Density Functional Theory

Systematic benchmarking of exchange and correlation functionals for the G2 dataset

Universidade de Coimbra

João Abreu

Supervisors

Dr. Micael Oliveira

Dr. Fernando Nogueira

Department of Physics

University of Coimbra

This dissertation is submitted for the degree of

Master of Science

October 2015

Acknowledgements

I would like to dedicate this thesis to my loving and wonderful family, that are my rock through the storms of life. With them I was able to rise and outdo easier from my stumbles and doubts.

I want to show my gratitude to my advisor's Dr. Micael Oliveira and Dr. Fernando Nogueira, for all the support and patience that helped me to overcome my problems and their guidance in the right path.

Finally and not least, I am want to give thanks for the joy and happiness that I received from my friends, it was fun and will continue to be.

Abstract

The density functional theory (DFT) used in this thesis is a powerful tool to simulate many-particle systems, however is not exact, the exchange-correlation potential (E_{xc}) represents an approximation of the particle interaction. With the development of latter approximations for E_{xc}, DFT becomes more useful and credible to the scientific world. However, the dispersion of information is becoming disturbing and confuse, so an agglomeration of this information is necessary. The goal of this thesis is to analyse a large quantity of exchange-correlation functionals and verify which ones gives an ionization energy closer to the experimental values in a set of well defined molecules, called the G2 test set.

Resumo

A teoria de funcional de densidade (DFT) usada nesta tese é uma poderosa ferramenta para simular sistemas de muitos corpos, no entanto, não é exacta, o potencial de troca e correlação (E_{xc}) representa a aproximação da interação entre partículas. Com o desenvolvimento destas aproximações em E_{xc}, DFT torna-se cada vez mais útil e credível aos olhos do mundo científico. Contudo, a dispersão de informação referente ao tema, começa a tornar-se confusa e perturbante, por isso um aglomerar desta informação é necessária. O objectivo desta tese é analisar a grande quantidade de funcionais de troca e correlação e verificar qual dará uma energia de ionização mais próxima dos valores experimentais num conjunto bem definido de moléculas, chamada de conjunto de testes G2.

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Part I

Introduction

In a world where we are dependent of material properties that help us improve our way of life it is necessary to study their properties so we can use them in our favour. These materials are constituted by clouds of electrons that fluctuate around a net of nuclei, where every particle interacts with each other within some order, and the key features of the material are due to the electronic properties.[1]

A system composed by electrons and nuclei, which represent that material, can be evaluated by the energies that act on them through the Hamiltonian operator $\hat{H}$. This operator applied to the particle system will determine the total energy of that system and can be written as

$$\begin{aligned}\hat{H} = &-\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 + \sum_{i,I}\frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \\ &- \sum_I \frac{\hbar^2}{2M_I}\nabla_I^2 + \frac{1}{2}\sum_{I\neq J}\frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|},\end{aligned}$$

where electrons are denoted by lower case subscripts and nuclei by upper case subscripts. The terms here included are the electrons and nuclei kinetic energy, the attraction between electrons and nuclei, the repulsion between pairs of electrons, and the repulsion between pairs of nuclei. One of the terms, the nuclei kinetic energy, can be considered small compared to the others in the system, due to the large value of the mass of the nuclei, and if we ignore it we still have a good approximation to the real system. This approximation is called the Born-Oppenheimer or adiabatic approximation.[2]

To know the characteristics and behaviour of a system we can use the time-independent Schrödinger equation, where an Hamiltonian is applied to the particle wave-function $|\Psi\left(\mathbf{r}_1, \ldots, \mathbf{r}_N\right)\rangle$, which contains all the information of the system,

$$\hat{H}|\Psi(\mathbf{r}_1, ..., \mathbf{r}_N)\rangle = E|\Psi(\mathbf{r}_1, ..., \mathbf{r}_N)\rangle. \tag{1}$$

The Schrödinger equation for interacting particles can be modified to an equivalent, but simpler, scheme in which the system is defined by the Kohn-Sham equation[3], where the particles do not interact and all the interaction effects are expressed as a potential energy, the exchange-correlation energy, E_{xc} [4]. The conversion between the two equations is developed in Part II.

The exchange-correlation energy is a very important term of the system and there are very good approximations to its exact form. In the Chapter 2, Part III, information about the exchange-correlation energy and its properties can be found.

The goal of this thesis is to verify the quality of a large list of E_{xc} constructions in a set of molecules, called G2 set test[5, 6] (Chapter 3, Part III). This set was a convenient choice, because there was a study already made to demonstrate the results of G2 theory with experimental values. The property of the system chosen as quality factor was the ionization potential (Chapter 4, Part III). This choice was made because it is easy to calculate, it is the property used in G2 theory and having a direct relation to the total energy is significantly important.

In Part IV, the methodology is presented, where is made an overview of the electronic structure software NWChem[7] that is used to solve the Kohn-Sham equation, with the assistance of the Libxc library[8] for the E_{xc} list and Pyxcbench application to organize the information in a database and where statistical calculations are performed.

Part II

Theory

Chapter 1

Density Functional Theory

One of the major problems in density functional theory[9] is to know an accurate and easy way to calculate the Coulomb energy that reproduces well the interaction between electrons,

$$\hat{V}_{ee} = \frac{1}{2} \sum_{i} \sum_{j \neq i} \frac{1}{|\mathbf{x}_i - \mathbf{x}_j|}. \tag{1.1}$$

In the early days of quantum theory, Thomas and Fermi[10, 11] replaced the expectation value $\left\langle \hat{V}_{ee} \right\rangle$ by the direct Coulomb functional energy that depends on the electron number density $n(\vec{r})$,

$$U[n] = \frac{1}{2} \int d^3x \int d^3x' \frac{n(\mathbf{x}) n(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|} \tag{1.2}$$

But it was observed a deficiency in an one-electron system, where a spurious self-interaction was found in this formulation.

To overcome this problem, the Hartree-Fock (HF)[12] approximation appeared, where the interaction between electrons is given by the sum of direct and exchange effects

$$\left\langle \hat{V}_{ee} \right\rangle = U[n] + E_x, \tag{1.3}$$

where the exchange energy is

$$E_x = -\frac{1}{2}\sum_{\sigma}\sum_{\alpha,\alpha'}\int d^3r \int d^3r' \frac{\Psi^*_{\alpha\sigma}(\mathbf{x})\Psi^*_{\alpha'\sigma}(\mathbf{x})\Psi_{\alpha'\sigma}(\mathbf{x})\Psi_{\alpha\sigma}(\mathbf{x})}{|\mathbf{x}-\mathbf{x}'|}. \tag{1.4}$$

The electron density is the sum of each state density,

$$n(\mathbf{x}) = \sum_{\alpha,\sigma} n_{\alpha\sigma}(\mathbf{x}), \tag{1.5}$$

and $n_{\alpha\sigma}(\mathbf{x})$ gives the probability of an electron being in that state,

$$n_{\alpha\sigma}(\mathbf{x}) = |\Psi_{\alpha\sigma}(\mathbf{x})|^2. \tag{1.6}$$

The Hartree-Fock approximation has a self-exchange energy which accurately cancels the self-interaction in the Coulomb energy $U[n]$, although this was an improvement, the HF solutions needed a more elaborated treatment. The total energy is dominated by high-density inner-shell electrons, but electronic properties has direct us to the low-density valence electrons, for which another factor needs to be considered, the correlation effect. Also the long range Coulomb interaction produces unrealistic description in the HF eigenvalues near the Fermi level.

To improve this method we turn up to the density functional theory (DFT) approach which is exact in principle and includes correlation explicitly in the total energy. In the next section we will clarify this approach by developing the Schrödinger equations into Kohn-Sham equations.

1.1 Many-Particle introduction

The Kohn-Sham[13] functional method uses N one-electron Schrödinger equations to find the ground state total energy and the spin densities that describes the same system with N interacting electrons.

In this section we will discuss how to simplify the complicated N interacting electrons system by using the Hohenberg-Kohn theorem[14] formulated for a local external potential that leads to a spin-independent and non-degenerated ground-state and then extend it to a spin-dependent degenerated ground state.

The non-relativistic time-independent Hamiltonian of a N particle system, in atomic units, is

$$\hat{H} = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 + \sum_{i=1}^{N} v(\mathbf{r}_i) + \frac{1}{2}\sum_{i=1}\sum_{j\neq i}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} = \hat{T} + \hat{V_{ext}} + \hat{V}_{ee}, \tag{1.7}$$

where the first term is the kinetic energy of the system, the second is an external potential affecting the electrons, and the third is a Coulomb interaction between the electrons. All the terms involving the nuclei are included in the external potential.

The Born-Oppenheimer approximation was used in the Hamiltonian (1.7), this consider that the electrons maintain the same state upon the movement of nuclei and we can ignore the kinetic energy of atoms, because of it's large mass. However, if we encounter degeneracy or near degeneracy electronic states, this approximation is no longer applicable.

The states of well-defined energy are the eigenstates of $\hat{H}$:

$$\hat{H}\Psi_k(\mathbf{x}_1, ..., \mathbf{x}_N) = E_k\Psi_k(\mathbf{x}_1, ..., \mathbf{x}_1), \tag{1.8}$$

where Ψ_k is a spin orbital with $\mathbf{x}_i = \{\mathbf{r}_i, \sigma_i\}$, ($\sigma_i = \frac{1}{2}$ or $\sigma_i = -\frac{1}{2}$), and k is the complete set of many-electron quantum numbers.

The electrons are fermions, so they follow the antisymmetry principle, a general statement of the Pauli exclusion principle, where a wave function must be antisymmetric with respect to the interchange of the coordinate $\mathbf{x}$ of any two electrons,

$$\Psi_k(\mathbf{x}_1, ..., \mathbf{x}_i, ..., \mathbf{x}_j, ..., \mathbf{x}_N) = -\Psi_k(\mathbf{x}_1, ..., \mathbf{x}_j, ..., \mathbf{x}_i, ..., \mathbf{x}_N). \tag{1.9}$$

The first postulate of quantum mechanics says that the wavefunctions must follow the normalization condition for probabilistic interpretation, so the N! distinct permutations that the antisymmetric property creates, imply the normalization condition:

$$\langle\Psi|\Psi\rangle = \frac{1}{N!}\sum_{\sigma_1...\sigma_N}\int d^3r_1 ... \int d^3r_N N!|\Psi(\mathbf{x}_1, ..., \mathbf{x}_N)|^2 = 1. \tag{1.10}$$

The probability for finding an electron with spin σ in volume element d^3r at $\mathbf{r}$ is found by calculating the electron spin density $n_\sigma(\mathbf{r})$. We find it by integrating over all other electrons

$$\begin{aligned} n_\sigma(\mathbf{r}) &= \frac{1}{(N-1)!}\sum_{\sigma_2 \ldots \sigma_N} \int d^3r_2 \ldots \int d^3r_N N! |\Psi(\mathbf{x}, \mathbf{x}_2, \ldots, \mathbf{x}_N)|^2 \\ &= N \sum_{\sigma_2 \ldots \sigma_N} \int d^3r_2 \ldots \int d^3r_N |\Psi(\mathbf{x}, \mathbf{x}_2, \ldots, \mathbf{x}_N)|^2, \end{aligned} \tag{1.11}$$

so it follows that

$$\sum_\sigma \int d^3r n_\sigma(\mathbf{r}) = N. \tag{1.12}$$

These conditions let us write the expectation value of the external potential with dependence on the electron density,

$$\langle \hat{V}_{ext} \rangle = \langle \Psi | \sum_{i=1}^{N} v(\mathbf{r}_i) | \Psi \rangle = \int d^3r n(\mathbf{r}) v(\mathbf{r}). \tag{1.13}$$

1.2 Hohenberg-Kohn theorem

To obtain the Kohn-Sham equation in terms of the system density, we are going to find an universal functional for the energy. To do this we use the Hohenberg-Kohn theorem, where the first part says that $v(\mathbf{r})$ is a unique functional of the density, apart from a trivial additive constant, and that the density uniquely determines the external potential.

To demonstrate this we will assume that another potential $\hat{V}'_{ext}$ with ground state Ψ' gives rise to the same density $n(\mathbf{r})$ as $\hat{V}_{ext}$ and Ψ, unless $\hat{V}_{ext} - \hat{V}'_{ext} = \text{const.}$ The wave function Ψ' cannot be equal to Ψ as they satisfy different Schrödinger equations. Since we know that the ground state energy is the lowest energy of the system and the ground state is non-degenerated

$$E_{gs} = \langle \Psi | \hat{H} | \Psi \rangle < \langle \Psi' | \hat{H} | \Psi' \rangle = \langle \Psi' | \hat{H}' + \hat{V}_{ext} - \hat{V}'_{ext} | \Psi' \rangle, \tag{1.14}$$

we find that

$$E_{gs} < E'_{gs} + \int n(\mathbf{r})[v(\mathbf{r}) - v'(\mathbf{r})]. \tag{1.15}$$

If we do the same, starting with E'_{gs}, we get

$$E'_{gs} < E_{gs} + \int n(\mathbf{r})[v'(\mathbf{r}) - v(\mathbf{r})]. \tag{1.16}$$

Summing both inequalities, we get the contradiction

$$E_{gs} + E'_{gs} < E_{gs} + E'_{gs}. \tag{1.17}$$

This means that $v(\mathbf{r})$, within a constant, is a unique functional of $n(\mathbf{r})$.

The second part of the Hohenberg-Kohn theorem establishes the variational procedure for the energy functional.

Since $\hat{H}$ is a functional of $n(\mathbf{r})$, so is the kinetic and the interaction energies. We can thus define an universal functional,

$$F_{\mathrm{HK}}[n] = \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle, \tag{1.18}$$

valid for any external potential. Thus the energy functional can be defined as

$$E_v[n] = \int v(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} + F_{\mathrm{HK}}[n]. \tag{1.19}$$

For an external potential $\hat{V}_{ext0}$ of a specific system, with ground state density $n_0(\mathbf{r})$ and ground state energy E_0, the variational principles shows that

$$E_0 < E_{v_0}[n] \quad for \quad n \neq n_0, \tag{1.20}$$

and

$$E_0 = E_{v_0}[n_0] \quad for \quad n = n_0, \tag{1.21}$$

so the exact ground state density can be determined by

$$E_0 = \min_n E_{v_0}[n]. \tag{1.22}$$

1.3 Extension to degenerate ground states

To extend this theory to include degenerate ground states, instead of a single ground state wave-function, each potential energy $\mathbf{V}$ will lead to a subspace spanned by an orthonormal system of degenerate ground states,

$$\mathbf{\Psi_V} = \left\{ \mid \Psi\rangle = \sum_{i=1}^{q} c_i \mid \Psi_i\rangle \right\}. \tag{1.23}$$

The same analogy can be made with the ground state densities. Nevertheless, this creates a problem: the universal functional uniqueness is no longer guaranteed. To overcome this, we will consider a ground state energy corresponding to an unique external potential $\hat{V}_{ext}[n]$ for a given density $n(\mathbf{r})$ that is the same for all degenerate ground state wave-functions

$$\langle\Psi|\hat{T} + \hat{V}_{ee} + \hat{V}_{ext}[n]|\Psi\rangle = \langle\Psi'|\hat{T} + \hat{V}_{ee} + \hat{V}_{ext}[n]|\Psi'\rangle = E. \tag{1.24}$$

The energy is fixed by the density to within a constant, which makes

$$F_{\mathrm{HK}}[n] = E - \int n(\mathbf{r})v(\mathbf{r})dr \tag{1.25}$$

an unique functional of the density and any possible ground state wave-function yielding the same density is allowed. [3]

1.4 v-Representability

A pure-state v-representability is a requirement to obtain physical solutions from the Schrõdinger equation. This characteristic means that a $n(\mathbf{r})$ function needs to be the ground state density with a suitable local external potential $v(\mathbf{r})$ of the Hamiltonian. The unique functional $F_{HK}[n]$ was defined only for pure-state v-representable functions. However, when applying the variational principle,

$$E_0 = \min_n E_{v_0}[n], \tag{1.26}$$

we need to be sure that the trial density belongs to the domain of pure-state v-representable densities. To find out if a density belongs to this domain, we can represent the variational principle by the following way

$$\frac{\delta}{\delta n(\mathbf{r})} E_{v_0}[n] = 0 \tag{1.27}$$

and choose the domain where the functional is differentiable in the vicinity of the minimum.

There are some functions that are non-v-representable. An example of this situation occurs when the density is an "ensemble of densities". The set of densities are represented by the density matrix which describes a system in a statistical mixture of states. To include this group we need to replace the subspace $\boldsymbol{\Psi}_V$ of degenerate ground states associated with a potential $V \in \mathcal{V}$ by a set of density matrices

$$\mathcal{D}_V = \left\{ \hat{D} = \sum_{i=1}^{q} d_i |\Psi_i\rangle\langle\Psi_i| \quad , \quad d_i^* = d_i >= 0 \quad , \quad \sum_{i=1}^{q} d_i = 1 \right\} \tag{1.28}$$

and an extension of the functional $F_{\mathrm{HK}}[n]$ of ensemble v-representable densities can be defined by

$$F_{\mathrm{EHK}}[n] = \mathrm{tr}\left\{ \hat{D}[n](\hat{T} + \hat{V}_{ee}) \right\}. \tag{1.29}$$

Other functions that do not correspond to the ground state of any external potential were found by Englisch and Englisch[15]. To find a more general domain so that $F_{\mathrm{HK}}[n]$ or $F_{\mathrm{EHK}}[n]$ can have a v-representable characteristic for an arbitrary non-negative function, it is used the constrained search found by Levy and Lieb [16, 17], where the functional F_{HK} is replaced by

$$F_{\mathrm{LL}} = \inf_{\Psi \to n} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle. \tag{1.30}$$

The infimum of the observable is going to be searched over all antisymmetric, normalised N-particle functions $\Psi(x_1, ..., x_N)$ whose density equals the function $n(\mathbf{r})$. So for all pure-state v-representable functions $n(\mathbf{r})$, $F_{\mathrm{LL}}[n] = F_{\mathrm{HK}}[n]$, since $F_{\mathrm{LL}}[n]$ is an extension of $F_{\mathrm{HK}}[n]$. To prove this extension we need to show that the total-energy functional

$$E_{v_0}[n] = F_{\mathrm{LL}}[n] + \int n(\mathbf{r}) v_0(\mathbf{r}) d\mathbf{r} \tag{1.31}$$

has its minimum at the correct ground state density $n_0(\mathbf{r})$, corresponding to the potential $v_0(\mathbf{r})$ and with the ground state energy value E_0. For the proof, we can use the Rayleigh-Ritz principle in the form of

$$\begin{aligned}
E_0 &= \inf_{\Psi} \langle \Psi | \hat{T} + \hat{V}_{ee} + \hat{V}_{ext0} | \Psi \rangle \\
&= \inf_{n(\mathbf{r})} \left[\inf_{\Psi \to n} \langle \Psi | \hat{T} + \hat{V}_{ee} + \hat{V}_{ext0} | \Psi \rangle \right] \\
&= \inf_{n(\mathbf{r})} \left[\inf_{\Psi \to n} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle + \int n(\mathbf{r}) v_0(\mathbf{r}) dr \right] \\
&= \inf_{n(\mathbf{r})} \left[\langle \Psi_n^{min} | \hat{T} + \hat{V}_{ee} | \Psi_n^{min} \rangle + \int n(\mathbf{r}) v_0(\mathbf{r}) dr \right] \\
&= \inf_{n(\mathbf{r})} \left[F_{\mathrm{LL}}[n] + \int n(\mathbf{r}) v_0(\mathbf{r}) dr \right] \\
&= \inf_{n(\mathbf{r})} \left[E_{v_0} \right].
\end{aligned}$$

This shows that the minimum of E_{v_0} is the ground state energy E_0.

The same reasoning can be used with $F_{\mathrm{EHK}}[n]$ for the functional

$$F_{\mathrm{L}}[n] = \inf_{\hat{D} \to n} tr \left\{ \hat{D}(\hat{T} + \hat{V}_{ee}) \right\} \tag{1.32}$$

and the corresponding total-energy functional

$$E_{v_0}[n] = F_{\mathrm{L}}[n] + \int n(\mathbf{r}) v_0(\mathbf{r}) dr. \tag{1.33}$$

The functional F_{LL} has a domain defined by all non-negative functions $n(\mathbf{r})$ with the condition that $\int n(\mathbf{r}) dr = N$ and can be represented as the density of some antisymmetric N-particle function $\Psi(x_1, ..., x_N)$. These density functions are considered N-representable. Since these functions are considered N-representable an ensemble of these densities are also considered as N-representable.

1.5 Kohn-Sham equations

The ground state energy, as we showed before, can be found by minimizing $\langle\Psi|\hat{H}|\Psi\rangle$ over all normalized, antisymmetric N-particle wavefunctions,

$$E = \min_{\Psi}\langle\Psi|\hat{H}|\Psi\rangle, \tag{1.34}$$

which is the same as the minimization of

$$E = \min_{\Psi}\left\{F[n] + \int d^3rv(\mathbf{r})n(\mathbf{r})\right\}, \tag{1.35}$$

where $v(\mathbf{r})$ is held fixed during the minimization and the minimized density is the ground-state density. We changed the notation of $F_{\mathrm{L}}[n]$ to $F[n]$ as it is the only functional for kinetic and interaction energy that we will be using for the rest of the section.

To find this minimum the variational principle will be used with a constraint on the number N of particles by using a Lagrange multiplier μ:

$$\delta\left\{F[n] + \int d^3rv(\mathbf{r})n(\mathbf{r}) - \mu\int d^3rn(\mathbf{r})\right\} = 0, \tag{1.36}$$

if we derive in order of n, by using the functional properties shown in appendix A, the solution we obtain is equivalent to the Euler equation

$$\frac{\delta F}{\delta n(\mathbf{r})} + v(\mathbf{r}) = \mu \tag{1.37}$$

and μ is adjusted until $\int d^3rn(\mathbf{r}) = N$ is verified.

We can write the last equation in form of energy and we can find that the Lagrangian multiplier μ is the exact chemical potential of the system

$$\mu = \frac{\delta F}{\delta n(\mathbf{r})} + v(\mathbf{r}) = \frac{\delta E}{\delta n} \to \frac{\partial E}{\partial N} \tag{1.38}$$

To find the Kohn-Sham equations, we define a system of non-interacting electrons, where $\hat{V}_{ee}$ vanishes from the Hamiltonian,

$$\hat{H} = \hat{T}_S + \hat{V}_{ext}, \tag{1.39}$$

and the exact solution for the Schrödinger equation with this non-interacting Hamiltonian system is

$$\hat{H}|\Psi_i\rangle = \epsilon_i|\Psi_i\rangle, \tag{1.40}$$

with a total energy of the system of

$$E_s[n] = \sum_i \epsilon_i. \tag{1.41}$$

We now introduce a classical electrostatic interaction potential V_H of the charge distribution $n(\mathbf{r})$ where

$$V_H(\mathbf{r}) = \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3r', \tag{1.42}$$

and the relation between the potential and it's energy is

$$V_H(\mathbf{r}) = \frac{\delta E_H}{\delta n(\mathbf{r})}. \tag{1.43}$$

Returning to our energy functional with the interacting particle system, we introduce the exchange and correlation energy functional E_{xc} to relate the interacting particle system with the non-interacting one,

$$\begin{aligned} E[n] &= (T+V_{ee})[n] + V_{ext}[n] \\ &= T_s[n] + E_H[n] + (T - T_s + V_{ee} - E_H)[n] + V_{ext}[n] \\ &= T_s[n] + E_H[n] + E_{xc}[n] + V_{ext}[n]. \end{aligned} \tag{1.44}$$

Using the relation of the chemical potential with this energy we get,

$$\mu = \frac{\delta E[n]}{\delta n(\mathbf{r})} = \frac{\delta T_s[n]}{\delta n(\mathbf{r})} + \frac{\delta E_H[n]}{\delta n(\mathbf{r})} + \frac{\delta E_{xc}}{\delta n(\mathbf{r})} + \frac{\delta V_{ext}[n]}{\delta n(\mathbf{r})}. \tag{1.45}$$

The functional derivatives are

$$\frac{\delta V_{ext}[n]}{\delta n(\mathbf{r})} = v(\mathbf{r}) \tag{1.46}$$

and

$$\frac{\delta E_{xc}}{\delta n(\mathbf{r})} = V_{xc}(\mathbf{r}). \tag{1.47}$$

By substituting these energy derivatives in (1.45) we get

$$\mu = \frac{\delta E[n]}{\delta n(\mathbf{r})} = \frac{\delta T_s[n]}{\delta n(\mathbf{r})} + V_H(\mathbf{r}) + V_{xc}(\mathbf{r}) + v(\mathbf{r}). \tag{1.48}$$

Comparing this last relation to the Euler equation (1.37) and finding the similarities to a non-interacting system where the Schrödinger equation is

$$\left(-\frac{1}{2}\nabla^2 + v\left(\mathbf{r}\right)\right)|\Psi_i\ \rangle = \epsilon_i|\Psi_i\ \rangle\,, \tag{1.49}$$

we see that if $v_s = V_H + V_{xc} + v$, and assuming that there exists a non-interacting system with exactly the same density as the interacting system of interest, the Kohn-Sham equation is written as

$$\left[-\frac{1}{2}\nabla^2 + v_s(\mathbf{r})\right]|\Psi_i\rangle = \left[-\frac{1}{2}\nabla^2 + V_H(\mathbf{r}) + V_{xc}(\mathbf{r}) + v(\mathbf{r})\right]|\Psi_i\rangle = \epsilon_i|\Psi_i\rangle \tag{1.50}$$

and the orbitals Ψ_i reproduce the density $n(\mathbf{r})$ from the original interacting system, since both are the ground state densities for the same external potential,

$$n(\mathbf{r}) = n_s(\mathbf{r}) = \sum_i^N |\Psi_i(\mathbf{r})|^2. \tag{1.51}$$

For the spin-dependent system, the total density is just divided into the sum of both density spins

$$n(\mathbf{r}) = n(\mathbf{r},\uparrow) + n(\mathbf{r},\downarrow). \tag{1.52}$$

with each spin-density state being the sum of the particles wave-functions with the spin established by the density spin state,

$$\begin{aligned} n(\mathbf{r},\uparrow) &= \sum_i^N |\Psi_i(\mathbf{r},\uparrow)|^2 \\ n(\mathbf{r},\downarrow) &= \sum_i^N |\Psi_i(\mathbf{r},\downarrow)|^2. \end{aligned} \tag{1.53}$$

With the Kohn-Sham equations well defined and giving an exact solution, we still have a problem: the exact form of the exchange-correlation energy is not known and the only solution is to find an approximation that gives an accurate result. In the next section we will see how we can find such functionals and their properties.

Chapter 2

Exchange and Correlation Functionals

2.1 Introduction

The exchange-correlation energy E_{xc} definition can be retrieved from the equation (1.44) and is the difference between the kinetic energies from the interacting particle system and the independent one and the difference of the potential of interacting particles and the classical electrostatic interaction energy. If the functional E_{xc} was known, then the exact ground state energy and it's density could be found.

The $E_{xc}[n]$ functional can be approximated as a local or non-local functional of the density. It can be separated in two terms, the exchange energy and the correlation energy

$$E_{xc}[n] = E_x[n] + E_c[n]. \tag{2.1}$$

In the next section we will start by specifying some properties and restrictions of the exchange and correlation functionals and in the following sections we will define these functionals in a system consisting of an uniform electron gas and in the two most popular approximations used for the exchange-correlation functionals, the Local Spin Density Approximation (LSDA/LDA/LDS) and the Generalized Gradient Approximation(GGA).

2.2 Properties and Restrictions

There are some restrictions that the density functionals are subject to and can give some guidance in the development of new approximations to the functionals.

To define some of the constraints we need first to look in a different perspective to the electron density interpretation. The alternative description can be related to the way the exchange and correlation effects tend to separate electrons apart and regard this effect as a hole involving an electron and keeping the others from approaching it. We will start with the description of the exchange-correlation energy with the coupling constant formulation[4]

$$E_{xc}[n] = \int_0^1 d\lambda \langle \Psi_n^{min,\lambda} | \hat{V}_{ee} | \Psi_n^{min,\lambda} \rangle - U[n], \tag{2.2}$$

where $\lambda = 0$ corresponds to the non-interacting case and $\lambda = 1$ to full interaction. The electron-electron potential and the Hartree electrostatic potential are dependent of the densities as

$$\langle \hat{V}_{ee} \rangle = \frac{1}{2} \int d^3r \int d^3r' \frac{\rho_2(\mathbf{r}', \mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} \tag{2.3}$$

and

$$U[n] = \frac{1}{2} \int d^3r \int d^3r' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \tag{2.4}$$

The two-electron reduced density matrix $\rho_2(\mathbf{r}', \mathbf{r})$ is a pair correlation function given by the density $n(\mathbf{r})$ of finding an electron in d^3r and $n_2(\mathbf{r}, \mathbf{r}')$ the conditional density of finding an electron in d^3r', given that there is one at $\mathbf{r}$.

$$\rho_2(\mathbf{r}', \mathbf{r}) = n(\mathbf{r}) n_2(\mathbf{r}, \mathbf{r}'). \tag{2.5}$$

The conditioned density $n_2(\mathbf{r}, \mathbf{r}')$ can be interpreted as having an electron in $\mathbf{r}'$ with the effects of an hole in $\mathbf{r}$

$$n_2(\mathbf{r}, \mathbf{r}') = n(\mathbf{r}') + n_{xc}^{\lambda}(\mathbf{r}, \mathbf{r}'), \tag{2.6}$$

where $n_{xc}^{\lambda}(\mathbf{r}, \mathbf{r}')$ is the exchange-correlation hole density.

The integral over space of the conditional density gives all the electrons in the system except the one in $\mathbf{r}$,

$$\int d^3r' n_2(\mathbf{r}, \mathbf{r}') = N - 1 \tag{2.7}$$

and given the integration of $n(\mathbf{r})$ from (1.12) on a unpolarized system,

$$\int d^3r n(\mathbf{r}) = N \tag{2.8}$$

we can define a constraint to the domain of the functionals.

Exchange-correlation hole density sum rule

This limitation to the electron densities implies, from (2.6), that the exchange-correlation hole density is an electron in $\mathbf{r}$ missing from the rest of the system

$$\int d^3r' n^{\lambda}_{xc}(\mathbf{r}, \mathbf{r}') = -1 \tag{2.9}$$

Defining the coupling-constant averaged hole density as

$$\bar{n}_{xc}(\mathbf{r}, \mathbf{r}') = \int_0^1 d\lambda n^{\lambda}_{xc}(\mathbf{r}, \mathbf{r}'), \tag{2.10}$$

we can rewrite the exchange-correlation energy (2.2) as

$$E_{xc}[n] = \frac{1}{2} \int d^3r \int d^3r' \frac{n(\mathbf{r})\bar{n}_{xc}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \tag{2.11}$$

For the Kohn-Sham non-interacting particle system $\lambda = 0$, the hole exchange density can be given by

$$n_x(\mathbf{r}, \mathbf{r}') = n^{\lambda=0}_{xc}(\mathbf{r}, \mathbf{r}') = -\sum_{\sigma} \frac{|\rho^{\lambda=0}_1(\mathbf{r}'\sigma, \mathbf{r}\sigma)|^2}{n(\mathbf{r})}, \tag{2.12}$$

where $\rho_1(\mathbf{r}'\sigma, \mathbf{r}\sigma)$ is the one-electron reduced density matrix.

Hole exchange density inequality

Since $\rho_1(\mathbf{r}'\sigma, \mathbf{r}\sigma)$ and $n(\mathbf{r})$ are positive, the hole exchange density (2.12) needs to be negative

$$n_x(\mathbf{r}, \mathbf{r}') \leq 0 \tag{2.13}$$

With $\lambda = 0$, the correlation effects, that represent the Coulomb interaction, disappear and the exchange-correlation energy becomes the exchange energy

$$E_x[n] = \frac{1}{2}\int d^3r \int d^3r' \frac{n(\mathbf{r})n_x(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}. \tag{2.14}$$

Exchange energy inequality

The dependence of the exchange energy functional with the hole exchange density, show us that the exchange-energy is constrained to negative values

$$E_x[n] \leq 0 \tag{2.15}$$

Exchange hole density sum rule

The constrain for the hole exchange-correlation density (2.9) is independent of the λ value so (2.12) says us that the exchange hole density also follows the same rule,

$$\int d^3r' n_x(\mathbf{r},\mathbf{r}') = -1. \tag{2.16}$$

Knowing that we can separate the exchange from the correlation terms in the energy, the same happens to the density, particulary with the average of the hole density

$$\bar{n}_{xc}(\mathbf{r},\mathbf{r}') = n_x(\mathbf{r},\mathbf{r}') + \bar{n}_c(\mathbf{r},\mathbf{r}'). \tag{2.17}$$

Correlation hole density sum rule

The sum rule can also be applied to the correlation hole density

$$\int d^3r' \bar{n}_c(\mathbf{r},\mathbf{r}') = 0 \tag{2.18}$$

Applying the coordinate scaling[18] to the density, we can find out how the functionals that depend on the density will be transformed by this change. When scaling the density $\mathbf{r} \rightarrow \gamma\mathbf{r}$ with a scale parameter $\gamma > 0$, the scaled density appears as

$$n_\gamma(\mathbf{r}) = \gamma^3 n(\gamma\mathbf{r}), \tag{2.19}$$

where this new density also conserves the electron number: $\int d^3r n_\gamma(\mathbf{r}) = N$

If $\gamma > 1$, we have higher and more contracted densities or if $\gamma < 1$, the scaled density will be lower and more expanded than $n(\mathbf{r})$.

Scaling properties

Using this scaling method[18] in the Hartree electrostatic self-repulsion of the electrons, the non-interacting kinetic energy, and the exchange energy functional, we can verify how these energies scale by

$$\begin{aligned} U[n_\gamma] &= \gamma U[n] \\ T_s[n_\gamma] &= \gamma^2 T_s[n] \\ E_x[n_\gamma] &= \gamma E_x[n] \end{aligned} \tag{2.20}$$

The correlational functional does not have a simple scaling, but a general inequality is obtained,

$$\begin{aligned} E_c[n_\gamma] &> \gamma E_c[n] \quad (\gamma > 1) \\ E_c[n_\gamma] &< \gamma E_c[n] \quad (\gamma < 1) \end{aligned} \tag{2.21}$$

From the scaling relations in (2.20), we can verify that for the high-density limit, $\gamma \rightarrow \infty$, $T_s[n_\gamma]$ dominates $U[n_\gamma]$ and $E_x[n_\gamma]$, while in the low-density limit, $\gamma \rightarrow 0$, $U[n_\gamma]$ and $E_x[n_\gamma]$ dominate $T_s[n_\gamma]$.

While $E_c[n_\gamma]$ in the high-density limit tends to a negative constant, in the low-density limit it behaves as $E_c[n_\gamma] \approx \gamma D[n]$, where $D[n]$ is an appropriately chosen density functional.

The Lieb-Oxford bound

A useful condition for functional approximations are the lower bounds, Lieb and Oxford[19] have found that the non-interacting kinetic and exchange-correlation functionals possess a lower bound, coming from Thomas-Fermi theory

$$T_s[n] \geq 2.87 \int d^3 r n(\mathbf{r})^{5/3} \tag{2.22}$$

Since,

$$E_x[n] \geq E_{xc}[n] \geq E_{xc}^{\lambda=1}[n] \tag{2.23}$$

and

$$E_{xc}^{\lambda=1}[n] \geq -1.68 \int d^3 r n(\mathbf{r})^{4/3} \tag{2.24}$$

then this is also the lower bound for the exchange and exchange-correlation functionals.

The fundamental band-gap[20, 21] (the difference between the bottom of the conduction band and the top of the valence band) is a ground state quantity that can be expressed in terms of ground-state energies of N-1, N, and N+1 particle systems as

$$E_g = IP - EA = \left(E_g\left(N+1\right) - E_g\left(N\right)\right) - \left(E_g\left(N\right) - E_g\left(N-1\right)\right), \tag{2.25}$$

where IP is the ionization potential and EA the electron affinity.

When considering the Kohn-Sham systems of N and N+1 particles, the true band-gap can be obtained by the difference between the HOMO (highest-occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital):

$$E_g = \epsilon_{N+1}(N+1) - \epsilon_N(N) \tag{2.26}$$

but usually, what is available is the difference in HOMO and LUMO in a N-electron calculation

Derivative discontinuity

$$E_g = (\epsilon_{N+1}(N) - \epsilon_N(N)) + \Delta_{xc} \tag{2.27}$$

The term in parenthesis is the Kohn-Sham band-gap and Δ_{xc} is called the derivative discontinuity. By verifying a discontinuity in the difference of the density, we can conclude that the derivatives of (1.45) also have discontinuity, this loss is included in the exchange-correlation potential.

Size Consistency

To avoid complexity the energy and the density of a system should be able to be separated into subsystems.

$$E = E_1 + E_2 \tag{2.28}$$

and

$$n(\mathbf{r}) = n_1(\mathbf{r}) + n_2(\mathbf{r}) \tag{2.29}$$

The LDA or GGA approximations that follow this constraint are properly size consistent.

The functionals that are not size consistent should be avoided.

2.3 Uniform Electron Gas

The simplest system involving several electrons is a non-interacting uniform electron gas. This system can be characterized by a null (constant) Kohn-Sham potential $v_s(\mathbf{r})$ in a volume (V) with cyclic boundary conditions. The solution to this system are the plane waves

$$\Psi(\mathbf{r}) = \frac{1}{\sqrt{V}} exp(i\mathbf{k} \cdot \mathbf{r}) \tag{2.30}$$

where $\mathbf{k}$ is the wave vector, the energy is $k^2/2$ and the number of orbitals in a volume d^3k of wave-vector space is $2[V/(2\pi)^3]d^3k$.

The number of electrons in volume V that occupy the N lowest Kohn-Sham spin orbitals ($k < k_F$) is given by

$$N = V\frac{k_F^3}{3\pi^2}, \tag{2.31}$$

where k_F is the Fermi wavevector and the electronic density is

$$n(\mathbf{r}) = \frac{k_F^3}{3\pi^2} = \frac{3}{4\pi r_s^3} \tag{2.32}$$

where r_s is the Seitz radius, the radius of a sphere containing one electron.

The kinetic energy of the system is given by

$$t_s(n) = \frac{3}{5}\frac{k_F^2}{2} = \frac{3}{10}(3\pi^2 n)^{2/3} = \frac{3}{10}\frac{(9\pi/4)^{2/3}}{r_s^2}. \tag{2.33}$$

Whe can evaluate the exchange energy in the homogeneous electron gas by using the description of this contribution in terms of a hole surrounding each electron and keeping other electrons from approaching them, as this kind of energy tend to keep electrons apart.

The one-matrix electron density of spin σ is given by[9]

$$\rho_1^{\lambda=0}(\mathbf{r}+\mathbf{u}\sigma, \mathbf{r}\sigma) = \frac{k_F^3}{2\pi^2}\frac{\sin(k_F u) - k_F u\cos(k_F)u}{(k_F u)^3}. \tag{2.34}$$

Using it to calculate the exchange hole density (2.12), we obtain

$$n_x(u) = -2\frac{|\rho_1^{\lambda=0}(\mathbf{r}+\mathbf{u}\sigma, \mathbf{r}\sigma)|^2}{n}. \tag{2.35}$$

The exchange energy per electron is then,

$$e_x(n) = \int_0^\infty du 2\pi u n_x(u) = -\frac{3}{4\pi}k_F = -\frac{3}{4\pi}(3\pi^2 n)^{1/3} = -\frac{3}{4\pi}\frac{(9\pi/4)^{1/3}}{r_s} \tag{2.36}$$

In a uniform gas the self-interaction correction vanishes, and the Pauli exclusion principle is the only effect to consider.

While kinetic and exchange energies were obtained exactly, the correlation energy can only be obtained in the same form for high and low limits.[4]

In these limits the correlation energy can by given by many-body perturbation theory for weak-coupling limit and from Madelung electrostatic and zero-point vibrational energies of the Wigner crystal for the strong coupling limit or also using expressions fitted to Quantum Monte Carlo calculations.

With the well established formulation for the limits at high density where the system approaches a perfect gas and at low density approaches the structure of a crystal, intermediate phases in the density, with small energy differences between them, need to be found. The Quantum Monte Carlo method is used because of it's capability to give a solution of two orders of magnitude smaller than an an approximate trial wave function. [22]

2.4 Local Spin Density Approximation

In the LSDA we assume that the density of a system is locally homogeneous, so we can write the exchange-correlation energy density as

$$E_{xc}^{LSDA}[n^{\uparrow}, n^{\downarrow}] = \int d^3r n(\mathbf{r}) \left[\epsilon_x^{hom}(n^{\uparrow}(\mathbf{r}), n^{\downarrow}(\mathbf{r})) + \epsilon_c^{hom}(n^{\uparrow}(\mathbf{r}), n^{\downarrow}(\mathbf{r}))\right] . \quad (2.37)$$

In unpolarized systems the following settings are found $n^{\uparrow}(\mathbf{r}) = n^{\downarrow}(\mathbf{r}) = n(\mathbf{r})/2$.

It is expected that this approximation will work better with some solid than with inhomogeneous cases like atoms and small molecules, because of the nearly-free-electron characteristics similar to the homogeneous electron gas.

The Local Spin Density Approximation is exact for uniform densities and nearly-exact for slowly-varying ones. The satisfactory results that show for many systems is from application of the constrains, from previous section (section 2.2), in the exchange and correlation functionals.

There is a constraint that LDA and GGA do not follow because of their local and semi-local density structure, they predict a zero derivative discontinuity, giving a poor approximations to the experimental gaps, by a factor of $\tilde{2}$.

2.5 Generalized-Gradient Approximation

The GGA[23] functionals have emerged to improve the LDA functionals. GGA can be more accurate than the LDA functionals, as adding the dependency on the gradient of the density allows for a better description of inhomogeneous systems than LSDA does.

The GGA arises from the gradient expansions approximation (GEA) introduced into LDSA, where the electrons are treated as in a homogeneous system. The first term of the expansion, ∇n, disappears due the random direction of electrons and only appears the 2nd order term, $\nabla^2 n$. The terms of this expansion are found by creating a weak external perturbation and finding out the response of the energy.

The result obtained was good for the kinetic energy, acceptable for the exchange energy, but poor in the correlation energy and, consequently, in the exchange-correlation energy. The improvements upon LSDA were found for high densities but display an inaccurate behaviour for small densities. With this approximation, oscillations in the exchange density hole disobey the constraint (2.13) and converges to -1 only with a convergence factor (2.16), while the correlation density hole do not integrate to 0 (2.18).

The non-empirical generalized gradient approximation emerges from GEA by applying a cut off to the large-u contributions, so that the constrains are fulfilled correctly

$$E_{xc}^{GGA}[n^{\uparrow}, n^{\downarrow}] = \int d^3r f(n^{\uparrow}(\mathbf{r}), n^{\downarrow}(\mathbf{r}), \nabla n^{\uparrow}(\mathbf{r}), \nabla n^{\downarrow}(\mathbf{r})). \tag{2.38}$$

Chapter 3

Ionization Potential

The ionization potential[24] can be classified in two definitions the vertical ionization energy and the adiabatic ionization energy.

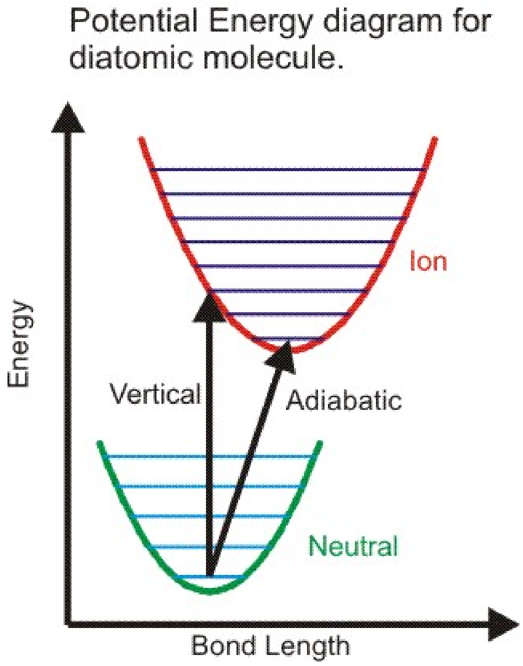


Fig. 3.1 Difference between vertical ionization energy and adiabatic ionization energy

When referring to the vertical ionization energy we can retrieve its interpretation from Koopmans' theorem in the Hartree-Fock theory, which states that the relaxation of the HF energy from a removal of an electron in an unrelaxed orbital state $\alpha\sigma$ is related to the HF eigenvalue as

$$\Delta E^{\mathrm{HF}}_{\alpha\sigma}|_{unrel} = -\epsilon^{\mathrm{HF}}_{\alpha\sigma} \tag{3.1}$$

the difference between the unrelaxed energy and the relaxed one is established by the orbital relaxation energy $\Sigma^{HF}_{\alpha\sigma}$ by

$$\Delta E^{\mathrm{HF}}_{\alpha\sigma}|_{rel} = \Delta E^{\mathrm{HF}}_{\alpha\sigma}|_{unrel} + \Sigma^{\mathrm{HF}}_{\alpha\sigma}|_{unrel}. \tag{3.2}$$

The Koopmans' theorem can give an acceptable removal energy from a single calculation of the eigenvalues for a N-electron system.

However, when we work in a system with localized states the relaxation effect $\Sigma_{\alpha\sigma}$ are significant, additional transitions may exist between the ground state of the neutral molecule and the excited state of the positive ion. There can also exist an intrinsic self-interaction effect, like the one electron in the DFT theory.

Unless there is a functional that cancels the negative relaxation energy which approximates the energy eigenvalue $-\epsilon_{\alpha\sigma}$ to the relaxed excitation energy, another method to accurately calculate the ionization energy should be used and this method is the adiabatic ionization energy.

The adiabatic ionization energy is a more correct way to calculate the ionization energy. With this method we need to evaluate two calculation of the total energy with different molecule geometries, because the lack of an electron the equilibrium modifies the atomic positions, so the difference between the two energy with different geometries gives a more accurate ionization energy, without the additional transitions and the self-interaction effect can be cancel.

Part III

Methodology

Chapter 4

Benchmark Dataset

In order to test the functionals, a suitable set of systems has to be chosen. There are several such databases. They cover systems ranging from atoms, small molecules and small ions to bulk structures. As the property we intended to use as benchmarks for the functionals was the ionization potential, the most adequate datasets would be sets of small, well-know, molecules.

There are several such datasets available: G1, G2, G3, etc

4.1 G2 Benchmark

The choice for the molecules from the list of Gaussian-2 theory[5, 6], was primarily due to having already experimental and theoretical data evaluated and we can use that previous work in our advantage.

The Gaussian-2 theory is an upgrade of the Gaussian-1 theory, some corrections were made in G1 energy to G2 energy. The G1 theory is mainly based in the Møller-Plesset perturbation theory, a post-Hartree-Fock ab initio method. This method improves HF theory by adding electron correlation effects by means of Rayleigh-Schrödinger perturbation theory normally used between 2nd (MP2) to 4th (MP4) order.

The main goal of this theory is to obtain an equilibrium geometry, a total electronic energy and a set of harmonic frequencies for each structure associated with a local minimum on a potential surface.

The steps to achieve the objectives starts by using the Hartree-Fock theory with 6-31G* basis to get initial equilibrium structures using spin-restricted for single states and spin-unrestricted for all other multiplicities. Then the final structures are obtained by using MP2 and 6-31 G* basis set, with full electron correlation. The calculation of the energy from this geometry, where the electron correlation is treated only with the valence ones using the frozen-core approximation, are carried by the full fourth-order Møller-Plesset theory (MP4SDTQ).

After the main calculations some corrections are made, like the inclusion of diffuse sp basis functions important for anions and molecules with lone pairs of electrons, corrections in higher polarization functions on non-hydrogen atoms and corrections of the deficiencies of Møller-Plesset theory truncated at fourth order, with problems occuring in unsaturated radicals or molecules with multiple bounds. Beside these corrections, the basis set also creates deficiencies and to solve this issue, arrangements in the total energy are made.

The change from G1 to G2 theory occurs with three corrections in G1 energy. The first result from non-additivity caused by the assumption of separate basis set extensions for diffuse sp functions and higher polarization functions. The second one there is an addition of a third d functions to the non-hydrogen atoms and a second p function to the hydrogen. The last is a better fit to experimental atomization energies of 55 molecules, to correct energy calculation error in the H_2 molecule and H atom .

We use the molecules studied by the Gaussian-2 theory and use them to compare the DFT theory with the experimental data (Table 6.2), we not only used the same molecules, but the same atomic geometry was applied.

Chapter 5

Application of DFT

5.1 Density Functional Theory calculations in a Gaussian basis set

The solutions of the Kohn-Sham equation needs to be calculated by methods that solve differential equations. The potentials used in the Hamiltonian are the classical Coulomb and the Hartree contributions, besides the exchange-correlations potential.

$$(-\frac{1}{2}\nabla^2 + v^c(\mathbf{r}))\Psi_i(\mathbf{r}) + \int v^{xc}(\mathbf{r}, \mathbf{r}')\Psi_i(\mathbf{r}')d\mathbf{r}' = \epsilon_i \Psi_i(\mathbf{r}) \tag{5.1}$$

with

$$v^c(\mathbf{r}) = -\sum_a \frac{Z_a}{|\mathbf{R_a} - \mathbf{r}|} + \int \frac{\rho(\mathbf{r}, \mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \tag{5.2}$$

where $\rho(\mathbf{r}, \mathbf{r})$ is the diagonal of the electron density matrix

$$\rho(\mathbf{r}, \mathbf{r}') = \sum_\alpha \Psi^*_\alpha(\mathbf{r})\Psi_\alpha(\mathbf{r}') \tag{5.3}$$

To obtain more easily the solutions of equation (5.1) the single-particle orbitals $\Psi_i(\mathbf{r})$ can be expanded in terms of a finite basis set.

There are two main types of basis set that can be used in NWChem[7], the local basis implementation, that uses atom-centred Gaussian type orbitals (GTO) and the plane wave implementation, which uses PSPW (pseudo-potential plane wave), band structures and PAW (projector augmented plane-wave).

In this project, the GTO basis are going to be use, as is more simple for small molecules calculations, these orbitals are decompose into

$$\Phi_\mu(\mathbf{r}) = x^l y^m z^n e^{-ar^2} \tag{5.4}$$

or in radial-angular description

$$\Phi_\mu(\mathbf{r}) = R_l(\mathbf{r}) Y_{lm}(\theta, \phi). \tag{5.5}$$

They can also be in linear combinations (contracted GTO's).

The single-particle orbitals are written in terms of the GTO functions

$$\Psi_i(\mathbf{r}) = \sum_\mu c_{i\mu} \Phi_\mu(\mathbf{r} - \mathbf{R}_{\mathbf{a}_\mu}). \tag{5.6}$$

Using the expansion of (5.6), the equation (5.1) can be transformed into the matrix form

$$\mathbf{FC} = \mathbf{SCE} \tag{5.7}$$

where $\mathbf{C} = \{c_{i\mu}\}$ is the matrix of expansion coefficients, $\mathbf{E} = \{\epsilon_i\}$ the eigenvalue matrix and $\mathbf{S}$ the overlap matrix

$$\mathbf{S}_{\mu\nu} = \int \Phi_\mu(\mathbf{r}) \Phi_\nu(\mathbf{r}) d\mathbf{r}. \tag{5.8}$$

The Fock matrix, $\mathbf{F}$, consists on the kinetic, Coulomb and exchange-correlation matrix elements

$$\mathbf{F}_{\mu\nu} = t_{\mu\nu} + v^c_{\mu\nu} + v^{xc}_{\mu\nu} \tag{5.9}$$

where

$$\begin{aligned} t_{\mu\nu} &= -\frac{1}{2}\int \Phi_\mu(\mathbf{r})\nabla^2\Phi_\nu(\mathbf{r})d\mathbf{r} \\ v^c_{\mu\nu} &= \int \Phi_\mu(\mathbf{r})v^c(\mathbf{r})\Phi_\nu(\mathbf{r})d\mathbf{r} \\ v^{xc}_{\mu\nu} &= \int\int \Phi_\mu(\mathbf{r})v^{xc}(\mathbf{r},\mathbf{r}')\Phi_\nu(\mathbf{r}')d\mathbf{r}d\mathbf{r}' \end{aligned} \tag{5.10}$$

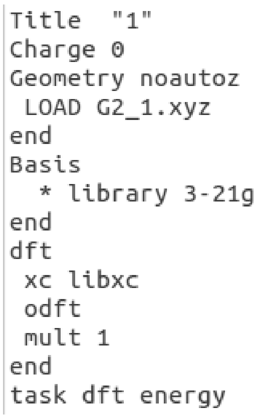
The generalized non-linear eigenvalue equation (5.7) is solved using a self-consistent field (SCF) procedure. The two main computational steps involve the construction of the Fock matrix and its diagonalization.

The Coulomb term and non-local component of the exchange-correlation energy give a complexity of $O(n^4)$ and different methods can be used to reduce them to $O(n^3)$, using charge density (CD) fitting or the resolution of identity (RI) approach. While the local part of the exchange-correlation potential has to be evaluated numerically on the radial grids with $O(n^3)$.

5.2 Input Files

Calculations in NWChem are done by creating input files and run them through the software. They are free-format text files that contain start-up directives, definition of the chemical system, specifications of parameters for calculations and task directives.

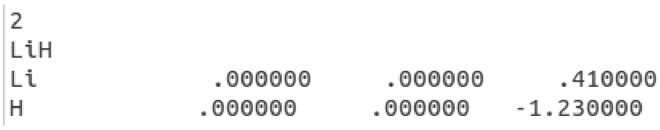
An example of input file is:



```
Title  "1"
Charge 0
Geometry noautoz
 LOAD G2_1.xyz
end
Basis
  * library 3-21g
end
dft
 xc libxc
 odft
 mult 1
end
task dft energy
```

Fig. 5.1 Example of an input file

where the .xyz file is



```
2
LiH
Li             .000000     .000000     .410000
H             .000000     .000000   -1.230000
```

Fig. 5.2 Example of a xyz file

The start-up directives are the ones that define the general features of the calculation, including available memory, database name, file locations and other global options. Once the start-up directives are processed, the parameters for the calculation will be searched. During this process the only procedure that is happening is saving these parameters to the database file, so when it parses through the task directives the extraction of relevant data starts and appropriate computational calculations are made.

We can see from the example, fig.(5.1), that the file title is a number, this number represents the molecule ID in the G2 benchmark, from the line that adds or removes a charge particle to the molecule is shown that the molecule is neutral.

The geometry is in Cartesian format inside a xyz file and the basis set used for all atoms is the 3-21G. In the DFT parameters part, the Libxc[8] library is used to call the functionals, in the next section we will discuss more about this library, and the multiplicity in a open-shell system (ODFT) is 1.

Finally the task to calculate the energy ends the input file. After we run it through NWChem an output file will be created with all calculations and the chosen and default options.

5.3 Functionals Dataset

Since DFT began to have solid foundations, the improvement of this theory and consequently the construction of new and more accurate exchange-correlation energies started to emerge to give more precise results for different systems and observable quantities. With the creation of a great number of E_{xc} functionals where all information was spread around and as new electronic structure software simulator appeared in this new technology view of the world with dependence on the functionals, a library was created so all the information could be located in one place and be easily used by the new electronic structure software.

It was made an effort to include not only new functionals, but the functionals that were used in the beginning of the density functional theory. Besides the functionals, their derivatives of several orders were included in the analytic form, so the numerical errors and instabilities are not introduced in the calculations. The possibility to use the Libxc in several software codes, is an advantage to make a comparison between them for any existing functional.

We can retrieve the functionals by using the functional id or functional name and we obtain the information about it like it's family or authors. The project is still growing in code access and number of functionals, so we can expect more from it.

5.4 Database and Statistical calculation

The Pyxcbench project is still being developed and is a fundamental tool for this thesis. The Pyxcbench is a set of Python modules that can be used to evaluate functionals by comparing them with others, by estimating the accuracy of a system property calculated with any electronic structure software for any kind of system. The data is stored in a data base and statistical studies can be made with the information obtained.

In this thesis the system evaluated are the molecules from the G2 test set, where the geometry and multiplicity are given and this information is used into the NWChem software. A number of 1 exchange and 21 correlation functionals from LDA and 45 exchange and 21 correlation functionals from GGA are studied. The neutral and ionic molecule geometries were given and the energies were obtain from the output files, then the Ionized Potential is calculated and this value is compared to the experimental ones.

The statistical studies made in the thesis are presented in the following chapter with graphics and tables where is analysed the mean relative values or smallest relative values by comparison of the different exchange and correlation functionals and different molecules.

Part IV

Results and Conclusion

Chapter 6

Results

6.1 Exchange-Correlation Functional

After executing the NWChem electronic structure software through the pyxcbench python library, the useful information was gathered into a database ready for analyze and interpretation.

The relative error value for each valid run was obtained by comparing the adiabatic ionization potential with it's experimental value,

$$\mathrm{re} = \frac{|\mathrm{IP} - \mathrm{IP}_{\mathrm{exp}}|}{\mathrm{IP}_{\mathrm{exp}}} * 100\%. \tag{6.1}$$

The relative mean deviation was obtained from calculating how much the result is a part from the mean value of the parameter being studied

$$\mathrm{rmd} = \frac{\frac{1}{n}\sum_{i=1}^{n} |x_i - \bar{x}|}{|\bar{x}|} \tag{6.2}$$

For a first analyze we found out the mean values of the relative errors for all molecules and determine where those values fit in small intervals of error.

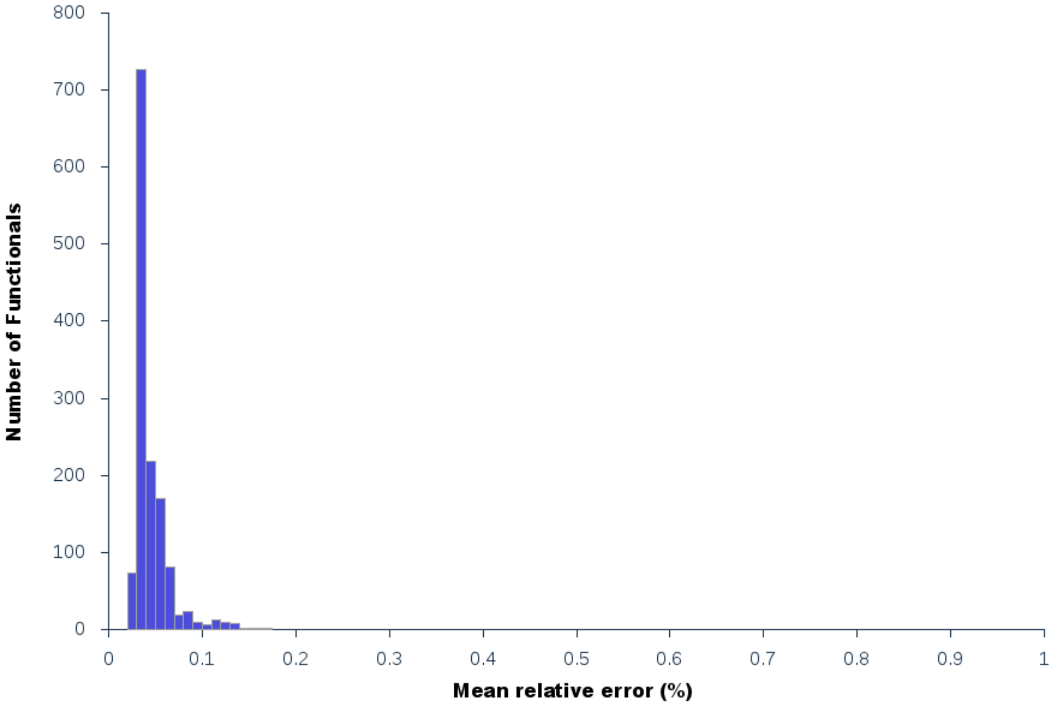


Fig. 6.1 Number of exchange-correlation functionals within the same range of 0.01% of the Ionization Potential mean relative error

The majority of the functionals have a mean relative error less than 0.1%. The biggest number of functionals belong to the interval between 0.02% and 0.03% with 726 functionals in a total of 1361 with relative error less than 1.0%. The relative error of most of functional is an acceptable value since the experimental value is determined with an uncertainty of 0.2%. [25]

From this list of functionals we gave attention to the top ten functionals and presented them in the following table (6.1).

Table 6.1 Top ten functionals of the G2 test set.

Exchange Functional	Correlation Functional	Mean relative Error (%)
GGA_X_SSB_SW	GGA_C_SOGGA11_X	0.02653
GGA_X_SSB	GGA_C_SOGGA11_X	0.02755
GGA_X_PW91	GGA_C_SOGGA11_X	0.02766
GGA_X_APBE	GGA_C_SOGGA11_X	0.02785
GGA_X_B86_MGC	GGA_C_SOGGA11_X	0.02799
GGA_X_B86	GGA_C_SOGGA11_X	0.02814
GGA_X_XPBE	GGA_C_SOGGA11_X	0.02814
GGA_X_DK87_R2	GGA_C_SOGGA11_X	0.02818

GGA_X_PBE	GGA_C_SOGGA11_X	0.02822
GGA_X_HJS_PBE	GGA_C_SOGGA11_X	0.02822

We can notice that the exchange-correlation energy was best obtained by the arrangement of the correlation functional GGA_C_SOGGA11_X, and the exchange functional GGA_X_SSB_SW.

The correlation functional GGA_C_SOGGA11_X overcomes any other in the top ten, while the exchange functional varies and the GGA_X_SSB_SW is a modification from the succeeding functional, a different version from the same authors.

From this result, we can see how the correlation functional is sensitive and are they who affect in higher order the accuracy of an exchange-correlation functional. The difference between GGA_C_SOGGA11 and GGA_C_SOGGA11_X is the addition of a term in the exchange energy and a few additional databases with experimental result. The general shape of these functionals are

$$E_{xc}^{SOGGA11} = E_x^{SOGGA11} + E_c^{SOGGA11} \tag{6.3}$$

and for SOGGA11-X,

$$E_{xc}^{SOGGA11-X} = \left(\frac{X}{100}\right) E_x^{HF} + \left(1 - \frac{X}{100}\right) E_x^{SOGGA11} + E_c^{SOGGA11}. \tag{6.4}$$

In the both functionals the same constrains were imposed, the uniform electron gas limit (UEG) and the limitation to the second-order density-gradient expansion.

The Monte Carlo fit of these functionals was made in conjunction with the exchange term and by improving the exchange part on the exchange-correlation functional, the coefficients for the correlation part also improved the accuracy in the correlation part. So this improvement of the GGA_C_SOGGA11_X took it to the top of the table.

Strangely, from the exchange functional GGA_X_SSB to GGA_X_SSB_SW was the opposite of an improvement from the same authors. They began with GGA_X_SSB_SW and then they enhanced to GGA_X_SSB.

The GGA_X_SSB_SW was a mix between GGA_X_PBE and GGA_X_OPTX functionals by using a switching function that changes between them in a smoothly way when altering from a low reduced density gradient to a high one. But, supposedly, this functional has a poor performance for spin states and reaction barriers.

From a study made by Swart, Solà and Bickelhaupt, the optimization for a kind of property will loose the accuracy for others. So by mixing the old GGA_X_SSB_SW with GGA_X_KT1, they improved the overall performance, but the atomization energies were improved.

To have a big picture from the big set of functionals used in this work, a color map with the mean relative error was generated and showed in (Fig. 6.2) with an interval between 0% and 0.1% since the values above 0.1% don't contribute for a better analyze of the functionals.

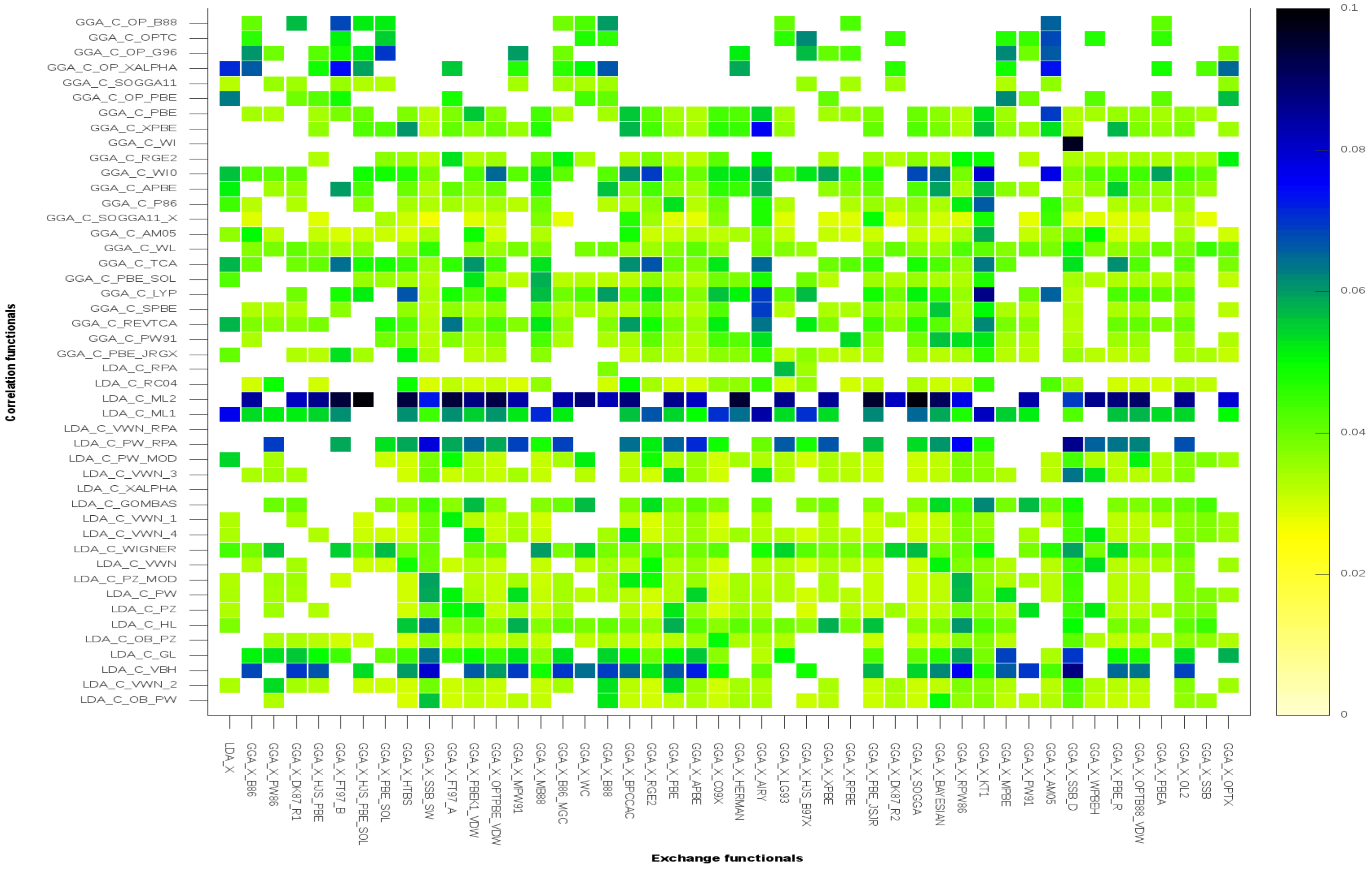


Fig. 6.2 Color map of the mean relative error of Exchange functionals with Correlation functionals in a more restrictive error interval, between 0% and 0.1%.

From the map color figure we can notice some lines with bad accuracy in the correlation functional part, most of them in the LDA side. This shows how sensible this term is for the calculation of ionization potential. We can see also a few lines in the exchange side, which start to show their differences when comparing in a smaller relative error percentage, below 0.1%.The white spots can be one of the three options: calculations that are still being made; divergence during the calculation of the result; or mean relative error higher than 0.1%.

6.2 Exchange Functional and Correlation Functional

By doing a statistical mean value in one of the type of functionals, e.g. exchange functional, we can regard how the other type, e.g. correlation functional, affects the system and verify what is the error value more probably to encounter for any given exchange functional energy.

If the mean relative error of the exchange/correlation functional is low, it can mean that the correlation/exchange functional will not affect much the result of the system total energy, while if the error is high it can perturb drastically the Kohn-Sham equation solution.

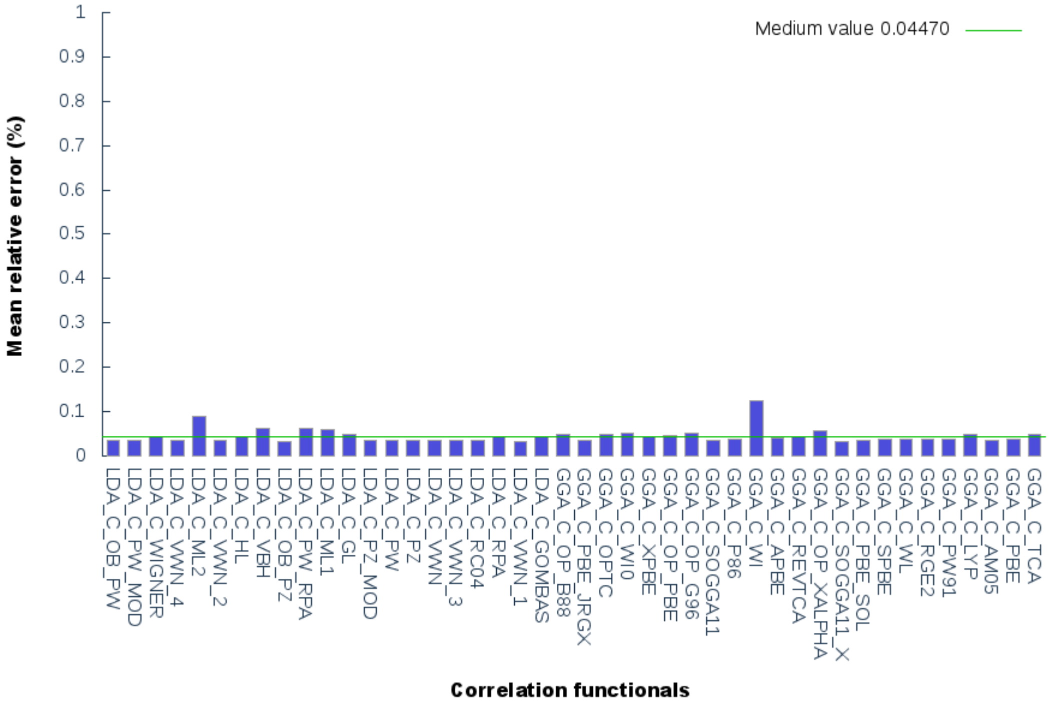


Fig. 6.3 Mean error value of each correlation functional with the exchange one averaged

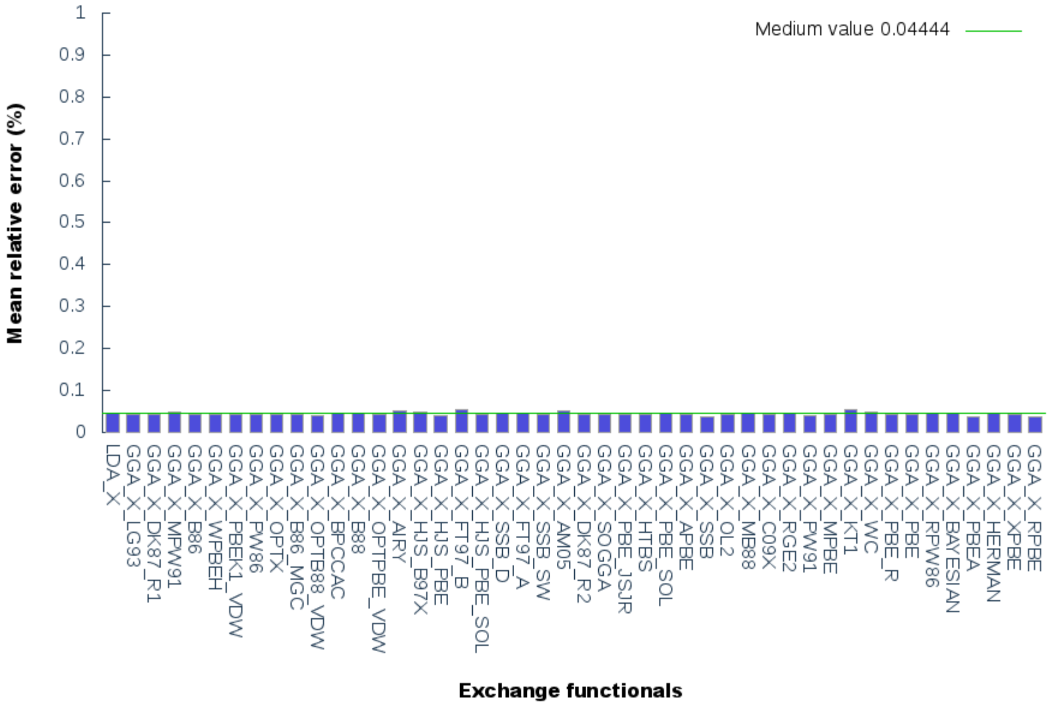


Fig. 6.4 Mean error value of each exchange functional with the correlation one averaged

We can see from the mean relative error of the correlation functionals with dependence in the exchange functionals, that there is no much change between functionals, they have all approximately the same value as the mean value of 0.044%.

By regarding the analysis of both graphics, Fig.(6.3) and Fig.(6.4), we can check that the most important term in the exchange-correlation functional energy is the correlation one. Since there is an higher fluctuation around the mean value with the variance of the correlation functional, this means that we need to have to chose more carefully the correlation functional to have a more accurate value for our ionization potential.

6.3 Molecules

Another way to classify the functionals is to see how they behave with different molecules, the mean relative error for all functionals to each molecule was calculated and is showed in the graphic below

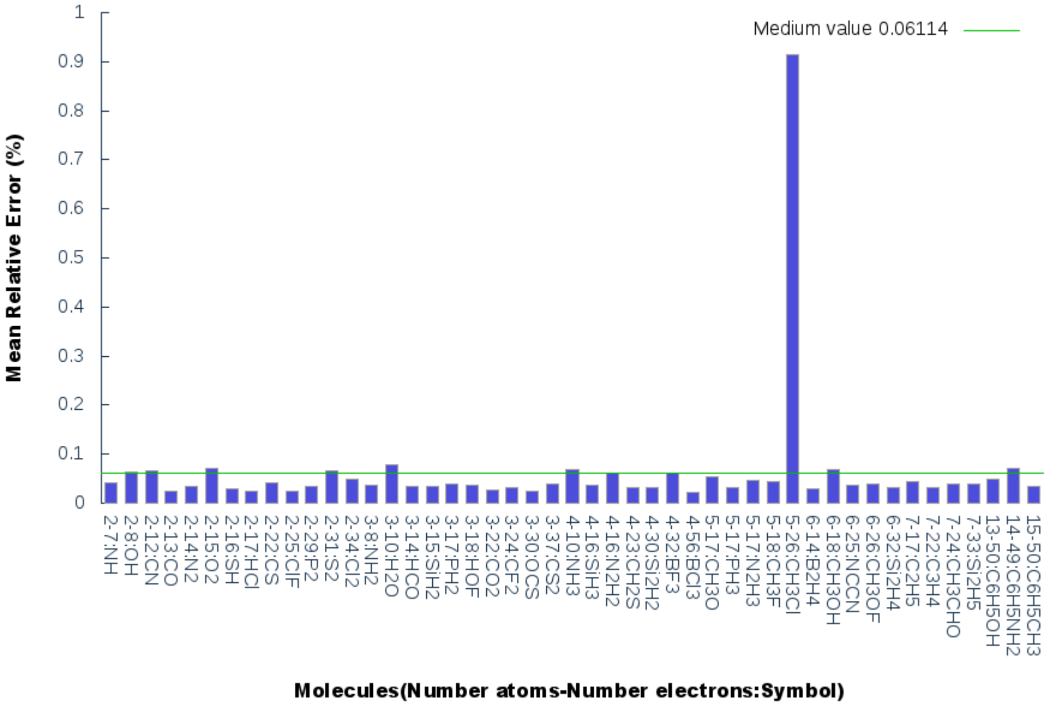


Fig. 6.5 Mean relative error value of each molecule sorted by number of atoms and number of electrons.

We can see that there is an high fluctuation in the mean relative error of the molecules, but there is only one that goes out of the 0.1%. The CH3Cl (Chloromethane) with a near 0.9% error. From LDA we can retrieve that the more similar the system is from an uniform electron cloud the better should be the solution. So, with this, it is suppose that the higher the number of electrons the system have the lesser should be the error, but is not noticeable in this graphic.

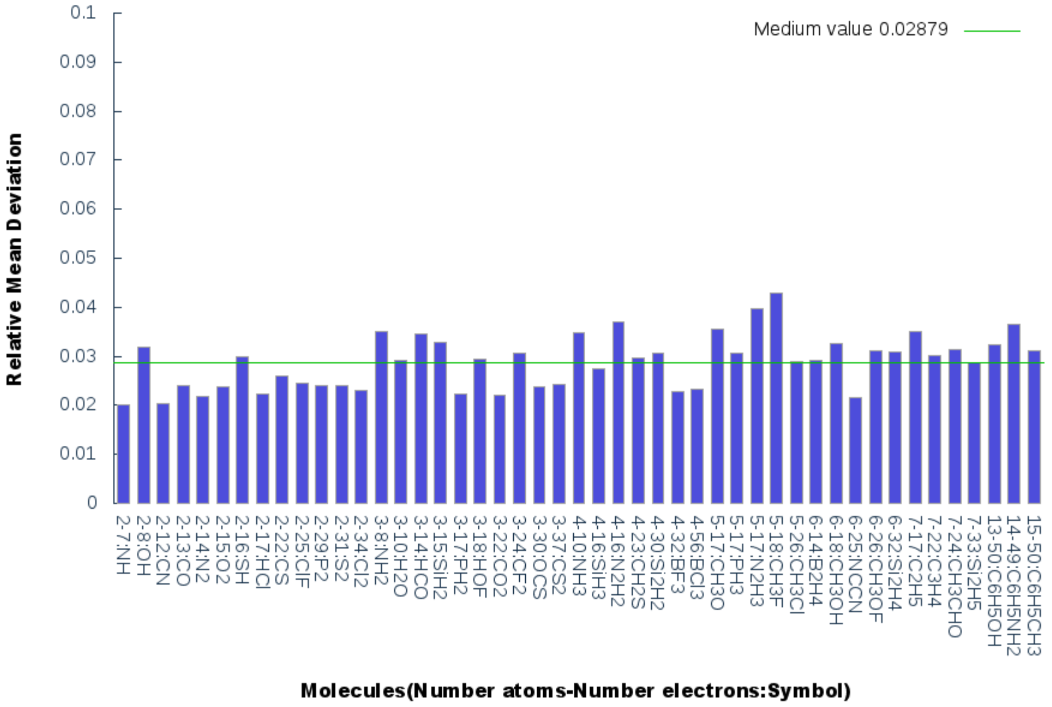


Fig. 6.6 Relative Mean Deviation of each molecule sorted by number of atoms and number of electrons.

From the Fig. (6.6), we can regard that the relative mean deviation is low, so the exchange-correlation functionals don't deviate from the mean value too much, which indicates, that the molecule CH3Cl has all functionals give an high error solution to the Kohn-Sham equation.

In the next graphic instead of the mean relative error we will see the functional that gives the smallest relative error to each molecule.

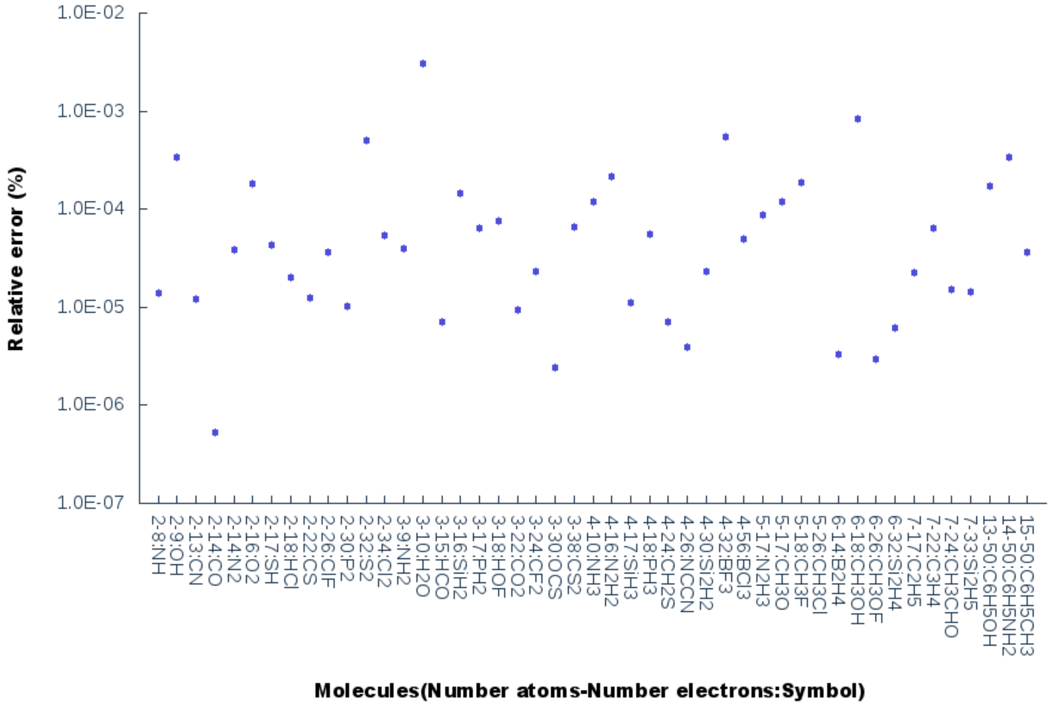


Fig. 6.7 Smallest error value of each molecule sorted by number of atoms and number of electrons.

There is a limitation of the range for the y axis to $1e-2$ so we can see closer how is the behaviour of the different molecules. The CH3Cl is the only not represented in the graphic because of it's high value of 0.6%.

For higher number of electrons and atomic mass it seams that the relative error values are converging to a specific short limited interval, this observation can give some reason to the property of LDA referred above about the uniform electron cloud.

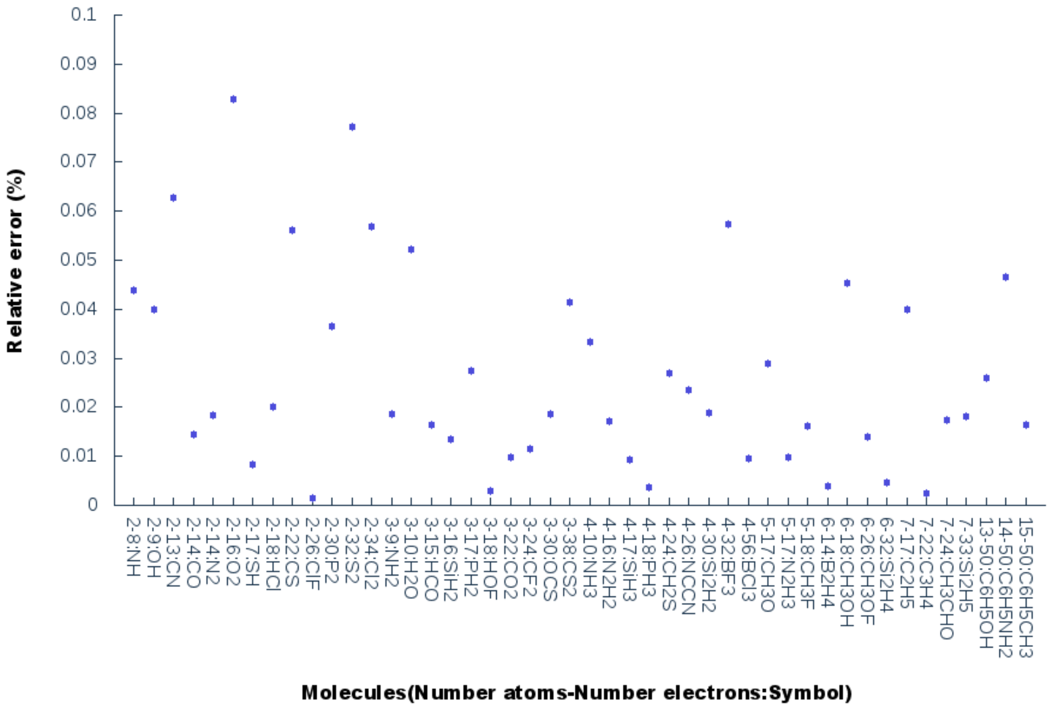


Fig. 6.8 Error value of the GGA_X_SSB_SW + GGA_C_SOGGA11_X for each molecule sorted by number of atoms and number of electrons.

The best functional of our top ten, doesn't have the lowest errors in the list of functionals, the smallest value is the ClF with an error of $1.43e-3$, they are quite high by comparing with the Table (6.2). But instead of very high and very low results they are in general well behaved. As we mentioned before the relative error seams to be starting to decrease with the electron numbers.

Table 6.2 List with the ionization potential with the smallest relative error for each molecule and it's experimental results

Molecule symbol	Ionization Potential (Ha)	Ionization (exp) Potential (Ha)	Smallest relative error (%)
NH	0.481416	0.481423	1.4e-05
OH	0.47853	0.47837	3.3e-04
CN	0.499804	0.499798	1.2e-05
CO	0.51501258	0.51501231	5.2e-07
N2	0.572577	0.572599	3.9e-05
O2	0.44349	0.44357	1.8e-04
SH	0.383023	0.383007	4.3e-05
HCl	0.468349	0.468340	2.0e-05

CS	0.416381	0.416376	1.3e-05
ClF	0.468176	0.468193	3.7e-05
P2	0.386980	0.386976	1.0e-05
S2	0.34709	0.34692	5.0e-04
Cl2	0.421948	0.421925	5.5e-05
NH2	0.396914	0.396898	4.0e-05
H2O	0.4624	0.4638	3.1e-03
HCO	0.2976758	0.2976737	7.1e-06
SiH2	0.32703	0.32707	1.5e-04
PH2	0.361054	0.361030	6.4e-05
HOF	0.466688	0.466723	7.5e-05
CO2	0.5071526	0.5071478	9.3e-06
CF2	0.418958	0.418948	2.3e-05
OCS	0.4115992	0.4115983	2.4e-06
CS2	0.371149	0.371173	6.5e-05
NH3	0.36828	0.36823	1.2e-04
N2H2	0.35287	0.35280	2.1e-04
SiH3	0.297677	0.297674	1.1e-05
PH3	0.362741	0.362721	5.5e-05
CH2S	0.3454461	0.3454485	7.2e-06
NCCN	0.4924460	0.4924479	4.0e-06
Si2H2	0.301356	0.301349	2.3e-05
BF3	0.57665	0.57697	5.5e-04
BCl3	0.426277	0.426298	4.9e-05
N2H3	0.279323	0.279299	8.7e-05
CH3O	0.39318	0.39322	1.2e-04
CH3F	0.45929	0.45937	1.9e-04
CH3Cl	0.67	0.42	6.0e-01
B2H4	0.3564747	0.3564735	3.3e-06
CH3OH	0.39657	0.39690	8.4e-04
CH3OF	0.4152745	0.4152732	3.0e-06
Si2H4	0.2976719	0.2976737	6.2e-06
C2H5	0.297680	0.297674	2.3e-05
C3H4	0.356496	0.356473	6.3e-05
CH3CHO	0.374854	0.374848	1.5e-05
Si2H5	0.279295	0.279299	1.4e-05
C6H5OH	0.31232	0.31237	1.7e-04
C6H5NH2	0.28288	0.28297	3.4e-04
C6H5CH3	0.323410	0.323399	3.7e-05

In the following table we have the best three functionals for each molecule and is very variable between the LDA and GGA functionals, as we can see the top functional rarely appears in this list, but in general has a high outcome.

Table 6.3 Top three functionals for each molecule.

Molecule	Exchange Functional	Correlation Functional	Mean relative Error (%)
CH3OF	GGA_X_LG93	LDA_C_RPA	2.96e-06
	GGA_X_XPBE	LDA_C_PW	2.19e-05
	GGA_X_XPBE	LDA_C_PW_MOD	2.23e-05
C6H5NH2	GGA_X_BPCCAC	LDA_C_GL	3.36e-04
	GGA_X_B88	LDA_C_GL	5.78e-04
	GGA_X_PBE	LDA_C_GL	7.46e-04
C6H5OH	GGA_X_OL2	LDA_C_GL	1.71e-04
	GGA_X_OPTX	LDA_C_VWN_1	4.49e-04
	GGA_X_SSB_SW	LDA_C_OB_PW	5.54e-04
N2H2	GGA_X_OPTPBE_VDW	LDA_C_GL	2.13e-04
	GGA_X_HJS_B97X	LDA_C_PW_RPA	5.63e-04
	GGA_X_HJS_B97X	LDA_C_VBH	1.56e-03
B2H4	GGA_X_SSB_D	GGA_C_SOGGA11_X	3.33e-06
	GGA_X_PBE	GGA_C_PBE_SOL	4.98e-05
	GGA_X_MPW91	GGA_C_PBE_SOL	5.39e-05
HOF	GGA_X_HJS_PBE	LDA_C_VWN_2	7.53e-05
	GGA_X_PBE	LDA_C_VWN_2	8.01e-05
	GGA_X_B86_MGC	LDA_C_GOMBAS	1.18e-04
N2H3	GGA_X_FT97_A	LDA_C_PW_MOD	8.73e-05
	GGA_X_FT97_A	LDA_C_PW	8.78e-05
	GGA_X_WPBEH	LDA_C_WIGNER	9.37e-05
Si2H4	GGA_X_PBE_R	GGA_C_RGE2	6.23e-06
	GGA_X_HJS_PBE	GGA_C_PBE	9.40e-06
	GGA_X_PBE	GGA_C_PBE	1.89e-05

Si2H2	GGA_X_DK87_R1	GGA_C_APBE	2.35e-05
	GGA_X_PW91	GGA_C_APBE	2.61e-05
	GGA_X_RPBE	GGA_C_SOGGA11_X	6.41e-05
N2	GGA_X_OL2	LDA_C_VWN_1	3.90e-05
	GGA_X_OPTX	LDA_C_VWN_1	1.51e-04
	GGA_X_RPW86	LDA_C_VWN_1	1.69e-04
SH	GGA_X_PBE_SOL	LDA_C_GOMBAS	4.32e-05
	GGA_X_MPBE	GGA_C_SPBE	7.01e-05
	GGA_X_BAYESIAN	GGA_C_PBE_SOL	8.06e-05
BCl3	GGA_X_HJS_B97X	LDA_C_PW	4.94e-05
	GGA_X_HJS_B97X	LDA_C_PW_MOD	4.97e-05
	GGA_X_HJS_B97X	LDA_C_VWN_4	5.68e-05
CH3O	GGA_X_PW86	LDA_C_PZ_MOD	1.20e-04
	GGA_X_PW86	LDA_C_PZ	1.49e-04
	GGA_X_SSB_D	LDA_C_OB_PZ	1.83e-04
CO	GGA_X_HJS_PBE_SOL	GGA_C_AM05	5.24e-07
	GGA_X_PBE_SOL	GGA_C_AM05	5.31e-06
	GGA_X_RPW86	GGA_C_PW91	4.35e-05
HCO	GGA_X_PBEA	GGA_C_PBE_SOL	7.07e-06
	GGA_X_MB88	LDA_C_VWN_3	1.73e-05
	GGA_X_APBE	GGA_C_PW91	7.96e-05
CH3Cl	GGA_X_RPW86	GGA_C_WI	6.04e-01
	GGA_X_APBE	GGA_C_WI	6.11e-01
	GGA_X_PBE_JSJR	GGA_C_WI	6.62e-01
CN	GGA_X_PBE_JSJR	LDA_C_ML2	1.22e-05
	GGA_X_HERMAN	LDA_C_ML2	8.47e-05
	GGA_X_SSB_SW	GGA_C_WI	4.58e-04
ClF	GGA_X_SOGGA	LDA_C_PZ_MOD	3.67e-05
	GGA_X_SOGGA	LDA_C_PZ	5.39e-05
	GGA_X_SSB_SW	GGA_C_PBE_SOL	6.29e-05

	GGA_X_OL2	LDA_C_PW_RPA	8.39e-04
CH3OH	GGA_X_OPTPBE_VDW	LDA_C_PW_RPA	8.60e-04
	GGA_X_OL2	LDA_C_VBH	8.91e-04
	GGA_X_KT1	GGA_C_APBE	1.25e-05
CS	GGA_X_BAYESIAN	GGA_C_WI0	1.02e-04
	GGA_X_MB88	GGA_C_APBE	1.20e-04
	GGA_X_PBE_JSJR	LDA_C_ML1	5.47e-05
Cl2	GGA_X_HTBS	LDA_C_ML1	1.41e-03
	GGA_X_AIRY	GGA_C_WI0	1.59e-03
	GGA_X_OPTB88_VDW	GGA_C_AM05	3.96e-05
NH2	GGA_X_HERMAN	LDA_C_OB_PZ	4.04e-05
	GGA_X_FT97_B	GGA_C_AM05	1.21e-04
	GGA_X_RGE2	GGA_C_LYP	1.41e-05
NH	GGA_X_RGE2	LDA_C_ML1	3.33e-05
	GGA_X_KT1	GGA_C_APBE	1.20e-04
	GGA_X_B88	LDA_C_GL	3.35e-04
OH	GGA_X_PBE_JSJR	LDA_C_PW_RPA	8.47e-04
	GGA_X_OPTPBE_VDW	LDA_C_PW_RPA	8.73e-04
	GGA_X_B88	LDA_C_GL	1.18e-04
NH3	GGA_X_PBE	LDA_C_GL	3.26e-04
	GGA_X_HJS_PBE	LDA_C_GL	3.42e-04
	GGA_X_RPW86	LDA_C_VBH	3.09e-03
H2O	GGA_X_SSB_SW	LDA_C_GL	3.21e-03
	GGA_X_SSB_D	LDA_C_GL	4.80e-03
	GGA_X_PBE_JSJR	LDA_C_PZ	2.32e-05
CF2	GGA_X_PBEK1_VDW	LDA_C_GOMBAS	2.91e-05
	GGA_X_PBE_JSJR	LDA_C_PZ_MOD	3.23e-05
	GGA_X_PBEK1_VDW	LDA_C_HL	3.66e-05
C6H5CH3	GGA_X_SSB_SW	GGA_C_SPBE	9.41e-05
	GGA_X_PW86	LDA_C_GOMBAS	9.46e-05

C2H5	GGA_X_OL2	GGA_C_LYP	2.26e-05
	GGA_X_MPBE	LDA_C_ML1	4.77e-05
	GGA_X_OPTX	GGA_C_OP_G96	1.06e-04
CH3F	GGA_X_SSB	LDA_C_OB_PW	1.88e-04
	GGA_X_AM05	GGA_C_WI0	1.89e-04
	GGA_X_SSB	LDA_C_OB_PZ	1.93e-04
CH2S	GGA_X_RGE2	GGA_C_P86	7.16e-06
	GGA_X_SSB	GGA_C_WI0	6.55e-05
	GGA_X_HERMAN	GGA_C_PBE_SOL	1.19e-04
CH3CHO	GGA_X_APBE	LDA_C_HL	1.52e-05
	GGA_X_XPBE	LDA_C_VWN_1	2.58e-05
	GGA_X_MPW91	LDA_C_VWN_3	6.19e-05
SiH3	GGA_X_B86	GGA_C_SOGGA11_X	1.10e-05
	GGA_X_XPBE	GGA_C_SOGGA11_X	1.02e-04
	GGA_X_C09X	GGA_C_PW91	1.10e-04
NCCN	GGA_X_HTBS	GGA_C_WL	3.96e-06
	GGA_X_OL2	GGA_C_WL	2.34e-05
	GGA_X_OPTPBE_VDW	GGA_C_WL	3.23e-05
Si2H5	GGA_X_MPBE	GGA_C_OPTC	1.42e-05
	GGA_X_PBE_R	GGA_C_SOGGA11_X	4.80e-05
	GGA_X_RPBE	GGA_C_SOGGA11_X	5.46e-05
PH2	LDA_X	GGA_C_TCA	6.38e-05
	GGA_X_MB88	GGA_C_SOGGA11_X	1.09e-04
	GGA_X_PBE_R	GGA_C_LYP	2.03e-04
SiH2	GGA_X_WC	GGA_C_RGE2	1.46e-04
	GGA_X_OPTPBE_VDW	GGA_C_SOGGA11_X	1.72e-04
	GGA_X_B88	GGA_C_PW91	1.84e-04
S2	GGA_X_APBE	LDA_C_ML2	5.00e-04
	GGA_X_AIRY	GGA_C_LYP	5.19e-04
	GGA_X_KT1	LDA_C_ML1	5.54e-04

P2	GGA_X_SSB_D	LDA_C_ML1	1.02e-05
	GGA_X_BAYESIAN	GGA_C_REVTCA	1.97e-05
	GGA_X_DK87_R1	GGA_C_OP_PBE	4.90e-05
PH3	GGA_X_MB88	LDA_C_PZ	5.50e-05
	GGA_X_MB88	LDA_C_PZ_MOD	5.80e-05
	GGA_X_C09X	LDA_C_PZ	1.48e-04
OCS	GGA_X_PBE_R	LDA_C_WIGNER	2.39e-06
	GGA_X_PBE_R	GGA_C_SPBE	2.98e-05
	GGA_X_PBEK1_VDW	LDA_C_RC04	5.30e-05
HCl	GGA_X_HTBS	GGA_C_SOGGA11_X	2.01e-05
	GGA_X_KT1	GGA_C_AM05	9.97e-05
	GGA_X_PBE_JSJR	GGA_C_SOGGA11_X	1.48e-04
O2	GGA_X_BAYESIAN	LDA_C_ML2	1.83e-04
	GGA_X_SSB_D	GGA_C_WI	6.83e-04
	LDA_X	LDA_C_ML1	1.04e-03
C3H4	GGA_X_FT97_A	LDA_C_GOMBAS	6.34e-05
	GGA_X_HJS_PBE_SOL	LDA_C_VWN_4	8.66e-05
	GGA_X_PBE_SOL	LDA_C_VWN_4	9.00e-05
CO2	GGA_X_DK87_R1	LDA_C_PW	9.33e-06
	GGA_X_WC	LDA_C_PW	1.06e-04
	GGA_X_WC	LDA_C_PW_MOD	1.07e-04
BF3	GGA_X_WC	LDA_C_VBH	5.52e-04
	GGA_X_SSB_D	LDA_C_PW_RPA	2.19e-03
	GGA_X_SSB_D	LDA_C_VBH	3.08e-03
CS2	GGA_X_SSB_SW	LDA_C_ML1	6.51e-05
	GGA_X_B86	GGA_C_OP_B88	9.04e-05
	GGA_X_WC	GGA_C_OP_PBE	1.89e-04

Chapter 7

Conclusion

With the development of this thesis, was made an improvement, for a better analyze and organization, in the pyxcbench structure.

We found out the importance of the correlation functionals are of very important matter to the exchange-correlation energy accuracy. They have higher fluctuations than the exchange functionals and so picking the correct correlation functional is very important.

The GGA_C_SOGGA11_X show us that is important to include a good exchange term when doing the fitting for best coefficients in a list of datasets. By including a big set of databases and giving excellent results in contrast to the studies made in GGA_X_SSB, this can mean that the choice of the right constrains and the functional terms that depend on the density is important. The GGA_X_SSB was overcome by it's previous version GGA_X_SSB_SW probably because of these factors.

The reason for why no functional gave good results for the molecule CH3Cl should be studied.

The LDA and GGA have similar high numbers as the best correlation functional for each molecule, this occurs because they both use Monte Carlo method for fitting, while the LDA of exchange even by being one, is rare to appear in the molecule list, because it is only an approximation to the uniform electron gas, i. e., it has a non-empirical form.

Part V

Future Work

For the future I propose to continue improving the pyxbench application, to include other properties, such as electron affinities, vibrational energy, spectrums and much more. Beside the NWChem, the electronic software APE is already in pyxbench but we can include much more like Abinit or Octopus. Another factor to take into account is the systems, other types of systems should be included, like solids.

As a database, pyxbench can also include the experimental data so we can use it to build a better functional. With the access of a supercomputer, we can try to produce a exchange-correlation functional with a considerable quantity of terms and use a Monte Carlo method to fit that functional to the databases that would be added.

Appendix A

Functionals

Definition

A functional F maps functions $\psi(x)$ to numbers $F[\psi]$. An example of a functional is doing the integration,

$$F[\psi] = \int dx \psi^2(x). \tag{A.1}$$

We can define the functional derivative $\frac{\delta F}{\delta \psi(x)}$ by

$$\int dx f(x) \frac{\delta F[\psi]}{\delta \psi(x)} = \lim_{\epsilon \to 0} \frac{F[\psi + \epsilon f] - F[\psi]}{\epsilon}, \tag{A.2}$$

where f is an arbitrary function of function space called test function and ϵ represents a real (or any other type of number) variable.

We will use this definition to calculate the functional derivative of example (A.1).

$$\lim_{\epsilon \to 0} \frac{F[\psi + \epsilon f] - F[\psi]}{\epsilon} = \lim_{\epsilon \to 0} \frac{1}{\epsilon} \int dx \left\{ (\psi(x) + \epsilon f(x))^2 - \psi^2(x) \right\} = \int dx f(x) 2\psi(x) \tag{A.3}$$

consequently,

$$\frac{\delta F[\psi]}{\delta \psi(x)} = 2\psi(x) \tag{A.4}$$

The functional properties reviewed here are helpful through all the work and mainly in the density functional theory, since the use of functional's in the potential energy of the Kohn-Sham equation.

Appendix B

List of Functionals

Table B.1 List of functionals used through this work.

LDA Functionals

	LDA Exchange	
LDA_X	Slater exchange	[26, 27]

	LDA Correlation	
LDA_C_WIGNER	Wigner	[28]
LDA_C_HL	Hedin & Lundqvist	[29]
LDA_C_GL	Gunnarson & Lundqvist	[30]
LDA_C_XALPHA	Slater's Xalpha	[31]
LDA_C_VWN	Vosko, Wilk & Nusair (VWN5)	[32]
LDA_C_PZ	Perdew & Zunger	[33]
LDA_C_PZ_MOD	Perdew & Zunger (Modified)	[33]
LDA_C_OB_PZ	Ortiz & Ballone (PZ parametrization)	[33–35]
LDA_C_PW	Perdew & Wang	[36]
LDA_C_PW_MOD	Perdew & Wang (modified)	[36]
LDA_C_OB_PW	Ortiz & Ballone (PW parametrization)	[34, 35, 37]
LDA_C_VBH	von Barth & Hedin	[38]
LDA_C_GOMBAS	Gombas	[39]

LDA_C_PW_RPA	Perdew & Wang (fit to the RPA energy)	[37]
LDA_C_VWN_1	Vosko, Wilk & Nusair (VWN1)	[40]
LDA_C_VWN_2	Vosko, Wilk & Nusair (VWN2)	[40]
LDA_C_VWN_3	Vosko, Wilk & Nusair (VWN3)	[40]
LDA_C_VWN_4	Vosko, Wilk & Nusair (VWN4)	[40]
LDA_C_RPA	Random Phase Approximation (RPA)	[41]
LDA_C_RC04	Ragot-Cortona	[42]
LDA_C_ML2	Modified LSD (version 2) of Proynov and Salahub	[43]
LDA_C_ML1	Modified LSD (version 1) of Proynov and Salahub	[43]
LDA_C_VWN_RPA	Vosko, Wilk & Nusair (VWN5_RPA)	[44]

	LDA Exchange-Correlation	
LDA_XC_TETER93	Teter 93	[45]

GGA Functionals

	GGA Exchange	
GGA_X_SSB_SW	Swarta, Sola and Bickelhaupt correction to PBE	[46]
GGA_X_SSB	Swarta, Sola and Bickelhaupt	[47]
GGA_X_SSB_D	Swarta, Sola and Bickelhaupt dispersion	[47]
GGA_X_BPCCAC	BPCCAC (GRAC for the energy)	[48]
GGA_X_PBE	Perdew, Burke & Ernzerhof	[23, 49]
GGA_X_PBE_R	Revised PBE from Zhang & Yang	[50]
GGA_X_B86	Becke 86	[51, 52]
GGA_X_HERMAN	Herman Xalphabeta GGA	[53, 54]
GGA_X_B86_MGC	Becke 86 with modified gradient correction	[51, 55]
GGA_X_B88	Becke 88	[56]
GGA_X_PW86	Perdew & Wang 86	[57]

GGA_X_PW91	Perdew & Wang 91	[37]
GGA_X_OPTX	Handy & Cohen OPTX 01	[58]
GGA_X_DK87_R1	dePristo & Kress 87 version R1	[59]
GGA_X_DK87_R2	dePristo & Kress 87 version R2	[59]
GGA_X_LG93	Lacks & Gordon 93	[60]
GGA_X_FT97_A	Filatov & Thiel 97 (version A)	[61]
GGA_X_FT97_B	Filatov & Thiel 97 (version B)	[61]
GGA_X_PBE_SOL	Perdew, Burke & Ernzerhof SOL	[62]
GGA_X_RPBE	Hammer, Hansen, and Nørskov	[63]
GGA_X_WC	Wu & Cohen	[64]
GGA_X_MPW91	mPW91 of Adamo & Barone	[65]
GGA_X_AM05	Armiento & Mattsson 05	[66, 67]
GGA_X_PBEA	Madsen 07	[68]
GGA_X_MPBE	Adamo & Barone modification to PBE	[69]
GGA_X_XPBE	Extended PBE by Xu & Goddard III	[70]
GGA_X_BAYESIAN	Bayesian best fit for the enhancement factor	[71]
GGA_X_PBE_JSJR	Reparametrized PBE by Pedroza, Silva & Capelle	[72]
GGA_X_OPTB88_VDW	opt-Becke 88 for vdW	[73]
GGA_X_PBEK1_VDW	Reparametrized PBE for vdW	[73]
GGA_X_OPTPBE_VDW	Reparametrized PBE for vdW	[73]
GGA_X_RGE2	Regularized PBE	[74]
GGA_X_RPW86	Refitted Perdew & Wang 86	[75]
GGA_X_KT1	Keal and Tozer, version 1	[76]
GGA_X_MB88	Modified Becke 88 for proton transfer	[77]
GGA_X_SOGGA	Second-order generalized gradient approximation	[78]
GGA_X_C09X	C09x to be used with the VdW of Rutgers-Chalmers	[79]
GGA_X_LB	van Leeuwen & Baerends	[80]
GGA_X_LBM	van Leeuwen & Baerends modified	[81]
GGA_X_OL2	Exchange form based on Ou-Yang and Levy v.2	[82, 83]

GGA_X_APBE	mu fixed from the semiclassical neutral atom	[84]
GGA_X_HTBS	Haas, Tran, Blaha, and Schwarz	[85]
GGA_X_AIRY	Constantin et al based on the Airy gas	[86]
GGA_X_WPBEH	short-range part of the PBE (default w=0 gives PBEh)	[87]
GGA_X_HJS_PBE	HJS screened exchange PBE version	[88]
GGA_X_HJS_PBE_SOL	HJS screened exchange PBE_SOL version	[88]
GGA_X_HJS_B97X	HJS screened exchange B97x version	[88]
	GGA Correlation	
GGA_C_SPBE	PBE correlation to be used with the SSB exchange	[47]
GGA_C_REVTCA	Tognetti, Cortona, Adamo (revised)	[89]
GGA_C_TCA	Tognetti, Cortona, Adamo	[90]
GGA_C_PBE	Perdew, Burke & Ernzerhof	[23, 49]
GGA_C_LYP	Lee, Yang & Parr	[91, 92]
GGA_C_P86	Perdew 86	[93]
GGA_C_PBE_SOL	Perdew, Burke & Ernzerhof SOL	[62]
GGA_C_PW91	Perdew & Wang 91	[37, 94]
GGA_C_AM05	Armiento & Mattsson 05	[66]
GGA_C_XPBE	Extended PBE by Xu & Goddard III	[95]
GGA_C_PBE_JRGX	Reparametrized PBE by Pedroza, Silva & Capelle	[72]
GGA_C_RGE2	Regularized PBE	[74]
GGA_C_WL	Wilson & Levy	[96]
GGA_C_WI	Wilson & Ivanov	[97]
GGA_C_WI0	Wilson & Ivanov initial version	[97]
GGA_C_SOGGA11_X	To be used with hyb_gga_x_SOGGA11-X	[98]

GGA_C_APBE	mu fixed from the semiclassical neutral atom	[84]
GGA_C_OP_B88	one-parameter progressive functional (B88 version)	[99]
GGA_C_OPTC	Optimized correlation functional of Cohen and Handy	[100]
GGA_C_OP_G96	one-parameter progressive functional (G96 version)	[101]
GGA_C_OP_XALPHA	one-parameter progressive functional (Xalpha version)	[101]
GGA_C_SOGGA11	Second-order generalized gradient approximation 2011	[102]
GGA_C_OP_PBE	one-parameter progressive functional (PBE version)	[101]

	GGA Exchange-Correlation	
GGA_XC_HCTH_407P	HCTH/407+	[103]
GGA_XC_HCTH_P76	HCTH p=1/4	[104]
GGA_XC_HCTH_P14	HCTH p=1/4	[104]
GGA_XC_B97_GGA1	Becke 97 GGA-1	[105]
GGA_XC_HCTH_A	HCTH-A	[106]
GGA_XC_KT2	Keal and Tozer, version 2	[76]
GGA_XC_EDF1	EDF1	[107]
GGA_XC_XLYP	XLYP	[95]
GGA_XC_B97	Becke 97	[52]
GGA_XC_B97_1	Becke 97-1	[106]
GGA_XC_B97_2	Becke 97-2	[108]
GGA_XC_B97_D	Becke 97-D	[109]
GGA_XC_B97_K	Boese-Martin for Kinetics	[110]
GGA_XC_B97_3	Becke 97-3	[111]
GGA_XC_PBE1W	PBE1W	[112]
GGA_XC_MPWLYP1W	mPWLYP1w	[112]
GGA_XC_PBELYP1W	PBELYP1W	[112]
GGA_XC_MOHLYP	Functional for organometallic chemistry	[113]
GGA_XC_MOHLYP2	Functional for barrier heights	[114]
GGA_XC_TH_FL	Tozer and Handy v. FL	[115]

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