Orbital dependent functionals in non-collinear spin systems

Pedro Miguel Monteiro Campos de Melo

Department of Physics

University of Coimbra

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To my Parents, for all the books and stories.

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Abstract

Here is presented an initial attempt to develop the necessary equations and algorithms to study non-collinear spin phenomena using the orbital dependent functionals with the open source code OCTOPUS. The main equations derived from the OEP method which allow one to evaluate the exact exchange potential are derived. After, the results for single atoms are presented, together with tests to the numerical implementation when the system is subjected to an initial magnetization direction. The results for the spectra of the Xe_3^+ cluster are presented afterwards and compared with what is obtained from using the LSDA functional with the spin-orbit correction.

Resumo

Aqui apresenta-se uma tentativa inicial de desenvolver as equações e algorítmos necessários para estudar fenómenos relacionados com spin não colinear usando funcionais dependentes de orbitais com o código aberto OCTOPUS. As equações principais que permitem determinar o potencial de troca exacto são derivadas do método OEP. A seguir, apresentam-se os resultados para átomos isolados, juntamente com testes à implementação numérica quando o sistema é sujeito a uma direcção inicial de magnetização. Os resultados para o espectro de absorção do agregado de Xe_3^+ são apresentados depois e comparados com o que é obtido usando o funcional da LDSA com a correcção de spin-órbita.

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Chapter 1

Introduction

1.1 Motivation

Numerical simulation of *ab-initio* theoretical models of many-body systems has been hindered by computational cost, due to the fact that the amount of data needed to be stored increases very quickly with the number of particles. One way to avoid this is by using Density Functional Theory (DFT), which through use of the Hohenberg-Kohn theorems make the ground state particle density the key object. The density is easily obtained from the auxiliar Kohn-Sham system of independent fermions.

Still, the theory needs approximations as the effects of the interaction between the particles are placed in the exchange-correlation energy functional, which exact form is unknown. Approximations can be built through different methods and have become more accurate, propelling the growth of the use of DFT. Despite this, the theory is not flawless.

In [18] the authors have studied the time-dependent DFT results for the photoabsorption of small cationic xenon clusters. When ionized, rare-gas clusters shift their absorption spectrum from the ultra-violet to the visible region. The authors found good agreement between the calculated and experimental peak positions of the spectra, but there were deviations between the strengths of the oscillators. In their analysis, the authors attributed this effect partially to an
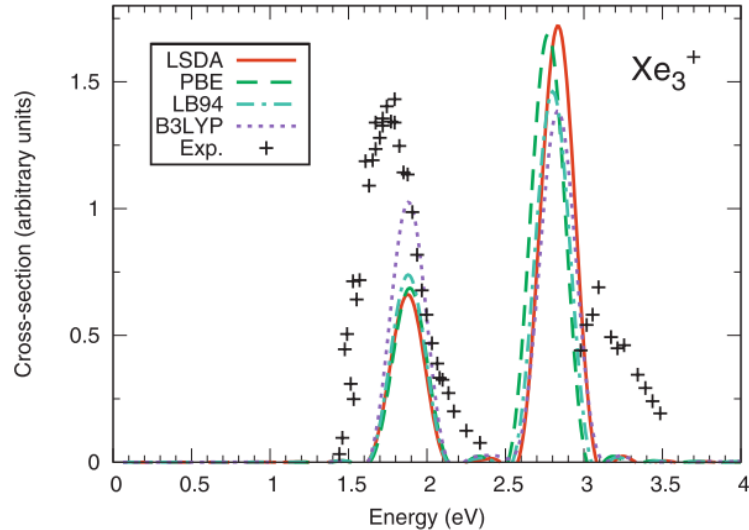
Figure 1.1: Absorption spectrum of the Xe_3^+ cluster, from [18]

unsatisfactory treatment of the exchange energy functional. From preliminary calculations, the authors noticed that the results were improved when adding a fraction of exact exchange, via the B3LYP functional [**?**].

Also, very few numerical implementations have incorporated exact exchange within non-collinear spin DFT, which is needed when one wishes to take into account the effects from spin-orbit coupling, and they are not (mostly) available to the community.

1.2 Objectives

The main objective is to obtain the absorption spectrum of the Xe_3^+ cluster. Doing so will require to study the effects of the exact exchange functional when developed within the formalism of non-collinear spin Density Functional Theory (SDFT) and to implement the resulting equations in the open source code OCTOPUS. As such, it is intended that the following steps are to be taken:

- Development of the equations needed to obtain the exchange potential in

systems with non-collinear spin using the Optimized Effective Potential method (OEP);

- Use the Krieger-Li-Yafrate (KLI) approach to obtain a working approximation of the equations obtained for the exchange potential;

- Implement the equations in the code OCTOPUS;

- Compare the obtained results with the ones given from collinear spin DFT for simple systems;

It should be noted that, since the numerical implementation is general, it can (in theory) be applied to any system.

1.3 Thesis' outline

This section aims to give a general idea of the structure of the thesis, along with the motivation behind it.

In the second chapter an introduction to the N-electron problem in Quantum Mechanics is given. After introducing the Born-Oppenheimer approximation, the Hartree-Fock (HF) method is presented and the expression for the Hartree-Fock exchange energy will be derived, along with the self-consistent formulation of the HF method and the definition of the classical correlation energy. It follows a small introduction to Density Functional Theory, starting with the Hohenberg-Kohn theorems and the Kohn-Sham scheme. Then the ladder of approximations for the xc functional is presented, along with the main difficulties that arise from the choice of each kind of functional. The Optimized Effective Potential (OEP) is explained next, along with its advantages and disadvantages in comparison with the other xc functionals. Finally, in the end of this chapter one has a short introduction to the Time-Dependent Density Functional theory, since one of the objectives of the work present in this thesis is to obtain the absorption spectra of the Xe_3^+ cluster.

In the third chapter one is presented with the formalism behind non-collinear spin Density Functional Theory (SDFT), starting with a derivation of Pauli's equation and followed by what one needs to consider in order to have the non-collinear spin version of the Hohenberg-Kohn theorems. The auxiliary KS system is defined after these considerations, along with the components of the KS potential and magnetic field. Afterwards are discussed the OEP method and the KLI approximation in SDFT and the main equations which allow one to evaluate the exchange potential are derived.

Chapter four contains the results and their analysis. In the first part one has the results obtained for atoms of the first three periods of the Periodic table and the comparison with what was obtained for the same atoms but with the collinear spin formalism. The second part presents the results obtained for the absorption spectra of the Xe_3^+ cluster from both formalisms and the analysis of the simulation data.

Through the appendices one can find more information omitted in the chapters for the sake of brevity. Appendix A contains a few remarks on the conditions needed in order to use the OEP method in non-collinear SDFT. Appendix B has the modifications done upon the final equations in Chapter 3 so that they could be implemented in a subroutine of OCTOPUS and in Appendix C one will find a transcript of said subroutine.

Chapter 2

The N-electron problem in Quantum Mechanics

2.1 The Many-body Hamiltonian

Consider a system of N electrons and M nuclei in condensed matter or molecular physics. For all the practical purpose nuclei can be considered as point like charges and the electrostatic interaction between electrons and nuclei can be described using the usual Coulomb potential in a full non-relativistic scheme. This first part follows what is done in [23]. The full Hamiltonian of the system, in the real space representation, is (in atomic units)[1]

$$\hat{H} = -\sum_{i=1}^{N} \frac{\nabla_i^2}{2} - \sum_{A=1}^{M} \frac{\nabla_A^2}{2m_A} - \sum_{i,A=1}^{N,M} \frac{Z_A}{|\boldsymbol{R}_A - \boldsymbol{r}_i|} + \frac{1}{2}\sum_{\substack{i,j=1 \\ i\neq j}}^{N} \frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} + \frac{1}{2}\sum_{\substack{A,B=1 \\ A\neq B}}^{M} \frac{Z_A Z_B}{|\boldsymbol{R}_A - \boldsymbol{R}_B|}$$

(2.1)

where m_A is the relative mass of the nucleus with respect to the electron, Z_A is the atomic number of the nucleus, $\boldsymbol{R}_A$ represents the nuclear space-coordinates and $\boldsymbol{r}_i$ represents the space coordinates of each electron.

---

[1]Atomic units $\hbar = m_e = e = 4\pi\epsilon_0 = 1$ will be used almost in the entire thesis, except in some specific parts where the reader will be warned.

The usual approach is to use the Born-Oppenheimer approximation [23] in order to solve the time-independent Schrödinger equation. One writes the wave function $\Psi(\boldsymbol{r}_i, \boldsymbol{R}_A)$ as

$$\Psi(\boldsymbol{r}_i, \boldsymbol{R}_A) = \psi(\boldsymbol{r}_i; \boldsymbol{R}_A)\chi(\boldsymbol{R}_A) \tag{2.2}$$

where $\psi(\boldsymbol{r}_i; \boldsymbol{R}_A)$ is a function of the set of coordinates $\boldsymbol{r}_i$ and depends parametrically on $\boldsymbol{R}_A$ and $\chi(\boldsymbol{R}_A)$ is an explicit function of $\boldsymbol{R}_A$.

Now, as the nuclei's mass is greater than that of the electrons (a proton's mass is about 1830 times the mass of an electron) the time it takes for the electrons to readjust their position in response to the nuclear motion can be neglected. This means that the electrons move adiabatically with the nuclei. Also, due to their much larger mass, the nuclei wave function will be extremely more localized, almost like the classical description of point charges. So, there must be a region in space where

$$|\nabla_A \chi(\boldsymbol{R}_A)| \gg |\nabla_A \psi(\boldsymbol{r}_i; \boldsymbol{R}_A)| \tag{2.3}$$

So, when applying the operator of the nuclei kinetic energy to the wave function, one can ignore the variation of the electronic part in comparison with the nuclear one. This will lead to the following equation

$$\frac{\left[\hat{T}_e + \hat{V}_{ee}(\boldsymbol{r}_i) + \hat{V}_{eN}\left(\boldsymbol{r}_i, \boldsymbol{R}_A\right)\right]\psi(\boldsymbol{r}_i; \boldsymbol{R}_A)}{\psi(\boldsymbol{r}_i; \boldsymbol{R}_A)} + \frac{\left[\hat{T}_N + \hat{V}_{NN}(\boldsymbol{R}_A)\right]\chi(\boldsymbol{R}_A)}{\chi(\boldsymbol{R}_A)} = E \tag{2.4}$$

where one can identify the following operators as the electron kinetic energy,

$$\hat{T}_e = -\sum_{i=1}^{N} \frac{\nabla_i^2}{2} \tag{2.5}$$

the electron-nuclei potential,

$$\hat{V}_{eN}\left(\boldsymbol{r}_i, \boldsymbol{R}_A\right) = -\sum_{i,A=1}^{N,M} \frac{Z_A}{|\boldsymbol{R}_A - \boldsymbol{r}_i|} \tag{2.6}$$

the electron-electron potential,

$$\hat{V}_{ee}(\boldsymbol{r}_i) = \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^{N} \frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} \tag{2.7}$$

the nuclei-nuclei potential

$$\hat{V}_{NN}(\boldsymbol{R}_A) = \frac{1}{2} \sum_{\substack{A,B=1 \\ A \neq B}}^{M} \frac{Z_A Z_B}{|\boldsymbol{R}_A - \boldsymbol{R}_B|} \tag{2.8}$$

and the nuclei kinetic energy

$$\hat{T}_N = -\sum_{A=1}^{M} \frac{\nabla_A^2}{2m_A} \tag{2.9}$$

respectively. By defining a parametric function

$$\epsilon(\boldsymbol{R}_A) = E - \frac{\left[\hat{T}_N + \hat{V}_{NN}(\boldsymbol{R}_A)\right] \chi(\boldsymbol{R}_A)}{\chi(\boldsymbol{R}_A)} \tag{2.10}$$

equation (2.3) can be decoupled in one equation for the nuclei and one equation for the electrons, respectively

$$\left[\hat{T}_N + \hat{V}_{NN}(\boldsymbol{R}_A) + \epsilon(\boldsymbol{R}_A)\right] \chi(\boldsymbol{R}_A) = E\chi(\boldsymbol{R}_A)$$
$$\left[\hat{T}_e + \hat{V}_{ee}(\boldsymbol{r}_i) + \hat{V}_{eN}(\boldsymbol{r}_i, \boldsymbol{R}_A)\right] \psi(\boldsymbol{r}_i; \boldsymbol{R}_A) = \epsilon(\boldsymbol{R}_A)\psi(\boldsymbol{r}_i; \boldsymbol{R}_A) \tag{2.11}$$

Although a quantum mechanical treatment for the nuclei is possible under such approximation, they are most often considered as classical particles described by Newtonian Mechanics. So, now one only has to find solutions for the second equation of (2.11), which can be re-written more simply by omitting the parametric dependence on $\boldsymbol{R}_A$

$$\hat{H}_e \psi_n(\boldsymbol{r}_i) = \left[\hat{T}_e + \hat{V}_{ee}(\boldsymbol{r}_i) + \hat{V}_{eN}(\boldsymbol{r}_i)\right] \psi_n(\boldsymbol{r}_i) = \epsilon_n \psi_n(\boldsymbol{r}_i) \tag{2.12}$$

As electrons are fermions, solutions for equation (2.12) must obey Pauli's exclusion principle, which states that a wave function of a system of N fermions must be antisymmetric, that is, when subjected to a singular permutation operation between two particles, its sign must change. Let $\hat{P}_{i,j}$ be an exchange operator that switches the particles i and j in the wave function. So

$$\hat{P}_{i,j}\psi_n\left(\boldsymbol{r}_1, ..., \boldsymbol{r}_i, ..., \boldsymbol{r}_j, ...\boldsymbol{r}_N\right) = -\psi_n\left(\boldsymbol{r}_1, ..., \boldsymbol{r}_j, ..., \boldsymbol{r}_i, ...\boldsymbol{r}_N\right) \qquad (2.13)$$

but as quantum mechanical particles cannot be distinguished, the new wave function must also be an eigenvector of the electronic hamiltonian. This remains true no matter how many permutation operators one applies to the original eigenvector, so any anti-symmetrized wave function would be an eigenvector and obey equation (2.12). This will also hold true for any linear combination of eigenvectors under a permutation.

Although it looks simple, equation (2.12) is only solvable, either numerically or arithmetically, for simple models or cases with few electrons. In order to go around this problem, physicists and quantum chemists developed approximation methods.

2.2   Hartree-Fock approximation

As said before, even with the Born-Oppenheimer approximation, the N-electron problem is still far from solvable. So, one usually has to apply additional approximations. The most simple approximation is the Hartree-Fock, which neglects all interactions between particles except those due to Fermi statistics. The latter is named exchange interaction. Since this is central in this thesis, the Hartree-Fock method is briefly presented.

2.2.1   The Hartree-Fock method

In section 2.1, one could see that any linear combination of eigenvectors subjected to a permutation operator (2.13) was also a solution of the N-electron problem. Let such wave function be called $|\Psi\rangle$ and let the eigenvectors of $\hat{H}_e$ be $|1_1 2_2 ... N_N\rangle$

where i_j represents the group of quantum numbers i that characterizes the state of the particle j. As particles in Quantum Mechanics are indistinguishable, in such a wave function the contribution of each anti-symmetrized eigenvector must be the same in absolute value. So, by defining the anti-symmetric operator

$$\hat{A} = \frac{1}{\sqrt{N!}} \sum_{\alpha} \varepsilon_{\alpha} \hat{P}_{\alpha} \tag{2.14}$$

(here α can represent either the particle or the set of quantum numbers which characterizes the state) such a wave function can be written as

$$|\Psi\rangle = \hat{A}|1_1...N_N\rangle = \frac{1}{\sqrt{N!}} \sum_{j_1,...,j_N} \varepsilon_{j_1,...,j_N} |1_{j_1}...N_{j_N}\rangle = \frac{1}{\sqrt{N!}} \sum_{j_1,...,j_N} \varepsilon_{j_1,...,j_N} |j_{1_1}...j_{N_N}\rangle \tag{2.15}$$

where ε_{α} is 1 if the permutation is even and -1 if it is odd. The Hartree-Fock approximation enters here. In (2.12), the electrostatic potential couples the coordinates of the electrons, so a solution using the separation of variables method is not optimal. Ignoring this interaction one can use an *ansatz* [23] in the form of

$$|1_1...N_N\rangle = |1_1\rangle|2_2\rangle...|N_N\rangle \tag{2.16}$$

with $\langle i_k|j_k\rangle = \delta_{ij}$. Equation (2.12) can then be separated in a set of N solvable independent equations. Slater [23] later realized that such a wave function could be written as a symbolic determinant, now known as a Slater determinant

$$|\Psi\rangle = \frac{1}{\sqrt{N!}} \begin{vmatrix} |1_1\rangle & |1_2\rangle & \cdots & |1_N\rangle \\ |2_1\rangle & |2_2\rangle & \cdots & |2_N\rangle \\ \vdots & \vdots & \ddots & \vdots \\ |N_1\rangle & |N_2\rangle & \cdots & |N_N\rangle \end{vmatrix} \tag{2.17}$$

When such a solution is used to evaluate the corresponding energy $E[\Psi] = \langle\Psi|\hat{H}_e|\Psi\rangle$, using the full N-electron hamiltonian, one gets

$$
\begin{aligned}
E[\Psi, \Psi^*] = \sum_{i=1}^{N} \int d^3 r\, \psi_i^*(\boldsymbol{r}) \left[-\frac{\nabla^2}{2} + v_{eN}(\boldsymbol{r}) \right] \psi_i(\boldsymbol{r}) + \\
+ \frac{1}{2} \sum_{i,j=1}^{N} \iint \left| \frac{|\psi_i(\boldsymbol{r})|^2 |\psi_i(\boldsymbol{r}')|^2}{|\boldsymbol{r} - \boldsymbol{r}'|} - \frac{\psi_i^*(\boldsymbol{r})\psi_j(\boldsymbol{r})\psi_j^*(\boldsymbol{r}')\psi_i(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} \right\}
\end{aligned}
\tag{2.18}
$$

and here $\langle x|i\rangle = \chi_i(x) = \psi_i(\boldsymbol{r})\sigma(s)$ with $x = \{\boldsymbol{r}, s\}$ (the spin functions disappear from the expression, because in the evaluation of E one has to sum up all spin values). The first term corresponds to the energy of a system of N independent electrons, while the second to the classic Coulomb interaction between two charge distributions and the third to the energy due to exchange interaction[1]. This last term is called the Hartree-Fock exchange energy

$$
E_x^{HF}[\{\psi_i, \psi_i^*\}] = -\frac{1}{2} \sum_{i,j=1}^{N} \iint d^3 r\, d^3 r'\, \frac{\psi_i^*(\boldsymbol{r})\psi_j(\boldsymbol{r})\psi_j^*(\boldsymbol{r}')\psi_i(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|}
\tag{2.19}
$$

and this functional form is central in this thesis.

A self consistent Hartree-Fock method can now be derived from the variational principle [23]. As seen before, the energy of the N-electron system is a functional of Ψ (and $\Psi^\dagger$) but is restricted to Slater determinants whose elements are orthogonal. One can, then, construct the following Lagrangean

$$
\mathcal{L}[\{\chi_a\}] = E_0[\{\chi_a\}] - \sum_{a,b} \varepsilon_{ab}(\langle a|b\rangle - \delta_{ab})
\tag{2.20}
$$

where ε_{ab} are the Lagrangean multipliers and E_0 is the Hartree-Fock energy given by (2.18). One now has to evaluate the variations of the Hartree-Fock wave function, $|\Psi_0\rangle \rightarrow |\Psi_0\rangle + |\delta\Psi_0\rangle$ that keep the Lagrangean invariant, that is, $\delta\mathcal{L} = 0$.

---

[1]To obtain the total energy of the system, one should also add the energy corresponding to the nuclear interaction.

By defining the Coulomb operator

$$\hat{\jmath}_b \chi_a(x_1) = \int d^3 r_2 \frac{|\chi_b(x_2)|^2}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} \chi_a(x_1) \tag{2.21}$$

and the exchange operator

$$\hat{\mathcal{K}}_b \chi_a(x_1) = \int d^3 r_2 \frac{\chi_b^*(x_2)\chi_a(x_2)}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} \chi_b(x_1) \tag{2.22}$$

it is possible to write the Hartree-Fock equation

$$\hat{\mathcal{F}}|a\rangle = \left[\hat{h} + \sum_{b=1}^{N}\left(\hat{\jmath}_b - \hat{\mathcal{K}}_b\right)\right]|a\rangle = \sum_{b=1}^{N}\varepsilon_{ab}|b\rangle \tag{2.23}$$

with $\hat{\mathcal{F}}$ being the Fock operator, $\hat{h}$ the one-electron Hamiltonian

$$\hat{h} = -\frac{\nabla^2}{2} - \sum_{A=1}^{M}\frac{Z_A}{|\boldsymbol{r} - \boldsymbol{R}_A|} \tag{2.24}$$

By introducing an unitary transformation which diagonalizes the matrix of the Lagrangian multipliers, (2.23) can be transformed in an eigenvalue equation (also called the canonical form of the Hartree-Fock equation).

The Hartree-Fock method neglects correlation effects between the electrons and therefore, if one defines the energy of the N-electron system calculated by the Hartree-Fock method as E_{HF} and the exact one has E_0, it is possible to define the classical correlation energy E_C [23] as

$$E_C = E_0 - E_{HF} \tag{2.25}$$

and since Hartree-Fock is a variational method, one will always have $E_{HF} > E_0$, so the correlation energy defined by (2.25) will always be negative.

2.3 Density Functional Theory (DFT)

It is easy to see that in order to perform a calculation of any expectation value of a quantum mechanical observable, the data that must be stored increases rapidly with the number of electrons (if the atom has n electrons, one must store $3n$ positions, each one with m entries, which leads to m^{3n} entries in total). One can ask if all the information stored in the many-particle wave function is useful, or if one could calculate another quantity which requires a lesser amount of data to be stored (the reduced density matrix for instance).

In 1964, in an article by Hohenberg and Kohn [12], it was proved that all quantum mechanical observables could be expressed as a (implicit or explicit) functional of the ground state density. This is a remarkable thing, as in principle one could study very large systems just using a real scalar function of three variables (and hence the name of the theory).

2.3.1 The Hohenberg-Kohn theorems

The purpose of Density Functional Theory is to solve the problem expressed by the Schrödinger equation (2.12). It is assumed that the electrons are subjected to an external potential of the form

$$\hat{V} = \sum_{i=1}^{N} v(\boldsymbol{r}_i) \tag{2.26}$$

so to better distinguish it from the electron-electron interaction, one changes the $\hat{V}_{ee}$ in (2.7) to $\hat{W}$

$$\hat{W} = \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^{N} \frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} \tag{2.27}$$

Now, the key quantity is not the many-particle wave function, but the electronic ground state density

$$n_0(\boldsymbol{r}) = N \sum_{\sigma} \int d\nu_2 ... \int d\nu_N |\psi_0(\boldsymbol{r}, \sigma, x_2, ..., x_N)|^2 \tag{2.28}$$

with ψ_0 being the ground state wave function and using the notation $\int d\nu_i = \sum_{\sigma_i} \int d^3 r_i$. The ground state of the system is assumed to be non-degenerate (see [10] for the case of a degenerate ground state).

Looking at equation (2.12), one should note that the operators $\hat{T}$ and $\hat{W}$ are the same if the number of electrons N is fixed and, therefore, the solution should be uniquely determined by the external potential. This means that there must exist a functional relation $n_0 = n[v(\boldsymbol{r})]$. It is convenient now to think in terms of mappings between three groups.

The ground state density is obtained from the ground state wave function, which obeys Schrödinger's equation. One can define three groups:

- $\mathbb{V}$ which contains all physical external potentials which differ from each other by more than a constant and give non-degenerate ground state wave functions;

- $\mathbb{W}$ which contains all physical ground state wave functions (square normalizable, non-divergent, continuous and differentiable) of interacting systems which differ from each other by more than a constant phase factor;

- $\mathbb{D}$ which contains all physical ground state densities of interacting systems;

If A is the mapping between $\mathbb{V}$ and $\mathbb{W}$ and B is the mapping between $\mathbb{W}$ and $\mathbb{D}$, one can define $C = B \circ A$. The mappings A and B represent a functional relation between the elements of each group, as the ground state is considered to be non-degenerate and one cannot obtain two different densities from the same wave function. Now, to invert such relations, one must be sure that A and B are injective (and therefore C will also be injective)[1]

$$
\begin{array}{ccccc}
A : \mathbb{V} \rightarrow \mathbb{W} & B : \mathbb{W} \rightarrow \mathbb{D} & & C : \mathbb{V} \rightarrow \mathbb{D} \\
\hat{V} \rightarrow |\psi_0\rangle & |\psi_0\rangle \rightarrow n_0(\boldsymbol{r}) & \Rightarrow & \hat{V} \rightarrow n_0(\boldsymbol{r})
\end{array}
\tag{2.29}
$$

---

[1] The correspondences $\mathbb{D} \equiv C(\mathbb{V})$, $\mathbb{D} \equiv B(\mathbb{W})$ and $\mathbb{W} \equiv A(\mathbb{V})$ which make each mapping a bijection are not needed as long as one restricts oneself to the counter domain of each group.

The proof that A is injective goes as follows: let $\hat{V}$ and $\hat{V}'$ be two external potentials which differ from more than a constant c and $|\psi_0\rangle$ and $|\psi_0'\rangle$ their respective ground state wave functions. Now, if one assumes that the wave functions are equal and subtracts the corresponding Schrödinger equations, one gets

$$(\hat{V} - \hat{V}')|\psi_0\rangle = (\epsilon_0 - \epsilon_0')|\psi_0\rangle \tag{2.30}$$

which contradicts the assumption that the potentials differ from more than a simple constant. So, by *reduction ad absurdum*, the mapping A is shown to be injective, and therefore invertible. For this mapping, the criteria of being a bijection also holds. If a ground state wave function $|\psi_0\rangle$ is given it is possible to evaluate the corresponding potential by inverting the Schödinger's equation, giving

$$\sum_{i=1}^{N} v(\boldsymbol{r}_i) = -\frac{1}{2} \sum_{i=1}^{N} \frac{\nabla_i^2 \psi_0(\{\boldsymbol{r}_i\})}{\psi_0(\{\boldsymbol{r}_i\})} + W(\{\boldsymbol{r}_i\}) + \text{const.} \tag{2.31}$$

Now one must prove that the mapping B is also injective. This is also done by *reduction ad absurdum*. Let $|\psi_0\rangle$ and $|\psi_0'\rangle$, which differ by more than a constant phase factor, be each a solution of the Schrödinger's equation for the external potentials $\hat{V}$ and $\hat{V}'$, respectively. Assuming that the ground state density given by each wave function is the same, that is, $n_0(\boldsymbol{r}) = n_0'(\boldsymbol{r})$, then ground the state energy associated with each one is

$$E_0 = \langle \psi_0 | \hat{H}_0 | \psi_0 \rangle \qquad E_0' = \langle \psi_0' | \hat{H}' | \psi_0' \rangle \tag{2.32}$$

Using the Rayleigh-Ritz variational principle, one has

$$E_0' < \langle \psi_0 | \hat{H}' | \psi_0 \rangle = \langle \psi_0 | \hat{H} + \hat{V}' - \hat{V} | \psi_0 \rangle = E_0 + \int d^3 r \left[v'(\boldsymbol{r}) - v(\boldsymbol{r}) \right] n_0(\boldsymbol{r})$$

$$E_0 < \langle \psi_0' | \hat{H} | \psi_0' \rangle = \langle \psi_0' | \hat{H}' + \hat{V} - \hat{V}' | \psi_0' \rangle = E_0' + \int d^3 r \left[v(\boldsymbol{r}) - v'(\boldsymbol{r}) \right] n_0(\boldsymbol{r}) \tag{2.33}$$

So, adding both equations, one arrives to the following contradiction

$$E_0 + E_0' < E_0 + E_0' \tag{2.34}$$

which proves that n_0 and n'_0 must be different. Therefore, the mapping B is also an injection between the groups $\mathbb{W}$ and $\mathbb{D}$ and $C = B \circ A$ is also an injection between $\mathbb{V}$ and $\mathbb{D}$, so there is a functional relation $v = v[n_0(\boldsymbol{r})]$. This proof forms what is known as the first Hohenberg-Kohn theorem [24]:

HK theorem 1. *In a finite system with N interacting electrons the external potential $v(\boldsymbol{r})$, and therefore the ground state energy E_0 are unique functionals of the ground state density $n_0(\boldsymbol{r})$.*

The second Hohenberg-Kohn theorem is a consequence of the Rayleigh-Ritz variational principle. By looking at the expression for the ground state energy, one notes that it can be rewritten in the form

$$E[n_0] = \langle \psi_0[n_0] | \hat{T} + \hat{V} + \hat{W} | \psi_0[n_0] \rangle = F[n_0] + \int d^3 r n_0(\boldsymbol{r}) v(\boldsymbol{r}) \qquad (2.35)$$

where

$$F[n_0] = \langle \psi_0[n_0] | \hat{T} + \hat{W} | \psi_0[n_0] \rangle \qquad (2.36)$$

is unknown. For another wave function $|\psi[n]\rangle$ associated with an electronic density $n \neq n_0$ the energy can be written as a v-representable functional, with v not related with n

$$E_v[n] = F[n] + \int d^3 r n(\boldsymbol{r}) v(\boldsymbol{r}) \qquad (2.37)$$

and by the Rayleigh-Ritz variational principle, one has that

$$E_v[n] > E_v[n_0] \qquad (2.38)$$

which is translated in the following theorem

HK theorem 2. *The ground state energy E_0 can be obtained variationally and to the exact ground state density n_0 corresponds to the exact ground state energy.*

Now all that is needed is a method through which n_0 can be evaluated. Such a method was proposed by Kohn and Sham in 1965 [13] and will be explained next.

2.3.2 The Kohn-Sham scheme

The variational character of the Hohenberg-Kohn theorems allows one to write a variational principle not in terms of the wave function but using the ground state density. Using (2.37) the exact n_0 would be the one that leaves the energy functional invariant under a change in the density, under the restriction that

$$N = \int d^3r n_0(\boldsymbol{r}) \tag{2.39}$$

So, by defining the Lagrange multiplier μ the problem would be reduced to solving the Euler equation

$$\frac{\delta}{\delta n(\boldsymbol{r})}\left[F[n] + \int d^3r n(\boldsymbol{r})v(\boldsymbol{r}) - \mu\left(\int d^3r n(\boldsymbol{r}) - N\right)\right] = 0 \tag{2.40}$$

Defined in (2.36) $F[n]$ is called the *universal functional*, in the sense that its expression in terms of the density is independent of the external potential to which the system is being subjected to. It only depends on the number of electrons present in the system. With this, (2.40) turns to

$$\frac{\delta F[n]}{\delta n(\boldsymbol{r})} + v(\boldsymbol{r}) = \mu \tag{2.41}$$

Of course, as the exact form of $F[n]$ is unknown, (2.41) is not of much use in practice. In order to transform DFT in a workable theory, Kohn and Sham devised a method that would take advantage of a simpler system: the system of N independent fermions [13].

In such a system, the interaction operator $\hat{W}$ disappears from (2.1). Let the new Hamiltonian be called $\hat{H}_s$. In real space, one has that

$$\hat{H}_s|\psi_{k,s}\rangle = \sum_{i=1}^{N}\left[-\frac{\nabla_i^2}{2} + v_s(\boldsymbol{r}_i)\right]|\psi_{k,s}\rangle = \epsilon_{k_s}|\psi_{k,s}\rangle \tag{2.42}$$

By application of the HK theorems, there is a functional relation between v_s and the ground state density of this system, $n_{0,s}$. The total energy functional (2.37)

changes to

$$E_{v_s}[n] = T_s[n] + \int d^3 r n(\boldsymbol{r}) v_s(\boldsymbol{r}) \tag{2.43}$$

and the universal functional coincides with the noninteracting kinetic energy functional $T_s[n]$. The Euler equation (2.40) is simplified to

$$\frac{\delta T_s[n]}{\delta n(\boldsymbol{r})} + v_s(\boldsymbol{r}) = \mu_s \tag{2.44}$$

As the exact form of $T_s[n]$ is unknown, it is best to work on a solution for (2.42). As seen in section 2.2, for a system of independent fermions, the solution can be written as a Slater determinant like (2.17) of single-particle orbitals $\phi_i(\boldsymbol{r})$, with each one satisfying

$$\left(-\frac{\nabla^2}{2} + v_s(\boldsymbol{r}) \right) \phi_i(\boldsymbol{r}) = \epsilon_i \phi_i(\boldsymbol{r}) \tag{2.45}$$

and the electronic density is written as

$$n_s(\boldsymbol{r}) = \sum_{i=1}^{N} \theta_i |\phi_i(\boldsymbol{r})|^2 \tag{2.46}$$

with θ_i being the occupation function for the state with index i. The kinetic energy is an explicit functional of the orbitals

$$T_s[n_0] = -\frac{1}{2} \sum_{i=1}^{N} \int d^3 r \phi_i^\dagger[n_0](\boldsymbol{r}) \nabla^2 \phi_i[n_0](\boldsymbol{r}) \tag{2.47}$$

but due to the HK theorems, it will also be an implicit functional of the ground state density.

The idea of Kohn and Sham was to rewrite equation (2.37) by adding and subtracting terms

$$
\begin{aligned}
E[n] &= T[n] + W[n] + \int d^3 r n(\boldsymbol{r}) v(\boldsymbol{r}) \\
&= (T[n] - T_s[n]) + (W[n] - E_H[n]) + T_s[n] + E_H[n] + \int d^3 r n(\boldsymbol{r}) v(\boldsymbol{r}) \\
&= T_s[n] + E_H[n] + \int d^3 r n(\boldsymbol{r}) v(\boldsymbol{r}) + E_{xc}[n]
\end{aligned}
\tag{2.48}
$$

where the functional $E_H[n]$ is the classical Coulomb energy or the Hartree energy

$$
E_H[n] = \frac{1}{2} \iint d^3 r d^3 r' \frac{n(\boldsymbol{r}) n(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|}
\tag{2.49}
$$

The last term in (2.48), $E_{xc}[n]$ is called the exchange-correlation functional. It is defined as

$$
E_{xc}[n] = T[n] - T_s[n] + W[n] - E_H[n]
\tag{2.50}
$$

and it is easy to see that it contains information concerning the difference between the non-interacting system and the real one. If one now inserts (2.48) in the Euler equation (2.40), the result is

$$
\frac{\delta T_s[n]}{\delta n(\boldsymbol{r})} + v[n](\boldsymbol{r}) + \int d^3 r' \frac{n(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} + \frac{\delta E_{xc}[n]}{\delta n(\boldsymbol{r})} = \mu
\tag{2.51}
$$

So, in order to reproduce the exact ground state density, subtraction of (2.44) and (2.51) gives

$$
v_s[n](\boldsymbol{r}) = v[n](\boldsymbol{r}) + \int d^3 r' \frac{n(\boldsymbol{r})}{|\boldsymbol{r} - \boldsymbol{r}'|} + (\mu - \mu_s) + \frac{\delta E_{xc}[n]}{\delta n(\boldsymbol{r})}
\tag{2.52}
$$

and by choosing the asymptotic limit of the functional derivative of E_{xc}, the difference in the Lagrange multipliers can be absorbed and one finally writes

$$
v_s[n](\boldsymbol{r}) = v[n](\boldsymbol{r}) + \int d^3 r' \frac{n(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} + v_{xc}[n](\boldsymbol{r}), \text{ with } v_{xc}[n](\boldsymbol{r}) = \frac{\delta E_{xc}[n]}{\delta n(\boldsymbol{r})}
\tag{2.53}
$$

The exchange-correlation energy is usually split in two additive components: the exchange part E_x and the correlation part E_c. For the exchange part, one can derive a expression with the same form of (2.19)

$$E_x[n] = \langle\phi[n]|\hat{W}|\phi[n]\rangle - \frac{1}{2}\iint d^3r d^3r' \frac{n(\boldsymbol{r})n(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} \tag{2.54}$$

and in the limit of exact exchange, the previous expression changes to

$$E_x[n] = -\frac{1}{2}\sum_{i,j=1}^{N}\theta_i\theta_j \iint d^3r d^3r' \frac{\phi_i^*(\boldsymbol{r})\phi_j(\boldsymbol{r})\phi_j^*(\boldsymbol{r}')\phi_i(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} \tag{2.55}$$

It is important to note that the difference in notation is not just a coincidence. In (2.19) the orbitals involved are obtained by solving the Schrödinger equation with a non-local Coulomb potential, while in (2.55) the orbitals are the eigenvectors of the Kohn-Sham equation for a local potential. So, although both expressions have the same functional dependence, they evaluate different quantities.

Through the use of second quantization and Many-body perturbation theory, it is actually possible to derive an exact expression for $E_{xc}[n]$ (see [7]). First of all, the KS Hamiltonian operator can be written as

$$\hat{H}_s = \hat{T} + \int d^3r \hat{n}(\boldsymbol{r}) v_s(\boldsymbol{r}) \tag{2.56}$$

where $\hat{n}(\boldsymbol{r})$ is the density operator. The ground state wave function of (2.56) can be written in terms of the vacuum state $|0\rangle$ and the creation operator $a_k^\dagger$

$$|\Phi_0\rangle = \prod_{\epsilon_k \leq \epsilon_F} a_k^\dagger |0\rangle \tag{2.57}$$

and as usual

$$\left\{a_k^\dagger, a_l^\dagger\right\} = 0 = \{a_k, a_l\} \qquad \left\{a_k, a_l^\dagger\right\} = \delta_{kl} \tag{2.58}$$

In this formalism, one defines the KS field operators (in the Heisenberg picture)

$$\hat{\psi}_0(\boldsymbol{r}, t) = e^{i\hat{H}_s t}\hat{\psi}(\boldsymbol{r})e^{-i\hat{H}_s t} = \sum_k \hat{b}_k \phi_k(\boldsymbol{r})e^{-i\epsilon_k t} \tag{2.59}$$

and the KS time-ordered Green's function

$$G_s(\boldsymbol{r}, t; \boldsymbol{r}', t') = -i\langle\Phi_0|T\hat{\psi}_0(\boldsymbol{r}, t)\hat{\psi}^\dagger(\boldsymbol{r}', t')|\Phi_0\rangle =$$
$$- i\theta(t - t') \sum_{\epsilon_k \leq \epsilon_F} \phi(\boldsymbol{r})\phi_k^\dagger(\boldsymbol{r})e^{-i\epsilon_k(t-t')} +$$
$$+ i\theta(t' - t) \sum_{\epsilon_k \leq \epsilon_F} \phi(\boldsymbol{r})\phi_k^\dagger(\boldsymbol{r})e^{-i\epsilon_k(t-t')} \tag{2.60}$$

With these ingredients, one can evaluate a perturbative expansion for the ground state energy using the coupling constant technique. Let $\hat{H}_1$ be the difference between the full interaction Hamiltonian operator $\hat{H}$ and the KS hamiltonian operator. Then, one has

$$\hat{H}_1 = \hat{W} - \int d^3r\hat{n}(\boldsymbol{r})\left[v_H(\boldsymbol{r}) + v_{xc}(\boldsymbol{r})\right] \Rightarrow \hat{H}(g) = \hat{H}_s + g\hat{H}_1 \tag{2.61}$$

with g being the coupling constant which allows one to turn on and off the correction to the KS Hamiltonian. After some calculations, it is possible to arrive to the following expression for the exchange-correlation energy functional

$$E_{xc}[n] = \frac{1}{2}\iint d^3r d^3r' \frac{1}{|\boldsymbol{r} - \boldsymbol{r}'|}\left[\langle\Phi_0|\hat{\psi}^\dagger(\boldsymbol{r})\hat{\psi}^\dagger(\boldsymbol{r}')\hat{\psi}(\boldsymbol{r}')\hat{\psi}(\boldsymbol{r})|\Phi_0\rangle - n(\boldsymbol{r})n(\boldsymbol{r}')\right] +$$
$$+ \lim_{\epsilon\to 0}\sum_{n=1}^\infty \frac{(-i)^n}{(n+1)!}\int_{-\infty}^{+\infty} dt_1 ... \int_{-\infty}^{+\infty} dt_n e^{-\epsilon(|t_1|+...+|t_2|)} \times$$
$$\times \langle\Psi_0|T\hat{H}_{1,I}(0)\hat{H}_{1,I}(t_1)...\hat{H}_{1,I}(t_n)|\Psi_0\rangle_l \tag{2.62}$$

The first term is obviously the exchange part while the remaining series is the correlation part. Here, $\hat{H}_{1,I}$ represents the perturbation in Dirac's picture (also known as the interaction picture)

$$\hat{H}_{1,I}(t) = e^{i\hat{H}_s t}\hat{H}_1 e^{-i\hat{H}_s t} \tag{2.63}$$

and the index l removes the contribution of non-linked diagrams in the evaluation of (2.62) (done with help of Wick's theorem). Although this expression is exact, it holds a rather complicated functional dependence, as v_{xc} is part of $\hat{H}_1$, making E_{xc} functionally dependent on it is own derivative.

In order to go around the impossibility of obtaining exact expressions for E_c and thus for E_{xc}, one usually uses approximations. In principle, the higher the complexity of the approximation the closer to reality, but this usually also involves an higher "computational" cost.

2.3.3 E_{xc} functionals and Jacob's ladder

Described in the Book of Genesis, Jacob's ladder appears in a dream to the character of the same name, creating a path between Heaven and Earth. This metaphor can be applied to the different approximations for the functional E_{xc} accuracy. As one climbs up, the approximation gets closer to what can be called *Chemical Heaven*.[1]

The first step on the ladder corresponds to the Local-density approximation (LDA) proposed in 1965 by Kohn and Sham. The idea is to approximate the xc energy of the inhomogeneous electron cloud to an integral of the homogeneous electron liquid xc energy density. In such a system, the exchange energy density is known and given by (in three dimensions) [24]

$$e_x[n] = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3} n^{4/3}(\boldsymbol{r}) \tag{2.64}$$

and the correlation energy density is usually obtained through an interpolation formula. At the high density limit, the interpolation formula is

$$e_c \approx a\ln(r_s) + b + r_s\left[c\ln(r_s) + b\right] \tag{2.65}$$

and at the low density limit [24]

$$e_c \approx \frac{1}{2}\left(\frac{\alpha_0}{r_s} + \frac{\alpha_1}{r_s^{3/2}} + ...\right) \tag{2.66}$$

---

[1]All trademark resemblances with this expression are purely coincidental.

with the Wigner-Seitz radius r_s being (in three dimensions)

$$r_s = \left(\frac{3}{4\pi n}\right)^{1/3} \tag{2.67}$$

and the parameters are usually obtained by interpolation of numerical results from quantum Monte Carlo calculations. A good LDA functional usually gives values for energies, geometrical parameters and vibrational frequencies with a low percentage error. As systems diverge from the uniform limit, the effectiveness range of LDA can be estimated by comparison with the magnitude of the Fermi wave vector, $k_F(\boldsymbol{r})$,

$$k_F(\boldsymbol{r}) \gg \frac{\nabla n(\boldsymbol{r})}{n(\boldsymbol{r})} \tag{2.68}$$

though this condition is often violated.

Although it is a very good starting point for a calculation and works perfectly well in a lot of systems, the LDA approximation fails, e.g., for long range interactions due to the wrong asymptotic limit of v_{xc}^{LDA}. The potential is often not deep enough to allow another electron to be bound, so negative ions cannot be created within this approximation.

In the second step in the approximation ladder one adds terms that depend on the gradient of the density, the gradient expansion approximation (GEA). The idea is to express $E_{xc}[n]$ as a functional not only of the density but its gradient in real space. The most usual way is to define a parameter involving the condition (2.68). One thus defines [24]

$$s(\boldsymbol{r}) = \frac{|\nabla n(\boldsymbol{r})|}{2n(\boldsymbol{r})k_F(\boldsymbol{r})} \tag{2.69}$$

as the parameter of the power expansion. For the exchange correlation energy, the expression is usually [24]

$$E_{xc}^{GEA}[n] = \int d^3r \left[e_{xc}^h(\boldsymbol{r}) + C_{xc}^{(2)}[n]s^2 + ...\right] \tag{2.70}$$

Chemical accuracy

$\psi_i(\mathbf{r})$ (empty) —————— EXX with partial exact correlation

$\psi_i(\mathbf{r})$ (occupied) —————— EXX with correlation

$\nabla^2 n(\mathbf{r}), \tau(\mathbf{r})$ —————— meta-GGA

$\nabla n(\mathbf{r})$ —————— GGA

$n(\mathbf{r})$ —————— LDA

Hartree world
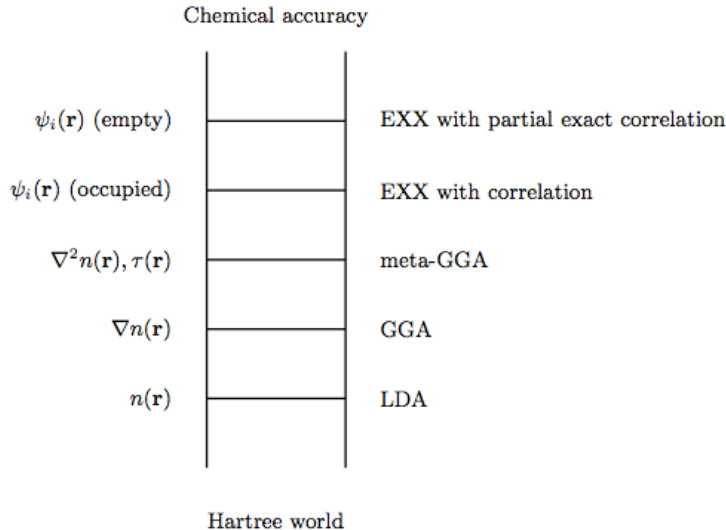
Figure 2.1: Functional ladder, from [17]

and further terms in the expansion can be obtained through response theory. Unfortunately, gradient expansions are difficult to deal with in terms of convergence and such functionals can give worse results than LDA. Another order of functionals which use the density's gradient uses the generalized gradient approximation (GGA), where [24]

$$E_{xc}^{GGA} = \int d^3r e_{xc}(n(\boldsymbol{r}), \nabla n(\boldsymbol{r})) \tag{2.71}$$

Now, while the GEA can be built analytically, the same does not happen with GGA. Expansions in this case are built by introducing terms which satisfy some known exact properties and, as there is no recipe for it, sometimes one uses a set of empirical parameters. As such, the number of GGA functionals one can find is usually immense. GGA's exchange-correlation functionals often give good results for integrated quantities due to error cancelation with the correlation and exchange effects, but sometimes fail to reproduce the asymptotic behavior of v_{xc}.

The next step on the ladder has the Meta-GGAs functionals, in which one includes more terms [24]

$$E_{xc}^{MGGA} = \int d^3 r e_{xc}^{MGGA}(n, \nabla n, \nabla^2 n, \tau) \qquad (2.72)$$

with $\tau = \frac{1}{2} \sum_{i=1}^{N} \theta_i |\nabla \phi_i(\boldsymbol{r})|^2$. Unfortunately this last parameter is only implicitly dependent on the density, so a direct evaluation of v_{xc}^{MGGA} is impossible. Still, this is actually the way the next steps in the ladder go. If one goes up, the next functionals will contain some portion of the exact exchange functional (2.55). The ones that depend on the density, its derivatives of first and second order and the exact exchange are called hyper-GGAs. They haven't been particularly successful in general, but a certain subclass of them seems to be working quite well. These hybrid functionals express the exchange-correlation functional as a linear combination of the exchange and correlation parts of LDA, GGA and exact exchange, with the linear coefficients being of some semi-empirical nature.

2.3.4 The Optimized Effective Potential (OEP) method

The initial purpose of DFT was to eliminate the need of the N-electron wave function in the calculations so that the computational cost would decrease. But, as seen before, as one climbs the ladder of approximations in the functionals, the KS orbitals are introduced once again leading to the concept of orbital functionals. Two examples of such entities already appeared in the form of $T_s[n]$ and the exact exchange functional. As seen in section 1.1, there are a few reasons to go back to using the wave functions explicitly. Also, LDA and GGA functionals often present some problems [7]:

- Heavy Metals: LDA underestimates the bonding energy and overestimates the bond length. GGA diverges from experimental data for high nuclear charge;

- Negative Ions: LDA and GGA fail to reproduce the asymptotic behavior of the xc-potential (this is also true for any finite system);

- Dispersion forces: Due to their short range behavior, both LDA and GGA fail to reproduce dispersion forces;

- Strong correlated systems: LDA and GGA fail to predict the correct behavior of some anti-ferromagnetic insulators, presenting them as metals;

There is also a mathematical reason to use orbital functionals. If one takes into account the expression (2.62) and expands the exchange correlation functional in powers of e^2 (with e being the absolute value of the electron's charge), one will get [7]

$$E_{xc}[n] = \sum_{j=1}^{+\infty} e^{2j} E_{xc}^{(j)}[n] = E_x^{exact}[n] + E_c^{(2)}[n] + ... \tag{2.73}$$

and taking the functional derivative

$$v_{xc}[n] = \sum_{j=1}^{+\infty} e^{2j} v_{xc}^{(j)}[n] = v_x^{exact}[n] + v_c^{(2)}[n] + ... \tag{2.74}$$

So, in first order approximation, $E_{xc}[n]$ can be taken as almost equal to the exact exchange functional.

Let one consider the following equality obtained using the chain rule for functional derivatives

$$\begin{aligned}
\frac{\delta E_{xc}[n]}{\delta v_s(\boldsymbol{r})} &= \int d^3 r' \frac{\delta E_{xc}}{\delta n(\boldsymbol{r}')} \frac{\delta n(\boldsymbol{r}')}{\delta v_s(\boldsymbol{r})} = \\
&= \sum_{k=1}^{N} \left\{ \int d^3 r' \left[\frac{\delta E_{xc}}{\delta \phi(\boldsymbol{r}')} \frac{\delta \phi(\boldsymbol{r}')}{\delta v_s(\boldsymbol{r})} + c.c. \right] + \frac{\delta \epsilon_k}{\delta v_s(\boldsymbol{r})} \frac{\partial E_{xc}}{\partial \epsilon_k} \right\}
\end{aligned} \tag{2.75}$$

which is valid as through the HK theorems E_{xc} is a functional of n and through the definition (2.62) a functional of the KS eigenvectors and eigenvalues. Using general first order perturbation theory applied to the KS Hamiltonian, one can

derive easily the following identities [7]

$$\frac{\delta\phi_k(\boldsymbol{r}')}{\delta v_s(\boldsymbol{r})} = \sum_{\substack{j=1 \\ j\neq i}}^{N} \frac{\phi_j(\boldsymbol{r}')\phi_j^*(\boldsymbol{r})}{\epsilon_i - \epsilon_j}\phi_k(\boldsymbol{r}) = -G_k(\boldsymbol{r}',\boldsymbol{r})\phi_k(\boldsymbol{r}) \tag{2.76}$$

$$\frac{\delta n(\boldsymbol{r}')}{\delta v_s(\boldsymbol{r})} = \chi_s(\boldsymbol{r}',\boldsymbol{r}) = -\sum_{k=1}^{N} \theta_k \left[\phi_k^*(\boldsymbol{r}')G_k(\boldsymbol{r}',\boldsymbol{r})\phi_k(\boldsymbol{r}) + c.c.\right] \tag{2.77}$$

$$\frac{\delta\epsilon_k}{\delta v_s(\boldsymbol{r})} = |\phi_k(\boldsymbol{r})|^2 \tag{2.78}$$

with $\chi_s(\boldsymbol{r}',\boldsymbol{r})$ being the linear response function and $G_k(\boldsymbol{r}',\boldsymbol{r})$ the Green's function. This leads to the known OEP equation

$$\int d^3r' \chi_s(\boldsymbol{r}',\boldsymbol{r})v_{xc}(\boldsymbol{r}') = \Lambda_{xc}(\boldsymbol{r})$$

$$\Lambda_{xc}(\boldsymbol{r}) = \sum_{k=1}^{N} \left\{ |\phi_k(\boldsymbol{r})|^2 \frac{\partial E_{xc}}{\partial \epsilon_k} - \int d^3r' \left[\frac{\delta E_{xc}}{\delta\phi(\boldsymbol{r}')}G_k(\boldsymbol{r}',\boldsymbol{r})\phi_k(\boldsymbol{r}) + c.c.\right]\right\} \tag{2.79}$$

This is a Fredholm equation of the first kind, with $\Lambda_{xc}(\boldsymbol{r})$ being the inhomogeneity. As it can be expressed as a linear operator acting on E_{xc}, each one of its components can be treated separately, and solving (2.79) eliminates the need to insert the density in $v_{xc}[n]$.

There is a problem with the efficiency of these equations. As the Green's functions need the complete spectrum of eigenvectors and eigenvalues (both occupied and unoccupied) the amount of data needed to be stored is very large and also, they don't have analytic expressions. One of the many approximations was proposed by Krieger-Li-Yafrate [7],[16],[15] and it has the following philosophy: the higher levels of the spectrum of a system are very close to each other, so that one can replace the difference in the denominator in the Green's function as an average value $\Delta\epsilon$. With this, and taking into account the completeness relation

for the KS eigenvectors, one can write

$$G_k(\boldsymbol{r}', \boldsymbol{r}) \approx= \frac{1}{\Delta\epsilon} \sum_{\substack{j=1 \\ j \neq k}}^{N} \phi_j(\boldsymbol{r}')\phi_j^*(\boldsymbol{r}) = \frac{1}{\Delta\epsilon}\left(\delta(\boldsymbol{r}-\boldsymbol{r}') - \phi_k(\boldsymbol{r}')\phi_k^*(\boldsymbol{r})\right) \qquad (2.80)$$

and insertion in (2.79) gives

$$v_{xc}^{KLI}(\boldsymbol{r}) = \frac{1}{2n(\boldsymbol{r})} \sum_{k=1}^{N} \left\{ \left[\frac{\delta E_{xc}}{\delta\phi_k(\boldsymbol{r})}\phi_k(\boldsymbol{r}) + c.c.\right] + |\phi_k(\boldsymbol{r})|^2 \left[\Delta v_k - \Delta\epsilon\frac{\partial E_{xc}}{\partial\epsilon_k}\right]\right\}$$

$$\Delta v_k = \int d^3 r \left[\theta_k|\phi_k(\boldsymbol{r})|^2 v_{xc}(\boldsymbol{r}) - \frac{\delta E_{xc}}{\delta\phi_k(\boldsymbol{r})}\phi_k(\boldsymbol{r})\right] + c.c.$$

$$(2.81)$$

Of course there is an ambiguity in the expression above, as $\Delta\epsilon$ is present through the dependence of E_{xc} in the KS eigenvalues and fitting this parameter would require some extra calculations for each system. If one wants to solve the full OEP equation with this approximation, the dependency on the eigenvalues can be eliminated since it only introduces a new energy scale. As this is a non-relativistic formalism, there is no problem in rescaling the energies so that such dependency is eliminated.

In the limit of the exact exchange, such problem is not part of one's concern, as (2.55) has no explicit dependency on ϵ_k. This immediately gives

$$v_x^{KLI}(\boldsymbol{r}) = \frac{1}{2n(\boldsymbol{r})} \sum_{k=1}^{N} \left\{ \left[\frac{\delta E_{xc}}{\delta\phi_k(\boldsymbol{r})}\phi_k(\boldsymbol{r}) + c.c.\right] + |\phi_k(\boldsymbol{r})|^2 \Delta v_k^{KLI}\right\} \qquad (2.82)$$

This equation can be solved either iteratively by starting with an approximation for Δv_x^{KLI} obtained from some approximate functional (LDA or GGA for example) and then iterate until convergence is obtained. Alternatively one can rewrite the equations in order to obtain a set of linear equations for Δv_x^{KLI} that can be then evaluated directly. The latter is implemented in OCTOPUS [4] and goes as

follows: one starts by rewriting (2.82) as

$$v_x^{KLI}(\boldsymbol{r}) = v_{slater}(\boldsymbol{r}) + \frac{1}{n(\boldsymbol{r})} \sum_{k=1}^{N} |\phi_k(\boldsymbol{r})|^2 \langle k | v_x^{KLI}(\boldsymbol{r}) - u_{x,k}^*(\boldsymbol{r}) | k \rangle \qquad (2.83)$$

with the exchange potential $u_{x,k(\boldsymbol{r})}$ being defined as

$$\frac{\delta E_x}{\delta \phi_k^*(\boldsymbol{r})} = u_{x,k}^*(\boldsymbol{r}) \phi_k(\boldsymbol{r}) \qquad (2.84)$$

and the Slater potential

$$v_{slater}(\boldsymbol{r}) = \frac{1}{2n(\boldsymbol{r})} \sum_{k=1}^{N} \left[\frac{\delta E_{xc}}{\delta \phi_k(\boldsymbol{r})} \phi_k(\boldsymbol{r}) + c.c. \right] \qquad (2.85)$$

which was initially proposed by Slater in [22] as a local approximation simplification to Hartree-Fock.

Evaluating the diagonal terms of v_x^{KLI} one gets that

$$\langle i | v_x^{KLI}(\boldsymbol{r}) | i \rangle = \langle i | v_{slater}(\boldsymbol{r}) | i \rangle + \sum_{k=1}^{N} M_{i,k} \Delta v_k^{KLI}, \quad M_{i,k} = \int d^3 r \frac{|\phi_i(\boldsymbol{r})|^2 |\phi_k(\boldsymbol{r})|^2}{n(\boldsymbol{r})}$$
$$(2.86)$$

and so, by adding and subtracting diagonal element $\langle i | u_{x,i}(\boldsymbol{r}) | i \rangle$, one arrives to the matrix equation

$$\sum_{k=1}^{N} (\delta_{i,k} - M_{i,k}) \Delta v_k^{KLI} = \langle i | v_{slater}(\boldsymbol{r}) | i \rangle - \langle i | u_{x,i}(\boldsymbol{r}) | i \rangle \qquad (2.87)$$

that allows the evaluation of Δv_k^{KLI}.

2.4 Time-Dependent Density Functional Theory (TDDFT)

DFT can be extended to the time-dependent regime, where the Hamiltonian of (2.12) contains an explicitly time-dependent scalar potential $v(\boldsymbol{r}, t)$. The evolution of the system is now governed by the time-dependent Schödinger equation

$$\hat{H}|\Psi\rangle = i\frac{\partial}{\partial t}|\Psi\rangle \tag{2.88}$$

which is used to propagate an initial state $|\Psi_0\rangle$ from an instant t_0 to t_1. It is usually convenient to consider that for $t < t_0$ the system was in the ground state under the effect of a static potential $v_0(\boldsymbol{r})$ and that at t_0 a time-dependent component is switched on. Analytically, this is expressed as

$$v(\boldsymbol{r}, t) = v_0(\boldsymbol{r}) + \theta(t - t_0)v_1(\boldsymbol{r}, t) \tag{2.89}$$

As in DFT, the key idea is to establish the density of the system (now time-dependent), $n(\boldsymbol{r}, t)$, as the key ingredient from which all observables can be evaluated once they are written as a functional of the density. In 1984 [21], Runge and Gross proved that, under certain conditions, the mapping between the time-dependent potential and density could be inverted and stated what is known as the Runge-Gross theorem [21]

Runge-Gross theorem. *Two densities $n(\boldsymbol{r}, t)$ and $n'(\boldsymbol{r}, t)$, evolving from a common initial many-body state Ψ_0 under the influence of two different potentials $v(\boldsymbol{r}, t)$ and $v'(\boldsymbol{r}, t) \neq v(\boldsymbol{r}, t) + c(t)$ (both assumed to be Taylor-expandable around t_0), will start to become different infinitesimally later than t_0. Therefore, there is a one-to-one correspondence between densities and potentials, for any fixed initial many-body state.*

Still, the theorem as limitations. To begin with, it excludes vector potentials which are essential to study the effects of electromagnetic waves or time-dependent magnetic fields (although such potentials can be included through the use of time-dependent current-DFT, but such theory is out of the scope of this

thesis). The theorem is also restricted to finite systems, since in its proof a surface integral should vanish. This problem can be avoided by taking into account potentials that come only from finite normalizable external charge distributions (this problem is also surpassed in the TDCDFT formalism, see [24]). Another limitation is that, since the potential must be analytic around t_0, potentials that are adiabatically switched from $t_0 = -\infty$ using a function $e^{\gamma t}$ (with $0 < \gamma < 1$) cannot be included, since the switch function has a singularity at $t = -\infty$. Numerically this doesn't turn out to be a significant problem if one chooses a sufficient large although finite negative instant t_0.

Another importan result is the van Leeuwen theorem [25] which is stated as follows

van Leeuwen theorem . *For a time-dependent density $n(\boldsymbol{r}, t)$ associated with a many-body system with a given particle-particle interaction, external potential and initial state, there is a different many-body system with another particle-particle interaction and time-dependent external potential (up to a $c(t)$ function) which reproduces the same time-dependent density. The initial state of the system Ψ_0 must be chosen such that it correctly gives the same density and its derivative at the initial time t_0*

This theorem gives the theoretical justification for the use of the Kohn-Sham auxiliary system, in which the particle-particle interaction is null. Time-dependent KS simulations usually start with a ground state calculation using equation (2.45) with the ground state density given by equation (2.46) and the ground state KS potential by equation (2.53). Right after the instant t_0, the time-dependent part of the potential begins to act. The KS eigenvectors follow the time-dependent KS equation

$$\left[-\frac{\nabla^2}{2} + v_s[n](\boldsymbol{r}, t) \right] \varphi_i(\boldsymbol{r}, t) = i\frac{\partial}{\partial t}\varphi_i(\boldsymbol{r}, t) \tag{2.90}$$

given that $\varphi_i(\boldsymbol{r}, t_0) = \phi_i(\boldsymbol{r})$. The time-dependent density is given by

$$n(\boldsymbol{r}, t) = \sum_{i=1}^{N} \theta_i |\varphi_i(\boldsymbol{r}, t)|^2 \tag{2.91}$$

and the effective KS potential in (2.90) is given by

$$v_s[n](\boldsymbol{r}, t) = v(\boldsymbol{r}, t) + \int d^3r \frac{n(\boldsymbol{r}', t)}{|\boldsymbol{r} - \boldsymbol{r}'|} + v_{xc}[n](\boldsymbol{r}, t) \qquad (2.92)$$

It is important to say that the xc potential used for the ground state calculation and the time-dependent xc potential used for the time propagation must match at the initial time in order to guarantee that the density remains static if no time-dependent potential is applied to the system at $t > t_0$ or to any sudden change at $t = t_0$.

It should also be stated that starting from the ground state is not actually necessary. The equations will still hold if one starts from another energy configuration as long as the many-body wave function is still a Slater determinant. The only difference is that in this case the potential will be a functional of the initial state.

Chapter 3

Non collinear spin Density Functional Theory (SDFT)

3.1 Pauli's equation

The full relativistic description of the interaction between fermions and an electromagnetic field requires the use of Dirac's equation [9][1]

$$(i\gamma^\mu \hat{\pi}_\mu - m)|\psi\rangle = 0 \tag{3.1}$$

where $\psi(x)$ is a four-dimension Dirac spinor, $\hat{\pi}_\mu$ is the canonical conjugated momentum, $\hat{\pi}_\mu = \hat{p}_\mu - q\hat{A}_\mu$, where A_μ is the four-vector potential and q is the charge of the particle. γ^μ are Dirac's gamma matrices, whose algebra is defined by the anti-commutation relation [9]

$$\gamma^\mu \gamma^\nu + \gamma^\nu \gamma^\mu = 2g^{\mu\nu} \tag{3.2}$$

with $g^{\mu\nu} = diag(1, -1, -1, -1)$ being the Minkowski metric. Now, if one isn't interested in studying the full relativistic description of a system of electrons, Dirac's equation can be brought to an approximate form [9]. First, as usual in

---

[1]For now the atomic units are abandoned and one only has $\hbar = c = 1$.

Relativistic Quantum Mechanics, any Dirac spinor can be written as

$$\psi = \begin{pmatrix} \bar{\varphi} \\ \bar{\chi} \end{pmatrix} \tag{3.3}$$

and in Pauli-Dirac's representation of the gamma matrices, Dirac's equation for a particle with charge q and spin $1/2$ assumes the form

$$i\partial_t \begin{pmatrix} \bar{\varphi} \\ \bar{\chi} \end{pmatrix} = \begin{pmatrix} \boldsymbol{\sigma} \cdot \hat{\boldsymbol{\pi}} \bar{\chi} + qA_0 \bar{\varphi} + m\bar{\varphi} \\ \boldsymbol{\sigma} \cdot \hat{\boldsymbol{\pi}} \bar{\varphi} + qA_0 \bar{\chi} - m\bar{\chi} \end{pmatrix} \tag{3.4}$$

with

$$\boldsymbol{\sigma} = \sigma_1 \hat{\boldsymbol{i}} + \sigma_2 \hat{\boldsymbol{j}} + \sigma_3 \hat{\boldsymbol{k}} \tag{3.5}$$

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{3.6}$$

and one should remember the relation which defines the algebra of this matrices

$$\sigma_i \sigma_j = \mathbb{I}_{2\times2} \delta_{i,j} + i\epsilon_{ijk}\sigma_k \tag{3.7}$$

where ϵ_{ijk} is the Levi-Civita andy-symmetric tensor. Now, taking the ansatz $\begin{pmatrix} \bar{\varphi} \\ \bar{\chi} \end{pmatrix} = e^{-imt} \begin{pmatrix} \varphi \\ \chi \end{pmatrix}$ and assuming that $|i\partial_t \chi| << |m\chi|$ and $|qA_0\chi| << |m\chi|$ one gets that

$$\chi = \frac{\boldsymbol{\sigma} \cdot \hat{\boldsymbol{\pi}} \varphi}{2m} \tag{3.8}$$

which immediately leads to the Pauli equation

$$i\partial_t \varphi = \frac{(\boldsymbol{\sigma} \cdot \hat{\boldsymbol{\pi}})^2}{2m}\varphi + qA_0\varphi = \left[\frac{(\hat{\boldsymbol{p}} - q\boldsymbol{A})^2}{2m} + qA_0 - \mu_B \boldsymbol{\sigma} \cdot \boldsymbol{B} \right] \varphi \tag{3.9}$$

with μ_B being Bohr's magneton (note that external potentials other than those coming from electromagnetic interactions are being neglected). Assuming a time-separable solution, it is trivial to express the energy of such particle as (for a

normalized solution)

$$
\begin{aligned}
E &= \frac{1}{2m} \int d^3r\, \varphi^\dagger(\boldsymbol{r})(\hat{\boldsymbol{p}} - q\boldsymbol{A})^2 \varphi(\boldsymbol{r}) + q \int d^3r\, A_0(\boldsymbol{r})n(\boldsymbol{r}) - \int d^3r\, \boldsymbol{m}(\boldsymbol{r}) \cdot \boldsymbol{B}(\boldsymbol{r}) \\
&= T + V + U_m
\end{aligned}
\tag{3.10}
$$

with the magnetization density vector being defined as

$$
\boldsymbol{m}(\boldsymbol{r}) = \mu_B \varphi^\dagger(\boldsymbol{r})\boldsymbol{\sigma}\varphi(\boldsymbol{r})
\tag{3.11}
$$

In case of weak magnetic fields, the vector potential can be discarded and one only works the magnetic field. Furthermore, the magnetic field resulting from the interaction between the nuclei and the electrons can also be ignored, so only the external magnetic field is considered.

3.2 The HK theorems in SDFT

It is clear from the previous section that in SDFT, due to the presence of a magnetic field in the Hamiltonian, one needs three extra ground state densities in order to establish something with the same idea as normal DFT. This section follows what was done for the relativist version of DFT [6].

Like in DFT, one starts by assuming that there must be a unique correspondence between the external potential and magnetic field, and the density and magnetization density.[1] Following the same arguments as in section 2.3.1, one assumes that there are two four vectors $(v(\boldsymbol{r}), \boldsymbol{B}(\boldsymbol{r}))$ and $(v'(\boldsymbol{r}), \boldsymbol{B}'(\boldsymbol{r}))$ which differ from each other by more than a constant vector but whose ground state wave function $|\psi_0\rangle$ and $\psi_0'\rangle$ (which should differ from each other by more than a constant phase) are equal. Like in (2.30), one gets that

$$
\left[\hat{V} - \hat{V}' + \mu_B \boldsymbol{\sigma} \cdot (\boldsymbol{B} - \boldsymbol{B}') \right] |\psi_0\rangle = (\epsilon_0 - \epsilon_0')|\psi_0\rangle
\tag{3.12}
$$

---

[1]Instead of $\boldsymbol{B}$ and $\boldsymbol{m}$ one could also establish a relation between $\boldsymbol{A}$ and $\boldsymbol{j}$ (the current density), but as $\boldsymbol{B}$ and $\boldsymbol{m}$ are uniquely determined from $\boldsymbol{A}$ and $\boldsymbol{j}$ once a certain gauge is fixed, both formalisms would be equivalent.

so, as long as two external potentials and magnetic fields differ from each other by more than a constant, there is a unique relation between the pair $(v(\boldsymbol{r}), \boldsymbol{B}(\boldsymbol{r}))$ and the (non-degenerate) ground state wave function.

The second part requires a bit more thought. Going with the same arguments as in section 2.3.1, one gets

$$E_0 < E_0' + \int d^3r \left[v(\boldsymbol{r}) - v'(\boldsymbol{r})\right] n_0(\boldsymbol{r}) - \mu_B \int d^3r' \left[\boldsymbol{B}(\boldsymbol{r}) - \boldsymbol{B}'(\boldsymbol{r})\right] \cdot \boldsymbol{m}(\boldsymbol{r}) \quad (3.13)$$

and the extra term also appears in the equation equivalent to the second part of (2.33). Now one should be reminded that what defines the magnetic field is the vector potential. Using Gauss' theorem and a property of the *del* operator, one easily gets that

$$\int d^3r \, \boldsymbol{m}(\boldsymbol{r}) \cdot \boldsymbol{B}(\boldsymbol{r}) = \int d^3r \boldsymbol{A}(\boldsymbol{r}) \cdot \boldsymbol{j}(\boldsymbol{r}) - \oiint_S dA \left[\boldsymbol{m}(\boldsymbol{r}) \times \boldsymbol{A}(\boldsymbol{r})\right] \cdot \hat{\boldsymbol{n}} \quad (3.14)$$

and as the surface terms should vanish when $r \rightarrow +\infty$, one can change the last term in (3.13) to

$$\int d^3r' \left[\boldsymbol{A}(\boldsymbol{r}) - \boldsymbol{A}'(\boldsymbol{r})\right] \cdot \boldsymbol{j}(\boldsymbol{r}) \quad (3.15)$$

Now, if the vector potentials differ from each other by a gauge transformation such that

$$\boldsymbol{A}'(\boldsymbol{r}) = \boldsymbol{A}(\boldsymbol{r}) + \nabla g(\boldsymbol{r}) \qquad \nabla \cdot \boldsymbol{A}'(\boldsymbol{r}) = 0 \Rightarrow \nabla^2 g(\boldsymbol{r}) = 0 \quad (3.16)$$

one immediately gets that

$$\int d^3r \nabla g(\boldsymbol{r}) \cdot \boldsymbol{j}(\boldsymbol{r}) = - \oiint_S dA \left[g(\boldsymbol{r})\boldsymbol{j}(\boldsymbol{r})\right] \cdot \hat{\boldsymbol{n}} + \int d^3r g(\boldsymbol{r}) \nabla \cdot \boldsymbol{j}(\boldsymbol{r}) \quad (3.17)$$

and as the currents should vanish in the infinite and because of the continuity equation, the integral is zero. So, the HK theorems for spin DFT require not only that the electrostatic potentials differ by more than an additive constant, but also that the vector potentials from which the external magnetic fields are evaluated differ by more than a gauge transformation that respects (3.16)

So, it is possible to establish an equivalent to the first HK theorem for spin DFT. The second theorem can also be easily extended, as it only reflects the nature of the Rayleigh-Ritz variational principle. As such, and due to the unique relation between the vector potential and the magnetic field (once a certain gauge is fixed), and the current and magnetization, it is possible to write

$$E[n(\boldsymbol{r}), \boldsymbol{m}(\boldsymbol{r})] = F[n(\boldsymbol{r}), \boldsymbol{m}(\boldsymbol{r})] + \int d^3 r n(\boldsymbol{r}) v(\boldsymbol{r}) - \int d^3 r' \boldsymbol{m}(\boldsymbol{r}) \cdot \boldsymbol{B}(\boldsymbol{r}) \quad (3.18)$$

with $F[n(\boldsymbol{r}), \boldsymbol{m}(\boldsymbol{r})] = T[n(\boldsymbol{r}), \boldsymbol{m}(\boldsymbol{r})] + W[n(\boldsymbol{r}), \boldsymbol{m}(\boldsymbol{r})]$ being the universal functional.

With the HK theorems, one can now assume the existence of a Kohn-Sham auxiliary system. For an electron that interacts with an external weak electromagnetic field, the Kohn-Sham equation is

$$\left[\frac{1}{2} (\boldsymbol{\sigma} \cdot \hat{\boldsymbol{p}})^2 + v_s(\boldsymbol{r}) \mathbb{I}_{2\times 2} + \mu_B \boldsymbol{\sigma} \cdot \boldsymbol{B}_s(\boldsymbol{r}) \right] \phi_i(\boldsymbol{r}) = \epsilon_i \phi_i(\boldsymbol{r}) \quad (3.19)$$

The sign difference in the Stern-Gerlach term with respect to (3.9) is due to the use of atomic units. Using the KS system, the universal functional can be written as

$$F[n(\boldsymbol{r}), \boldsymbol{m}(\boldsymbol{r})] = T_s[n(\boldsymbol{r}), \boldsymbol{m}(\boldsymbol{r})] + E_H[n(\boldsymbol{r})] + E_{xc}[n(\boldsymbol{r}), \boldsymbol{m}(\boldsymbol{r})] \quad (3.20)$$

By defining the ground state density and ground state magnetization density of the N electron system respectively as

$$n(\boldsymbol{r}) = \sum_{k=1}^{N} \theta_k \phi_k^\dagger(\boldsymbol{r}) \phi_k(\boldsymbol{r}) \quad (3.21)$$

$$\boldsymbol{m}(\boldsymbol{r}) = -\mu_B \sum_{k=1}^{N} \theta_k \phi_k^\dagger(\boldsymbol{r}) \boldsymbol{\sigma} \phi_k(\boldsymbol{r}) \quad (3.22)$$

one can define the KS potential and magnetic field as

$$v_s(\boldsymbol{r}) = \left(\frac{\delta E[n, \boldsymbol{m}]}{\delta n(\boldsymbol{r})}\right)_{\boldsymbol{m}} = v_{ext}(\boldsymbol{r}) + v_H(\boldsymbol{r}) + \left(\frac{\delta E_{xc}[n, \boldsymbol{m}]}{\delta n(\boldsymbol{r})}\right)_{\boldsymbol{m}} \tag{3.23}$$

$$\boldsymbol{B}_s(\boldsymbol{r}) = -\left(\frac{\delta E[n, \boldsymbol{m}]}{\delta \boldsymbol{m}(\boldsymbol{r})}\right)_{n} = \boldsymbol{B}_{ext}(\boldsymbol{r}) - \left(\frac{\delta E_{xc}[n, \boldsymbol{m}]}{\delta \boldsymbol{m}(\boldsymbol{r})}\right)_{n} \tag{3.24}$$

and thus, one can define the exchange-correlation potential and magnetic field

$$v_{xc}(\boldsymbol{r}) = \left(\frac{\delta E_{xc}[n, \boldsymbol{m}]}{\delta n(\boldsymbol{r})}\right)_{\boldsymbol{m}} \qquad \boldsymbol{B}_{xc}(\boldsymbol{r}) = -\left(\frac{\delta E_{xc}[n, \boldsymbol{m}]}{\delta \boldsymbol{m}(\boldsymbol{r})}\right)_{n} \tag{3.25}$$

3.3 OEP in SDFT

Having established the grounds for spin DFT the remaining work now is to develop approximate functionals for the exchange-correlation energy in order to work with the ground state density and magnetization density. This section follows the derivation of the OEP method done in [6] and [20]

Using Many-Body theory it is possible to derive a functional expansion for $E_{xc}[n, \boldsymbol{m}]$ in terms of powers of e^2, much like (2.73)

$$E_{xc}[n, \boldsymbol{m}] = \sum_{j=1}^{+\infty} e^{2j} E_{xc}^{(j)}[n, \boldsymbol{m}] = E_x[n, \boldsymbol{m}] + E_c^{(2)}[n, \boldsymbol{m}] + ... \tag{3.26}$$

$$v_{xc}[n, \boldsymbol{m}] = \sum_{j=1}^{+\infty} e^{2j} v_{xc}^{(j)}[n, \boldsymbol{m}] = v_x[n, \boldsymbol{m}] + v_c^{(2)}[n, \boldsymbol{m}] + ... \tag{3.27}$$

and again, one can choose as first order approximation the exact exchange energy, which has the same expression as (2.55)

$$E_x[n, \boldsymbol{m}] = -\frac{1}{2} \sum_{i,j}^{N} \theta_i \theta_j \iint d^3r d^3r' \frac{\phi_i^\dagger(\boldsymbol{r})\phi_j(\boldsymbol{r})\phi_j^\dagger(\boldsymbol{r}')\phi_i(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} \tag{3.28}$$

although now one is working with the Kohn-Sham spinors, solutions of (3.19).

The rest of the derivation goes in a similar way. One starts by writing the following equalities

$$
\frac{\delta E_x}{\delta v_s(\boldsymbol{r})} = \int d^3 r' \left[\frac{\delta E_x}{\delta n(\boldsymbol{r}')} \frac{\delta n(\boldsymbol{r}')}{\delta v_s(\boldsymbol{r})} + \frac{\delta E_x}{\delta \boldsymbol{m}(\boldsymbol{r}')} \cdot \frac{\delta \boldsymbol{m}(\boldsymbol{r}')}{\delta v_s(\boldsymbol{r})} \right] =
$$
$$
= \int d^3 r' \sum_{k=1}^{N} \left[\frac{\delta \phi_k^\dagger(\boldsymbol{r}')}{\delta v_s(\boldsymbol{r})} \frac{\delta E_x}{\delta \phi_k^\dagger(\boldsymbol{r}')} + c.c. \right]
\tag{3.29}
$$

$$
\frac{\delta E_x}{\delta \boldsymbol{B}_s^{(i)}(\boldsymbol{r})} = \int d^3 r' \left[\frac{\delta E_x}{\delta n(\boldsymbol{r}')} \frac{\delta n(\boldsymbol{r}')}{\delta \boldsymbol{B}_s^{(i)}(\boldsymbol{r})} + \sum_{j=1}^{3} \frac{\delta E_x}{\delta \boldsymbol{m}^{(j)}(\boldsymbol{r})} \frac{\delta \boldsymbol{m}^{(j)}(\boldsymbol{r}')}{\delta \boldsymbol{B}_s^{(i)}(\boldsymbol{r})} \right] =
$$
$$
= \int d^3 r' \sum_{k=1}^{N} \left[\frac{\delta \phi_k^\dagger(\boldsymbol{r}')}{\delta \boldsymbol{B}_s^{(i)}(\boldsymbol{r})} \frac{\delta E_x}{\delta \phi_k^\dagger(\boldsymbol{r}')} + c.c. \right]
\tag{3.30}
$$

Through the use of perturbation theory, one can derive the sixteen components of the linear response tensor

$$
\chi_{nn}(\boldsymbol{r}', \boldsymbol{r}) = \frac{\delta n(\boldsymbol{r}')}{\delta v_s(\boldsymbol{r})} = -\sum_{k=1}^{N} \theta_k \left[\phi_k^\dagger(\boldsymbol{r}') G_k(\boldsymbol{r}', \boldsymbol{r}) \phi_k(\boldsymbol{r}) + c.c. \right]
\tag{3.31}
$$

$$
\boldsymbol{\chi}_{nm}(\boldsymbol{r}', \boldsymbol{r}) = \frac{\delta n(\boldsymbol{r}')}{\delta \boldsymbol{B}_s(\boldsymbol{r})} = -\mu_B \sum_{k=1}^{N} \theta_k \left[\phi_k^\dagger(\boldsymbol{r}) \boldsymbol{\sigma} G_k(\boldsymbol{r}, \boldsymbol{r}') \phi_k(\boldsymbol{r}') + c.c. \right]
\tag{3.32}
$$

$$
\boldsymbol{\chi}_{mn}(\boldsymbol{r}', \boldsymbol{r}) = \frac{\delta \boldsymbol{m}(\boldsymbol{r}')}{\delta v_s(\boldsymbol{r})} = \mu_B \sum_{k=1}^{N} \theta_k \left[\phi_k^\dagger(\boldsymbol{r}) G_k(\boldsymbol{r}, \boldsymbol{r}') \boldsymbol{\sigma} \phi_k(\boldsymbol{r}') + c.c. \right]
\tag{3.33}
$$

$$
\chi_{mm}^{(i,j)}(\boldsymbol{r}', \boldsymbol{r}) = \frac{\delta \boldsymbol{m}^{(i)}(\boldsymbol{r}')}{\delta \boldsymbol{B}_s^{(j)}(\boldsymbol{r})} = \mu_B^2 \sum_{k=1}^{N} \theta_k \left[\phi_k^\dagger(\boldsymbol{r}) \sigma_j G_k(\boldsymbol{r}, \boldsymbol{r}') \sigma_i \phi_k(\boldsymbol{r}') + c.c. \right]
\tag{3.34}
$$

which are obtained by using the following relations

$$
\frac{\delta \phi_k(\boldsymbol{r}')}{\delta v_s(\boldsymbol{r})} = \sum_{\substack{j \neq k \\ j=1}}^{N} \frac{\phi_j(\boldsymbol{r}') \phi_j^\dagger(\boldsymbol{r})}{\epsilon_k - \epsilon_j} \phi_k(\boldsymbol{r}) = -G_k(\boldsymbol{r}', \boldsymbol{r}) \phi_k(\boldsymbol{r})
\tag{3.35}
$$

$$\frac{\delta\phi_k(\boldsymbol{r}')}{\delta\boldsymbol{B}_s(\boldsymbol{r})} = \sum_{\substack{j\neq k \\ j=1}}^{N} \frac{\phi_j(\boldsymbol{r}')\phi_j^\dagger(\boldsymbol{r})}{\epsilon_k - \epsilon_j}\boldsymbol{\sigma}\phi_k(\boldsymbol{r}) = -\mu_B G_k(\boldsymbol{r}',\boldsymbol{r})\boldsymbol{\sigma}\phi_k(\boldsymbol{r}) \tag{3.36}$$

Using equations (3.31) to (3.36) in equations (3.29) and (3.30), the functional derivatives of E_x can be written as a set of four coupled integral equations

$$\int d^3r'\left\{v_x(\boldsymbol{r}')\chi_{nn}(\boldsymbol{r}',\boldsymbol{r}) - \boldsymbol{B}_x(\boldsymbol{r}')\cdot\boldsymbol{\chi}_{mn}(\boldsymbol{r}',\boldsymbol{r})\right\} =$$
$$= -\int d^3r'\sum_k\left\{\phi_k^\dagger(\boldsymbol{r})G_k(\boldsymbol{r},\boldsymbol{r}')\frac{\delta E_x}{\delta\phi_k^\dagger(\boldsymbol{r}')} + c.c.\right\} \tag{3.37}$$

$$\int d^3r'\left\{v_x(\boldsymbol{r}')\boldsymbol{\chi}_{nm}^{(i)}(\boldsymbol{r}',\boldsymbol{r}) - \sum_{j=1}^{3}\boldsymbol{B}_x^{(j)}(\boldsymbol{r}')\chi_{mm}^{(j,i)}(\boldsymbol{r}',\boldsymbol{r})\right\} =$$
$$= -\mu_B\int d^3r'\sum_k\left\{\phi_k^\dagger(\boldsymbol{r})\boldsymbol{\sigma}_i G_k(\boldsymbol{r},\boldsymbol{r}')\frac{\delta E_x}{\delta\phi_k^\dagger(\boldsymbol{r}')} + c.c.\right\} \quad i = 1,2,3 \tag{3.38}$$

3.3.1 KLI approximation in SDFT

Now one can apply the KLI approximation. Using the same arguments as in section 2.3.5, the linear response functions can be approximated to[1]

$$\chi_{nn}(\boldsymbol{r}',\boldsymbol{r}) = -2n(\boldsymbol{r})\delta^{(3)}(\boldsymbol{r}-\boldsymbol{r}') + 2\sum_k\theta_k|\phi_k(\boldsymbol{r})|^2|\phi_k(\boldsymbol{r}')|^2 \tag{3.39}$$

$$\boldsymbol{\chi}_{nm}(\boldsymbol{r}',\boldsymbol{r}) = 2\boldsymbol{m}(\boldsymbol{r})\delta^{(3)}(\boldsymbol{r}-\boldsymbol{r}') + 2\mu_B\sum_k\theta_k\phi_k^\dagger(\boldsymbol{r}')\boldsymbol{\sigma}\phi_k(\boldsymbol{r}')|\phi_k(\boldsymbol{r})|^2 \tag{3.40}$$

$$\boldsymbol{\chi}_{mn}(\boldsymbol{r}',\boldsymbol{r}) = -2\boldsymbol{m}(\boldsymbol{r})\delta^{(3)}(\boldsymbol{r}-\boldsymbol{r}') - 2\mu_B\sum_k\theta_k|\phi_k(\boldsymbol{r})|^2\phi_k^\dagger(\boldsymbol{r}')\boldsymbol{\sigma}\phi_k(\boldsymbol{r}') \tag{3.41}$$

---

[1]The coefficient $\Delta\epsilon$ is ignored in the expressions and from now on, as in the exact exchange limit it is irrelevant.

$$\chi_{mm}^{(i,j)}(\boldsymbol{r}',\boldsymbol{r}) = 2\mu_B^2 n(\boldsymbol{r})\delta_{ij}\delta^{(3)}(\boldsymbol{r}-\boldsymbol{r}') - \mu_B^2 \sum_k \theta_k \left[\phi_k^\dagger(\boldsymbol{r})\sigma_j\phi_k(\boldsymbol{r})\phi_k^\dagger(\boldsymbol{r}')\sigma_i\phi_k(\boldsymbol{r}') + c.c.\right]$$

$$(3.42)$$

An interesting thing happens during the evaluation of χ_{mm} within KLI. One can notice that two of its elements can be written as

$$\mu_B^2 \sum_k \theta_k \phi_k^\dagger(\boldsymbol{r}) \{\sigma_i, \sigma_j\} \phi_k(\boldsymbol{r}) \tag{3.43}$$

as one should sum two terms that are the complex conjugate of each other and $(\sigma_i\sigma_j)^\dagger = \sigma_j\sigma_i$, this will lead to the elimination of a pure imaginary term in χ_{mm}

$$2i\mu_B^2 \left[\boldsymbol{m}(\boldsymbol{r}) \times \boldsymbol{B}_x(\boldsymbol{r})\right]_i \tag{3.44}$$

which is a direct contribution from the torque of the exchange magnetic field.

Each right hand side of equations (3.29) and (3.30) can now be written as

$$-\sum_k \left[\phi_k^\dagger(\boldsymbol{r})\frac{\delta E_x}{\delta\phi_k^\dagger(\boldsymbol{r})} - |\phi_k(\boldsymbol{r})|^2 \int d^3r' \phi_k^\dagger(\boldsymbol{r}')\frac{\delta E_x}{\delta\phi_k^\dagger(\boldsymbol{r}')} + c.c.\right] \tag{3.45}$$

$$-\mu_B \sum_k \left[\phi_k^\dagger(\boldsymbol{r})\sigma_i\frac{\delta E_x}{\delta\phi_k^\dagger(\boldsymbol{r})} - \phi_k^\dagger(\boldsymbol{r})\sigma_i\phi_k(\boldsymbol{r}) \int d^3r' \phi_k^\dagger(\boldsymbol{r}')\frac{\delta E_x}{\delta\phi_k^\dagger(\boldsymbol{r}')} + c.c.\right] \tag{3.46}$$

So, one can finally write an inhomogeneous system of equations which when solved would give the expressions for v_x and $\boldsymbol{B}_x$. As one has to deal with the relations between two groups of four objects, it is convenient to use Einstein's summation convention and the usual notation from Special Relativity [8]. Due to the use of atomic units, one should define the metric matrix as $\eta^{\mu\nu} = diag(1,1,1,1) = \mathbb{I}_{4\times4}$. If one defines the four vector exchange potential and the four density as

$$v_x^\mu(\boldsymbol{r}) = (v_x(\boldsymbol{r}), \mu_B\boldsymbol{B}_x(\boldsymbol{r})) \quad n^\mu(\boldsymbol{r}) = \left(n(\boldsymbol{r}), \frac{\boldsymbol{m}(\boldsymbol{r})}{\mu_B}\right) \tag{3.47}$$

and by establishing the following four vector

$$\sigma^\mu = (\mathbb{I}_{2\times 2}, \boldsymbol{\sigma}) \tag{3.48}$$

one can rewrite the four equations in the KLI approximation [(3.29) and (3.30)] in the compact form

$$M^{\mu\nu}(\boldsymbol{r})v_{x,\nu}(\boldsymbol{r}) = \Lambda_x^\mu(\boldsymbol{r}) \tag{3.49}$$

with

$$M^{\mu\nu}(\boldsymbol{r}) = \begin{pmatrix} n(\boldsymbol{r}) & -\frac{m_x(\boldsymbol{r})}{\mu_B} & -\frac{m_y(\boldsymbol{r})}{\mu_B} & -\frac{m_z(\boldsymbol{r})}{\mu_B} \\ -\frac{m_x(\boldsymbol{r})}{\mu_B} & n(\boldsymbol{r}) & 0 & 0 \\ -\frac{m_y(\boldsymbol{r})}{\mu_B} & 0 & n(\boldsymbol{r}) & 0 \\ -\frac{m_z(\boldsymbol{r})}{\mu_B} & 0 & 0 & n(\boldsymbol{r}) \end{pmatrix} \tag{3.50}$$

and

$$\Lambda_x^\mu(\boldsymbol{r}) = \frac{1}{2}\sum_{k=1}^N \left\{ \left[\phi_k^\dagger(\boldsymbol{r})\sigma^\mu \frac{\delta E_x}{\delta \phi_k(\boldsymbol{r})} + c.c. \right] + \phi_k^\dagger(\boldsymbol{r})\sigma^\mu \phi_k(\boldsymbol{r}) \Delta v_k^{KLI} \right\} \tag{3.51}$$

with the exchange potential difference now being

$$\Delta v_k^{KLI} = \int d^3 r \left\{ \theta_k \phi_k^\dagger(\boldsymbol{r}) \left[v_x(\boldsymbol{r}) + \mu_B \boldsymbol{\sigma} \cdot \boldsymbol{B}_x(\boldsymbol{r}) - u_{x,k}^\dagger(\boldsymbol{r}) \right] \phi_k(\boldsymbol{r}) + c.c. \right\} \tag{3.52}$$

as long as the potential $u_{x,k}^\dagger(\boldsymbol{r})$ (now a 2×2 matrix) is defined as

$$\frac{\delta E_x}{\delta \phi_k^\dagger(\boldsymbol{r})} = u_{x,k}^\dagger(\boldsymbol{r})\phi_k(\boldsymbol{r}) \tag{3.53}$$

The system of equations can be inverted in order to obtain a set of coupled integral equations which can be solved iteratively in order to evaluate the exchange potential and magnetic field. Inverting the matrix $M^{\mu\nu}$ in (3.49) yields[1]

$$v_x^\mu(\boldsymbol{r}) = \Gamma(\boldsymbol{r})N^{\mu\nu}(\boldsymbol{r})\Lambda_{x,\nu}(\boldsymbol{r}) \tag{3.54}$$

---

[1]One should note that there is no difference between the covariant and contravariant forms of the vectors and matrices, since the metric is purely an identity matrix. Again, the notation is used only because of its usefulness when dealing with four-vectors and 4×4 matrices and one should remind oneself that this is not a relativistic theory.

with

$$[\Gamma(\boldsymbol{r})]^{-1} = n(\boldsymbol{r}) \left[n^2(\boldsymbol{r}) - \frac{\boldsymbol{m}(\boldsymbol{r}) \cdot \boldsymbol{m}(\boldsymbol{r})}{\mu_B^2} \right] \tag{3.55}$$

and

$$N^{00}(\boldsymbol{r}) = n^2(\boldsymbol{r}) \qquad N^{0i}(\boldsymbol{r}) = n(\boldsymbol{r}) \frac{m_i(\boldsymbol{r})}{\mu_B} = N^{i0}(\boldsymbol{r})$$

$$\tag{3.56}$$

$$N^{ii}(\boldsymbol{r}) = n^2(\boldsymbol{r}) + \sum_{j=1}^{3} (\delta_{ij} - 1) \frac{m_j^2(\boldsymbol{r})}{\mu_B^2} \quad N_{i \neq j}^{ij}(\boldsymbol{r}) = \frac{m_i(\boldsymbol{r}) m_j(\boldsymbol{r})}{\mu_B^2}$$

Obviously, there is the question of whenever or not $[\Gamma(\boldsymbol{r})]^{-1}$ (which when multiplied by the density is the determinant of $M^{\mu\nu}(\boldsymbol{r})$) is zero. Contrary to what happens in relativistic-spin DFT (see [3]) where it can be proven that the determinant of the correspondent matrix will be always positive, as off the date of this thesis such statement cannot be said for the case of SDFT (Appendix A contains a few calculations on the conditions for $\Gamma(\boldsymbol{r})$ to be different than zero).

The set of equations (3.54) can be solved iteratively or through the same method from which equation (2.87) is obtained. It is obvious at first sight that one cannot simply write $\langle i | v_x^\mu(\boldsymbol{r}) | i \rangle$ and just add the resulting components. Looking at (3.19), it is obvious that the right way to combine the elements of v_x^μ is through the scalar product $\sigma_\mu v_x^\mu$. First, one gets that

$$\sigma_\mu v_x^\mu = \Gamma \sigma_\mu N^{\mu\nu} \Lambda_{x,\nu} = \Gamma \begin{pmatrix} N^{0\nu} \Lambda_{x,\nu} + N^{3\nu} \Lambda_{x,\nu} & N^{1\nu} \Lambda_{x,\nu} - i N^{2\nu} \Lambda_{x,\nu} \\ N^{1\nu} \Lambda_{x,\nu} + i N^{2\nu} \Lambda_{x,\nu} & N^{0\nu} \Lambda_{x,\nu} - N^{3\nu} \Lambda_{x,\nu} \end{pmatrix} \tag{3.57}$$

and it can be easily obtained that

$$N^{0\nu}(\boldsymbol{r}) \Lambda_{x,\nu}(\boldsymbol{r}) = n(\boldsymbol{r}) \sum_{k=1}^{N} \left\{ \phi_k^\dagger(\boldsymbol{r}) \left[\frac{n(\boldsymbol{r})}{2} + \boldsymbol{\sigma} \cdot \frac{\boldsymbol{m}(\boldsymbol{r})}{2\mu_B} \right] \left[u_{x,k}^\dagger(\boldsymbol{r}) + \frac{\Delta v_k^{KLI}}{2} \right] \phi_k(\boldsymbol{r}) + c.c. \right\}$$

$$\tag{3.58}$$

$$
N^{i\nu}(\boldsymbol{r})\Lambda_{x,\nu}(\boldsymbol{r}) = \frac{m_i(\boldsymbol{r})}{\mu_B} \sum_{k=1}^{N} \left\{ \phi_k^\dagger(\boldsymbol{r}) \left[\frac{n(\boldsymbol{r})}{2} + \boldsymbol{\sigma} \cdot \frac{\boldsymbol{m}(\boldsymbol{r})}{2\mu_B} \right] \left[u_{x,k}^\dagger(\boldsymbol{r}) + \frac{\Delta v_k^{KLI}}{2} \right] \phi_k(\boldsymbol{r}) +
$$
$$
+ c.c. \right\} + \frac{1}{2\Gamma(\boldsymbol{r})n(\boldsymbol{r})} \sum_{k=1}^{N} \left\{ \phi_k^\dagger(\boldsymbol{r})\sigma_i \left[u_{x,k}^\dagger(\boldsymbol{r}) + \frac{\Delta v_k^{KLI}}{2} \right] \phi_k(\boldsymbol{r}) + c.c. \right\}
$$
$$(3.59)$$

provided that one keeps in mind the metric defined previously due to the use of atomic units. The factor of $1/2$ in Δv_k shows up because in (3.51) the complex conjugate part of the second term is already inside the definition of Δv_k.

Combining (3.58), (3.59) and (3.57) the resulting expression for $\sigma_\mu v_x^\mu(\boldsymbol{r})$ is

$$
\sigma_\mu v_x^\mu(\boldsymbol{r}) = 2\Gamma(\boldsymbol{r}) \left[\frac{n(\boldsymbol{r})}{2} + \boldsymbol{\sigma} \cdot \frac{\boldsymbol{m}(\boldsymbol{r})}{2\mu_B} \right] \sum_{k=1}^{N} \left\{ \phi_k^\dagger(\boldsymbol{r}) \left[\frac{n(\boldsymbol{r})}{2} + \boldsymbol{\sigma} \cdot \frac{\boldsymbol{m}(\boldsymbol{r})}{2\mu_B} \right] \times \right.
$$
$$
\times \left[u_{x,k}^\dagger(\boldsymbol{r}) + \frac{\Delta v_k^{KLI}}{2} \right] \phi_k(\boldsymbol{r}) + c.c. \right\} +
$$
$$
+ \frac{1}{2n(\boldsymbol{r})} \sum_{k=1}^{N} \left\{ \Sigma_{x,k}(\boldsymbol{r}) + \Sigma_{x,k}^\dagger(\boldsymbol{r}) + \Delta_k(\boldsymbol{r})\Delta v_k^{KLI} \right\}
$$
$$(3.60)$$

with

$$
\Sigma_{x,k}(\boldsymbol{r}) = \begin{pmatrix} \phi_k^\dagger(\boldsymbol{r})\sigma_3 u_{x,k}^\dagger(\boldsymbol{r})\phi_k(\boldsymbol{r}) & \phi_k^\dagger(\boldsymbol{r})(\sigma_1 - i\sigma_2)u_{x,k}^\dagger(\boldsymbol{r})\phi_k(\boldsymbol{r}) \\ \phi_k^\dagger(\boldsymbol{r})(\sigma_1 + i\sigma_2)u_{x,k}^\dagger(\boldsymbol{r})\phi_k(\boldsymbol{r}) & -\phi_k^\dagger(\boldsymbol{r})\sigma_3 u_{x,k}^\dagger(\boldsymbol{r})\phi_k(\boldsymbol{r}) \end{pmatrix} \quad (3.61)
$$

$$
\Delta_k(\boldsymbol{r}) = \begin{pmatrix} \phi_k^\dagger(\boldsymbol{r})\sigma_3\phi_k(\boldsymbol{r}) & \phi_k^\dagger(\boldsymbol{r})(\sigma_1 - i\sigma_2)\phi_k(\boldsymbol{r}) \\ \phi_k^\dagger(\boldsymbol{r})(\sigma_1 + i\sigma_2)\phi_k(\boldsymbol{r}) & -\phi_k^\dagger(\boldsymbol{r})\sigma_3\phi_k(\boldsymbol{r}) \end{pmatrix} \quad (3.62)
$$

There is no factor $1/2$ before Δv_k in the second sum as one should note that $\Delta_k(\boldsymbol{r}) = \Delta_k^\dagger(\boldsymbol{r})$.

It is convenient now, due to the form of equations (3.57) - (3.60), that one changes the main objects of spin DFT from four vectors to two by two hermitian

matrices. Let the following matrices

$$V_s(\boldsymbol{r}) = \sigma_\mu v_s^\mu(\boldsymbol{r}) = \begin{pmatrix} v_s^{\alpha\alpha}(\boldsymbol{r}) & v_s^{\alpha\beta}(\boldsymbol{r}) \\ v_s^{\beta\alpha}(\boldsymbol{r}) & v_s^{\beta\beta}(\boldsymbol{r}) \end{pmatrix} \tag{3.63}$$

be the KS potential in its matrix form and

$$\rho(\boldsymbol{r}) = \frac{n(\boldsymbol{r})}{2}\mathbb{I}_{2\times 2} + \boldsymbol{\sigma} \cdot \frac{\boldsymbol{m}(\boldsymbol{r})}{2\mu_B} = \sum_{i=1}^{N} \theta_i \begin{pmatrix} |\phi_i^\beta(\boldsymbol{r})|^2 & -\phi_i^{*\beta}(\boldsymbol{r})\phi_i^\alpha(\boldsymbol{r}) \\ -\phi_i^{*\alpha}(\boldsymbol{r})\phi_i^\beta(\boldsymbol{r}) & |\phi_i^\alpha(\boldsymbol{r})|^2 \end{pmatrix} \tag{3.64}$$

the ρ matrix be (aside a factor which is the determinant of the density) the inverse of the density of the system in its matrix form, which is given by

$$\mathcal{N}(\boldsymbol{r}) = \frac{n(\boldsymbol{r})}{2}\mathbb{I}_{2\times 2} - \boldsymbol{\sigma} \cdot \frac{\boldsymbol{m}(\boldsymbol{r})}{2\mu_B} \tag{3.65}$$

Thus equation (3.60) can be rewritten as[1]

$$V_x(\boldsymbol{r}) = 2\Gamma(\boldsymbol{r})\rho(\boldsymbol{r})\sum_{k=1}^{N}\left\{\phi_k^\dagger(\boldsymbol{r})\rho(\boldsymbol{r})\left[u_{x,k}^\dagger(\boldsymbol{r}) + \frac{\Delta v_k^{KLI}}{2}\right]\phi_k(\boldsymbol{r}) + c.c.\right\} + $$
$$+ \frac{1}{2n(\boldsymbol{r})}\sum_{k=1}^{N}\left\{\Sigma_{x,k}(\boldsymbol{r}) + \Sigma_{x,k}^\dagger(\boldsymbol{r}) + \Delta_k(\boldsymbol{r})\Delta v_k^{KLI}\right\} \tag{3.66}$$

Like in 2.3.5, this equation can be separated in two main components, giving

$$V_x(\boldsymbol{r}) = V_{slater}(\boldsymbol{r}) + \sum_{k=1}^{N}\left\{2\Gamma(\boldsymbol{r})\rho(\boldsymbol{r})\phi_k^\dagger(\boldsymbol{r})\rho(\boldsymbol{r})\phi_k(\boldsymbol{r})+ \right.$$
$$\left. + \frac{1}{2n(\boldsymbol{r})}\Delta_k(\boldsymbol{r})\right\}\Delta v_k^{KLI} \tag{3.67}$$

---

[1]Using the matrices ρ and V_s as the key components, one should note that the function $\Gamma(\boldsymbol{r})$ is now expressed as $[\Gamma(\boldsymbol{r})]^{-1} = 4\left[\rho^{\alpha\alpha}(\boldsymbol{r}) + \rho^{\beta\beta}(\boldsymbol{r})\right]\det(\rho(\boldsymbol{r}))$

by redefining the Slater part as

$$V_{slater}(\boldsymbol{r}) = \sum_{k=1}^{N} \left\{ 2\Gamma(\boldsymbol{r})\rho(\boldsymbol{r}) \left[\phi_k^\dagger(\boldsymbol{r})\rho(\boldsymbol{r})u_{x,k}^\dagger(\boldsymbol{r})\phi_k(\boldsymbol{r}) + c.c. \right] + \right. \\ \left. + \frac{1}{2n(\boldsymbol{r})} \left[\Sigma_{x,k}(\boldsymbol{r}) + \Sigma_{x,k}^\dagger(\boldsymbol{r}) \right] \right\} \tag{3.68}$$

So, in order to obtain a equation for Δv_k^{KLI} like (2.87), once should write

$$\langle i|V_s|i\rangle - \langle i|u_{x,i}^\dagger|i\rangle = \langle i|V_{slater}|i\rangle - \langle i|u_{x,i}^\dagger|i\rangle + \sum_{k=1}^{N} M_{i,k}\Delta v_k \\ \langle i|V_s^\dagger|i\rangle - \langle i|u_{x,i}|i\rangle = \langle i|V_{slater}^\dagger|i\rangle - \langle i|u_{x,i}|i\rangle + \sum_{k=1}^{N} M_{i,k}\Delta v_k \tag{3.69}$$

and by adding both, one obtains

$$\sum_{k=1}^{N}[\delta_{i,k} - 2M_{i,k}]\Delta v_k^{KLI} = \langle i|V_{slater}(\boldsymbol{r}) - u_{x,i}^\dagger(\boldsymbol{r})|i\rangle + c.c. \tag{3.70}$$

but the matrix elements are now

$$M_{i,k} = \int d^3r \left\{ 2\Gamma(\boldsymbol{r})\phi_i^\dagger(\boldsymbol{r})\rho(\boldsymbol{r})\phi_i(\boldsymbol{r})\phi_k^\dagger(\boldsymbol{r})\rho(\boldsymbol{r})\phi_k(\boldsymbol{r}) + \right. \\ \left. + \frac{1}{2n(\boldsymbol{r})}\phi_i^\dagger(\boldsymbol{r})\Delta_k(\boldsymbol{r})\phi_i(\boldsymbol{r}) \right\} \tag{3.71}$$

For some specific details concerning the implementation of the equations in OCTOPUS see Appendix B. The code file is transcript in Appendix C.

Chapter 4

Numerical results and analysis

In this section the results obtained through simulation using OCTOPUS, ([4], [1]) will be presented and analyzed. In Sections 4.1 and 4.2 are presented results for ground state calculations within KLI and Slater approximations on atoms of the first three periods and Xe, that have been done to validate the implementation. The atoms are arranged in the tables in accordance to their pseudo-potential description.

In Section 4.3 are the results for the Xe_3^+ cluster obtained by real-time propagation.

Octopus solves the equations (Kohn-Sham and time-dependent Kohn-Sham) in real space by sampling the wave functions in a grid and using an high finite difference order method to evaluate derivatives. The grid is defined by spheres centers on the atoms with a given radius and spacing, that are input parameters in the simulation. Standard LDA's and GGA's functionals are available from the LibXC [17].

4.1 Validation of the implementation: orbital energies of single atoms

Results were obtains by preforming a ground state calculation over a real space grid. The Tables 4.1 to 4.12 contain the results obtained through OCTOPUS for the KS eigenvalues (e_{KS}) and average value of each spin moment for each KS eigenstate (S_x, S_y, S_z)

$$\langle S_i \rangle = \frac{1}{2} \int d^3 r \, \phi^\dagger(\boldsymbol{r}) \sigma_i \phi(\boldsymbol{r}) \tag{4.1}$$

They also show the order of magnitude of the difference between the eigenvalues calculated with the non-collinear spin expressions and the collinear spin formalism, which will be represented by δ. Significant differences were not expected since there were no added corrections to the simulation (e.g. there was no relativistic correction). The radius, spacing and starting guess for the wave functions are indicated in each table.

In this section there should be no results for H and alkali atoms. As it is explained in Appendix A, it would be impossible to obtain results for these systems since they are described as only having one occupied state. Still, by making the determinant of (3.64) not zero but something very small (10^{-20} was the value chosen in this case) it is possible to get good results for the atoms of the first group, as it can be seen in Table 4.1

Table 4.1: Values of e_{KS}, average values of S_x, S_y, S_z and values of δ for each state of the atoms H, Li and Na (radius = 4.5 Å, spacing = 0.4 Å, starting from LSDA)

Atom	State	e_{KS} (eV)	Occupancy	$\langle S_x \rangle$	$\langle S_y \rangle$	$\langle S_z \rangle$	δ (eV)
H	1	-13.050	1	0.000	0.000	-0.500	0.1
Li	1	-5.380	1	0.000	0.000	-0.500	-
Na	1	-5.167	1	0.000	0.000	0.500	-

Table 4.2: Values of e_{KS}, average values of S_x, S_y, S_z and values of δ for each state of the atoms He, Be and Mg (radius = 4.5 Å, spacing = 0.15 Å, starting from LCAO)

Atom	State	e_{KS} (eV)	Occupancy	$\langle S_x \rangle$	$\langle S_y \rangle$	$\langle S_z \rangle$	δ (eV)
He	1	-25.462	1	0.000	0.000	-0.500	0.00
	2	-25.462	1	0.000	0.000	0.500	0.00
Be	1	-8.425	1	0.000	0.000	-0.500	0.00
	2	-8.425	1	0.000	0.000	0.500	0.00
Mg	1	-6.961	1	0.000	0.000	-0.500	0.00
	2	-6.961	1	0.000	0.000	0.500	0.00

For the He, Be and Mg atoms (Table 4.2), calculations where performed starting from the LCAO states available in OCTOPUS. The results match the ones evaluated from the spin-polarized KLI calculation up to the numerical precision given by the code. This was expected, as they are described as a core of effective charge $2e$ (e being the absolute value of the electron charge) with two electrons in a s orbital.

Note that in fact, for one and two electron systems KLI coincides with the Slater approximation. Concerning the performance of the Slater potential, Tabels 4.6, 4.8, 4.10 and 4.12 show that the collinear spin limits is reproduced within 10^{-3} to 10^{-4} eV, depending on the system.

The results obtained within KLI require a more extensive discussion.

For the atoms of the 18th group, OCTOPUS gives a residual polarization along the Ox axis in the case of Ar and Xe. It is possible to reduce this remnant along Ox by changing the grid spacing, as it can be seen in Table 4.4, but most likely this is just a numerical artifact that does not disappear during the SCF cycle, since in the first iteration OCTOPUS puts some states with a polarization component along Ox. It may also depend on the starting point.

Table 4.3: Values of e_{KS}, average values of S_x, S_y, S_z and values of δ for each state of the atoms Ne, Ar and Xe (radius = 4.5 Å, spacing = 0.15 Å, starting from LCAO)

Atom	State	e_{KS} (eV)	Occupancy	$\langle S_x \rangle$	$\langle S_y \rangle$	$\langle S_z \rangle$	δ (eV)
Ne	1	-53.606	1	0.000	0.000	0.500	10^{-4}
	2	-53.606	1	0.000	0.000	-0.500	10^{-4}
	3	-21.691	1	0.000	0.000	-0.500	10^{-4}
	4	-21.691	1	0.000	0.000	-0.500	10^{-4}
	5	-21.691	1	0.000	0.000	-0.500	10^{-4}
	6	-21.691	1	0.000	0.000	0.500	10^{-4}
	7	-21.691	1	0.000	0.000	0.500	10^{-4}
	8	-21.691	1	0.000	0.000	0.500	10^{-4}
Ar	1	-30.084	1	-0.015	0.000	-0.499	10^{-5}
	2	-30.084	1	0.015	0.000	0.499	10^{-5}
	3	-16.183	1	-0.015	0.000	-0.499	10^{-5}
	4	-16.183	1	-0.015	0.000	-0.499	10^{-5}
	5	-16.183	1	-0.015	0.000	-0.499	10^{-5}
	6	-16.183	1	0.015	0.000	0.499	10^{-5}
	7	-16.183	1	0.015	0.000	0.499	10^{-5}
	8	-16.183	1	0.015	0.000	0.499	10^{-5}
Xe	1	-24.034	1	-0.010	0.000	0.499	10^{-5}
	2	-24.034	1	0.010	0.000	-0.499	10^{-5}
	3	-12.434	1	0.010	0.000	-0.499	10^{-5}
	4	-12.434	1	0.010	0.000	-0.499	10^{-5}
	5	-12.434	1	0.010	0.000	-0.499	10^{-5}
	6	-12.434	1	-0.010	0.000	0.499	10^{-5}
	7	-12.434	1	-0.010	0.000	0.499	10^{-5}
	8	-12.434	1	-0.010	0.000	0.499	10^{-5}

Table 4.4: Variation of $|\langle S_x \rangle|$ for Ar with the grid spacing

Spacing	$|\langle S_x \rangle|$
0.12	0.0048
0.15	0.0151
0.18	0.0022
0.21	0.0013

Table 4.5: Values of e_{KS}, average values of S_x, S_y, S_z and values of δ for each state of the atoms C and Si with the KLI response (radius = 4.5 Å, spacing = 0.4 Å, starting from LCAO)

Atom	State	e_{KS} (eV)	Occupancy	$\langle S_x \rangle$	$\langle S_y \rangle$	$\langle S_z \rangle$	δ (eV)
C	1	-22.314	1	0.000	0.000	-0.500	10^{-4}
	2	-19.362	1	0.000	0.000	0.500	10^{-4}
	3	-7.856	0	0.000	0.000	-0.500	10^{-4}
	4	-7.856	0	0.000	0.000	-0.500	10^{-4}
	5	-7.856	0	0.000	0.000	-0.500	10^{-4}
	6	-5.726	2/3	0.000	0.000	0.500	10^{-4}
	7	-5.726	2/3	0.000	0.000	0.500	10^{-4}
	8	-5.726	2/3	0.000	0.000	0.500	10^{-4}
Si	1	-13.326	1	-0.027	0.000	-0.499	10^{-4}
	2	-12.118	1	0.027	0.000	0.499	10^{-4}
	3	-6.389	0	-0.027	0.000	-0.499	10^{-4}
	4	-6.389	0	-0.027	0.000	-0.499	10^{-4}
	5	-6.389	0	-0.027	0.000	-0.499	10^{-4}
	6	-5.519	2/3	0.027	0.000	0.499	10^{-4}
	7	-5.519	2/3	0.027	0.000	0.499	10^{-4}
	8	-5.519	2/3	0.027	0.000	0.499	10^{-4}

Table 4.6: Values of e_{KS}, average values of S_x, S_y, S_z and values of δ for each state of the atoms C and Si for the Slater part only (radius = 4.5Å, spacing = 0.15Å, starting from LCAO for C and random w.f. for Si)

Atom	State	e_{KS} (eV)	Occupancy	$\langle S_x \rangle$	$\langle S_y \rangle$	$\langle S_z \rangle$	δ (eV)
C	1	-18.481	1	-0.061	0.000	-0.496	10^{-4}
	2	-16.046	1	0.061	0.000	0.496	10^{-4}
	3	-9.997	2/3	-0.061	0.000	-0.496	10^{-4}
	4	-9.997	2/3	-0.061	0.000	-0.496	10^{-4}
	5	-9.997	2/3	-0.061	0.000	-0.496	10^{-4}
	6	-8.029	0	0.061	0.000	0.496	10^{-4}
	7	-8.029	0	0.061	0.000	0.496	10^{-4}
	8	-8.029	0	0.061	0.000	0.496	10^{-4}
Si	1	-13.802	1	0.091	0.000	-0.492	10^{-4}
	2	-12.337	1	-0.091	0.000	0.492	10^{-4}
	3	-6.944	2/3	0.091	0.000	-0.492	10^{-4}
	4	-6.944	2/3	0.091	0.000	-0.492	10^{-4}
	5	-6.944	2/3	0.091	0.000	-0.492	10^{-4}
	6	-5.848	0	-0.091	0.000	0.492	10^{-4}
	7	-5.848	0	-0.091	0.000	0.492	10^{-4}
	8	-5.848	0	-0.091	0.000	0.492	10^{-4}

Table 4.7: Values of e_{KS}, average values of S_x, S_y, S_z and values of δ for each state of the atoms N and P with the KLI response (radius = 4.5 Å, spacing = 0.4 Å, starting from LSDA)

Atom	State	e_{KS} (eV)	Occupancy	$\langle S_x \rangle$	$\langle S_y \rangle$	$\langle S_z \rangle$	δ (eV)
N	1	-32.976	1	0.000	0.000	0.500	10^{-5}
	2	-30.640	1	0.000	0.000	-0.500	10^{-5}
	3	-11.281	1	0.000	0.000	0.500	10^{-4}
	4	-11.281	1	0.000	0.000	0.500	10^{-4}
	5	-11.281	1	0.000	0.000	0.500	10^{-4}
	6	-8.458	0	0.000	0.000	-0.500	10^{-4}
	7	-8.458	0	0.000	0.000	-0.500	10^{-4}
	8	-8.458	0	0.000	0.000	-0.500	10^{-4}
P	1	-19.556	1	0.000	0.000	0.500	10^{-5}
	2	-15.387	1	0.000	0.000	-0.500	10^{-4}
	3	-10.719	1	0.000	0.000	0.500	10^{-4}
	4	-10.719	1	0.000	0.000	0.500	10^{-4}
	5	-10.719	1	0.000	0.000	0.500	10^{-4}
	6	-6.975	0	0.000	0.000	-0.500	10^{-4}
	7	-6.975	0	0.000	0.000	-0.500	10^{-4}
	8	-6.975	0	0.000	0.000	-0.500	10^{-4}

Table 4.8: Values of e_{KS}, average values of S_x, S_y, S_z and values of δ for each state of the atoms N and P for the Slater part only (radius = 4.5Å, spacing = 0.15Å, starting from random w.f.)

Atom	State	e_{KS} (eV)	Occupancy	$\langle S_x \rangle$	$\langle S_y \rangle$	$\langle S_z \rangle$	δ (eV)
N	1	-28.474	1	0.061	0.000	0.496	10^{-4}
	2	-19.242	1	-0.061	0.000	-0.496	10^{-4}
	3	-16.742	1	0.061	0.000	0.496	10^{-4}
	4	-16.742	1	0.061	0.000	0.496	10^{-4}
	5	-16.742	1	0.061	0.000	0.496	10^{-4}
	6	-8.383	0	-0.061	0.000	-0.496	10^{-4}
	7	-8.383	0	-0.061	0.000	-0.496	10^{-4}
	8	-8.383	0	-0.061	0.000	-0.496	10^{-4}
P	1	-20.192	1	0.124	0.000	0.484	10^{-4}
	2	-14.607	1	-0.124	0.000	-0.484	10^{-4}
	3	-11.542	1	0.124	0.000	0.484	10^{-4}
	4	-11.542	1	0.124	0.000	0.484	10^{-4}
	5	-11.542	1	0.124	0.000	0.484	10^{-4}
	6	-6.671	0	-0.124	0.000	-0.484	10^{-4}
	7	-6.671	0	-0.124	0.000	-0.484	10^{-4}
	8	-6.671	0	-0.124	0.000	-0.484	10^{-4}

Table 4.9: Values of e_{KS}, average values of S_x, S_y, S_z and values of δ for each state of the atoms O and S with the KLI response (radius = 4.5 Å, spacing = 0.4 Å, starting from LSDA)

Atom	State	e_{KS} (eV)	Occupancy	$\langle S_x \rangle$	$\langle S_y \rangle$	$\langle S_z \rangle$	δ (eV)
O	1	-47.256	1	0.000	0.000	0.500	1.0
	2	-31.534	1	0.000	0.000	-0.500	10^{-4}
	3	-16.562	1	0.000	0.000	0.500	10^{-4}
	4	-16.562	1	0.000	0.000	0.500	10^{-4}
	5	-16.562	1	0.000	0.000	0.500	10^{-4}
	6	-2.287	1/3	0.000	0.000	-0.500	10^{-4}
	7	-2.287	1/3	0.000	0.000	-0.500	10^{-4}
	8	-2.287	1/3	0.000	0.000	-0.500	10^{-4}
S	1	-25.825	1	0.000	0.000	0.500	1.0
	2	-14.523	1	0.000	0.000	0.500	1.0
	3	-14.523	1	0.000	0.000	0.500	1.0
	4	-14.523	1	0.000	0.000	0.500	1.0
	5	-13.337	1	0.000	0.000	-0.500	0.1
	6	-3.137	1/3	0.000	0.000	-0.500	10^{-4}
	7	-3.137	1/3	0.000	0.000	-0.500	10^{-4}
	8	-3.137	1/3	0.000	0.000	-0.500	10^{-4}

Table 4.10: Values of e_{KS}, average values of S_x, S_y, S_z and values of δ for each state of the atoms O and S for the Slater part only (radius = 4.5Å, spacing = 0.15Å, starting from LCAO)

Atom	State	e_{KS} (eV)	Occupancy	$\langle S_x \rangle$	$\langle S_y \rangle$	$\langle S_z \rangle$	δ (eV)
O	1	-36.059	1	-0.017	0.000	0.499	10^{-5}
	2	-23.566	1	0.017	0.000	-0.499	10^{-4}
	3	-20.156	1	-0.017	0.000	0.499	10^{-4}
	4	-20.156	1	-0.017	0.000	0.499	10^{-4}
	5	-20.156	1	-0.017	0.000	0.499	10^{-4}
	6	-8.183	1/3	0.017	0.000	-0.499	10^{-4}
	7	-8.183	1/3	0.017	0.000	-0.499	10^{-4}
	8	-8.183	1/3	0.017	0.000	-0.499	10^{-4}
S	1	-24.004	1	-0.269	0.000	-0.422	10^{-4}
	2	-16.631	1	0.269	0.000	0.422	10^{-4}
	3	-13.599	1	-0.269	0.000	-0.422	10^{-4}
	4	-13.599	1	-0.269	0.000	-0.422	10^{-4}
	5	-13.599	1	-0.269	0.000	-0.422	10^{-4}
	6	-6.684	1/3	0.269	0.000	0.422	10^{-4}
	7	-6.684	1/3	0.269	0.000	0.422	10^{-4}
	8	-6.684	1/3	0.269	0.000	0.422	10^{-4}

Table 4.11: Values of e_{KS}, average values of S_x, S_y, S_z and values of δ for each state of the atoms F and Cl with the KLI response (radius = 4.5 Å, spacing = 0.4 Å, starting from LSDA)

Atom	State	e_{KS} (eV)	Occupancy	$\langle S_x \rangle$	$\langle S_y \rangle$	$\langle S_z \rangle$	δ (eV)
F	1	-39.643	1	0.000	0.000	0.500	1.0
	2	-29.620	1	0.000	0.000	-0.500	10^{-4}
	3	-19.440	1	0.000	0.000	0.500	10^{-4}
	4	-19.440	1	0.000	0.000	0.500	10^{-4}
	5	-19.440	1	0.000	0.000	0.500	10^{-4}
	6	-10.295	2/3	0.000	0.000	-0.500	10^{-4}
	7	-10.295	2/3	0.000	0.000	-0.500	10^{-4}
	8	-10.295	2/3	0.000	0.000	-0.500	10^{-4}
Cl	1	-30.142	1	0.000	0.000	0.500	1.0
	2	-22.041	1	0.000	0.000	-0.500	10^{-4}
	3	-16.545	1	0.000	0.000	0.500	1.0
	4	-16.545	1	0.000	0.000	0.500	1.0
	5	-16.545	1	0.000	0.000	0.500	1.0
	6	-9.085	2/3	0.000	0.000	-0.500	10^{-4}
	7	-9.085	2/3	0.000	0.000	-0.500	10^{-4}
	8	-9.085	2/3	0.000	0.000	-0.500	10^{-4}

Table 4.12: Values of e_{KS}, average values of S_x, S_y, S_z and values of δ for each state of the atoms F and Cl for the Slater part only (radius = 4.5Å, spacing = 0.15Å, starting from LCAO)

Atom	State	e_{KS} (eV)	Occupancy	$\langle S_x \rangle$	$\langle S_y \rangle$	$\langle S_z \rangle$	δ (eV)
F	1	-44.392	1	0.009	0.000	0.499	10^{-3}
	2	-35.879	1	-0.009	0.000	-0.499	10^{-3}
	3	-22.354	1	0.009	0.000	0.499	10^{-3}
	4	-22.354	1	0.009	0.000	0.499	10^{-3}
	5	-22.354	1	0.009	0.000	0.499	10^{-3}
	6	-14.294	2/3	-0.009	0.000	-0.499	10^{-3}
	7	-14.294	2/3	-0.009	0.000	-0.499	10^{-3}
	8	-14.294	2/3	-0.009	0.000	-0.499	10^{-3}
Cl	1	-27.734	1	0.084	0.000	-0.493	10^{-4}
	2	-22.807	1	-0.084	0.000	0.493	10^{-4}
	3	-15.541	1	0.084	0.000	-0.493	10^{-4}
	4	-15.541	1	0.084	0.000	-0.493	10^{-4}
	5	-15.541	1	0.084	0.000	-0.493	10^{-4}
	6	-10.962	2/3	-0.084	0.000	0.493	10^{-4}
	7	-10.962	2/3	-0.084	0.000	0.493	10^{-4}
	8	-10.962	2/3	-0.084	0.000	0.493	10^{-4}

For the atoms of the 14th to 17th groups (Tables 4.5, 4.7, 4.9 and 4.11), the KLI results show good agreement with the spin-polarized simulations. There are some larger differences of O and S (Table 4.9), and F and CL(Table 4.11) in the eigenvalues.

Note that for C and Si (Table 4.5) one needs to force an hole below the Fermi energy to reproduce the spin-polarized results, in which the (unoccupied) minority p-down-spin orbitals are lower in energy that the corresponding (occupied) majority p-up-spin orbitals.

For F and Cl (Table 4.11), the states corresponding to the majority spin channel in the spin polarized calculations present a larger error of 1 eV. By inspecting results more carefully, once finds that those states are rigidly shifted be -1.472 eV (F) and by 1.226 eV (Cl) with respect to the spin-polarized results.

These differences can be understood since with respect to the spin-polarized case, fixing the xc potential gauge (e.g. value of the potential at $+\infty$) is far from trivial.

Within spin-unpolarized KLI, the gauge is fixed by subtracting the highest occupied atomic/molecular orbital before solving the linear equation which determines the potential (2.87). Within polarized spin-collinear KLI, one has two independent equations for each spin-channel and the gauge is fixed, as in the spin unpolarized case, for booths channels.[1]

Within non-collinear spin, one has one equation to fix the gauge for the two components of the spinor. Since a general condition to fix the gauge was not found, it was decided to use the iterative solution of the KLI, as it is presented in Appendix B. In this case one of the gauge is 'chosen' by the procedure (the other one is fixed to zero as in the unpolarized case) and is system dependent. It seems that this gauge depends strongly on how the starting value for the KLI

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[1]The problem with the gauge choice was found by Myrta Grüning.

potential is chosen. To the results presented here, the KLI potential at the first iteration is chosen to be equal to the Slater one.

An alternative implementation of the code gives similarly good results though the "gauge problem" shows up for all atoms in the 14-17th group and the results are more dependent on the starting point.

4.2 Rotation of the magnetization direction

As further validation of the implementation, this sub-section shows the test results for the non-collinear Slater behavior when used to calculate the ground state configuration over initial LSDA results, with the state polarization along Ox, Oy or Oz. The previous tests only shown if the implementation would predict correctly the results in the spin-polarized limit, but did not test the behavior of the off-diagonal components. The tests were done with the N atom.

The expected behavior is that non-collinear Slater should keep each state polarization and only improve the results given by LSDA, as it can be seen in Appendix B.

Analyzing Tables 4.13 to 4.15, one can see that, within a small margin of error, the results for the eigenvalues are very close to each other and that each state polarization is kept the same after the non-collinear KLI calculation over the LSDA results. The larger errors may be due to these simulations also being affected by the "gauge problem". Still, the maximum error is in the order of the $1eV$ and this gives some confidence that the implementation is behaving as expected from Appendix B.

4.3 Optical response of the Xe_3^+ cluster

In the Introduction was said that one of the objectives of this thesis is to obtain the optical response of the Xe_3^+ cluster and compare it with the results from [18].

Table 4.13: Values of e_{KS}, average values of S_x, S_y, S_z and values of δ for each state of the N atom with LSDA and non-collinear Slater with an initial polarization along Ox (radius = 5.0Å, spacing = 0.2Å)

Approximation	State	e_{KS} (eV)	Occupancy	$\langle S_x \rangle$	$\langle S_y \rangle$	$\langle S_z \rangle$
LSDA	1	-19.438	1	0.500	0.000	0.000
	2	-14.847	1	-0.500	0.000	0.000
	3	-8.512	1	0.500	0.000	0.000
	4	-8.512	1	0.500	0.000	0.000
	5	-8.512	1	0.500	0.000	0.000
	6	-4.188	0	-0.500	0.000	0.000
	7	-4.188	0	-0.500	0.000	0.000
	8	-4.188	0	-0.500	0.000	0.000
KLI	1	-27.003	1	0.500	0.000	0.000
	2	-19.122	1	-0.500	0.000	0.000
	3	-15.865	1	0.500	0.000	0.000
	4	-15.865	1	0.500	0.000	0.000
	5	-15.865	1	0.500	0.000	0.000
	6	-8.553	0	-0.500	0.000	0.000
	7	-8.553	0	-0.500	0.000	0.000
	8	-8.553	0	-0.500	0.000	0.000

Table 4.14: Values of e_{KS}, average values of S_x, S_y, S_z and values of δ for each state of the N atom with LSDA and non-collinear Slater with an initial polarization along Oy (radius = 5.0Å, spacing = 0.2Å)

Approximation	State	e_{KS} (eV)	Occupancy	$\langle S_x \rangle$	$\langle S_y \rangle$	$\langle S_z \rangle$
LSDA	1	-19.438	1	0.000	0.500	0.000
	2	-14.847	1	0.000	-0.500	0.000
	3	-8.512	1	0.000	0.500	0.000
	4	-8.512	1	0.000	0.500	0.000
	5	-8.512	1	0.000	0.500	0.000
	6	-4.188	0	0.000	-0.500	0.000
	7	-4.188	0	0.000	-0.500	0.000
	8	-4.188	0	0.000	-0.500	0.000
KLI	1	-27.003	1	0.000	0.500	0.000
	2	-19.122	1	0.000	-0.500	0.000
	3	-15.865	1	0.000	0.500	0.000
	4	-15.865	1	0.000	0.500	0.000
	5	-15.865	1	0.000	0.500	0.000
	6	-8.553	0	0.000	-0.500	0.000
	7	-8.553	0	0.000	-0.500	0.000
	8	-8.553	0	0.000	-0.500	0.000

Table 4.15: Values of e_{KS}, average values of S_x, S_y, S_z and values of δ for each state of the N atom with LSDA and non-collinear Slater with an initial polarization along Oz (radius = 5.0Å, spacing = 0.2Å)

Approximation	State	e_{KS} (eV)	Occupancy	$\langle S_x \rangle$	$\langle S_y \rangle$	$\langle S_z \rangle$
LSDA	1	-19.438	1	0.000	0.000	0.500
	2	-14.847	1	0.000	0.000	-0.500
	3	-8.512	1	0.000	0.000	0.500
	4	-8.512	1	0.000	0.000	0.500
	5	-8.512	1	0.000	0.000	0.500
	6	-4.188	0	0.000	0.000	-0.500
	7	-4.188	0	0.000	0.000	-0.500
	8	-4.188	0	0.000	0.000	-0.500
KLI	1	-27.003	1	0.000	0.000	0.500
	2	-19.122	1	0.000	0.000	-0.500
	3	-15.865	1	0.000	0.000	0.500
	4	-15.865	1	0.000	0.000	0.500
	5	-15.865	1	0.000	0.000	0.500
	6	-8.553	0	0.000	0.000	-0.500
	7	-8.553	0	0.000	0.000	-0.500
	8	-8.553	0	0.000	0.000	-0.500

In this system, the spin-orbit effects are important, hence the use of non-collinear spin.

Ground state calculations were performed in a grid with 4.5 $\mathring{A}$ and 0.42 $\mathring{A}$ spacing and the starting point where the LCAO states. The geometry of the cluster and the pseudo potential were provided by [11]. The ions were initially magnetized along the Oz axis.

The time-dependent Kohn-Sham equations are solved by time propagation. The system is initially perturbed by a delta-like field, that excites the system in all the frequencies. Time-propagation used 4000 steps of 0.01 fs, with the Lanczos method for the time propagator [5]. The strength of the perturbation was set to 0.002. The grid spacing and radius were the same that were used for the ground state calculations.

4.3.1 Results with the Slater potential

As it can be seen in Figure 4.1, while the numerical data obtained from the Slater potential calculation using the non-collinear expressions inverted the strength of the peaks with respect to LSDA, it worsen the peaks' position with respect to the experiment.

It should be said that the Slater results do not include correlation effects, so some effects which will wide the distance in between the peaks might be missing. Also, as it was said in [18], the spin-orbit coupling strength affects the position of the peaks, so its effect in the simulations using the Slater potential should be investigated.

4.3.2 Results with full KLI

The results from the full KLI calculation were not so good. It can be seen that the obtained spectra shows a significant negative part. In order to see where the problem might be, the time variation of the total energy (Figure 4.3), dipole
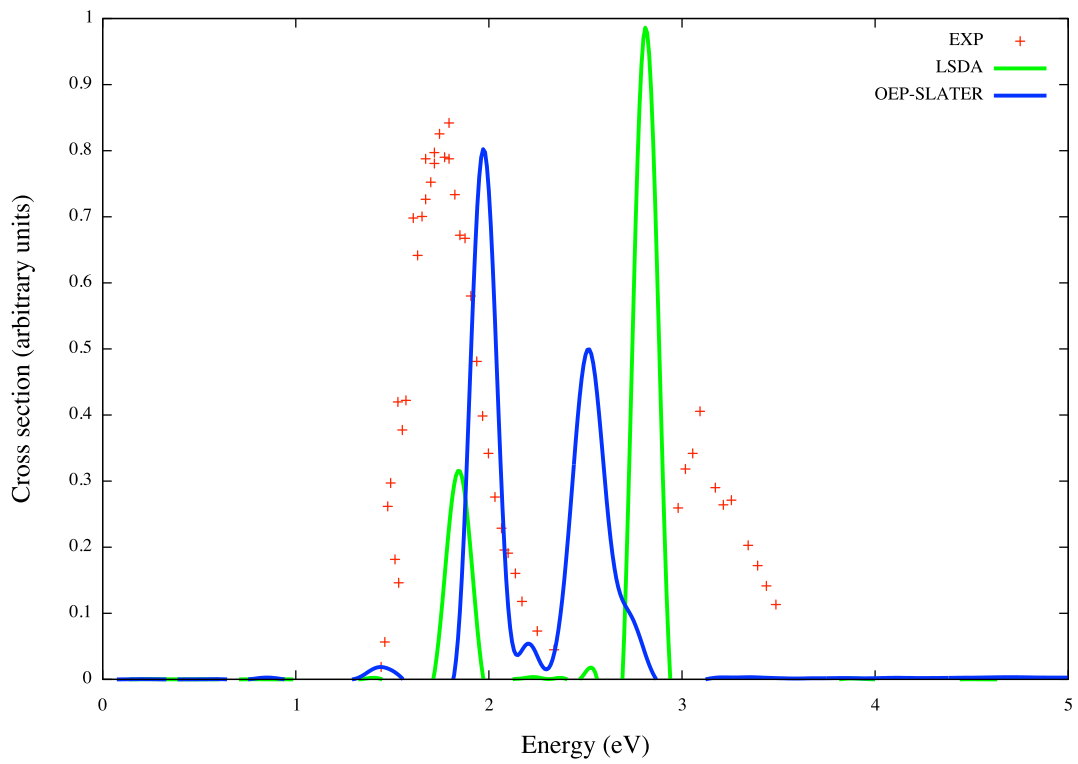
Figure 4.1: Absorption cross section for the Xe_3^+ cluster obtained from both LSDA and the Slater part of the non-collinear formalism.
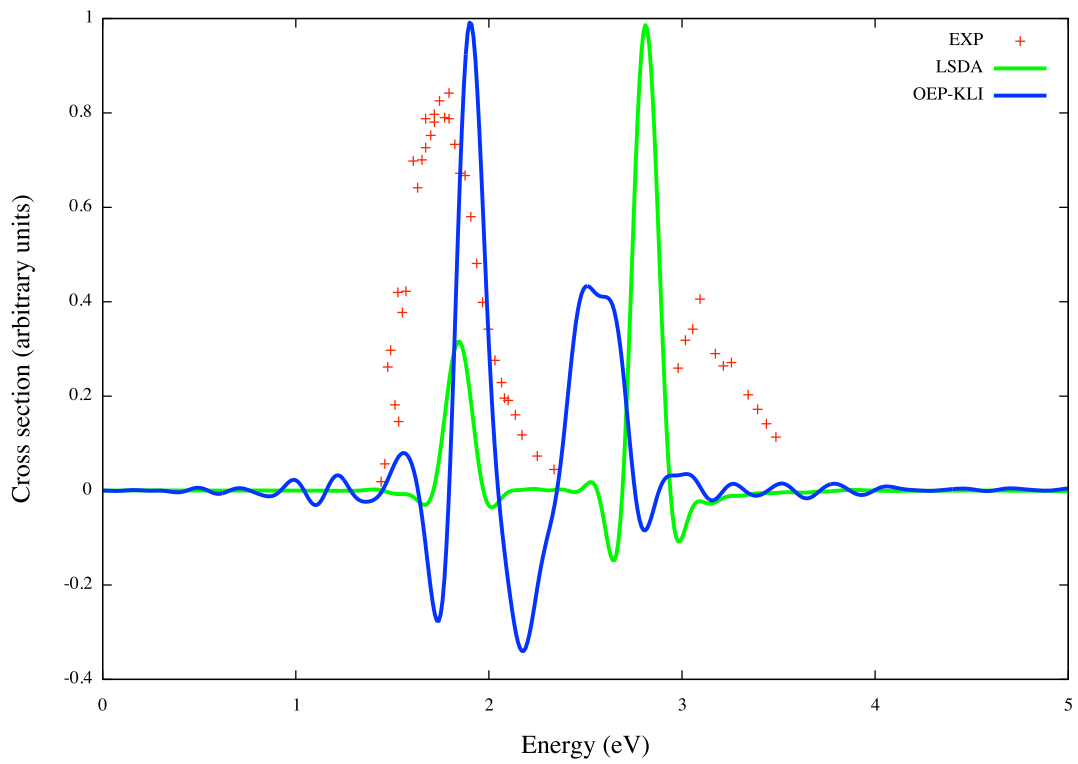
Figure 4.2: Absorption cross section for the Xe_3^+ cluster obtained from both LSDA and the KLI response of the non-collinear formalism.

moments (Figures 4.5) and electronic density (Figure 4.4) for the KLI calculation where plotted and compared with the results from the Slater only calculation.

In Figure 4.3, it is clearly shown that the KLI calculation is not conserving the total energy of the system. Taking this and with the help of Figure 4.4, it is clear that after 15 fs, the system starts to transfer electronic charge from the spin-up states to the spin-down ones and vice-versa. Such a thing does not happen with the Slater only calculations.

By looking at Figures 4.5 and 4.6, it is also clear that the dipole moments have larger oscillations when the time-propagation is running with the full KLI response than when only the Slater part is used.

One possible reason for this is that what may have been found during the ground state calculation might not have been an absolute minimum, but a local one. As such, during the time-propagation, OCTOPUS may have found a lower energy configuration and started to switch to it, and thus the non-conservation of the total energy.

Note that for the time-evolution it was used as initial guess for the KLI in the iteration procedure the potential found in the previous step. Test are now in progress for an alternative algorithm in which the initial guess is the Slater potential. This algorithm was the one already used for the results of atoms.
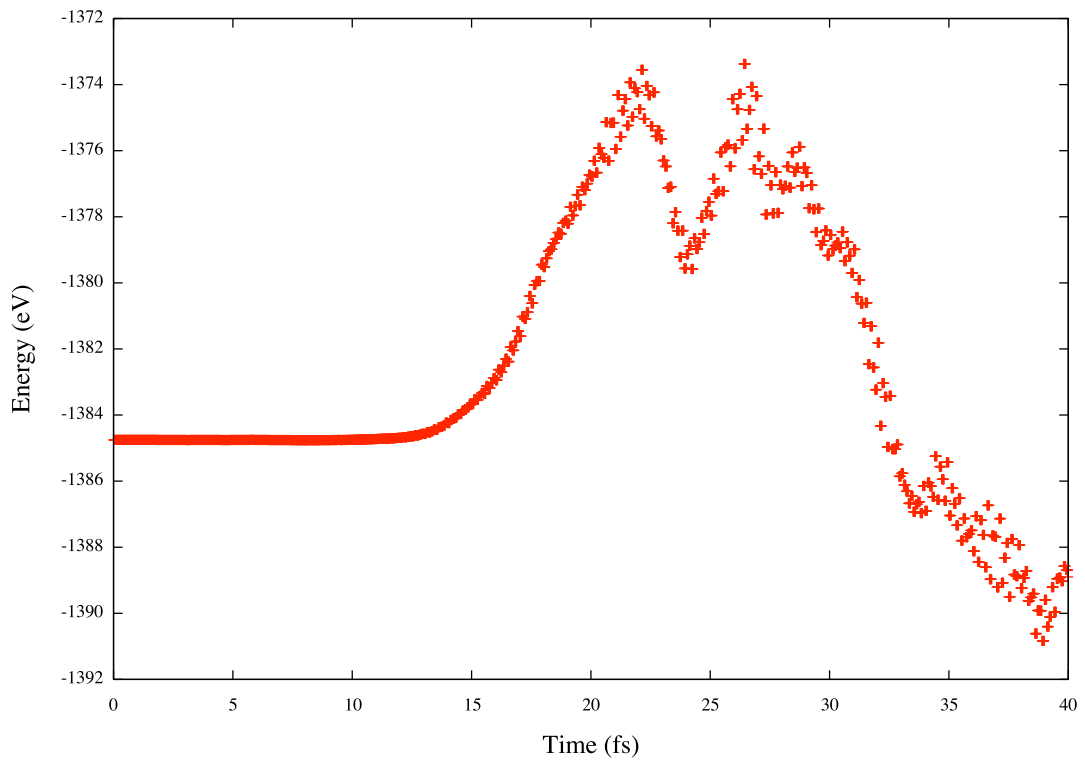
Figure 4.3: Time variation of the total energy during the propagation using the full KLI response.
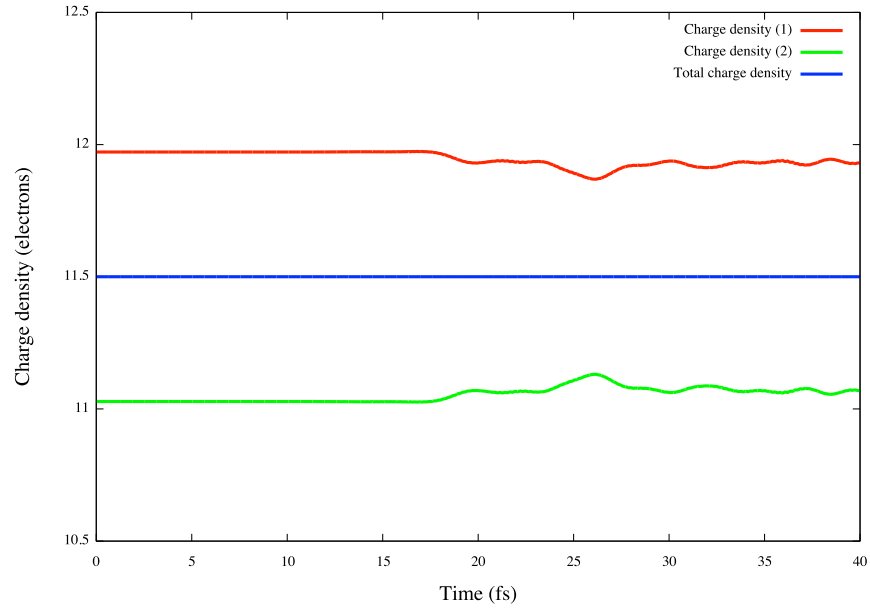
(a)
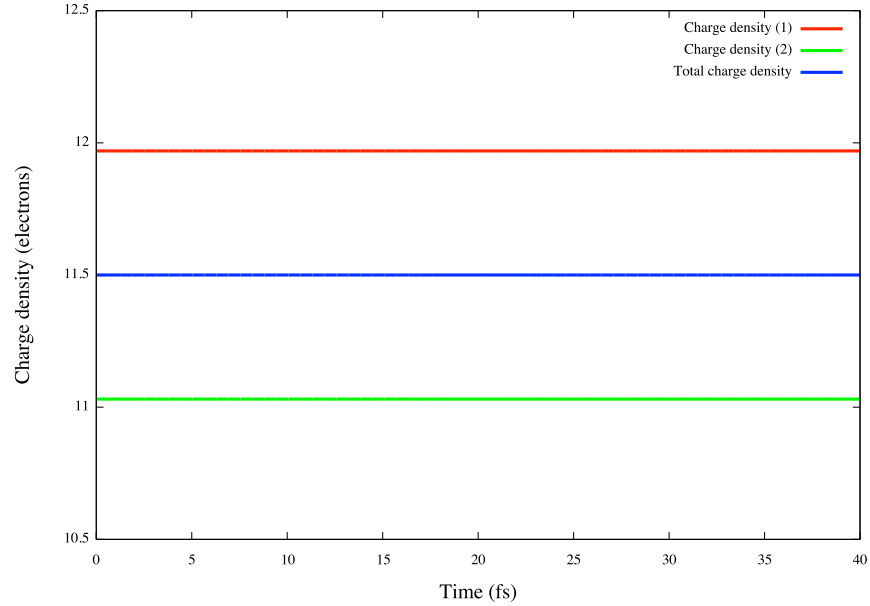
(b)

Figure 4.4: Diagonal elements of the electronic density matrix obtained from the Slater part only and full KLI response using the non-collinear formalism.
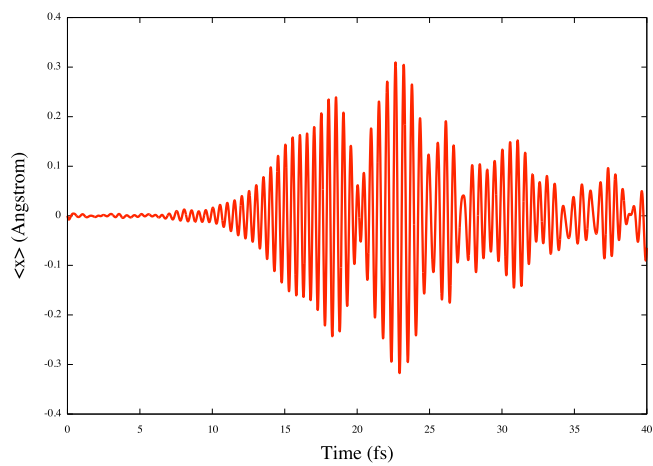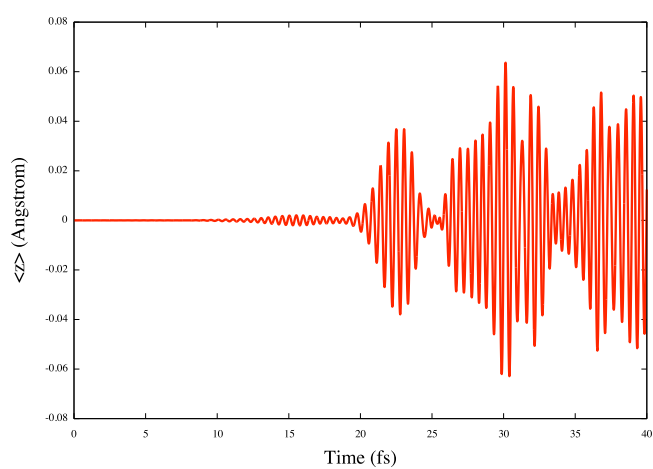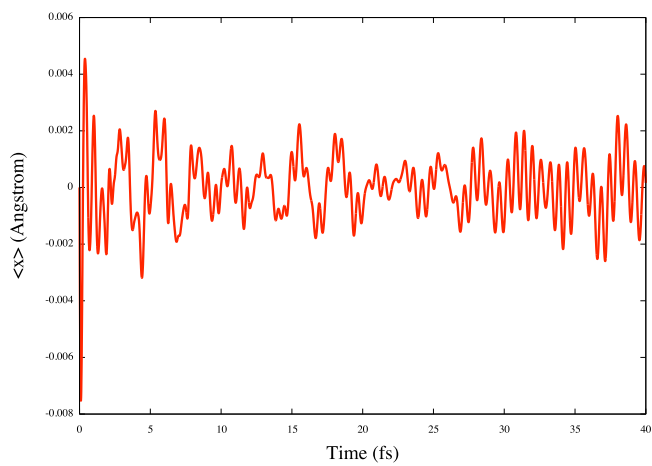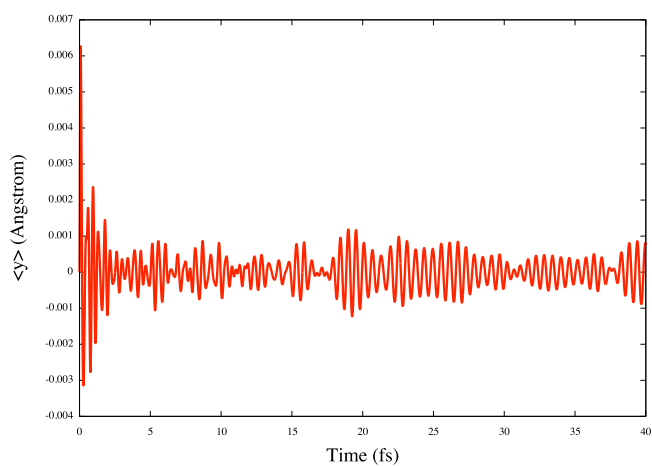
(a)
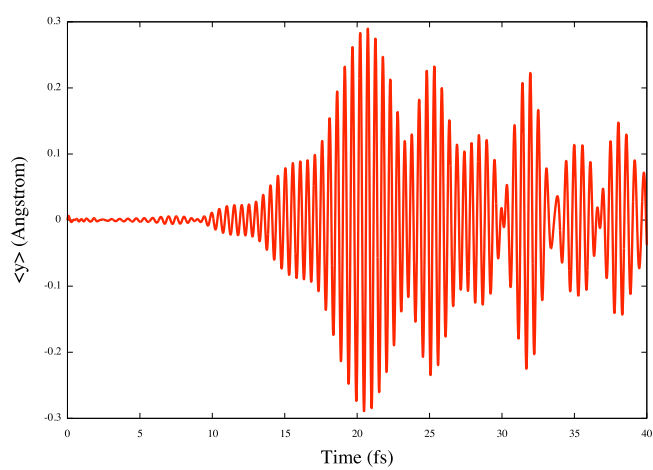
(b)

(c)

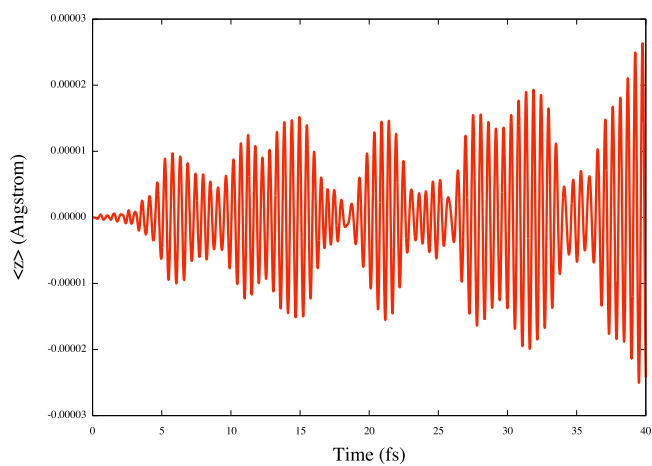Figure 4.5: Dipole moments obtained from the full KLI response using the non-collinear formalism.

(a)

(b)

(c)

Figure 4.6: Dipole moments obtained from the Slater part only using the non-collinear formalism.

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Chapter 5

Conclusions and future work

5.1 Conclusions

It is important to note that, although these are just preliminary results and likely as it is that some of them may change in the future, along with their analysis and derived conclusions.

Regarding the equations that were derived for this thesis, it is important to note that they predict the known limits of the unpolarized and spin-polarized systems. Not only that, but it has also been shown when the equations cannot be applied, as seen in Appendix A, although this barrier can be surpassed with a numerical artifact.

Regarding the numerical results, the Slater-only and full KLI results on atoms are close to what is predicted by the spin-polarized formalism. The results for full KLI have larger errors when there was a shift, but otherwise they show good agreement with the spin-polarized limit.

The full KLI passed the tests concerning the rotation of the magnetization, where the behavior of the off-diagonal terms was important. The behavior of the Slater potential was tested, but the results were not presented for brevity.

In what concerns the optical response of the Xe_3^+ cluster, the Slater-only results were able to invert the intensity of the peaks, although the peaks' position is worse than what was predicted by LSDA. The full KLI results also manage to invert the intensities, but due to the fact that the calculations did not conserve the total energy of the system and appears to be very susceptible to the gauge choice, this simulation must be repeated. KLI is also showing a strong dependence on the initial guess for the wave functions. This may be due to the the fact that in the used version there are two self consistent cycles running, one for the KLI potential and another for the ground state. This may lead to setting the ground state or the KLI potential in a local minimum and not an absolute one.

5.2 Future work

It will be important to study on why does the exact exchange improve the peaks' relative weight. There might be self interacting errors in LDA, so it would be interesting to see the results for LDA with Self-Interaction Correction (SIC) [19]. This may correct the asymptotic behavior as well.

The exact exchange spoils the peak position agreement of LSDA. It would be important to study the interference of the spin-orbit coupling strength as well as to see what results may come from using SIC in the simulations in order to include correlation effects.

Since the Slater potential is working and managed to invert the relative strength of the peaks, it would be interesting to see if approximations to Slater are working (e.g. Becke-Roussel, [2]).

Appendix A - On the inversion of $M^{\mu\nu}(\boldsymbol{r})$

In Chapter 3 it was shown that in order to evaluate the exchange potential and magnetic field one would need to invert the matrix $M^{\mu\nu}(\boldsymbol{r})$ in (3.49). For that, $[\Gamma(\boldsymbol{r})]^{-1}$ must be different than zero. Looking at the expression

$$[\Gamma(\boldsymbol{r})]^{-1} = 4\left[\rho^{\alpha\alpha}(\boldsymbol{r}) + \rho^{\beta\beta}(\boldsymbol{r})\right]\det(\rho(\boldsymbol{r})) \tag{5.1}$$

the two ways for such a thing not to happen are if $n(\boldsymbol{r})$ is zero or $\det(\rho(\boldsymbol{r}))$ is zero. The ground state density is assumed to be always positive (see [14]) so any problem concerning the inversion must come from the determinant of $\rho(\boldsymbol{r})$.

In [3] it was shown that for relativistic-spin DFT, such problem does not show up, since the determinant of the matrix in question is proportional to

$$1 - \frac{\boldsymbol{j}^2(\boldsymbol{r})}{n^2(\boldsymbol{r})} = 1 - \frac{\boldsymbol{v}^2(\boldsymbol{r})}{c^2} > 0 \tag{5.2}$$

since $\boldsymbol{v}(\boldsymbol{r})$ would be the velocity field and a particle with mass cannot reach the speed of light. If one tries to use the same argument for SDFT, one will get (using Einstein summation convention from here on)

$$\boldsymbol{m}^2 = \epsilon_{ijk}\epsilon_{ilm}\frac{\partial(nv_k)}{\partial x_j}\frac{\partial(nv_m)}{\partial x_l} = \frac{\partial(nv_k)}{\partial x_j}\left[\frac{\partial(nv_k)}{\partial x_j} - \frac{\partial(nv_j)}{\partial x_k}\right] \tag{5.3}$$

taking into account that $\epsilon_{ijk}\epsilon_{ilm} = \delta_{j,l}\delta_{k,m} - \delta_{i,m}\delta_{k,l}$. This relation is not very helpful since there are no upper bounds for the derivatives of n or the velocity field.

Expanding n and the components of $\boldsymbol{m}$ in the components of the spinors, one easily gets that

$$n = \theta_i \left(|\phi_i^\alpha|^2 + |\phi_i^\beta|^2 \right) \tag{5.4}$$

$$m_x = -\mu_B \theta_i \left(\phi_i^{*\alpha}\phi_i^\beta + c.c. \right) \tag{5.5}$$

$$m_y = i\mu_B \theta_i \left(\phi_i^{*\alpha}\phi_i^\beta - c.c. \right) \tag{5.6}$$

$$m_z = -\mu_B \theta_i \left(|\phi_i^\alpha|^2 - |\phi_i^\beta|^2 \right) \tag{5.7}$$

From here and taking into account that

$$n^2 - \frac{\boldsymbol{m}^2}{\mu_b^2} = \theta_i \theta_j \left[|\phi_i|^2 |\phi_j|^2 - \phi_i^\dagger \sigma_k \phi_i \phi_j^\dagger \sigma_k \phi_j \right] \tag{5.8}$$

one arrives at the final expression

$$n^2 - \frac{\boldsymbol{m}^2}{\mu_b^2} = 2\theta_i \theta_j \left(\phi_i^{*\alpha}\phi_j^{*\beta} - \phi_i^{*\beta}\phi_j^{*\alpha} \right) \left(\phi_i^\alpha \phi_j^\beta - \phi_i^\beta \phi_j^\alpha \right) \tag{5.9}$$

which, besides the obvious case that at least one of the spinors is zero at a given point, will be zero if there is only one occupied state or if the the states are fully polarized (one of the components of the spinor is zero).

Appendix B - Transformation of the equations and rotation

The following equations show how the formulas in Chapter 3 where transformed in order to be implemented in a subroutine in OCTOPUS and they follow the notes of Myrta Grüning. One starts by writing for the Slater part of (3.54)

$$v_x^\mu(\boldsymbol{r}) = \Gamma(\boldsymbol{r}) N^{\mu\nu}(\boldsymbol{r}) \Lambda_{x,\nu}(\boldsymbol{r}) \tag{5.10}$$

with

$$[\Gamma(\boldsymbol{r})]^{-1} = n(\boldsymbol{r}) \left[n^2(\boldsymbol{r}) - \frac{\boldsymbol{m}(\boldsymbol{r}) \cdot \boldsymbol{m}(\boldsymbol{r})}{\mu_B^2} \right] \tag{5.11}$$

$$v_x^\mu(\boldsymbol{r}) = (v_x(\boldsymbol{r}), \mu_B \boldsymbol{B}_x(\boldsymbol{r})) \tag{5.12}$$

$$\Lambda_x^\mu(\boldsymbol{r}) = \frac{1}{2} \sum_{k=1}^{N} \left[\phi_k^\dagger(\boldsymbol{r}) \sigma^\mu \frac{\delta E_x}{\delta \phi_k(\boldsymbol{r})} + c.c. \right], \quad \mu = 0, 1, 2, 3 \tag{5.13}$$

One now can write

$$N^{0\mu} = n \begin{pmatrix} n \\ m_x/\mu_B \\ m_y/\mu_b \\ m_z/\mu_B \end{pmatrix} \quad N^{i\mu} = \frac{m_i}{\mu_B} \begin{pmatrix} n \\ m_x/\mu_B \\ m_y/\mu_b \\ m_z/\mu_B \end{pmatrix} + \frac{u^i}{n\Gamma} \tag{5.14}$$

so that

$$N^{\nu} = \mathcal{N}^{\nu}\mathcal{N} + \frac{u^{\nu}}{n\Gamma} \tag{5.15}$$

with $\mathcal{N} = (n(\boldsymbol{r}), \boldsymbol{m}(\boldsymbol{r})/\mu_B)$ and $u^{\nu} = (0, \delta v_1, \delta v_2, \delta v_3)$. Then, one can rewrite (5.10) as

$$v_x^{\mu}(\boldsymbol{r}) = n(\boldsymbol{r})\Gamma(\boldsymbol{r})N^{\mu\mu}(\boldsymbol{r})\mathcal{N}^{\mu}(\boldsymbol{r})\Lambda_x(\boldsymbol{r}) + \frac{u^{\mu}(\boldsymbol{r})\Lambda(\boldsymbol{r})}{n(\boldsymbol{r})} \tag{5.16}$$

Now it is possible to define the previous expression in terms of

$$\rho = \sum_{i=1}^{N} \theta_i \left(|\phi_i^{\alpha}|^2, |\phi_i^{\beta}|^2, Re(\phi_i^{\alpha}\phi_i^{*\beta}), Im(\phi_i^{\alpha}\phi_i^{*\beta})) \right)^T = \left(n - \frac{m_z}{\mu_B}, n + \frac{m_z}{\mu_B}, -\frac{m_x}{\mu_B}, \frac{m_y}{\mu_B} \right)^T \tag{5.17}$$

and, by analogy,

$$V = \left(V^{\alpha\alpha}, V^{\beta\beta}, Re(V^{\alpha\beta}), Im(V^{\alpha\beta}) \right)^T = (v_x + \mu_B B_z, v_x - \mu_B B_z, \mu_B B_x, -\mu_B B_y)^T \tag{5.18}$$

Transformation between ρ and $\mathcal{N}$ is done via the matrix

$$T_1 = \begin{pmatrix} 1/2 & 0 & 0 & -1/2 \\ 1/2 & 0 & 0 & 1/2 \\ 0 & -1/2 & 0 & 0 \\ 0 & 0 & 1/2 & 0 \end{pmatrix}, \quad (T_1^T)^{-1} = \begin{pmatrix} 1 & 0 & 0 & -1 \\ 1 & 0 & 0 & 1 \\ 0 & -2 & 0 & 0 \\ 0 & 0 & 2 & 0 \end{pmatrix} \tag{5.19}$$

while v_x and V transform via

$$T_2 = \begin{pmatrix} 1 & 0 & 0 & 1 \\ 1 & 0 & 0 & -1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \end{pmatrix} \tag{5.20}$$

Starting with the transformation of the product

$$\mathcal{N}^T \Lambda \to (T_1 \mathcal{N})^T [(T_1^T)^{-1}\Lambda] \tag{5.21}$$

and defining

$$w^{\alpha\beta} = \sum_{k=1}^{N} \phi_k^{*\alpha} \left(\frac{\delta E_x}{\delta \phi^\dagger}\right)^\beta \qquad \Lambda = \begin{pmatrix} Re(w^{\alpha\alpha} + w^{\beta\beta}) \\ Re(w^{\alpha\beta} + w^{\beta\alpha}) \\ -Im(w^{\alpha\beta} - w^{\beta\alpha}) \\ Re(w^{\alpha\alpha} - w^{\beta\beta}) \end{pmatrix} \tag{5.22}$$

then

$$(T_1^T)^{-1}\Lambda = 2 \begin{pmatrix} Re(w^{\beta\beta}) \\ Re(w^{\alpha\alpha}) \\ -Re(w^{\alpha\beta} - w^{\beta\alpha}) \\ -Im(w^{\alpha\beta} - w^{\beta\alpha}) \end{pmatrix} = \hat{\Lambda} \tag{5.23}$$

One will also get that

$$T_2 \mathcal{N} = 2\left(\rho_2, \rho_1, -\rho_3, -\rho_4\right)^T \qquad T_2(u^\nu \Lambda) = \begin{pmatrix} Re(w^{\alpha\alpha} - w^{\beta\beta}) \\ -Re(w^{\alpha\alpha} - w^{\beta\beta}) \\ Re(w^{\alpha\beta} + w^{\beta\alpha}) \\ Im(w^{\alpha\beta} - w^{\beta\alpha}) \end{pmatrix} \tag{5.24}$$

And thus

$$\begin{pmatrix} V^{\alpha\alpha} \\ V^{\beta\beta} \\ Re(V^{\alpha\beta}) \\ -Im(V^{\alpha\beta}) \end{pmatrix} = \frac{1}{n} \begin{pmatrix} \rho^{\beta\beta} \\ \rho^{\alpha\alpha} \\ -Re(\rho^{\alpha\beta}) \\ -Im(\rho^{\alpha\beta}) \end{pmatrix} \frac{\rho\hat{\Lambda}}{2\lambda} + \begin{pmatrix} Re(w^{\alpha\alpha} - w^{\beta\beta}) \\ -Re(w^{\alpha\alpha} - w^{\beta\beta}) \\ Re(w^{\alpha\beta} + w^{\beta\alpha}) \\ Im(w^{\alpha\beta} - w^{\beta\alpha}) \end{pmatrix} \tag{5.25}$$

with $\Gamma = 4n\lambda$, $\lambda = \frac{1}{4}(n^2 - \frac{m^2}{\mu_B^2}) = [\rho_1\rho_2 - (|\rho_3|^2 + |\rho_4|^2)]$.

In the limit of unpolarized spin, one has that $\rho_1 = \rho_2 = \frac{\rho_0}{2}$, $\rho_3 = \rho_4 = 0$ and that $\hat{\Lambda}_1 = \hat{\Lambda}_2 = w_0$, $\hat{\Lambda}_3 = \hat{\Lambda}_4 = 0$. Thus, one will obtain

$$V^{\alpha\alpha} = \frac{w_0}{\rho_0} = V^{\beta\beta} \qquad V^{\alpha\beta} = 0 \tag{5.26}$$

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For the case of collinear spin with polarization along Oz, $\rho_1 = \frac{\rho_0 + \delta}{2}$, $\rho_2 = \frac{\rho_0 - \delta}{2}$, $\rho_3 = \rho_4 = 0$. The transformed potentials are $\hat{\Lambda}_1 = w_0 - \Delta$, $\hat{\Lambda}_2 = w_0 + \Delta$ and $\hat{\Lambda}_3 = \hat{\Lambda}_4 = 0$. After some algebra, one will arrive at

$$V^{\alpha\alpha} = \frac{w_0 + \Delta}{\rho_0 + \delta} \qquad V^{\beta\beta} = \frac{w_0 - \Delta}{\rho_0 - \delta} \qquad V^{\alpha\beta} = 0 \tag{5.27}$$

which is the result for the spin-polarized limit along Oz.

Now, for the limit where the polarization lies along Ox, $\hat{\Lambda}_1 = \hat{\Lambda}_2 = w_0$ and $\hat{\rho}_1 = \hat{\rho}_2 = \frac{\rho_0}{2}$. As there is no polarization along Oy, $\hat{\Lambda}_4 = 0$ and $\hat{\rho}_4 = 0$, but $\hat{\Lambda}_3 = -2\Delta$ and $\hat{\rho}_3 = \frac{\delta}{2}$. After some calculations one will get

$$V^{\alpha\alpha} = V^{\beta\beta} = \frac{1}{2}\left(\frac{w_0 - \Delta}{\rho_0 - \delta} - \frac{w_0 + \Delta}{\rho_0 + \delta} \right) \tag{5.28}$$

$$Re(V^{\alpha\beta}) = \frac{1}{2}\left(\frac{w_0 + \Delta}{\rho_0 + \delta} - \frac{w_0 - \Delta}{\rho_0 - \delta} \right) \qquad Im(V^{\alpha\beta}) = 0 \tag{5.29}$$

Now, the matrices

$$\begin{pmatrix} \rho^{\alpha\alpha} & \rho^{\alpha\beta} \\ \rho^{\beta\alpha} & \rho^{\beta\beta} \end{pmatrix} \qquad \begin{pmatrix} V^{\alpha\alpha} & V^{\alpha\beta} \\ V^{\beta\alpha} & V^{\beta\beta} \end{pmatrix} \tag{5.30}$$

will transform in the same way as σ_3 transforms to σ_1, which is through the matrix

$$\frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \tag{5.31}$$

So, one will have

$$\begin{pmatrix} \rho_1 & 0 \\ 0 & \rho_2 \end{pmatrix} \rightarrow \frac{1}{2} \begin{pmatrix} \rho_1 + \rho_2 & \rho_1 - \rho_2 \\ \rho_1 - \rho_2 & \rho_1 + \rho_2 \end{pmatrix} \tag{5.32}$$

$$\begin{pmatrix} V_1 & 0 \\ 0 & V_2 \end{pmatrix} \rightarrow \frac{1}{2} \begin{pmatrix} V_1 + V_2 & v_1 - V_2 \\ V_1 - V_2 & V_1 + V_2 \end{pmatrix} \tag{5.33}$$

which when replaced by the values of the spin-polarized limit along Oz match the results for the Ox case.

When the polarization is along Oy, the matrix transformation is done by

$$\frac{1}{\sqrt{2}} \begin{pmatrix} 1 & -i \\ -i & 1 \end{pmatrix} \tag{5.34}$$

and so,

$$\begin{pmatrix} \rho_1 & 0 \\ 0 & \rho_2 \end{pmatrix} \rightarrow \frac{1}{2} \begin{pmatrix} \rho_1 + \rho_2 & -i(\rho_1 - \rho_2) \\ i(\rho_1 - \rho_2) & \rho_1 + \rho_2 \end{pmatrix} \tag{5.35}$$

and W and V will transform in the same way. For $V^{\alpha\alpha}$ and $V^{\beta\beta}$ the expressions are the same, but in this case $Re(V^{\alpha\beta}) = 0$ and

$$-Im(V^{\alpha\beta}) = -\frac{1}{2} \left(\frac{w_0 + \Delta}{\rho_0 + \delta} - \frac{w_0 - \Delta}{\rho_0 - \delta} \right) \tag{5.36}$$

When adding the KLI response part, one will arrive at the following equation

$$\begin{pmatrix} V_{KLI}^{\alpha\alpha} \\ V_{KLI}^{\beta\beta} \\ Re(V_{KLI}^{\alpha\beta}) \\ -Im(V_{KLI}^{\alpha\beta}) \end{pmatrix} = \begin{pmatrix} V_S^{\alpha\alpha} \\ V_S^{\beta\beta} \\ Re(V_s^{\alpha\beta}) \\ -Im(V_S^{\alpha\beta}) \end{pmatrix} + \frac{1}{n} \begin{pmatrix} \rho_2 \\ \rho_1 \\ -\rho_3 \\ -\rho_4 \end{pmatrix} \frac{\rho\hat{\Delta}}{2\lambda} + \sum_{k=1}^{N} \begin{pmatrix} \phi_k^{\alpha\alpha} - \phi_k^{\beta\beta}) \\ -(\phi_k^{\alpha\alpha} - \phi_k^{\beta\beta}) \\ 2Re(\phi_k^{\alpha\beta}) \\ -2Im(\phi_k^{\alpha\beta}) \end{pmatrix} \frac{\Delta v_k^{KLI}}{2} \tag{5.37}$$

with $\phi_k^{\alpha\beta} = \phi_k^{*\beta}\phi_k^\alpha$ and

$$\hat{\Delta} = \sum_{k=1}^{N} \begin{pmatrix} \phi_k^{\beta\beta} \\ \phi_k^{\alpha\alpha} \\ -2Re(\phi_k^{\alpha\beta}) \\ 2Im(\phi_k^{\alpha\beta}) \end{pmatrix} \Delta v_k^{KLI} = \sum_{k=1}^{N} \hat{P}_k \Delta v_k^{KLI} \tag{5.38}$$

Going back to the definition of Δv_k^{KLI}, one defines

$$\Delta v^{KLI} = \sum_{k=1}^{N} \int d^3r \left\{ \theta_k \phi_k^\dagger(\boldsymbol{r}) \left[v_x(\boldsymbol{r}) + \mu_B \boldsymbol{\sigma} \cdot \boldsymbol{B}_x(\boldsymbol{r}) - u_{x,k}^\dagger(\boldsymbol{r}) \right] \phi_k(\boldsymbol{r}) + c.c. \right\} \tag{5.39}$$

$$\sum_{k=1}^{N}\phi_k^\dagger(\boldsymbol{r})\left[v_x(\boldsymbol{r})+\mu_B\boldsymbol{\sigma}\cdot\boldsymbol{B}_x(\boldsymbol{r})\right]\phi_k(\boldsymbol{r})=\Delta V \to [(T_2^{-1})^T\Delta]V \tag{5.40}$$

$$\bar{u}_k^*=\int d^3r\,\phi_k^\dagger u_{x,k}^\dagger(\boldsymbol{r})\phi_k(\boldsymbol{r}) \tag{5.41}$$

and

$$\hat{\Delta}'=\sum_{k=1}^{N}\begin{pmatrix}\phi_k^{\alpha\alpha}\\\phi_k^{\beta\beta}\\2Re(\phi_k^{\alpha\beta})\\-2Im(\phi_k^{\alpha\beta})\end{pmatrix}=\sum_{k=1}^{N}\hat{P}_k' \tag{5.42}$$

To evaluate Δv^{KLI}, one has to multiply (5.37) by $(\hat{P}_i')^T$ on the right and on the left, then subtract from both sides $\bar{u}_i^*$, sum on i and integrate in $\boldsymbol{r}$, thus arriving at

$$\Delta v^{KLI}=\sum_{i=1}^{N}\int [(\hat{P}_i')^T V_S-\bar{u}_i^*]d^3r+$$

$$+\sum_{i=1}^{N}\sum_{k=1}^{N}\int\frac{1}{2n\lambda}(\hat{P}_i')^T\begin{pmatrix}\rho_2\\\rho_1\\-\rho_3\\-\rho_4\end{pmatrix}(\rho\hat{P}_k)d^3r\Delta v^{KLI}+$$

$$+\sum_{i=1}^{N}\sum_{k=1}^{N}\int(\hat{P}_i')^T\begin{pmatrix}\phi_k^{\alpha\alpha}\\\phi_k^{\beta\beta}\\2Re(\phi_k^{\alpha\beta})\\-2Im(\phi_k^{\alpha\beta})\end{pmatrix}d^3r\Delta v^{KLI} \tag{5.43}$$

Appendix C - The algorithm

```
! ————————————————————————————————————————————————————
subroutine xc_KLI_Pauli_solve(mesh, st, oep)
  type(mesh_t),   intent(in)    :: mesh
  type(states_t), intent(in)    :: st
  type(xc_oep_t), intent(inout) :: oep
  !
  integer :: is, ip, ii, jj, ist, eigen_n, it, kssi
  FLOAT    :: rho(mesh%np,4),lambda(mesh%np),n(mesh%np),T_rho(mesh%np,4)
  FLOAT, allocatable :: T_V(:,:),V(:,:),rhoV(:),V_m1(:,:),P_i(:,:,:),T_Vi(:,:,:),  Delta_V(:),Vs(:,:)
  CMPLX, allocatable :: weighted_hf(:,:,:),rho_i(:,:,:,:)
  FLOAT :: reached_threshold(4)
  logical, save :: first = .true.
  !
  call profiling_in(C_PROFILING_XC_KLI)
  PUSH_SUB(xc_KLI_Pauli_solve)
  !
  ! Density related quantities
  !
  rho = st%rho
  do ip = 1,mesh%np
```

```fortran
    do is = 1,2
       if (rho(ip,is).lt.CNST(1e-20)) rho(ip,is) = CNST(1e-20)
    end do
  end do
  !
  n(:) = rho(:,1) + rho(:,2)
  lambda(:) = rho(:,1)*rho(:,2) - (rho(:,3)**2 + rho(:,4)**2)
  !
  ! Potential related quantities
  ! (Built from HF potentials weighted with orbital densities)
  !
  SAFE_ALLOCATE(weighted_hf(mesh%np,st%d%dim,st%d%dim))
  weighted_hf = M_Z0
  !
  ! w_{up,down} = \sum_i \phi_{i,down}^* u_x^{i,up}^* \phi_{i,up}
  !
  do ii = 1,st%d%dim
    do jj = 1,st%d%dim
      do ist = st%st_start,st%st_end
        weighted_hf(:,ii,jj) = weighted_hf(:,ii,jj) + &
          &oep%socc*st%occ(ist,1)*conjg(st%zpsi(:,jj,ist,1)*oep%zlxc(:,ist,ii))
          ! oep%zlxc => (\phi_j)^*u_x^j
      end do
    end do
  end do
  !
  SAFE_ALLOCATE(T_V(mesh%np,4))
  T_V = M_ZERO
  !
  T_V(:,1) = real(weighted_hf(:,2,2),REAL_PRECISION)
  T_V(:,2) = real(weighted_hf(:,1,1),REAL_PRECISION)
  T_V(:,3) = -real(weighted_hf(:,1,2) + weighted_hf(:,2,1),REAL_PRECISION)
  T_V(:,4) = -aimag(weighted_hf(:,1,2) - weighted_hf(:,2,1))
  !
  SAFE_DEALLOCATE_A(weighted_hf)
  !
  SAFE_ALLOCATE(V(mesh%np,4))
  V = M_ZERO
  !
  V(:,1) = T_V(:,2)-T_V(:,1)
  V(:,2) = -V(:,1)
  V(:,3) = -T_V(:,3)
  V(:,4) = -T_V(:,4)
  !
  ! Combine them to obtain Slater part
  !
  SAFE_ALLOCATE(rhoV(mesh%np))
  rhoV = M_ZERO
  forall (ip = 1:mesh%np) rhoV(ip) = sum(rho(ip,:)*T_V(ip,:))
  rhoV = rhoV/lambda
```

```
SAFE_DEALLOCATE_A(T_V)
!
T_rho(:,1) = rho(:,2)
T_rho(:,2) = rho(:,1)
T_rho(:,3:4) = -rho(:,3:4)
!
forall (ip = 1:mesh%np) V(ip,:) = (V(ip,:) + T_rho(ip,:)*rhoV(ip))/n(ip)
!
if(oep%level == XC_OEP_SLATER) then ! if Slater exit here
  !
  oep%vxc = V
  !
  call profiling_out(C_PROFILING_XC_KLI)
  POP_SUB(X(xc_KLI_Pauli_solve))
  SAFE_DEALLOCATE_A(V)
  SAFE_DEALLOCATE_A(rhoV)
  !
  return
end if
!
SAFE_ALLOCATE(Vs(mesh%np,4))
Vs = V ! Slater part
!
! iteration criteria
!
call scf_tol_init(oep%scftol,"KLI",def_maximumiter=20)
!
! get the HOMO state
!
call xc_oep_AnalyzeEigen(oep, st, 1)
eigen_n = oep%eigen_n
!
if (eigen_n == 0) then
  oep%vxc = Vs
  return
end if
!
! orbital densities
!
SAFE_ALLOCATE(rho_i(mesh%np,st%d%dim,st%d%dim,eigen_n))
rho_i = M_Z0
!
do ii = 1, st%d%dim
  do jj = ii, st%d%dim
    do ist = 1, eigen_n
      kssi = oep%eigen_index(ist)
      rho_i(:,ii,jj,ist) = oep%socc*st%occ(kssi,1)*conjg(st%zpsi(:,jj,kssi,1))*&
          &st%zpsi(:,ii,kssi,1)
      rho_i(:,jj,ii,ist) = conjg(rho_i(:,ii,jj,ist))
    end do
```

```fortran
    end do
end do
!
! arrange them in a 4-vector
!
SAFE_ALLOCATE( P_i ( mesh%np , 4 , eigen_n ) )
P_i = M_ZERO
!
P_i ( : , 1 , : ) = real ( rho_i ( : , 1 , 1 , : ) )
P_i ( : , 2 , : ) = real ( rho_i ( : , 2 , 2 , : ) )
P_i ( : , 3 , : ) = M_TWO * real ( rho_i ( : , 1 , 2 , : ) , REAL_PRECISION )
P_i ( : , 4 , : ) = M_TWO * aimag ( rho_i ( : , 1 , 2 , : ) )
!
SAFE_DEALLOCATE_A( rho_i )
!
! Calculate iteratively response part
!
SAFE_ALLOCATE( V_m1 ( mesh%np , 4 ) )
SAFE_ALLOCATE( Delta_V ( eigen_n ) )
SAFE_ALLOCATE( T_Vi ( mesh%np , 4 , eigen_n ) )
!
if ( first ) then !
   V = M_ZERO
   first = .false.
else
   V = oep%vxc - Vs
end if
!
KLI_iteration: do it = 1 , oep%scftol%max_iter
   V_m1 = Vs + V
   !
   ! Delta_V^KLI
   !
   Delta_V = M_ZERO
   do ist = 1 , eigen_n
      kssi = oep%eigen_index ( ist )
      do is = 1 , st%d%nspin
         Delta_V ( ist ) = Delta_V ( ist ) + dmf_dotp ( mesh , P_i ( 1 : mesh%np , is , ist ) , V_m1 ( 1 : mesh%np , is ) )
      end do
      Delta_V ( ist ) = Delta_V ( ist ) - real ( sum ( oep%uxc_bar ( kssi , : ) ) )
   end do
   !
   !
   T_Vi ( : , 1 , : ) = P_i ( : , 2 , : )
   T_Vi ( : , 2 , : ) = P_i ( : , 1 , : )
   T_Vi ( : , 3 , : ) = -P_i ( : , 3 , : )
   T_Vi ( : , 4 , : ) = -P_i ( : , 4 , : )
   !
   forall ( ip = 1 : mesh%np , is = 1 : st%d%nspin ) T_Vi ( ip , is , : ) = T_Vi ( ip , is , : ) * Delta_V ( : )
   !
```

```
    V = M_ZERO
    do ip=1,mesh%np
      V(ip,1) = sum(T_Vi(ip,2,:)-T_Vi(ip,1,:))
      V(ip,2) = -V(ip,1)
      V(ip,3) = -sum(T_Vi(ip,3,:))
      V(ip,4) = -sum(T_Vi(ip,4,:))
    end do
    !
    rhoV = M_ZERO
    do ip = 1,mesh%np
      do ist=1,eigen_n
        rhoV(ip) = rhoV(ip) + sum(rho(ip,:)*T_Vi(ip,:,ist))
      end do
    end do
    rhoV = rhoV/lambda
    !
    forall (ip = 1:mesh%np) V(ip,:) = (V(ip,:) + T_rho(ip,:)*rhoV(ip))/n(ip)
    !
    do is = 1,4
      reached_threshold(is) = dmf_nrm2(mesh,(Vs(1:mesh%np,is) + V(1:mesh%np,is) - &
        &V_m1(1:mesh%np,is)))
    end do
    !
    if (all(reached_threshold(:).le. oep%scftol%conv_abs_dens)) exit
  end do KLI_iteration
  !
  write(message(1), '(a,i4,a,es14.6)') &
      &"Info: After ", it, " iterations, KLI converged to ", maxval(reached_threshold(:))
  message(2) = ''
  call messages_info(2)
  !
  oep%vxc = V_m1
  !
  call profiling_out(C_PROFILING_XC_KLI)
  POP_SUB(xc_KLI_Pauli_solve)
  !
  SAFE_DEALLOCATE_A(T_Vi)
  SAFE_DEALLOCATE_A(P_i)
  SAFE_DEALLOCATE_A(rhoV)
  SAFE_DEALLOCATE_A(Delta_V)
  !
end subroutine xc_KLI_Pauli_solve
```

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