UNIVERSIDAD DE LA LAGUNA

Study of the electronic structure of atoms

Rubén Santana Alonso

Directores

Dr. José Diego Bretón Peña

Dr. Javier Hernández Rojas

Facultad de Ciencias

Sección de Física

La Laguna, July 10, 2023

Acknowledgment

Firstly, I want to thank to my family and childhood friends who have supported me during all these years. I am aware that they will hold my back any time I need it. Also, thank my supervisors to calm me down when results were not positives and guide me through this project. Last but not least, thank to the new people that I had the pleasure to met here, during my studies.

Contents

Tables

List of plots

Chapter 1

Summary

En este trabajo se estudiará la energía del estado fundamental de distintos átomos de la tabla periódica. Para ello, se utilizará el método de la Teoría del Funcional de la Densidad (DFT), haciendo comparaciones con los datos obtenidos con el método Hartree-Fock, post Hartree-Fock (MP2) y los datos de referencia obtenidos de la tabla de datos del *National Institute of standards and technology* (NIST) [1]. Cabe destacar que el estudio realizado es únicamente para átomos, aunque puede prestarse para el estudio de moléculas. Además, se hará desde la perspectiva del método DFT no relativista.

En el marco teórico, se hará un resumen del fundamento teórico sobre el método y sus distintas aproximaciones. El DFT es un método variacional empleado para obtener la energía del estado fundamental de átomos y moléculas. El objetivo es minimizar el funcional de la energía electrónica con respecto a la densidad electrónica. Esto reduce el número de cálculos, ya que se pasa de resolver una ecuación de 3N variables (la ecuación de Schrödinger depende de 3 variables espaciales para cada uno de los N electrones) a una que depende de solo tres coordenadas espaciales (la densidad electrónica). Existen diferentes variantes o métodos del DFT, cada uno de los cuales utiliza diferentes aproximaciones y modelos para calcular la energía y otras propiedades de los sistemas. Este es un resumen de algunos de los métodos más comunes del DFT y que se explicará en el marco teórico:

LDA (Local Density Approximation): Es el método más simple del DFT, que se basa en aproximar la energía de intercambio y correlación en función de la densidad electrónica local en cada punto del sistema. Es computacionalmente eficiente, el LDA no tiene en cuenta la dependencia de la densidad electrónica en la posición relativa de los electrones.

GGA (Generalized Gradient Approximation): Los métodos GGA mejoran el LDA al tener en cuenta el gradiente de la densidad electrónica. Esto hace posible describir de forma más precisa la energía de intercambio y correlación.

Meta-GGA (Meta-Generalized Gradient Approximation): Los métodos Meta-GGA son una mejora adicional de los GGA, en el marco teórico de ahondará sobre las mejoras.

Hybrid Functionals: Estos métodos combinan la aproximación del DFT con un intercambio y correlación exactos o semilocalmente exactos, junto con una fracción de intercambio y correlación obtenida de cálculos de Hartree-Fock. Son computacionalmente más cos-

tosos que los métodos anteriores.

Cada método tiene sus ventajas y desventajas, la elección del método depende de la naturaleza del sistema objeto de estudio y de la precisión requerida en los cálculos. Se ha incluido en este trabajo un capítulo dedicado a la explicación del uso del programa informático *Northwest Computational Chemistry Package* (NWChem), adjuntando, además, un ejemplo de fichero de entrada en el apéndice A. Se utiliza dicho programa ya que el método DFT es de carácter iterativo, llevándose a cabo estos cálculos de forma rápida y cómoda. La rapidez y comodidad es algo que se valorará al final de este TFG, junto con los resultados obtenidos para determinar los funcionales que podrían utilizarse para cada átomo. El problema fundamental de el DFT es que *a priori* se desconoce el funcional con el que se conseguirá un resultado más próximo a la energía del estado fundamental. Por eso mismo, el objetivo ha sido estudiar los átomos de los cuatro primeros períodos de la tabla periódica, juzgando así qué funcionales se ajustan mejor al estudio concreto de la energía del estado fundamental de dichos átomos. La idea principal es organizar los átomos por períodos y/ grupos para sacar mejores conclusiones. Aunque este es el objetivo principal, en las conclusiones se reflejarán los resultados obtenidos y qué podemos pensar al respecto (también pequeños detalles sobre el coste computacional, algo a tener que cuenta).

Chapter 2

Introduction

The many-body system has always been a difficult question to solve in physics. Since solving the Schrödinger equation for many-body systems is virtually impossible, a way to obtain the ground state energy has to be found. The many-body wave function is substituted for the density, which only depends on the three spatial coordinates. Non-relativistic considerations have been taken in the study, since the basis set used is non-relativistic and the atoms studied are not formed by a huge number of electrons (Spin-Orbit effects increase as the number of electrons increase [2]). What makes the density functional theory possible is the restriction to ground states. The DFT gives a practical computational resolution of the Kohn-Sham equations [3]. The equations are very similar to the Hartree-Fock equations, although they include both exchange and correlation effects. As it will be explained later, the main problem of this theory is to improve the approximate form of the energy functionals.

The simplest systems are single and isolated atoms. The dynamical treatment is required only for the electrons. The Hamiltonian can be separated into a part governing the translational motion of the atom and the motion of the electrons relative to the center of mass. It should be said that the origin of the center of mass is essentially the position of the nucleus. So, it is an electronic problem and the nucleus is an electrostatic external source. Due to the self-consistent nature of the solution of the problem, it is needed to use a quantum chemistry package: the NWChem. Because a certain level of accuracy is demanded.

Chapter 3

Theoretical Background

En este capítulo se expondrá brevemente la Teoría del funcional de la densidad. Se darán ciertos matices teóricos que giren en torno a dicha teoría. Además de las aproximaciones que tiene la teoría, desde la aproximación local de la densidad hasta los funcionales híbridos. En resumen, se partirá desde el planteamiento de la teoría y los problemas presentados hasta las últimas aproximaciones.

3.1   Density Functional Theory

The fundamental mathematical theorems proven by Kohn-Hohenberg (KH) [4] and the derivation of a set of equations by Kohn-Sham (KS) [4] are the basis of the whole field of density functional theory. KH postulated the following:

"The ground-state energy suited by Schrödinger's equation is a unique functional of the electron density." [4]

In simple words, it states that there is a one-to-one correspondence between the ground-state wavefunction and the ground-state electron density. So, the ground-state energy is expressed as a functional of the electronic density: $E[n(\mathbf{r})]$. This result is hugely important, meaning that it is possible to solve the Schrödinger equation by finding a function of only three spatial variables (the electron density), unlike a function of 3N variables (the wave function). Also, there is a problem: the theorem only proves that the functional exists, but there is no information about what the functional really is.

The second theorem becomes more interesting. It defines an important property that must have the functional:

"The electron density that minimizes the energy of the overall functional is the true electron density corresponding to the full solution of the Schrödinger equation." [4]

Later in this final degree work, the results will be analysed and this theorem will be much clearer. Let's suppose that the form of the functional is well known: the only thing that could be done is to vary the electron density until the energy from the functional is minimized, finding the electron density.

The situation we are studying is where multiple electrons are interacting each other and the nuclei. The Schrödinger equation that describes this situation is:

$$\left[\frac{h^2}{2m} \sum_{i=1}^{N} \nabla_i^2 + \sum_{i=1}^{N} V(\mathbf{r}_i) + \sum_{i=1}^{N} \sum_{j<i} U(\mathbf{r}_i, \mathbf{r}_j) \right] \psi = E\psi \tag{3.1}$$

The Hamiltonian terms in the equation refer to the kinetic energy of each electron, the interaction energy between each electron and the atomic nuclei and the interaction energy between electrons, respectively (m is the mass of the electron and h the Planck's constant). The ground state energy is independent of time, that is why the time-independent Schrödinger equation is shown.

The electronic density is written in terms of the single-electron wave functions $\psi_i(\vec{r})$:

$$n(\mathbf{r}) = 2 \sum_i \psi_i^*(\mathbf{r}) \psi_i(\mathbf{r}) \tag{3.2}$$

This summation goes over all the electron wave functions that are occupied by electrons, the term in the summation is the probability of finding an electron in individual wave function located at the position $\mathbf{r}$. It is multiplied by two because of the electron spin.

It is assumed that for the ground state of any atom, the electron density minimizes the energy functional $E_{TF}[n(\mathbf{r})]$ (energy functional of the Thomas-Fermi theory of atoms) [4] under the restriction:

$$N = N[n(\mathbf{r})] = \int n(\mathbf{r}) d\mathbf{r} \tag{3.3}$$

Since n determines N (number of electrons) and v (the external potential) and hence all properties of the ground state, for example, the kinetic energy $T[n]$, the potential energy $V[n]$, and the total energy $E[n]$ (according to Thomas-Fermi model). To make explicit the dependence on v, it can be written

$$E[n] = T[n] + V[n] + V_{ee}[n] = \int n(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} + F_{HK}[n] \tag{3.4}$$

Where

$$F_{HK}[n] = T[n] + V_{ee}[n] \tag{3.5}$$

$$V_{ee} = J[n] + unknown\,quantum\,term \tag{3.6}$$

As

$$J[n] = \frac{1}{2} \int \int \frac{1}{r_{12}} n(\mathbf{r}_1) n(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \tag{3.7}$$

is the electron-electron repulsion energy for classical charges, where the 1/2 term avoids the double counting. The *unknown quantum term* is also noted as the pair correlation function, which incorporates all nonclassical effects [5].

According to the second Hohenberg-Kohn theorem: "For a trial density $\tilde{n}(\mathbf{r})$, such that $\tilde{n}(\mathbf{r}) \geq 0$ and $\int \tilde{n}(\mathbf{r}) d\mathbf{r} = N$ "

$$E_0 \leq E[\tilde{n}] \tag{3.8}$$

Where $E[\tilde{n}]$ is the energy functional of Eq. 3.4. This is similar to the known variational principle for wave functions:

$$E[\psi] \geq E_0 \tag{3.9}$$

A density is v-representable if the density is associated with the antisymmetric ground state wave function of a Hamiltonian of the following form:

$$\hat{H} = \sum_{i=1}^{N} (\frac{1}{2}) \nabla_i^2 + \sum_{i=1}^{N} v(\mathbf{r}_i) + \sum_{i<j}^{N} \frac{1}{\mathbf{r}_{ij}} \tag{3.10}$$

Also, the functional $F_{HK}[n]$ is particularly important,

$$F_{HK}[n] = \langle \psi | \hat{T} + \hat{V}_{ee} | \psi \rangle \tag{3.11}$$

where ψ is the ground state wave function associated with n (has to be v-representable) with some external potential v($\mathbf{r}$). It can be confirmed the first Hohenberg-Kohn theorem as the fact that there is a one to one correspondence between the ground state wave functions and a v-representable electron densities. The second Hohenberg-Kohn theorem states that for all v-representable densities

$$E[n] \equiv F_{HK}[n] + \int v(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} \geq E[n_0] \tag{3.12}$$

where $E[n_0]$ is the ground state energy of the Hamiltonian of v($\mathbf{r}$) as external potential, while n_0 is the ground state density. The variational principle 3.12 fails in practical calculations if the trial densities are not v-representable. Also, the conditions for a density to be v-representable remain unknown [4]. Then, a weaker condition has to be obtained, this is the N-representability condition. A density is N-representable if it can be obtained

from some antisymmetric wave function. A density n($\mathbf{r}$) is N-representable if it satisfies the following conditions:

$$n(\mathbf{r}) \geq 0 \tag{3.13}$$

$$\int n(\mathbf{r})d\mathbf{r} = N \tag{3.14}$$

$$\int |\nabla n(\mathbf{r})^{1/2}|^2 d\mathbf{r} < \infty \tag{3.15}$$

The minimum-energy principle for the ground state is

$$\langle \psi_{n_0}|\hat{H}|\psi_{n_0}\rangle \geq \langle \psi_0|\hat{H}|\psi_0\rangle = E_0 \tag{3.16}$$

where $\hat{H}$ is the Hamiltonian for the N-electron system. Since the external field v($\mathbf{r}$) is characterized by the functional of density, it is obtained

$$\langle \psi_{n_0}|\hat{T} + \hat{V}_{ee}|\psi_{n_0}\rangle + \int v(\mathbf{r})n_0(\mathbf{r})d\mathbf{r} \geq \langle \psi_0|\hat{T} + \hat{V}_{ee}|\psi_0\rangle + \int v(\mathbf{r})n_0(\mathbf{r})d\mathbf{r} \tag{3.17}$$

Therefore,

$$\langle \psi_{n_0}|\hat{T} + \hat{V}_{ee}|\psi_{n_0}\rangle \geq \langle \psi_0|\hat{T} + \hat{V}_{ee}|\psi_0\rangle \tag{3.18}$$

the ground state ψ_0 minimizes the expectation value $\langle \hat{T} + \hat{V}_{ee}\rangle$. Comparing Eq. 3.18 with Eq. 3.11 we obtain:

$$F_{HK}[n_0] = \langle \psi_0|\hat{T} + \hat{V}_{ee}|\psi_0\rangle = \underset{\psi \to n_0}{\text{Min}} \langle \psi|\hat{T} + \hat{V}_{ee}|\psi\rangle \tag{3.19}$$

This statement provides the first theorem of Hohenberg and Kohn and eliminates the problem in the original approach about the v-representability. This is the Levy and Lieb's constrained search method. Also, this last method applies to degenerate ground states, contrary to Hohenberg and Kohn's method. Assuming the differenciability of $E[n]$, the variational principle 3.8 requires that the ground state density satisfies

$$\delta \left\{ E[n] - \mu \left[\int n(\mathbf{r})d\mathbf{r} - N \right] \right\} = 0 \tag{3.20}$$

the stationary principle, resulting the Euler-Lagrange equation:

$$\mu = \frac{\delta E[n]}{\delta n(\mathbf{r})} = v(\mathbf{r}) + \frac{\delta F_{HK}[n]}{\delta n(\mathbf{r})} \tag{3.21}$$

Where μ is the chemical potential. Kohn and Sham introduced orbitals into the problem

so the kinetic energy can be computed to an acceptable accuracy. Starting with the exact formula for the ground state kinetic energy,

$$T = \sum_i^N n_i \langle \psi_i | (-\frac{1}{2}\nabla^2)|\psi_i\rangle \tag{3.22}$$

where ψ_i and n_i are natural spin orbitals and their occupation numbers respectively. This kinetic energy is a functional of the total electron density

$$n(\mathbf{r}) = \sum_i^N n_i \sum_s |\psi(\mathbf{r},s)|^2 \tag{3.23}$$

as the Pauli principle requires, the occupation number is a positive integer or zero, $0 \le n_i \le 1$. Also, s denotes the spin. For any interacting system there are an infinite number of terms in Eq. 3.22 or Eq. 3.23.

It was showed that a theory using simpler formulas could be built, if $n_i = 1$ for N orbitals and $n_i = 0$ for the rest, we have:

$$T_s[n] = \sum_i^N \langle \psi_i | (-\frac{1}{2}\nabla^2)|\psi_i\rangle \tag{3.24}$$

$$n(\mathbf{r}) = \sum_i^N \sum_s |\psi_i(\mathbf{r},s)|^2 \tag{3.25}$$

This $T_s[n]$ is still not the exact kinetic energy functional $T[n]$. Kohn and Sham set a problem making $T_s[n]$ is its kinetic energy component, exactly. To produce the objective separation of $T_s[n]$ as the kinetic energy component, rewriting Eq. 3.5

$$F[n] = T_s[n] + J[n] + E_{xc}[n] \tag{3.26}$$

where E_{xc} is called as the *exchange-correlation* energy. Which can be written as

$$E_{xc}[n] = T[n] - T_s[n] + V_{ee}[n] - J[n] \tag{3.27}$$

containing the difference between T and T_s and the nonclassical part of $V_{ee}[n]$.

The Euler-Lagrange equation 3.21 can be written as

$$\mu = v_{eff}(\mathbf{r}) + \frac{\delta T_s[n]}{\delta n(\mathbf{r})} \tag{3.28}$$

Defining the KS effective potential and the exchange-correlation potential as

$$v_{eff}(\mathbf{r}) = v(\mathbf{r}) + \frac{\delta J[n]}{\delta n(\mathbf{r})} + \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} = v(\mathbf{r}) + \int \frac{n(\mathbf{r'})}{|\mathbf{r} - \mathbf{r'}|} d\mathbf{r'} + v_{xc}(\mathbf{r}) \qquad (3.29)$$

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} \qquad (3.30)$$

respectively.

3.1.1   Steps made to face the problem

The main problem is that the density functional is not known. So, to describe the system accurately, it is needed an effective number of iterations.

Firstly, the electron density must be defined. There is an initial trial electron density so there must not be a problem of how different it actually is from the real one. Secondly, the KS equations have to be solved using that trial electron density. Solving these equations, the single-electron wave functions should be found. Thirdly, the electron density defined by the single-electron wave functions would be calculated. Lastly, the result is compared to the electron density used in the first place. If the two densities are the same, then the ground-state electron density is found (this can be used to calculate the total energy). If not, the trial electron density must be changed.

3.1.2   Uniform Electron Gas (UEG)

The uniform electron gas is a theoretical model used in condensed matter physics to study the behavior of electrons in a solid. It assumes that the electron density is constant throughout the system, neglecting any spatial variations. Despite its simplicity, the uniform electron gas provides valuable insights into the electronic properties of real materials.

The connection between the uniform electron gas and DFT lies in the fact that the uniform electron gas serves as a reference system for developing practical approximations to the exchange-correlation functional, a key ingredient in DFT calculations. The exchange-correlation functional captures the effects of electron-electron interactions, which are crucial for an accurate description of electronic properties.

By studying the uniform electron gas, researchers have derived approximate exchange-correlation functionals, such as the local density approximation (LDA) and the generalized gradient approximation (GGA), which can be used in DFT calculations for real materials. These functionals approximate the exchange and correlation effects of the electrons in a material based on their local density, making DFT calculations computationally tractable.

In summary, the uniform electron gas serves as a starting point for developing practical approximations to the exchange-correlation functional in DFT calculations. These functionals enable the study of the electronic structure and properties of real materials.

Considering a system with electrons moving in a box (a cubical box of side length l, for example), in which there is uniformly extended a positive charge enough to make the system neutral. A UEG is alike a system in the limit $N \to \infty$, $V \to \infty$ with density $\rho = \frac{N}{V}$ remaining finite [1]. The total ground state energy of a UEG,

$$E[\rho] = T_s[\rho] + \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} + J[\rho] + E_{xc}[\rho] + E_b \tag{3.31}$$

where the external potential, due to the positive charge density n($\mathbf{r}$), and E_b, the electrostatic energy of the positive background, respectively are written as

$$v(\mathbf{r}) = -\int \frac{n(\mathbf{r})}{|\mathbf{r} - \mathbf{r'}|}d\mathbf{r'} \tag{3.32}$$

$$E_b = \frac{1}{2}\int\int \frac{n(\mathbf{r})n(\mathbf{r'})}{|\mathbf{r} - \mathbf{r'}|}d\mathbf{r}d\mathbf{r'} \tag{3.33}$$

Considering that the system is neutral in all the space, $\rho(\mathbf{r}) = n(\mathbf{r})$. As a consequence, we have:

$$\int n(\mathbf{r})v(\mathbf{r})d\mathbf{r} + J[n] + E_b = 0 \tag{3.34}$$

Hence [4]

$$E[n] = T_s[n] + E_{xc}[n] \tag{3.35}$$
$$= T_s[n] + E_x[n] + E_c[n] \tag{3.36}$$
$$= \int n\epsilon_t[n]d\mathbf{r} + \int n\epsilon_x[n]d\mathbf{r} + \int n\epsilon_c[n]d\mathbf{r} \tag{3.37}$$

The KS equations are satisfied by the plane waves under the condition $n = N/V$, which is a constant,

$$\psi_k(\mathbf{r}) = \frac{1}{V^{1/2}}e^{i\mathbf{k}\mathbf{r}} \tag{3.38}$$

Whose boundary conditions in a cubic box demand:

---

[1]Here, we will use $\rho(\mathbf{r})$ for electron density and $n(\mathbf{r})$ for positive charge density.

$$k_x = \frac{2\pi}{l} n_x \tag{3.39}$$

$$k_y = \frac{2\pi}{l} n_y \tag{3.40}$$

$$k_z = \frac{2\pi}{l} n_z \tag{3.41}$$

$$n_x, n_y, n_z = 0, \pm 1, \pm 2, ... \tag{3.42}$$

Kinetic energy and exchange energy of a system described by those set of orbitals, each doubly occupied (paired electrons) are expressed as [4]

$$T_s^0[n] = C_s \int n^{5/3} d\mathbf{r} \tag{3.43}$$

$$\epsilon_t^0(n) = C_s n^{2/3} = \frac{1.1049}{r_s^2} \tag{3.44}$$

$$E_x^0[n] = C_x \int n^{4/3} d\mathbf{r} \tag{3.45}$$

$$\epsilon_x^0(n) = C_x n^{1/3} = \frac{0.4582}{r_s} \tag{3.46}$$

where the superscript 0 denotes the spin polarization (is zero because all the electrons are paired). The term r_s is the radius of a sphere whose volume is the effective volume of an electron, in other words

$$\frac{1}{n} = \frac{4}{3} \pi r_s^3 \tag{3.47}$$

This can be related to the Fermi wavevector, k_F. Let $N = nV$ the be the number of electrons in a volume V. Electrons occupy the N lowest KS spin orbitals, in other words, those with $k < k_F$.

$$N = 2 \sum_k \theta(k_F - k) = 2 \frac{V}{(2\pi)^3} \int_0^{k_f} 4\pi k^2 dk = V \frac{k_F^3}{3\pi^2} \tag{3.48}$$

The Fermi wavelength $2\pi/k_F$ is the shortest de Broglie wavelength for the non-interacting electrons. So, the Seitz radius r_s, using Eq. 3.47 can be related to the Fermi wavevector as it follows:

$$n = \frac{3}{4\pi r_s^3} = \frac{k_F^3}{3\pi^2} \tag{3.49}$$

Linear response

It is going to be detailed now the linear response of the spin-unpolarized UEG to a weak, static, external potential $\delta v(\mathbf{r})$. It has to be taken into account that:

$$\delta v(\mathbf{r}) = \delta v(\mathbf{q}) exp(i\mathbf{q} \cdot \mathbf{r}) \tag{3.50}$$

Is a wave of wavevector $\mathbf{q}$ and small amplitude $\delta v(\mathbf{q})$. The density response function of the interacting UEG is:

$$\chi(q) = \frac{\chi_s(q)}{\epsilon_s(q)} \tag{3.51}$$

Where $\chi_s(q)$ is the density response function for the non-interacting UEG. And $\epsilon_s(q)$:

$$\epsilon_s(q) = 1 - \frac{4\pi}{q^2} \left[1 - G_{XC}(q) \right] \chi_s(q) \tag{3.52}$$

The coefficient $\frac{4\pi}{q^2}$ is the Fourier transform of the Coulomb interaction $1/|\mathbf{r} - \mathbf{r'}|$. Also, $G_{XC}(q)$ is the local field factor.

The second order change δE in the total energy can be found from the Hellmann-Feynmann theorem. [4]

$$\delta E = \frac{1}{2}\delta n(-\mathbf{q})\delta v(\mathbf{q}) \tag{3.53}$$

Where $\delta v(\mathbf{q})$ is an external potential.[4]

3.1.3   Exchange-Correlation Functional

There is a problem solving the KS equations: the exchange-correlation functional must be specified. The existence of the exchange-correlation functional is guaranteed by the KH theorem, but, their form is not known. It is usual to decompose the total xc-energy functional $E_{xc}[n]$ into an exchange part $E_x[n]$ and a correlation functional $E_c[n]$ (the spatial coordinates have been eliminated to make the notation simpler.)

On the other hand, there is a way of finding this functional exactly: the key is the UEG, where the electron density is constant at all points. The UEG gives a practical way to use the KS equations properly [4]. For this, we set:

$$V_{XC}(\mathbf{r}) = V_{XC}^{ueg}[n(\mathbf{r})] \tag{3.54}$$

The equation sets the exchange-correlation potential at each position as the known exchange-correlation potential from the UEG at the electron density observed at that position.This approximation is called as "the local density approximation (LDA)". It is important to know that these equations do not exactly solve the true Schrödinger equation (as the true exchange-correlation functional is not used).

3.1.4   Local Density Approximation (LDA)

The simplest approximation to the KS functional is the LDA. The LDA can be applied to any in-homogeneous systems without complications. However, its universality does not implies it exactly works in any system. One would expect the LDA to be so consistent for systems that share many properties with the UEG, like simple metals. This is one of the objectives of this work, to compare many functionals for many atoms and see which ones fit better witch each other. In the following equation:

$$V_{xc}^{LDA}(\mathbf{r}) = V_{xc}^{UEG}[n(\mathbf{r})] \tag{3.55}$$

The local exchange-correlation potential is defined as the exchange-correlation potential for the UEG with the same density as the local electron density. In other words, in the LDA the exchange-correlation energy density of the inhomogeneous system with density $n(\mathbf{r})$ is locally approximated to the exchange-correlation density of an UEG with density $n_0 = n(\mathbf{r})$:

$$E_{xc}^{LDA}[n] = \int e_{xc}^{UEG}(n_0 = n(\mathbf{r}))d^3r \tag{3.56}$$

Since in Eq. 3.55 the LDA exchange-correlation potential is related to the UEG exchange-correlation one:

$$v_{xc}^{LDA}(\mathbf{r}) = \frac{\delta E_{xc}^{LDA}[n]}{\delta n(\mathbf{r})} = \int d^3r' \frac{de_{xc}^{UEG}(n_0)}{dn_0}\bigg|_{n_0=n(\mathbf{r'})} \frac{\delta n(\mathbf{r'})}{\delta n(\mathbf{r})} = \frac{de_{xc}^{UEG}(n_0)}{dn_0}\bigg|_{n_0=n(\mathbf{r})} \tag{3.57}$$

where it has been used Eq. 3.30 and Eq. 3.56 in the first and second equalities. It only depends on the local density (really short range). So, as a consequence, the LDA vanishes exponentially in the asymptotic region ($r \to \infty$) of finite systems, as the density decays exponentially [4]. LDA as have been seen only takes into account the value of the electron density at each point in space (not in the derivative of the electron density or the KS orbitals). The LDA does not depend on any free parameters that introduce some physical scale. Also, as an alternative, you can use numerical *Monte Carlo* results in the LDA. Moreover, the LDA is consistent with the *ab-initio* concept of DFT.

3.1.5   Local Spin Density Approximation

The LSD approximation to any energy moment "G" is the expressed as it follows:

$$G^{LSD}[n_\uparrow, n_\downarrow] = \int d^3r\, n(\mathbf{r})g(n_\uparrow, n_\downarrow(\mathbf{r})) \tag{3.58}$$

Being $g(n_\uparrow, n_\downarrow(\mathbf{r}))$ the energy component per particle in an EG (electron gas) with uniform spin densities $n_\uparrow$ and $n_\downarrow$. LSD gives a good account of the linear response of the spin-unpolarized UEG. As:

$$\frac{\delta^2 E_{XC}^{LSD}}{\delta n(\mathbf{r})\delta n(\mathbf{r'})} = \delta(\mathbf{r} - \mathbf{r'})\frac{\partial^2[ne_{XC}(n)]}{\partial n^2} \tag{3.59}$$

The input $e_{XC}(n_\uparrow, n_\downarrow)$ to LSD is in essence unique, as there is a posible system in which $n_\uparrow$ and $n_\downarrow$ are constant, for that LSD is exact. [4]

3.1.6 Generalized Gradient Approximation (GGA)

As it was said before, most of the systems in nature are inhomogeneous, so the accuracy of the LDA is not clear *a priori*. It is an approach that evolves from another one: the gradient expansion (GE). The GE consists in varying only the density very slowly with **r** [4].

One important variable in the GE is the reduced density gradient:

$$\zeta = \frac{|\nabla n|}{2nk_F} = \frac{|\nabla n|}{2(3\pi^2)^{1/3}n^{4/3}} = \frac{3}{2}\left(\frac{4}{9\pi}\right)^{1/3}|\nabla r_s| \tag{3.60}$$

It tells how fast and how much the density varies on the scale of the local Fermi wavelength $2\pi/k_F$, obtained in Eq. 3.49. Correlation introduces another length scale, the screening length, $1/k_\zeta$, so we have other reduced density gradient:

$$t = \frac{|\nabla n|}{2k_\zeta n} = \left(\frac{\pi}{4}\right)^{1/2}\left(\frac{9\pi}{4}\right)^{1/6}\frac{\zeta}{r_s^{1/2}} \tag{3.61}$$

It is interesting to comment here that in the high-density limit (when $r_s \to 0$), the screening length ($1/k_\zeta \sim r_s^{1/2}$) is the most important length scale for the correlation hole. Moreover, under the uniform density scaling of $\zeta(\mathbf{r}) \to \zeta_\gamma(\mathbf{r}) = \zeta(\gamma\mathbf{r})$, the functionals $T_s[n]$ and $E_x[n]$ scale as the theory of functionals explains, so their gradient expansions are:

$$T_s[n] = A_s \int d^3r\, n^{5/3}\left[1 + \alpha s^2 + ...\right], \tag{3.62}$$

$$E_x[n] = A_x \int d^3r\, n^{4/3}\left[1 + \mu s^2 + ...\right] \tag{3.63}$$

It is noteworthy that the previous equations refer to the non-interacting kinetic energy functional and the exchange energy functional respectively.

$$E_c[n] = \int d^3r\, n\left[e_c(n) + \beta(n)t^2 + ...\right] \tag{3.64}$$

The variable $e_c(n)$ does not approach to a constant as $n \to \infty$, however, $\beta(n)$ does.

The second order GE has many problems as it follows. Its potential diverges for exponentially decaying densities. Also, it gives only lowly accurate exchange energies. Moreover, it does not lead to a significantly improvement over the LDA. The structure of gradient-dependent functionals is semi-local, this means that are computationally highly less demanding than calculations with fully non-local functionals.

The GEA form of 3.62, 3.63 and 3.64 is a special case of the GGA form:

$$E_{XC}^{GGA}[n_\uparrow, n_\downarrow] = \int d^3r \, f(n_\uparrow, n_\downarrow, \nabla n_\uparrow, \nabla n_\downarrow) \tag{3.65}$$

The input $f(n_\uparrow, n_\downarrow, \nabla n_\uparrow, \nabla n_\downarrow)$ to GGA is not unique.

GGAs include the density and its first derivative in the Exchange-Correlation potential. Also, there is another improvement, further than GGAs: the Meta-GGAs. Meta-GGA functionals are a development of Generalized Gradient Approximation (GGA) functionals. A Meta-GGA functional in its original form also includes, contrary to a GGA functional, the second derivative of the electron density (the Laplacian).

However, Meta-GGA functionals nowadays are not the same as they were formulated in the beginning. There exist Meta-GGA functionals that do not include the Laplacian of the electron density, this is because new Meta-GGA functionals are characterised by taking into account the local kinetic energy density, which is more accurate for chemical bonds compared to LDA and GGA. The most general expression for Meta-GGA functionals is [5]:

$$E_{xc}[n] = \int e_{xc}(\rho(\vec{r}), \nabla\rho(\vec{r}), \tau(\vec{r})) d\vec{r} \tag{3.66}$$

Where e_{xc} is an ordinary function, also, the kinetic-energy density, $\tau(\vec{r})$ is given by:

$$\tau(\vec{r}) = \frac{1}{2} \sum_{i=1}^{occupied} \left| \nabla \psi_i(\vec{r}) \right|^2 \tag{3.67}$$

Where ψ_i are the KS orbitals [6].

3.1.7   Hybrid functionals

These functionals are a class of aproximations to the Exchange-Correlation energy functional which incorporate a portion of exact exchange (or HF exchange) from HF method with the rest of the Exchange-Correlation energy functionals from other sources. The exact exchange energy is expressed in terms of the KS orbitals rather than the density. So, it can be said that Hybrid Exchange-Correlation functionals are a linear combination of the HF exact exchange functional and any number of Exchange-Correlation explicit density functionals.

The exchange energy of electrons with the same spin [2] is the most important contribution to the total exchange correlation energy [7]. So, what is expected is to obtain

---

[2]Also called "Fermi hole". Electrons which share the same spin are correlated in HF, while different-spin electrons are not. This is a direct consequence of the Pauli exclusion principle, this is, two electrons with same spin cannot be at the same place.

accurate results if the approximated semilocal exchange functional is replaced with a HF equation for exchange energy :

$$E_x^{Exact} = -\frac{1}{2} \sum_{\sigma=\alpha,\beta} \sum_{i_\sigma,j_\sigma}^{occ} \int \int \frac{\phi_{i_\sigma}(\vec{r})\phi_{j_\sigma}(\vec{r})\phi_{i_\sigma}(\vec{r'})\phi_{j_\sigma}(\vec{r'})}{\left|\vec{r}-\vec{r'}\right|} \tag{3.68}$$

There are a few terms that should be noted about the equation 3.68. Takes into account the α and β electrons (spin $\uparrow$ and $\downarrow$ respectively), also, the occupied orbitals by those electrons (i_σ and j_σ) and their respective monoelectronic orbital functions.
Taking into account:

$$E_{xc} = E_x^{exact} + E_c \tag{3.69}$$

There is a problem with this functional's form. Is proven to be inapplicable to description of chemical bonds in molecules. However, it is accordingly good for one-center systems (for example, atoms). To check how theory of hybrid functionals is developed and what could be the weak points in this development of functionals in DFT theory, read ref. [7].

The GGA functionals used in this study are : becke88, perdew86, hcth, xtpss03, becke97 and m06-L. All the functionals used in the work (unless one, the becke97) are GGA functionals or meta GGA functionals, this decision was made based on the research done previously (ref. [4] and ref. [5]). However, there are many differences between them, which are goint to be explained next. For example, between becke88 and perdew86: they are GGA functionals, but they also are exchange and correlation functionals respectively. In other words, for one, there is a term of exchange energy but not correlation and vice-versa. This was done on purpose to analyze how powerful would be the absence of the exchange or correlation terms. Taking into account that the exchange terms refers to the quantum mechanical effect of electron indistinguishability. It represents the tendency of electrons to avoid each other due to their antisymmetrization requirement under the Pauli exclusion principle. Also, the correlation term in the exchange-correlation functional captures the collective behavior of electrons. It accounts for the fact that the motion of one electron is influenced by the presence of all other electrons in the system. We can predict which will be important as the number of electrons increases. On the other hand, there is the hcth, which is a GGA functional that takes into account both terms. Also, there are the meta GGA functionals, these two are from different nature: while xtpss03 considers only the exchange term, the m06-L keeps both in mind.

The remaining functional is a exhcange-correlation GGA hybrid functional, the becke97. This is the only functional in the study that incorporates a portion of exact exchange from HF with the rest of the exchange-correlation terms from studies.

3.1.8 Pseudopotentials

Pseudopotentials are approximations used to simplify the electronic structure calculations. The idea behind pseudopotentials is that the valence electrons, which are primarily responsible for the chemical bonding and electronic properties, are well-behaved and localized near the atomic cores. Pseudopotentials replace the full electron-nucleus interaction potential with an effective potential that represents the core electrons and their screening effects on the valence electrons. It becomes possible to represent the valence electron wave functions with a smaller number of basis functions, reducing the computational cost significantly. This allows for the study of larger systems and longer timescales that would be computationally prohibitive otherwise. The basis for pseudopotentials lies in the fact that only a few electrons are responsible for chemical bond formation, while most tightly bound electrons are essentially uninvolved. Pseudopotentials effectively remove these unimportant electrons and replace the complex electron-nuclear interactions with a smooth ionic pseudopotential that acts on the relevant electrons. Quantum effects and Fermi statistics lead to cancellations, enabling this simplification [8].

Let us suppose that the core states $|\chi_n\rangle$ satisfy: $H|\chi_n\rangle = E_n|\chi_n\rangle$. A valence state, call it $|\psi\rangle$, can be substituted by a smoother pseudofunction, $|\phi\rangle$, expanding the remaining part in terms of the core states,

$$|\psi\rangle = |\phi\rangle + \sum_n^{core} a_n |\chi_n\rangle \tag{3.70}$$

Since the valence state must be orthogonal to all the core states, we write:

$$\langle\chi_m|\psi\rangle = \langle\chi_m|\phi\rangle + a_m \tag{3.71}$$

$$|\psi\rangle = |\phi\rangle - \sum_n^{core} |\chi_n\rangle \langle\chi_n|\phi\rangle \tag{3.72}$$

So, the eigenvalue equation will look like:

$$\hat{H}\left(|\phi\rangle - \sum_n^{core} \langle\chi_n|\phi\rangle |\chi_n\rangle\right) = E\left(|\phi\rangle - \sum_n^{core} \langle\chi_n|\phi\rangle |\chi_n\rangle\right) \tag{3.73}$$

$$\hat{H}|\phi\rangle + \sum_n^{core} (E - E_n) |\chi_n\rangle \langle\chi_n|\phi\rangle = E|\phi\rangle \tag{3.74}$$

Where we can write:

$$\hat{V}_{nl} = \sum_n^{core} (E - E_n) |\chi_n\rangle \langle\chi_n|\phi\rangle \tag{3.75}$$

So, it can be fully expressed as:

$$(H + V_{nl}) \left| \phi \right\rangle = E \left| \phi \right\rangle \tag{3.76}$$

This additional potential, $\hat{V}_{nl}$ is localised in the core. That potential is constructed such that it includes a repulsive component that cancels out the attractive Coulomb potential between the valence electrons and the atomic nucleus. This is done to effectively remove the core electrons from the calculation and simplify the treatment of the valence electrons. [9]. Since the objective of the study is to analyse the different functionals" behaviour through the ground state energy for different atoms, we will not analyse the impact of the pseudopotentials. Also, pseudopotentials are used for compounds, because the aim of this approximation is to focus on the chemical bonds and forget the inner electrons.

3.1.9 Basis sets

Basis sets are a set of functions (that are also called basis functions) which form part of linear combinations to develop atomic and molecular orbitals [10]. It is convenient for these functions to be atomic orbitals centered on atoms. These functions are introduced in quantum chemical calculations (such as HF or DFT). Basis sets have been optimized over the years, however, the computational cost intensifies as the basis sets grows. The construction of these basis sets relies on Slater, Gaussian, plane wave and delta functions. The basis sets that are most commonly used and offer good approximate results are contracted sets of atom-centered Gaussian functions.

So, to calculate the molecular orbitals (which are unknown), is usually helpful to expand them in terms of known wave functions (atomic orbitals, which are basis functions), this expansion is linear and its form is the following:

$$\psi_i = \sum_j c_{ij} \phi_j \tag{3.77}$$

This expansion is introduced in the HF equations, since HF is a variational method. It can get started with a simple trial set of atomic orbitals coefficients and finally obtain a set of coefficients which determines a self-consistent field solution [11]. Take into account that a good basis set would be available for any atom, however, computational cost would be so expensive.

Types of basis sets

The most used basis functions in electronic structure calculations are Slater-type orbitals (STO) and Gaussian-type orbitals (GTO). STO have the general form:

$$\chi_{\zeta,n,l,m}(r, \theta, \phi) = N Y_{l,m}(\theta, \phi) r^{n-1} e^{-\zeta r} \tag{3.78}$$

Where N is the normalization factor, $Y_{l,m}$ are spherical harmonic functions, while ζ is the orbital exponent and n the principal quantum number. This type of basis functions do not posses radial nodes. Instead, they are introduced by making linear combinations of STOs.

The STO functions can be replaced by GTO functions and solve the limitations they have (they become inefficient in the calculation). On the other hand, GTOs are very efficient in calculation, but they offer a worse reproduction of the orbitals (contrary to the STO functions). This is why STO functions are adjusted as a linear combination of GTOs [12]. GTO functions are written in terms of the spherical harmonics or cartesian coordinates:

$$\chi_{\zeta,n,l,m}(r,\theta,\phi) = NY_{l,m}(\theta,\phi)r^{2n-2-1}e^{-\zeta r^2} \tag{3.79}$$

$$\chi_{\zeta,l_x,l_y,l_z} = Nx^{l_x}y^{l_y}z^{l_z}e^{-\zeta r^2} \tag{3.80}$$

GTO functions are written in terms of polar (3.79) or cartesian (3.80) form. Also, the type of orbital in equation 3.80 is determined by the sum of l_x, l_y and l_z. The combination of the complete set of basis functions is called primitive GTOs (PGTOs). This combination into a smaller set of functions forms linear combinations and is called contraction of the basis set, the resulting functions are named as CGTOs[11].

For example, in this study, the chosen basis was: 6-31G* [13]. Is able to represent electronic wave function for atoms from hydrogen to krypton. 6-31 means that each inner shell STO is a linear combination of 6 primitive Gaussian functions and each valence shell STO is divided into an inner and outer part (due to the term ζ) which use, respectively, 3 and 1 primitive Gaussian functions.

Polarization functions are used as tools to increase the size of the basis set. They are used on the orbitals whose angular momentum is the highest and allows polarizing the atomic electron density to a get a better resolution. According to the previous explanation of the basis set used in this DFT calculation, 6-31G*, the asterisk means that contains a set of Gaussian polarization functions. *Pople* style basis sets are STOs consisting of n Polarized Gaussian type orbitals. As only one set of polarization is used, the notation used is with the asterisk, for example, 6-31G* is the same as 6-31G(d). This basis set adds a set of d functions to the atoms which belong to the first and second rows (without counting on H and noble gases). Polarization functions are those whose angular momentum is higher than the corresponding for the atom they belong.

Chapter 4

NWChem

En este capítulo se hará una breve introducción sobre el programa informático utilizado en este trabajo. Se realizará una breve descripción de los comandos utilizados en el fichero de entrada, así como la naturaleza de los funcionales objetos de estudio.

NWChem is a free product of computational ab initio chemistry package created by the Experimental Molecular Science Laboratory (EMSL), located at the Pacific Norwest National Laboratory (PNNL) in Washington State. It is possible to make the extremely rough calculations of HF methods or DFT and much more. [14]

It is needed to make clear that is not only for quantum mechanics use, it is used for classical physics as well. Also, allows relativistic and non-relativistic calculations. The package was developed to make molecular calculations in the context of biomolecules, nanostructures, and solid-state but it was adapted to the atomic domain. The calculations were carried in node 41 of the cluster Molec3 in the Department of Physics of the University of La Laguna. An example of input file is going to be shown next, with all the instructions and its meaning.

4.1 Structure of the input file

NWChem has a manual for the user, there is a whole chapter of DFT calculations and representation of the charge density, so it is not difficult to follow the instructions [15].

- START. This instruction will name the files related as the word written next to the directive and their extensions. This can be skipped and write it in the console with the properly commands, as the output file.

- GEOMETRY. It is used to specify the geometry of the system, the atoms are named by its symbol and the cartesian coordinates (x,y,z) where the nucleus is fixed.

- BASIS. It has to be specified if the spherical or cartesian projection is used. Also, the type of orbital must be specified if the calculation involves many of them. The default is "ao basis", which involves the atomic orbital.

- DFT. This is the type of calculation method whose result is wanted. Here, is where the user decides to put: HF, DFT...

- MULT. Defines the multiplicity of the system, being the value as it follows: $(2S+1)$

- MAXITER. This is the maximum number of iterations.

- SET TOLGUESS. The number written after this command fixes the accuracy in Ha of the calculations.

- DPLOT. The instruction to plot the vectors obtained in the DFT calculation.

- LIMITXYZ. Establishes the limits of the cell to be plotted, similar to many functions in different languages of programs. It is always convenient to limit the coordinates in the plots. The units by default are in Angstroms.

- SPIN TOTAL. It specifies what kind of density is computed. There are several types of spin densities: alpha and beta densities, spidens and total. Alpha electrons, and beta electrons are well known. Spidens are the difference between them, and the total spin density indicates the value of the total value of spin (M_s).

- GAUSSIAN. Is used to give as an output the Gaussian Cube format. Using the program *Visual Molecular Dynamics* (VMD) the Gaussian Cube format can be read.

An example of input file of the VMD program and NWChem is shown in the **Appendix** A and **Appendix** B

Chapter 5

Results and Discussion

En este capítulo se expondrán los resultados obtenidos para las energías del estado fundamental de los distintos átomos que se han organizado por periodos. Además, se indica cómo se ha procedido a evaluar dichos átomos en el programa, ya que su multiplicidad de spin se ha de tener en cuenta en el fichero de entrada. Finalmente, se buscarán patrones y se discutirá la efectividad de determinados funcionales.

5.1 Study for Different Periods

The electronic structure of atoms depends on the electronic configuration. The study will not only focus on the nature of atoms, it must be taken into account which shells and sub-shells are completed, following the *Aufbau Principle* [1]. So, it was decided to start with the most easy to understand elements (apart from the simplest one: the Hydrogen), the Helium and the second period of the periodic table.

It should be noticed that in these results it is being referred as "best option", or "best functional" to the "appropriate" functional in a specific situation. It does not mean that anyone could find any functional that works better than these. These functionals were chosen by their nature (GGA, exchange, correlation, hybrid, meta...) to show which one could be the "appropriate" for every family of elements. The purpose of this project is to study these atoms with different functionals. The electronic ground state energy of atoms are written in Hartrees (Ha) (energy atomic unit) and is equal to $27.211eV$ or $219474.6^{-1}cm$.[17]

To establish the electron spin multiplicity of atoms in the periodic table, it is needed to consider the number of unpaired electrons present in the atom's electron configuration. The spin multiplicity is determined by the total number of unpaired electrons. The Aufbau principle governs the construction of electronic configurations: in other words, the

---

[1]Following the order in which the orbitals are filled, as Feynman wrote [16], it is obtained the also known *Aufbau principle.*

energies of the central field approximation. Hund's rules give the order of energy levels arising from a given electronic configuration.

1. Aufbau Principle: Electrons occupy the lowest energy orbitals available before filling higher energy ones.

2. Pauli Exclusion Principle: No two electrons in an atom can have the same set of quantum numbers. This means that each orbital can hold a maximum of two electrons with opposite spins.

3. Hund's Rule of Maximum Multiplicity: When electrons occupy orbitals of equal energy (degenerate orbitals), they maximize the total spin by placing one electron in each orbital before pairing them up.

There have been selected many different functionals to guess which one is the best depending on the family of atoms selected (this will be discussed later). It is not known at first sight what type of functional will work better, so, it was a comparison task. Different DFT calculations have been made with the same basis set, 6-31G*. It might not be the best basis chosen for the study, because the larger the base, the higher the accuracy of the results would be. The results are grouped into their correspondent periods (apart from Hydrogen and Helium). Also, in every subsection are two tables: one for the electronic configuration and ground level for every atom and the table of the data collected from the DFT calculation (the ground state energy) for every functional and the reference ground state energy (obtained from the NIST [1]). To calculate binding energies, it is added up all relevant ionization energies. The uncertainties in ionization energies from the same source are combined in a straightforward manner, assuming they are mainly affected by systematic factors. On the other hand, uncertainties arising from different sources are combined using a method called quadrature. If the uncertainty of a particular ionization energy used in the calculation is unknown, it is approximated as ten times the value of the least significant figure of that ionization energy. Some binding energies require combining two or more ionization energies. The tables are formed of 8 columns. The first two columns correspond to the atom's element and the ground state energy of reference, respectively. Then, they are followed by the 6 ground state energies obtained from the different functionals commented before in this work. The order of appearance is not relevant as it only reflects in which order they have been studied.

5.1.1 Hydrogen

Element	Electronic configuration	Ground level
H	$1s^1$	$^2S_{1/2}$

Table 5.1: Electronic configuration and ground level for Hydrogen atom.

In Table 5.1 there are three columns: the name of the atom studied, the electronic configuration and the spectroscopic notation. The form of the spectroscopic notation is :

$^{2S+1}L_J$, where the sub-index J denotes the total angular momentum quantum number, S is the total spin quantum number and L is the total orbital angular quantum number. This notation reveals the fine structure of the terms (weakly relativistic character).

Element	E_{ref}	$E_{becke88}$	$E_{perdew86}$	E_{hcth}	Extpss03	$E_{becke97}$	E_{m06-L}
H	-0.50000	-0.49545	-	-0.50375	-0.49785	-0.50055	-0.50181

Table 5.2: The values in this table are the ground state energies in Hartree (Ha).

In Table 5.2 the value of E_{ref} is the analytical value of the ground state energy of Hydrogen, which is possible to calculate. There is no calculation of ground state energy using the perdew86 functional because is a correlation functional, for hydrogen this term is null (there is only one electron). However, there exists an exchange term, which should be equal (with opposite sign) to the electrostatic energy and cancel it, see Eq. 3.6. In other words: $n_\uparrow(\mathbf{r}) = n(\mathbf{r})$, so $E_{xc}[n_\uparrow, n_\downarrow] = E_x[n_\uparrow, n_\downarrow]$. Depending on accuracy, the exchange term would not be cancelling the electrostatic term, generating the so called spurious self-interaction term [18]. Taking this into account, the most accurate functional for hydrogen atom is becke97. This makes sense (since is a hybrid functional), since the exact Hartree potential would vanish with the correct exchange potential for hydrogen atom.

To make the study clearer, the values of the table written before were plotted. Is a useful way to determine where the functionals fail the most. In Figure 5.1 there can be
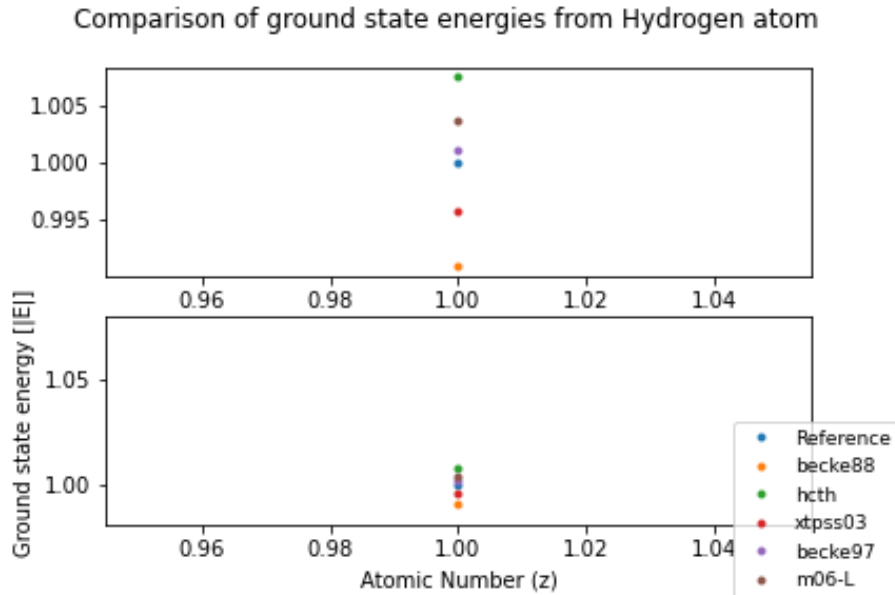

Figure 5.1: Relative ground state energy against atomic number (Z).

seen two subplots. Both correspond to the same study. The Y axis reflects $\frac{|E_i|}{|E_{ref}|}$, finally called $|E|$ to make the plot cleaner. Where E_i denotes the ground state energies obtained from the different functionals. Other way to see it as percents: $E = \frac{100E_i}{E_{ref}}$. On the one

hand, the first subplot is not zoomed to the region of interest (close to the reference value). On the other hand, the second subplot is the zoomed region, since for hydrogen atom and helium this action would be irrelevant, in the upcoming results this will be determinant to analyse the way the functionals behave in many regions. In this case, it can be seen how three functionals (hcth,m06-L and becke97) overestimate the hydrogen's ground state energy.

5.1.2 Helium

Element	Electronic configuration	Ground level
He	$1s^2$	$^1S_0$

Table 5.3: Electronic configuration and ground level for Helium atom.

Element	E_{ref}	$E_{becke88}$	$E_{perdew86}$	E_{hcth}	Extpss03	$E_{becke97}$	E_{m06-L}
He	-2.90339	-2.85400	-1.95432	-2.91041	-2.85930	-2.90230	-2.90393

Table 5.4: The values in this table are the ground state energies in Hartree (Ha).

Contrary to the hydrogen atom, the functional that calculates the best the ground state energy is m06-L. This can be seen in Figure 5.2.

5.1.3 Second Period

Element	Electronic configuration	Ground level
Li	$[He]2s$	$^2S_{1/2}$
Be	$[He]2s^2$	$^1S_0$
B	$[He]2s^22p$	$^2P_{1/2}$
C	$[He]2s^22p^2$	$^3P_0$
N	$[He]2s^22p^3$	$^4S_{3/2}$
O	$[He]2s^22p^4$	$^3P_2$
F	$[He]2s^22p^5$	$^2P_{3/2}$
Ne	$[He]2s^22p^6$	$^1S_0$

Table 5.5: Electronic configurations and ground levels for second period atoms.

Element	E_{ref}	$E_{becke88}$	$E_{perdew86}$	E_{hcth}	Extpss03	$E_{becke97}$	E_{m06-L}
Li	-7.47798	-7.42641	-5.75733	-7.49246	-7.43799	-7.48653	-7.48512
Be	-14.66844	-14.56063	-12.08599	-14.66496	-14.57915	-14.66274	-14.65825
B	-24.65809	-24.51454	-21.00683	-24.64147	-24.54239	-24.64394	-24.64410
C	-37.85579	-37.67235	-32.94426	-37.82744	-37.70211	-37.83176	-37.83573
N	-54.61161	-54.37610	-48.21642	-54.57062	-54.40810	-54.56765	-54.58373
O	-75.10984	-74.78902	-67.10519	-75.03477	-74.83032	-75.03473	-75.05395
F	-99.80710	-99.38031	-89.94208	-99.68564	-99.42185	-99.68348	-99.70789
Ne	-129.05250	-128.49643	-117.08527	-128.87563	-128.53827	-128.85853	-128.88763

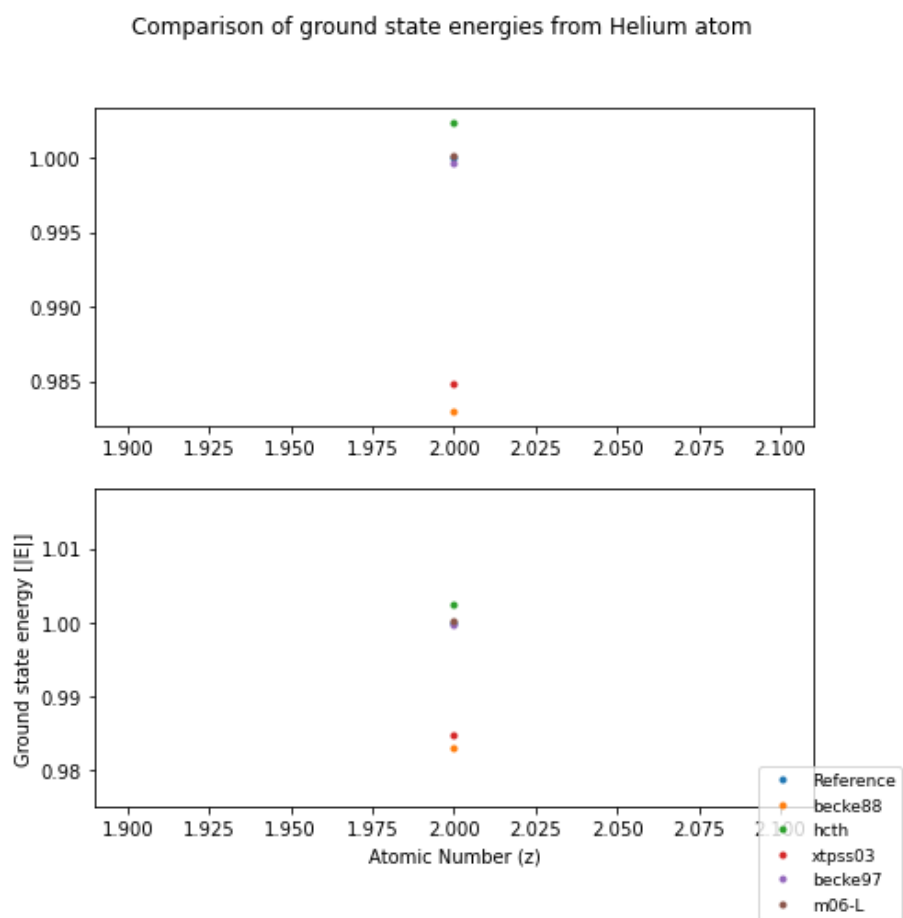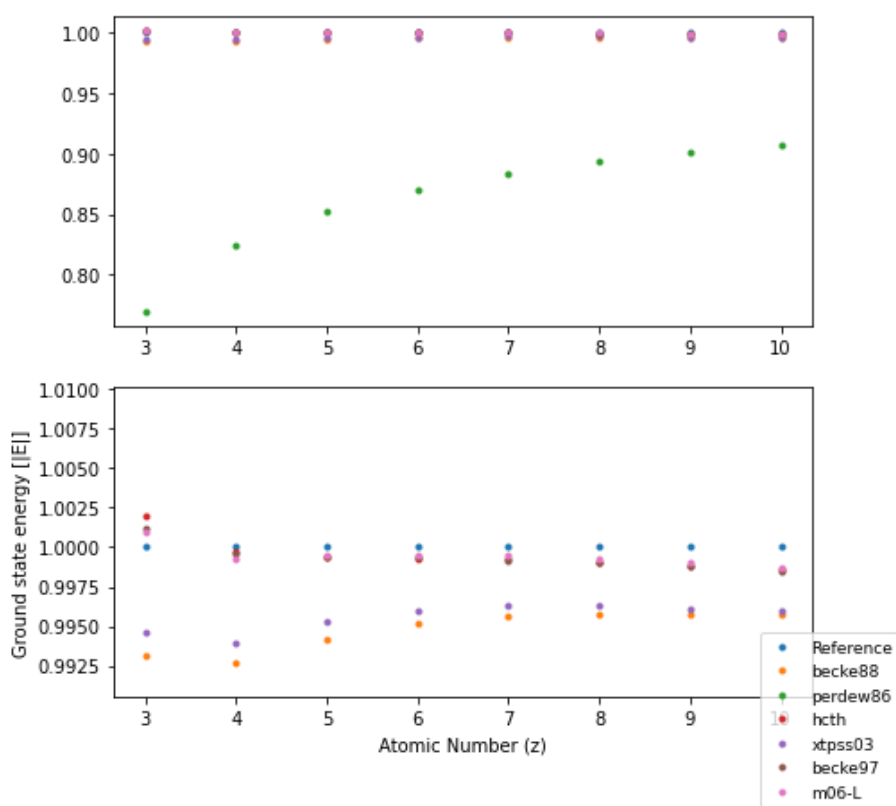Table 5.6: The values in this table are the ground state energies in Hartree (Ha).

Figure 5.2: Relative ground state energy against atomic number (Z).

Figure 5.3: Relative ground state energy against atomic number (Z).

In Figure 5.3, the only functional which is not good enough to provide accurate results is perdew86. This has been seen along the study and there is no need to mention it again in the following conclusions (this is due to correlation effects, they are not important for light atoms, later on, this will be discussed). Correlations effects are negligible comparing to exchange effects, this is something that can be seen in the figure, also, which functionals overstimate the ground state energy (technically the term is "understimate", because we are working with absolute values).

These functionals are the best working functionals in this study (hcth,becke97 and m06-L), while the others (except perdew86) are close to the reference value. Also, in Figure 5.3 it can be seen that for higher atomic number values perdew86 works better, but it is not enough to get close to the reference values. Also, the three "best" functionals (they are exchange-correlation functionals) tend to understimate the ground state energy for light atoms. At the end of the graph, for Ne ($Z = 10$), there is no functional which understimates the ground state energy. Also, Table 5.5 has also been written to make clearer conclusions about the data of Table 5.6.

5.1.4 Third Period

Element	Electronic configuration	Ground level
Na	$[Ne]3s$	$^2S_{1/2}$
Mg	$[Ne]3s^2$	$^1S_0$
Al	$[Ne]3s^23p$	$^2P_{1/2}$
Si	$[Ne]3s^23p^2$	$^3P_0$
P	$[Ne]3s^23p^3$	$^4S_{3/2}$
S	$[Ne]3s^23p^4$	$^3P_2$
Cl	$[Ne]3s^23p^5$	$^2P_{3/2}$
Ar	$[Ne]3s^23p^6$	$^1S_0$

Table 5.7: Electronic configurations and ground levels for third period atoms.

Element	E_{ref}	$E_{becke88}$	$E_{perdew86}$	E_{hcth}	Extpss03	$E_{becke97}$	E_{m06-L}
Na	-162.43200	-161.85777	-148.51856	-162.26231	-161.90478	-162.23451	-162.24296
Mg	-200.32300	-199.60529	-184.37305	-200.07021	-199.65416	-200.02819	-200.03931
Al	-242.72700	-241.85851	-224.60841	-242.36886	-241.91179	-242.31110	-242.32978
Si	-289.89800	-288.82479	-269.44195	-289.38784	-288.88040	-289.31017	-289.33745
P	-341.98000	-340.67301	-319.03930	-341.29780	-340.73034	-341.19365	-341.23718
S	-399.08000	-397.45665	-373.53835	-398.15880	-397.51842	-398.03324	-398.07911
Cl	-461.44000	-459.42579	-433.09753	-460.21002	-459.48859	-460.05906	-460.11045
Ar	-529.22000	-526.74507	-497.87143	-527.62004	-526.80835	-527.43623	-527.49843

Table 5.8: The values in this table are the ground state energies in Hartree (Ha).

For this period, results are very different from the ones seen before and can be read in Table 5.8. In the third period the only atom whose ground state energy was determined
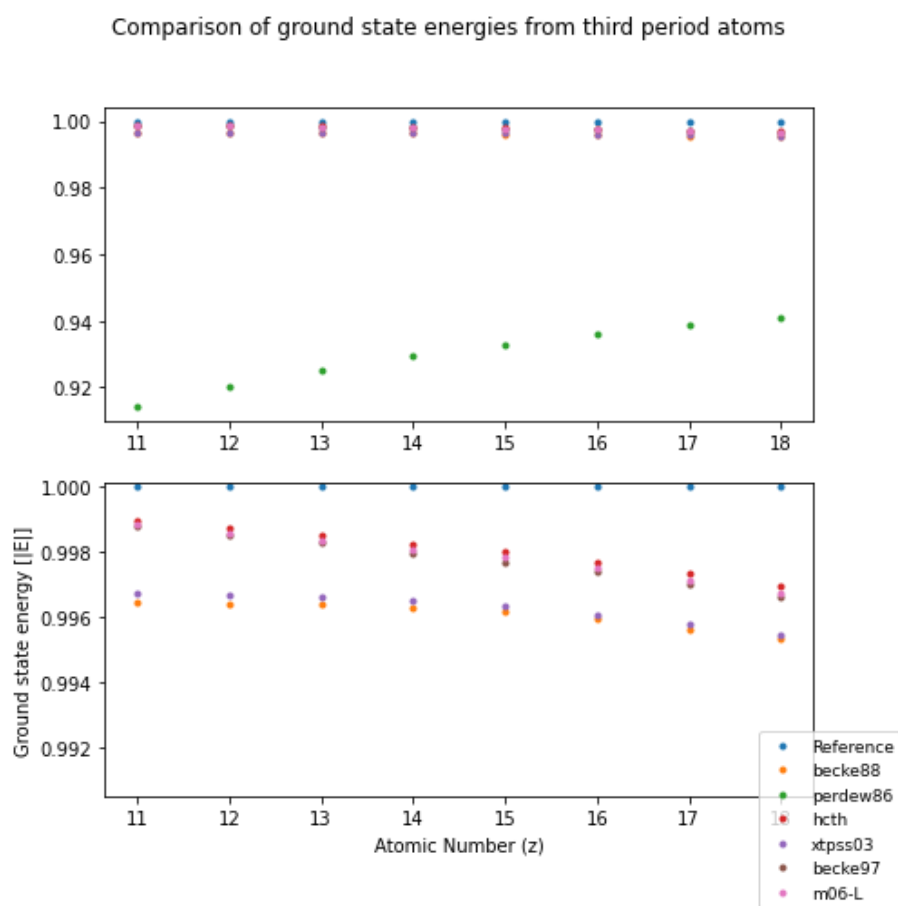
Figure 5.4: Relative ground state energy against atomic number (Z).

accurately by a functional different from the hcth (it was the m06-L), was the Argon. The reason is unknown, and purely speculative. Analysing Table 5.7, one could think that functional m06-L works accurately for ground level $^1S_0$ (this is the same scenario as He). However, there is a contradiction with this thought, because, the functional that offers the best result for Mg, for example, is the hcth. The functional hcth is over m06-L for third period atoms in Figure 5.4 (and closer to the reference data) until Ar (they switch and m06-L is over hcth). Also, it seems that most of the functionals tend to get far from the reference data as Z increases (unlike perdew86).

5.1.5 Fourth period

Element	Electronic configuration	Ground level
K	$[Ar]4s$	$^2S_{1/2}$
Ca	$[Ar]4s^2$	$^1S_0$
Sc	$[Ar]4s^23d$	$^2D_{3/2}$
Ti	$[Ar]4s^23d^2$	$^3F_2$
V	$[Ar]4s^23d^3$	$^4F_{3/2}$
Cr	$[Ar]4s3d^5$	$^7S_3$
Mn	$[Ar]4s^23d^5$	$^6S_{5/2}$
Fe	$[Ar]4s^23d^6$	$^5D_4$
Co	$[Ar]4s^23d^7$	$^4F_{9/2}$
Ni	$[Ar]4s^23d^8$	$^3F_4$
Cu	$[Ar]4s3d^10$	$^2S_{1/2}$
Zn	$[Ar]4s^23d^10$	$^1S_0$
Ga	$[Ar]4s^23d^{10}4p$	$^2P_{1/2}$
Ge	$[Ar]4s^23d^{10}4p^2$	$^3P_0$
As	$[Ar]4s^23d^{10}4p^3$	$^4S_{3/2}$
Se	$[Ar]4s^23d^{10}4p^4$	$^3P_2$
Br	$[Ar]4s^23d^{10}4p^5$	$^2P_{3/2}$
Kr	$[Ar]4s^23d^{10}4p^6$	$^1S_0$

Table 5.9: Electronic configurations and ground levels for fourth period atoms.

Element	E$_{ref}$	E$_{becke88}$	E$_{perdew86}$	E$_{hcth}$	Extpss03	E$_{becke97}$	E$_{m06-L}$
K	-602.03000	-599.09096	-567.51308	-600.01533	-599.15350	-599.79736	-599.85026
Ca	-680.22000	-676.69117	-642.66337	-677.69541	-676.74946	-677.43857	-677.49354
Sc	-763.96000	-759.69389	-723.16682	-760.78295	-759.74833	-760.47397	-760.51968
Ti	-853.36000	-848.35862	-808.81507	-849.54659	-848.40758	-849.17878	-849.22816
V	-948.90000	-942.84239	-900.30284	-944.14504	-942.88427	-943.70523	-943.75258
Cr	-1050.40000	-1043.26688	-997.38508	-1044.69474	-1043.28749	-1044.15291	-1044.19254
Mn	-1158.10000	-1149.78644	-1100.67945	-1151.35620	-1149.80077	-1150.74259	-1150.79260
Fe	-1272.20000	-1262.37394	-1209.93609	-1264.07783	-1262.37920	-1263.38809	-1263.42425
Co	-1392.80000	-1381.33659	-1325.40535	-1383.18339	-1381.33485	-1382.41016	-1382.43156
Ni	-1519.80000	-1506.77814	-1447.22162	-1508.78756	-1506.75606	-1507.91282	-1507.94196
Cu	-1653.80000	-1638.83408	-1575.51995	-1640.99552	-1638.78746	-1640.03150	-1639.99771
Zn	-1794.90000	-1777.68278	-1710.44956	-1780.06588	-1777.61619	-1778.94904	-1778.96686
Ga	-1942.80000	-1923.14921	-1852.30956	-1925.66801	-1923.06970	-1924.44612	-1924.47770
Ge	-2097.70000	-2075.19591	-2000.52009	-2077.87369	-2075.10298	-2076.54411	-2076.57580
As	-2259.00000	-2234.02240	-2155.42907	-2236.86565	-2233.91561	-2235.42252	-2235.45222
Se	-2428.10000	-2399.61609	-2317.11108	-2402.63831	-2399.49438	-2401.08519	-2401.11069
Br	-2604.40000	-2572.15156	-2485.64887	-2575.35486	-2572.01453	-2573.68779	-2573.70743
Kr	-2788.00000	-2751.72098	-2661.13071	-2755.11090	-2751.56867	-2753.32437	-2753.33592

Table 5.10: The values in this table are the ground state energies in Hartree (Ha).

The values obtained and written in the tables are plotted and can be observed in Figure 5.5. Analysing the figure, we can get several conclusions. It seems that most of the functionals tend to get far from the reference data as Z increases (like in the third period). In the last period, the most efficient by far was the hcth functional (for any atom) and it can be seen also in Table 5.10. As the atomic nuclei gets bigger (and the atoms have more electrons), correlation effects are important and are taken into account, results are getting better (but not accurate enough to be taken into account as principal functional for DFT calculation). We can consider heavy atoms after $Z = 20$, and argue that for heavy single atoms, the correlation effects are stronger than exchange effects (this in the condition which let those functionals obtain accurate enough values). Also, this could be the reason why hcth works efficiently enough to surpass the m06-L results after the second period. Analysing Table 5.9, the inner electrons of three closed shells are interacting with each other, this would lead to bigger correlation effects, making the hcth the best functional among the chosen ones to study these atoms (in general lines).
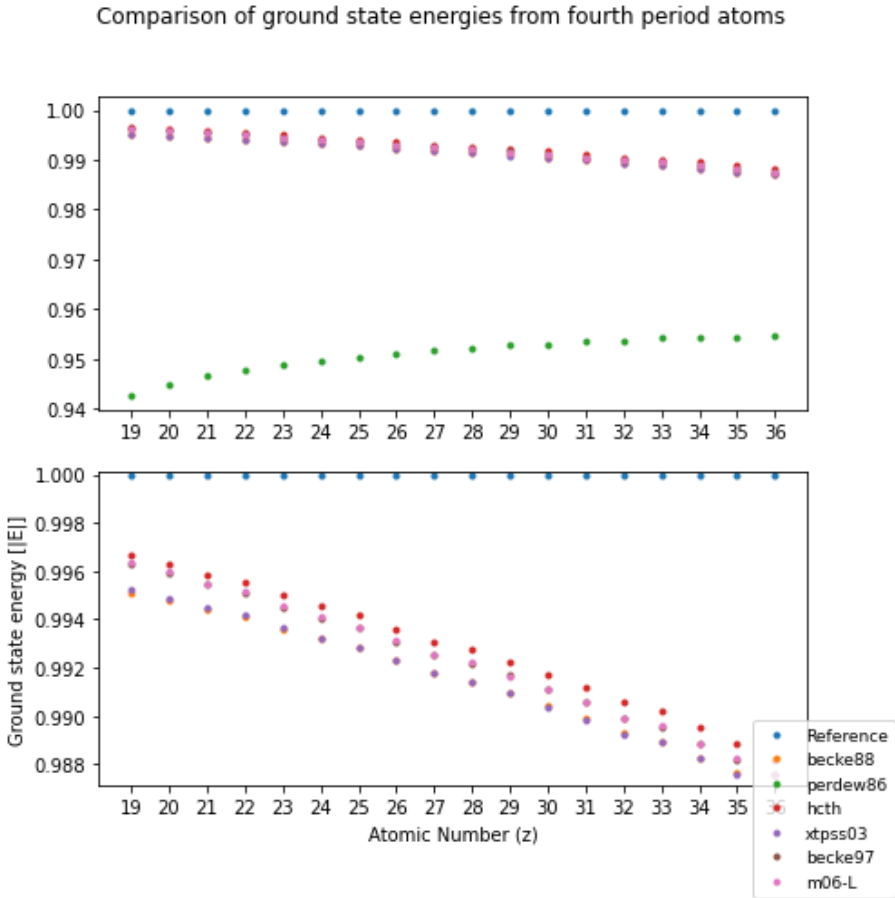
Figure 5.5: Relative ground state energy against atomic number (Z).

Chapter 6

Conclusion

Finalmente, se discute la efectividad de los funcionales propuestos para logar un resultado preciso sobre la energía del estado fundamental de los átomos estudiados de la tabla periódica.

As the results have indicated, there is no best functional "*a priori*" to determine the ground state energy for isolated atoms. For example, in theory, the best functionals are hybrid exchange-correlation ones, however, in this study, they did not offer accurate enough values as, for example in many cases, a GGA exchange-correlation functional.

Comparing the data obtained during this study with those extracted from **Appendix** C.1, DFT is a method that should be consider seriously. Maybe the accuracy of the values obtained in relation with the reference data is not the best. Also, HF and MP2 ground state energies cannot be compared from the ones obtained in this study because a different basis set was used and the maximum number of iterations is also different. For example, in the input file used in **Appendix** A, the maximum number of iterations is 1000, while in the input file used for **Appendix** C.1 the maximum number of iterations is set to 2000. However, the same basis was not used for the calculation. In the reference, the basis used were 6-311G* for atoms H to Ca and Ga to Kr, while the basis aug-cc-pvdz (typical basis set of post HF calculation) was used for the transition metals. It should also be considered the computational cost.

Also, computational cost has to be taken into account (for example, the time the program needs to run the input file). For Kr, which is a heavy atom, the time needed to run all the operations was 0.9s, while for Cr or Ni was 1.2s and 1772.1s respectively (all times for hcth). If we compare these times for the same elements but using the hybrid functional becke97, we obtain 0.9s, 14.2s and 475.9s respectively. Now we have seen that for different functionals, we obtain different running times, this is not a surprise, since we know one is a GGA exchange-correlation functional and the other is a hybrid GGA exchange-correlation functional. Maybe the reason in the decreasing running time for the Ni (comparing the two different functionals) is because it takes less iterations to converge and maybe more time for Cr due to the calculation of the exact exchange.

Now, forgetting the basis sets (which are important, though), the different behaviours of the functionals are still an interrogant. For hydrogen, the choice of functional may indeed have less impact compared to heavier atoms because hydrogen is a simple system with a single electron. In this case, the electron correlation effects are null, and simpler functionals like GGA or even LDA can provide reasonable accuracy (this is why results are so close between them for hydrogen).

However, as you move to heavier atoms, the electron correlation effects become more significant, and the choice of functional becomes crucial. Hybrid functionals, which incorporate a fraction of Hartree-Fock exchange, often provide improved accuracy for systems with stronger electron correlation, such as heavier atoms. It is not always necessary to use hybrid functionals for heavier atoms. The choice of functional depends on the atom or group of atoms, the property of interest, and the level of accuracy required. While hybrid functionals are generally more accurate for many systems, they can be computationally more expensive than GGA or Meta-GGA functionals.

Elements from the first and second rows of the periodic table, such as carbon, oxygen, and nitrogen, tend to have less electron correlation effects compared to heavier elements. GGA functionals can often yield reasonable accuracy for their electronic structures and properties.The electron correlation effects generally increase as you move across the periodic table, especially for transition metals and heavier elements, this is something to take into account.

On the other hand, GGA functionals can still provide reasonable results for some properties of these elements, they may not fully capture the strong electron correlation effects that are characteristic of transition metals and heavier atoms, this can be seen in Table 5.10. Hybrid functionals, due to their inclusion of Hartree-Fock exchange, are often better suited for accurately describing the electronic structure and properties of these systems [19]. It is important to note that the sensitivity to electron correlation effects can vary depending on the specific property and the context of the study. This might be the reason why the hybrid functional does not predict as accurate as the GGA functional the ground state energy of heavier atoms. GGA functionals like hcth primarily capture electron correlation effects through the exchange-correlation energy functional based on the electron density. On the other hand, meta-GGA functionals like m06-L and hybrid functionals like Becke97 incorporate additional terms that account for electron density gradients, Laplacians, and Hartree-Fock exchange [20]. The inclusion of these additional terms may introduce certain approximations or assumptions that could impact the accuracy for transition metals.

It's worth noting that the performance of DFT functionals can vary, and there is no universally "best" functional for all systems and properties. It is often recommended to perform benchmark calculations and compare the results with reference data or higher-level theoretical methods to assess the accuracy and suitability of different functionals.

For example, hcth functional used is also called hcth/93, where 93 energetic data were fit. Only the first two rows of atoms in periodic table is part of this energetic fitting. The rest corresponds to cations of those rows and several molecules (this is a reason why the results might have decay in the heavier elements)[21]. Also, we would think about the second best functional in this study, the m06-L, used commonly for transition metals and noncovalent interactions [22]. As hcth this functional was developed with a purpose, to study deeply the compounds formed by transition metals and offering the best results, so, it is understandable that using a basis set for 36 atoms and study the ground state energy for nonmetal elements is not the properly way to obtain accurate results with this functional. However, it has been a good idea to study many atoms (with the same basis set) with these functionals which differ from each other in their nature.

In **Appendix** D there can be seen the results analysed in the last section reorganised into atom's groups. Many things are important here. For alkaline earth metals, the ground level term is $^1S_0$, the most accurate functional for them is hcth. Moreover, for noble gases, whose ground level term is also $^1S_0$, the most suitable functional for them is the m06-L (unless the Kr, whose ground state energy is closer to the reference value, using the hcth functional). On the other hand, in the non-metal atoms we cannot establish a relation between the ground state energy and the ground level term, since N and O have the same ground level term as P and S, respectively. This is were correlation effects begin to be important and should be considered in the functionals.

The uncompleted tasks that should be interesting for another work are: the visualization of ".cube" files in python, creating 3D isosurfaces of the electron density (and 2D representations to see how it varies against r) and electrostatic potential maps. Since the NWChem gives so much information, it could be somehow downloaded to visualize the data. Also, apart from using the VMD, it would be interesting to represent the atomic orbitals.

Appendices

Appendix A

Input NWChem file

All input files have the same structure, but many variables must be changed to study different atoms and functionals.

```
start H1
geometry units au
H 0.0 0.0 0.0
end
basis
 H library 6-31G*
end
dft
  vectors output H1.movecs
  xc becke88
  MULT 2
  maxiter 1000
end
set tolguess 1e-7
dplot
  TITLE HOMO
  vectors H1.movecs
  LimitXYZ units au
  -4.0 4.0 39
  -4.0 4.0 39
  -4.0 4.0 39
  spin total
  gaussian
  output H1dens.cube
end
task dft
task dplot
```

Following the guide provided in Chapter 4, the input file can be easily understood step by step. This file consists in a DFT calculation of the Hydrogen atom. The atom center

is located at the origin (units should be written, otherwise, default units are Angstrom). The basis is chosen according to the atoms subject to study. Also, the vectors are given to later use the function "dplot" (to obtain the electron density), taking into account that the functional used is the becke88. Multiplicity of atoms should also be given. The maximum number of iterations have been set to 1000 and the accuracy demanded was set to 10E-7.

Right below, the parameters to obtain the output (cube file) are written, like the dimensions of the cube and the number of divisions in each axis (n+1, in this case, 40). This input was specifically written to see how would change the radii with the highest electron density and compare if making a bigger cube would be a better solution to accurately plot the electron density.

Appendix B

VMD input
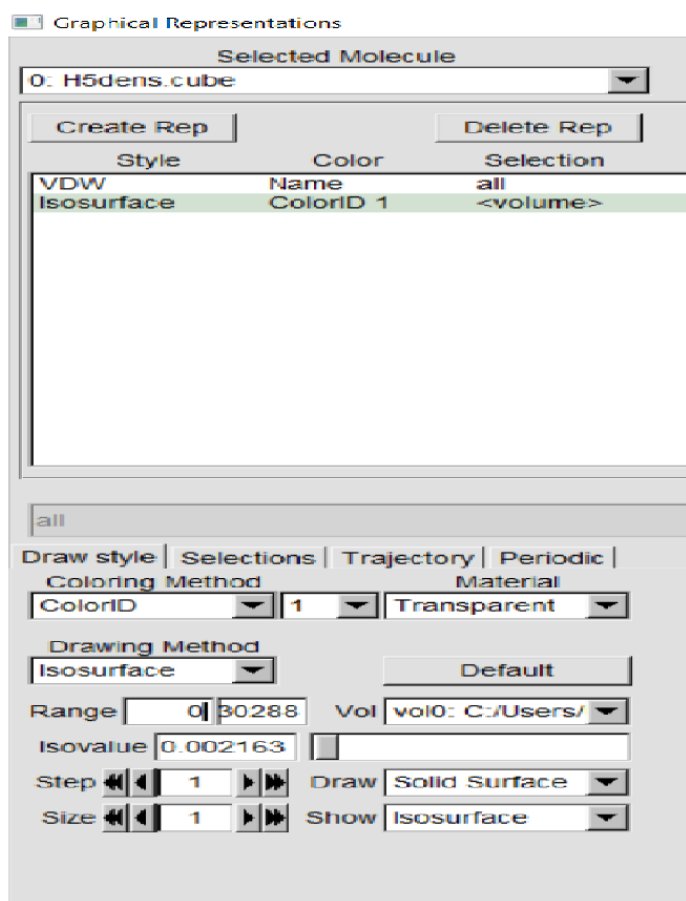
This is an intuitive input example and the guide can be found on the internet [23].The cube file is loaded and then you can create as many representations as you want. In this case, there were added two. VDW is used to visualize the atomic nuclei. On the other hand, the electron density has been displayed as an isosurface (which can be colored

and select if the representation is opaque, transparent...). The isovalue bar selects the value for which isosurface is going to be computed. Step and size are used to skip or modificate the voxels/number of divisions (affecting the resolution). Moreover, "Draw" indicates what type of representations can be set (for example, instead of solid surface, points can be used) and "show" is to select what the user will see (the cube, only the isosurface, the isosurface and the cube...). The '.cube' file format is commonly associated with computational chemistry software, such as NWChem. It is used to store three-dimensional volumetric data, particularly electron density, molecular orbitals, or other related properties obtained from quantum chemical calculations. It contains a grid of regularly spaced points in three-dimensional space, where each point corresponds to a particular value of the property being represented (e.g., electron density). The values are typically stored as floating-point numbers, allowing for a high degree of precision. The '.cube' file format includes header information specifying the dimensions of the grid, the origin of the coordinate system, and the spacing between grid points. Additionally, it provides information about the nature of the property represented, such as whether it represents electron density, a molecular orbital, or another related quantity. The data in a '.cube' file can be visualized using specialized software or molecular visualization tools that support this file format (VMD is one of them). In Figure B.1 can be seen
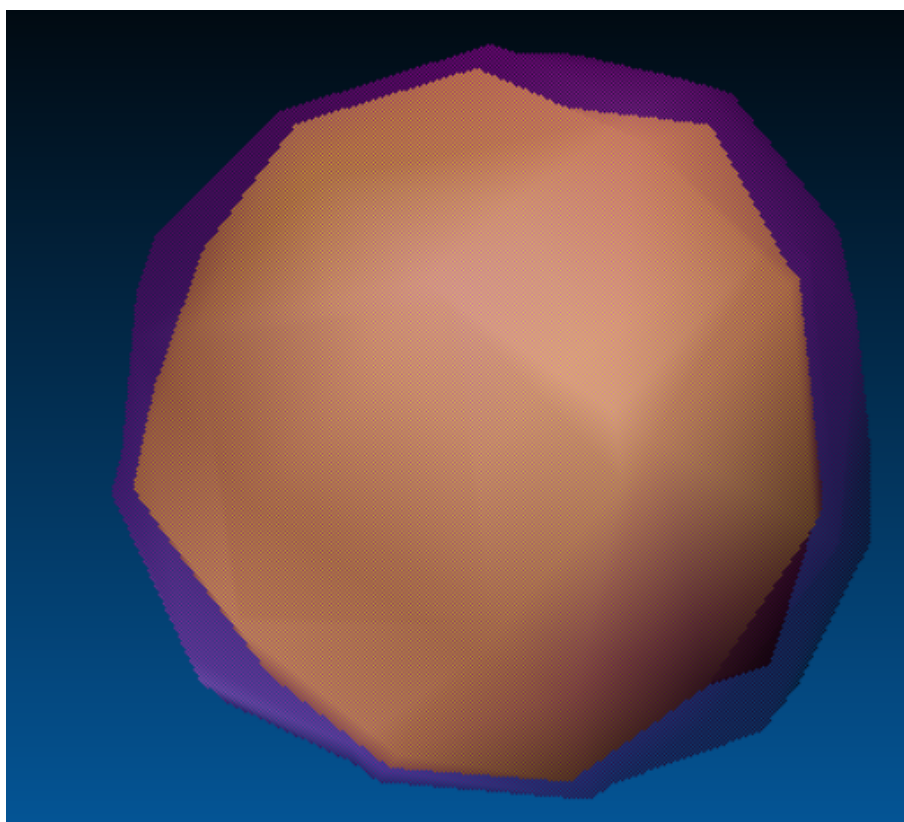

Figure B.1: .

the representation of the electron density of helium. Is should have spherical symmetry (taking into account its electronic configuration).

Appendix C

HF-MP2,DFT table

Element	E_{ref}	E_{HF}	E_{MP2}	E_{hcth}
H	-0.50000	-0.49981	-	-0.50375
He	-2.90339	-2.85990	-2.87280	-2.91041
Li	-7.47798	-7.43212	-7.44509	-7.49246
Be	-14.66844	-4.57189	-14.61405	-14.66496
B	-24.65809	-24.53015	-24.58715	-24.64147
C	-37.85579	-37.68915	-37.76495	-37.82744
N	-54.61161	-54.39814	-54.49704	-54.57062
O	-75.10984	-74.80526	-74.94257	-75.03477
F	-99.80710	-99.39689	-99.58113	-99.68564
Ne	-129.05250	-128.52267	-128.76113	-128.87563
Na	-162.43200	-161.84605	-161.97775	-162.26231
Mg	-200.32300	-199.60699	-199.75886	-200.07021
Al	-242.72700	-241.87225	-242.02909	-242.36886
Si	-289.89800	-288.85044	-289.01812	-289.38784
P	-341.98000	-340.70784	-340.89310	-341.29780
S	-399.08000	-397.49847	-397.70304	-398.15880
Cl	-461.44000	-459.47356	-459.63555	-460.21002
Ar	-529.22000	-526.80683	-527.00923	-527.62004
K	-602.03000	-599.14932	-599.42504	-600.01533
Ca	-680.22000	-676.74067	-677.05213	-677.69541
Sc	-763.96000	-759.68153	-759.84703	-760.78295
Ti	-853.36000	-848.33654	-848.57264	-849.54659
V	-948.90000	-942.89032	-943.21129	-944.14504
Cr	-1050.40000	-1043.35577	-1043.73938	-1044.69474
Mn	-1158.10000	-1149.86823	-1150.26921	-1151.35620
Fe	-1272.20000	-1262.38433	-1262.90067	-1264.07783
Co	-1392.80000	-1381.36370	-1381.96089	-1383.18339
Ni	-1519.80000	-1506.82711	-1507.50883	-1508.78756
Cu	-1653.80000	-1638.96235	-1639.76725	-1640.99552
Zn	-1794.90000	-1777.84675	-1778.65294	-1780.06588
Ga	-1942.80000	-1923.18223	-1923.62564	-1925.66801
Ge	-2097.70000	-2075.27982	-2075.71910	-2077.87369
As	-2259.00000	-2234.15408	-2234.60007	-2236.86565
Se	-2428.10000	-2399.78581	-2400.24480	-2402.63831
Br	-2604.40000	-2572.35545	-2572.85334	-2575.35486
Kr	-2788.00000	-2751.96296	-2752.46125	-2755.11090

Table C.1: The values in this table are the ground state energies in Hartree (Ha) calculated by different methods. DFT ground state energies were obtained by the author, the HF and MP2 ground state energies were collected from [24]

Appendix D

Groups of atoms

Noble Gases

Element	E_{Exp}	E_{becke88}	E_{perdew86}	E_{hcth}	E_{xtpss03}	E_{becke97}	$E_{\text{m06-L}}$
He	-2.90339	-2.85400	-1.95432	-2.91041	-2.85930	-2.90230	-2.90393
Ne	-129.05250	-128.49643	-117.08527	-128.87563	-128.53827	-128.85853	-128.88763
Ar	-529.22000	-526.74507	-497.87143	-527.62004	-526.80835	-527.43623	-527.49843
Kr	-2788.00000	-2751.72098	-2661.13071	-2755.11090	-2751.56867	-2753.32437	-2753.33592

Table D.1: The values in this table are the ground state energies in Hartree (Ha).

Non-Metals

Element	E_{Exp}	E_{becke88}	E_{perdew86}	E_{hcth}	E_{xtpss03}	E_{becke97}	$E_{\text{m06-L}}$
H	-0.49973	-0.49545	-	-0.50375	-0.49785	-0.50055	-0.50181
C	-37.85579	-37.67235	-32.94426	-37.82744	-37.70211	-37.83176	-37.83573
N	-54.61161	-54.37610	-48.21642	-54.57062	-54.40810	-54.56765	-54.58373
O	-75.10984	-74.78902	-67.10519	-75.03477	-74.83032	-75.03473	-75.05395
P	-341.98000	-340.67301	-319.03930	-341.29780	-340.73034	-341.19365	-341.23718
S	-399.08000	-397.45665	-373.53835	-398.15880	-397.51842	-398.03324	-398.07911
Se	-2428.10000	-2399.61609	-2317.11108	-2402.63831	-2399.49438	-2401.08519	-2401.11069

Table D.2: The values in this table are the ground state energies in Hartree (Ha).

Alkali Metals

Element	E_{Exp}	E_{becke88}	E_{perdew86}	E_{hcth}	E_{xtpss03}	E_{becke97}	$E_{\text{m06-L}}$
Li	-7.47798	-7.42641	-5.75733	-7.49246	-7.43799	-7.48653	-7.48512
Na	-162.43200	-161.85777	-148.51856	-162.26231	-161.90478	-162.23451	-162.24296
K	-602.03000	-599.09096	-567.51308	-600.01533	-599.15350	-599.79736	-599.85026

Table D.3: The values in this table are the ground state energies in Hartree (Ha).

Alkaline Earth Metals

Element	E_{Exp}	E_{becke88}	E_{perdew86}	E_{hcth}	E_{xtpss03}	E_{becke97}	$E_{\text{m06-L}}$
Be	-14.66844	-14.56063	-12.08599	-14.66496	-14.57915	-14.66274	-14.65825
Mg	-200.32300	-199.60529	-184.37305	-200.07021	-199.65416	-200.02819	-200.03931
Ca	-680.22000	-676.69117	-642.66337	-677.69541	-676.74946	-677.43857	-677.49354

Table D.4: The values in this table are the ground state energies in Hartree (Ha).

Metaloids, Aluminum and Gallium

Element	E_{Exp}	E_{becke88}	E_{perdew86}	E_{hcth}	E_{xtpss03}	E_{becke97}	$E_{\text{m06-L}}$
B	-24.65809	-24.51454	-21.00683	-24.64147	-24.54239	-24.64394	-24.64410
Al	-242.72700	-241.85851	-224.60841	-242.36886	-241.91179	-242.31110	-242.32978
Si	-289.89800	-288.82479	-269.44195	-289.38784	-288.88040	-289.31017	-289.33745
Ga	-1942.80000	-1923.14921	-1852.30956	-1925.66801	-1923.06970	-1924.44612	-1924.47770
Ge	-2097.70000	-2075.19591	-2000.52009	-2077.87369	-2075.10298	-2076.54411	-2076.57580
As	-2259.00000	-2234.02240	-2155.42907	-2236.86565	-2233.91561	-2235.42252	-2235.45222

Table D.5: The values in this table are the ground state energies in Hartree (Ha).

Halogens

Element	E_{Exp}	E_{becke88}	E_{perdew86}	E_{hcth}	E_{xtpss03}	E_{becke97}	$E_{\text{m06-L}}$
F	-99.80710	-99.38031	-89.94208	-99.68564	-99.42185	-99.68348	-99.70789
Cl	-461.44000	-459.42579	-433.09753	-460.21002	-459.48859	-460.05906	-460.11045
Br	-2604.40000	-2572.15156	-2485.64887	-2575.35486	-2572.01453	-2573.68779	-2573.70743

Table D.6: The values in this table are the ground state energies in Hartree (Ha).

Transition Metals

Element	E_{Exp}	E_{becke88}	E_{perdew86}	E_{hcth}	E_{xtpss03}	E_{becke97}	$E_{\text{m06-L}}$
Sc	-763.96000	-759.69389	-723.16682	-760.78295	-759.74833	-760.47397	-760.51968
Ti	-853.36000	-848.35862	-808.81507	-849.54659	-848.40758	-849.17878	-849.22816
V	-948.90000	-942.84239	-900.30284	-944.14504	-942.88427	-943.70523	-943.75258
Cr	-1050.40000	-1043.26688	-997.38508	-1044.69474	-1043.28749	-1044.15291	-1044.19254
Mn	-1158.10000	-1149.78644	-1100.67945	-1151.35620	-1149.80077	-1150.74259	-1150.79260
Fe	-1272.20000	-1262.37394	-1209.93609	-1264.07783	-1262.37920	-1263.38809	-1263.42425
Co	-1392.80000	-1381.33659	-1325.40535	-1383.18339	-1381.33485	-1382.41016	-1382.43156
Ni	-1519.80000	-1506.77814	-1447.22162	-1508.78756	-1506.75606	-1507.91282	-1507.94196
Cu	-1653.80000	-1638.83408	-1575.51995	-1640.99552	-1638.78746	-1640.03150	-1639.99771
Zn	-1794.90000	-1777.68278	-1710.44956	-1780.06588	-1777.61619	-1778.94904	-1778.96686

Table D.7: The values in this table are the ground state energies in Hartree (Ha).

Bibliography

[1] Kramida, A., Ralchenko, Yu., Reader, J. and NIST ASD Team. "NIST Atomic Spectra Database" , version 5.10, 2022. `https://www.nist.gov/pml/atomic-spectra-database`

[2] B.H. Bransden. "Physics of Atoms & Molecules", Dorling Kindersley Pvt Ltd, 2 ed., 2006.

[3] David S.Sholl, Janice A.Steckel. "Density Functional Theory: A Practical Introduction", Wiley-Interscience, 1 ed., 2009.

[4] Carlos Fiolhais, Fernando Nogueira, Miguel A.L. Marques."A Primer in Density Functional Theory", Springer-Verlag Berlin Heidelberg,1 ed., 2003.

[5] Robert G. Parr, Yang Weitao. "Density-Functional Theory of Atoms and Molecules", Oxford University Press, Reprinted ed., 1989.

[6] Teffanie Goh, University of Chicago. " Exchange-Correlation Functionals: GGA vs. meta-GGA ", 2020.

[7] A. V. Arbuznikov. "Hybrid exchange correlation functionals and potentials: Concept elaboration", J Struct Chem 48 (Suppl 1), S1–S31, 2007.

[8] A. Filippetti, G.B. Bachelet. "Encyclopedia of Condensed Matter Physics", Academic Press, 1 ed., 2005.

[9] Ersen Mete. "DFT in practice: Part II", Department of Physics, Balıkesir University, Balıkesir - Turkey, 2009.

[10] Jarrod R. McClean, Kevin J. Sung, Ian D. Kivlichan, Yudong Cao, Chengyu Dai, E. Schuyler Fried, Craig Gidney, Brendan Gimby, Pranav Gokhale, Thomas Häner, Tarini Hardikar, Vojtěch Havlíček, Oscar Higgott, Cupjin Huang, Josh Izaac, Zhang Jiang, Xinle Liu, Sam McArdle, Matthew Neeley, Thomas O"Brien, Bryan O"Gorman, Isil Ozfidan, Maxwell D. Radin, Jhonathan Romero, Nicholas Rubin, Nicolas P. D. Sawaya, Kanav Setia, Sukin Sim, Damian S. Steiger, Mark Steudtner, Qiming Sun, Wei Sun, Daochen Wang, Fang Zhang and Ryan Babbush. "OpenFermion: The Electronic Structure Package for Quantum Computers", arXiv:1710.07629. 2017. `https://manual.q-chem.com/5.3/Ch8.S1.html`

[11] Rosa Mary López Álvarez."Basis Functions in Computational Chemistry: Analysis of the Second Period Diatomic Hydrides", Universidad de Oviedo, Facultad de Química, 2021.

[12] Ignacio Nilo Tuñón García de Vicuña. "Introduction to Computational Chemistry and the working environment ", Universidad de Valencia, Facultad de Química, 2018.

[13] Theresa Julia Zielinski, Erica Harvey, Robert Sweeney, and David M. Hanson. "Quantum States of Atoms and Molecules", J. Chem. Educ. 2005, 82, 12, 1880, 2005.

[14] M. Valiev, E.J. Bylaska, N. Govind, K. Kowalski, T.P. Straatsma, H.J.J. van Dam, D. Wang, J. Nieplocha, E. Apra, T.L. Windus, W.A. de Jong. "NWChem: a comprehensive and scalable open-source solution for large scale molecular simulations", Comput. Phys. Commun. 181, 1477, 2010.

[15] E. Aprà, E. J. Bylaska, W. A. de Jong, N. Govind, K. Kowalski, T. P. Straatsma, M. Valiev, H. J. J. van Dam, Y. Alexeev, J. Anchell, V. Anisimov, F. W. Aquino, R. Atta-Fynn, J. Autschbach, N. P. Bauman, J. C. Becca, D. E. Bernholdt, K. Bhaskaran-Nair, S. Bogatko, P. Borowski, J. Boschen, J. Brabec, A. Bruner, E. Cauët, Y. Chen, G. N. Chuev, C. J. Cramer, J. Daily, M. J. O. Deegan, T. H. Dunning Jr., M. Dupuis, K. G. Dyall, G. I. Fann, S. A. Fischer, A. Fonari, H. Früchtl, L. Gagliardi, J. Garza, N. Gawande, S. Ghosh, K. Glaesemann, A. W. Götz, J. Hammond, V. Helms, E. D. Hermes, K. Hirao, S. Hirata, M. Jacquelin, L. Jensen, B. G. Johnson, H. Jónsson, R. A. Kendall, M. Klemm, R. Kobayashi, V. Konkov, S. Krishnamoorthy, M. Krishnan, Z. Lin, R. D. Lins, R. J. Littlefield, A. J. Logsdail, K. Lopata, W. Ma, A. V. Marenich, J. Martin del Campo, D. Mejia-Rodriguez, J. E. Moore, J. M. Mullin, T. Nakajima, D. R. Nascimento, J. A. Nichols, P. J. Nichols, J. Nieplocha, A. Otero-de-la-Roza, B. Palmer, A. Panyala, T. Pirojsirikul, B. Peng, R. Peverati, J. Pittner, L. Pollack, R. M. Richard, P. Sadayappan, G. C. Schatz, W. A. Shelton, D. W. Silverstein, D. M. A. Smith, T. A. Soares, D. Song, M. Swart, H. L. Taylor, G. S. Thomas, V. Tipparaju, D. G. Truhlar, K. Tsemekhman, T. Van Voorhis, Á. Vázquez-Mayagoitia, P. Verma, O. Villa, A. Vishnu, K. D. Vogiatzis, D. Wang, J. H. Weare, M. J. Williamson, T. L. Windus, K. Woliński, A. T. Wong, Q. Wu, C. Yang, Q. Yu, M. Zacharias, Z. Zhang, Y. Zhao, and R. J. Harrison. "NWChem: Past, present, and future", The Journal of Chemical Physics 152, 184102, 2020. URL: `https://nwchemgit.github.io/Home.html`

[16] Richard P. Feynman, Matthew Sands. "The Feynman Lectures on Physics, Vol. III", Basic Books, The New Millennium Edition, 2011.

[17] The National Institute of Standards and Technology (NIST). "Computational Chemistry Comparison and Benchmark DataBase", 2013. `https://cccbdb.nist.gov/hartree.asp#:~:text=A$%$20hartree$%$20is$%$20a$%$20unit,$%$2C$%$20and$%$20219474.6$%$20cm-1.`

[18] W. Nelson, P. Bokes, Patrick Rinke, R. W. Godby. "Self-interaction in Green's-function theory of the hydrogen atom", PHYSICAL REVIEW A 75, 032505, 2007.

[19] A. V. Arbuznikov. "Hybrid exchange correlation functionals and potentials: Concept elaboration", J Struct Chem 48 (Suppl 1), S1–S31, 2007.

[20] F. Zahariev, S.S. Leang, Mark S. Gordon."Functional derivatives of meta-generalized gradient approximation (meta-GGA) type exchange-correlation density functionals", J. Chem. Phys. 138, 244108, 2013.

[21] A. Daniel Boese, Nikos L. Doltsinis, Nicholas C. Handy, and Michiel Sprik. "New generalized gradient approximation functionals", Journal of Chemical Physics volume 112, number 4, 2000.

[22] Ying Wang, Xinsheng Jin, Haoyu S. Yu, Donald G. Truhlar, Xiao He. "Revised M06-L functional for improved accuracy on chemical reaction barrier heights, noncovalent interactions, and solid-state physics", Proceedings of the National Academy of Sciences 114(32), 2017.

[23] Humphrey, W., Dalke, A. and Schulten, Klaus. "VMD - Visual Molecular Dynamics", J. Molec. Graphics, 1996, vol. 14, pp. 33-38. `http://www.ks.uiuc.edu/Research/vmd/`

[24] Pablo Martínez Martínez. "Ab initio studies on the electronic structure of atoms", Universidad de La Laguna, Facultad de Ciencias, sección de Física, 2021.