



Universidad de Oviedo

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**WAVEFUNCTION ANALYSIS:  
ELECTRON POPULATIONS**

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## Introduction

In order to analyze the electron population of certain molecules it is needed to use common approximations of the electronic Schrödinger equation with quantum chemical methods to find where the electrons are placed around the atoms.

The Schrödinger equation is usually solved in stationary states that are not dependent on time, so it does not determine the state of the function, and the energy is calculated in a function dependent on the position of the nucleus. Position is solved with Gaussian type orbital functions (GTOs) using the computational program Orca, in which the output includes the different calculations of electron population and an extension to use the Quantum Theory of Atoms in Molecules (QTAIM) calculating with the AIMAll computational program.

This thesis will compare the different ways of analyzing the electron population taking into account the advantages and disadvantages of the main kinds of analysis. Calculations are done under three different basis sets: the most superficial one 6-311G\*, a triple Z basis that is cc-pVTZ and the most complete of the three chosen basis cc-pVQZ either for restricted Hartree-Fock or B3LYP methods.

## Theoretical Foundations

### History of Quantum Mechanics

Quantum mechanics is one of the principal tools for understanding the physical world, it studies matter and its interactions from a microscopic, atomic and molecular perspective. This understanding of microscopic properties leads to a further knowledge on macroscopic objects and their behavior. Quantum mechanics was born after the discovery of several inconsistencies in classical mechanics and experimental incongruencies between the classical predictions and the observed real behavior of systems.

The beginning of quantum mechanics is usually marked by the interpretation provided in 1900 of the thermal radiation spectrum emitted by a black body by Max Planck, which can be summarized in a relation that expresses the possible values of energy exchanges for a microscopic particle at a certain wavelength:

$$\Delta E = n \cdot (h \cdot \nu) \quad (1)$$

being  $h$  the Planck constant ( $6.6262 \cdot 10^{-34}$  J·s) and  $n$  an integer. Later it was proposed that it was not only the energy exchange but the energy of the particle itself that it was

in this way *quantized*. The energy is not any possible quantity, it is expressed in certain amounts that are multiples of Planck's constant, where these amounts are called quanta.

Based on this quantification of energy Albert Einstein stated that light could also be quantized in this case in particles called photons and discovered the photoelectric effect that earned him the Nobel prize in 1921.

After Rutherford's experiment in 1909, which consolidated the nuclear model of the atom, it was Niels Bohr in 1913 who rationalized simple atomic spectra by proposing that the electronic orbits around the nuclei were also quantized. This led to the different propositions that properties of atoms are given by electronic configurations, confirmed by Moseley in 1913, who ordered the elements by increasing atomic number.

In 1923 de Broglie enounced the particle-wave duality, according to which microscopic particles (as electrons) sometimes show wave behavior, which allowed Heisenberg to state his uncertainty principle, since lowering the deviation on the measurement of position makes bigger uncertainties in speed measurement and vice versa. In this period, it was also found that elementary particles possessed an intrinsic angular momentum called the spin, which led to the statement of Pauli's exclusion principle, according to which an electron cannot have the same quantum numbers as another electron placed in the same atom. These advances helped Erwin Schrödinger to formulate the first quantum mechanical calculation method with the Schrödinger wave equation (SWE),

$$H \cdot \Psi = E \cdot \Psi \quad (2)$$

being  $\Psi$  the wavefunction of the particle, a function that contains all the information that can be obtained from a system,  $E$  the energy of the system and  $H$  a linear operator called the Hamiltonian. Following progress in the area of quantum mechanics was made by improvements and approximations to solve the SWE either in a simpler way or more precisely. [1,2,3]

## The Schrödinger Wave Equation

The time dependent SWE contains the first derivative of the wavefunction, that gives all the information that could possibly be known about the system that is describing, being Quantum mechanics a probabilistic theory. For a one-particle one-dimensional system, for instance, the Copenhagen interpretation establishes that the (complex) square of the wavefunction can be understood as the probability density of finding the particle along the  $x$  axes at a certain time  $t$ .

$$|\Psi(x,t)|^2 dx \quad (3)$$

Most chemical problems involving the SWE use Hamiltonians that do not depend explicitly on time, so that the time variable can be separated in the SWE, giving rise to the time-independent SWE whose solutions are the so-called stationary states that do not depend on time. In this way, the SWE is applied to a system containing  $N$  electrons and  $M$  nuclei (working in atomic units) obtaining the time-independent Schrödinger equation [1], that is represented by:

$$\hat{H} \cdot \psi(x_1, \dots, x_N; R_1, \dots, R_M) = E \cdot \psi(x_1, \dots, x_N; R_1, \dots, R_M) \quad (4)$$

referring  $x_i$  and  $r_i$  to the spatial coordinates of electrons and the spin coordinates respectively, and  $R_i$  to the spatial coordinates of the nuclei.  $\hat{H}$  is the Hamiltonian operator, which for a molecular system can be written as:

$$\hat{H} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 - \frac{1}{2} \sum_{A=1}^M \frac{1}{M_A} \nabla_A^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{|r_i - R_A|} + \sum_{i>j}^N \frac{1}{|r_i - r_j|} + \sum_{A>B}^M \frac{Z_A Z_B}{|R_A - R_B|} \quad (5)$$

indexes  $i$  and  $j$  represent electrons and nuclei, being the first two terms the expression for the kinetic energy of electrons and nuclei, with  $\nabla_i^2$  the Laplacian operator of particle  $i$  and the final last terms the repulsive interactions of nuclei and electrons. [4]

As the Schrödinger equation cannot be solved exactly except in one-electron systems there is a series of approximations that can be taken in order to determine the solution.

## The Born-Oppenheimer Approximation

The Born-Oppenheimer (BO) approximation states that as nuclei are much heavier than the electrons the speed of the electrons is much higher, so it can be considered as a good approximation that the nucleus is fixed and the electrons move freely around it. Thus, as nuclei are considered motionless, terms of the Hamiltonian related to kinetic energy of the nuclei can be neglected and Schrödinger equation can be written just for the electronic motion and the terms involving it,

$$\hat{H}_{elec} = \hat{T} + \hat{V}_{NE} + \hat{V}_{EE} \quad (6)$$

being  $\hat{T}$  the kinetic energy of the electrons,  $\hat{V}_{EE}$  the potential of repulsion of electrons and  $\hat{V}_{NE}$  the potential of repulsion of nuclei and electron. Internuclear repulsions are also neglected because nuclei are fixed and thus, coordinates and distances remain constant; it can also be proven that a constant term does not affect the result of the Hamiltonian operator, in this way the Hamiltonian and Schrödinger equation have only the electronic terms and it is described as electronic Hamiltonian and electronic wavefunction.

From now on, the BO approximation will be taken in all calculations, so electronic subindexes and any other application of the approximation will not be mentioned. Applying this approximation one-electron problems can be solved, but for the solution of many electron systems further approximations need to be taken. [1,4]

## Approximate Methods

### The Variational Theorem

The basic idea of the variational method is the guessing of a trial wavefunction in order to have its energy minimized, the parameters used for the minimization of the energy are called variation parameters. The parameters and the trial wavefunction are the variational approximations to the exact wavefunction and its energy. In this way an upper bound for the ground-state energy of the system is calculated, being any estimated energy equal or higher than the exact wavefunction.

If the variational theorem is applied in the way it is previously explained it can only extract information about the energy of the ground-state and the wavefunction, although the variational theorem can be extended to estimate the energy of the first excited state using orthogonal normalized functions to the ground-state energy. [4,5]

### Perturbative Methods

In opposition to the variational theorem, the Hamiltonian operator can be split into a part that it is known how it can be solved (reference or unperturbed Hamiltonian) and a part that it has no known solution (perturbation). It is interesting because if the unperturbed Hamiltonian has a bigger influence in the result than the perturbation, solution can be approximated to the unperturbed Hamiltonian, or maybe the perturbation can be guessed with respect to the reference Hamiltonian. There is also the possibility of correcting the unperturbed Hamiltonian with respect to the perturbation to minimize the error. [6]

## Quantum Chemistry

Quantum chemistry is the application of quantum mechanics to chemistry. The importance of quantum chemistry has only increased in the last century for its applications in favor of the knowledge of the structure of the molecules and the atoms. The solution of Schrödinger equation has led to a better understanding of the properties of atoms and chemical bonding.

### SWE solution for the Hydrogen Atom

The hydrogen atom only consists of a proton and an electron, so assuming both particles as point masses and the Born-Oppenheimer approximation, the problem reduces to that of a single particle moving around a central force, whose interaction is given by Coulomb's Law. The interaction between proton and electron still depends only on their distance, but its quantum dynamics instead of being represented by Newton's Law as in classical mechanics, it is replaced with the time independent SWE.

As it is mentioned before, the Hydrogen atom can be taken as a particle moving around a force center and the equation is mathematically expressed in spherical polar coordinates considering a system similar to the Sun-Earth system. The Hamiltonian in this way would be:

$$\hat{H} = \frac{-1}{2m} \nabla^2 - \frac{Z}{r} \quad (7)$$

being  $m$  the electron's mass,  $Z=1$  the nuclear charge,  $r$  the distance between the electron and the proton, and  $\nabla^2$  the Laplacian operator depending on spherical polar coordinates.

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{r^2 \sin \theta} \frac{\partial^2}{\partial \varphi^2} \quad (8)$$

Other atoms or molecules can be solved using variations of this model of a particle moving around a central force in Hydrogen-like atoms in which there is only one electron around a fixed nucleus. [1,7]

### Antisymmetric Functions: Slater Determinants

For many-electron atoms it was discovered in 1929 by Slater that a determinant fulfills the antisymmetry conditions needed for these systems. Antisymmetric determinants can represent in this way the wavefunctions of molecules with more than one electron having each electron an associated function or orbital in a determinant with the same rows and columns than electrons.

Taking the simplest example of a molecule with two electrons being  $x_1$  and  $x_2$  the spatial and spin coordinates of the electron, the solution of wavefunction will be the determinant:

$$\psi(x_1, x_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \chi_1(x_1) & \chi_2(x_1) \\ \chi_1(x_2) & \chi_2(x_2) \end{vmatrix} \quad (9),$$

it can be appreciated that the determinant satisfies the antisymmetry conditions of the system, being the Slater determinant extendable to any number of electrons possible.

$$\psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(x_1) & \chi_2(x_1) & \chi_N(x_1) \\ \chi_1(x_2) & \chi_2(x_2) & \chi_N(x_2) \\ \chi_1(x_N) & \chi_2(x_N) & \chi_N(x_N) \end{vmatrix} \quad (10)$$

Something to notice in this notation is the indistinguishability of the electrons, being associated each electron to an orbital. [1,8]



## The Hartree-Fock (HF) Approximation Method

The Hartree-Fock method is the basis of the Molecular Orbital (MO) theory, which describes the electron motion by means of a single-particle function (orbital) that neglects the instantaneous movement and interactions with other electrons. It is important to consider that these orbitals are just mathematical constructs that are only an approximation to reality, actual behavior can differ from the orbitals predicted, only Hydrogen atom satisfies completely this model (or Hydrogen like atoms with only one electron).

As the only solvable SWE in Chemistry is the Hydrogenoid atom, the Hartree-Fock method is normally introduced for the next simplest atom possible in which there are only two electrons. As a starting point it is considered that the two electrons do not interact with each other in order to have a Hamiltonian separable in two, being the wavefunction the product of two Hydrogen atom wavefunctions (this is called the Hartree product). As a reminder, the approximation of non-interacting electrons is not very accurate because electrons normally interact with each other, although it is easier to start with this assumption. In this way the antisymmetry principle is not fulfilled, so coordinates must be swapped, and this is not always correct. [9]

This approximation can be restricted (Restricted Hartree-Fock, RHF) or unrestricted (Unrestricted Hartree-Fock, UHF) depending on whether the alpha and beta electrons share the same spatial orbital or not. For closed-shell systems the RHF method is used and for open-shell systems both can be used, the Restricted Open-Shell Hartree-Fock (ROHF) or the UHF, which gives well defined orbital energies.

When the HF orbitals are written as linear combinations of an otherwise fixed set of functions called the basis set, the RHF equations transform into a set of coupled algebraic equations that determine the best possible orbitals iteratively. These are known as the Roothaan-Hall equations [7]. This procedure is also known as the LCAO (Linear Combination of Atomic Orbitals). [10]

## Self-Consistent Field (SCF) Theory

As it is already seen, SWE can only be exactly solved for one electron systems, in this way approximations should be used. Based on the variational principle the "best" trial wavefunction is generated minimizing the energy using variational parameters, making trial wavefunction consist of a single Slater determinant that allows us to not consider the approximation of the electron interactions, or just the electron-electron repulsion as an average effect.

There are techniques based on the SCF to solve the Roothaan-Hall equations making the Fock matrix depend on its own solutions, solving these equations iteratively. For this resolution there are some steps until convergence is reached: calculate one and two electron integrals, generate a proper guess for MO coefficients, form an initial density matrix, form the Fock matrix, diagonalize the Fock matrix and form the new density matrix until it is close enough to the previous matrix. [7]

## Post Hartree-Fock Methods and Configuration Interaction (CI)

The basic approximation of the HF method, that takes the independence of the electron movement, is freed in what is known as post Hartree-Fock methods, where the position of the electrons depends on the immediate position of the other electrons and their interactions. We say that their motion is correlated, being zero the probability that two electrons with parallel spins are found at the same position (Pauli's principle). Correlation of these electrons has an associated energy lowering given by the energy of the exact non-relativistic energy minus the limit energy of the Hartree-Fock contribution. This is known as correlation energy.

One of these post-HF methods is the Configuration Interaction (CI) procedure, improving the description of the electronic structure building the wavefunction as a linear combination of Slater determinants. The CI function (just according to the variational method) provides the best possible approximation to the wavefunction from a given basis set, and if the number of basis function is complete enough (tends to an infinite number of functions) the CI function approaches the exact solution of the. Basis function that can be taken are the Slater-type Orbitals (STO's), usually taken for atomic calculations and Gaussian-type Orbitals (GTO's), taken for molecular calculations.

For precise results, the CI calculations need accurate trial wavefunctions for finding out the solution of many-electron systems, in this way CI calculations are tedious and need a lot of time. [1,4,7]

## Density Functional Theory (DFT)

The several nuclei in polyatomic molecules make the quantum-mechanical calculation much harder than for atoms and diatomic molecules. Density functional theory (DFT) provides another method based on a theorem that states that the energy of the ground state is a functional of the electron density ( $\rho$ ). In this way, the calculation of the wavefunction is by-passed. DFT is conceptually and computationally similar to Hartree-Fock but its results are more accurate, which makes it the most popular method at the moment, however DFT cannot systematically get better results and it fails explaining important chemical interactions as Van der Waals.

In order to explain DFT there are two key concepts to define. The electronic density: it is the multiple integral of the square of the wavefunction over the spatial coordinates and the spin of all electrons but one, determining the number of electrons per unit of volume. The electronic density is observable by X ray diffraction and it has a local maximum around the nuclei, it is also a simple mathematical function because it is always positive, it has zero asymptotes at infinity and its integral gives the total number of electrons. The functional concept: it is a function that takes as an argument other function, for instance, a function of the full electron density is called a functional of the electron density. In the case of DFT the basic idea is expressing the electronic energy as a functional of the density. [4,11]

DFT was formulated by Pierre Hohenberg and Walter Kohn in 1964, it stated that ground state energy can be expressed by a functional that only depends on the electronic density in this state. [12]

## Population Analysis

The Roothaan equations can be applied to molecular orbitals that are formed by a linear combination of atomic orbitals (LCAO-MO) in a method called Roothaan's SCF LCAO-MO method. Wavefunction calculations done by this method are certainly accurate (there are other magnitudes that can be calculated more accurately with this method like ionization potentials, other excitation energy calculations can be done but less precisely). Once a wavefunction has been obtained, the first interesting chemical outcome beyond its energy is related to how the electrons of the molecule distribute around the different nuclei, i.e. to how they concentrate in some atoms and become depleted from others. Such a partition of the total electron population into atomic (and possibly interatomic) terms is called population analysis. There are a large number of techniques that try to extract such information from the LCAO coefficients of the computed orbitals. Population analyses provide access to chemically cherished concepts such as polarity, partial atomic charges, etc. [13]

Since in the HF scheme electrons are independent, the electron density at a point in space can be obtained by adding the probability densities to find an electron at that point for all the occupied orbitals of a system. Taking one of them, expanded in a set of basis functions,

$$\phi_i = \sum_{\alpha}^{M_{basis}} c_{\alpha i} \cdot \chi_{\alpha} \quad (11)$$

$$\phi_i^2 = \sum_{\alpha\beta}^{M_{basis}} c_{\alpha i} \cdot c_{\beta i} \cdot \chi_{\alpha} \cdot \chi_{\beta} \quad (12)$$

and integrating over all occupied MO's gives the total number of electrons.

$$\sum_i^{N_{occ}} \int \phi_i^2 dr = \sum_i^{N_{occ}} \sum_{\alpha\beta}^{M_{basis}} c_{\alpha i} c_{\beta i} \int \chi_{\alpha} \chi_{\beta} dr = \sum_i^{N_{occ}} \sum_{\alpha\beta}^{M_{basis}} c_{\alpha i} c_{\beta i} S_{\alpha\beta} = N_{elec} \quad (13)$$

The sum of the product of MO coefficients and the occupation numbers is the density matrix ( $D_{\alpha\beta}$ ) and the sum over the product of the density and overlap matrices elements equals to the number of electrons of the molecule.

$$D_{\gamma\delta} = \sum_j^{N_{occ}} c_{\gamma j} \cdot c_{\delta j} \quad (14)$$

The total number of electrons of a system can then be recovered from the trace (the sum of the diagonal elements) of the product of the  $D$  and  $S$  matrices.

## Mulliken Population Analysis

It uses  $D \cdot S$  matrix product for distributing easily the electrons into atomic contributions. If we isolate all the elements in  $\text{Tr}(DS)$  that share basis functions centered at a given nucleus, then we come to a partition of  $N$  into atomic centers. This was proposed by Robert S. Mulliken, and is known as Mulliken's population analysis. Mulliken's scheme divides the contribution equally between atoms over the overlap density.

$$N_A = \sum_{\alpha \in A}^{M_{basis}} \sum_{\beta}^{M_{basis}} D_{\alpha\beta} S_{\alpha\beta} \quad (15)$$

Sometimes we refer not to  $N_A$ , but to  $Z_A - N_A$ , the net (or partial) charge of an atom.

## Loewdin Population Analysis

Loewdin analysis uses instead of the  $D \cdot S$  product the equivalent  $S^{1/2} \cdot D \cdot S^{1/2}$  matrix and it is equivalent to a population analysis of the density matrix in the orthogonalized basis set. Mulliken and Loewdin methods are particular examples of a family of populations analysis using matrix products in the form of  $S^n \cdot D \cdot S^{n-1}$ .

Mulliken and Loewdin analysis give numerically different atomic charges but there is no evidence on which of them is better, but both have several problems in comparison with the most actual types of population analysis. [7]

## Mayer Population Analysis

This analysis uses a Mulliken-like partition (in Hilbert space) using the product of matrices  $(D \cdot S)^k$  but including in this case the bond orders defined by Wiberg and István Mayer. The introduction of bond orders solves problems in dissociations of molecules such as ethene. The problem of this kind of analysis is that the Mulliken-like partitioning used limits the basis that are reasonable to select. For the systems that will be analyzed on this thesis Mayer analysis will be the same as Mulliken analysis because we will only be referring to restricted HF or DFT calculations for diatomic molecules. [14,15]

## Quantum Theory of Atoms in Molecules (QTAIM)

Once a wavefunction has been found, its chemical interpretation is far from trivial. The quantum theory of atoms in molecules (QTAIM) uses the electron density topology in the tridimensional space in order to study the chemical bond. Richard F. W. Bader stated that atoms within molecules can be isolated as three-dimensional subsystems in real space which hold a single nucleus to simplify the interpretation. Bonds between them are also defined when these regions satisfy certain order relationships.

The virial theorem relates the average kinetic energy to the negative total energy of a system with inverse square forces at equilibrium geometries. The QTAIM postulates the fulfilment of an equivalent atomic virial theorem, and warrants that if the charge distribution of an atom is identical in two different systems, it contributes identical amounts of energy in both systems, being the sum of atomic energies the total energy of the molecule. The postulation of the atomic virial theorem is confirmed because of its consequences (as Bader reports) and it is the complete quantum description of the topological properties of the atom, nevertheless even though space can be separated in regions the quantum mechanics of each subsystem requires careful consideration of the observable properties and their equation of motion. [16,17]

The QTAIM works for a more useful interpretation of the experimental electron density distribution rather than a theoretical one, in fact calculated wavefunctions contain more information than just the electron density. [18]

## Results and Discussion

The aim of this thesis is the comparison of the different basis and methods used and the statistical study of the variation of their atomic populations for the hydrides and fluorides of the elements of the second period. This study will be carried out using the ab initio, DFT and semiempirical SCF-MO computational program ORCA [19], the driver application for QTAIM calculations AIMAll [20] and the molecule editor and visualizer program Avogadro [21], all free open source, except AIMAll, that has a free trial version that does not cover several complex calculations (as  $\text{CF}_4$  and bigger molecules).

## Basis Functions

The analysis of population must be carried out using different types of basis sets to compare the difference in the result, basis are from different complexities and using different methods. The larger and the more complex the basis is the longer and the more difficult are the resulting calculations.

Two methods are used in these calculations, the RHF (explained before in the Hartree-Fock approximation) method and simple density functional calculations using the B3LYP functional, a hybrid functional that takes a part of the exact exchange in HF theory. As it is mentioned above there are some basis that show much better results for different methods, because some molecular properties make the results of some analysis decline their quality, so this comparison will be very useful. Any method will be proven with all the basis selected and the data is shown with a forced symmetry, and some calculations will be done with a wider selection of basis to establish a better comparison.

All geometry optimizations have been made with a forced optimization using the BFGS (Broyden-Fletcher-Goldfarb-Shanno) algorithm, that is an iterative method used to solve non-linear optimization problems by employing the curvature information as a starting point to get to a convergence of the iteration.

There different basis sets have been chosen :

- 6-311G\*: This basis is from the basis sets implemented by John Pople (Nobel prize winner). The basis set is the most popular among all ab initio molecular calculations, there are basis from all complexities and it is a very versatile basis set.  
As in the basis name there are three numbers it means that it is a triple-zeta basis (it contains three times as many primitives as the minimum basis), the \* means that the function is d-type polarized in the non-Hydrogen atoms, another \* would mean another type of polarization. [22]
- cc-pVTZ: It corresponds to the electron correlation consistent basis set (cc) that it is an upgrade from the Dunning basis set. The cc basis set have a similar contribution of the correlation energy for all valence electrons.  
The p indicates that the basis is polarized, the V represents that it is for only valence electrons and the TZ means that a triple-zeta basis is used.
- cc-pVQZ: cc-pVQZ basis correspond to the same basis set than cc-pVTZ but using a quadruple- zeta basis, this means that the basis employs at least four times as many functions as the minimum basis. [23]

For further discussion of evolution of other properties (such as equilibrium distance) there would be a wider selection of basis (mainly from the basis set recently explained) to have a better statistical evolution of these magnitudes.

## Detailed Analysis of two Systems with Limiting Behavior

All population analyses have been obtained with all the basis and methods explained before with the help of the computational programs already mentioned for all the hydrides and fluorides of elements of the first two periods, in this way in order to test the different basis and methods, two molecules with a very different behavior are chosen: LiH and HF, behaving the first one almost as an ionic compound and the second one as a polar covalent molecule, based on the difference of electronegativity of the atoms in the same molecule taking as a reference the Pauling electronegativity table showed below (figure 1).

	IA	IIA	IIIB	IVB	VB	VIB	VII B	VIII B	VIII B	VIII B	IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
1	H 2,2																	He
2	Li 1	Be 1,6											B 2	C 2,6	N 3	O 3,4	F 4	Ne
3	Na 0,9	Mg 1,3											Al 1,6	Si 1,9	P 2,2	S 2,6	Cl 3,2	Ar
4	K 0,8	Ca 1	Sc 1,4	Ti 1,5	V 1,6	Cr 1,7	Mn 1,6	Fe 1,8	Co 1,9	Ni 1,9	Cu 1,9	Zn 1,7	Ga 1,8	Ge 2	As 2,2	Se 2,6	Br 3	Kr 3
5	Rb 0,8	Sr 1	Y 1,2	Zr 1,3	Nb 1,6	Mo 2,2	Tc 1,9	Ru 2,2	Rh 2,3	Pd 2,2	Ag 1,9	Cd 1,7	In 1,8	Sn 1,8	Sb 2,1	Te 2,1	I 2,7	Xe 2,6
6	Cs 0,8	Ba 0,9	La 1,1	Hf 1,3	Ta 1,5	W 2,4	Re 1,9	Os 2,2	Ir 2,2	Pt 2,3	Au 2,5	Hg 2	Tl 1,6	Pb 2,3	Bi 2	Po 2	At 2,2	Rn 2,2
7	Fr 0,7	Ra 0,9	Ac 1,1															

Ce 1,1	Pr 1,1	Nd 1,1	Pm 1,1	Sm 1,2	Eu 1,2	Gd 1,2	Tb 1,1	Dy 1,2	Ho 1,2	Er 1,2	Tm 1,3	Yb 1,1	Lu 1,3
Th 1,3	Pa 1,5	U 1,4	Np 1,4	Pu 1,3	Am 1,1	Cm 1,3	Bk 1,3	Cf 1,3	Es 1,3	Fm 1,3	Md 1,3	No 1,3	Lr 1,3

Figure 1: Pauling electronegativity table. Taken from reference [24]

The study is carried out focusing on the convergence of the electron populations obtained with different methods, some basis will work better in some methods and for some kind of molecules, so the distribution of the data is going to be done in this case in the form of graphs that statistically show the variance of the results for each base and for each kind of population analysis.

**Table 1: Population analysis of LiH using RHF.**

Electron Population							
Method	Molecule	Atoms	Basis	Mulliken Analysis	Loewdin Analysis	Mayer Analysis	QTAIM
RHF	LiH	Li	6-311G*	0,3256	0,2335	0,3256	0,9108
			cc-pVTZ	0,2058	0,1562	0,2058	0,9132
			cc-pVQZ	0,3064	0,0983	0,3064	0,9138
		1 H	6-311G*	-0,3256	-0,2335	-0,3256	-0,9108
			cc-pVTZ	-0,2058	-0,1562	-0,2058	-0,9132
			cc-pVQZ	-0,3064	-0,0983	-0,3064	-0,9138

**Table 2: Population analysis of LiH using B3LYP.**

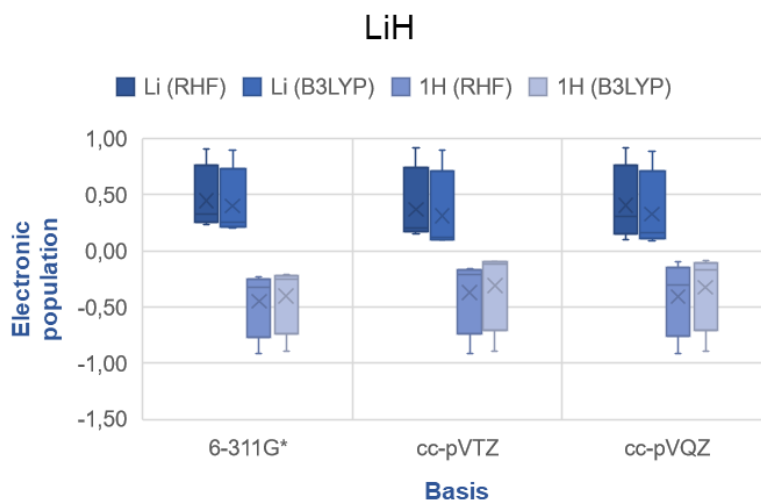
Electron Population							
Method	Molecule	Atoms	Basis	Mulliken Analysis	Loewdin Analysis	Mayer Analysis	QTAIM
B3LYP	LiH	Li	6-311G*	0,2516	0,2078	0,2516	0,8950
			cc-pVTZ	0,1011	0,1440	0,1011	0,8944
			cc-pVQZ	0,1641	0,0885	0,1641	0,8900
		1 H	6-311G*	-0,2516	-0,2078	-0,2516	-0,8950
			cc-pVTZ	-0,1011	-0,1440	-0,1011	-0,8944
			cc-pVQZ	-0,1641	-0,0885	-0,1641	-0,8900

**Table 3: Population analysis of HF using RHF.**

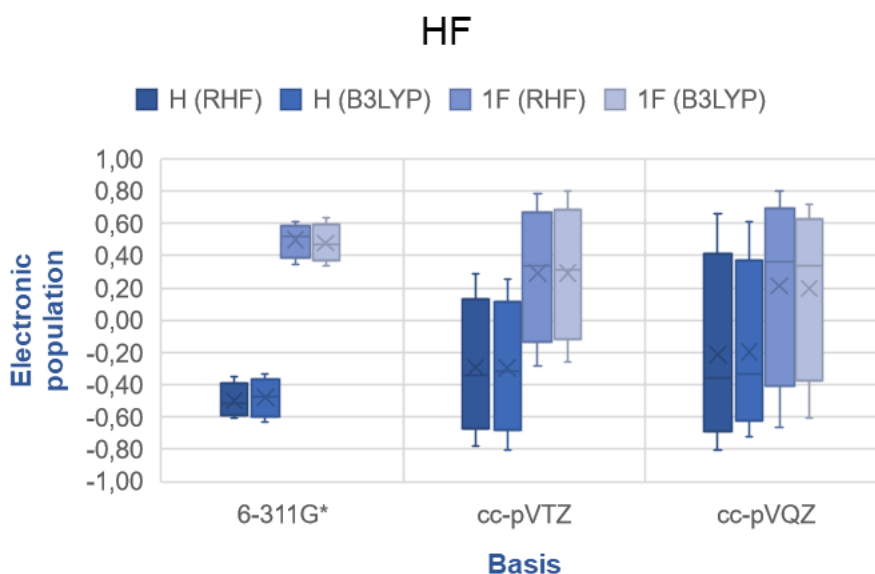
Electron Population							
Method	Molecule	Atoms	Basis	Mulliken Analysis	Loewdin Analysis	Mayer Analysis	QTAIM
RHF	HF	F	6-311G*	-0,5162	-0,3500	-0,5162	-0,6096
			cc-pVTZ	-0,3383	0,2861	-0,3383	-0,7819
			cc-pVQZ	-0,3585	0,6647	-0,3585	-0,8041
		1 H	6-311G*	0,5162	0,3500	0,5162	0,6096
			cc-pVTZ	0,3383	-0,2861	0,3383	0,7819
			cc-pVQZ	0,3585	-0,6647	0,3585	0,8041

**Table 4: Population analysis of HF using B3LYP.**

Electron Population							
Method	Molecule	Atoms	Basis	Mulliken Analysis	Loewdin Analysis	Mayer Analysis	QTAIM
B3LYP	HF	F	6-311G*	-0,4732	-0,3345	-0,4732	-0,6344
			cc-pVTZ	-0,3138	0,2575	-0,3138	-0,8041
			cc-pVQZ	-0,3363	0,6095	-0,3363	-0,7197
		1 H	6-311G*	0,4732	0,3345	0,4732	0,6344
			cc-pVTZ	0,3138	-0,2575	0,3138	0,8041
			cc-pVQZ	0,3363	-0,6095	0,3363	0,7197



**Figure 2: Comparison of electron populations depending on the basis chosen for LiH.**



**Figure 3: Comparison of electron populations depending on the basis chosen for HF.**

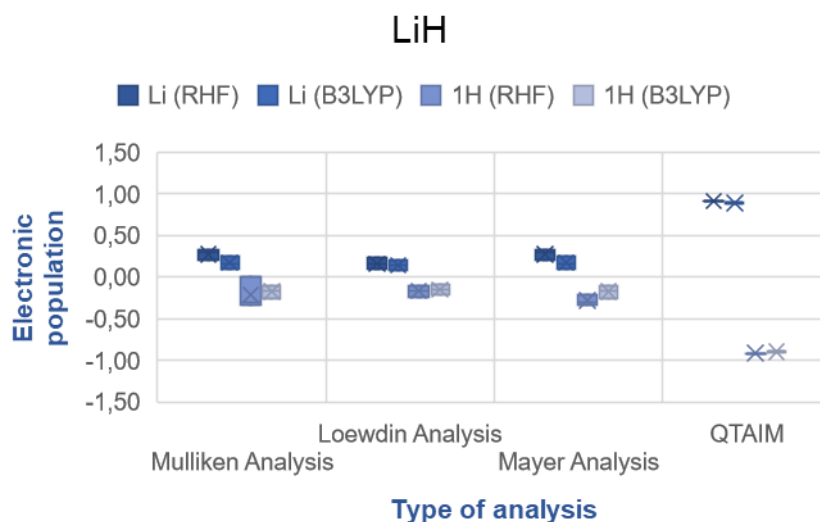
Looking at the picture of the results of the LiH it is appreciated that the results for the different basis are very similar and the only difference between them is the method used, in which the RHF gives more difference in electron population between Li and H than the B3LYP, but the variation in the electronic population from any basis is not significant. The only thing to point as a difference from the basis is that cc-pVQZ gives a closer difference between the electron population of Li and H.

In the case of HF there is only one basis that shows reasonable results, the 6-311G\* is the only one that does not give positive electron population for the Hydrogen, what would not make sense taking into account the electronegativity table (figure 1), as Fluorine is much more electronegative its electron population should be bigger than the Hydrogen one. cc-pVTZ and cc-pVQZ have an enormous variation in their results depending on the analysis used, Loewdin analysis results are the ones that makes the electron population of the Hydrogen positive (in this way Loewdin analysis for this molecule cannot be trusted), and Mulliken and Mayer analysis (in this basis have

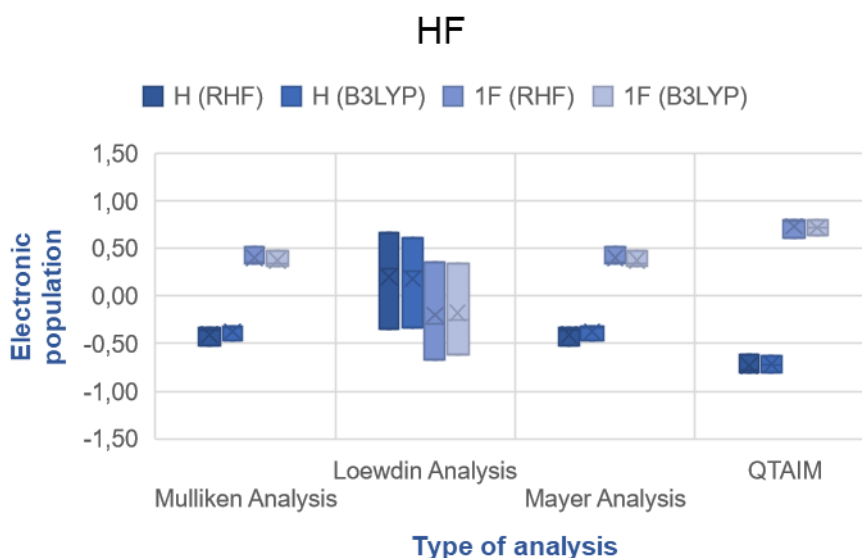


identical results) have a great difference with the QTAIM results obtained with AIMAll (tables 3 and 4).

Some general considerations for the basis comparison in molecules that show extreme behavior, taking the example of LiH as an ionic molecule and HF as a covalent one, are that the covalent character makes a huge deviation in the results for the more complex basis (electron correlation consistent ones) and that in covalent molecules the results depend strongly on the analysis performed. Results for ionic molecules are more consistent as it is show in the graphic of LiH (figure 2).



**Figure 4: Comparison of results depending on the analysis made.**



**Figure 5: Comparison of results depending on the analysis made for HF.**

For the comparison of the different kinds of population analysis (figure 4) for LiH all the analysis give reasonable results, but it is remarkable the precision of the results

of QTAIM, having a very small difference between the results depending on the basis, results for Loewdin analysis are the ones that are closer respect to the other analysis.

On the other hand, results for the same comparison of HF (figure 5) depend much more on the analysis, showing as it is already said that Loewdin analysis is not valid for the cc basis in covalent compounds, and having a little bit more of separation between the electron population of H and F for the QTAIM than for the Mayer and Mulliken analysis.

The conclusion that QTAIM works very well for ionic behavior can be taking because of the precision of measurements in LiH, while in more covalent behavior results can be also trusted but they are not as precise. Mayer and Mulliken analysis show consistent result in all molecules, but when the size of the basis increases the results for these analysis starts to show erratic behavior. Finally, Loewdin analysis depend much more on the basis used and the molecules analyzed (much worse for cc basis showing impossible results for covalent and polar compounds).

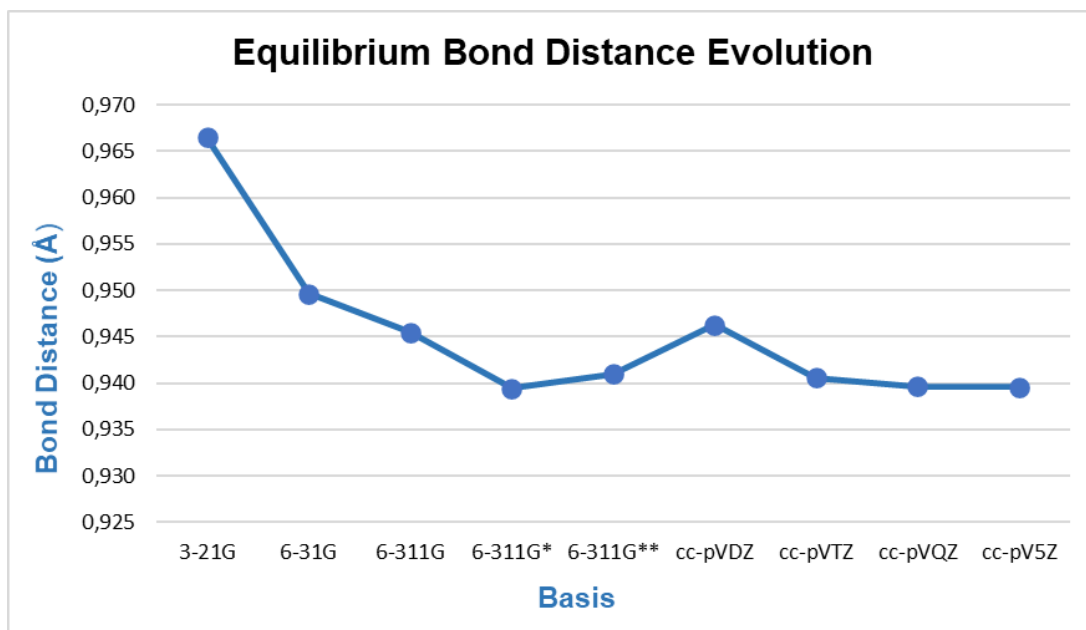
## Equilibrium Bond Distance and Angles

It is also interesting to examine how the equilibrium bond distance evolves in a molecule depending on the base used to perform the analysis, all of these calculations are optimized by the BFGS algorithm and done under the RHF approximations. Selection of basis should be wider to obtain any valid conclusion of the analysis, basis chosen are from the two basis sets explained before and arranged inside the sets by order of complexity, from less to more complex: 3-21G, 6-31G, 6-311G, 6-311G\*, 6-311G\*\*, cc-pVDZ, cc-pVTZ, cc-pVQZ, cc-pV5Z.

The data obtained will be compared with the experimental values (all checked in the NIST webbook) [23], using also as a compliment the bond angle. The molecule used will be water because the study of these magnitudes has already been done in an exact manner, the bond distance of water is 0,958 Å and the bond angle of 104,48°.

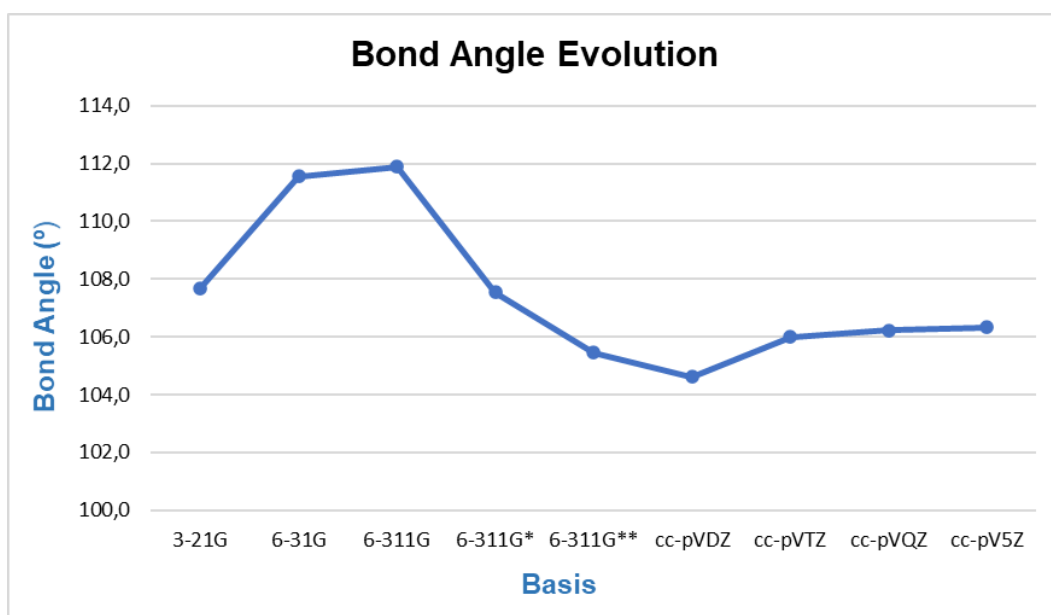
**Table 5: Bond distance and bond angle evolution for H<sub>2</sub>O for different basis.**

H <sub>2</sub> O		
Basis	Distance ( Å )	Angle (°)
3-21G	0,967	107,7
6-31G	0,950	111,5
6-311G	0,945	111,9
6-311G*	0,939	107,5
6-311G**	0,941	105,5
cc-pVDZ	0,946	104,6
cc-pVTZ	0,941	106,0
cc-pVQZ	0,940	106,2
cc-pV5Z	0,940	106,3



**Figure 6: Equilibrium distance evolution for H<sub>2</sub>O for different basis.**

As the Figure shows (figure 6), the bond distances start from a higher value in the lower complexity basis and decreases slowly until it reaches a kind of convergence in more complex basis. Is it reasonable to think that polarization in Pople's basis make a small jump with respect to the non-polarized functions, while the cc basis do not show any significant jump. Comparison with the experimental value (0,958 Å) [23] tells that even though the most complex basis have a convergence at 0.940 Å, weirdly, the most similar values are the ones obtained with less complex basis; it is due to a cancelation of successive errors, the data could improve using the B3LYP method, that will be tested afterwards.



**Figure 7: Bond angle evolution for H<sub>2</sub>O for different basis.**

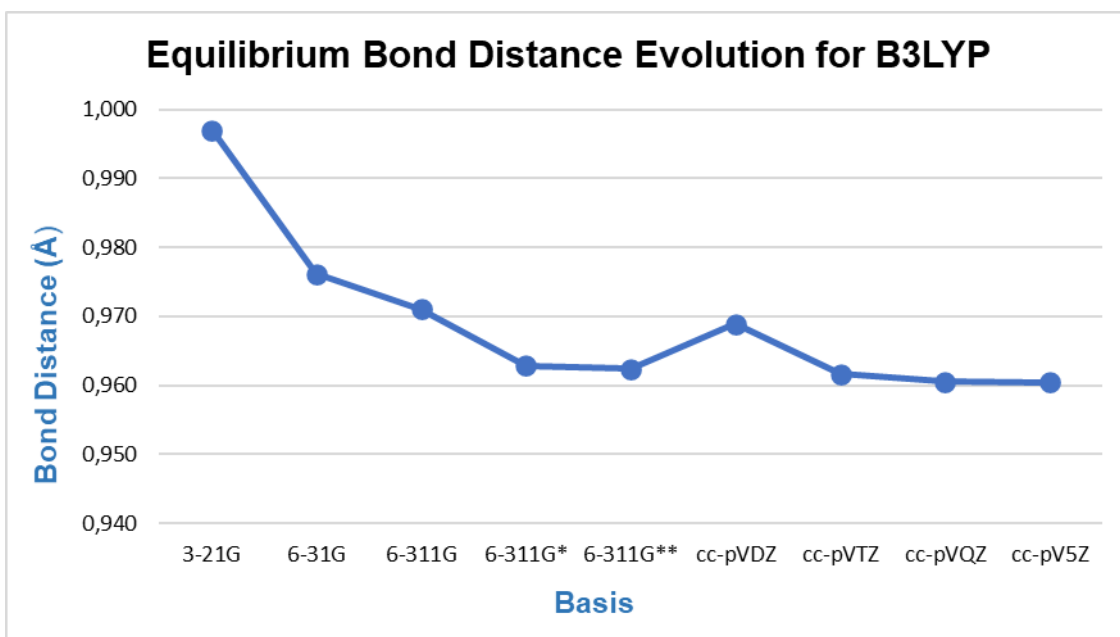
Behavior of the bond angle evolution with respect of the basis set fits what it is expected for Pople's, there is a convergence on the most complex basis (polarized ones) having a big gap between polarized basis and non-polarized basis. In the case of electron correlation consistent basis the closest value to the experimental data is the simplest base, nevertheless all values are pretty similar, the values of bond angles increase while the base gets more functions (increases complexity), values go getting further of the experimental value.

However, even though there were incongruences with the complexity of the basis used and the similarity to the experimental data it is not conclusive that the simplest basis are better for these calculations, the bond angle and the bond distance have a strong dependence on temperature and other magnitudes. Calculations are done theoretically, and it is not considered the other magnitudes dependence, in this way the results obtained cannot be taken as a certainty.

As it is mentioned above the DFT hybrid functional could improve the results and the same calculations to find out the evolution of bond distances and bond angles but in this case with the B3LYP method.

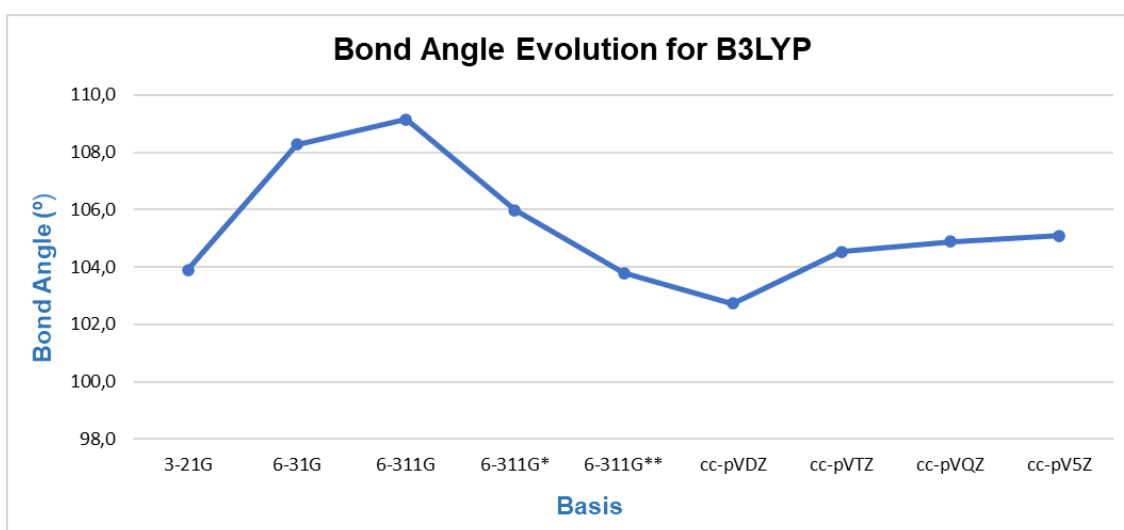
**Table 6: Bond distance and bond angle evolution for B3LYP for different basis.**

H <sub>2</sub> O for B3LYP		
Basis	Distance ( Å )	Angle (°)
3-21G	0,997	103,9
6-31G	0,976	108,3
6-311G	0,971	109,2
6-311G*	0,963	106,0
6-311G**	0,962	103,8
cc-pVDZ	0,969	102,7
cc-pVTZ	0,962	104,5
cc-pVQZ	0,961	104,9
cc-pV5Z	0,960	105,1



**Figure 8: Equilibrium bond distance evolution for H<sub>2</sub>O in B3LYP for the different basis.**

In this case it can be appreciated that the shape of the graph is the same for RHF than for B3LYP but looking at the values for B3LYP get really close to the experimental value obtained from NIST (0,958 Å) [23], so it can be stated that the DFT approximation methods are much better for the calculation of this property. The evolution is the same than the RHF and the rising complexity of the basis also improves the results as it does for the study of bond distance evolution for RHF method.



**Figure 9: Bond angle evolution for H<sub>2</sub>O in B3LYP for the different basis.**

The bond angle evolution among the different basis is similar for RHF and B3LYP and in the comparison occurs the same as the comparison of bond distances, but the bond angle values do not get the accuracy of the results for the bond distance, even though the same conclusions can be obtained because the shape of the graph of evolution is similar for both methods and the results improve with the complexity of the basis but the accuracy of the results is bigger for B3LYP.

## Evolution of net charges

The analysis of the net charges is done over all the fluorides and hydrides of the second period with RHF and B3LYP, the raw data is organized in Appendix 1 in tables (tables 16,17,18,19) and the discussion will be carried to see how the charges evolve depending on the analysis employed and on the basis used. The results and molecules that will be commented are the cases that are useful to express the differences according to the properties of the molecules (polarity, electronegativity difference...).

The most interesting cases to comment are the combinations with Bromine, because in the case of the hydride the difference in electronegativity is very small and in the case of the fluoride the difference is much higher, so for these examples it can be done an analysis of the evolution of the charges and the suitability of the population analysis and the basis depending on the differences in electronegativity. Comparison of the regression standard deviation (RSD) for measurements of the different population analysis for the same base.

**Table 7: Electron population analysis of BH<sub>3</sub> on RHF.**

Electron Population								
Method	Molecule	Atoms	Basis	Mulliken Analysis	Loewdin Analysis	Mayer Analysis	QTAIM	RSD
RHF	BH <sub>3</sub>	B	6-311G*	-0,1353	0,0181	-0,1353	1,9842	1,0367
			cc-pVTZ	-0,0857	0,1659	-0,0857	2,1327	1,0738
			cc-pVQZ	0,1730	0,2617	0,1730	2,1750	0,9871
		3 H	6-311G*	0,0451	-0,0060	0,0451	-0,6614	0,3456
			cc-pVTZ	0,0286	-0,0553	0,0286	-0,7109	0,3579
			cc-pVQZ	-0,0577	-0,0872	-0,0577	-0,7250	0,3290

**Table 8: Electron population analysis of BH<sub>3</sub> on B3LYP.**

Electron Population								
Method	Molecule	Atoms	Basis	Mulliken Analysis	Loewdin Analysis	Mayer Analysis	QTAIM	RSD
B3LYP	BH <sub>3</sub>	B	6-311G*	-0,1876	-0,0150	-0,1876	1,6882	0,9128
			cc-pVTZ	-0,1591	0,1485	-0,1591	1,8631	0,9707
			cc-pVQZ	0,1387	0,2540	0,1387	1,8671	0,8467
		3 H	6-311G*	0,0625	0,0050	0,0625	-0,5627	0,3043
			cc-pVTZ	0,0530	-0,0495	0,0530	-0,6210	0,3236
			cc-pVQZ	-0,0462	-0,0847	-0,0462	-0,6224	0,2822

The difference in electronegativity between Bromine and Hydrogen is small, so all data of charges in electron population is expected to be small. However, the Bader

charges (QTAIM analysis), that are the most trustable and the analysis that is normally closer to experimental data, are the ones with higher results and with more difference between B and H. As QTAIM is the one that can be taken as a reference what can be stated is that the electronic population of B should be positive and the electronic population of H should be negative, in this way it is shown that the basis with more functions have more acceptable results, and that the Loewdin analysis is the one that works better for small differences of electronegativity (as an opposition of its malfunction for the covalent compounds in electron correlation consistent basis as it is explained for the detailed analysis of cases with extreme behavior).

Analysis of the huge standard deviation is not that useful in this case; it only shows that Mulliken and Mayer analysis (already mentioned that for all these molecules are always the same) do not fit in any base except for the most complex one. Nevertheless, even RSD does not give a great information for this example it can be used as a comparison between the basis and which of them has the lower deviation. As a general consideration that can be extracted from this information is that the greater standard deviations are given by analysis that do not fit with certain magnitudes that have influence on the charges (as difference in electronegativity in this case).

**Table 9: Electron population analysis of BF<sub>3</sub> on RHF.**

Electron Population								
Method	Molecule	Atoms	Basis	Mulliken Analysis	Loewdin Analysis	Mayer Analysis	QTAIM	RSD
RHF	BF <sub>3</sub>	B	6-311G*	0,6900	-0,3560	0,6900	2,5173	1,1945
			cc-pVTZ	0,7002	-1,2602	0,7002	2,5992	1,5757
			cc-pVQZ	0,9931	-2,0812	0,9931	2,6172	1,9632
		3 F	6-311G*	-0,2300	0,1187	-0,2300	-0,8391	0,3982
			cc-pVTZ	-0,2334	0,4201	-0,2334	-0,8664	0,5252
			cc-pVQZ	-0,3310	0,6937	-0,3310	-0,8724	0,6544

**Table 10: Electron population analysis of BF<sub>3</sub> on B3LYP.**

Electron Population								
Method	Molecule	Atoms	Basis	Mulliken Analysis	Loewdin Analysis	Mayer Analysis	QTAIM	RSD
B3LYP	BF <sub>3</sub>	B	6-311G*	0,4942	-0,4766	0,4942	2,3528	1,1832
			cc-pVTZ	0,5205	-1,3247	0,5205	2,4639	1,5469
			cc-pVQZ	0,8353	-2,0786	0,8353	2,4819	1,8974
		3 F	6-311G*	-0,1647	0,1589	-0,1648	-0,7843	0,3944
			cc-pVTZ	-0,1735	0,4416	-0,1735	-0,8213	0,5156
			cc-pVQZ	-0,2784	0,6929	-0,2784	-0,8273	0,6325

First conclusion that is easy to obtain comparing with the other analysis is that the Loewdin analysis does not make any sense and should not be considered for any information that is given, so RSD is totally useless because Loewdin analysis data is far away from any reasonable result, and it is not even useful for a mere comparison of the difference of the data of the several analyses. A conclusion that has already been taken is that Loewdin analysis is not valid for big electronegativity differences.

The basis has not a big influence on the result of Bader charges, that are completely reasonable compared to the expected results, and these can be taken as a reference of the electron population for this molecule.

Methane is a very well-known non-polar substance with small difference of electronegativity between its atoms and it can be taken as a reference of a nonpolar molecule.

**Table 11: Electron population analysis of CH<sub>4</sub> on RHF.**

Electron Population								
Method	Molecule	Atoms	Basis	Mulliken Analysis	Loewdin Analysis	Mayer Analysis	QTAIM	RSD
RHF	CH <sub>4</sub>	C	6-311G*	-0,8348	-0,4132	-0,8348	0,3800	0,5727
			cc-pVTZ	-0,3702	0,1421	-0,3702	0,1720	0,3047
			cc-pVQZ	-0,2680	0,4397	-0,2680	0,2845	0,3693
		4 H	6-311G*	0,2087	0,1033	0,2087	-0,0950	0,1432
			cc-pVTZ	0,0926	-0,0355	0,0926	-0,0430	0,0762
			cc-pVQZ	0,0670	-0,1099	0,0670	-0,0711	0,0923

**Table 12: Electron population analysis of CH<sub>4</sub> on B3LYP.**

Electron Population								
Method	Molecule	Atoms	Basis	Mulliken Analysis	Loewdin Analysis	Mayer Analysis	QTAIM	RSD
B3LYP	CH <sub>4</sub>	C	6-311G*	-0,8393	-0,4402	-0,8393	-0,1151	0,3504
			cc-pVTZ	-0,4121	0,1228	-0,4121	0,0207	0,2825
			cc-pVQZ	-0,3642	0,4175	-0,3642	0,1329	0,3870
		4 H	6-311G*	0,2098	0,1101	0,2098	0,0288	0,0876
			cc-pVTZ	0,1030	-0,0307	0,1030	-0,0052	0,0706
			cc-pVQZ	0,0910	-0,1044	0,0911	-0,0332	0,0967

It is on non-polar molecules where the Loewdin analysis have the most concordant results with the Bader charges and where the Mulliken and Mayer analysis have poorer results, not coinciding even with the sign of the electron population expected. The evolution of charges with respect to the basis make completely sense with the complexity of the basis, the more complex the basis is the more acceptable is the result. It is important to notice that even Bader charge has a not credible result in the analysis made with 6-311G\* base in B3LYP.

As in BF<sub>3</sub> the standard deviation information is useless, but in this case, it is due to the small differences in values because of the small difference of electronegativity of the molecule, that implies very small numbers in absolute value in all the results.

The OF<sub>2</sub> is a molecule that is polar due to its geometry and can represent the characteristics of the polar molecules, but the difference in electronegativity of its atoms is not very high and will be suitable to use it as a test to prove the conclusions that are extracted from the previous molecules.



**Table 13: Electron population analysis of OF<sub>2</sub> on RHF.**

Electron Population								
Method	Molecule	Atoms	Basis	Mulliken Analysis	Loewdin Analysis	Mayer Analysis	QTAIM	RSD
RHF	OF <sub>2</sub>	O	6-311G*	0,2275	0,1304	0,2275	0,2923	0,0668
			cc-pVTZ	0,1825	0,0145	0,1825	0,3342	0,1306
			cc-pVQZ	0,1965	-0,1253	0,1965	0,3432	0,1978
		2 F	6-311G*	-0,1137	-0,0652	-0,1137	-0,1462	0,0334
			cc-pVTZ	-0,0912	-0,0073	-0,0912	-0,1671	0,0653
			cc-pVQZ	-0,0983	0,0626	-0,0983	-0,1716	0,0989

**Table 14: Electron population analysis of OF<sub>2</sub> on B3LYP.**

Electron Population								
Method	Molecule	Atoms	Basis	Mulliken Analysis	Loewdin Analysis	Mayer Analysis	QTAIM	RSD
B3LYP	OF <sub>2</sub>	O	6-311G*	0,1774	0,1171	0,1774	0,2302	0,0462
			cc-pVTZ	0,1428	0,0244	0,1428	0,2661	0,0987
			cc-pVQZ	0,1531	-0,0910	0,1531	0,2686	0,1514
		2 F	6-311G*	-0,0887	-0,0586	-0,0887	-0,1151	0,0231
			cc-pVTZ	-0,0714	-0,0122	-0,0714	-0,1330	0,0493
			cc-pVQZ	-0,0766	0,0455	-0,0766	-0,1343	0,0757

As it was already assumed the Loewdin analysis shows wrong results even in the sign of the values with less difference in electronegativity for polar molecules, in these cases in which there is a low difference in electronegativity is where Mayer and Mulliken analysis better work.

It is also remarkable that the RSD is really small and as in the case of BF<sub>3</sub> it is due to the difference of electronegativity that make electron population very low, but comparing to the Bromine fluoride it is even lower because the results are more consistent; so, even though standard deviation is not that important for the information obtained in many cases it can be compared and stated that information of OF<sub>2</sub> is more accurate than values for BF<sub>3</sub>.

## Dipole Moment

The dipole moment is also included in the output of the ORCA computational program, it is given as a vector in the three-dimensional space, but maybe it is more interesting to compare just the module of the magnitude. The molecules that will be studied are H<sub>2</sub>O, because as in the study of bond distances and bond angles it is a very well-known molecule and there is a lot of study of it, LiH and HF, because they can be representative of extreme cases because of the difference of electronegativity of their atoms (figure 1). Values obtained on calculations are going to be compared with the reference standard values at room temperature of the NIST webbook [25], and every calculation is done with RHF method.

**Table 15: Dipole moment depending on the basis for H<sub>2</sub>O.**

Dipole Moment H <sub>2</sub> O					
Basis	X Coordinate	Y Coordinate	Z Coordinate	Module (a.u.)	Module (Debyes)
3-21G	0,5423	0,7666	-0,0226	0,9393	2,3874
6-31G	0,5680	0,6918	0,4082	0,9838	2,5006
6-311G	0,5652	0,6884	0,4061	0,9789	2,4881
6-311G*	0,5263	-0,7236	0,1744	0,9116	2,3170
6-311G**	0,4856	0,5914	0,3489	0,8410	2,1377
cc-pVDZ	0,4643	0,5656	0,3337	0,8043	2,0443
cc-pVTZ	0,4515	0,5500	0,3245	0,7821	1,9878
cc-pVQZ	0,4463	0,5436	0,3207	0,7730	1,9649
cc-pV5Z	0,4445	0,5414	0,3194	0,7699	1,9570

The experimental value of H<sub>2</sub>O is 1.855 Debyes, which is lower from any value obtained with the different basis employed, although, as it is show in the data (table 6), the values follow a consistent trend slowly decreasing while complexity of basis increases. It can be assumed that, even though the results were a little bit different than the experimental value, the complexity of the basis (increasing while the number of functions of the basis increases) makes results closer to the experimental value. The trend of the evolution of the dipolar moment follows the expected behavior, but there is still room to improve because theoretical calculations do not take into account the influence of the temperature (as in bond angles and distances) that researchers have already stated that it has a great importance on the value. [26]

The values of the vector depending on the coordinates do not give much information because they depend on the position in which the molecule it is analyzed, so this could be relatively arbitrary if the position is not forced to be the same. However, the dipole moment according to the coordinates could be useful to compare the evolution of the results with the one of B3LYP.

**Table 16: Dipole moment depending on the basis for HF.**

Dipole Moment HF		
Basis	Module (a.u.)	Module (Debye)
3-21G	0,8551	2,1736
6-31G	0,9053	2,3012
6-311G	0,9148	2,3253
6-311G*	0,8505	2,1618
6-311G**	0,7789	1,9798
cc-pVDZ	0,7548	1,9185
cc-pVTZ	0,7493	1,9046
cc-pVQZ	0,7455	1,8948
cc-pV5Z	0,7448	1,8932

Studying the case of the HF it is interesting to relate the dipolar moment to the geometry, as the molecule is linear the dipolar moment vector will be zero in two dimensions, and it will only have numerical value for one coordinate.

The experimental value of dipolar moment of HF is 2,0830 Debyes, the trend of the evolution of dipolar moment with respect to the basis used is the one that can be expected, but the decreasing of the dipole moment values overtake the experimental reference; even though, this can be explained by the influence of temperature or other external magnitudes, the same that happens with water.

**Table 17: Dipole moment depending on the basis for LiH.**

Dipole Moment LiH		
Basis	Module (a.u.)	Module (Debye)
3-21G	2,3560	5,9884
6-31G	2,3681	6,0193
6-311G	2,3781	6,0446
6-311G*	2,3765	6,0405
6-311G**	2,3708	6,0261
cc-pVDZ	2,3584	5,9947
cc-pVTZ	2,3660	6,0140
cc-pVQZ	2,3673	6,0172
cc-pV5Z	2,3699	6,0237

The case of the LiH is the same case regarding the relation of dipolar moment and geometry than the HF, so the dipole moment will only be shown in one dimension. However, in this case (as it happens) it is expected to be in the opposite sign than HF because the difference of electronegativity, the electronegativity of Fluor is higher than the electronegativity of Hydrogen and this one is higher than the one of Lithium; in this way the order of the atoms has only influence on the sign of the value, and the location of atoms will conserve the module but the spatial distribution (values in coordinates) will be different.

The standard experimental value of the dipolar moment of LiH is 5,5927 Debyes, it can also be explained like in H<sub>2</sub>O y HF by the influence of the other magnitudes the inconsistency of the basis to improve the results, even so it is remarkable that the increasing of complexity of the basis does not make results closer to the reference.

**Table 18: Dipole moment depending on the basis in B3LYP for H<sub>2</sub>O.**

Dipole Moment H <sub>2</sub> O					
Basis	X Coordinate	Y Coordinate	Z Coordinate	Module (a.u.)	Module (Debyes)
3-21G	0,5074	-0,5482	0,4623	0,8784	2,2328
6-31G	0,5440	-0,5871	0,4949	0,9411	2,3920
6-311G	0,5508	-0,5944	0,5004	0,9524	2,4207
6-311G*	0,5127	-0,5533	0,4656	0,8864	2,2531
6-311G**	0,4697	-0,5069	0,4265	0,8121	2,0641
cc-pVDZ	0,4394	-0,4744	0,3997	0,7602	1,9322
cc-pVTZ	0,4352	-0,4698	0,3951	0,7525	1,9127
cc-pVQZ	0,4296	-0,4642	0,3899	0,7430	1,8886
cc-pV5Z	0,4262	-0,4612	0,3870	0,7377	1,8750

The analysis of the dipole moment of H<sub>2</sub>O in B3LYP is a very useful trial to compare the methods as it is done in the bond distances and angles, showing the same kind of results. The dipole moment in B3LYP is closer to the experimental data (1.855D), this can certify that this method is better for these associated properties. As in RHF the complexity of the base has a great influence on the values obtained, a trend followed in every calculation. The spatial coordinates of the vector can be used to compare with the RHF results, it is observable that the values are much more consistent in B3LYP; in RHF there is more deviation in the evolution of the dipole moment depending on the basis.

## General Discussion and Comparison of Basis Sets and Population Analysis

In order to compare the results of the basis sets for the different molecules it should be useful to use the information given by the regression standard deviation, but as it is already stated there are big problems with this statistic, there is some molecules with certain properties that make certain analysis completely wrong, which interferes with the information that RSD can give, but in some cases, it can be used to establish very good comparisons. This is easy to see because as it is already mentioned on the charge evolution there are many molecules, (specially very polar or with high covalent character) in which the Loewdin analysis does not give reasonable results, and for other molecules (some non-polar molecules) Mayer and Mulliken analysis does not work as it is expected. Although it cannot be obtained a lot of information of the basis with the RSD there is already bibliography about the basis, and it is known that the basis are much better depending on the number of functions they have, increasing the complexity of the basis in terms of number of functions also make the calculation of other magnitudes much more accurate.

Comparison of the different types of population analysis is easier to obtain than the comparison of basis, because even though there is a big influence on the basis employed the results obtained depending on the basis are much more consistent. QTAIM AIMAll values correspond to the expected electron population and are usually the closest to the experimental data, the Mulliken and the Mayer analysis are much more dependent on the basis used and work better for the more polar molecules (giving completely wrong results for non-polar molecules) and Loewdin analysis present decent results for the less polar molecules (poor results for very polar molecules and high covalent characters).

Approximation methods used have also influence on the results, but much less significant than basis and population analysis. The hybrid DFT method (the B3LYP) show lower results in absolute value than the RHF, it is not conclusive that one obtains better results than the other, but the results obtained employing RHF are closer to the Bader charges, but all Bader charges use to be far from other analysis' results, in this way it cannot be assumed that RHF works more precisely. Although a comparison that is much clearer is the one it is done for the other properties studied, the B3LYP shows the better results in terms of accuracy and the evolution of the data is more or less similar, so in this way the DFT approximation method would be better for these properties

## Conclusions

Having easy to compute, stable and chemically intuitive atomic electron populations is of great importance in quantum chemistry, since much of our chemical intuition rests on fuzzy concepts related to how electrons redistribute when atoms form molecules or molecules react among themselves. This endeavor is far from settled, and a large number of methods exist in the literature, each characterized by failures and successes.

The evolution in this area is totally visible, from the early 1930's where Mulliken developed the first population analysis to the latest methods used in the quantum theory of atoms in molecules. In this thesis this evolution has been examined, because those first analysis are the Loewdin, Mayer and Mulliken charges and the analysis usually employed nowadays are the AIMAll analysis that give the Bader charges, during all the thesis Bader charges are taken as a reference against traditional analysis because they are more reliable and much closer to the expected data while other charges are normally further away to those values. Traditional methods these days are in abandonment while QTAIM is the most popular.

Basic conclusions about the approximation methods used can also be extracted, because even though DFT calculations (in this case with the hybrid functional B3LYP) are commonly more accurate and so more popular, DFT fails to explain some intermolecular interactions as the Van der Waals interactions.

The most important information obtained from the calculations was the variance in the results depending on the properties of different molecules and the influence of these properties on the basis and the analysis used. Results show the impact of the difference of electronegativity and polarity of the molecules on the charges calculated and the types of calculations, this is the main point of this thesis and it is shown how for higher polarities Loewdin analysis does not work properly and for low differences in electronegativity Mulliken and Mayer analysis show incorrect results.

Population analysis resolution can be also used for the calculation of the properties seen in the thesis like bond angles, bond distances and dipolar moment. The calculation of these properties varies significantly by the basis and the methods used, and this can be taken as a meaningful evidence of the influence that can have the improvement and evolution of the population analysis.

## Bibliography

- [1] Levine, I. N., 1991. *Quantum Chemistry*. 5th ed. USA: Prentice Hall.
- [2] Weinberg, S., 1977. Notes for a History of Quantum Field Theory. *Discoveries and Interpretations: Studies in Contemporary Scholarship Volume II*, 106(4) 17-35.
- [3] Garriz, A., 2014. Historia de la química cuántica. *Educ. quím.*, 25(E1) 170-175.

- [4] Menéndez San Francisco, M., 2015. *Nuevas herramientas para el estudio del enlace químico en el espacio real*. Tesis doctoral. Oviedo: Universidad de Oviedo.
- [5] *The Variation Method*, 2006. David Sherrill [last seen 26 June 2021]. Available in <http://vergil.chemistry.gatech.edu/notes/quantrev/node28.html>
- [6] *Perturbation Theory*, 2006. David Sherrill [last seen 26 June 2021]. Available in <http://vergil.chemistry.gatech.edu/notes/quantrev/node27.html>
- [7] Jensen, F., 2006. *Introduction to Computational Chemistry*. 2nd ed. Denmark: John Wiley & Sons, Ltd.
- [8] Slater, J. C., 1929. The Theory of Complex Spectra. *The Physical Review*, 34(10) 1294-1322.
- [9] Sherrill, D., 2000. *An Introduction to Hartree-Fock Molecular Orbital Theory*. Georgia Institute of Technology, School of Chemistry and Biochemistry.
- [10] García de la Vega, J. M., Miguel, B., 2009. *Basis Sets for Computational Chemistry*. Departamento de Química Física Aplicada, Facultad de Ciencias, Universidad Autónoma de Madrid.
- [11] Bokanowski, O., Grebert, B., 1998. Utilization of Deformations in Molecular Quantum Chemistry and Application to Density Functional Theory. *International Journal of Quantum Chemistry*, 68(4).
- [12] Hohenberg, P., Kohn, W., 2001. Inhomogeneous Electron Gas. *The Physical Review B*, 136 864-971.
- [13] Paupelier, P., 2000. *Atoms in Molecules an Introduction*. Prentice Hall an imprint by Pearson Education.
- [14] Bader, R. F. W., 1994. *Atoms in Molecules a Quantum Theory*. Clarendon Press Oxford, Department of Chemistry of McMaster University, Ontario Canada.
- [15] Macchi, P., 2017. The future of Topological Analysis in Experimental Charge Density Research. *Structural Science Crystal Engineering Materials*.
- [16] Mulliken, R. S., 1955. Electronic Population Analysis on LCAO-MO Molecular Wavefunctions. *J. Chem. Phys.* 1833 (23).
- [17] Mayer, I., 2003. *Simple Theorems, Proofs, and Derivations in Quantum Chemistry*. Spring Science+Business Media New York.
- [18] Cooper, D. L., Ponec, R., Karadakov, P. B., 2020. Investigating István Mayer's "improved" definition of bond orders and free valence for correlated single-state wavefunctions. *International Journal of Quantum Chemistry*.

- [19] Neese, F., 2012. The ORCA Program System. *Wiley Interdisciplinary Reviews – Computational Molecular Science*, 2(1) 73-78.
- [20] AIMAll software package for quantitative and visual QTAIM calculations by Todd A. Keith [last seen 4 June 2021] <http://aim.tkgristmill.com/manual/aimqb/aimqb.html> .
- [21] Avogadro: Molecular Editor and Visualization by Taylor Cornell and Geoffrey Hutchinson, University of Pittsburgh, Pennsylvania 2015 [last seen 4 June 2021] <https://avogadro.cc/docs/> .
- [22] Krishnan, R., Binkley, J. S., Seeger, R., Pople, J. A., 1980. Self-consistent Molecular Orbital Methods. XX. A Basis Set for Correlated Wave Functions. *J. Chem. Phys.*, 650 (72) 650-654.
- [23] Peterson, K. A., Keshewani, M. K., Martin, J. M. L., 2014. The cc-pV5Z-F12 Basis Set: Reaching the Basis Set Limit in Explicitly Correlated Calculations. *Molecular Physics: An International Journal at the Interference Between Chemistry and Physics*.
- [24] Figure taken from online resource <https://www.quimicas.net/2015/06/ejemplos-de-electronegatividad.html> [last seen 26 June 2021]
- [25] NIST (National Institute of Standards and Technology) Chemistry Webbook, U.S. Department of Commerce <https://webbook.nist.gov/chemistry/> [last seen 22 June 2021]
- [26] Gubskaya, A. V., Kusalik, P. G., 2002. The total molecular dipole moment for liquid water. *Journal of Chemical Physics*, 117 (11).

# Appendices

## Appendix 1: Raw Data

**Table 19: Electron population for hydrides of the second period in RHF method.**

Electron Population								
Method	Molecule	Atoms	Basis	Mulliken Analysis	Loewdin Analysis	Mayer Analysis	QTAIM	RSD
RHF optimized	H <sub>2</sub> O	O	6-311G*	-0,8668	-0,5463	-0,8668	-1,1404	0,2429
			cc-pVTZ	-0,4754	0,4091	-0,4754	-1,2727	0,6871
			cc-pVQZ	-0,5124	0,9089	-0,5124	-1,2626	0,9074
		2 H	6-311G*	0,4334	0,2731	0,4334	0,5702	0,1215
			cc-pVTZ	0,2377	-0,2046	0,2377	0,6363	0,3435
			cc-pVQZ	0,2562	-0,4544	0,2562	0,6313	0,4537
		Total	6-311G*	0,0000	0,0000	0,0000	0,0000	0,0000
			cc-pVTZ	0,0000	0,0000	0,0000	-0,0001	0,0001
			cc-pVQZ	0,0000	0,0000	0,0000	0,0000	0,0000
	CH <sub>4</sub>	C	6-311G*	-0,8348	-0,4132	-0,8348	0,3800	0,5727
			cc-pVTZ	-0,3702	0,1421	-0,3702	0,1720	0,3047
			cc-pVQZ	-0,2680	0,4397	-0,2680	0,2845	0,3693
		4 H	6-311G*	0,2087	0,1033	0,2087	-0,0950	0,1432
			cc-pVTZ	0,0926	-0,0355	0,0926	-0,0430	0,0762
			cc-pVQZ	0,0670	-0,1099	0,0670	-0,0711	0,0923
		Total	6-311G*	0,0000	0,0000	0,0000	0,0000	0,0000
			cc-pVTZ	0,0000	0,0000	0,0002	0,0000	0,0001
			cc-pVQZ	0,0000	0,0000	0,0000	0,0001	0,0000
	BeH <sub>2</sub>	Be	6-311G*	0,1748	0,1865	0,1748	1,6943	0,7578
			cc-pVTZ	0,1686	0,1518	0,1686	1,7184	0,7777
			cc-pVQZ	0,4721	0,2091	0,4721	1,7276	0,6829
		2H	6-311G*	-0,0874	-0,0933	-0,0874	-0,8472	0,3789
			cc-pVTZ	-0,0843	-0,0759	-0,0843	-0,8592	0,3889
			cc-pVQZ	-0,2361	-0,1045	-0,2361	-0,8638	0,3415
		Total	6-311G*	0,0000	0,0000	0,0000	-0,0001	0,0001
			cc-pVTZ	0,0000	0,0000	0,0000	0,0000	0,0000
			cc-pVQZ	0,0000	0,0000	-0,0001	0,0000	0,0000
	LiH	Li	6-311G*	0,3256	0,2335	0,3256	0,9108	0,3110
			cc-pVTZ	0,2058	0,1562	0,2058	0,9132	0,3627
			cc-pVQZ	0,3064	0,0983	0,3064	0,9138	0,3523
		1 H	6-311G*	-0,3256	-0,2335	-0,3256	-0,9108	0,3110
			cc-pVTZ	-0,2058	-0,1562	-0,2058	-0,9132	0,3627
			cc-pVQZ	-0,3064	-0,0983	-0,3064	-0,9138	0,3523
		Total	6-311G*	0,0000	0,0000	0,0000	0,0000	0,0000
			cc-pVTZ	0,0000	0,0000	0,0000	0,0000	0,0000
			cc-pVQZ	0,0000	0,0000	0,0000	0,0000	0,0000
NH <sub>3</sub>	N	6-311G*	-1,0221	-0,5797	-1,0221	-1,0619	0,2286	



Electron Population								
Method	Molecule	Atoms	Basis	Mulliken Analysis	Loewdin Analysis	Mayer Analysis	QTAIM	RSD
			cc-pVTZ	-0,4957	0,3411	-0,4957	-1,1128	0,5969
			cc-pVQZ	-0,5219	0,7970	-0,5219	-1,1614	0,8232
		3 H	6-311G*	0,3407	0,1932	0,3407	0,3540	0,0762
			cc-pVTZ	0,1652	-0,1137	0,1652	0,3709	0,1990
			cc-pVQZ	0,1740	-0,2657	0,1740	0,3871	0,2744
		Total	6-311G*	0,0000	0,0000	0,0000	0,0000	0,0000
			cc-pVTZ	0,0000	0,0000	0,0000	0,0000	0,0000
			cc-pVQZ	0,0000	0,0000	0,0000	0,0000	0,0000
		BH <sub>3</sub>	B	6-311G*	-0,1353	0,0181	-0,1353	1,9842
	cc-pVTZ			-0,0857	0,1659	-0,0857	2,1327	1,0738
	cc-pVQZ			0,1730	0,2617	0,1730	2,1750	0,9871
	3 H		6-311G*	0,0451	-0,0060	0,0451	-0,6614	0,3456
			cc-pVTZ	0,0286	-0,0553	0,0286	-0,7109	0,3579
			cc-pVQZ	-0,0577	-0,0872	-0,0577	-0,7250	0,3290
	Total		6-311G*	0,0000	0,0000	0,0000	0,0000	0,0000
			cc-pVTZ	0,0000	0,0000	0,0000	0,0000	0,0000
			cc-pVQZ	0,0000	0,0000	0,0000	0,0000	0,0000
	HF	F	6-311G*	-0,5162	-0,3500	-0,5162	-0,6096	0,1081
			cc-pVTZ	-0,3383	0,2861	-0,3383	-0,7819	0,4391
			cc-pVQZ	-0,3585	0,6647	-0,3585	-0,8041	0,6224
		1 H	6-311G*	0,5162	0,3500	0,5162	0,6096	0,1081
			cc-pVTZ	0,3383	-0,2861	0,3383	0,7819	0,4391
			cc-pVQZ	0,3585	-0,6647	0,3585	0,8041	0,6224
		Total	6-311G*	0,0000	0,0000	0,0000	0,0000	0,0000
			cc-pVTZ	0,0000	0,0000	0,0000	0,0000	0,0000
			cc-pVQZ	0,0000	0,0000	0,0000	0,0000	0,0000

Table 20: Electron population for hydrides of the second period in B3LYP method.

Electron Population								
Method	Molecule	Atoms	Basis	Mulliken Analysis	Loewdin Analysis	Mayer Analysis	QTAIM	RSD
B3LYP optimized	H <sub>2</sub> O	O	6-311G*	-0,7954	-0,5248	-0,7954	-1,0228	0,2037
			cc-pVTZ	-0,4296	0,3716	-0,4296	-1,1203	0,6099
			cc-pVQZ	-0,4813	0,8430	-0,4813	-1,1341	0,8301
		2 H	6-311G*	0,3977	0,2624	0,3977	0,5114	0,1018
			cc-pVTZ	0,2148	-0,1858	0,2148	0,5602	0,3050
			cc-pVQZ	0,2407	-0,4215	0,2407	0,5671	0,4151
		Total	6-311G*	0,0000	0,0000	0,0000	0,0000	0,0000
			cc-pVTZ	0,0000	0,0000	0,0000	0,0000	0,0000
			cc-pVQZ	0,0000	0,0000	0,0000	0,0000	0,0000
	CH <sub>4</sub>	C	6-311G*	-0,8393	-0,4402	-0,8393	-0,1151	0,3504
			cc-pVTZ	-0,4121	0,1228	-0,4121	0,0207	0,2825

Electron Population									
Method	Molecule	Atoms	Basis	Mulliken Analysis	Loewdin Analysis	Mayer Analysis	QTAIM	RSD	
		4 H	cc-pVQZ	-0,3642	0,4175	-0,3642	0,1329	0,3870	
			6-311G*	0,2098	0,1101	0,2098	0,0288	0,0876	
			cc-pVTZ	0,1030	-0,0307	0,1030	-0,0052	0,0706	
		Total	cc-pVQZ	0,0910	-0,1044	0,0911	-0,0332	0,0967	
			6-311G*	0,0000	0,0000	0,0000	0,0000	0,0000	
			cc-pVTZ	0,0000	0,0000	0,0000	0,0001	0,0000	
		BeH <sub>2</sub>	Be	6-311G*	0,1316	0,1679	0,1316	1,6434	0,7500
				cc-pVTZ	-0,0025	0,1286	-0,0025	1,6565	0,8100
				cc-pVQZ	0,2669	0,1923	0,2669	1,6630	0,7114
	2 H		6-311G*	-0,0658	-0,0840	-0,0658	-0,8217	0,3750	
			cc-pVTZ	0,0013	-0,0643	0,0013	-0,8283	0,4050	
			cc-pVQZ	-0,1335	-0,0961	-0,1335	-0,8315	0,3557	
	Total		6-311G*	0,0000	0,0000	0,0000	0,0000	0,0000	
			cc-pVTZ	0,0000	0,0000	0,0000	0,0000	0,0000	
			cc-pVQZ	0,0000	0,0000	0,0000	0,0000	0,0000	
	LiH	Li	6-311G*	0,2516	0,2078	0,2516	0,8950	0,3296	
			cc-pVTZ	0,1011	0,1440	0,1011	0,8944	0,3900	
			cc-pVQZ	0,1641	0,0885	0,1641	0,8900	0,3772	
		1 H	6-311G*	-0,2516	-0,2078	-0,2516	-0,8950	0,3296	
			cc-pVTZ	-0,1011	-0,1440	-0,1011	-0,8944	0,3900	
			cc-pVQZ	-0,1641	-0,0885	-0,1641	-0,8900	0,3772	
		Total	6-311G*	0,0000	0,0000	0,0000	0,0000	0,0000	
			cc-pVTZ	0,0000	0,0000	0,0000	0,0000	0,0000	
			cc-pVQZ	0,0000	0,0000	0,0000	0,0000	0,0000	
	NH <sub>3</sub>	N	6-311G*	-0,9622	-0,5701	-0,9622	-0,9788	0,1990	
			cc-pVTZ	-0,4779	0,3114	-0,4779	-0,9951	0,5391	
			cc-pVQZ	-0,5542	0,7463	-0,5542	-1,0496	0,7691	
		3 H	6-311G*	0,3207	0,1900	0,3208	0,3259	0,0663	
			cc-pVTZ	0,1593	-0,1038	0,1593	0,3317	0,1797	
			cc-pVQZ	0,1847	-0,2488	0,1847	0,3499	0,2564	
		Total	6-311G*	0,0000	0,0000	0,0001	-0,0010	0,0005	
			cc-pVTZ	0,0000	0,0000	-0,0001	0,0001	0,0001	
			cc-pVQZ	0,0000	0,0000	0,0000	0,0000	0,0000	
	BH <sub>3</sub>	B	6-311G*	-0,1876	-0,0150	-0,1876	1,6882	0,9128	
			cc-pVTZ	-0,1591	0,1485	-0,1591	1,8631	0,9707	
			cc-pVQZ	0,1387	0,2540	0,1387	1,8671	0,8467	
		3 H	6-311G*	0,0625	0,0050	0,0625	-0,5627	0,3043	
			cc-pVTZ	0,0530	-0,0495	0,0530	-0,6210	0,3236	
			cc-pVQZ	-0,0462	-0,0847	-0,0462	-0,6224	0,2822	
		Total	6-311G*	0,0000	0,0000	0,0000	0,0000	0,0000	
			cc-pVTZ	0,0000	0,0000	-0,0001	0,0000	0,0000	
			cc-pVQZ	0,0000	0,0000	0,0000	0,0000	0,0000	

Electron Population								
Method	Molecule	Atoms	Basis	Mulliken Analysis	Loewdin Analysis	Mayer Analysis	QTAIM	RSD
	HF	F	6-311G*	-0,4732	-0,3345	-0,4732	-0,6344	0,1226
			cc-pVTZ	-0,3138	0,2575	-0,3138	-0,8041	0,4340
			cc-pVQZ	-0,3363	0,6095	-0,3363	-0,7197	0,5664
		1 H	6-311G*	0,4732	0,3345	0,4732	0,6344	0,1226
			cc-pVTZ	0,3138	-0,2575	0,3138	0,8041	0,4340
			cc-pVQZ	0,3363	-0,6095	0,3363	0,7197	0,5664
		Total	6-311G*	0,0000	0,0000	0,0000	0,0000	0,0000
			cc-pVTZ	0,0000	0,0000	0,0000	0,0000	0,0000
			cc-pVQZ	0,0000	0,0000	0,0000	0,0000	0,0000

Table 21: Electron population for fluorides of the second period in RHF method.

Electron Population								
Method	Molecule	Atoms	Basis	Mulliken Analysis	Loewdin Analysis	Mayer Analysis	QTAIM	RSD
RHF optimized	LiF	Li	6-311G*	0,6923	0,2782	0,6923	0,9374	0,2735
			cc-pVTZ	0,5880	0,0372	0,5880	0,9340	0,3708
			cc-pVQZ	0,6044	-0,4176	0,6044	0,9395	0,5884
		1 F	6-311G*	-0,6923	-0,2782	-0,6923	-0,9374	0,2735
			cc-pVTZ	-0,5880	-0,0372	-0,5880	-0,9340	0,3708
			cc-pVQZ	-0,6044	0,4176	-0,6044	-0,9395	0,5884
		Total	6-311G*	0,0000	0,0000	0,0000	0,0000	0,0000
			cc-pVTZ	0,0000	0,0000	0,0000	0,0000	0,0000
			cc-pVQZ	0,0000	0,0000	0,0000	0,0000	0,0000
	BeF <sub>2</sub>	Be	6-311G*	0,9283	-0,0763	0,9283	1,7766	0,7578
			cc-pVTZ	0,6917	-0,7787	0,6917	1,8041	1,0595
			cc-pVQZ	0,9339	-1,3829	0,9338	1,8103	1,3683
		2 F	6-311G*	-0,4642	0,0382	-0,4642	-0,8883	0,3789
			cc-pVTZ	-0,3459	0,3894	-0,3459	-0,9020	0,5297
			cc-pVQZ	-0,4669	0,6915	-0,4669	-0,9052	0,6842
		Total	6-311G*	0,0000	0,0000	-0,0001	0,0000	0,0000
			cc-pVTZ	0,0000	0,0000	-0,0001	0,0001	0,0001
			cc-pVQZ	0,0000	0,0000	0,0000	-0,0001	0,0000
	BF <sub>3</sub>	B	6-311G*	0,6900	-0,3560	0,6900	2,5173	1,1945
			cc-pVTZ	0,7002	-1,2602	0,7002	2,5992	1,5757
			cc-pVQZ	0,9931	-2,0812	0,9931	2,6172	1,9632
		3 F	6-311G*	-0,2300	0,1187	-0,2300	-0,8391	0,3982
			cc-pVTZ	-0,2334	0,4201	-0,2334	-0,8664	0,5252
			cc-pVQZ	-0,3310	0,6937	-0,3310	-0,8724	0,6544
		Total	6-311G*	0,0000	0,0000	0,0000	0,0000	0,0000
			cc-pVTZ	0,0000	0,0000	0,0000	0,0000	0,0000
			cc-pVQZ	0,0000	0,0000	0,0001	0,0000	0,0001
CF <sub>4</sub>	C	6-311G*	1,0691	0,2035	1,0691	2,5594	0,9785	
		cc-pVTZ	0,7406	-0,6064	0,7406	2,8259	1,4173	

Electron Population									
Method	Molecule	Atoms	Basis	Mulliken Analysis	Loewdin Analysis	Mayer Analysis	QTAIM	RSD	
		4 F	cc-pVQZ	1,0075	-1,3723	1,0075		1,3740	
			6-311G*	-0,2673	-0,0509	-0,2673	-0,6399	0,2446	
			cc-pVTZ	-0,1851	0,1516	-0,1851	-0,7065	0,3543	
		Total	cc-pVQZ	-0,2519	0,3431	-0,2519		0,3435	
			6-311G*	0,0000	0,0000	0,0000	-0,0001	0,0000	
			cc-pVTZ	0,0000	0,0000	0,0001	-0,0001	0,0001	
		NF <sub>3</sub>	N	6-311G*	0,6388	0,1938	0,6388	1,0713	0,3583
				cc-pVTZ	0,4782	-0,2349	0,4782	1,1498	0,5654
				cc-pVQZ	0,4831	-0,6457	0,4831	1,1918	0,7599
	3 F		6-311G*	-0,2129	-0,0646	-0,2130	-0,3571	0,1194	
			cc-pVTZ	-0,1594	0,0783	-0,1594	-0,3832	0,1885	
			cc-pVQZ	-0,1610	0,2152	-0,1610	-0,3972	0,2533	
	Total		6-311G*	0,0000	0,0000	-0,0001	0,0001	0,0001	
			cc-pVTZ	0,0000	0,0000	0,0001	0,0002	0,0001	
			cc-pVQZ	0,0000	0,0000	0,0001	0,0002	0,0001	
	OF <sub>2</sub>	O	6-311G*	0,2275	0,1304	0,2275	0,2923	0,0668	
			cc-pVTZ	0,1825	0,0145	0,1825	0,3342	0,1306	
			cc-pVQZ	0,1965	-0,1253	0,1965	0,3432	0,1978	
		2 F	6-311G*	-0,1137	-0,0652	-0,1137	-0,1462	0,0334	
			cc-pVTZ	-0,0912	-0,0073	-0,0912	-0,1671	0,0653	
			cc-pVQZ	-0,0983	0,0626	-0,0983	-0,1716	0,0989	
		Total	6-311G*	0,0000	0,0000	0,0001	-0,0001	0,0001	
			cc-pVTZ	0,0000	0,0000	0,0001	0,0000	0,0000	
			cc-pVQZ	0,0000	0,0000	-0,0001	0,0000	0,0001	

Table 22: Electron population for fluorides of the second period in B3LYP method.

Electron Population								
Method	Molecule	Atoms	Basis	Mulliken Analysis	Loewdin Analysis	Mayer Analysis	QTAIM	RSD
B3LYP optimized	LiF	Li	6-311G*	0,5622	0,1820	0,5622	0,9132	0,2986
			cc-pVTZ	0,4471	-0,0518	0,4471	0,9242	0,3985
			cc-pVQZ	0,4732	-0,4735	0,4732	0,9185	0,5864
		1 F	6-311G*	-0,5622	-0,1820	-0,5622	-0,9132	0,2986
			cc-pVTZ	-0,4471	0,0518	-0,4471	-0,9242	0,3985
			cc-pVQZ	-0,4732	0,4735	-0,4732	-0,9185	0,5864
		Total	6-311G*	0,0000	0,0000	0,0000	0,0000	0,0000
			cc-pVTZ	0,0000	0,0000	0,0000	0,0000	0,0000
			cc-pVQZ	0,0000	0,0000	0,0000	0,0000	0,0000
	BeF <sub>2</sub>	Be	6-311G*	0,6749	-0,2146	0,6749	1,7147	0,7888
			cc-pVTZ	0,4903	-0,8625	0,4903	1,7505	1,0671
			cc-pVQZ	0,8327	-1,4069	0,8327	1,7539	1,3453

Electron Population									
Method	Molecule	Atoms	Basis	Mulliken Analysis	Loewdin Analysis	Mayer Analysis	QTAIM	RSD	
		2 F	6-311G*	-0,3374	0,1073	-0,3375	-0,8574	0,3944	
			cc-pVTZ	-0,2451	0,4312	-0,2452	-0,8753	0,5335	
			cc-pVQZ	-0,4164	0,7034	-0,4164	-0,8770	0,6727	
		Total	6-311G*	0,0000	0,0000	0,0000	-0,0001	0,0001	
			cc-pVTZ	0,0000	0,0000	0,0000	0,0000	0,0000	
			cc-pVQZ	0,0000	-0,0001	-0,0001	-0,0001	0,0000	
		BF <sub>3</sub>	B	6-311G*	0,4942	-0,4766	0,4942	2,3528	1,1832
				cc-pVTZ	0,5205	-1,3247	0,5205	2,4639	1,5469
				cc-pVQZ	0,8353	-2,0786	0,8353	2,4819	1,8974
	3 F		6-311G*	-0,1647	0,1589	-0,1648	-0,7843	0,3944	
			cc-pVTZ	-0,1735	0,4416	-0,1735	-0,8213	0,5156	
			cc-pVQZ	-0,2784	0,6929	-0,2784	-0,8273	0,6325	
	Total		6-311G*	0,0000	0,0000	-0,0001	0,0000	0,0000	
			cc-pVTZ	0,0000	0,0000	0,0000	0,0000	0,0000	
			cc-pVQZ	0,0000	0,0000	0,0000	-0,0001	0,0000	
	CF <sub>4</sub>	C	6-311G*	0,7932	0,0746	0,7932	1,9080	0,7572	
			cc-pVTZ	0,5724	-0,6700	0,5724	2,1195	1,1422	
			cc-pVQZ	0,8012	-1,3389	0,8012		1,2356	
		4 F	6-311G*	-0,1983	-0,0186	-0,1983	-0,4770	0,1893	
			cc-pVTZ	-0,1431	0,1675	-0,1431	-0,5299	0,2856	
			cc-pVQZ	-0,2003	0,3347	-0,2003		0,3089	
		Total	6-311G*	0,0000	0,0000	0,0000	0,0000	0,0000	
			cc-pVTZ	0,0000	0,0000	0,0000	-0,0001	0,0000	
			cc-pVQZ	0,0000	0,0000	0,0000	0,0000	0,0000	
	NF <sub>3</sub>	N	6-311G*	0,4619	0,1848	0,4619	0,7868	0,2461	
			cc-pVTZ	0,3550	-0,1894	0,3550	0,8599	0,4285	
			cc-pVQZ	0,3650	-0,5397	0,3650	0,8912	0,5943	
		3 F	6-311G*	-0,1540	-0,0616	-0,1540	-0,2623	0,0821	
			cc-pVTZ	-0,1183	0,0631	-0,1183	-0,2866	0,1428	
			cc-pVQZ	-0,1217	0,1799	-0,1216	-0,2970	0,1981	
		Total	6-311G*	0,0000	0,0000	0,0000	-0,0001	0,0001	
			cc-pVTZ	0,0000	0,0000	0,0000	0,0001	0,0000	
			cc-pVQZ	0,0000	0,0000	0,0001	0,0001	0,0001	
	OF <sub>2</sub>	O	6-311G*	0,1774	0,1171	0,1774	0,2302	0,0462	
			cc-pVTZ	0,1428	0,0244	0,1428	0,2661	0,0987	
			cc-pVQZ	0,1531	-0,0910	0,1531	0,2686	0,1514	
		2 F	6-311G*	-0,0887	-0,0586	-0,0887	-0,1151	0,0231	
			cc-pVTZ	-0,0714	-0,0122	-0,0714	-0,1330	0,0493	
			cc-pVQZ	-0,0766	0,0455	-0,0766	-0,1343	0,0757	
		Total	6-311G*	0,0000	0,0000	0,0000	0,0000	0,0000	
			cc-pVTZ	0,0000	0,0000	0,0001	0,0001	0,0001	
			cc-pVQZ	0,0000	0,0000	-0,0001	0,0001	0,0001	

## Appendix 2: xyz Files with Equilibrium Geometries (Orca Outputs)

All coordinates in Angstroms.

- BeF<sub>2</sub> in 6-311G\* for RHF  
3  
Coordinates from ORCA-job bef2  
Be -1.40408107572612 4.92740744177771 0.00000311609412  
F -0.05657280635402 4.68126759642405 -0.00000237000157  
F -2.75158611791984 5.17356496179824 -0.00000074609255
- BeF<sub>2</sub> in 6-311G\* for B3LYP  
3  
Coordinates from ORCA-job bef2b3lyp  
Be -1.40407338537644 4.92745084792810 0.00001330709486  
F -0.04410983845261 4.68019707853060 0.00002050636946  
F -2.76405677617094 5.17459207354127 -0.00003381346432
- BeF<sub>2</sub> in cc-pVQZ for RHF  
3  
Coordinates from ORCA-job bef2lar  
Be -1.40407861543624 4.92742178178188 -0.00002770223658  
F -0.06477822099571 4.68295445611364 0.00000724703295  
F -2.74338316356804 5.17186376210446 0.00002045520363
- BeF<sub>2</sub> in cc-pVQZ for B3LYP  
3  
Coordinates from ORCA-job bef2larb3lyp  
Be -1.40407706047045 4.92743744115339 -0.00000439559775  
F -0.05057091822053 4.68147551768448 0.00040396664653  
F -2.75759202130902 5.17332704116211 -0.00039957104878
- BeF<sub>2</sub> in cc-pVTZ for RHF  
3  
Coordinates from ORCA-job bef2med  
Be -1.40408031074581 4.92741165310169 0.00000174772487  
F -0.06173490052594 4.68171158993232 -0.00000170601647  
F -2.74642478872824 5.17311675696598 -0.00000004170840
- BeF<sub>2</sub> in cc-pVTZ for B3LYP  
3  
Coordinates from ORCA-job bef2med  
Be -1.40408031074581 4.92741165310169 0.00000174772487  
F -0.06173490052594 4.68171158993232 -0.00000170601647  
F -2.74642478872824 5.17311675696598 -0.00000004170840
- BeH<sub>2</sub> in 6-311G\* for RHF  
3  
Coordinates from ORCA-job beh2  
Be -2.67072999999883 1.50435000926174 -0.00000000932704

- |   |                   |                  |                  |
|---|-------------------|------------------|------------------|
| H | -1.34194087961128 | 1.50434999536913 | 0.00000000466352 |
| H | -3.99951912038989 | 1.50434999536913 | 0.00000000466352 |
- BeH<sub>2</sub> in cc-pVQZ for RHF
    - 3
    - Coordinates from ORCA-job beh2lar

Be	-2.24055000011387	3.07175001029638	-0.00000001037010
H	-0.91552819873683	3.07174999485181	0.00000000518505
H	-3.56557180114930	3.07174999485181	0.00000000518505
  - BeH<sub>2</sub> in cc-pVTZ for RHF
    - 3
    - Coordinates from ORCA-job beh2med

Be	-1.20092999979027	2.11689998170490	-0.00000001840675
H	0.12568417170911	2.11690000914755	0.00000000920338
H	-2.52754417191884	2.11690000914755	0.00000000920338
  - BF<sub>3</sub> in 6-311G\* for RHF
    - 4
    - Coordinates from ORCA-job bf3

B	1.32192245444438	2.99518241267016	-0.00000000000007
F	2.60638531841885	2.81242681182149	0.00000000000002
F	0.52141987071969	1.97418293891760	0.00000000000002
F	0.83796235641709	4.19893783659074	0.00000000000002
  - BF<sub>3</sub> in 6-311G\* for B3LYP
    - 4
    - Coordinates from ORCA-job bf3b3lyp

B	1.32206573456518	2.99504863577074	-0.00000000971905
F	2.62535759350194	2.80985285874870	0.00000000324080
F	0.50949551434351	1.95943721017501	0.00000000323975
F	0.83077115758937	4.21639129530555	0.00000000323850
  - BF<sub>3</sub> in cc-pVQZ for RHF
    - 4
    - Coordinates from ORCA-job bf3lar

B	1.32192247960085	2.99518245945748	-0.00000000000007
F	2.60245766206279	2.81298558496461	0.00000000000002
F	0.52386769140996	1.97730499190262	0.00000000000002
F	0.83944216692639	4.19525696367528	0.00000000000002
  - BF<sub>3</sub> in cc-pVQZ for B3LYP
    - 4
    - Coordinates from ORCA-job bf3larb3lyp

B	1.32177040236318	2.99519290322462	0.00000000018292
F	2.62262055806619	2.81006160724373	-0.00000000006085
F	0.51141167268769	1.96117969812382	-0.00000000006101
F	0.83188736688293	4.21429579140782	-0.00000000006106

- BF<sub>3</sub> in cc-pVTZ for RHF  
4  
Coordinates from ORCA-job bf3med  

B	1.32192247972696	2.99518245930256	-0.000000000000030
F	2.60368773966545	2.81281056779034	0.000000000000010
F	0.52310108216179	1.97632722162277	0.000000000000010
F	0.83897869844581	4.19640975128433	0.000000000000010
- BF<sub>3</sub> in cc-pVTZ for B3LYP  
4  
Coordinates from ORCA-job bf3medb3lyp  

B	1.32204982048218	2.99502802263052	0.00000001579423
F	2.62398054163804	2.81005312770207	-0.00000000526641
F	0.51037017420024	1.96057974302286	-0.00000000526508
F	0.83128946367953	4.21506910664455	-0.00000000526273
- BH<sub>3</sub> in 6-311G\* for RHF  
4  
Coordinates from ORCA-job bh3  

B	-0.39425560391475	2.81954328907731	-0.00000218845037
H	0.79801394682754	2.81952578387413	0.00000044983348
H	-0.99055892675839	2.67566945377194	-1.02198717478431
H	-0.99055941615440	2.96337147327662	1.02198891340120
- BH<sub>3</sub> in cc-pVQZ for RHF  
4  
Coordinates from ORCA-job bh3lar  

B	-0.39447340903566	2.81954526236105	-0.00000246620379
H	0.79334282197109	2.81952511445620	0.00000054223612
H	-0.98811446187708	2.67614679971004	-1.01859115106835
H	-0.98811495105835	2.96289282347270	1.01859307503601
- BH<sub>3</sub> in cc-pVTZ for RHF  
4  
Coordinates from ORCA-job bh3med  

B	-0.39429497331369	2.81954489267571	-0.00000241352179
H	0.79432139967585	2.81952523860925	0.00000052515362
H	-0.98869296877210	2.67607786678472	-1.01908177432983
H	-0.98869345759007	2.96296200193032	1.01908366269800
- CF<sub>4</sub> in 6-311G\* for RHF  
5  
Coordinates from ORCA-job cf4  

C	0.59508244545520	4.03019269919372	0.000000000000000
F	1.95524716475067	3.86522771783234	0.000000000000000
F	0.76006253795579	5.39039282572689	0.000000000000000
F	0.43014950631431	2.67005304950430	0.000000000000000
F	-0.76509165447596	4.19517370774274	0.000000000000000



- CF<sub>4</sub> in 6-311G\* for B3LYP  
5  
Coordinates from ORCA-job cf4b3lyp
 

C	0.59508698892474	4.03017904642546	0.0000000000000000
F	1.99476463781718	3.86044929595678	0.0000000000000000
F	0.76484353878570	5.42989526842791	0.0000000000000000
F	0.42534113364680	2.63054512496520	0.0000000000000000
F	-0.80458629917442	4.19997126422465	0.0000000000000000
- CF<sub>4</sub> in cc-pVQZ for RHF  
5  
Coordinates from ORCA-job cf4lar
 

C	0.59509048634192	4.03018922729491	0.0000000000000000
F	1.95355865314757	3.86545816143803	0.0000000000000000
F	0.75985041151879	5.38867786435197	0.0000000000000000
F	0.43032473281854	2.67175013627303	0.0000000000000000
F	-0.76337428382682	4.19496461064205	0.0000000000000000
- CF<sub>4</sub> in cc-pVQZ for B3LYP  
Coordinates from ORCA-job cf4larb3lyp
 

C	0.59508713563762	4.03017575772995	0.0000000000000000
F	1.99220693017229	3.86076162264542	0.0000000000000000
F	0.76453438750951	5.42733848439239	0.0000000000000000
F	0.42565041147837	2.63310279669054	0.0000000000000000
F	-0.80202886479780	4.19966133854170	0.0000000000000000
- CF<sub>4</sub> in cc-pVTZ for RHF  
5  
Coordinates from ORCA-job cf4med
 

C	0.59509047330963	4.03019043881245	0.0000000000000000
F	1.95427726275261	3.86537050640107	0.0000000000000000
F	0.75993758448147	5.38939646756835	0.0000000000000000
F	0.43023787254557	2.67103093944710	0.0000000000000000
F	-0.76409319308928	4.19505164777103	0.0000000000000000
- CF<sub>4</sub> in cc-pVTZ for B3LYP  
5  
Coordinates from ORCA-job cf4medb3lyp
 

C	0.59508682039945	4.03017736936366	0.0000000000000000
F	1.99289427658332	3.86067772446159	0.0000000000000000
F	0.76461786559795	5.42802521030611	0.0000000000000000
F	0.42556708083384	2.63241573701160	0.0000000000000000
F	-0.80271604341456	4.19974395885702	0.0000000000000000
- CH<sub>4</sub> in 6-311G\* for RHF  
5  
Coordinates from ORCA-job ch4
 

C	-1.21854913087008	0.65745273664788	-0.00030346097452
H	-0.12730080458849	0.65782639136951	0.00022686854462
H	-1.58273468398268	0.33424893123163	0.97579418033696

- |   |                   |                   |                   |
|---|-------------------|-------------------|-------------------|
| H | -1.58305311956430 | -0.02609890300999 | -0.76825261594939 |
| H | -1.58266226099445 | 1.66452084376097  | -0.20746497195766 |
- CH<sub>4</sub> in cc-pVQZ for RHF  
5  
Coordinates from ORCA-job ch4lar

C	0.30498562087088	2.90976214588219	0.00021029972066
H	1.39316198256503	2.90942365066737	-0.00017054545681
H	-0.05836936824116	3.61108106646697	0.74820940166914
H	-0.05808162752124	1.91104468395125	0.23316057703676
H	-0.05812660767351	3.20672845303221	-0.98140973296974
  
  - CH<sub>4</sub> in cc-pVTZ for RHF  
5  
Coordinates from ORCA-job ch4med

C	-1.36194215551334	3.14382658922703	0.00022249552539
H	-0.27307894739665	3.14399537830509	-0.00010611152546
H	-1.72543162975835	2.75774195351975	-0.95059628791575
H	-1.72525423908582	4.16020712561392	0.14071899672749
H	-1.72555302824584	2.51331895333422	0.80976090718833
  
  - H<sub>2</sub>O in 6-311G\* for RHF  
3  
Coordinates from ORCA-job h2o

O	-2.49909793350217	2.38569508434671	0.01057030577623
H	-1.53667773082287	2.38968421999357	-0.01861228593714
H	-2.79202433567497	2.50990069565972	-0.89805801983909
  
  - H<sub>2</sub>O in 6-311G\* for RHF  
3  
Coordinates from ORCA-job h2olar

O	-0.11733670859474	2.95649539647429	-0.00860392142036
H	0.84240728152871	2.92639600736286	0.01525267187210
H	-0.40105057293398	2.23731859616285	0.56141124954826
  
  - H<sub>2</sub>O in 6-311G\* for RHF  
3  
Coordinates from ORCA-job h2omed

O	-0.08269745207803	1.27308583278661	0.01526745936204
H	0.87796644465356	1.26520636792008	-0.02556968869031
H	-0.36369899257553	1.09886779929330	-0.88765777067173
  
  - HF in 6-311G\* for RHF  
2  
Coordinates from ORCA-job hf

F	-1.00819920838062	4.27883000000000	0.00000000000000
H	-0.08348079161938	4.27883000000000	0.00000000000000

- HF in cc-pVQZ for RHF  
2  
Coordinates from ORCA-job hflar  
F -1.00660993745028 4.27883000000000 0.00000000000000  
H -0.08507006254972 4.27883000000000 0.00000000000000
- HF in cc-pVTZ for RHF  
2  
Coordinates from ORCA-job hfmed  
F -1.00702364681536 4.27883000000000 0.00000000000000  
H -0.08465635318464 4.27883000000000 0.00000000000000
- LiF in 6-311G\* for RHF  
2  
Coordinates from ORCA-job lif  
Li 1.00398132064468 4.44546068831818 0.00000000000000  
F 2.56296867935532 4.45451931168182 0.00000000000000
- LiF in 6-311G\* for B3LYP  
2  
Coordinates from ORCA-job lifb3lyp  
Li 1.00129244327320 4.44544506437662 0.00000000000000  
F 2.56565755672680 4.45453493562338 0.00000000000000
- LiF in cc-pVQZ for RHF  
2  
Coordinates from ORCA-job liflar  
Li 1.00665636201898 4.44547623186454 0.00000000000000  
F 2.56029363798102 4.45450376813545 0.00000000000000
- LiF in cc-pVQZ for B3LYP  
2  
Coordinates from ORCA-job liflarb3lyp  
Li 1.00148210874679 4.44544616644335 0.00000000000000  
F 2.56546789125321 4.45453383355665 0.00000000000000
- LiF in cc-pVTZ for RHF  
2  
Coordinates from ORCA-job lifmed  
Li 0.99993318585731 4.44543716630040 0.00000000000000  
F 2.56701681414269 4.45454283369960 0.00000000000000
- LiF in cc-pVTZ for B3LYP  
2  
Coordinates from ORCA-job lifmedb3lyp  
Li 0.99502267601722 4.44540863338196 0.00000000000000  
F 2.57192732398278 4.45457136661804 0.00000000000000

- LiH in 6-311G\* for RHF  
2  
Coordinates from ORCA-job lih  
Li -1.47295085176786 3.32398000000000 0.00000000000000  
H 0.12335085176786 3.32398000000000 0.00000000000000
- LiH in cc-pVQZ for RHF  
2  
Coordinates from ORCA-job lihlar  
Li -1.46990613917742 3.32398000000000 0.00000000000000  
H 0.12030613917742 3.32398000000000 0.00000000000000
- LiH in cc-pVTZ for RHF  
2  
Coordinates from ORCA-job lihmed  
Li -1.46994916853547 3.32398000000000 0.00000000000000  
H 0.12034916853547 3.32398000000000 0.00000000000000
- NF<sub>3</sub> in 6-311G\* for RHF  
4  
Coordinates from ORCA-job nf3  
N 3.01003581333899 2.45782706832146 -0.11674741474305  
F 2.98149627017197 1.14069688867179 -0.09781314031622  
F 2.25313954444301 2.75596369448185 -1.15331202234504  
F 2.25075837204602 2.78566234852490 0.90905257740431
- NF<sub>3</sub> in 6-311G\* for B3LYP  
4  
Coordinates from ORCA-job nf3b3lyp  
N 3.03973613677054 2.47115294834880 -0.11688743145116  
F 2.99151783572158 1.09185273336325 -0.09712600972114  
F 2.23333087361914 2.77309613709936 -1.19576734738777  
F 2.23084515388873 2.80404818118859 0.95096078856007
- NF<sub>3</sub> in cc-pVQZ for RHF  
4  
Coordinates from ORCA-job nf3lar  
N 3.01097345341121 2.45823060521873 -0.11675215803894  
F 2.98086556036638 1.14125212876498 -0.09782185458611  
F 2.25298529749928 2.75549388902889 -1.15263909551612  
F 2.25060568872312 2.78517337698740 0.90839310814118
- NF<sub>3</sub> in cc-pVQZ for B3LYP  
4  
Coordinates from ORCA-job nf3larb3lyp  
N 3.03991361694351 2.47115871768268 -0.11691418563352  
F 2.99026616718731 1.09454141305002 -0.09711095587798  
F 2.23385468806451 2.77182554462471 -1.19318509022990  
F 2.23139552780467 2.80262432464259 0.94839023174140

- $\text{NF}_3$  in cc-pVTZ for RHF  
4  
Coordinates from ORCA-job nf3med
 

N	3.01137624259363	2.45841548036443	-0.11675435452710
F	2.98106846044933	1.14043379632470	-0.09780983787003
F	2.25268328668446	2.75580021320739	-1.15336648862944
F	2.25030201027258	2.78550051010347	0.90911068102656
- $\text{NF}_3$  in cc-pVTZ for B3LYP  
4  
Coordinates from ORCA-job nf3medb3lyp
 

N	3.04053437385892	2.47154839560224	-0.11688892711225
F	2.99045898174724	1.09342830208135	-0.09714852650646
F	2.23345672559106	2.77213400719956	-1.19421644327338
F	2.23097991880278	2.80303929511686	0.94943389689209
- $\text{NH}_3$  in 6-311G\* for RHF  
4  
Coordinates from ORCA-job nh3
 

N	0.18426120836490	1.86797393615041	-0.02893419807670
H	1.19857912275289	1.85398659632587	0.01626092222039
H	-0.13188743573785	2.49619828363000	0.70325386293227
H	-0.13168289537994	0.93840118389372	0.22947941292404
- $\text{NH}_3$  in cc-pVQZ for RHF  
4  
Coordinates from ORCA-job nh3lar
 

N	0.18496070252227	1.86727736270270	-0.02672743402103
H	1.19698406520344	1.85414300638846	0.01603483600946
H	-0.13137617920876	2.49562264257967	0.70198829177738
H	-0.13129858851695	0.93951698832917	0.22876430623419
- $\text{NH}_3$  in cc-pVTZ for RHF  
4  
Coordinates from ORCA-job nh3med
 

N	0.18377627632185	1.86836319916699	-0.03023747545709
H	1.19669170410458	1.85366631857276	0.01739594431080
H	-0.13068318460985	2.49446710991638	0.70281692520441
H	-0.13051479581659	0.94006337234387	0.23008460594188
- $\text{OF}_2$  in 6-311G\* for RHF  
3  
Coordinates from ORCA-job of2
 

O	-0.51428219290753	3.86293413855685	0.00000000000000
F	0.81960932945579	3.89426215956531	0.00000000000000
F	-0.86097713654826	5.15136370187784	0.00000000000000

- OF<sub>2</sub> in 6-311G\* for B3LYP  
3  
Coordinates from ORCA-job of2b3lyp  
O -0.53067366789227 3.84108268122700 0.00000000000000  
F 0.87652759934967 3.86876049329685 0.00000000000000  
F -0.90150393145740 5.19871682547615 0.00000000000000
- OF<sub>2</sub> in cc-pVQZ for RHF  
3  
Coordinates from ORCA-job of2lar  
O -0.51480789310358 3.86223134560207 0.00000000000000  
F 0.81812464320203 3.89592073961110 0.00000000000000  
F -0.85896675009845 5.15040791478684 0.00000000000000
- OF<sub>2</sub> in cc-pVQZ for B3LYP  
3  
Coordinates from ORCA-job of2larb3lyp  
O -0.53004809671517 3.84193898118934 0.00000000000000  
F 0.87150852987126 3.87185854266754 0.00000000000000  
F -0.89711043315609 5.19476247614312 0.00000000000000
- OF<sub>2</sub> in cc-pVTZ for RHF  
3  
Coordinates from ORCA-job of2med  
O -0.51523272442965 3.86166339837202 0.00000000000000  
F 0.81977678107489 3.89512778047978 0.00000000000000  
F -0.86019405664524 5.15176882114820 0.00000000000000
- OF<sub>2</sub> in cc-pVTZ for B3LYP  
3  
Coordinates from ORCA-job of2medb3lyp  
O -0.53037329402762 3.84153444087065 0.00000000000000  
F 0.87316337476217 3.87095312461054 0.00000000000000  
F -0.89844008073454 5.19607243451881 0.00000000000000
- H<sub>2</sub>O in 3-21G for RHF  
3  
Coordinates from ORCA-job H2O-3-21G  
O -3.89356416707724 2.66978182157201 0.00016526404114  
H -2.92702212685023 2.68486654182911 -0.00027846729654  
H -4.20151370607253 3.58568163659888 -0.02677679674460
- H<sub>2</sub>O in 6-31G for RHF  
3  
Coordinates from ORCA-job H2O-6-31G  
O -3.86414712954271 8.27548416233271 1.20273885691289  
H -2.91467071297261 8.26068057240064 1.19400510346415  
H -4.19684215748468 9.04154526526665 1.65469603962295

- H<sub>2</sub>O in 6-311G for RHF  
3  
Coordinates from ORCA-job H2O-6-311G  
O -3.86235613899240 8.27766564052509 1.20402587531677  
H -2.91711656138588 8.26053402549274 1.19391864439793  
H -4.19618729962172 9.03951033398217 1.65349548028530
- H<sub>2</sub>O in 6-311G\* for RHF  
3  
Coordinates from ORCA-job H2O-6-311GS  
O -3.49340442830962 1.33965012497325 0.00061438141475  
H -2.55413330122606 1.32426453466855 0.00432147318948  
H -3.79157227046432 0.47360534035819 0.20928414539577
- H<sub>2</sub>O in 6-311G\*\* for RHF  
3  
Coordinates from ORCA-job H2O-6-311GSS  
O -3.87787804156451 8.25875952011945 1.19287172993361  
H -2.93747705375126 8.28711352451572 1.20959989417065  
H -4.16030490468424 9.03183695536483 1.64896837589573
- H<sub>2</sub>O in cc-pVDZ for RHF  
3  
Coordinates from ORCA-job H2O-cc-pVDZ  
O -3.88125478198307 8.25464655937050 1.19044518439361  
H -2.93581740498958 8.28918749747292 1.21082348713362  
H -4.15858781302735 9.03387594315658 1.65017132847277
- H<sub>2</sub>O in cc-pVTZ for RHF  
3  
Coordinates from ORCA-job H2O-cc-pVTZ  
O -3.87643042830743 8.26052275471700 1.19391199491784  
H -2.93625810048968 8.28504873325588 1.20838171818298  
H -4.16297147120289 9.03213851202712 1.64914628689918
- H<sub>2</sub>O in cc-pVQZ for RHF  
3  
Coordinates from ORCA-job H2O-cc-pVQZ  
O -3.87564099633719 8.26148430525286 1.19447928605109  
H -2.93641845882904 8.28442523034592 1.20801386682293  
H -4.16360054483377 9.03180046440122 1.64894684712598
- H<sub>2</sub>O in cc-pV5Z for RHF  
3  
Coordinates from ORCA-job H2O-cc-pV5Z  
O -3.87536727240877 8.26181772374164 1.19467599474740  
H -2.93614926771909 8.28401123143681 1.20776961766332  
H -4.16414345987214 9.03188104482154 1.64899438758928

- H<sub>2</sub>O in 3-21G for B3LYP  
3  
Coordinates from ORCA-job H2O1  
O -4.55908276943650 4.60724641596858 -0.01911610975417  
H -3.56328592032963 4.57020893216851 0.01214118011991  
H -4.84531131023387 3.87732465186290 0.59669492963426
- H<sub>2</sub>O in 6-31G for B3LYP  
3  
Coordinates from ORCA-job H2O2  
O -4.54269555354062 4.58950097556513 -0.00414463340086  
H -3.56649913297002 4.58176393174795 0.00239252966100  
H -4.85848531348936 3.88351509268693 0.59147210373985
- H<sub>2</sub>O in 6-311G for B3LYP  
3  
Coordinates from ORCA-job H2O3  
O -4.53920957316923 4.58572641945395 -0.00096011521843  
H -3.56813811750520 4.58370531972418 0.00075462062320  
H -4.86033230932557 3.88534826082187 0.58992549459523
- H<sub>2</sub>O in 6-311G\* for B3LYP  
3  
Coordinates from ORCA-job H2O4  
O -4.54566664766032 4.59271424865541 -0.00685560825714  
H -3.58321257078042 4.57032216962896 0.01204544811128  
H -4.83880078155926 3.89174358171564 0.58453016014586
- H<sub>2</sub>O in 6-311G\*\* for B3LYP  
3  
Coordinates from ORCA-job H2O5  
O -4.55115415827929 4.59866572314924 -0.01187674924582  
H -3.58996095783386 4.56222205880943 0.01887921051230  
H -4.82656488388684 3.89389221804133 0.58271753873352
- H<sub>2</sub>O in cc-pVDZ for B3LYP  
3  
Coordinates from ORCA-job H2O6  
O -4.55540513294002 4.60327471563146 -0.01576526480087  
H -3.58815033014013 4.55975128290493 0.02096375051906  
H -4.82412453691985 3.89175400146361 0.58452151428181
- H<sub>2</sub>O in cc-pVTZ for B3LYP  
3  
Coordinates from ORCA-job H2O7  
O -4.54906448160915 4.59642068150821 -0.00998265194738  
H -3.58828757116416 4.56481743122897 0.01668958644789  
H -4.83032794722668 3.89354188726282 0.58301306549949



- H<sub>2</sub>O in cc-pVQZ for B3LYP  
3  
Coordinates from ORCA-job H2O8  
O -4.54790047623557 4.59517615866005 -0.00893267254128  
H -3.58813674198453 4.56583954358459 0.01582726132557  
H -4.83164278177990 3.89376429775536 0.58282541121571
- H<sub>2</sub>O in cc-pV5Z for B3LYP  
3  
Coordinates from ORCA-job H2O9  
O -4.54732848883711 4.59471833134418 -0.00854641123518  
H -3.58757623195082 4.56657061460579 0.01521048340066  
H -4.83277527921207 3.89349105405003 0.58305592783452
- HF in 3-21G for RHF  
2  
Coordinates from ORCA-job HF-3-21G  
F -3.76098906844954 1.81759000000000 0.00000000000000  
H -2.82354093155046 1.81759000000000 0.00000000000000
- HF in 6-31G for RHF  
2  
Coordinates from ORCA-job HF-6-31G  
F -3.75269147972680 1.81759000000000 0.00000000000000  
H -2.83183852027320 1.81759000000000 0.00000000000000
- HF in 6-311G for RHF  
2  
Coordinates from ORCA-job HF-6-311G  
F -3.74753431279718 1.81759000000000 0.00000000000000  
H -2.83699568720282 1.81759000000000 0.00000000000000
- HF in 6-311G\* for RHF  
2  
Coordinates from ORCA-job HF-6-311GS  
F -3.74092127992616 1.81759000000000 0.00000000000000  
H -2.84360872007384 1.81759000000000 0.00000000000000
- HF in 6-311G\*\* for RHF  
2  
Coordinates from ORCA-job HF-6-311GSS  
F -3.74024770215458 1.81759000000000 0.00000000000000  
H -2.84428229784542 1.81759000000000 0.00000000000000
- HF in cc-pVDZ for RHF  
2  
Coordinates from ORCA-job HF-cc-pVDZ  
F -3.74300794351448 1.81759000000000 0.00000000000000  
H -2.84152205648552 1.81759000000000 0.00000000000000

- HF in cc-pVTZ for RHF  
2  
Coordinates from ORCA-job HF-cc-pVTZ  
F -3.74123600286576 1.81759000000000 0.00000000000000  
H -2.84329399713424 1.81759000000000 0.00000000000000
- HF in cc-pVQZ for RHF  
2  
Coordinates from ORCA-job HF-cc-pVQZ  
F -3.74071239389902 1.81759000000000 0.00000000000000  
H -2.84381760610098 1.81759000000000 0.00000000000000
- HF in cc-pV5Z for RHF  
2  
Coordinates from ORCA-job HF-cc-pV5Z  
F -3.74074170455950 1.81759000000000 0.00000000000000  
H -2.84378829544050 1.81759000000000 0.00000000000000
- LiH in 3-21G for RHF  
2  
Coordinates from ORCA-job LiH-3-21G  
Li -4.31629940547108 2.78942000000000 0.00000000000000  
H -2.67636059452892 2.78942000000000 0.00000000000000
- LiH in 6-31G for RHF  
2  
Coordinates from ORCA-job LiH-6-31G  
Li -4.31613822980290 2.78942000000000 0.00000000000000  
H -2.67652177019710 2.78942000000000 0.00000000000000
- LiH in 6-311G for RHF  
2  
Coordinates from ORCA-job LiH-6-311G  
Li -4.29914116510590 2.78942000000000 0.00000000000000  
H -2.69351883489409 2.78942000000000 0.00000000000000
- LiH in 6-311G\* for RHF  
2  
Coordinates from ORCA-job LiH-6-311GS  
Li -4.30041089127172 2.78942000000000 0.00000000000000  
H -2.69224910872827 2.78942000000000 0.00000000000000
- LiH in 6-311G\*\* for RHF  
2  
Coordinates from ORCA-job LiH-6-311GSS  
Li -4.29989815531805 2.78942000000000 0.00000000000000  
H -2.69276184468195 2.78942000000000 0.00000000000000

- LiH in cc-pVDZ for RHF  
2  
Coordinates from ORCA-job LiH-cc-pVDZ  
Li -4.30519893198485 2.78942000000000 0.00000000000000  
H -2.68746106801515 2.78942000000000 0.00000000000000
- LiH in cc-pVTZ for RHF  
2  
Coordinates from ORCA-job LiH-cc-pVTZ  
Li -4.30000705849111 2.78942000000000 0.00000000000000  
H -2.69265294150889 2.78942000000000 0.00000000000000
- LiH in cc-pVQZ for RHF  
2  
Coordinates from ORCA-job LiH-cc-pVQZ  
Li -4.29911176305028 2.78942000000000 0.00000000000000  
H -2.69354823694972 2.78942000000000 0.00000000000000
- LiH in cc-pV5Z for RHF  
2  
Coordinates from ORCA-job LiH-cc-pV5Z  
Li -4.29907184920890 2.78942000000000 0.00000000000000  
H -2.69358815079110 2.78942000000000 0.00000000000000