18513
O	2.27191	-1.46176	-0.28273
H	2.88361	-1.70536	0.42227
H	2.30001	-0.47596	-0.30983
O	-2.27099	1.46124	0.28617
H	-2.88119	1.70334	-0.42063
H	-2.29929	0.47554	0.31467

$(H_2O)_6$ 4199

18

O	-1.79811	-1.11803	0.29643
H	-1.60791	-1.24303	-0.64937
H	-1.90481	-0.14133	0.33103
O	-1.49921	1.63167	-0.11147
H	-1.23721	1.33877	-1.00197
H	-0.64911	1.77147	0.34383
O	-0.60861	-0.21643	-2.21377
H	-0.54641	-0.30363	-3.17257
H	0.31869	-0.28453	-1.88357
O	1.81129	-0.36793	-0.93297
H	1.92129	0.49077	-0.49267
H	1.58999	-0.94653	-0.17997
O	0.57579	-1.27763	1.49293
H	-0.34651	-1.31923	1.11233
H	0.61399	-1.96433	2.16943
O	1.06539	1.44067	1.26373
H	1.37399	1.97167	2.00813
H	0.92749	0.53757	1.62053

BIBLIOGRAPHY

[1] Julen Munárriz, Rubén Laplaza, A. Martín Pendás, and Julia Contreras-García. A first step towards quantum energy potentials of electron pairs. *Physical Chemistry Chemical Physics*, 21(8):4215–4223, 2019. doi: 10.1039/c8cp07509c. URL `https://doi.org/10.1039/c8cp07509c`.

[2] José Manuel Guevara-Vela, Eduardo Romero-Montalvo, Víctor Arturo Mora Gómez, Rodrigo Chávez-Calvillo, Marco García-Revilla, Evelio Francisco, Ángel Martín Pendás, and Tomás Rocha-Rinza. Hydrogen bond cooperativity and anticooperativity within the water hexamer. *Physical Chemistry Chemical Physics*, 18(29):19557–19566, 2016. doi: 10.1039/c6cp00763e. URL `https://doi.org/10.1039/c6cp00763e`.

[3] Víctor Manuel Castor-Villegas, José Manuel Guevara-Vela, Wilmer E. Vallejo Narváez, Ángel Martín Pendás, Tomás Rocha-Rinza, and Alberto Fernández-Alarcón. On the strength of hydrogen bonding within water clusters on the coordination limit. *Journal of Computational Chemistry*, 41(26):2266–2277, August 2020. doi: 10.1002/jcc.26391. URL `https://doi.org/10.1002/jcc.26391`.

[4] E. Francisco A. Martín Pendás. Promelf. a ELF/IQA code (available from the authors upon request). 2001.

[5] J.R.B. Sánchez and A.G. Belmar. *La revolución química: Entre la historia y la memoria*. Col·lecció Oberta: Història. Publicacions de la Universitat de València, 2006. ISBN 9788437065496. URL `https://books.google.com.mx/books?id=5gd9HoGGShgC`.

[6] J Lee. *Concise Inorganic Chemistry*. Wiley-Blackwell, London, 5 edition, 1996.

[7] Anmol Kumar, Shridhar R. Gadre, Neetha Mohan, and Cherumuttathu H. Suresh. Lone pairs: An electrostatic viewpoint. *The Journal of Physical Chemistry A*, 118 (2):526–532, January 2014. doi: 10.1021/jp4117003. URL `https://doi.org/10.1021/jp4117003`.

[8] Justin P. Gallivan and Dennis A. Dougherty. Can lone pairs bind to a π system? the water $\cdots$ hexafluorobenzene interaction. *Organic Letters*, 1(1):103–106, May 1999. doi: 10.1021/ol990577p. URL `https://doi.org/10.1021/ol990577p`.

[9] N. A. Campbell, B. Williamson, and R. J. Heyden. *Biology: Exploring Life*. Pearson Prentice Hall, 2006. ISBN 0132508826.

[10] J. E. McMurry. *Organic Chemistry (with InfoTrac Printed Access Card)*. Brooks Cole, 2003. ISBN 0534389996.

[11] D. Voet and J. G. Voet. *Biochemistry*. Wiley, 2010. ISBN 0470570954.

[12] John A. Dean, editor. *Lange's Handbook of Chemistry*. McGraw-Hill, New York, 14th edition, 1992.

[13] R. T. Morrison and R. N. Boyd. *Organic Chemistry*. Prentice Hall, 1992. ISBN 0136400612.

[14] R.A. Serway and J.S. Faughn. *Física*. Pearson Educación, 2001. ISBN 9789702600152. URL `https://books.google.com.mx/books?id=KCvdzVRb4I4C`.

[15] CRC Handbook. *CRC Handbook of Chemistry and Physics, 88th Edition*. CRC Press, 88 edition, 2007. ISBN 0849304881. URL `http://www.amazon.com/CRC-Handbook-Chemistry-Physics-88th/dp/0849304881/ref=sr_1_5?ie=UTF8&qid=1302802093&sr=8-5`.

[16] J. D. Smith, C. D. Cappa, K. R. Wilson, R. C. Cohen, P. L. Geissler, and R. J. Saykally. Unified description of temperature-dependent hydrogen-bond rearrangements in liquid water. *Proc. Natl. Acad. Sci. USA*, 102:14171–4, 2005. ISSN 0027-8424. doi: 10.1073/pnas.0506899102.

[17] Thomas Steiner. The hydrogen bond in the solid state. *Angew. Chem. Int. Ed.*, 41:48–76, 2002. ISSN 1521-3773. doi: 10.1002/1521-3773(20020104)41:1<48::AID-ANIE48>3.0.CO;2-U. URL `http://dx.doi.org/10.1002/1521-3773(20020104)41:1<48::AID-ANIE48>3.0.CO;2-U`.

[18] Denis Quane. The reception of hydrogen bonding by the chemical community, 1920–1937. *Bull. Hist. Chem*, 7:3–13, 1990.

[19] JOEL H Hildebrand. Wendell mitchell latimer. *Biogr. Mem. Nat. Acad. Sci*, 32:224–237, 1958.

[20] Wendell M. Latimer and Worth H. Rodebush. POLARITY AND IONIZATION FROM THE STANDPOINT OF THE LEWIS THEORY OF VALENCE. *Journal of the American Chemical Society*, 42(7):1419–1433, July 1920. doi: 10.1021/ja01452a015. URL `https://doi.org/10.1021/ja01452a015`.

[21] Irving Langmuir. Types of valence. *Science*, 54(1386):59–67, July 1921. doi: 10.1126/science.54.1386.59. URL `https://doi.org/10.1126/science.54.1386.59`.

[22] Maurice L. Huggins. Atomic structure. *Science*, 55(1426):459–460, April 1922. doi: 10.1126/science.55.1426.459. URL `https://doi.org/10.1126/science.55.1426.459`.

[23] M. L. Huggins. Electronic structures of atoms. *The Journal of Physical Chemistry*, 26(7):601–625, October 1922. doi: 10.1021/j150223a001. URL `https://doi.org/10.1021/j150223a001`.

[24] Nevil Vincent Sidgwick and Robert Kenneth Callow. LXVII.—abnormal benzene derivatives. *J. Chem. Soc., Trans.*, 125(0):527–538, 1924. doi: 10.1039/ct9242500527. URL `https://doi.org/10.1039/ct9242500527`.

[25] Gastone Gilli and Paola Gilli. *The Nature of the Hydrogen Bond: Outline of a Comprehensive Hydrogen Bond Theory (International Union of Crystallography Monographs on Crystallography)*. Oxford University Press, USA, 2009. ISBN 0199558965.

[26] R. Chang. *Chemistry*. McGraw-Hill Science/Engineering/Math, 2006. ISBN 0073221031.

[27] S. Scheiner. *Hydrogen Bonding: A Theoretical Perspective (Topics in Physical Chemistry)*. Oxford University Press, USA, 1997. ISBN 019509011X.

[28] E. Arunan, G. R. Desiraju, R. A. Klein, J. Sadlej, S. Scheiner, I. Alkorta, D. C. Clary, R. H. Crabtree, J. J. Dannenberg, P. Hobza, H. G. Kjaergaard, A. C. Legon, B. Mennucci, and D. J. Nesbitt. Definition of the hydrogen bond (IUPAC Recommendations 2011). *Pure Appl. Chem.*, 83:1637–1641, 2011. ISSN 0033-4545. doi: 10.1351/PAC-REC-10-01-02. URL `http://iupac.org/publications/pac/83/8/1637/`.

[29] K. Liu and J. D. Cruzan. Water clusters. *Science*, 271:929–933, 1996. URL `http://www.sciencemag.org/content/271/5251/929.short`.

[30] O. Mó, M. Yáñez, and J. Elguero. Cooperative (nonpairwise) effects in water trimers: An ab initio molecular orbital study. *The Journal of Chemical Physics*, 97(9):6628–6638, November 1992. doi: 10.1063/1.463666. URL `https://doi.org/10.1063/1.463666`.

[31] Thom H. Dunning. Gaussian basis sets for use in correlated molecular calculations. i. the atoms boron through neon and hydrogen. *The Journal of Chemical Physics*, 90(2):1007–1023, January 1989. doi: 10.1063/1.456153. URL `https://doi.org/10.1063/1.456153`.

[32] A. Einstein. Über einen die erzeugung und verwandlung des lichtes betreffenden heuristischen gesichtspunkt. *Annalen der Physik*, 322(6):132–148, 1905. doi: 10.1002/andp.19053220607. URL `https://doi.org/10.1002/andp.19053220607`.

[33] E. Schrödinger. An undulatory theory of the mechanics of atoms and molecules. *Physical Review*, 28(6):1049–1070, December 1926. doi: 10.1103/physrev.28.1049. URL `https://doi.org/10.1103/physrev.28.1049`.

[34] Paul Adrien Maurice Dirac. The quantum theory of the electron. *Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character*, 117(778):610–624, February 1928. doi: 10.1098/rspa.1928.0023. URL `https://doi.org/10.1098/rspa.1928.0023`.

[35] Francis Halzen and Alan D. Martin. *Quarks and Leptons: An Introductory Course in Modern Particle Physics*. Wiley, 1984. ISBN 0471887412.

[36] S. W. Hawking. Black hole explosions? *Nature*, 248(5443):30–31, March 1974. doi: 10.1038/248030a0. URL `https://doi.org/10.1038/248030a0`.

[37] A. Szabo and N. S. Ostlund. *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory (Dover Books on Chemistry)*. Dover Publications, 1996. ISBN 0486691861.

[38] C. C. J. Roothaan. A study of two-center integrals useful in calculations on molecular structure. i. *The Journal of Chemical Physics*, 19(12):1445–1458, December 1951. doi: 10.1063/1.1748100. URL `https://doi.org/10.1063/1.1748100`.

[39] I. N. Levine. *Quantum Chemistry*. Prentice Hall, 1999. ISBN 8120330641.

[40] M. Moshinsky. How good is the hartree-fock approximation. *American Journal of Physics*, 36(1):52–53, January 1968. doi: 10.1119/1.1974410. URL `https://doi.org/10.1119/1.1974410`.

[41] Douglas J DeFrees, Krishnan Raghavachari, H Bernhard Schlegel, and John A Pople. Effect of electron correlation of theoretical equilibrium geometries. 2. Comparison of third-order perturbation and configuration interaction results with experiment. *Journal of the American Chemical Society*, 104(21):5576–5580, 1982.

[42] Carlos A. Jiménez-Hoyos, Thomas M. Henderson, Takashi Tsuchimochi, and Gustavo E. Scuseria. Projected hartree–fock theory. *The Journal of Chemical Physics*, 136(16):164109, April 2012. doi: 10.1063/1.4705280. URL `https://doi.org/10.1063/1.4705280`.

[43] Yang Weitao Robert G. Parr. *Density-Functional Theory of Atoms and Molecules*. Oxford University Press Inc, 1994. ISBN 978-0-19-509276-9.

[44] Hidetaka Kasai, Kasper Tolborg, Mattia Sist, Jiawei Zhang, Venkatesha R. Hathwar, Mette Ø. Filsø, Simone Cenedese, Kunihisa Sugimoto, Jacob Overgaard, Eiji Nishibori, and Bo B. Iversen. X-ray electron density investigation of chemical bonding in van der waals materials. *Nature Materials*, 17(3):249–252, February 2018. doi: 10.1038/s41563-017-0012-2. URL `https://doi.org/10.1038/s41563-017-0012-2`.

[45] P. Coppens and A. Vos. Electron density distribution in cyanuric acid. II. Neutron diffraction study at liquid nitrogen temperature and comparison of X-ray neutron diffraction results. *Acta Crystallographica Section B Structural Crystallography and Crystal Chemistry*, 27(1):146–158, January 1971. doi: 10.1107/s0567740871001808. URL `https://doi.org/10.1107/s0567740871001808`.

[46] Per-Olov Löwdin. Quantum theory of many-particle systems. i. Physical interpretations by means of density matrices, natural spin-orbitals, and convergence problems in the method of configurational interaction. *Physical Review*, 97(6):1474–1489, March 1955. doi: 10.1103/physrev.97.1474. URL `https://doi.org/10.1103/physrev.97.1474`.

[47] R. McWeeny and B. T. Sutcliffe. *Methods of Molecular Quantum Mechanics (Theoretical chemistry; a series of monographs)*. Academic Press Inc, 1969. ISBN 012486550X.

[48] M. Hazewinkel, editor. *Encyclopaedia of Mathematics*. Springer Netherlands, 1990. doi: 10.1007/978-94-009-5991-0. URL `https://doi.org/10.1007/978-94-009-5991-0`.

[49] P. Hohenberg and W. Kohn. Inhomogeneous electron gas. *Physical Review*, 136 (3B):B864–B871, November 1964. doi: 10.1103/physrev.136.b864. URL `https://doi.org/10.1103/physrev.136.b864`.

[50] W. Kohn and L. J. Sham. Self-consistent equations including exchange and correlation effects. *Physical Review*, 140(4A):A1133–A1138, November 1965. doi: 10.1103/physrev.140.a1133. URL `https://doi.org/10.1103/physrev.140.a1133`.

[51] L. H. Thomas. The calculation of atomic fields. *Mathematical Proceedings of the Cambridge Philosophical Society*, 23(5):542–548, January 1927. doi: 10.1017/s0305004100011683. URL `https://doi.org/10.1017/s0305004100011683`.

[52] Enrico Fermi. Statistical method to determine some properties of atoms. *Rend. Accad. Naz. Lincei*, 6(602-607):5, 1927.

[53] Erich Runge and E. K. U. Gross. Density-functional theory for time-dependent systems. *Physical Review Letters*, 52(12):997–1000, March 1984. doi: 10.1103/physrevlett.52.997. URL `https://doi.org/10.1103/physrevlett.52.997`.

[54] Wolfram Koch and Max C. Holthausen. *A Chemist's Guide to Density Functional Theory*. Wiley, July 2001. doi: 10.1002/3527600043. URL https://doi.org/10.1002/3527600043.

[55] J. C. Slater and James C. Phillips. Quantum Theory of Molecules and Solids vol. 4: The Self-consistent Field for Molecules and Solids. *Physics Today*, 27(12):49–50, December 1974. doi: 10.1063/1.3129035. URL https://doi.org/10.1063/1.3129035.

[56] S. H. Vosko, L. Wilk, and M. Nusair. Accurate spin-dependent electron liquid correlation energies for local spin density calculations: a critical analysis. *Canadian Journal of Physics*, 58(8):1200–1211, August 1980. doi: 10.1139/p80-159. URL https://doi.org/10.1139/p80-159.

[57] D. M. Ceperley and B. J. Alder. Ground state of the electron gas by a stochastic method. *Physical Review Letters*, 45(7):566–569, August 1980. doi: 10.1103/physrevlett.45.566. URL https://doi.org/10.1103/physrevlett.45.566.

[58] J. P. Perdew and Alex Zunger. Self-interaction correction to density-functional approximations for many-electron systems. *Physical Review B*, 23(10):5048–5079, May 1981. doi: 10.1103/physrevb.23.5048. URL https://doi.org/10.1103/physrevb.23.5048.

[59] A. D. Becke. Density-functional exchange-energy approximation with correct asymptotic behavior. *Physical Review A*, 38(6):3098–3100, September 1988. doi: 10.1103/physreva.38.3098. URL https://doi.org/10.1103/physreva.38.3098.

[60] Carlo Adamo and Vincenzo Barone. Exchange functionals with improved long-range behavior and adiabatic connection methods without adjustable parameters: The mPW and mPW1pw models. *The Journal of Chemical Physics*, 108(2):664–675, January 1998. doi: 10.1063/1.475428. URL https://doi.org/10.1063/1.475428.

[61] Chengteh Lee, Weitao Yang, and Robert G. Parr. Development of the colle-salvetti correlation-energy formula into a functional of the electron density. *Physical Review B*, 37(2):785–789, January 1988. doi: 10.1103/physrevb.37.785. URL https://doi.org/10.1103/physrevb.37.785.

[62] CF von Weizsäcker. Zur theorie der kernmassen. *Zeitschrift für Physik*, 96(7):431–458, 1935.

[63] Renato Colle and Oriano Salvetti. Approximate calculation of the correlation energy for the closed shells. *Theoretica Chimica Acta*, 37(4):329–334, 1975. doi: 10.1007/bf01028401. URL https://doi.org/10.1007/bf01028401.

[64] John P. Perdew. Density-functional approximation for the correlation energy of the inhomogeneous electron gas. *Physical Review B*, 33(12):8822–8824, June 1986. doi: 10.1103/physrevb.33.8822. URL https://doi.org/10.1103/physrevb.33.8822.

[65] Jianwei Sun, Richard C. Remsing, Yubo Zhang, Zhaoru Sun, Adrienn Ruzsinszky, Haowei Peng, Zenghui Yang, Arpita Paul, Umesh Waghmare, Xifan Wu, Michael L. Klein, and John P. Perdew. Scan: An efficient density functional yielding accurate structures and energies of diversely-bonded materials, 2015. URL https://arxiv.org/abs/1511.01089.

[66] Troy Van Voorhis and Gustavo E. Scuseria. A novel form for the exchange-correlation energy functional. *The Journal of Chemical Physics*, 109(2):400–410, July 1998. doi: 10.1063/1.476577. URL https://doi.org/10.1063/1.476577.

[67] A. Gonis, N. Kioussis, and M. Ciftan, editors. *Electron Correlations and Materials Properties*. Springer US, 1999. doi: 10.1007/978-1-4615-4715-0. URL https://doi.org/10.1007/978-1-4615-4715-0.

[68] Axel D. Becke. Density-functional thermochemistry. III. the role of exact exchange. *The Journal of Chemical Physics*, 98(7):5648–5652, April 1993. doi: 10.1063/1.464913. URL https://doi.org/10.1063/1.464913.

[69] Matthias Ernzerhof and John P. Perdew. Generalized gradient approximation to the angle- and system-averaged exchange hole. *The Journal of Chemical Physics*, 109(9):3313–3320, September 1998. doi: 10.1063/1.476928. URL https://doi.org/10.1063/1.476928.

[70] Yan Zhao and Donald G. Truhlar. The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals. *Theoretical Chemistry Accounts*, 120(1-3):215–241, July 2007. doi: 10.1007/s00214-007-0310-x. URL https://doi.org/10.1007/s00214-007-0310-x.

[71] Yan Zhao, Nathan E. Schultz, and D. G. Truhlar. Exchange-correlation functional with broad accuracy for metallic and nonmetallic compounds, kinetics, and noncovalent interactions. *The Journal of Chemical Physics*, 123(16):161103, October 2005. doi: 10.1063/1.2126975. URL https://doi.org/10.1063/1.2126975.

[72] Leonhard Euler. *Solutio problematis ad geometriam situs pertinentis*. Euler Archive - All Works, 1736.

[73] J.B. Listing. *Vorstudien zur Topologie*. Vandenhoeck und Ruprecht, 1848.

[74] Gerda Fritsch Rudolf. *The Four-Color Theorem*. Springer, 1998. ISBN 978-1-4612-1720-6.

[75] Tony Crilly. *50 cosas que hay que saber sobre matemáticas*. Ariel, 2014. ISBN 6079377640.

[76] R. F. W. Bader. *Atoms in Molecules: A Quantum Theory (International Series of Monographs on Chemistry)*. Oxford University Press, USA, 1994. ISBN 0198558651.

[77] C. F. Matta. *Applications of the Quantum theory of atoms in molecules to chemical and biochemical problems*. PhD thesis, McMaster University, 2002.

[78] Tibor S. Koritsanszky and Philip Coppens. Chemical applications of X-ray charge-density analysis. *Chemical Reviews*, 101(6):1583–1628, June 2001. doi: 10.1021/cr990112c. URL https://doi.org/10.1021/cr990112c.

[79] Todd Keith. Aimall web site, 2012. http://aim.tkgristmill.com.

[80] Friedrich W. Biegler-könig, Richard F. W. Bader, and Ting-Hua Tang. Calculation of the average properties of atoms in molecules. II. *Journal of Computational Chemistry*, 3(3):317–328, September 1982. doi: 10.1002/jcc.540030306. URL https://doi.org/10.1002/jcc.540030306.

[81] M. A. Blanco, A. Martín Pendás, and E. Francisco. Interacting quantum atoms: a correlated energy decomposition scheme based on the quantum theory of atoms in molecules. *Journal of Chemical Theory and Computation*, 1(6):1096–1109, August 2005. doi: 10.1021/ct0501093. URL https://doi.org/10.1021/ct0501093.

[82] Andreas Savin, Ove Jepsen, Jürgen Flad, Ole Krogh Andersen, Heinzwerner Preuss, and Hans Georg von Schnering. Electron localization in solid-state structures of the elements: the diamond structure. *Angewandte Chemie International Edition in English*, 31(2):187–188, February 1992. doi: 10.1002/anie.199201871. URL `https://doi.org/10.1002/anie.199201871`.

[83] A. Martín Pendás, E. Francisco, and M.A. Blanco. Electron–electron interactions between ELF basins. *Chemical Physics Letters*, 454(4-6):396–403, March 2008. doi: 10.1016/j.cplett.2008.02.029. URL `https://doi.org/10.1016/j.cplett.2008.02.029`.

[84] Peter Maxwell, Ángel Martín Pendás, and Paul L. A. Popelier. Extension of the interacting quantum atoms (IQA) approach to B3LYP level density functional theory (DFT). *Phys. Chem. Chem. Phys.*, 18:20986–21000, 2016.

[85] Hicham Fenniri, Packiarajan Mathivanan, Kenrick L. Vidale, Debra M. Sherman, Klaas Hallenga, Karl V. Wood, and Joseph G. Stowell. Helical rosette nanotubes: design, self-assembly, and characterization. *Journal of the American Chemical Society*, 123(16):3854–3855, March 2001. doi: 10.1021/ja005886l. URL `https://doi.org/10.1021/ja005886l`.

[86] Peter A Kollman. Noncovalent interactions. *Accounts of Chemical Research*, 10(10): 365–371, 1977.

[87] Julia Contreras-García, Erin R. Johnson, Shahar Keinan, Robin Chaudret, Jean-Philip Piquemal, David N. Beratan, and Weitao Yang. NCIPLOT: A program for plotting noncovalent interaction regions. *Journal of Chemical Theory and Computation*, 7(3):625–632, January 2011. doi: 10.1021/ct100641a. URL `https://doi.org/10.1021/ct100641a`.

[88] Julia Contreras-García, Weitao Yang, and Erin R. Johnson. Analysis of hydrogen-bond interaction potentials from the electron density: Integration of noncovalent interaction regions. *The Journal of Physical Chemistry A*, 115(45):12983–12990, July 2011. doi: 10.1021/jp204278k. URL `https://doi.org/10.1021/jp204278k`.

[89] Christophe Narth, Zeina Maroun, Roberto A. Boto, Robin Chaudret, Marie-Laure Bonnet, Jean-Philip Piquemal, and Julia Contreras-García. A complete NCI perspective: From new bonds to reactivity. In *Challenges and Advances in Computational Chemistry and Physics*, pages 491–527. Springer International Publishing, 2016. doi: 10.1007/978-3-319-29022-5_18. URL `https://doi.org/10.1007/978-3-319-29022-5_18`.

[90] Joseph R. Lane, Julia Contreras-García, Jean-Philip Piquemal, Benjamin J. Miller, and Henrik G. Kjaergaard. Are bond critical points really critical for hydrogen bonding? *Journal of Chemical Theory and Computation*, 9(8):3263–3266, July 2013. doi: 10.1021/ct400420r. URL `https://doi.org/10.1021/ct400420r`.

[91] Yan Zhao and Donald G. Truhlar. Density functional for spectroscopy: no long-range self-interaction error, good performance for rydberg and charge-transfer states, and better performance on average than B3LYP for ground states. *J. Phys. Chem. A*, 110(49):13126–13130, December 2006. doi: 10.1021/jp066479k. URL `https://doi.org/10.1021/jp066479k`.

[92] Rick A. Kendall, Thom H. Dunning, and Robert J. Harrison. Electron affinities of the first-row atoms revisited. systematic basis sets and wave functions. *The Journal of Chemical Physics*, 96(9):6796–6806, May 1992. doi: 10.1063/1.462569. URL `https://doi.org/10.1063/1.462569`.

[93] David E. Woon and Thom H. Dunning. Gaussian basis sets for use in correlated molecular calculations. III. the atoms aluminum through argon. *The Journal of Chemical Physics*, 98(2):1358–1371, January 1993. doi: 10.1063/1.464303. URL https://doi.org/10.1063/1.464303.

[94] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox. Gaussian~16 Revision C.01, 2016. Gaussian Inc. Wallingford CT.

[95] Fernando Jiménez-Grávalos, José Luis Casals-Sainz, Evelio Francisco, Tomás Rocha-Rinza, Ángel Martín Pendás, and José Manuel Guevara-Vela. DFT performance in the IQA energy partition of small water clusters. *Theoretical Chem. Accounts*, 139(1), November 2019. doi: 10.1007/s00214-019-2514-2. URL https://doi.org/10.1007/s00214-019-2514-2.

[96] F. Fuster S. Noury, X. Krokidis and B. Silvi. Topmod package. 1997.

[97] Roberto A. Boto, Francesca Peccati, Rubén Laplaza, Chaoyu Quan, Alessandra Carbone, Jean-Philip Piquemal, Yvon Maday, and Julia Contreras-García. NCIPLOT4: Fast, robust, and quantitative analysis of noncovalent interactions. *Journal of Chemical Theory and Computation*, 16(7):4150–4158, May 2020. doi: 10.1021/acs.jctc.0c00063. URL https://doi.org/10.1021/acs.jctc.0c00063.

[98] William Humphrey, Andrew Dalke, and Klaus Schulten. VMD – Visual Molecular Dynamics. *Journal of Molecular Graphics*, 14:33–38, 1996.

[99] Koichi Momma and Fujio Izumi. VESTA for three-dimensional visualization of crystal, volumetric and morphology data. *Journal of Applied Crystallography*, 44(6):1272–1276, October 2011. doi: 10.1107/s0021889811038970. URL https://doi.org/10.1107/s0021889811038970.

[100] Berhane Temelso, Kaye A. Archer, and George C. Shields. Benchmark structures and binding energies of small water clusters with anharmonicity corrections. *The Journal of Physical Chemistry A*, 115(43):12034–12046, October 2011. doi: 10.1021/jp2069489. URL https://doi.org/10.1021/jp2069489.

[101] Ewa Papajak, Jingjing Zheng, Xuefei Xu, Hannah R. Leverentz, and Donald G. Truhlar. Perspectives on basis sets beautiful: Seasonal plantings of diffuse basis functions. *Journal of Chemical Theory and Computation*, 7(10):3027–3034, August 2011. doi: 10.1021/ct200106a. URL https://doi.org/10.1021/ct200106a.

[102] Camelia Muñoz-Caro and Alfonso Niño. Effect of anharmonicities on the thermodynamic properties of the water dimer. *The Journal of Physical Chemistry A*, 101(22):4128–4135, May 1997. doi: 10.1021/jp9701348. URL https://doi.org/10.1021/jp9701348.

[103] T. Rocha-Rinza. *Estudio de las propiedades topológicas de la densidad electrónica de cúmulos de agua*. Tesis para obtener el título de Químico, Facultad de Química, UNAM, 2003.