Atomic ionization energies with hybrid functionals

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”You tried your best and you failed miserably.
The lesson is, never try.” - Homer Simpson

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> No man is an island.
>
> John Donne

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Abstract

We proceed to describe an implementation of hybrid functionals formalism in the open source code Atomic Pseudopotential Engine (APE), starting with a description of the Hartree-Fock method implementation required to calculate them. A report on the obtained results is presented.

Resumo

Descreve-se uma implementação do formalismo de funcionais híbridos no código aberto Atomic Pseudopotential Engine (APE), começando na descrição da implementao do método de Harree-Fock necessário para tal. Apresenta-se uma discussão dos resultados obtidos.

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Chapter 1

Introduction

Modern studies of many-body systems often rely on Density Functional Theory (DFT) due to its affordable computational effort. One of the advantages of this formulation resides on the separation of the several parts of the Hamiltonian, with the effects of the interaction between particles being placed in the Hartree and exchange-correlation energy functionals, although the exact form of the latter is unknown. In fact, the used functionals are only approximations (usually using as starting point the local density approximation and adding correction terms), built from physical intuition and obeying several rules, arising from the theoretical formulation (for example, coordinate scaling and asymptotic behaviour) [17].

Currently there is a large variety of exchange-correlation energy functionals available, ranging from the local density approximation (LDA) to the more complex generalized-gradient approximations (GGA's). There is a particular kind of functionals that seeks to include a portion of the exact exchange (coming from Hartree-Fock calculations) with any other functional. These are hybrid functionals, so called because they mix functionals with explicit dependence on the density, with an orbital dependent functional (obtained from Hartree-Fock calculations).

The overall good results of hybrids [9] are the main motivation for this work. As such we expect to implement a solution to the Hartree-Fock equations within the Atomic Pseudopotential Engine (APE) and, along with the functional library LIBXC [25], use it to make calculations with hybrid functionals. With this we expect to compute the ionization potentials for several atoms of the Periodic Table which are easily compared with the experimental data [20].

We hope this work will be the basis for a more ambitious project: the generation of hybrid functionals pseudopotentials, to be used in computational simulation.

This thesis is structured as follows: in the first chapter, we present some theoretical background for both Hartree-Fock and DFT formulations. Then we proceed to present some details on the implementation and results. Finally, we present some conclusions and prospects for future work.

Chapter 2

The N-electron problem for atoms

2.1 Introduction

As a physical system the atom is a complicated one. This fact arises from all the interactions happening on it: electrostatic, electron spin-electron spin, nucleus spin-electron spin... However, the more complicated interactions are usually of higher order than electrostatic ones and can be negleted allowing therefore a non relativistic treatment of the system.

By doing this, the atom can be described as a point like static nucleus of charge Z, surrounded by N electrons. Neglecting the spin dependent interactions, the corresponding Hamiltonian is written as (using atomic units[1]):

$$\hat{H} = -\sum_{i=1}^{N} \frac{1}{2}\nabla_i^2 - \sum_{i=1}^{N} \frac{Z}{r_i} + \sum_{i=1}^{N}\sum_{j>i}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \,, \tag{2.1}$$

where $\mathbf{r}_i$ are the electron coordinates.

In spite of neglecting the electron spin in the Hamiltonian (2.1), an electronic wavefunction is only fully described if the spins are specified. In this way, the electronic wavefunction is a function of $3N$ spacial coordinates and N spin coordinates, $\mathbf{x}_i = \{\mathbf{r}_i, s_i\}$, that is, $\psi(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N)$. This wavefunction, must obey the

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[1] In this case, atomic units mean that $e = m_e = \hbar = \frac{1}{4\pi\epsilon_0} = 1$

spin-statistics theorem, which states that a many-electron wavefunction must be antisymmetric with respect to the interchange of any two electrons:

$$\hat{P}_{ij}\,\psi(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_i, ..., \mathbf{x}_j, ..., \mathbf{x}_N) = -\psi(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_j, ..., \mathbf{x}_i, ..., \mathbf{x}_N)\ , \tag{2.2}$$

where $\hat{P}_{ij}$ is an operator that permutes the coordinates (both space and spin) of the i and j electrons. Furthermore, since the electrons are indistinguishable any permutation of coordinates in (2.2) must also be the same solution to the Hamiltonian (2.1).

Although knowledge of the Hamiltonian and the requisite of the antisymmetry allow to obtain a solution to the electronic problem, it is still far from solvable. In order to advance some assumptions about the form of the wavefunctions must be made.

2.2 The Hartree-Fock method

If the electrons were non interacting, the Hamiltonian (2.1) would merely be written as the sum of single particle operators:

$$\hat{H} = \sum_{i}^{N} \hat{h}(\mathbf{r}_i) \tag{2.3}$$

where,

$$\hat{h}(\mathbf{r}_i) = -\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i}. \tag{2.4}$$

This operator has itself a set of orthogonal eigenvalues and eigenfunctions,

$$\hat{h}(\mathbf{r}_i)\phi_j(\mathbf{x}_i) = \epsilon_j \phi_j(\mathbf{x}_i), \tag{2.5}$$

which allows to write a solution to (2.3) as a product of $\phi_j(\mathbf{x}_i)$

$$\psi = \phi_i(\mathbf{x}_1)\phi_j(\mathbf{x}_2)...\phi_k(\mathbf{x}_N),$$

representing what is called a Hartree Product. Although mathematically correct, this product presents crucial deficiencies from the physical point of view: it specifically distinguishes electrons and is not antisymmetric with respect to the change of any two electron coordinates.

To overcome these problems we make use of the spin-statistics theorem and the indistinguishability of the electrons, and define an antisymetrization operator[1]

$$\mathcal{A} = \frac{1}{N!}\sum_{\alpha} \epsilon_\alpha \hat{P}_\alpha, \tag{2.6}$$

which applied to an Hartree product gives

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \sum_{\alpha\beta\cdots\omega} \epsilon_{\alpha\beta\cdots\omega} \phi_\alpha(\mathbf{x}_1)\phi_\beta(\mathbf{x}_2)\cdots\phi_\omega(\mathbf{x}_N)\ , \tag{2.7}$$

where the $\epsilon_{\alpha\beta\cdots\omega}$ symbol indicates the sign of the permutation in the sum. This wavefunction can also be written as a determinant,

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_i(\mathbf{x}_1) & \phi_j(\mathbf{x}_1) & \cdots & \phi_k(\mathbf{x}_1) \\ \phi_i(\mathbf{x}_2) & \phi_j(\mathbf{x}_2) & \cdots & \phi_k(\mathbf{x}_2) \\ \vdots & \vdots & & \vdots \\ \phi_i(\mathbf{x}_N) & \phi_j(\mathbf{x}_N) & \cdots & \phi_k(\mathbf{x}_N) \end{vmatrix}, \tag{2.8}$$

called a Slater determinant and it represents the basic *ansatz* of the Hartree-Fock method: approximate the multi electronic wavefunction as a sum of products of independent single electron wavefunctions.

The energy of the system is the expectation value of the Hamiltonian,

$$E = \left\langle \Psi \middle| \hat{H} \middle| \Psi \right\rangle . \tag{2.9}$$

In Hartree-Fock theory, using (2.7) and (2.1), this is written as (following the notation of [37])

$$E[\{\phi_\alpha\}] = \sum_a \langle a|\hat{h}|a\rangle + \frac{1}{2}\sum_{ab}\left[\langle ab|ab\rangle - \langle ab|ba\rangle\right] \tag{2.10}$$

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[1] The α here represents any of the available permutations for the applied function, in such manner that ϵ_α is the signal of the permutation.

where the one electron integral is given by

$$\langle a|\hat{h}|b\rangle = \int \mathrm{d}\mathbf{x}_1 \; \phi_a^\dagger(\mathbf{x}_1)\hat{h}(\mathbf{x}_1)\phi_b(\mathbf{x}_1) \; , \tag{2.11}$$

and the two electron integral

$$\langle ab|cd\rangle = \int \mathrm{d}\mathbf{x}_1 \; \mathrm{d}\mathbf{x}_2 \; \phi_a^\dagger(\mathbf{x}_1)\phi_b^\dagger(\mathbf{x}_2)\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}\phi_c(\mathbf{x}_1)\phi_d(\mathbf{x}_2) \; . \tag{2.12}$$

Expression (2.10) is separated in three terms. The first parcel is easily identified as the kinetic and nuclear-electron interaction energies. The last two are, accordingly, the Hartree and exchange energies.

In order to obtain the integro-differential equations for the orbitals, the energy functional must be minimized subjected to the orthonormality constrains. This is done by introducing a set of Lagrange multipliers, ϵ_{ab}, and requiring the functional

$$\mathcal{F}[\{\phi_\alpha\}] = E[\{\phi_\alpha\}] - \sum_{ab} \epsilon_{ab} \left(\langle a|b\rangle - \delta_{ab}\right) \tag{2.13}$$

to be stationary, $\delta\mathcal{F} = 0$, with respect to infinitesimal changes of the orbitals, i.e. $\phi_a \to \phi_a + \delta\phi_a$. The final result of such procedure gives a set of N differential equations [37]

$$\left[\hat{h}(\mathbf{x}_1) + \sum_{b=1}^{N} \left(\mathcal{J}_b(\mathbf{x}_1) - \mathcal{K}_b(\mathbf{x}_1)\right)\right] \psi_a(\mathbf{x}_1) = \sum_{b=1}^{N} \epsilon_{ab}\phi_b(\mathbf{x}_1), \tag{2.14}$$

where we define the Coulomb operator,

$$\mathcal{J}_b(\mathbf{x}_1)\phi_a(\mathbf{x}_1) = \int \mathrm{d}\mathbf{x}_2 \frac{\phi_b^\dagger(\mathbf{x}_2)\phi_b(\mathbf{x}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}\phi_a(\mathbf{x}_1) \; , \tag{2.15}$$

and the Exchange operator,

$$\mathcal{K}_b(\mathbf{x}_1)\phi_a(\mathbf{x}_1) = \int \mathrm{d}\mathbf{x}_2 \frac{\phi_b^\dagger(\mathbf{x}_2)\phi_a(\mathbf{x}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}\phi_b(\mathbf{x}_1) \; . \tag{2.16}$$

Since the sum of the Coulomb and exchange operators is invariant with respect to a unitary transformation, it is possible to transform the wavefunctions, diagonalizing the Lagrange multipliers matrix. When such procedure is taken one usually refers to the canonical Hartree-Fock equations.

The value for the energy obtained through the solutions of (2.14) is larger than the real value[1], since it is obtained by a variational principle. The difference between these two values is called the correlation energy[2] [24],

$$E_C = E_0^{(real)} - E_0^{(HF)}, \tag{2.17}$$

and is, by construction, negative. The value of E_C reflects the failures of the Hartree-Fock method to correctly describe electron correlation due to being a mean field approximation theory.

Conceptually, the correlation energy can be divided in two types: static and dynamic. Static correlation is associated with situations where there are nearly degenerate states and a single determinant is no longer an acceptable approximation for the wavefunction. On the other hand, dynamic correlation is related to the dynamics of electron-electron interaction: in Hartree-Fock theory, the motion of opposite spins electrons is not correlated. These problems are tackled by going beyond Hartree-Fock and using more than one determinant while describing the wavefunction. For example, the configuration interaction [37], which uses a sum of excited determinants with fixed orbitals (obtained from Hartree-Fock calculations) and minimizes the expansion coefficients, and multiconfiguration methods [7], where the orbitals are also varied thus making it a more costly method. In general however, direct implementation of these methods becomes prohibitive for large systems.

2.2.1 Koopman's theorem

Consider a configuration of N electrons. If, by any means, an electron, lets say j, were to be removed, and therefore form the $N-1$ configuration, the ionization

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[1] Strictly speaking, it could also be equal but this only happens for the hydrogen case in which Hartree-Fock is exact.

[2] This definition is commonly applied in determinantal methods. In the case of density functional theory another definition applies.

potential for the process would be written as

$$\mathrm{IP} = E_0^{(N)} - E_j^{(N-1)} \ . \tag{2.18}$$

Supposing the removal of the electron does not affect the form of the remaining orbital (i.e. neglecting orbital relaxation), this difference can be written simply as

$$\mathrm{IP} = -\langle j|\hat{h}|j\rangle \ . \tag{2.19}$$

This is a statement of Koopman's Theorem: the ionization potential of a electron from a given configuration is equal to the negative of it's orbital energy. From the derivation of Koopman's theorem an accurate result is not expected, since orbital relaxation actually happens in a real ionization process.

Despite the approximated nature of this theorem, it gives an explicit meaning to orbital energies in the Hartree-Fock method. Also, it gives a consistency test when calculating ionization potentials of a given system, since we expect the value obtained from the theorem to be close to the one calculated correctly.

2.3 Radial Hartree-Fock

For a N electron atom, the general single determinant Hartree-Fock, requires a set of N differential equations to be solved in 3 dimensions. This number can be reduced if subsequent approximations are made.

In the non-relativistic regime, a spin orbital is specified by a set of four quantum numbers (n, l, m_l and m_s). In order to reduce the number of orbitals, we neglect the angular and spin projection numbers, m_l and m_s respectively, which means a restricted formulation is assumed. Here neglect means that the final description of the wavefunctions will not depend on these numbers. We get rid of m_s by assuming the spatial part of orbitals with spin up and spin down are equal; m_l disappears after spherically averaging the atom as will be seen in section 2.3.3 (which leads to a spherical atom). This way, since the one electron wavefunctions with same n and l numbers are equal, the number of wavefunctions to calculate is reduced from N (the number of electrons) to m (the number of shells). By doing this, the electronic structure of the atom is specified by a set of orbitals and their occupations, ω_{nl},

$$(n_1 l_1)^{(\omega_{n_1 l_1})}(n_2 l_2)^{(\omega_{n_2 l_2})}...(n_m l_m)^{(\omega_{n_m l_m})} \, . \tag{2.20}$$

Using a method identical to the hydrogen atom, separation of variables for the wavefunctions can be considered,

$$\phi_{nlmm_s}(\mathbf{x}) = R_{nl}(r) Y_{lm}(\theta, \varphi) \chi_{m_s} \, , \tag{2.21}$$

where the R_a are the radial wavefunctions, Y_{lm} the spherical harmonics and χ the spin wavefunction, and by doing so, reduce the problem to one dimension. The radial wavefunctions should obey the orthonormality relations for the same angular number l

$$\int_0^\infty \mathrm{d}r \; r^2 R^*_{n_a l} R_{n_b l} = \delta_{n_a, n_b}. \tag{2.22}$$

These tools will allow for a radial formulation of the Hartree-Fock equations.

2.3.1 One Electron Integrals

The first term of (2.10) is the simplest to rewrite in a radial formulation. Since the one electron part of the Hamiltonian only depends on the coordinates, the integration over spin is immediate. Furthermore, since the Coulomb potential does not depend on the angular coordinates, and the laplacian is separable into [21]

$$\nabla^2 = \frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2 \frac{\mathrm{d}}{\mathrm{d}r}\right) - \frac{1}{r^2}\hat{L}^2,$$

the term can be rewritten as

$$\sum_{\{nlm_l m_s\}}^{N} \langle a|h|a\rangle = \sum_{\{nl\}}^{m} \omega_a \int r^2 \mathrm{d}r R^*_a \left[-\frac{1}{2}\frac{\mathrm{d}^2}{\mathrm{d}r^2} - \frac{1}{r}\frac{\mathrm{d}}{\mathrm{d}r} + \frac{l_a(l_a+1)}{2r^2} - \frac{Z}{r} \right] R_a \; ; \tag{2.23}$$

the summation is now limited only to (nl) since the radial part of every orbital sharing the same n and l numbers is, by construction, equal.

2.3.2 Two Electron Integrals

The two electron integrals of the exchange and correlation energies are more complicated to integrate. This happens because the Coulomb kernel, $1/_{|\mathbf{r}-\mathbf{r}'|}$, is a function of both the radial and angular coordinates. To overcome this, we expand the kernel using the spherical harmonics as [16]

$$\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}=\sum_{k=0}^{\infty}\sum_{m=-k}^{k}\frac{4\pi}{2k+1}\frac{r_<^k}{r_>^{k+1}}Y_{km}^*(\hat{r}_1)Y_{km}(\hat{r}_2), \tag{2.24}$$

where $r_> = \max\{|\mathbf{r}_1|, |\mathbf{r}_2|\}$ and $r_< = \min\{|\mathbf{r}_1|, |\mathbf{r}_2|\}$.

Introducing equation (2.24) in (2.12) and integrating over the spins, the two electron integral becomes

$$\begin{aligned}\langle ab|cd\rangle = \sum_{k=0}^{\infty}\sum_{m=-k}^{k}&\frac{4\pi}{2k+1}\delta(m_{sa},m_{sc})\delta(m_{sb},m_{sd})\\ &\times\int \mathrm{d}\Omega_1\; Y_{km}(\hat{r}_1)Y_{l_am_{la}}^*(\hat{r}_1)Y_{l_cm_{lc}}(\hat{r}_1)\\ &\times\int \mathrm{d}\Omega_2\; Y_{km}^*(\hat{r}_2)Y_{l_dm_{ld}}(\hat{r}_2)Y_{l_bm_{lb}}^*(\hat{r}_2)\\ &\times\iint \mathrm{d}r_1\mathrm{d}r_2\; r^2r_2^2R_a^*(r_1)R_b^*(r_2)\frac{r_<^k}{r_>^{k+1}}R_c(r_1)R_d(r_2)\ .\end{aligned}$$

The angular and radial parts can be further manipulated. In the angular case we see that each line contains a term that is the complex conjugate of the other two. Using the relation $Y_{lm} = (-1)^m Y_{l-m}^*$ it becomes possible to change the integrands into trios of spherical harmonics, and, by doing so, the usage of the property

$$\begin{aligned}&\int \mathrm{d}\Omega\; Y_{l_1m_1}(\hat{r})Y_{l_2m_2}(\hat{r})Y_{l_3m_3}(\hat{r}) =\\ &\qquad=\sqrt{\frac{(2l_1+1)(2l_2+1)(2l_3+1)}{4\pi}}\begin{pmatrix} l_1 & l_2 & l_3\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} l_1 & l_2 & l_3\\ m_1 & m_2 & m_3\end{pmatrix}\end{aligned} \tag{2.25}$$

allows to write the angular integrals in terms of the Wigner 3j symbols.

For the radial part, following the notation on [6], the quantity

$$R^k_{ab;cd} = \iint \mathrm{d}r'\mathrm{d}r\ r^2 r'^2 R^*_a(r) R^*_b(r') \frac{r^k_<}{r^{k+1}_>} R_c(r) R_d(r') \tag{2.26}$$

is defined, along with the particular cases, $F^k_{a;b} = R^k_{ab;ab}$ and $G^k_{a;b} = R^k_{ab;ba}$.

With this information in mind, the only thing left to do is write the specific form for the Coulomb and exchange integrals. Acording to their definition, the Coulomb integrals are given by

$$\langle ab|ab\rangle = \sum_{k=0}^{2\min\{l_a,l_b\}} a^k_{a,b} F^k_{a;b}, \tag{2.27}$$

where

$$\begin{aligned} a^k_{(l_a m_{la};l_b m_{lb})} = (-1)^{m_{la}+m_{lb}}(2l_a+1)(2l_b+1) \begin{pmatrix} k & l_a & l_a \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} k & l_b & l_b \\ 0 & 0 & 0 \end{pmatrix} \\ \times \begin{pmatrix} k & l_a & l_a \\ 0 & -m_{la} & m_{la} \end{pmatrix} \begin{pmatrix} k & l_b & l_b \\ 0 & m_{lb} & -m_{lb} \end{pmatrix}. \end{aligned} \tag{2.28}$$

In the same manner, for the exchange integrals we have

$$\langle ab|ba\rangle = \delta(m_{sa}, m_{sb}) \sum_{k=|l_a-l_b|}^{l_a+l_b} b^k_{(l_a m_{la};l_b m_{lb})} G^k_{a;b}, \tag{2.29}$$

where

$$b^k_{(l_a m_{la};l_b m_{lb})} = (2l_a+1)(2l_b+1) \begin{pmatrix} k & l_a & l_b \\ m_{la}-m_{lb} & -m_{la} & m_{lb} \end{pmatrix}^2 \begin{pmatrix} k & l_a & l_b \\ 0 & 0 & 0 \end{pmatrix}^2. \tag{2.30}$$

2.3.3 Spherically Averaged Atom

The main interest of the radial formulation is to be able to write the Hartree-Fock equations in terms of the radial coordinate only. The previously calculated quantities, although written in terms of radial integrals, still present a dependence on the angular part of the atom through the angular quantum numbers.

To remove this dependency, it is necessary to average the integrals over all the possible configurations for a given set of shells, effectively spherically averaging the atom.

In spite of the effective independent particle potential in the Hartree-Fock method not being truly spherical (this only happens for closed shell systems), the true many body potential is actually spherically symmetric [10]. Physically this is attained by having partial equal occupations on every sub-shell (which are degenerate in this level of approximation) and it gives physical motivation to the averaging process.

This process is thoroughly described in [34]. In short, it starts by separating pairs of equivalent (same shells) and non-equivalent electrons (different shells) and calculate the average of the exchange and Coulomb energies for a given type of pair. After calculating the number of possible combinations for each type, the result is immediate.

As a final result, the energy of the averaged atom can be written as [11]

$$\begin{aligned} E[\{R_a\}] = \sum_{a=1}^{m} w_a I(a,a) + \sum_{a=1}^{m} \sum_{k=0}^{2l_a} w_a \frac{w_a - 1}{2} f_{l_a}^k F_{a,b}^k + \\ + \frac{1}{2} \sum_{a=1}^{m} \sum_{\substack{b=1 \\ b\neq a}}^{m} w_a w_b \left(F_{a,b}^0 + \sum_{k=|l_a-l_b|}^{l_a+l_b} g_{l_a,l_b}^k G_{a,b}^k \right), \end{aligned} \tag{2.31}$$

where

$$f_{l_a}^k = \begin{cases} 1 & \text{for } k = 0 \\ -\dfrac{4l_a+2}{4l_a+1} \begin{pmatrix} l_a & k & l_a \\ 0 & 0 & 0 \end{pmatrix}^2 & \text{for } k > 0 \end{cases} \tag{2.32}$$

and

$$g_{l_a,l_b}^k = -\frac{1}{2} \begin{pmatrix} l_a & k & l_b \\ 0 & 0 & 0 \end{pmatrix}^2 . \tag{2.33}$$

Rearranging the terms, a more explicit form can be obtained, dividing the energy on its several contributions [39]:

$$E = \sum_{a=1}^{m} w_a I(a,a) + E_H + E_x \; , \tag{2.34}$$

where the Hartree energy is written as

$$E_H = \frac{1}{2}\sum_{pq} \omega_p \omega_q R^0_{pq;qp} \tag{2.35}$$

and the exchange energy,

$$E_x = -\frac{1}{2}\sum_{pq} \sum_{L=|l_p-l_q|}^{l_p+l_q} \Theta^L_{pq} R^L_{pq;qp} \tag{2.36}$$

with

$$\Theta^L_{pq} = \begin{cases} \frac{1}{2}\omega_p\omega_q \begin{pmatrix} l_p & L & l_q \\ 0 & 0 & 0 \end{pmatrix}^2 & \text{for } p \neq q \\ \frac{1}{2}\omega_p(\omega_p - 1)\frac{4l_p+2}{4l_p+1} \begin{pmatrix} l_p & L & l_p \\ 0 & 0 & 0 \end{pmatrix}^2 & \text{for } p = q \text{ and } L \neq 0 \\ \omega_p & \text{for } p = q \text{ and } L = 0 \end{cases} \tag{2.37}$$

It can be shown that the weight factor (2.37) cancels the self interaction term of the Hartree energy. The energy expressions presented are both equivalent; equation (2.31), although more complicated, has the advantage of not having double counts, but usage of equations (2.35) and (2.36) makes explicit the physical meaning of the terms.

2.3.4 Differential Equations

The desired radial functions are the ones that minimize the energy funcional, while subjected to the orthogonality constraint (equation (2.22)). Following the same procedure as in subsection 2.2, we introduce the Lagrange multipliers, λ_{ab}, and require the functional

$$F[\{R_a\}] = E[\{R_a\}] - \sum_{ab} \lambda_{ab}\delta_{l_a l_b}\left[\left(\int_0^\infty \mathrm{d}r r^2\; R^*_{n_a l_a} R_{n_b l_b}\right) - \delta_{n_a,n_b}\right] \tag{2.38}$$

to be stationary with respect to infinitesimal changes in the wavefunctions (i.e. for $R_a \to R_a + \delta R_a$ we have that $\delta F = 0$). Therefore, taking the functional derivative in order to $R_a(r)$ of (2.38) and equalling to zero we obtain the radial Hartree-Fock equations for a spherically averaged atom [11]:

$$\begin{aligned}\left(-\frac{1}{2}\frac{\mathrm{d}^2}{\mathrm{d}r^2} - \frac{1}{r}\frac{\mathrm{d}}{\mathrm{d}r} + \frac{l_a(l_a+1)}{2r^2} - \frac{Z}{r} + \frac{Y_a(r)}{r} - \epsilon_{aa}\right) R_a(r) = \\ -\frac{X_a(r)}{r} + \sum_{b\neq a}^{m} \delta_{l_a l_b}\epsilon_{ab}R_b(r)\ ,\end{aligned} \tag{2.39}$$

where the off-diagonal energy parameters, ϵ_{ab}, are related to the Lagrange multipliers by

$$\epsilon_{ab} = \frac{\lambda_{ab}}{\omega_a}. \tag{2.40}$$

The non-linear term is

$$X_a(r) = \sum_{\substack{b=1\\ b\neq a}}^{m} w_b \sum_{k=|l_a-l_b|}^{(l_a+l_b)} g^k_{l_a,l_b} Y^k_{ab}(r) R_b(r) \tag{2.41}$$

and the local potential term,

$$Y_a(r) = (w_a - 1)\sum_{k=0}^{2l_a} f^k_{l_a} Y^k_{aa}(r) + \sum_{\substack{b=1\\ b\neq a}}^{m} w_b Y^0_{bb}(r)\ , \tag{2.42}$$

where

$$Y^k_{ab}(r) = r\int_0^\infty r'^2 \frac{r^k_<}{r^{k+1}_>} R_a(r') R_b(r')\mathrm{d}r' \tag{2.43}$$

are the Hartree screening functions.

As with equations (2.14), the implicit dependence of the potential terms on the wavefunctions require the system to be solved in a self consistent manner.

2.4 Density Functional Theory

Traditionally speaking, all quantum mechanical observables can be derived in terms of expectation values using the wavefunction. However, for some systems (molecules for example) wavefunction approximations beyond Hartree-Fock must be considered (e.g. Configuration Interaction) for good results. In practice these methods scale poorly with the particle number (for a N electron system there are $3N$ space coordinates which in a mesh with M points means at least M^{3N} entries) making them unsuitable for said systems.

In 1964, Hohenberg and Kohn presented a paper [15] where was shown that quantum mechanical observables can be considered unique functionals of the ground state density. Although their work was based on the non relativistic workframe, in the following years it was generalized to include degenerate ground states and time and spin dependent formulations. Using this knowledge one could, in principle, study any system by using only the density which is a three variable scalar function. This represents the basis of Density Functional Theory (DFT).

2.4.1 Hohenberg-Kohn Theorems

The Hohenberg-Kohn theorems are the cornerstone of DFT as they establish a relation between the external potential and the ground state density. Since they are extensively discussed in the literature (see for example [38] [17] [26]) only a simple exposition is done here.

Lets start by considering the non-relativistic Hamiltonian, with the kinetic operator

$$\hat{T} = \sum_{i=1}^{N} -\frac{1}{2}\nabla_i^2, \tag{2.44}$$

the potential operator

$$\hat{V} = \sum_{i=1}^{N} v_i(\mathbf{r}_i) = v(\mathrm{r}), \tag{2.45}$$

and the electron-electron interaction

$$\hat{W} = \frac{1}{2} \sum_{\substack{i,j \\ i \neq j}}^{N} \omega(\mathbf{r}_i, \mathbf{r}_j). \tag{2.46}$$

In this case, the potential operator represents the nuclei-electron electrostatic interaction and $\omega(\mathbf{r}_i, \mathbf{r}_j) = \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$, although the exact form of the electron-electron interaction is not relevant as long as it is symmetric and spin independent.

Let $\mathcal{V}$ be the set of all external potentials, $\hat{V}$, differing from each other by more than a constant and that originate a physical non degenerate ground state wavefunction, Ψ_0, and $\mathcal{W}$ the set of physical non degenerate ground states that differ from each other by more than a phase factor. Also, let $\mathcal{N}$ be the set of physical ground state densities. By construction any map between any of these sets is surjective. If A to be the map from $\mathcal{V}$ to $\mathcal{W}$ and B the map from $\mathcal{W}$ to $\mathcal{N}$ the first Hohenberg-Kohn theorem states that the map $A \circ B$ is invertible. To prove this, one must prove that both A and B are invertible.

Going from the potential to the density is trivial. If we consider an element of $\mathcal{V}$, its mapping to $\mathcal{W}$ is simply done by the Schrödinger equation. Moreover, since we are restricted to non degenerate ground states, no element of $\mathcal{V}$ can be mapped to two different elements of $\mathcal{W}$.

The mapping $\mathcal{W} \to \mathcal{N}$ is done by the definition of density,

$$n_0(\mathbf{r}) = N \sum_{\sigma_1, \cdots, \sigma_N} \int \mathrm{d}\mathbf{r}_2 \cdots \mathrm{d}\mathbf{r}_N \, |\Psi_0(\mathbf{r}, \sigma_1, \mathbf{x}_2, \cdots, \mathbf{x}_N)|^2 \tag{2.47}$$

which also shows that no element of $\mathcal{W}$ can be mapped to two different densities.

We must now analyse the inverse direction of mapping starting with the map $A : \mathcal{W} \to \mathcal{V}$. Consider two different potentials, $\hat{V}$ and $\hat{V}'$, which, by assumption, have the same ground state. Then, using Schrödinger equation

$$\begin{cases} \left[\hat{T} + \hat{V} + \hat{W}\right] |\Psi_0\rangle = E_0 \, |\Psi_0\rangle \\ \left[\hat{T} + \hat{V}' + \hat{W}\right] |\Psi_0\rangle = E_0' \, |\Psi_0\rangle \end{cases}, \tag{2.48}$$

which upon subtraction give

$$\left[\hat{V} - \hat{V}'\right] |\Psi_0\rangle = [E_0 - E_0'] |\Psi_0\rangle \,. \tag{2.49}$$

This statement contradicts the premise that the elements of $\mathcal{V}$ differ by more than a constant and so, by *reductio ad absurdum* we conclude no two elements of $\mathcal{V}$ can map the same element of $\mathcal{W}$. This allows us to say that the map A is injective and (since also surjective) invertible.

Now it is necessary to prove that B is also invertible. Proceeding by *reductio ad absurdum* we assume that the ground states (of different systems) Ψ_0 and Ψ_0' originate the same density $n_0(\mathbf{r}) = n_0'(\mathbf{r})$. The energy associated to each ground state is

$$E_0 = \langle\Psi_0|\hat{H}|\Psi_0\rangle \qquad E_0' = \langle\Psi_0|\hat{H}'|\Psi_0\rangle \,. \tag{2.50}$$

Using the variational principle[1] we can write

$$E_0' < \langle\Psi_0|\hat{H}'|\Psi_0\rangle = \langle\Psi_0|\hat{H} + \hat{V}' - \hat{V}|\Psi_0\rangle = E_0 + \int \mathrm{d}\mathbf{r}[v(\mathbf{r})' - v(\mathbf{r})] \,, \tag{2.51}$$

$$E_0 < \langle\Psi_0'|\hat{H}|\Psi_0'\rangle = \langle\Psi_0|\hat{H}' + \hat{V} - \hat{V}'|\Psi_0\rangle = E_0' + \int \mathrm{d}\mathbf{r}[v(\mathbf{r}) - v(\mathbf{r})'] \,. \tag{2.52}$$

Adding both equations we arrive at the following contradiction

$$E_0 + E_0' < E_0 + E_0' \tag{2.53}$$

which proves that $n_0(\mathbf{r}) \neq n_0'(\mathbf{r})$. These two arguments prove that B is unique (there is a one-to-one correspondence between the elements of $\mathcal{W}$ and $\mathcal{N}$).

Since both maps A and B are invertible then $A \circ B$ is also invertible, or in other words, $\hat{V}$, Ψ_0 and n_0 determine each other uniquely (up to a constant for $\hat{V}$ or a constant phase factor for Ψ_0) through some functional relation, conclusion that forms the first Hohenberg-Kohn theorem.

Theorem 1 *For any system of particles in an external potential, the potential v is uniquely determined, up to a constant, by the ground state density n_0.*

---

[1] It was already established that $\mathcal{V}$ and $\mathcal{W}$ are a bijection and therefore Ψ_0' cannot be the ground state of $\hat{H}$ (and vice-versa). Because of this the equality in the variational principle cannot occur for the cases presented.

As a consequence of the first Hohenberg-Kohn theorem, the existence of the functional $\Psi[n]$ means that every observable can be written as a functional of the density since

$$O[n] = \langle \Psi[n] | \hat{O} | \Psi[n] \rangle \, . \tag{2.54}$$

This is particularly true for the energy. Consider a ground state density, n_0, associated with a given potential, v_0.

$$E_{v_0}[n_0] = \langle \Psi_0[n_0] | \hat{T} + \hat{W} + \hat{V}_0 | \Psi_0[n_0] \rangle = F[n_0] + \int \mathrm{d}\mathbf{r} \; n_0(\mathbf{r}) v_0(\mathbf{r}) \; , \tag{2.55}$$

where the functional

$$F[n_0] = \langle \Psi_0[n_0] | \hat{T} + \hat{W} | \Psi_0[n_0] \rangle \tag{2.56}$$

contains all internal energies of the system. If we consider a different V-representable[1] density, say n, then, by the variational principle, the quantity

$$E_{v_0}[n] = F[n] + \int \mathrm{d}\mathbf{r} \; n(\mathbf{r}) v_0(\mathbf{r}) \tag{2.57}$$

must obey the inequality

$$E[n_0] < E[n], \tag{2.58}$$

which is a statement of the second Hohenberg-Kohn theorem.

Theorem 2 *For a particular* $v(\mathrm{r})$ *the ground state energy of the system is the global minimum of the energy functional; the density that minimizes it is the ground state density.*

Although the Hohenberg-Kohn theorems assure that an observable is a functional of the density, it does not provide a way to extract that information from the density. To do so, some method is necessary, like the scheme proposed by Kohn and Sham.

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[1] If there exists a physical density that is the ground state for a given potential, such density is said to be V-representable.

2.4.2 Kohn-Sham Ansatz

Using the Hohenberg-Kohn theorems we can find the ground state density by looking for the minimum of the energy functional with the restriction for the electron number

$$N = \int \mathrm{d}\mathbf{r}\; n(\mathbf{r}). \tag{2.59}$$

Introducing the Lagrange multiplier μ, we need only to solve the equation

$$\frac{\delta}{\delta n(\mathbf{r})}\left[F[n] + \int \mathrm{d}\mathbf{r}\; n(\mathbf{r})v(\mathbf{r}) - \mu\left(\int \mathrm{d}\;\mathbf{r}n(\mathbf{r}) - N\right)\right] = 0 \Leftrightarrow$$

$$\Leftrightarrow \frac{\delta F[n]}{\delta n(\mathbf{r})} + v(\mathbf{r}) = \mu\;. \tag{2.60}$$

This equation is not solvable since the exact form of $F[n]$ is unknown. Now enters the fundamental hypothesis of Kohn and Sham [19]: we assume the existence of a N non interacting particle system with the same density of the real one, to be used as an auxiliary system. In this system, the Hamiltonian, $\hat{H}_s$, presents only the kinetic and external potential terms,

$$\hat{H}_s = \hat{T}_s + \hat{V}_s.$$

The ground state density must be a solution to

$$\frac{\delta T_s[n(\mathbf{r})]}{\delta n(\mathbf{r})} + v_s(\mathbf{r}) = \mu \tag{2.61}$$

but the exact form of the implicit density functional $T_s[n(\mathbf{r})]$ is only known as an approximation at best. However, being an independent particle system, the ground state can be expressed as a Slater determinant (defined in (2.8)), and the respective orbitals must obey the equation

$$\left(-\frac{1}{2}\nabla^2 + v_s(\mathbf{r})\right)\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r}) \tag{2.62}$$

This also allows to write T_s as an explicit functional of the orbitals

$$T_s[\phi[n_{0s}]] = -\frac{1}{2}\sum_{i=1}^{N}\int \mathrm{d}\mathbf{r}\ \phi_i^\dagger[n_{0s}]\nabla^2\phi_i[n_{0s}]\ , \tag{2.63}$$

and the ground state density as

$$n_{0s}(\mathbf{r}) = \sum_{i=1}^{N}|\phi_i(\mathbf{r})|^2\ . \tag{2.64}$$

This allows to easily solve the independent particle problem. The Kohn-Sham approach now starts by rearranging the terms in the energy functional for the interacting system

$$\begin{aligned} E_{v_0}[n] &= T[n] + W[n] + \int \mathrm{d}\mathbf{r}\ n(\mathbf{r})v_0(\mathbf{r}) \\ &= (T[n] - T_s[n]) + (W[n] - E_H[n]) + T_s[n] + E_H[n] + \int \mathrm{d}\mathbf{r}\ n(\mathbf{r})v_0(\mathbf{r}) \\ &= T_s[n] + E_H[n] + \int \mathrm{d}\mathbf{r}\ n(\mathbf{r})v_0(\mathbf{r}) + E_{xc}\ , \end{aligned} \tag{2.65}$$

where E_H is the Hartree energy (the classical Coulomb interaction of the electron density with itself),

$$E_H[n] = \frac{1}{2}\iint \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\ . \tag{2.66}$$

The E_{xc} term, which is written as

$$E_{xc}[n] = T[n] - T_s[n] + W[n] - E_H[n]\ , \tag{2.67}$$

is called the exchange-correlation energy. It is a functional of the density and (in a certain way) represents the difference between the real system and the non interacting one (through the first two terms), and the non classical part of the electron-electron interaction (the last two terms).

Minimization of (2.65) translates into

$$\frac{\delta T_s[n(\mathbf{r})]}{\delta n(\mathbf{r})} + v(\mathbf{r}) + \int \mathrm{d}\mathbf{r}'\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \frac{\delta E_{xc}[n(\mathbf{r})]}{\delta n(\mathbf{r})} = \mu\ . \tag{2.68}$$

Comparing (2.61) with (2.68) we see that the two equations are formally identical if we identify (neglecting the constant terms)

$$v_s[n](\mathbf{r}) = v[n](\mathbf{r}) + \int \mathrm{d}\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + v_{xc}[n](\mathbf{r}) \ , \tag{2.69}$$

where the exchange-correlation potential is defined as

$$v_{xc}[n](\mathbf{r}) = \frac{\delta E_{xc}[n(\mathbf{r})]}{\delta n(\mathbf{r})} \ . \tag{2.70}$$

Substitution of (2.69) into (2.62) gives the Kohn-Sham equations, which solved self-consistently would give the exact ground state if the exact form of the exchange-correlation potential was known.

Before proceding, there are a couple of valuable observations to be made. In Kohn-Sham theory, the wavefunctions $\{\phi_i\}$ and eigenvalues $\{\epsilon_i\}$ do not have any direct physical interpretation, except that they allow to derive useful quantities (like the density). There is however one exception: for a finite system, the highest occupied eigenvalue equals minus the ionization energy [1]:

$$\epsilon_N = -IP \tag{2.71}$$

This quantity also relevant in describing the long range behaviour of the system since the asymptotic density is regulated by the occupied state with the highest eigenvalue [23].

Also, although both the Kohn-Sham and Hartree-Fock equations have the same functional form, the former contains only local terms while the later are evaluated using a non-local Coulomb term. Therefore, Kohn-Sham orbitals cannot be identified with Hartree-Fock orbitals.

2.4.3 Exchange-Correlation Functionals

Given the definition for the exchange-correlation energy in (2.67) it can be divided in two terms, the exchange and correlation energies

$$E_{xc}[n] = E_x[n] + E_c[n] \ , \tag{2.72}$$

Frequently $E_{xc}[n]$ is also written as an integral

$$E_{xc}[n] = \int \mathrm{d}\mathbf{r}\; n(\mathbf{r})\epsilon_{xc}(n(\mathbf{r}))\ , \tag{2.73}$$

where ϵ_{xc} is the exchange-correlation energy per particle of the system. This quantity is also separable in each of its (correlation and exchange) components.

Since the exact form of the functional is not known there is a certain liberty to the construction of the functional. In theory, however, the functional should obey a set of physical constrains (obeyed by the exact functional) [17]. For example, the exchange functional should scale as

$$\begin{aligned} n_\lambda(\mathbf{r}) &= \lambda^3 n(\mathbf{r}) \\ E_x[n_\lambda] &= \lambda E_x[n] \end{aligned}\ , \tag{2.74}$$

while the global exchange-correlation functional is restrained by the Lieb-Oxford condition

$$E_x[n_\lambda] \le E_{xc}[n_\lambda] \le 2.273 E_x^{LDA}[n_\lambda]\ . \tag{2.75}$$

Other properties apply, in particular the adiabatic connection formula [10].

Consider a normalized and antisymmetric wavefunction Ψ_n^λ that yields density n and also minimizes $\langle \hat{T} + \lambda \hat{W} \rangle$, where the constant λ belongs to the range $[0, 1]$. For the case $\lambda = 0$, $\Psi_n^{\lambda=0}$ represents the non-interacting wavefunction (the Kohn-Sham wavefunction) while in the case $\lambda = 1$ the interacting wavefunction is recovered. Using equation (2.67), the exchange-correlation energy for Ψ_n^λ is written as

$$\begin{aligned} E_{xc} &= \langle \Psi_n^\lambda | \hat{T} + \lambda \hat{W} | \Psi_n^\lambda \rangle \Big|_{\lambda=1} + \langle \Psi_n^\lambda | \hat{T} + \lambda \hat{W} | \Psi_n^\lambda \rangle \Big|_{\lambda=0} - E_H[n] \\ &= \int_0^1 \mathrm{d}\lambda \frac{\mathrm{d}}{\mathrm{d}\lambda} \langle \Psi_n^\lambda | \hat{T} + \lambda \hat{W} | \Psi_n^\lambda \rangle - E_H[n]\ , \end{aligned} \tag{2.76}$$

Using the Feynman-Hellman theorem

$$\frac{\mathrm{d}\langle O \rangle}{\mathrm{d}\lambda} = \langle \Psi | \frac{\mathrm{d}\hat{O}}{\mathrm{d}\lambda} | \Psi \rangle\ , \tag{2.77}$$

this last equation can be rewritten as

$$E_{xc}[n] = \int_0^1 \mathrm{d}\lambda \, \langle \Psi_n^\lambda | \hat{W} | \Psi_n^\lambda \rangle - E_H[n] \tag{2.78}$$

Since the wavefunctions originate the physical density, the Hartree energy term can be absorbed in the integral

$$\begin{aligned} E_{xc}[n] &= \int_0^1 \mathrm{d}\lambda \left[\langle \Psi_n^\lambda | \hat{W} | \Psi_n^\lambda \rangle - E_H[n] \right] \\ &= \int_0^1 \mathrm{d}\lambda \; E_{xc}^\lambda[n] \end{aligned} \tag{2.79}$$

so that the integrand is comprised of potentials terms only, the kinetic contribution to $E_{xc}[n]$ having been absorbed by the coupling constant integration. This formula is known as the adiabatic connection formula since it connects the non-interacting Kohn-Sham orbitals ($\lambda = 0$) to the real ones ($\lambda = 1$) through a set of partially interacting (and non physical) systems.

Available functionals do not always obey all of the requisites imposed by the theory. This has some implications on their effectiveness in calculations but nonetheless, it is possible to build increasingly precise (and therefore complex) functionals.

2.4.3.1 Jacob's Ladder

The several degrees of approximation for the exchange-correlation functional are usually presented in what is called the Jacob's Ladder[1]. This construction ranges from the rudimentary "Hartree World" (of no correlation) to the desired chemical accuracy and in the rungs between lay the several functional approximations to E_{xc}.

The simplest approximation for E_{xc} is the local density approximation (LDA). In this scheme, the exchange-correlation energy of the system is locally equal to the exchange-correlation energy of the homogeneous electron gas (heg) of the

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[1] In biblical terms, Jacob's ladder is a staircase ranging from Earth to Heaven (hence prompting the comparison) that appears in a dream to the biblical Patriarch Jacob. Said event is described in the Book of Genesis.

same density, ϵ_{xc}^{heg}, making E_{xc} the integral

$$\begin{aligned} E_{xc}^{LDA}[n] &= \int \mathrm{d}\mathbf{r}\; n(\mathbf{r})\epsilon_{xc}^{heg}(n(\mathbf{r})) \\ &= \int \mathrm{d}\mathbf{r}\; n(\mathbf{r})(\epsilon_{x}^{heg}(n(\mathbf{r})) + \epsilon_{c}^{heg}(n(\mathbf{r})))\;. \end{aligned} \tag{2.80}$$

Although the ϵ_x^{heg} term is exactly known,

$$\epsilon_x^{heg} = -\frac{3}{4\pi}(3\pi^2 n)^{1/3}\;, \tag{2.81}$$

for correlation term analytic expressions are known only for certain limits [10]: in the high-density case we have

$$\epsilon_c^{heg} \approx c_0 \ln(r_s) - c_1 + c_2 r_s \ln(r_s) - c_3 r_s + \cdots \tag{2.82}$$

and for the low-density case

$$\epsilon_c^{heg} \approx -\frac{d_0}{r_s} + \frac{d_1}{r_s^{3/2}} + \cdots\;, \tag{2.83}$$

where

$$r_s = \left(\frac{3}{4\pi n}\right)^{1/3} \tag{2.84}$$

is the Wigner-Seitz radius. For intermediate values of the density, ϵ_c^{heg} is calculated using Monte-Carlo methods, and the coefficients of (2.82) and (2.83) can be found by interpolation in the respective regimes.

The LDA works reasonably well for several properties (atomic and molecular energies, equilibrium geometries and vibrational frequencies are reproduced within a few percent error) but it presents some deficiencies: LDA does not produce stable negative ions and, due to wrong asymptotic behaviour, band gaps and eigenvalues typically present large errors.

In order to improve the approximations for E_{xc}, gradient terms are introduced, thus contemplating the effects of a non homogeneous electron gas. Historically, this was done by writing the xc-functional in a way reminiscent of a Taylor expansion, in what is called the gradient expansion approximation (GEA) [10],

$$E_{xc}[n] = \int \mathrm{d}\mathbf{r}\; n(\mathbf{r})\epsilon_{xc}^{heg}(n)F_{xc}(n, \nabla n, \nabla^2 n, \cdots) \tag{2.85}$$

$$\approx \int \mathrm{d}\mathbf{r}\; n(\mathbf{r})\left(\epsilon_{xc}^{heg}(n) + Cs^2 + \cdots\right)\ , \tag{2.86}$$

where the $F_{xc}(n, \nabla n)$ is a dimensionless term that presents all the corrections to the heg and

$$s = \frac{|\nabla n|}{2k_f n}\ , \tag{2.87}$$

is sometimes called the reduced density gradient [10] (k_f is the Fermi moment). Analytical expressions for this expansion can be calculated [14] [36], however, the lack of higher order terms results in violation of relevant constrains and often leads worse results than LDA.

In order to surpass the difficulties presented by GEA, the family of generalized gradient approximations (GGA), with general form

$$E_{xc}^{GGA}[n] = \int \mathrm{d}\mathbf{r}\; n(\mathbf{r})\epsilon_{xc}^{GGA}(n) \tag{2.88}$$

$$= \int \mathrm{d}\mathbf{r}\; n(\mathbf{r})\epsilon_{xc}^{heg}(n)F_{xc}^{GGA}(n, \nabla n)\ , \tag{2.89}$$

was developed.

Contrarily to GEA, GGA are not derived from systematic higher order derivation. Different approaches can be taken while building a GGA: although many are built to obey as many of the exact properties as possible by introducing adequate terms (some of which may have an empirical input) there is an important class of GGAs that only care about the results obtained with the functionals, regardless of the physical constrains they obey. Since there is a certain freedom to the construction, it is possible to find a myriad of functionals (B88 [2], LYP [22], PW91 [30] are some of them). As an example let us consider the GGA proposed by Perdew, Burk and Ernzerhof (PBE) [29]. The exchange part is

$$\begin{aligned} \epsilon_x^{PBE} &= \epsilon_x^{heg} F_x^{PBE} \\ F_x^{PBE} &= 1 + k - \frac{k}{1 + (\mu s^2/k)} \ . \end{aligned} \tag{2.90}$$

Here k and μ are both numerical factors with values $k = 0.804$ and $\mu = 0.21951$. The correlation part is, as usually, much more complicated to write, so it will not be presented here. Nonetheless, both parts depend up to the first derivative of the density.

In general, GGA present good results for energy calculations but fail to reproduce the asymptotic behaviour of v_{xc}.

Following GGA, the next functional family is the meta-generalized gradient approximation (meta-GGA, mGGA),

$$E_{xc}^{mGGA}[n] = \int \mathrm{d}\mathbf{r} \ n(\mathbf{r}) \epsilon_{xc}^{mGGA}(n, \nabla n, \nabla^2 n, \tau) \ . \tag{2.91}$$

These functionals include not only a second order derivative but also the Kohn-Sham orbital kinetic energy densities

$$\tau(\mathbf{r}) = \frac{1}{2} \sum_i |\nabla \phi_i|^2 \ , \tag{2.92}$$

which are implicit functionals of the density.

The next step of the ladder will show the hyper-GGA functionals which include an obrital dependency through the Hartree-Fock exchange. Hybrid functionals are a subset of the hyper-GGA. Further climbing will show functionals that depend on virtual orbitals.

2.4.3.2 Hybrid Functionals

Exchange is frequently the dominant part of the exchange-correlation functional giving motivation to treat this part of the functional exactly. The original idea for this method was proposed by Becke [3] and makes use of the adiabatic connection formula (2.78) by approximating it to an interpolation at the extremes

$$E_{xc}[n] = \int_0^1 \mathrm{d}\lambda \; E_{xc}^{\lambda}[n] \approx \frac{1}{2}(E_{xc}^{\lambda=0}[n] + E_{xc}^{\lambda=1}[n]) \; , \tag{2.93}$$

in what is called the "half-and-half" approximation. Here, $E_{xc}^{\lambda=1}[n]$ is simply the functional for the interacting system and it can be approximated by any other functional available (in his 1993 paper, Becke used the local spin density approximation). At the lower limit however, the functional reduces to the exact exchange which can be exactly calculated using the Kohn-Sham Slater determinant. In practice the Kohn-Sham determinant is approximated by the Hartree-Fock determinant.

More sophisticated functionals have since been presented in the literature. In 1996, Perdew, Burke and Ernzerhof proposed the hybrid [31]

$$E_{xc}^{\mathrm{hyb},\lambda} = E_{xc}^{\mathrm{DFA},\lambda} + (E_x - E_{xc}^{\mathrm{DFA}})(1-\lambda)^{m-1} \; , \tag{2.94}$$

where DFA is a LDA or a GGA and m an integer such that $m \geq 1$. Using equation (2.78) their functional is written as

$$E_{xc}^{\mathrm{hyb}} = \int_0^1 \mathrm{d}\lambda \; E_{xc}^{\mathrm{hyb},\lambda} = E_{xc}^{\mathrm{DFA}} + \frac{1}{m}(E_x - E_{xc}^{\mathrm{DFA}}) \; . \tag{2.95}$$

In order to obtain m they argue that its value should be equal to the lowest order of perturbation theory provinding adequate results in the λ expantion of the exact $E_{xc}^{hyb,\lambda}$

$$E_{xc}^{hyb,\lambda} \approx c_0 + c_1\lambda + \cdots + \lambda_{m-1}c_m \; , \tag{2.96}$$

which should differ according to the system in analysis; in practice the standard value is $m = 4$ [31]. The PBE0 functional is the particular case when DFA is the PBE.

Empirical hybrids also exist. One of the most famous is B3LYP (Becke, three-parameter, Lee-Yang-Parr) [35]

$$E_{xc}^{\mathrm{B3LYP}} = (1-a)E_x^{\mathrm{LDA}} + aE_x + bE_x^{\mathrm{B88}} + cE_c^{\mathrm{LYP}} + (1-c)E_c^{\mathrm{LDA}} \; , \tag{2.97}$$

where the constants a,b and c are chosen to best reproduce the data from the G2 set.

In general, hybrids are quite accurate in terms of energies but they will not satisfy the exact properties that their DFA does not, and therefore may fail for certain specific systems (for example, since B3LYP does not reproduce the correct homogeneous limit it fails for certain metals [38]).

Chapter 3

Implementation Details

In order to solve the Hartree-Fock equations the Atomic Pseudopotential Generator (APE) [28] program was modified as to include this set of differential equations. This program is capable of solving the Kohn-Sham equations (for both the non-relativistc and relativistc cases) in a radial real space grid, using the exchange-correlation functionals from the LIBXC library [25].

The code was written using FORTRAN 90 for the most part, but since numerical methods are computed using the GNU Scientific Library (GSL) [12], C interfaces are needed in order to call the functions.

3.1 Self-consistent field cycle

Due to the implicit nature of the exchange and potential terms, direct solution of the differential equations is not possible. Therefore, such as in solving the Kohn-Sham, an iterative method is used, dubbed self-consistent field cycle (SCF), and the algorithm goes as follows:

```
$t = 0$ ;
while $t \leq$ MaxIter do
    Orthogonalize $\{\phi_i^t\}$ ;
    Update $V$, $X$, $\epsilon_{ij}$ ;
    Solve (2.39) to obtain $\{\phi_i^{t+1}\}$ and $\{\epsilon_i^{t+1}\}$ ;
    if Calculation converged then
        exit ;
    else
        $\phi_i^{t+1} \leftarrow \mathrm{Mix}(\phi_i^{t+1}, \phi_i^t)$ ;
        $t \leftarrow t + 1$ ;
    end
end
```

The orthogonalization of the states batches was done using the modified Gram-Schmidt [13], in order to avoid numerical instability. Initially, the SCF cycle did not include the orthogonalization process. However, since the algorithm did not converge correctly when more than one orbital was present, and the final orbitals did not obey the orthogonality rules, the routine was implemented in order to analyse its influence (this is discussed in section 4.3).

Updating the potential and exchange terms merely implies computing equations (2.41) and (2.42) with the new iteration of the wavefunction. To calculate the off-diagonal energy parameters we use the same process as in [11]. We start by considering the equations for two distinct states and, for each one take the inner product with the other. Depending on the occupations the resulting equations are then summed or subbtracted. If the states have different occupation, subraction gives

$$\epsilon_{ij} = \frac{\theta_j}{\theta_j - \theta_i} \int \mathrm{d}r \; r \left[R_j X_i - R_i X_j + R_i (Y_i - Y_j) R_j \right] \;, \tag{3.1}$$

while for same occupation

$$2\epsilon_{ij} = \langle R_i | \mathcal{L} | R_j \rangle + \langle R_i | \mathcal{L} | R_j \rangle + \int \mathrm{d}r \; r \left[R_j X_i + R_i X_j + R_i (Y_i + Y_j) R_j \right] \tag{3.2}$$

where

$$\mathcal{L} = -\frac{1}{2}\frac{\mathrm{d}^2}{\mathrm{d}r^2} - \frac{1}{r}\frac{\mathrm{d}}{\mathrm{d}r} - \frac{Z}{r} + \frac{l(l+1)}{2r^2}\ . \tag{3.3}$$

After a cycle of the iteration the new wavefunctions are mixed with the ones of the previous iteration. This is commonly done in order to avoid large fluctuations in the solutions that would dificult convergence. Two types of mixing are available, linear and modified Broyden [18] methods. In the linear mixing method, as the name implies, the new iteration wavefunctions are merely a linear combination of the current and previous interations,

$$\phi_i^{t+1} = a\phi_i^t + (1-a)\phi_i^{t+1}\ . \tag{3.4}$$

The modified Broyden method is more complicated and its discussion is done in [18] but, in short, it is built using a least square minimization of the error in the iteration increment. This is the standard method of mixing since it greatly reduces the number of iterations needed to reach convergence.

The remaining important aspects of the algorithm (solution of (2.39) and some numerical aspects) are discussed bellow.

3.2 Solution of the eigenvalue problem

To solve the differential equations (2.39), the shooting method is used which allows to simultaneously find the eigenvalue and the wavefunctions. In order to apply this method we start by separating the second order differential equations on the wavefunction (here descrived by f) into a set of two first order differential equation on f and its derivative g. The method then goes as follows [28]

1. Choose an arbitrary value for the eigenvalue, ϵ;
2. Choose an arbitrary initial value for f at the practical origin (r_0) and practical infinity (r_∞);
3. Compute the initial values for $g(r_0)$ and $g(r_\infty)$. This is done using the small and large r expansions for the wavefunction;

4. Using the initial conditions, integrate f and g from r_0 up to an intermediate point, r_m, thus obtaining $f^{\rightarrow}(r)$ and $g^{\rightarrow}(r)$;

5. Integrate f and g from r_∞ to r_m, thus obtaining $f^{\leftarrow}(r)$ and $g^{\leftarrow}(r)$;

6. Multiply $f^{\leftarrow}(r)$ and $g^{\leftarrow}(r)$ by $\frac{f^{\rightarrow}(r_m)}{f^{\leftarrow}(r_m)}$. This process makes f continuous;

7. Evalulate $\tau(\epsilon) = \left[g^{\rightarrow}(r_m) - g^{\leftarrow}(r_m)\right]_\epsilon$.

Since whenever $\tau(\epsilon) = 0$ we have that ϵ is an eigenvalue of the functions, finding them is reduced to finding the roots of τ. Several possible eigenvalues may be found; in such case, to find the correct one, care must be taken to assure the calculated wavefunctions present the adequate number of nodes.

Integration of the differential equations is made resorting to adaptative step methods in order to obtain the best accuracy possible.

3.3 Grids

Due to the localized nature of atomic orbitals, in real space methods it becomes convenient to have a higher concentration of grid points near the regions where the wavefunction varies the most, in order to assure numerical precision. This can be assured, for example, using a coordinate transformation like Fischer [11],

$$\rho = \log(Zr) \Leftrightarrow r = \frac{e^\rho}{Z} \ , \tag{3.5}$$

and Chernysheva [5]

$$x = \alpha r + \beta \log(r) \ . \tag{3.6}$$

In the same spirit, APE has implemented two types of logarithmic grid to be used, defined as

$$r_i = b e^{ai} \ , \tag{3.7}$$

(which is equivalent to (3.5) through an appropriate choice of coefficients) and

$$r_i = b e^{a(i-1)} \ , \tag{3.8}$$

where the parameters a and b are determined by the extremes and the number of points of the grid. A linear mesh is also available.

Since the differential equation integration is usually made in an adaptative grid, passing to the logarithmic grid makes use of spline interpolation methods. Several methods are supplied by the GSL from which cubic splines are used (a description of the method is given in [33]). Numerical differentiation and integration are evaluated using spline interpolation, although the former can also be evaluated with finite difference methods.

Chapter 4

Numerical results

In this section we present the results obtained using the implementation done on the Atomic Pseudopotential Engine (APE) [28].

In short, the hydrogen and helium atoms are correctly solved but for lithium and above we found some issues that did not allow the correct solution to be found.

4.1 Hydrogenoid Series

The hydrogen atom is the only atom for which the Schrödinger equation is exactly solvable. As such the energy and wavefunctions are readily available and present (e.g. [21]) a good precision test for any atomic implementation. The energy of a hydrogenoid atom is simply given by

$$E_{teo} = -\frac{Z^2}{2} \ . \tag{4.1}$$

The calculated relative error,

$$\Delta = \frac{E_{calculated} - E_{teo}}{E_{teo}} \ , \tag{4.2}$$

for the hydrogenoid series is presented in figure 4.1. The obtained errors are of a small magnitude and only significant for large atomic numbers ($Z \geq 50$).

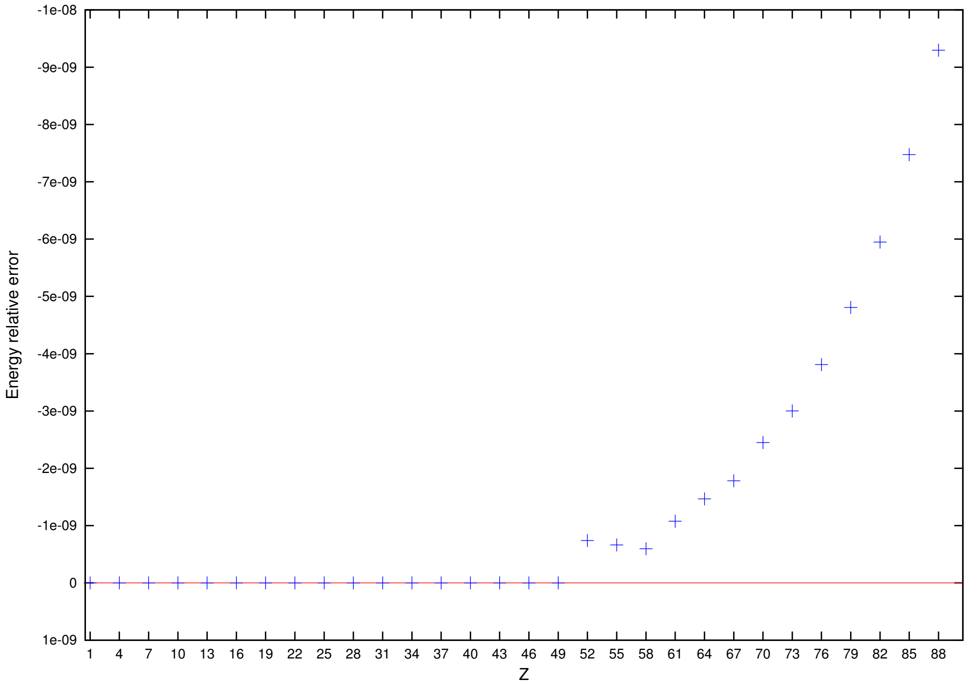

Figure 4.1: Relative errors (dots) for the hydrogenoid series.

4.2 Helium Atom

The Hartree-Fock results for the helium atom are presented in table 4.1 and figure 4.2. Our energy values are in good agreement with those obtained using ORCA (using an Ahlrichs triple zeta valence basis set) [27] and the results published by C. F. Fischer [11]; the wavefunctions are also superposable.

4.3 Lithium Atom

As previously stated, the Hartree-Fock calculation for the lithium atom did not converge to the expected values and, therefore, it is not possible to present any proper result. Still we present some data from the simulations in figure 4.3 and table 4.2

Since lithium presents the first atom with a second occupied shell, the orthogonalization process now becomes relevant. Although the scf converged without

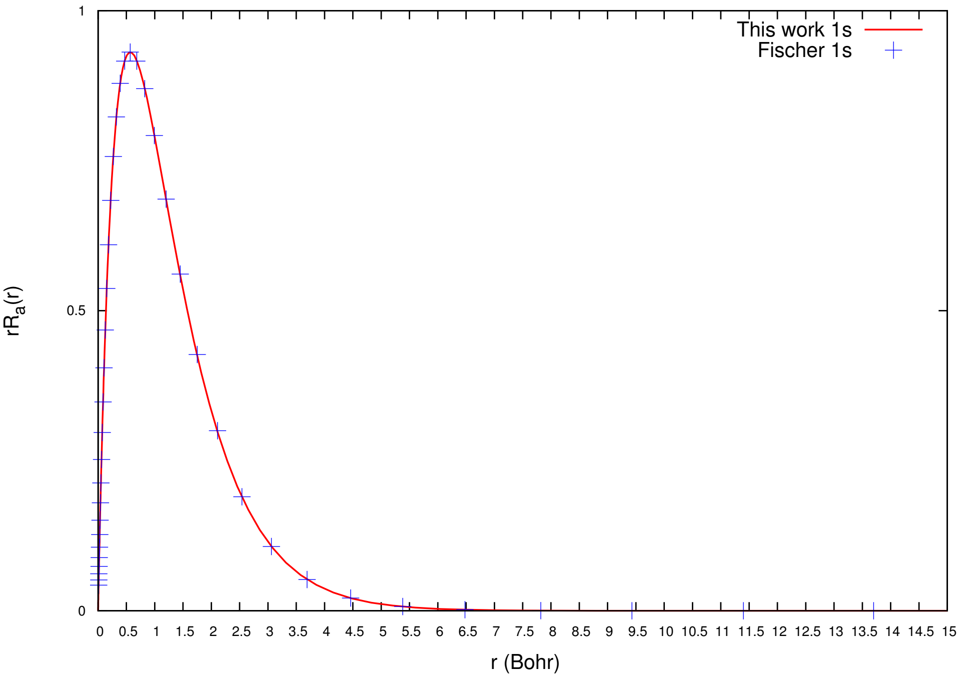

Figure 4.2: Comparison between $1s$ wavefunction of He obtained in this work and the results from C. F. Fischer [11].

Atom		This work		Ref [11]	Ref [27]
He	E_k	2.861679		2.861680	2.859894
	E_{ee}	2.051536	-5.723361	-5.723360	-5.719790
	E_{ne}	-6.749129			
	E_x	-1.025768			
	E_{tot}	-2.861681		-2.861680	-2.859895
	ϵ_{1s}	-0.91796		-0.91796	-0.91687

Table 4.1: Calculated energies for the helium atom. Here, E_k is the kinetic energy, E_{ee} the electron-electron interaction energy, E_{ne} the nucleus-electron interaction energy, E_x the exchange energy and ϵ_i the orbital energies. All energy values are in Hartree units. The ORCA values were computed using a Ahlrichs triple zeta valence basis set.

forcing the orthogonalization, the obtained orbitals ($1s$ and $2s$ in this case) were not orthogonal, violating equation (2.22).

One would expect the calculations to converge to orthogonal solutions, which happens naturally in solving the Kohn-Sham equations, but without the orthogonalization process this did not happen. However, the Hartree-Fock implementations found in literature present such a procedure, and a possible reason is because the computation of the off-diagonal energy parameters (the Lagrange multipliers) requires the orbitals to be orthogonal. Although this is true for the first iteration (when the orbitals are hydrogenoid) the presence of the non homogeneous term in the next iteration may lead to overlap, and ultimately a non orthogonal "solution".

A different implementation was attempted, using the set of differential equations obtained by minimizing the energy with the explicit form of the equations (2.35) and (2.36) (as done in [39]). This effectively makes the potential term equal for every orbital, by writing it as a sum of the Hartree,

$$v_H(r) = \sum_a \int \frac{\omega_a |R_a(r')|^2}{r_<} r'^2 \, \mathrm{d}r' \ , \tag{4.3}$$

and Coulomb potentials, and placing every orbital dependent term in the rewritten inhomogeneous term

$$X_a = -\sum_b \sum_{L=|l_a-l_b|}^{l_a+l_b} \frac{1}{\omega_a} \Theta^L_{ab} Y^L_{ab}(r) R_b(r) \ . \tag{4.4}$$

The main difference of this formulation is that here the inhomogeneous term is never null, making the solution of the hydrogen and helium atoms qualitatively similar to the lithium one in the original implementation.

It was found that the eigenvalues bracketing even for the hydrogen and helium atoms was not possible, due to the alteration created by the inhomogeneous term, the same effect saw in solving the lithium atom. This effect can be viewed in figure 4.4, where the logarithmic derivative of the $1s$ wavefunction of helium is plotted against the eigenvalue values near the correct eigenvalue (we choose to plot helium's data since there comparison with a successful calculation was

	$\langle R_{1s}\|R_{1s}\rangle$	$\langle R_{1s}\|R_{2s}\rangle$	$\langle R_{2s}\|R_{2s}\rangle$
With	1.000	0.000	1.000
Whithout	1.000	-0.232	1.000

	E_k	E_{pot}	E_{tot}	ϵ_{1s}	ϵ_{2s}
With	7.322731	-14.743800	-7.421070	-2.55763	-0.16031
Without	7.322027	-15.035199	-7.713171	-2.71609	-0.10128
Ref. [11]	7.432727	-14.865454	-7.432727	-2.47774	-0.19632

Table 4.2: Upper table: final results for the inner product of the $1s$ and $2s$ orbitals with and without the orthogonalization process. Lower table: Energy results for the lithium atom with and without orthogonalization process, and the results from C. F. Fischer. In here $E_{pot} = E_{ne} + E_{ee} + E_x$.

available). The Kohn-Sham plot was created using the default functionals in APE, Perdew-Wang LDA [32] correlation and LDA exchange [4] [8] functionals.

The exact origin of this problem is yet to be determined but it is known that it arises during the bracketing steps. It could be due to the long range behaviour of the inhomogeneous term introducing instabilities but this remains an hypothesis.

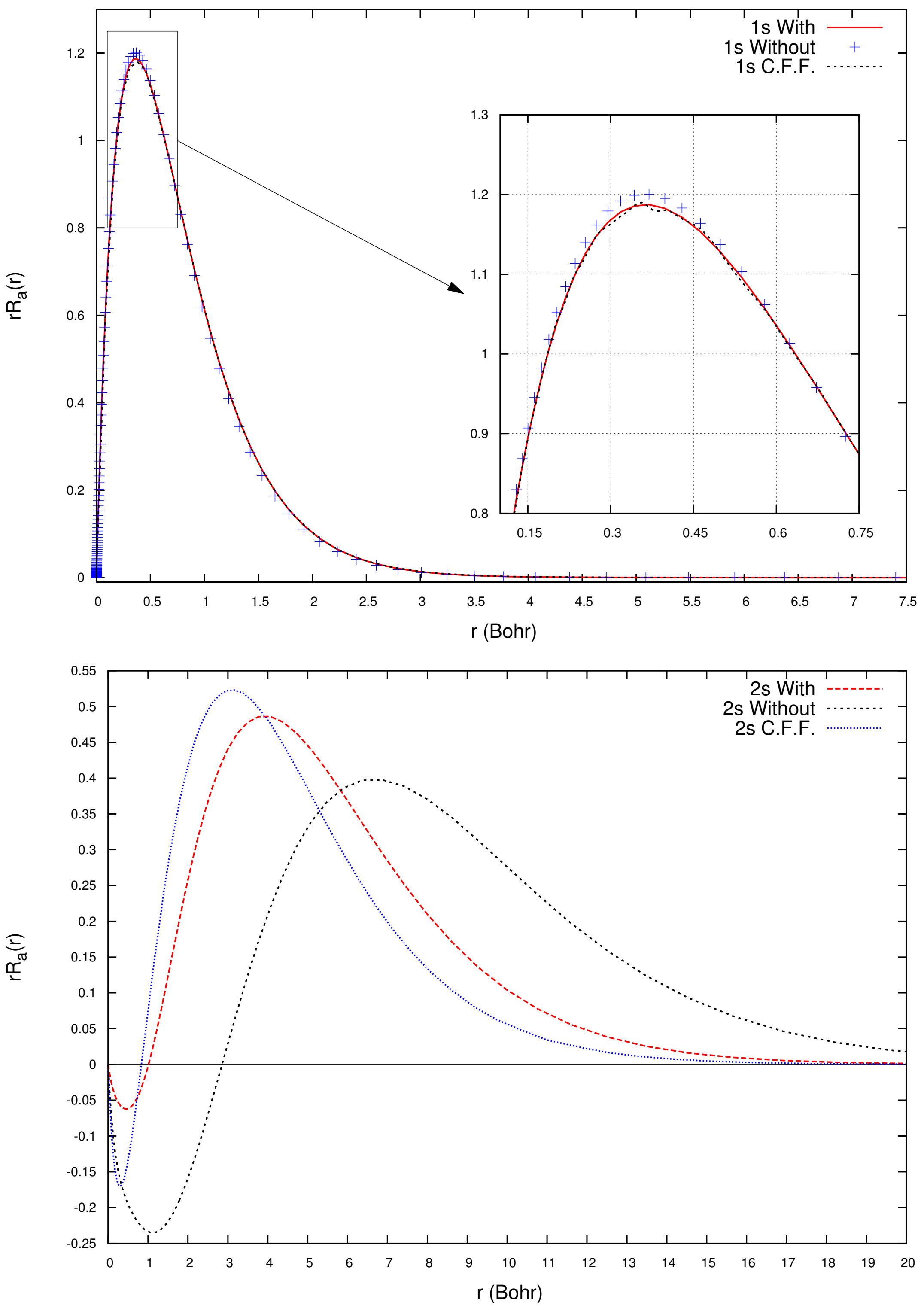

Figure 4.3: Comparison between the 1*s* (up) and 2*s* wavefunctions (down) obtained for Li, with and without orthogonalization process, and the results from C. F. Fischer [11].

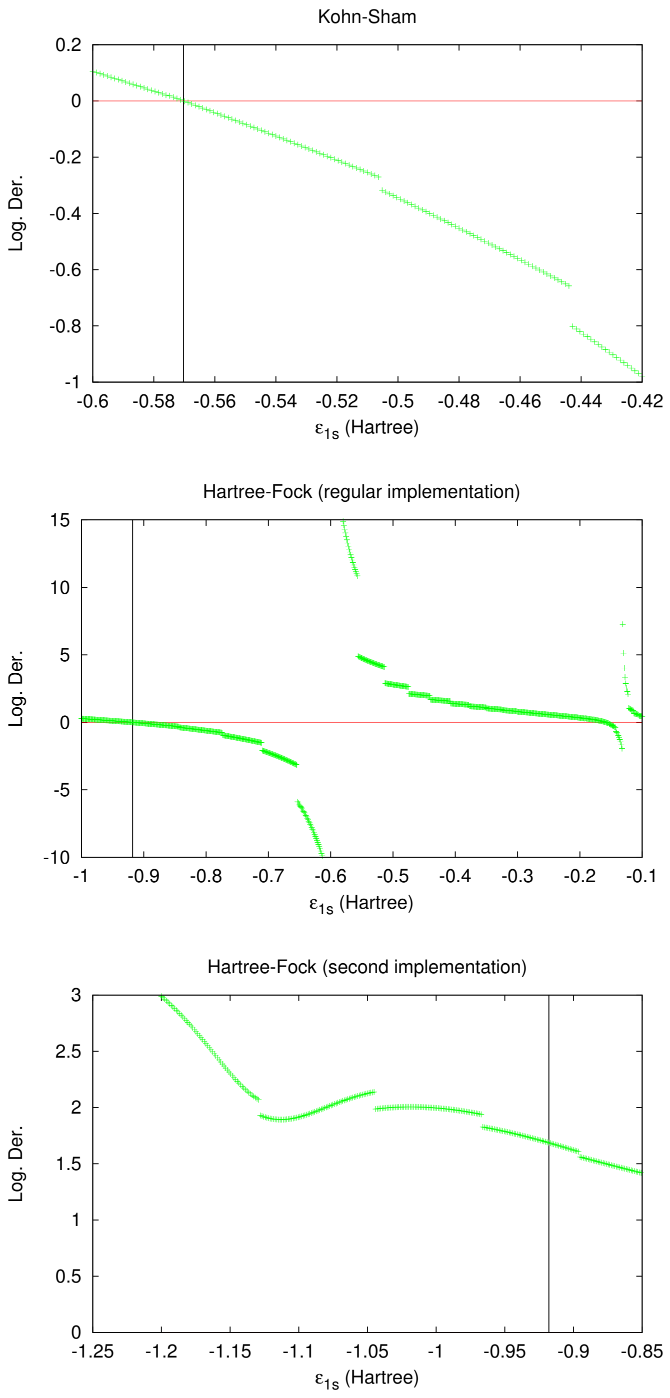

Figure 4.4: Logarithmic derivative curves against the $1s$ eigenvalue for helium, in the Kohn-Sham (KS) (top; functionals described in text), the Hartree-Fock (HF) (middle) and the altered Hartree-Fock (bottom) implementations. The vertical lines represent the correct eigenvalues ($\epsilon_{1s} = -0.57026$ for KS and $\epsilon_{1s} = -0.91796$ for HF) .

Chapter 5

Conclusions and future work

We report on the work done in the implementation of Hartree-Fock and hybrid formulation for atoms in the Atomic Pseudopotential Engine (APE). As said in previous chapters, the global goal of this work was not fully met; since the Hartree-Fock implementation was incomplete, the hybrid formalist could not be implemented and tested.

The main objective for future work is therefore to solve the problems with the Hartree-Fock part of the code. This step should be achieved quickly as no more implementation is required. Still finding the exact nature of the problem can turn out to be problematic as is common of this type of situations. It is also desirable to alter some aspects of the code, for example, create some data structures in order to reduce the amount of calculated quantities and the overall computation time.

Important as it is, this is not the most desirable goal as stated in the introduction: from here we want to proceed to a good implementation of hybrid functionals. This part is mostly comprised by extensive testing of the obtained results. Once achieved, this will allow to proceed even further, to the creation of adequate hybrid pseudopotentials.

References

[1] C.-O. Almbladh and U. von Barth. Exact results for the charge and spin densities, exchange-correlation potentials, and density-functional eigenvalues. *Phys. Rev. B*, **31**:3231–3244, Mar 1985. 21

[2] A. D. Becke. Density-functional exchange-energy approximation with correct asymptotic behavior. *Phys. Rev. A*, **38**:3098–3100, Sep 1988. 25

[3] Axel D. Becke. A new mixing of hartreefock and local densityfunctional theories. *The Journal of Chemical Physics*, **98**[2], 1993. 26

[4] F. Bloch. Bemerkung zur elektronentheorie des ferromagnetismus und der elektrischen leitfhigkeit. *Zeitschrift fr Physik*, **57**[7-8]:545–555, 1929. 38

[5] L.V. Chernysheva, N.A. Cherepkov, and V. Radojevi. Self-consistent field hartree-fock program for atoms. *Computer Physics Communications*, **11**[1]:57 – 73, 1976. 32

[6] E.U. Condon and G.H. Shortley. *The Theory of Atomic Spectra*. Cambridge Univ.Pr.209. Cambridge University Press, 1935. 11

[7] C.J. Cramer. *Essentials of Computational Chemistry: Theories and Models*. Wiley, 2005. 7

[8] P. A. M. Dirac. Note on exchange phenomena in the thomas atom. *Mathematical Proceedings of the Cambridge Philosophical Society*, **26**:376–385, 7 1930. 38

[9] Matthias Ernzerhof and Gustavo E. Scuseria. Assessment of the perdewburkeernzerhof exchange-correlation functional. *The Journal of Chemical Physics*, **110**[11], 1999. 1

[10] C. Fiolhais, F. Nogueira, and M.A.L. Marques. *A Primer in Density Functional Theory*. Lecture Notes in Physics. Springer, 2003. 12, 22, 24, 25

[11] C. Froese-Fischer, T. Brage, and P. Johnsson. *Computational Atomic Structure: An MCHF Approach*. Taylor & Francis, 1997. xi, 12, 14, 30, 32, 35, 36, 38, 39

[12] M. et al Galassi. *GNU Scientific Library Reference Manual*. 29

[13] L. Giraud, J. Langou, and M. Rozloznik. The loss of orthogonality in the gram-schmidt orthogonalization process. *Computers and Mathematics with Applications*, **50**[7]:1069 – 1075, 2005. Numerical Methods and Computational Mechanics. 30

[14] Frank Herman, John P. Van Dyke, and Irene B. Ortenburger. Improved statistical exchange approximation for inhomogeneous many-electron systems. *Phys. Rev. Lett.*, **22**:807–811, Apr 1969. 25

[15] P. Hohenberg and W. Kohn. Inhomogeneous electron gas. *Phys. Rev.*, **136**:B864–B871, Nov 1964. 15

[16] J.D. Jackson. *Classical electrodynamics*. Wiley, 1975. 10

[17] F. Jensen. *Introduction to Computational Chemistry*. Wiley, 2007. 1, 15, 22

[18] D. D. Johnson. Modified broyden's method for accelerating convergence in self-consistent calculations. *Phys. Rev. B*, **38**:12807–12813, Dec 1988. 31

[19] W. Kohn and L. J. Sham. Self-consistent equations including exchange and correlation effects. *Phys. Rev.*, **140**:A1133–A1138, Nov 1965. 19

[20] A. Kramida, Yu. Ralchenko, J. Reader, and and NIST ASD Team. NIST Atomic Spectra Database (ver. 5.2), [Online]. Available:

`http://physics.nist.gov/asd`. National Institute of Standards and Technology, Gaithersburg, MD., 2014. 2

[21] L.D. Landau and Lifshits E.M. *Quantum Mechanics: Non-relativistic Theory*. Course of Theoretical Physics. 9, 34

[22] Chengteh Lee, Weitao Yang, and Robert G. Parr. Development of the colle-salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B*, **37**:785–789, Jan 1988. 25

[23] Mel Levy, John P. Perdew, and Viraht Sahni. Exact differential equation for the density and ionization energy of a many-particle system. *Phys. Rev. A*, **30**:2745–2748, Nov 1984. 21

[24] Per-Olov Löwdin. Quantum theory of many-particle systems. iii. extension of the hartree-fock scheme to include degenerate systems and correlation effects. *Phys. Rev.*, **97**:1509–1520, Mar 1955. 7

[25] Miguel A.L. Marques, Micael J.T. Oliveira, and Tobias Burnus. Libxc: A library of exchange and correlation functionals for density functional theory. *Computer Physics Communications*, **183**[10]:2272 – 2281, 2012. 1, 29

[26] R.M. Martin. *Electronic Structure: Basic Theory and Practical Methods*. Cambridge University Press, 2004. 15

[27] Frank Neese. The orca program system. *Wiley Interdisciplinary Reviews: Computational Molecular Science*, **2**[1]:73–78, 2012. 35, 36

[28] Micael J.T. Oliveira and Fernando Nogueira. Generating relativistic pseudo-potentials with explicit incorporation of semi-core states using ape, the atomic pseudo-potentials engine. *Computer Physics Communications*, **178**[7]:524 – 534, 2008. 29, 31, 34

[29] John P. Perdew, Kieron Burke, and Matthias Ernzerhof. Generalized gradient approximation made simple. *Phys. Rev. Lett.*, **77**:3865–3868, Oct 1996. 26

[30] John P. Perdew, J. A. Chevary, S. H. Vosko, Koblar A. Jackson, Mark R. Pederson, D. J. Singh, and Carlos Fiolhais. Atoms, molecules, solids, and surfaces: Applications of the generalized gradient approximation for exchange and correlation. *Phys. Rev. B*, **46**:6671–6687, Sep 1992. 25

[31] John P. Perdew, Matthias Ernzerhof, and Kieron Burke. Rationale for mixing exact exchange with density functional approximations. *The Journal of Chemical Physics*, **105**[22], 1996. 27

[32] John P. Perdew and Yue Wang. Accurate and simple analytic representation of the electron-gas correlation energy. *Phys. Rev. B*, **45**:13244–13249, Jun 1992. 38

[33] W.H. Press. *Numerical Recipes in C: The Art of Scientific Computing.* Number bk. 4. Cambridge University Press, 1992. 33

[34] J.C. Slater. *Quantum theory of atomic structure. 1 (1960).* International series in pure and applied physics. McGraw-Hill Interamericana, 1960. 12

[35] P. J. Stephens, F. J. Devlin, C. F. Chabalowski, and M. J. Frisch. Ab initio calculation of vibrational absorption and circular dichroism spectra using density functional force fields. *The Journal of Physical Chemistry*, **98**[45]:11623–11627, 1994. 27

[36] P. S. Svendsen and U. von Barth. Gradient expansion of the exchange energy from second-order density response theory. *Phys. Rev. B*, **54**:17402–17413, Dec 1996. 25

[37] A. Szabo and N.S. Ostlund. *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory.* Dover Books on Chemistry Series. Dover Publications, 1996. 5, 6, 7

[38] C. Ullrich. *Time-Dependent Density-Functional Theory: Concepts and Applications.* Oxford Graduate Texts. OUP Oxford, 2012. 15, 28

[39] Xiao Xu and N. A. W. Holzwarth. Projector augmented wave formulation of hartree-fock calculations of electronic structure. *Phys. Rev. B*, **81**:245105, Jun 2010. 13, 37