

Influence of the Exchange and Correlation Functional in the Ionization Potentials of Atoms



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Aos meus Pais.

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Abstract

In this work we study the influence of the exchange and correlation functional on the ionization potentials of atoms, in the framework of Density Functional Theory. Here, we will present the results for 42 atoms of the periodic table, and for a total of almost 1000 different combinations of exchange and correlation functionals. A comparison between different levels of theory and a list of the combinations with smallest errors is given. We also present some results for 2 special exchange functionals with the correct asymptotic limit.

Resumo

Neste trabalho faz-se um estudo sobre a influência do funcional de troca e correlação nos potenciais de ionização atômicos, em Teoria do Funcional da Densidade. Apresentam-se os resultados para 42 átomos da tabela periódica, e para cerca de 1000 combinações diferentes de funcionais de troca e correlação. Faz-se também uma comparação entre os vários níveis de teoria, e apresenta-se uma lista com as combinações que originam os menores erros. Também se apresenta alguns resultados para 2 funcionais de troca que possuem o limite assintótico correcto.

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Chapter 1

Introduction

Density Functional Theory (DFT) has become one of the most widely used methods in the condensed matter simulations world. In its Kohn-Sham formulation, the very complicated many-body problem is reformulated as a set of effective single-particle Schrödinger-like equations, where the effective potential is a functional of the electronic density. The non-classical effects resulting from the interacting nature of the electrons are described by an exchange-correlation potential which has to be approximated. Over the years, the quest for better and better approximations originated dozens of different formulas for this functional. If we combine all the possible suggestions for this functional that exist on the literature we end up with an huge set of possibilities to choose from for our calculations. Since there is no "right" or "wrong" answer we usually make an educated guess based on previous calculations and benchmarks.

In this work we will study how the ionization potential of elements of the periodic table change with the exchange-correlation functional used. Atoms are simple systems, which some properties, like their ionization potentials, can easily be evaluated. The experimental values for the ionization potentials are known [1] which give us a direct way to compare results. The ultimate goal of this work is to use all the possible exchange-correlation combinations of the functionals in the LIBXC library [2], for all the atoms of the Periodic Table. Also, we will use three formulations of the Kohn-Sham equations: Schrödinger, Scalar Relativistic and Dirac, in their spin unpolarized and polarized forms. However, due to time

constraints¹, in this thesis we will use only a fraction of the periodic table, and not for all the combinations of functionals. We choose not to use the ones that presented numerical problems. Also, due to its complexity, calculations with the polarized Dirac equation are a lot more demanding from the computational point of view than the others cases, and no result with this scheme will be presented at this point. Even with these constraints, the number of calculations done in this work is far from small. We have almost 1000 combinations of exchange and correlation functionals, for 42 elements of the periodic table, and for 5 degrees of theory.

There are some benchmarks in the literature where the Ionization Potentials were used to evaluate the performance of exchange and correlation functionals [3] [4] [5]. However, these are usually done for a small set of atoms / molecules or for a small set of functionals. Also, usually only one of the formulations of the Kohn-Sham equations is used. Thus, such a comprehensive study as we propose to do was never performed before. With this work, our goal is to give further insights on the choice of the exchange-correlation functional.

This thesis is organized in the following way: in the second chapter we will provide a review of Density Functional Theory. The third chapter is an overview on how the DFT equations are solved in the code used. In the fourth we will present and discuss our results and finally, in the fifth chapter we will present our conclusions and point to some future work.

¹The total number of combinations of atoms, functionals and DFT formalisms is over half a million.

Chapter 2

Density Functional Theory

Lets start by considering a system of N non-relativistic electrons described by the time-independent Schrödinger equation, in the Born-Oppenheimer approximation [6]:

$$\hat{H}\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = E\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N). \quad (2.1)$$

The hamiltonian operator can be written as,

$$\hat{H} = \hat{T} + \hat{V}_{\text{ext}} + \hat{V}_{\text{ee}}, \quad (2.2)$$

where the kinetic energy, the external potential, and the electron-electron repulsion operators are respectively:

$$\hat{T} = - \sum_{i=1}^N \frac{1}{2} \nabla_i^2, \quad \hat{V}_{\text{ext}} = \sum_{i=1}^N v_{\text{ext}}(\mathbf{r}_i), \quad \text{and} \quad \hat{V}_{\text{ee}} = \sum_{i < j}^N \frac{1}{r_{ij}}, \quad (2.3)$$

with

$$v_{\text{ext}}(\mathbf{r}_i) = - \sum_{\alpha} \frac{Z_{\alpha}}{r_{i\alpha}} \quad \text{and} \quad r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|. \quad (2.4)$$

Here, α stands for the atom nuclei and \mathbf{x}_i comprehends the spatial and spin coordinates of electron i (\mathbf{r}_i, σ_i). Atomic units are use throughout. To obtain the total energy of the system we have also to add the nuclei-nuclei repulsive energy

contribution,

$$V_{\text{nn}} = \sum_{\alpha < \beta} \frac{Z_{\alpha} Z_{\beta}}{r_{\alpha\beta}}. \quad (2.5)$$

So, in principle, solving (2.1) would allow us to evaluate any physical quantity we want. There are couple of setbacks however. In the first place, Ψ is a function of $3N$ variables. Just storing the wave-function in memory is an impossible task, even for small systems. Also, due to the last term of (2.2) we can not solve the equation independently for each one of the N particles. A simple way of dealing with this is a theory known as Density Functional Theory (DFT).

In DFT we replace the wave-function by a much simpler quantity - the electronic density of the system $n(\mathbf{r})$, which is a function of just 3 variables, as the basic variable. We also recast the problem of interacting particles into one of non-interacting particles. The first approach to this idea was done in 1927 by Llewellyn Thomas and Enrico Fermi which, independently, idealized a model where the full many-body Schrödinger equation was replaced by one equation on the electronic density of the system. However it was only on the sixties that DFT was formulated as the accurate and widely used method we know today.

2.1 Hohenberg-Kohn Theorems

The crucial step to establish the idea of the electronic density as the fundamental variable was given by Hohenberg and Kohn in their landmark paper in 1964 [7]. Consider a N -electron system with a non-degenerate ground-state ruled by the hamiltonian (2.2). The first theorem states that the external potential $v_{\text{ext}}(\mathbf{r})$ is determined, within a additive constant, by the electronic ground state density $n_0(\mathbf{r})$ of the system. That is, there is a one-to-one correspondence between the electronic density of the system and the external potential. Let's prove this theorem in two steps via *reductio ad absurdum*. First, consider two external potentials V_{ext} and V'_{ext} , differing by more than a constant, leading to the same ground-state wave-function. If we subtract the two resulting Schrödinger equations we get $(V_{\text{ext}} - V'_{\text{ext}})|\Psi\rangle = (E_0 - E'_0)|\Psi\rangle$, which clearly violates our assumption. Second, we have to prove that two different ground-sate wave-functions can not produce

the same ground-state electronic density. Following the same philosophy we used for the first case, let's consider two ground-state wave-functions Ψ_0 and Ψ'_0 . As we already saw, these wave-functions must come from different hamiltonians, \hat{H} and \hat{H}' . If E_0 is the ground-state energy of \hat{H} ,

$$E_0 = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle \quad (2.6)$$

then, by the Rayleigh-Ritz [8] variational principle, we have:

$$\begin{aligned} E_0 < \langle \Psi'_0 | \hat{H} | \Psi'_0 \rangle &= \langle \Psi'_0 | \hat{H}' | \Psi'_0 \rangle + \langle \Psi'_0 | \hat{H} - \hat{H}' | \Psi'_0 \rangle \\ &= E'_0 + \int d\mathbf{r} n_0(\mathbf{r}) [v_{\text{ext}}(\mathbf{r}) - v'_{\text{ext}}(\mathbf{r})]. \end{aligned} \quad (2.7)$$

Repeating the same process for Ψ' and \hat{H}'

$$\begin{aligned} E'_0 < \langle \Psi_0 | \hat{H}' | \Psi_0 \rangle &= \langle \Psi_0 | \hat{H} | \Psi_0 \rangle + \langle \Psi_0 | \hat{H}' - \hat{H} | \Psi_0 \rangle \\ &= E_0 - \int d\mathbf{r} n_0(\mathbf{r}) [v_{\text{ext}}(\mathbf{r}) - v'_{\text{ext}}(\mathbf{r})]. \end{aligned} \quad (2.8)$$

Adding (2.7) with (2.8) we get $E_0 + E'_0 < E'_0 + E_0$, which is a contradiction. Thus, we have proved that a one-to-one correspondence between ground-state densities and potentials exist, which can be expressed as $v[n](\mathbf{r})$. In fact, we can write any observable of the system as a unique functional of the density,

$$\langle \Psi | \hat{O} | \Psi \rangle = O[n]. \quad (2.9)$$

For instance, we can write the total energy of the system under an external potential v_{ext} as a functional of the density:

$$\begin{aligned} E_{v_{\text{ext}}}[n] &= \langle \Psi | \hat{T} + \hat{V}_{\text{ext}} + \hat{V}_{\text{ee}} | \Psi \rangle + E_{\text{nn}} \\ &= F_{\text{HK}}[n] + \int d\mathbf{r} n(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) + E_{\text{nn}}, \end{aligned} \quad (2.10)$$

where

$$F_{\text{HK}}[n] = T[n] + V_{\text{ee}}[n] \quad (2.11)$$

is an universal functional, independent of the external potential, which is the same

for any N -electron system. The second theorem states that, for a non-negative trial density, \tilde{n} , and $\int \tilde{n} d\mathbf{r} = N$:

$$E_0 \leq E_{v_{\text{ext}}}[\tilde{n}]. \quad (2.12)$$

The exact ground-state density is then the one that minimizes the energy functional (2.10):

$$E_0 = \min_{\{n\}} E_{v_{\text{ext}}}[n]. \quad (2.13)$$

which can also be written as:

$$\frac{\delta}{\delta n(\mathbf{r})} \left[E_{v_{\text{ext}}}[n] - \mu \int n(\mathbf{r}) d\mathbf{r} \right] = \frac{\delta F_{\text{HK}}[n]}{\delta n(\mathbf{r})} + v_{\text{ext}}(\mathbf{r}) - \mu = 0, \quad (2.14)$$

where μ is a Lagrange multiplier which ensures the normalization to the total number of electrons. So, solving the last equation would give us the exact ground-state of any electronic system, if we knew the explicit form of F_{HK} , which unfortunately we do not.

An important remark here is that these theorems are only valid for *v-representable* densities. A function n is called *v-representable* if it belongs to some external potential. In other words, not all densities belong to some physical external potential. However, on a finite or infinite lattice, all ground-state densities are *v-representable* [9]. We have also considered only non-degenerated ground-states. This condition can be relaxed using the Levy constrained search formalism [8].

2.2 Kohn-Sham Equations

Let us consider a non-interacting system of electrons ($\hat{V}_{ee} = 0$ at equation (2.2)). In this case, the many-body ground-state wave-function can be written as a Slater

determinant of the single particle wavefunctions ψ_i ,

$$\Psi_s(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\mathbf{r}_1) & \psi_2(\mathbf{r}_1) & \cdots & \psi_N(\mathbf{r}_1) \\ \psi_1(\mathbf{r}_2) & \psi_2(\mathbf{r}_2) & \cdots & \psi_N(\mathbf{r}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(\mathbf{r}_N) & \psi_2(\mathbf{r}_N) & \cdots & \psi_N(\mathbf{r}_N) \end{vmatrix}, \quad (2.15)$$

satisfying:

$$\left[-\frac{1}{2}\nabla^2 + v_s(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}). \quad (2.16)$$

The ground-state density is obtained from the N lowest occupied orbitals,

$$n(\mathbf{r}) = \sum_{i=1}^N |\psi_i(\mathbf{r})|^2. \quad (2.17)$$

Proceeding in the same way we did in the previous section, the variational principle for this non-interacting system yields:

$$\frac{\delta}{\delta n(\mathbf{r})} \left[E_s[n] - \mu_s \int n(\mathbf{r}) d\mathbf{r} \right] = \frac{\delta T_s[n]}{\delta n(\mathbf{r})} + v_s(\mathbf{r}) - \mu_s = 0. \quad (2.18)$$

This is formally equivalent to equation (2.16). Now, let us consider again the interacting system. We can rewrite the functional (2.11) as

$$F_{\text{HK}}[n] = T_s[n] + E_{\text{H}}[n] + E_{\text{xc}}[n], \quad (2.19)$$

where $E_{\text{H}}[n]$ is the classic Coulomb energy, also known as the Hartree energy

$$E_{\text{H}}[n] = \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \quad (2.20)$$

and the non-classical part, the exchange-correlation energy

$$E_{\text{xc}}[n] = T[n] + V_{\text{ee}}[n] - T_s[n] - E_{\text{H}}[n]. \quad (2.21)$$

With these modifications the Euler equation (2.14) reads:

$$\frac{\delta T_s[n]}{\delta n(\mathbf{r})} + v_{\text{ext}}(\mathbf{r}) + \frac{1}{2} \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})} - \mu = 0. \quad (2.22)$$

We can rewrite this Euler equation as:

$$\frac{\delta T_s[n]}{\delta n(\mathbf{r})} + v_{\text{KS}}[n](\mathbf{r}) - \mu = 0, \quad (2.23)$$

where

$$v_{\text{KS}}[n](\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + v_{\text{H}}[n](\mathbf{r}) + v_{\text{xc}}[n](\mathbf{r}), \quad (2.24)$$

with

$$v_{\text{H}}[n](\mathbf{r}) = \frac{1}{2} \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad \text{and} \quad v_{\text{xc}}[n](\mathbf{r}) = \frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})}. \quad (2.25)$$

If we now compare this last equation with (2.14), we see that the two are identical and therefore, solving (2.23) has to be the same as solving the single-particle Schrödinger equation:

$$\left[-\frac{1}{2} \nabla^2 + v_{\text{KS}}[n](\mathbf{r}) \right] \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}), \quad (2.26)$$

where the ground-state density is given by:

$$n(\mathbf{r}) = \sum_{i=1}^N |\psi_i(\mathbf{r})|^2. \quad (2.27)$$

Equations (2.23) and (2.26) are known as the Kohn-Sham equations. They allow us to treat a system of interacting electrons as a non-interacting one, that yields the same ground-state density. This would be *exact* if we knew the exact form of E_{xc} , which we do not. Nevertheless, the major part of the electron-electron interaction (the Hartree energy) is treated exactly and so does the non-interacting kinetic energy. The remaining exchange-correlation energy is by far the one that has the smallest contribution to the total energy. It is however, the main responsible for the binding energy of matter, being a good approximation

to this term the key to obtain accurate results.

2.2.1 Spin Density Functional Theory

Up to this point we have only discussed the spin-independent formalism. Now we will look at the Kohn-Sham equations in their spin-dependent form [10]. We will consider only its collinear form in which $\mathbf{m} = (0, 0, m_z)$. The basic variables are now the ground-state density,

$$n(\mathbf{r}) = n^\uparrow(\mathbf{r}) + n^\downarrow(\mathbf{r}), \quad (2.28)$$

and the magnetization density,

$$m_z(\mathbf{r}) = n^\uparrow(\mathbf{r}) - n^\downarrow(\mathbf{r}), \quad (2.29)$$

where

$$n^\sigma(\mathbf{r}) = \sum_{i=1}^{N_\sigma} |\psi_i^\sigma(\mathbf{r})|^2. \quad (2.30)$$

In this case (assuming the absence of magnetic external fields), we end up with two sets of Kohn-Sham equations:

$$\left[-\frac{1}{2}\nabla^2 + v_{\text{H}}[n](\mathbf{r}) + v_{\text{ext}}^\sigma[n](\mathbf{r}) + v_{\text{xc}}^\sigma[n, m_z](\mathbf{r}) \right] \psi_i^\sigma(\mathbf{r}) = \epsilon_i \psi_i^\sigma(\mathbf{r}). \quad (2.31)$$

This formalism is more general than the spin-independent version through the inclusion of spin-dependent external potentials. The exchange-correlation potential is most commonly written as a functional of the spin up and down densities,

$$v_{\text{xc}}^\sigma[n^\uparrow, n^\downarrow](\mathbf{r}) = \frac{\delta E_{\text{xc}}[n^\uparrow, n^\downarrow]}{\delta n^\sigma(\mathbf{r})}. \quad (2.32)$$

2.2.2 Relativistic Spin Density Functional Theory

When relativistic effects become important, a relativistic extension of DFT has to be used. Here we will consider only systems not subject to external magnetic fields and, as before, $\mathbf{m} = (0, 0, m_z)$ [11]. The Dirac-Kohn-Sham equations are then:

$$[ic\boldsymbol{\alpha} \cdot \boldsymbol{\nabla} + (\beta - 1)c^2 + v_{\text{KS}}[n, m_z](\mathbf{r}) + \beta\Sigma_z B_{\text{xc}}[n, m_z](\mathbf{r})] \psi_k = \epsilon_k \psi_k, \quad (2.33)$$

where α and β are the usual Dirac matrices, v_{KS} is the usual Kohn-Sham effective potential like in (2.24), and

$$B_{\text{xc}}[n, m_z](\mathbf{r}) = \frac{\delta E_{\text{xc}}[n, m_z]}{\delta m_z(\mathbf{r})}, \quad (2.34)$$

which can also be written as functional of the spin up and down densities:

$$B_{\text{xc}}[n^\uparrow, n^\downarrow](\mathbf{r}) = \frac{1}{2} \left\{ \frac{\delta E_{\text{xc}}[n^\uparrow, n^\downarrow]}{\delta n^\uparrow(\mathbf{r})} - \frac{\delta E_{\text{xc}}[n^\uparrow, n^\downarrow]}{\delta n^\downarrow(\mathbf{r})} \right\}. \quad (2.35)$$

The ground-state density and the magnetization are constructed from the 4-component spinors by¹:

$$n(\mathbf{r}) = \sum_k \psi_k^\dagger(\mathbf{r}) \psi_k(\mathbf{r}), \quad (2.36)$$

$$m_z(\mathbf{r}) = -\mu_B \sum_k \psi_k^\dagger(\mathbf{r}) \beta \Sigma_z \psi_k(\mathbf{r}). \quad (2.37)$$

2.3 Exchange and Correlation Functionals

We already saw that we do not know the exact form of the exchange-correlation potential. We will now look at some of the most used families of approximations for this functional.

¹Vacuum states are excluded from the summation.

2.3.1 Local density approximation

The first, and also the simplest one, is the local spin density approximation (LSDA). It takes the following form:

$$E_{\text{xc}}^{\text{LDA}}[n^\uparrow, n^\downarrow] = \int d\mathbf{r} n(\mathbf{r}) \varepsilon_{\text{xc}}^{\text{HEG}}(n^\uparrow(\mathbf{r}), n^\downarrow(\mathbf{r})). \quad (2.38)$$

where $\varepsilon_{\text{xc}}^{\text{HEG}}(n^\uparrow, n^\downarrow)$ is the exchange-correlation energy per particle for an electron gas of uniform spin densities n^\uparrow, n^\downarrow [12]. The exchange energy of an homogeneous electron gas is known analytically. For the correlation part, the analytic expression is only known in the extreme limits of high and low densities. For the values in between, we only know the values for a few densities by Monte-Carlo simulations [13]. Most of the different proposed LSDA correlation functionals result from different parameterizations of these results.

The LSDA yields very good results for systems whose density varies slowly over space. Surprisingly, it also works well for systems which do not. This happens because LSDA has many physically correct features [10]. It has also some bad features. For instance, it is not exact in the one-electron limit. It does not take into account the fact that one electron does not interact with itself. As a consequence of this, the exchange-correlation potential has the wrong asymptotic limit - it goes to zero exponentially instead of going as $-1/r$ [14].

2.3.2 Generalized gradient approximations

The natural improvement over LSDA would be the gradients expansion approximation (GEA) [7]. However this does not improve the results consistently, since it broke some of the good features of LSDA. The goal is then a more general form for an exchange-correlation functional depending on the gradients, that conserve the good features of LSDA, and add new ones. This is known as the generalized gradient approximation (GGA):

$$E_{\text{xc}}^{\text{GGA}}[n^\uparrow, n^\downarrow] = \int d\mathbf{r} n \varepsilon_{\text{xc}}^{\text{GGA}}(n^\uparrow, n^\downarrow, \nabla n^\uparrow, \nabla n^\downarrow). \quad (2.39)$$

The function $\varepsilon_{\text{xc}}^{\text{GGA}}$ is built in such a way that the functional obeys some known physical constraints and there are dozens of proposed forms for this function [2].

The problems enumerated for the LSDA are partially eliminated with the GGA.

2.3.3 Meta-generalized Gradient Approximations

Another step further is the meta-generalized gradients approximation (MGGA). In this approximation:

$$E_{\text{xc}}^{\text{MGGA}}[n^\uparrow, n^\downarrow] = \int d\mathbf{r} n \varepsilon_{\text{xc}}^{\text{MGGA}}(n^\uparrow, n^\downarrow, \nabla n^\uparrow, \nabla n^\downarrow, \nabla^2 n^\uparrow, \nabla^2 n^\downarrow, \tau^\uparrow, \tau^\downarrow), \quad (2.40)$$

where $\tau^\sigma = \frac{1}{2} \sum_i |\nabla \psi_{i\sigma}(\mathbf{r})|^2$ is the Kohn-Sham orbital kinetic energy density for electrons of spin σ . Note that the functional dependence on $\nabla^2 n^\sigma$ is not present in some MGGAs.

2.4 Ionization Potentials

The ionization potential can be evaluated as the difference between the total energies:

$$IP = E(N^+) - E(N), \quad (2.41)$$

where $E(N)$ is the total energy of the atom and $E(N^+)$ the total energy of the correspondent cation.

In the Kohn-Sham theory there is no physical meaning for the orbitals $\psi_i(\mathbf{r})$. Their only purpose is to construct the ground-state density. Accordingly, the Kohn-Sham eigenvalues do not have any physical meaning either. There is however an exception – the eigenvalue of the highest occupied orbital (HOMO) – which is equal to minus the ionization potential (IP) [15]:

$$IP = -\epsilon_{\text{HOMO}}. \quad (2.42)$$

However, due to the limitations of the LDA presented above, we know in advance that the ionization potentials evaluated by this method will be approximately 30 – 50% off from the experimental value [14]. Even the GGA functionals do not

correct this problem completely.

Chapter 3

Procedure and numerical details

All the calculations for this work were done using the program APE (Atomic PseudoPotentials Engine) [16]. This program uses the LIBXC library [2] to evaluate the exchange-correlation potentials. In this work, we are going to use three formulations of Kohn-Sham theory: non-relativistic, scalar-relativistic and relativistic equations, both in their spin-unpolarized and polarized forms.

3.1 Kohn-Sham equations for atoms

As we are only dealing with atoms, spherical symmetry is assumed. In this case, the Kohn-Sham potential is spherically symmetric and the Kohn-Sham orbitals can be separated into an angular and a radial part.

3.1.1 Non-relativistic equations

In the case of non-relativistic calculation, the single-particle orbitals can be written as:

$$\psi_i(\mathbf{r}) = R_{nl}(r)Y_{lm}(\theta, \phi), \quad (3.1)$$

where R_{nl} are the radial wave functions and Y_{lm} are the spherical harmonics. The Kohn-Sham equation (2.26) for the radial part results in a one-dimensional

second-order differential equation:

$$\left(-\frac{1}{2} \frac{d^2}{dr^2} - \frac{1}{r} \frac{d}{dr} + \frac{l(l+1)}{2r^2} + v_{\text{KS}} \right) R_{nl} = \epsilon_{nl} R_{nl}, \quad (3.2)$$

and the radial electron density is given by:

$$n(r) = \sum_n \sum_{l=0}^{n-1} \Theta_{nl} \frac{|R_{nl}(r)|^2}{4\pi}. \quad (3.3)$$

where Θ_{nl} are the occupations of each nl sub-shells.

For a spin-dependent calculation, in which the spin-up and spin-down electrons feel a different Kohn-Sham potential (2.32), two sets of one-particle equations are solved.

3.1.2 Relativistic equations

3.1.2.1 Scalar-relativistic equation

This case is actually a simplification of the Dirac-KS equation. In this scheme proposed by Koelling and Harmon [17], all the relativistic effects are included, but the spin-orbit interaction is neglected. Without this term, and assuming again spherical symmetry, the radial Dirac-KS equation may be written as the following one-dimensional second-order differential equation:

$$\frac{1}{2M(r)} \left(-\frac{d^2}{dr^2} + \frac{1}{M(r)} \frac{dM(r)}{dr} \frac{d}{dr} - \frac{2}{r} \frac{d}{dr} + \frac{l(l+1)}{r^2} \right) R_{nl} + v_{\text{KS}} R_{nl} = \epsilon_{nl} R_{nl}, \quad (3.4)$$

with

$$M(r) = 1 + \frac{(\epsilon_{nl} - v_{\text{KS}}[n](r))}{2c^2}. \quad (3.5)$$

For the spin-dependent case, the same procedure of the non-relativistic calculation applies.

3.1.2.2 Spin-unpolarized Dirac-Kohn-Sham equation

In the unpolarized case, equation (2.33) becomes:

$$[ic\boldsymbol{\alpha} \cdot \boldsymbol{\nabla} + (\beta - 1)c^2 + v_{\text{KS}}[n](\mathbf{r})] \psi_i = \epsilon_i \psi_i, \quad (3.6)$$

since if $n^\uparrow = n^\downarrow$, then $B_{\text{xc}} = 0$. In this case, ψ_i is written as:

$$\psi_i(\mathbf{r}) = \begin{pmatrix} ig_{nlj}(r) \Omega_{jlm}(\theta, \phi) \\ -f_{nlj}(r) \Omega_{jl'm}(\theta, \phi) \end{pmatrix}, \quad (3.7)$$

where Ω_{jlm} are the spherical spinors and g_k and f_k are solutions of ($k \equiv nlj$):

$$c \left(\frac{d}{dr} + \frac{k+1}{r} \right) g_k = (\epsilon_k + 2c^2 - v_{\text{KS}}) f_k, \quad (3.8a)$$

$$c \left(\frac{d}{dr} + \frac{1-k}{r} \right) f_k = -(\epsilon_k - v_{\text{KS}}) g_k. \quad (3.8b)$$

The k quantum number is related with l by:

$$k = \begin{cases} -(l+1) & \text{for } j = l + \frac{1}{2}, \\ l & \text{for } j = l - \frac{1}{2}. \end{cases} \quad (3.9)$$

The radial electronic density is written as:

$$n(r) = \sum_n \sum_{l=0}^{n-1} \sum_{j=l-\frac{1}{2}}^{l+\frac{1}{2}} \Theta_k \frac{|f_k(r)|^2 + |g_k(r)|^2}{4\pi} \quad (3.10)$$

3.1.2.3 Spin-polarized Dirac-Kohn-Sham equation

For this equation, which was implemented in APE during the course of this work, we followed closely the implementation by E. Engel [11]. Here we have to distinguish states with $2|m_j| = 2l+1$ from states with $2|m_j| \neq 2l+1$. For the first case, which has the standard form of closed-subshell spinors with $j = l + 1/2$, the radial functions are solutions of the following set of coupled first-order differential

equations ($k \equiv nlm_j$):

$$c \left(\frac{d}{dr} - \frac{l}{r} \right) g_k = \left(\epsilon_k + 2c^2 - v_{\text{KS}} - \frac{2m_j}{2l+3} B_{\text{xc}} \right) f_k, \quad (3.11a)$$

$$c \left(\frac{d}{dr} + \frac{l+2}{r} \right) f_k = \left(-\epsilon_k + v_{\text{KS}} + \frac{2m_j}{2l+1} B_{\text{xc}} \right) g_k. \quad (3.11b)$$

For the second case, a superposition state of $j = l + 1/2$ with $j = l - 1/2$ spinors is used ($k \equiv nlm_j\sigma$):

$$\psi_k(\mathbf{r}) = \sum_{s=\pm 1} \begin{pmatrix} i g_k^s(r) \Omega_{jlm_j}(\theta, \phi) \\ -f_k^s(r) \Omega_{jlm_j}(\theta, \phi) \end{pmatrix}. \quad (3.12)$$

Here the quantum number σ is introduced to differentiate states with the same magnetic quantum number m_j , but different j . The resulting radial equations are:

$$c \left(\frac{d}{dr} - \frac{l}{r} \right) g_k^+ = \left(\epsilon_k + 2c^2 - v_{\text{KS}} - \frac{2m_j}{2l+3} B_{\text{xc}} \right) f_k^+, \quad (3.13a)$$

$$c \left(\frac{d}{dr} + \frac{l+2}{r} \right) f_k^+ = \left(-\epsilon_k + v_{\text{KS}} + \frac{2m_j}{2l+1} B_{\text{xc}} \right) g_k^+ + C_{lm_j} B_{\text{xc}} g_k^-, \quad (3.13b)$$

$$c \left(\frac{d}{dr} + \frac{l+1}{r} \right) g_k^- = \left(\epsilon_k + 2c^2 - v_{\text{KS}} + \frac{2m_j}{2l-1} B_{\text{xc}} \right) f_k^-, \quad (3.13c)$$

$$c \left(\frac{d}{dr} - \frac{l-1}{r} \right) f_k^- = \left(-\epsilon_k + v_{\text{KS}} - \frac{2m_j}{2l+1} B_{\text{xc}} \right) g_k^- + C_{lm_j} B_{\text{xc}} g_k^+, \quad (3.13d)$$

with

$$C_{lm_j} = -\frac{[(2l+1)^2 - (2m_j)^2]^{1/2}}{2l+1}. \quad (3.14)$$

3.1.3 Solving the Kohn-Sham equations

All the previous Kohn-Sham equations are either first-order differential equations, a set of coupled first order, or, being second-order, can be written as a set of first-orders. Thus, the numerical method to solve then is the same. Also, since v_{KS}

depends on the density which itself depends on ψ_i , the Kohn-Sham equations have to be solved self-consistently, and the eigenvalues and the eigenfunctions are obtained simultaneously. To solve these equations, we proceed in the following way: for each function f_k and g_k , values for the starting and ending points are chosen, subject to some boundary conditions. For a trial eigenvalue ϵ_k and using a suitable algorithm, both equations are integrated from r_0 (a point close to the origin) to r_m , and from r_∞ (a point very far away) to r_m , where r_m is a point in between ($r_0 < r_m < r_\infty$). One of the functions is forced to be continuous at $r = r_m$, and the mismatch in the remaining is used as a correction to the eigenvalue. For the special case of equation (3.13) a few more steps are required. First, instead of two equations f_k and g_k , we have four: f_k^+ , f_k^- , g_k^+ and g_k^- . Besides that, when searching for the boundary conditions, we end up with two independent sets of coupled solutions to integrate [11]. The functions resulting from the sum of these two sets are then matched as in the other cases (three functions are forced to match at $r = r_m$ in this case).

3.2 Generating Ionization Potentials

To obtain the ionizations potentials we proceeded in the following way: first, for each possible exchange-correlation functional, an all-electron calculation was performed for a ground-state configuration [1]. We used an algorithm proposed by Averill and Painter [18] that changes the occupations numbers, in order to obtain the lowest self-consistent total energy solution. The HOMO eigenvalue and the atom total energy are then saved. After that, one electron is removed and a new self-consistent calculation is performed. To finish, the total energy of the ionized and neutral atoms are used to evaluate the ionization potential by (2.41).

Chapter 4

Results and Discussion

In this Chapter we will present and discuss our results. First, we will choose a set of widely used exchange and correlation functionals and compare the results obtained for the different schemes: Schrödinger, Scalar Relativistic and Dirac equations, both in their unpolarized and polarized form, for the ionization potentials obtained through the total energy difference (equation 2.41). For the polarized Dirac case however, it was not possible to have the results ready on time, so no results will be presented for this scheme at the moment. After, we will choose the polarized Schrödinger equation, and look for the differences in the performance of the functionals. We will then finish with the results for the ionization potentials evaluated by the HOMO eigenvalue (equation 2.42). We choose a total of 42 atomic elements for our analysis - the first four lines of the periodic table and the remaining of groups I and II.

4.1 Comparing different levels of theory

For this section, we choose four combinations of exchange-correlation functionals: two LDA and two GGA. For the LDA, we choose the parametrization of S.H. Vosko, Wilk and Nusair (VWN)[19] and the one by Perdew and Wang (PW)[12]. For the GGA, the functional proposed by Perdew, Burke, and Ernzerhof (PBE)[20; 21], and the parametrization of Armiento and Mattsson (AM05)[22; 23]. In figures 4.1.1, 4.1.2 and 4.1.3, we present the relative errors for each of

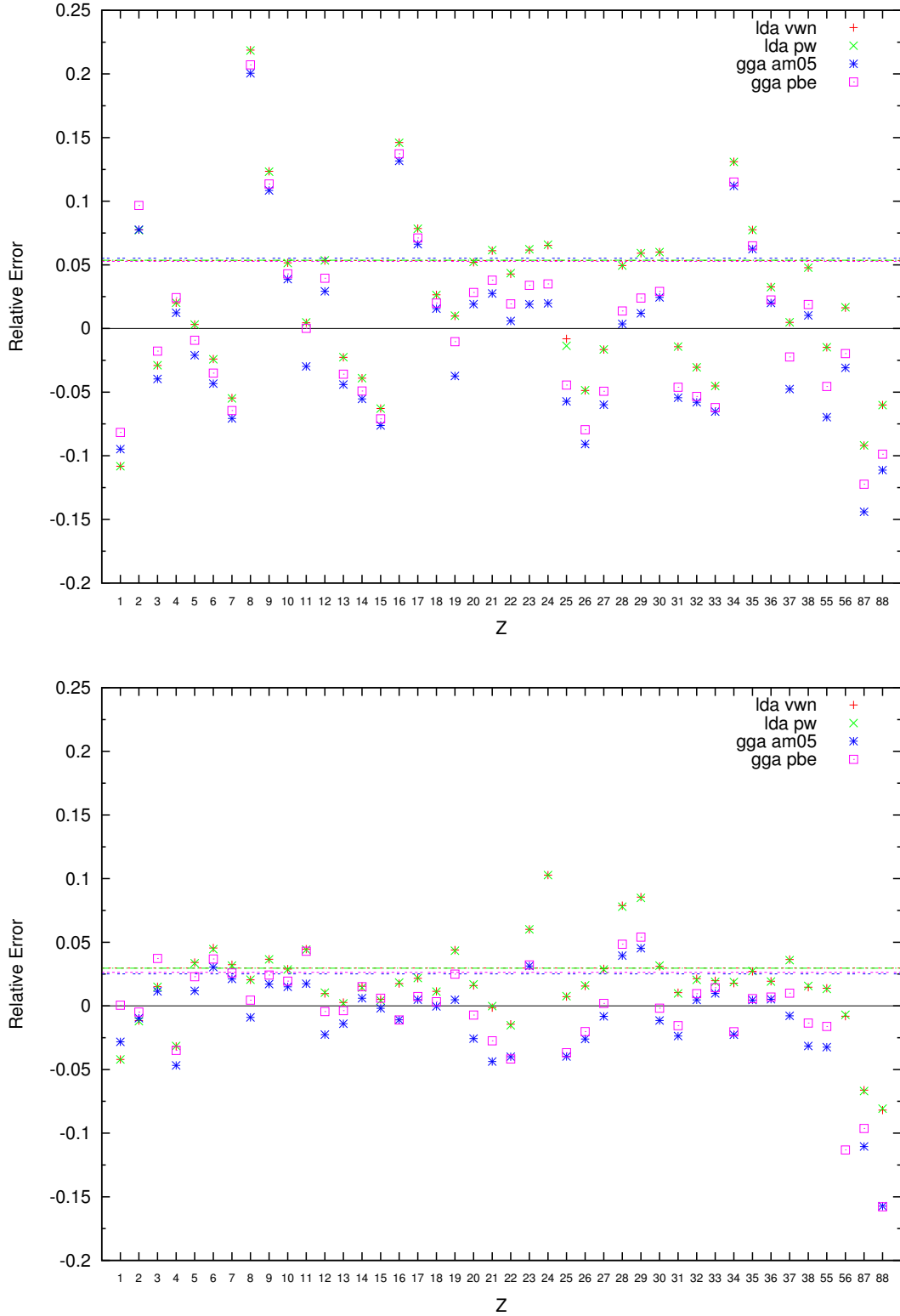


Figure 4.1.1: Relative errors (dots) and mean relative error (lines) for several combinations of functionals, obtained using the unpolarized Schrödinger (top) and polarized Schrödinger (bottom) equations, as a function of the atomic number Z .

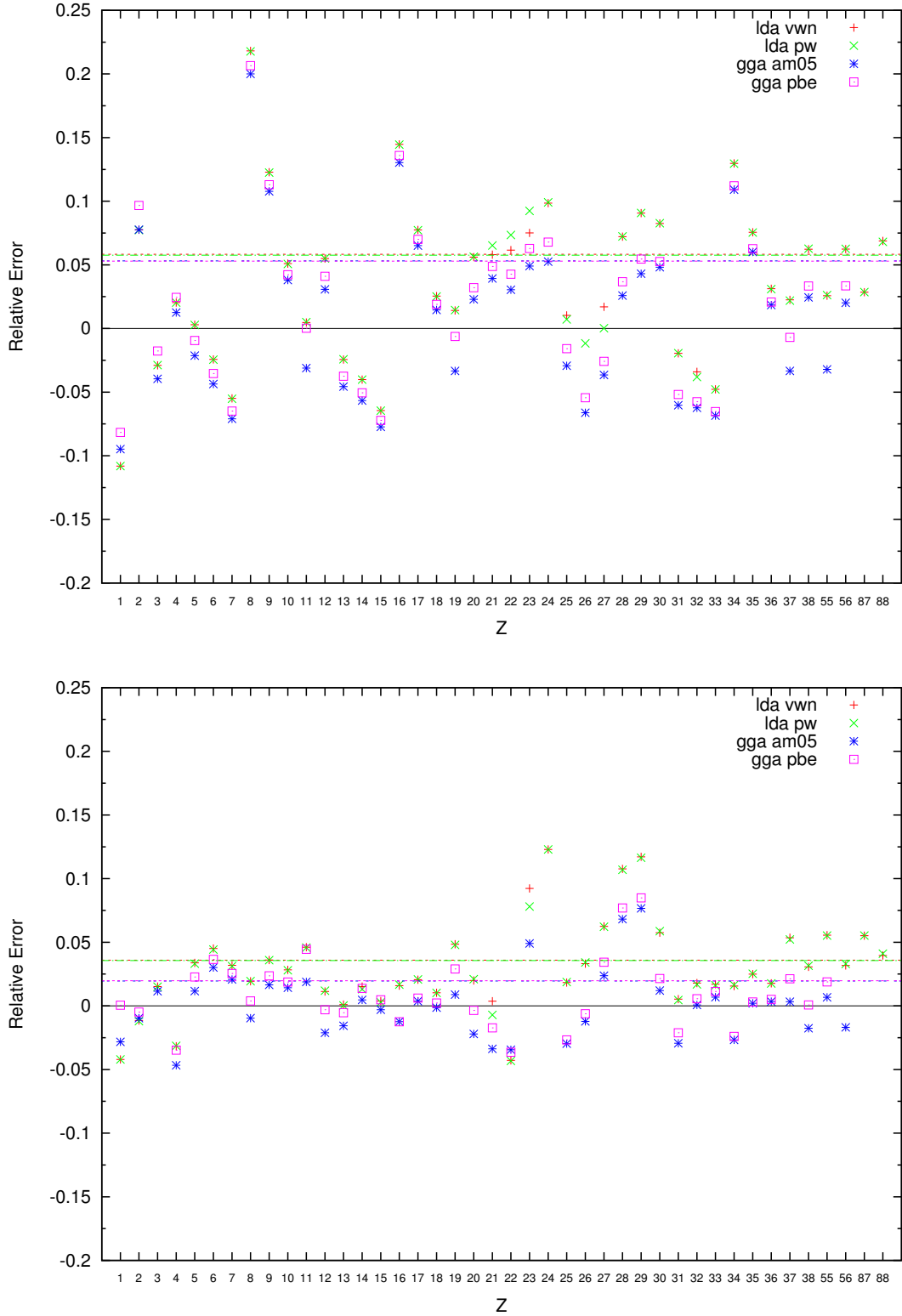


Figure 4.1.2: Relative errors (dots) and mean relative error (lines) for several combinations of functionals, obtained using the unpolarized Scalar Relativistic (top) and polarized Scalar Relativistic (bottom) equations, as a function of the atomic number Z .

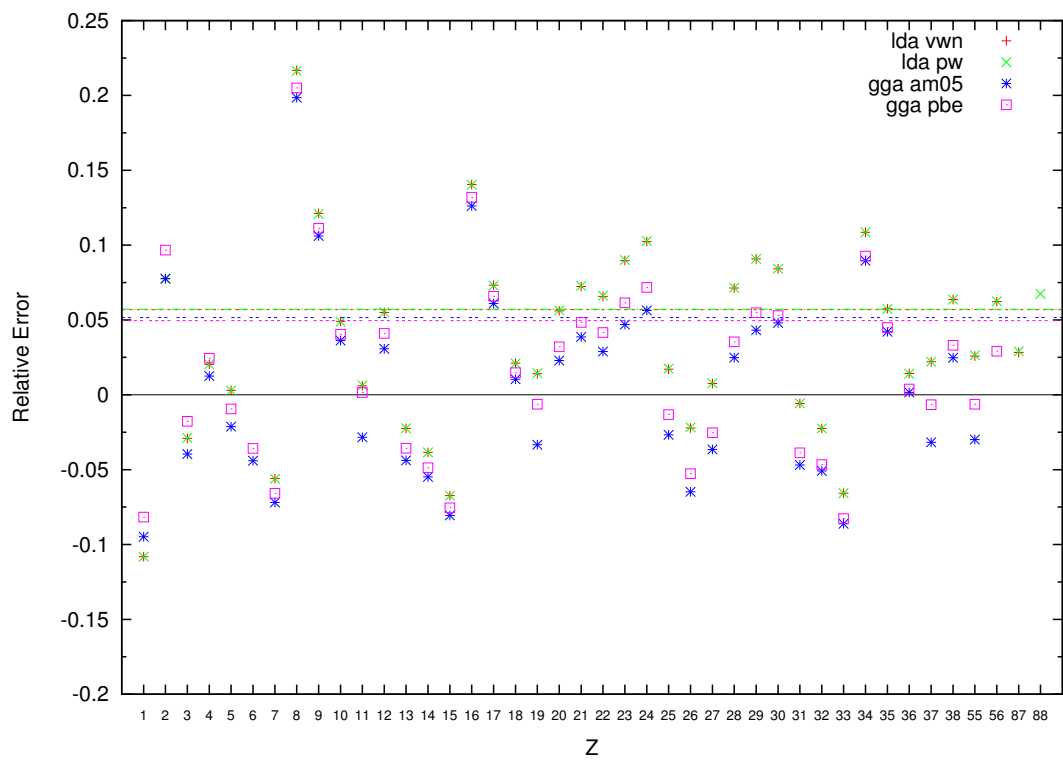


Figure 4.1.3: Relative errors (dots) and mean relative error (lines) for several combinations of functionals, obtained using the unpolarized Dirac equation, as a function of the atomic number Z .

these functionals, for each atom, and the corresponding mean absolute relative error for each functional:

$$\text{Relative Error} = \frac{IP_{calc} - IP_{exp}}{IP_{exp}}$$

For the mean values, the absolute relative errors were used.

In figures 4.1.1 and 4.1.2, we can clearly see that the errors are bigger for the unpolarized cases. Values missing in the figures are cases where we could not get the results (numerical problems). We can see this looking at the mean relative errors, which are smaller for the polarized case, or looking at the dispersion of the relative errors in respect to the mean values. This is a consequence of treating open-shell atoms with a closed-shell formalism. These errors are much smaller in the corresponding polarized calculations. For the same spin scheme, the mean error decreases when increasing the level of the theory (Schrödinger → Scalar Relativistic → Dirac) and spin-polarization effects should be bigger.

For the heaviest elements in our set (Cs, Ba, Fr and Ra), the difference between an unpolarized calculation and a polarized one dilutes. Relativistic effects have the biggest contribution to the error in this region, and thus, using relativistic equations should yield better results. This is something we also see in our results. The close similarity between the scalar relativistic and the Dirac equations results for these four elements is not surprising. Barium and Radium have closed s -shell orbitals, while Cesium and Francium only have one unpaired electron. We only expect to see some significant differences in the results of the two equations for elements with many unpaired electrons in the valence, where both spin-orbit (which is the main difference between the two equations) are bigger.

In tables 4.2.1 and 4.2.1, we present the mean relative errors for the same functionals we used before, and the respective variance. In table 4.2.1 we clearly see the improvement from a spin-independent to a spin-dependent calculation. Not only the mean relative errors are smaller, but also are the variances. For the second table we wanted to see the effects of relativity, the non-relativistic results seem better than the others. However, this is not a very conclusive result, since there are not many heavy atoms in our set. Because of this, we will think the polarized Schrödinger equation is enough for this set of atoms (it is also less

numerically demanding), and we will only use this equation in the next section.

4.2 Comparing different exchange-correlation potentials

In figure 4.2.1 we present the relative errors for all the combinations of exchange and correlation functionals considered in this work (for a complete list of the functionals, see Appendix 1) obtained using the spin-polarized Schrödinger equation. We divided the functionals by groups: functionals with only LDA exchange and correlations on the left, LDA correlations mixed with GGA exchanges and *vice-versa* on the center, and GGA only functionals on the right (the ticks on the x-axis mark the limits). We choose to leave out some functionals from the LIBXC that turned out to be numerically unstable and for which we were only able to get results for very few elements. Nevertheless, there is a total of 902 combinations of functionals in this figure. The dark spots correspond to functionals whose errors are greater than 60% or to cases where we could not get the ionization potentials (numerical problems). There are some vertical red/"greenish" lines (red for the LDA/GGA region, green for the GGA), almost periodical, that correspond to some particular bad combinations of exchange and correlation. The errors for the GGA only part are lower than for the others. There are some elements with consistently bigger errors (horizontal bands). This is the case Li, Na, K, Rb and Cs (group I), and V, Cr, Ni and Cu. The later are elements with reasonably large magnetic moments, which could be a reason for these larger errors. A bit surprisingly, because its the other way around for the majority of the other elements, errors for the heaviest elements are bigger for the GGA only functionals than from the LDA/GGA mixture. The reason for this may be the following: we know that one of the reasons to the accuracy of LDA is the cancelation of errors from the exchange and the correlation parts. Then, mixing LDA correlations with the GGA exchange, results in an uncompensated error that adds to the total energy in the (fortunate) "right" direction.

Another view of those is presented in figure 4.2.2. Here we averaged the error for the set of elements for each functional and count the number of functionals

that have mean relative errors in some given interval. The top histogram has all the 902 combinations of functionals that we consider (LDA + GGA + mixtures) and in the bottom one we split the groups of functionals (the LDA functionals are not present in this histogram because they are so few compared with the GGAs that they are negligible). From this figure we can conclude that, even when mixing exchanges and correlations functionals from different families, the mean relative error are almost all under 10%. Even more, roughly half of the combinations of functionals give errors under 5%. However, we can also see that GGA only functionals are still averaging better than the mixture of LDA and GGA functionals. This figure also tell us that roughly 40 combinations of functionals that have mean relative errors under 2%. Next, we are going to make a ranking of functionals. We are looking for the functionals that yield very good results, relative errors under 2%, and we are going to count for how many atoms each functional has relative error less than that error. These results are (partially) presented in table 4.2.3. From this figure we can see that there are some LDA correlations, mixed with GGA exchanges, that yield very good results, but there is none GGA correlation with the LDA exchange. Also, the Perdew 88 GGA correlation appears several times, mixed with various exchanges.

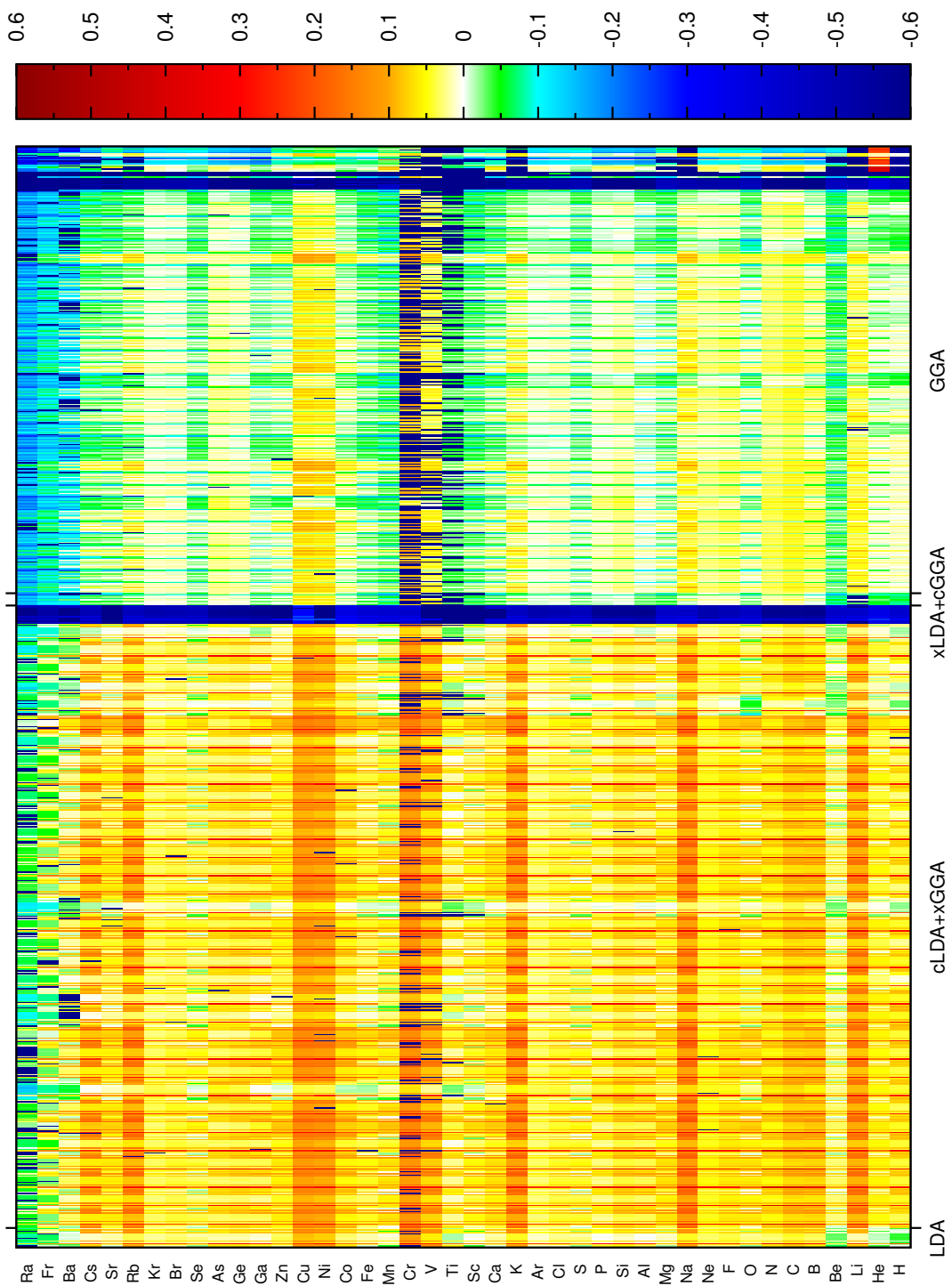


Figure 4.2.1: Relative errors for 902 functionals for each atom, for the spin-polarized Schrödinger equation.

Table 4.2.1: Comparison of the mean relative errors (Δ) and corresponding variances (σ) for some selected combinations of exchange-correlation functionals when considering or not spin-polarization, for both Schrödinger and scalar-relativistic equations.

Functional	Schrödinger				Scalar-relativistic			
	Unpolarized		Polarized		Unpolarized		Polarized	
	Δ	σ	Δ	σ	Δ	σ	Δ	σ
LDA VWN	0.0547	0.0019	0.0297	0.0006	0.0501	0.0011	0.0345	0.0008
LDA PW	0.0536	0.0018	0.0296	0.0006	0.0510	0.0011	0.0353	0.0008
GGA AM05	0.0564	0.0017	0.0251	0.0008	0.0471	0.0007	0.0183	0.0003
GGA PBE	0.0537	0.0017	0.0260	0.0010	0.0490	0.0008	0.0199	0.0004

Table 4.2.2: Mean relative errors (Δ) and corresponding variances (σ) for some selected combinations of exchange-correlation functionals using different wave-equations, but without considering spin-polarization.

Functional	Schrödinger		Scalar-rel.		Dirac	
	Δ	σ	Δ	σ	Δ	σ
LDA VWN	0.0547	0.0019	0.0501	0.0011	0.0516	0.0020
LDA PW	0.0536	0.0018	0.0510	0.0011	0.0522	0.0020
GGA AM05	0.0564	0.0017	0.0471	0.0007	0.0520	0.0015
GGA PBE	0.0537	0.0017	0.0490	0.0008	0.0483	0.0018

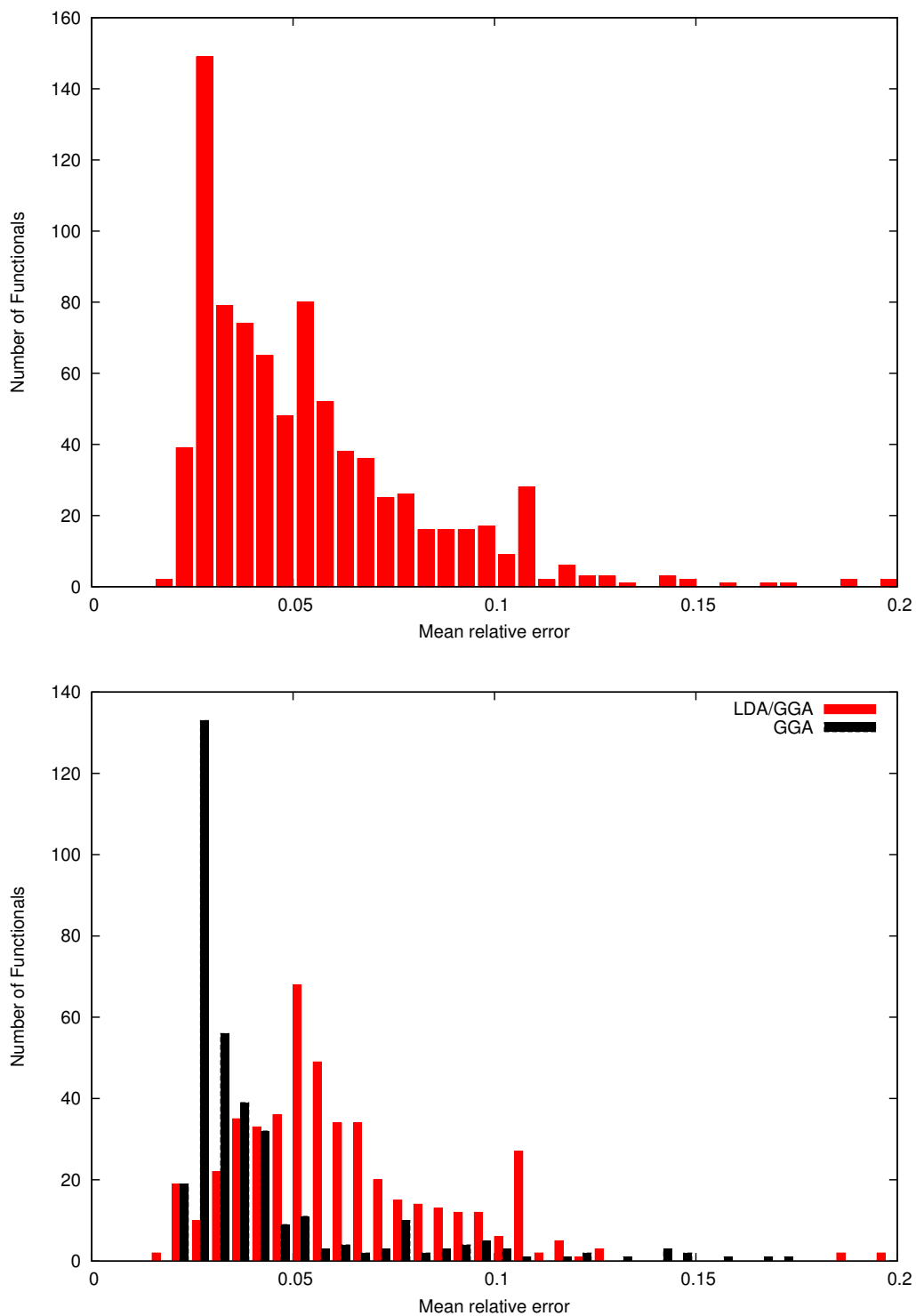


Figure 4.2.2: Histogram of the mean relative errors, for the total set of combinations of functionals (top), and for the GGA only and GGA/LDA combinations (bottom). Note that there are a total of 902 combinations of functionals in the complete set, 366 in the GGA only set, and 520 in the GGA/LDA mixture set.

Table 4.2.3: Number of atoms (N) for which a given combination of exchange-correlation functionals has one of the 100 smallest relative errors.

N	Correlation Functional	Exchange Functional
29	GGA - Perdew 86 [24]	GGA - Second-order generalized gradient approximation [25]
29	GGA - Perdew 86 [24]	GGA - Perdew, Burke and Ernzerhof SOL [26]
28	LDA - Ortiz and Ballone (PW parametrization) [27; 28; 29]	GGA - Keal and Tozer, version 1 [30]
28	LDA - Ortiz and Ballone (PW parametrization) [27; 28; 29]	GGA - Armiento and Mattsson 05 [22]
28	LDA - Perdew and Wang (modified) [12]	GGA - Keal and Tozer, version 1 [30]
28	LDA - Perdew and Wang [12]	GGA - Keal and Tozer, version 1 [30]
28	LDA - Ortiz and Ballone (PZ parametrization) [27; 28; 29]	GGA - Armiento and Mattsson 05 [22]
28	LDA - Perdew and Zunger (Modified) [29]	GGA - Keal and Tozer, version 1 [30]
28	LDA - Perdew and Zunger [29]	GGA - Keal and Tozer, version 1 [30]
28	LDA - Vosko, Wilk and Nusair [19]	GGA - Keal and Tozer, version 1 [30]
27	GGA - Perdew 86 [24]	GGA - Regularized PBE [31]
27	GGA - Perdew 86 [24]	GGA - Reparametrized PBE for vdW [32]
27	GGA - Perdew 86 [24]	GGA - Reparametrized PBE by Pedroza, Silva and Capelle [33]
27	LDA - Ortiz and Ballone (PW parametrization) [27; 28; 29]	GGA - Constantin et al based on the Airy gas [34]
27	LDA - Perdew and Wang (modified) [12]	GGA - Constantin et al based on the Airy gas [34]
27	LDA - Perdew and Wang [12]	GGA - Constantin et al based on the Airy gas [34]
27	LDA - Ortiz and Ballone (PZ parametrization) [27; 28; 29]	GGA - Keal and Tozer, version 1 [30]
27	LDA - Perdew and Zunger (Modified) [29]	GGA - Constantin et al based on the Airy gas [34]
27	LDA - Perdew and Zunger [29]	GGA - Constantin et al based on the Airy gas [34]

4.3 Ionization Potentials by the HOMO Eigenvalue

Up to this point, the ionization potentials presented, or strictly speaking, the relative errors in the ionization potentials, were evaluated by the difference on the total energies. The reason for this, is that, has already discussed in sections 2.3 - 2.4, almost all exchange-correlation potentials have the wrong asymptotic limit. This leads to huge errors in the ionization potentials evaluated by the HOMO eigenvalue, as shown in figure 4.3.1. The mean relative errors are about 50%. Remember that the exchange-correlation functionals used are the same as in figure 4.1.1, where the mean errors for the ionizations potentials evaluated by the total energy difference were around 10%. However, some functionals with the correct asymptotic limit exists. In this section, we will use two of these exchange functionals (GGA exchanges): the functional of Leeuwen and Baerends and a modified version of it [62][63].

In figure 4.3.2 are represented the mean relative errors for the 50 combinations of exchange and correlation functionals (resulting from mixing these two GGA exchanges with LDA and GGA correlations), for each atom. These functionals are harder to converge, and so there are some dark blue squares, that correspond to unfinished calculations. However we think that the remaining is still worth some discussion. From this figure, we see that the LB94 functional seems to be better for the lightest elements, in contrast with the its modified version, which is better for the heaviest elements. We can not concluded much about the differences between using LDA or GGA correlations, so a bit more study is need for this case.

What we can also conclude is that, with those two functionals, we can obtain errors of the same magnitude we had for the case where the ionization potentials were calculated using the total energies, but using the HOMO eigenvalue instead.

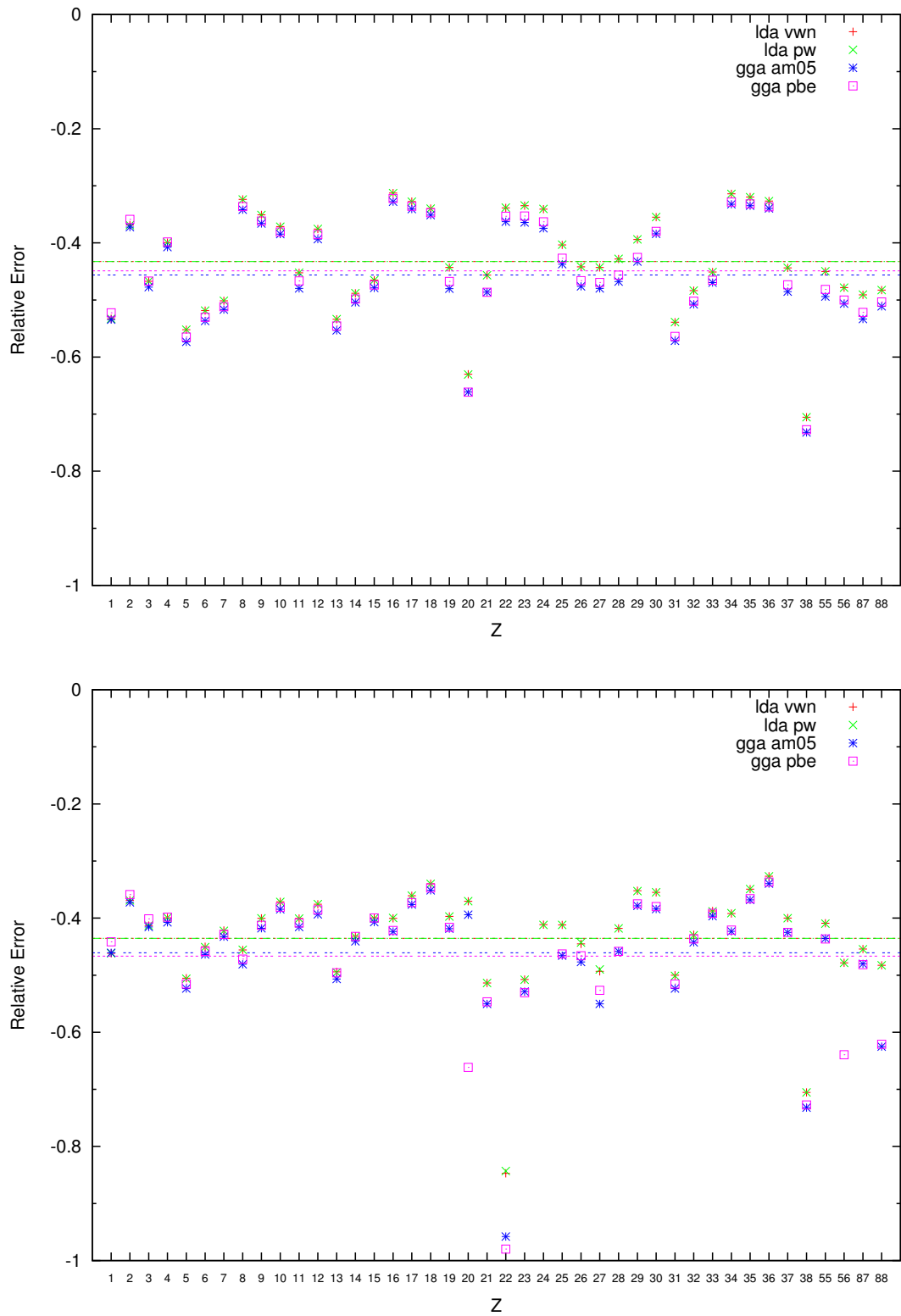


Figure 4.3.1: Relative errors (dots) and mean relative error (lines) for several functionals for the unpolarized Schrödinger (top) and polarized Schrödinger (bottom) equations.

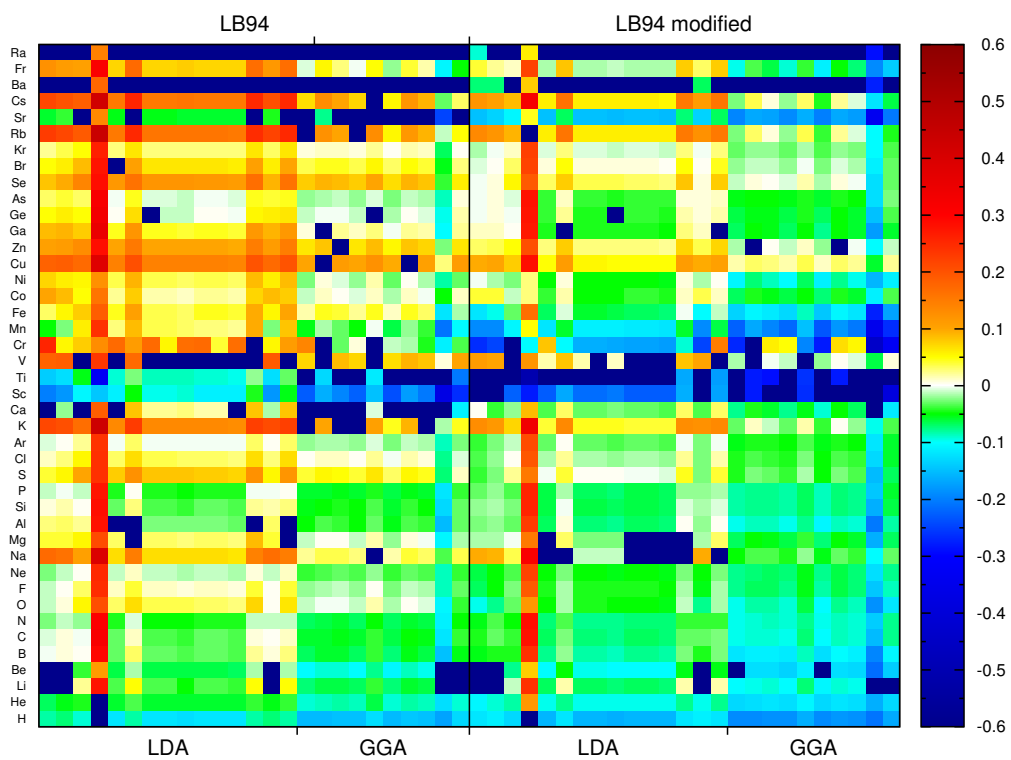


Figure 4.3.2: Relative errors for the LB94 [62] functional (left part) and the modified LB94m functional [63] (right part) combined with 25 LDA and GGA correlation functionals, for each atom, evaluated by the HOMO eigenvalue with the spin-polarized Schrödinger equation.

Chapter 5

Conclusions and Future Work

First, we have to stress the fact that this is just a preliminary study, and it may be that some conclusions change when all the calculations are done. Nevertheless, we have showed that even in the simplest approximation (LDA), density functional theory is able to reproduce within error of around 5% the experimental ionization potentials. We have also seen, unsurprisingly, that higher levels of theory give lower errors. We have constructed a list of some combinations of functionals that consistently yield the best results, across the set of atoms we have used.

For the ionizations potentials evaluated by the HOMO eigenvalues, we have shown that although the values obtained with the generality of the combinations of functionals, there are some which are able to reproduce the ionization potentials, within the same marge of error, as the remaining functionals do for the total energy difference case.

The results presented in this thesis are just a fraction of what we plan to do, and we think we have done only roughly 10% of the total. Finishing all the calculations and getting the results for the remaining part is then something we will do in the near future. We have still to get the first results for the polarized Dirac equation calculations, and we are curious about how different will they be comparing to the Scalar Relativistic case.

Even for these results, there are some things we did not have time to analyze yet, and could be interesting: are all the combinations predicting the same ground-state configuration? How does the errors vary with the magnetic moment?

Also, it would be interesting to know if the combinations of functionals we

discovered to be the best, will perform in the same way for other properties (electronic affinities, excitation energies, etc), and in another systems (molecules or solids).

Appendix A

Table 1: List of functionals used throughout this work with the corresponding LIBXC identifier.

LDA Functionals

LDA Exchange

XC_LDA_X	LDA exchange	[35; 36]
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LDA Correlation

XC_LDA_C_WIGNER	Wigner parametrization	[37]
XC_LDA_C_HL	Hedin & Lundqvist	[38]
XC_LDA_C_GL	Gunnarsson & Lundqvist	[39]
XC_LDA_C_XALPHA	Slater's $X\alpha$ (X-alpha)	
XC_LDA_C_VWN	Vosko, Wilk, & Nussair	[19]
XC_LDA_C_VWN_RPA	Vosko, Wilk, & Nussair (RPA)	[19]
XC_LDA_C_PZ	Perdew & Zunger	[29]
XC_LDA_C_OB_PZ	Ortiz & Ballone (PZ parametrization)	[27; 28; 29]
XC_LDA_C_PW	Perdew & Wang	[12]
XC_LDA_C_PW_RPA	Perdew & Wang fit to the RPA energy	[12]
XC_LDA_C_OB_PW	Ortiz & Ballone (PW parametrization)	[12; 27; 28]
XC_LDA_C_vBH	von Barth & Hedin	[40]

XC_LDA_C_GOMBAS	Gombas	[41]
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LDA Exchange-Correlation

XC_LDA_XC_TETER93	Teter 1993	[42]
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GGA Functionals

GGA Exchange

XC_GGA_X_PBE	Perdew, Burke & Ernzerhof ex- change	[20; 21]
XC_GGA_X_PBE_R	Perdew, Burke & Ernzerhof ex- change (revised)	[43]
XC_GGA_X_MPBE	Adamo & Barone modification to PBE	[44]
XC_GGA_X_XPBE	Extended PBE by Xu & Goddard III	[45]
XC_GGA_X_B86	Becke 86 Xalfa,beta,gamma	[46; 47]
XC_GGA_X_B86_MGC	Becke 86 Xalfa,beta,gamma (with mod. grad. correction)	[46; 48]
XC_GGA_X_B88	Becke 88	[49]
XC_GGA_X_PW86	Perdew & Wang 86	[50]
XC_GGA_X_PW91	Perdew & Wang 91	[51]
XC_GGA_X_OPTX	Handy & Cohen OPTX 01	[52]
XC_GGA_X_DK87_R1	dePristo & Kress 87 (version R1)	[53]
XC_GGA_X_DK87_R2	dePristo & Kress 87 (version R2)	[53]
XC_GGA_X_LG93	Lacks & Gordon 93	[54]
XC_GGA_X_FT97_A	Filatov & Thiel 97 (version A)	[55]
XC_GGA_X_FT97_B	Filatov & Thiel 97 (version B)	[55]
XC_GGA_X_PBE_SOL	Perdew, Burke & Ernzerhof ex- change (for solids)	[26]
XC_GGA_X_RPBE	Hammer, Hansen & Norskov (PBE-like)	[56]
XC_GGA_X_WC	Wu & Cohen	[57]

XC_GGA_X_AM05	Armiento & Mattsson 05 ex- change	[22; 23]
XC_GGA_X_PBEA	Madsen 07	[58]
XC_GGA_X_mPW91	mPW91 of Adamo & Barone	[59]
XC_GGA_X_BAYESIAN	Bayesian best fit for the enhance- ment factor	[60]
XC_GGA_X_PBE_JSJR	Reparametrized PBE by Pedroza, Silva & Capelle	[33]
XC_GGA_X_OPTB88_VDW	opt-Becke 88 for vdW	[32]
XC_GGA_X_PBEK1_VDW	Reparametrized PBE for vdW	[32]
XC_GGA_X_OPTPBE_VDW	Reparametrized PBE for vdW	[32]
XC_GGA_X_RGE2	Regularized PBE	[31]
XC_GGA_X_RPW86	Refitted Perdew & Wang 86	[61]
XC_GGA_X_KT1	Keal and Tozer, version 1	[30]
XC_GGA_X_LB	van Leeuwen & Baerends	[62]
XC_GGA_X_LBM	van Leeuwen & Baerends modi- fied	[63]
XC_GGA_X_MB88	Modified Becke 88 for proton transfer	[64]
XC_GGA_X_APBE	mu fixed from the semiclassical neutral atom	[65]
XC_GGA_X_HTBS	Haas, Tran, Blaha, and Schwarz	[66]
XC_GGA_X_AIRY	Constantin et al based on the Airy gas	[34]
XC_GGA_X_LAG	Local Airy Gas	[67]
XC_GGA_X_C09X	C09x to be used with the VdW of Rutgers-Chalmers	[68]
XC_GGA_X_SOGGA11	Second-order generalized gradient approximation 2011	[25]

GGA Correlation

XC_GGA_C_PBE	Perdew, Burke & Ernzerhof cor- relation	[20; 21]
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XC_GGA_C_XPBE	Extended PBE by Xu & Goddard III	[45]
XC_GGA_C_P86	Perdew 86	[24]
XC_GGA_C_PBE_SOL	Perdew, Burke & Ernzerhof correlation SOL	[26]
XC_GGA_C_PW91	Perdew & Wang 91	[51; 69]
XC_GGA_C_AM05	Armiento & Mattsson 05 correlation	[22]
XC_GGA_C_PBE_JRGX	Reparametrized PBE by Pedroza, Silva & Capelle	[33]
XC_GGA_C_RGE2	Regularized PBE	[31]
XC_GGA_C_WI	Wilson & Ivanov	[70]
XC_GGA_C_WI0	Wilson & Ivanov initial version	[70]
XC_GGA_C_APBE	mu fixed from the semiclassical neutral atom	[65]

GGA Exchange-Correlation

XC_GGA_XC_HCTH_93	HCTH functional fitted to 93 molecules	[71]
XC_GGA_XC_HCTH_120	HCTH functional fitted to 120 molecules	[72]
XC_GGA_XC_HCTH_147	HCTH functional fitted to 147 molecules	[72]
XC_GGA_XC_HCTH_407	HCTH functional fitted to 147 molecules	[73]
XC_GGA_XC_EDF1	Empirical functional from Adamson, Gill, and Pople	[74]
XC_GGA_XC_XLYP	XLYP functional	[75]
XC_GGA_XC_PBE1W	PBE1W (functional fitted for water)	[76]
XC_GGA_XC_MPWLYP1W	mPWLYP1w (functional fitted for water)	[76]

XC_GGA_XC_PBELYP1W	PBELYP1W (functional fitted for water)	[76]
XC_GGA_XC_KT2	Keal and Tozer, version 2	[30]
XC_GGA_XC_TH_FL	Tozer and Handy v. FL	[77]
XC_GGA_XC_TH_FC	Tozer and Handy v. FC	[77]
XC_GGA_XC_TH_FCFO	Tozer and Handy v. FCFO	[77]
XC_GGA_XC_TH_FCO	Tozer and Handy v. FCO	[77]
XC_GGA_XC_TH1	Tozer and Handy v. 1	[78]
XC_GGA_XC_TH2	Tozer and Handy v. 2	[79]
XC_GGA_XC_TH3	Tozer and Handy v. 3	[80]
XC_GGA_XC_TH3	Tozer and Handy v. 4	[80]

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