SORBONNE UNIVERSITY

INTERNSHIP REPORT

Development of functionals for observables

Student:
Ayoub Aouina

Supervisors:
Dr.Lucia Reining
Dr.Matteo Gatti

Laboratoire des solides irradiés
Ecole polytechnique

January 28, 2019

Acknowledgements

I would like to thank my supervisors Lucia Reining and Matteo Gatti. I am very grateful for their optimism and patience, excellent supervising and always having time to help.
I would like to thank Marco Vanzini for fruitful discussions.
I would like to acknowledge all the members in ETSF Palaiseau group!

Contents

Acknowledgements **i**

1 Introduction **1**

2 Theoretical framework **2**
2.1 Many electron problem 2
2.2 Density functional theory 3
2.2.1 Kohn-Sham method 3
2.2.2 Approximation of the exchange correlation potential 4
2.3 Time dependent density functional theory 5
2.3.1 Adiabatic local density approximation 5

3 Connector strategy **7**
3.1 General connector theory 7
3.2 Is that possible for the exchange correlation energy 8
3.2.1 Exchange energy 8
3.2.2 Correlation energy 9
3.3 Approximations 9
3.3.1 General discussion 9
3.3.2 The error canceling 10

4 Approximating the exchange correlation potential **12**
4.1 Linear approximation 12
4.1.1 Exchange correlation kernel 12
4.1.2 Design of the connector 13
4.1.3 Discussion 14
4.2 Examples : 14
4.2.1 Static case : 14
Cosinus density 14
4.2.2 Time dependent case 16
Cosinus density in permanent perturbation 16

5 Conclusion and outlook **19**

Bibliography **21**

Chapter 1

Introduction

Computational materials design reflects the dream to create new materials with desired properties in a guided way. This properties like color, conductivity, magnetization.. are the result of collective behaviors of particles and in order to understand it and be able to predict it we find ourselves in front of a many body problem.

From quantum mechanics we know that the state of an electron is completely specified by the wave function which is the solution of Schrödinger's equation. This is true also for an interacting electrons and so in principle, we need the many body wave function $\psi(\mathbf{r_1}, \mathbf{r_2}, \mathbf{r_3}, ..., \mathbf{r_n}, \mathbf{œ}, t)$ for a complete description of the system. This function depends on the position of Avogadro's number of electrons, which makes it impossible to be calculated numerically and stored. However in practice we just deal with observables, i.e. expectation values $\langle\psi| O |\psi\rangle = \int \psi^* O \psi d^N r$. Taking the integral means that efforts have been made to calculate too detailed information (the wave function) which is not economical and even impossible because of the size of the Hamiltonian matrix to diagonalize for many body system.

Density Functional Theory (DFT) comes as a solution to this problem, it tells us that the external potential, and therefore all observables, are functionals of the ground state density however the exact functionals are of course not known. Following the Kohn-Sham scheme, a system of interacting electrons can be transformed to a fictitious system of non-interacting electrons that has the same density of the ground state as the real system. The price to pay is that the effective potential of this new system contains an unknown part which we called the exchange-correlation potential. From DFT we know that this potential is a functional of the ground state density and much effort goes into the design of suitable approximations. In the Homogeneous electrons gas this potential has been already numerically calculated using the quantum Monte-Carlo method.

In my internship I have tried to explore a new strategy of approximation :"Connector theory", and I used it in order to profit from the calculation done in the homogeneous electron gas and approximate the exchange correlation potential in real systems identified by their density. In the first part I will talk about the theoretical framework of my internship then I will introduce the idea of the "connector" and why it's a promising theory and finally I will give and discuss my result as an application of this theory in the approximation of the exchange correlation potential.

Chapter 2

Theoretical framework

In this chapter, I will present the concepts and the methods that I have been used during my internship. I will start by the many electron problem which is the origin of the problem. Next, I will introduce density functional theory (DFT) as a solution from point of view of principle. I will discuss what makes this theory useful in practice and what are its limits. Finally, I will talk about the time dependent DFT, its standard approximation and the problems encountered by it.
In all the rest of my report equations are written in the Hartree units : $e^2 = \hbar = m_e = 1$ where e is the electron charge and m_e its mass.

2.1 Many electron problem

One of the most important purpose of condensed matter physics is to understand the electronic properties of metals this type of problem contains of order 10^{23} particles. In quantum mechanics the Hamiltonian of a system with N electrons and M nuclei can be written as :

$$\hat{H} = -\sum_i \frac{\nabla_i^2}{2} - \sum_I \frac{\nabla_I^2}{2M_I} + \frac{1}{2}\sum_{i\neq j} \frac{1}{|\mathbf{r_i} - \mathbf{r_j}|} + \frac{1}{2}\sum_{I\neq J} \frac{Z_I Z_J}{|\mathbf{R_I} - \mathbf{R_j}|} - \sum_{i,I} \frac{Z_I}{|\mathbf{r_i} - \mathbf{R_I}|},$$

where electrons and their positions are denoted by i and r_i, nucleus by I and R_I. M_I is the I-th nucleus mass and Z_I its atomic number. The first two terms represent the kinetic energy of electrons and nuclei. The next two terms represents electron-electron interaction and nucleus-nucleus interaction. The last term represent the electron-nucleus interaction which we will denote by V_{ext}.
The evolution of the system is described by the Schrödinger equation :

$$\hat{H}\psi(\{R\},\{r\}) = E\psi(\{R\},\{r\})$$

This equation can be solved analytically at most for two electrons and numerically for very few electrons, that's why we have to adopt approximations. As a first step we can consider the Born-Oppenheimer approximation, assuming that the motion of atomic nuclei and electrons in a molecule can be decoupled. Indeed the time scale of electrons is much shorter than the one of nuclei and so the latter can be frozen in their equilibrium positions. This yields to simpler Hamiltonian :

$$\mathcal{H} = \sum_i^N \left(\frac{\nabla_i^2}{2} + V_{ext}(\mathbf{r_i})\right) + \frac{1}{2}\sum_{i\neq j} \frac{1}{|\mathbf{r_i} - \mathbf{r_j}|}$$

But we still need to find the wave function of $N \sim 10^{23}$ electrons which is impossible! In practice we are interested in observables i.e., integrated variables, and the question arises if there is a way to extract this observables without finding the many electron wave function?

2.2 Density functional theory

The density functional theory (DFT) comes as a solution to the many-electron problem. According to this theory, the electronic density is the minimum and the sufficient information that we need to calculate all ground state observables. it is based on two theorems by Hohenberg-Kohn [5].

HK theorem I The ground state expectation value of any physical observable of a many-electron system is a unique functional of the electronic density $n(\mathbf{r})$.

HK theorem II The total energy functional has a minimum at the exact ground state density $n(\mathbf{r})$.

These theorems introduce the electronic density as the key variable of the system which is much simpler than the many body wave function. They prove the existence of the functionals of the ground state observables but they say nothing how to find them, which is not interesting from practical point of view. What makes DFT useful is the Kohn-Sham method [11].

2.2.1 Kohn-Sham method

The Kohn-Sham (KS) method is a reformulation of the many electron problem. The idea of this method consists of introducing a fictitious system of non interacting electrons subjected to an effective external potential, V_{KS}, with the property that it yields the same density as the real interacting system. Therefore the Hamiltonian of this fictitious system (KS system) can be written as :

$$\mathcal{H}_{KS} = -\frac{1}{2}\nabla^2 + V_{KS}(\mathbf{r})$$

The ground state density of the KS system is then obtained from the eigenfunctions φ_i of this Hamiltonian :

$$n(\mathbf{r}) = \sum_i^N |\varphi_i(\mathbf{r})|^2.$$

This density , according to the second HK theorem, is the minimum of the total energy functional which can be expressed as:

$$E_{KS}[n] = \int d\mathbf{r} n(\mathbf{r}) V_{ext} + T[n] + E_H[n] + E_{xc}[n],$$

with $T[n]$ is the kinetic energy functional which can be calculated as :

$$T = \sum_i^N \langle \varphi_i | -\frac{\nabla_i^2}{2} | \varphi_i \rangle .$$

$E_H[n]$ is the Hartree energy which is the result of the electrostatic interaction between electrons:

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

$E_{xc}[n]$ is the unknown part in the total energy functional, it encompasses the exchange correlation effects i.e., the electron-electron interaction beyond the electrostatic one.

Minimizing the energy functional of the KS system $E_{KS}[n]$ with the constraint that it yields the same ground state density as the real system implies :

$$\frac{\delta(E_{KS}[n] - \epsilon_i \int d\mathbf{r}' n(\mathbf{r}'))}{\delta n(\mathbf{r})} = 0.$$

In this way one can write a Schrödinger-like equation :

$$(-\frac{\nabla^2}{2} + V_{ext} + \frac{\delta E_H[n]}{\delta n(r)} + \frac{\delta E_{xc}[n]}{\delta n(r)})\varphi_i(\mathbf{r}) = \epsilon_i\varphi_i(\mathbf{r}).$$

Or :

$$(-\frac{\nabla^2}{2} + V_{KS}(\mathbf{r}))\varphi_i(\mathbf{r}) = \epsilon_i\varphi_i(\mathbf{r}),$$

with $V_{KS}(\mathbf{r}) = V_{ext}(\mathbf{r}) + \frac{\delta E_H[n]}{\delta n(r)} + \frac{\delta E_{xc}[n]}{\delta n(r)} = V_{ext}(\mathbf{r}) + V_H[n](\mathbf{r}) + V_{xc}[n](\mathbf{r})$.

In conclusion, the many body problem is reformulated to the problem of solving a set of self-consistent single-particle Schrödinger equations which is possible in practice. However, since we don't know the expression of $E_{xc}[n]$, the exchange correlation (xc) potential $V_{xc}[n](\mathbf{r})$ is unknown and at this level we must make approximations.

2.2.2 Approximation of the exchange correlation potential

As it has been shown in the previous section, using DFT in KS scheme, the central quantity that needs to be approximated is the xc potential functional $V_{xc}[n]$. The standard and the most used approximation is the local density approximation (LDA). It was presented in the same paper in which the KS method was developed [11]. In the case of the xc potential the LDA suggests to take it from a homogeneous electron gas (HEG), as a model system, with a density n^h equal to the local density of the real system $n(\mathbf{r})$, this yields :

$$V_{xc}^{LDA}[n](\mathbf{r}) = V_{xc}^{HEG}(n^h = n(\mathbf{r})),$$

where $V_{xc}^{HEG}(n^h)$ is the xc potential of the homogeneous electron gas, which is calculated and tabulated using methods based on the wave function. The Figure 2.1 illustrates how the LDA approximate the xc potential.

For a real system with a slowly varying density, the system can be seen locally as a HEG and then using the LDA is reasonable, which justify its success. However, this approximation fails to describe a various phenomena. For example, the problem of image potential [4].

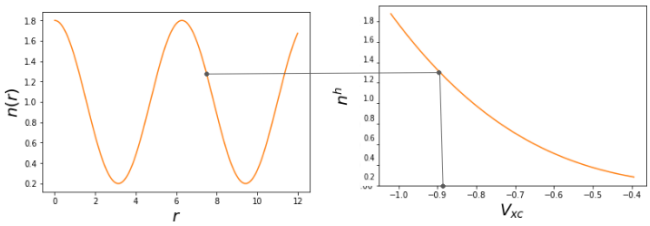

FIGURE 2.1: LDA scheme. Here we show how tu use the LDA to approximate the xc potential. First we read the density at some point r_0 in the the real system (left side graph) which is a number. Then we construct a HEG with a density equal to this number. In the table of the xc potential of HEG (right side graph) we determine $V_{xc}[n](\mathbf{r})$ at the point r_0

2.3 Time dependent density functional theory

The time dependent density functional theory (TDDFT) is the extension of the static DFT to the case of time-dependent external potentials. it's based on the Runge-Gross theorems :

RG theorem I The expectation value of any physical time-dependent observable many-electrons system is a unique functional of the time-dependent electron density $n(r,t)$ and of the initial state ψ_0.

RG theorem II The Hamiltonian action :

$$A = \int_{t_0}^{t_1} \langle \psi(t) | \, i\frac{\partial}{\partial t} - H(t) \, | \psi(t) \rangle \, .$$

has a stationary point corresponds to time-dependent Schrödinger equation with the initial condition $\psi(t=0) = \psi_0$.

Similarly to DFT, TDDFT proves the existence of functionals without determining them. In order to make it useful in practice, we can extend the KS method to this case and build a time dependent KS system. This yields :

$$(-\frac{\nabla^2}{2} + V_{KS}(\mathbf{r},t))\varphi_i(\mathbf{r},\mathbf{t}) = i\frac{\partial}{\partial t}\varphi_i(\mathbf{r},t),$$

with $n(\mathbf{r},t) = \sum_i^N |\varphi_i(\mathbf{r})|^2$. In analogy to the static case :

$$V_{KS}(\mathbf{r},t) = V_{ext}(\mathbf{r},t) + V_H[n](\mathbf{r},t) + V_{xc}[n](\mathbf{r},t).$$

Since the xc potential $V_{xc}[n](\mathbf{r},t)$ is unknown we have to adopt approximations.

2.3.1 Adiabatic local density approximation

The simplest and the widely used approximation in TDDFT calculation is the adiabatic local approximation (ALDA). Using this approximation for the xc potential, means that at each instant t we take for $V_{xc}[n](\mathbf{r},t)$ the xc potential calculated in LDA with density $n(\mathbf{r},t)$:

$$V_{xc}^{ALDA}(\mathbf{r},t) = V_{xc}^{LDA}(n(\mathbf{r},\mathbf{t})).$$

Note that this approximation is local both in space and time. Although studies have shown that the ALDA is able to describe properly a limited range of time-dependent physical systems [8], it exhibits serious deficiencies in the description of long range charge transfer [9], and the description of dynamical processes where the density changes significantly in time.

Chapter 3

Connector strategy

In physics, we usually want to calculate certain observables which contain a limited amount of information about the system. In principle, if we know every single detail about the system we can extract any information we want. However this way of dealing with the problem is not optimal and it is expensive in term of computation because we need to redo it for every system. In this internship, I have explored a different approach. It is based on the idea that the interaction effects are to some extent universal. The idea is to represent the real system by a model one which is simpler and which contains all parts of interaction including the non trivial one. In order to import results from calculations done in the model system into the real one we do approximations. The LDA, introduced in chapter 2, is an example. Although there are justifications for existing approximations, they don't start from an exact formulation, and they are therefore not systematic. In this chapter we introduce a general strategy which is an exactifying and generalization of these approximations i.e., an exact mapping between the model system and the real one. The task of this internship was to explore some general properties, which we discuss in this chapter, and to give the illustrations in chapter 4.

3.1 General connector theory

Suppose that we want to calculate a quantity $Q(x, [F])$ in a real system that depends on the variable x and the function F. Suppose also that this quantity can be expressed in a simpler way $\tilde{Q}(p)$ in a model system in which the calculations are done, stored in tables and targeted by a parameter p. Now we want to profit from the model calculation for the real system. The question is whether one can choose the parameter

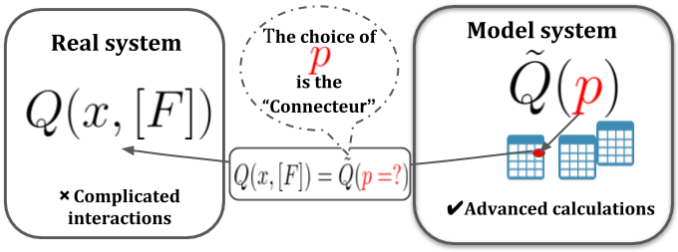

FIGURE 3.1: Schematic summary of the connector approach. The tables inside the model system are the results of advanced calculations that can be done in this system because it is simpler. These results are targeted by the parameter p. The prescription how to use them in the real system, is the connector

p in order to get the same quantity in the real system i.e.:

$$Q(x,[F]) = \tilde{Q}(p). \tag{3.1}$$

The prescription of how to import the quantity $\tilde{Q}$ to the real system is what we call "the connector". The enormous advantage of such a procedure is that the most complicated part of calculation is done only once and forever in the model system.

The exact way to import the quantity Q is to solve the equation 3.1 for p :

$$p = \tilde{Q}^{-1}(Q(x,[F])). \tag{3.2}$$

This is not necessarily possible. it is so only if the function $\tilde{Q}$ fulfills the following conditions:

- It has an inverse, ie., $\tilde{Q}^{-1}$ exists. it is not mandatory that the inverse is unique. Not uniqueness means that we have the possibilty to use more than one connector.
- It is onto, ie., the values of $Q(x,[F])$ that are to be covered must fall into the domain of the function $\tilde{Q}$. Else the connector will not be physical and for example divergence may appear in the quantity of interest.

3.2 Is that possible for the exchange correlation energy

According to the DFT we know that the exchange correlation energy $E_{xc}[n]$ is a functional of the density, however the expression of its universal functional is unknown. This quantity was computed in the case of the homogeneous electrons gas by Ceperley and Alder [1] using quantum Monte Carlo-method which deals directly with the wave function and gives results that are considered to be benchmarks. Taking the homogeneous electron gas as a model system, in this section we explore whether it is possible to import the quantum Monte Carlo results to a real system using the general connector theory.

The exchange correlation energy can be expressed as a sum of local contributions weighted by the local density, $E_{xc}[n] = \int d^3r n(\mathbf{r})\epsilon_{xc}(\mathbf{r})$. The local contribution $\epsilon_{xc}(\mathbf{r})$ can be separated into two parts, the density of the exchange energy $\epsilon_x(\mathbf{r})$ and the density of correlation energy $\epsilon_c(\mathbf{r})$.

3.2.1 Exchange energy

In the homogeneous electron gas (HEG), the density of the exchange energy can be written as [3] :

$$\epsilon_x^h = -\frac{3}{4}(\frac{3}{\pi})^{\frac{1}{3}}(n^h)^{\frac{1}{3}},$$

where n^h is the density of the HEG. If we want to import ϵ_x^h to a real system we need to invert ϵ_x^h. This yields :

$$n^h(\epsilon_x(\mathbf{r},[n])) = -\frac{64}{9}\pi(\epsilon_x(r,[n]))^3, \tag{3.3}$$

where $\epsilon_x(\mathbf{r},[n])$ is the exchange energy in the real system. The range of $\epsilon_x(r,[n])$ is $]-\infty,0]$ which implies $n^h(\epsilon_x(\mathbf{r},[n])) \geq 0$, so the inverse does exist and it is well defined.

3.2.2 Correlation energy

In the case of the HEG, an analytical expression for the correlation energy density has been proposed by Chachiyo [2]. It is a function of a density parameter [1] $r_s = (\frac{4}{3}\pi n^h)^{\frac{1}{3}}$, and it is of the form :

$$\epsilon_c^h = a \ln\left(1 + \frac{b}{r_s} + \frac{b}{r_s^2}\right)$$

with $a = \frac{ln(2)-1}{2\pi^2}$ and $b = 20.4562557$. This expression derived from many-body perturbation theory is valid for the full range of densities and it shows good agreement with the quantum Monte Carlo results, to within 2 milli-hartree.

So we have accurate results that are well described in the model system. The question now is if it is possible to use them to calculate $\epsilon_c(r,[n])$in any real system. To answer we need first to invert the function ϵ_c^h, this gives :

$$r_s(\epsilon_c(r,[n])) = \frac{2}{-1 + \sqrt{1 - 4(\frac{1-e^{\frac{\epsilon_c(r,[n])}{a}}}{b})}}$$

or, in terms of the density n^h :

$$n^h(\epsilon_c(r,[n]) = \frac{3}{4\pi {r_s}^3} = \frac{3}{32\pi}(-1 + \sqrt{1 + 4(\frac{e^{\frac{\epsilon_c(r,[n])}{a}} - 1}{b})})^3. \tag{3.4}$$

Since $a < 0$ and $\epsilon_c(r,[n]) \leq 0 \Rightarrow e^{\frac{\epsilon_c(r,[n])}{a}} - 1 \geq 0 \Rightarrow n^h(\epsilon_c(r,[n]) > 0$. This means that the inverse does exist and it is well defined, and so it is, in principle, possible to use the general connector strategy to profit from calculation done in the HEG.

The conclusion of this section gives a positive answer to the possibility of using the general connector strategy for the exchange correlation energy. This is interesting from the point of view of principle but it is useless in practice because both equation 3.3 and 3.4 require the expression of the exchange correlation energy i.e., $\epsilon_x(r,[n])$ and $\epsilon_c(r,[n])$ which we are looking for! That is why we have to do approximations on this quantities and it is precisely at this level where the utility of the connector strategy appears.

3.3 Approximations

3.3.1 General discussion

Before starting to approximate the exchange correlation energy. Let us first go back to our general discussion. As we have seen through the example of the previous section finding an exact solution to the equation 3.1 is useless because it needs an explicit formula for the quantity Q which is unknown. That's why we must make approximations to find the connector p. This implies:

$$p_{approx} = \tilde{Q}^{-1}_{approx}(Q_{approx}(x,[F])). \tag{3.5}$$

[1] Known as the Wigner-Seitz radius

At this point and since we know the exact [2] function of $\tilde{Q}$, one can say : why we use an approximated one in equation 3.5 ? To answer this question, we note first that using the exact function $\tilde{Q}$, i.e. calculating $p_{approx} = \tilde{Q}^{-1}(Q_{approx})$, would be equivalent to make the approximation directly to Q. Then we can forget for the story of the connector from the beginning. However, when we make the same approximation to both Q and $\tilde{Q}$, as we did in equation 3.5, this involves an error canceling which is expected a better connector and so better results.

3.3.2 The error canceling

The connector strategy, as it has been shown in [7] and [10], is a promising theory. The main reason behind this success is probably the fact that it involves an error canceling. To illustrate what we mean by that, we take a very simple example. Suppose that we make the same approximation to a quantity Q and $\tilde{Q}$ and this approximation makes an error of factor two i.e., $Q_{approx} = 2Q$ and $\tilde{Q}_{approx} = 2\tilde{Q}$. To find the connector we have to solve for p the following equation :

$$\tilde{Q}_{approx}(p) = Q_{approx}(x, [F]) \Leftrightarrow 2\tilde{Q}(p) = 2Q(x, [F]) \Leftrightarrow p = \tilde{Q}^{-1}(Q(x, [F]).$$

As it has been shown in this example, we started from an approximation and we end up with an exact connector due to error canceling.

Now, let us take a more realistic example. Considering a finite real system with a density $n(r)$, the Hartree potential V_H, which is our quantity Q, can be written as :

$$V_H(r) = \int dr' \frac{n(r')}{|r - r'|}. \tag{3.6}$$

Suppose that we don't know how to calculate this integral and in order to simplify it, we make the approximation of constant interaction : $\frac{1}{|r-r'|} \approx c$.

- If we make the last approximation directly in the quantity of interest we find :

$$V_H^{direct}(r) = c \int dr' n(r'). \tag{3.7}$$

- Now we want to use the connector strategy. As model system we choose a sphere of HEG of radius R. The condition to find the connector is :

$$V_H(r) = \tilde{V}_H \Leftrightarrow \int dr' \frac{n(r')}{|r - r'|} = n^h \int_R dr' \frac{1}{|r - r'|},$$

  where $\tilde{V}_H$ is the Hartree potential in the HEG and n^h its density.
  Using the approximation $\frac{1}{|r-r'|} \approx c$ and equation 3.5 we get :

$$n^h(r, [n]) = \tilde{V}^{-1}_{H,approx}(V_{H,approx}(r)) = \frac{3}{4\pi R^3} \int dr' n(r') = \bar{n}.$$

[2] We consider the interpolation of the results of advanced calculations, like quantum Monte Carlo in the last section, as exact

With this connector we import the Hartree potential from the calculation done in the HEG. Therefore the resulting potential is :

$$V_H^{connector}(r) = \bar{n} \int_R dr' \frac{1}{|r - r'|}. \tag{3.8}$$

In this example we can see that the result of making the approximation in the expression of the connector (equation 3.8) is not the same as making it directly on the potential (equation 3.7). Another important remark is that the result of the connector strategy is much better. Indeed the dependence on $\frac{1}{|r-r'|}$ of the Coulomb interaction is completely absent in the V_H^{direct} while it is present in $V_H^{connector}$. In addition, the equation 3.8 suggests to represent the real system as a HEG with a density equal to the average of the density of the real system $\bar{n}$ which is more reasonable than equation 3.7.

Chapter 4

Approximating the exchange correlation potential

In this chapter we apply the connector strategy to approximate the central quantity in DFT calculations which is the exchange correlation (xc) potential. We compare our results to the standard and the most used approximation, namely the LDA, and we explain why our strategy goes beyond it.

4.1 Linear approximation

As we have seen in chapter 3, in order to find a connector we have to apply an approximation to the quantity of interest, both in the HEG and in the real system. Here we choose a first order linear expansion.

4.1.1 Exchange correlation kernel

We know from DFT that, for a given real system, the xc potential is a functional of the density of this system which, in TDDFT, can also be time-dependent. In the following, we perform a first order expansion of the xc potential in the vicinity of some constant density $\bar{n}$:

$$v_{xc}[n] = v_{xc}[\bar{n}] + \int d^3r'dt'\delta n(\mathbf{r'},t')\frac{\delta v_{xc}(\mathbf{r},t)}{\delta n(\mathbf{r'},t')}|_{\bar{n}} \equiv v_{xc}[\bar{n}] + \Delta v_{xc}(\mathbf{r},t)[n,\bar{n}].$$

Defining $\frac{\delta v_{xc}(\mathbf{r},t)}{\delta n(\mathbf{r'},t')}|_{\bar{n}} \equiv f_{xc}(\mathbf{r}-\mathbf{r}';t-t')[\bar{n}]$ [1] :

$$\Delta v_{xc}(\mathbf{r},t)[n,\bar{n}] = \int d^3r'dt'\delta n(\mathbf{r}',t')f_{xc}(\mathbf{r}-\mathbf{r}';t-t')[\bar{n}]. \tag{4.1}$$

The quantity $f_{xc}(\mathbf{r}-\mathbf{r}';t-t')[\bar{n}]$ is known as the xc kernel. In our case this functional is evaluated at a constant density $\bar{n}$. This means that we are in a HEG and that's why it is translational invariant in space and time. M.Panholzer *et al.* [7] propose a non-adiabatic and non-local approximation to this kernel which was tabulated for a wide range of wave-vectors and frequencies. In the rest of the chapter we will profit from this calculation, and explore what happens when the results are imported to a non homogeneous system using the connector strategy.

Remarks :

[1] Since $\bar{n}$ is constant we can write $f_{xc}(\mathbf{r}-\mathbf{r}';t-t';\bar{n})$ but we choose to keep the general notation

- The kernel is wave vector and frequency dependent in the Fourier transform. This is the result of non-locality in both space and time.
- The kernel is, in general, complex, with real and imaginary parts related via Kramers-Kronig.
- The tabulated kernel, as we can see in Figure 4.1, can have poles related to the frequency of the plasmons [2] as it is explained in [7].
- Making the local approximation is equivalent to taking a kernel that does not depend on the wave-vector.
- Making the adiabatic approximation is equivalent to taking a kernel that is frequency-independent, which together with the local approximation, removes all features of the tabulated one.

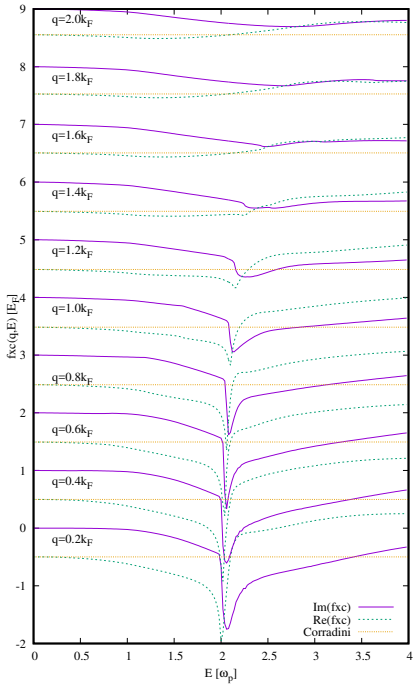

FIGURE 4.1: The xc kernel tabulated by Martin et *et al.*[7] in a HEG of density $n^h = 3.73 \times 10^{-3}$. The figure shows the xc kernel as a function of energy at momenta starting from $q = 0.2k_f$ to $q = 2k_f$ in steps of $0.2k_f$. k_f is the Fermi wave vector and w_p is the plasmon frequency

4.1.2 Design of the connector

Our aim is to make use of the tabulated kernel in order to design the connector, which tells us the density of the HEG that we should use to map the xc potential from the HEG to the real system.

Equation 4.1 can be written for a crystal as :

$$\Delta v^{xc}(\mathbf{r},t)[n,\bar{n}] = \frac{1}{V}\sum_{\mathbf{G},\mathbf{G}'}\sum_{\mathbf{q}}\int\frac{dw}{2\pi}e^{i(\mathbf{q}.\mathbf{r}-wt)}e^{i\mathbf{G}.\mathbf{r}}\delta n_{\mathbf{G}'}(\mathbf{q},w)f^{xc}_{\mathbf{G},\mathbf{G}'}(\mathbf{q},w)[\bar{n}], \tag{4.2}$$

where $f^{xc}_{\mathbf{G},\mathbf{G}',w}(\mathbf{k}) \equiv f^{xc}(\mathbf{k}+\mathbf{G},\mathbf{k}+\mathbf{G}',w)$ and $\mathbf{G}$, $\mathbf{G}'$ are reciprocal lattice vectors, $\mathbf{k}$ lies in the first Brillouin zone (BZ)and V is the total volume of the system.

Since n is constant the kernel is diagonal reciprocal space:

$$f^{xc}_{\mathbf{G},\mathbf{G}'}(\mathbf{q},w)[\bar{n}] = f^{xc}_{\mathbf{G},\mathbf{G}'}(\mathbf{q},w)[\bar{n}]\delta_{\mathbf{G}\mathbf{G}'}.$$

This yields :

$$\Delta v^{xc}(\mathbf{r},t)[n,\bar{n}] = \sum_{\mathbf{G}}\int_{1BZ}\frac{d^3q}{(2\pi)^3}\int\frac{dw}{2\pi}e^{i(\mathbf{q}.\mathbf{r}-wt)}e^{i\mathbf{G}.\mathbf{r}}\delta n_{\mathbf{G}}(\mathbf{q},w)f^{xc}_{\mathbf{G}}(\mathbf{q},w)[\bar{n}].$$

Or :

$$\Delta v^{xc}(\mathbf{r},t)[n,\bar{n}] = \int\frac{d^3k}{(2\pi)^3}\int\frac{dw}{2\pi}e^{i(\mathbf{k}.\mathbf{r}-wt)}\delta n(\mathbf{k},w)f^{xc}(\mathbf{k},w)[\bar{n}]. \tag{4.3}$$

[2] collective oscillation of electrons

In the case of the homogeneous electron gas v_{xc} is a function of the constant density n^h and so:

$$\Delta v^h_{xc}(n^h) = \frac{dv_{xc}}{dn}|_{\bar{n}}(n^h - \bar{n}) = f^{xc}_h(\bar{n})\delta n^h, \tag{4.4}$$

Where $f^{xc}_h(\bar{n}) = f^{xc}_h(\mathbf{k} \to 0)[\bar{n}] = f^{\mathrm{CODP}}(0)[\bar{n}]$. Here, $f^{\mathrm{CODP}}(\mathbf{k})[\bar{n}]$ is the Fourier transform of the static xc kernel of Corradini *et al.*, which corresponds in this limit to the kernel of M.Panholzer *et al.* [7]
Now let us determine the density n^h that we should use in the model system i.e. the homogeneous gas so that $\Delta v^h_{xc}(n^h) = \Delta v_{xc}(n^h)$, using the equation 4.3 and 4.4 we get :

$$n^h = \bar{n} + \frac{1}{f^{CODP}(0)[\bar{n}]} \int \frac{d^3k}{(2\pi)^3} \int \frac{dw}{2\pi} e^{i(\mathbf{k}.\mathbf{r} - wt)} \delta n(\mathbf{k}, w) f^{xc}(\mathbf{k}, w)[\bar{n}]. \tag{4.5}$$

4.1.3 Discussion

From equation 4.5, if the kernel f_{xc} is constant in the k-space (short range in r) we get the LDA, since the kernel drops out and the Fourier transform of the density appears. If $f_{xc} \sim \delta(\mathbf{k})$ (constant is $\mathbf{r}$ space) we get the average density as connector. Since f_{xc} lies in between, we expect a result that interpolates between these limits. if f_{xc} is constant in ω (instantaneous in time), we get the adiabatic approximation. If it is $\sim \delta(\omega)$, again the average survive.

4.2 Examples :

The internship was too short to apply the new expression in real systems. Therefore we use in the following some model cases for illustrations.

4.2.1 Static case :

We will first consider a static density, which is modulated in real space.

Cosinus density

Let us consider for example, in the static case, a crystal with the following density:

$$n(\mathbf{r}) = A + B\cos(\mathbf{a}.\mathbf{r}),$$

where $B \leq A$ are positive constants, and $\mathbf{a}$ is a vector of the reciprocal space.

Taking $A = \bar{n}$, the density in the vicinity of which we perform the expansion. This means that we make the variation around the middle of our initial density, which is not the unique choice. So we have :

$$\delta n(\mathbf{r}) = B\cos(\mathbf{a}.\mathbf{r}).$$

Performing the Fourier transform we get :

$$\delta n(\mathbf{k}) = (2\pi)^3 \frac{B}{2}[\delta(\mathbf{k} + \mathbf{a}) + \delta(\mathbf{k} - \mathbf{a})].$$

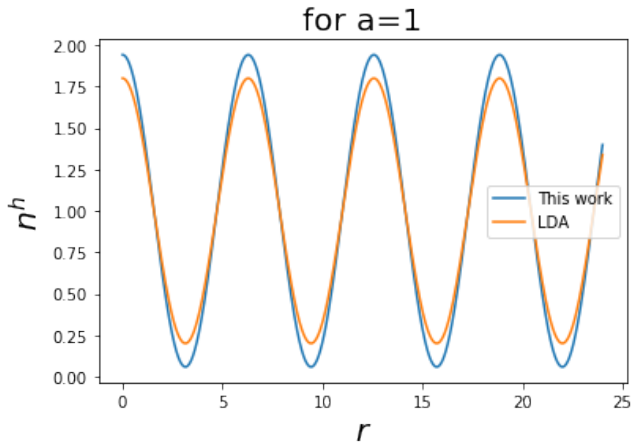

FIGURE 4.2: Comparison between LDA and connector strategy. For slowly varying density in space the results are close

Calculating n^h from equation 4.5 :

$$\Rightarrow n^h_{\mathbf{r}} = \bar{n} + \frac{1}{f^{CODP}(0)[\bar{n}]} \int \frac{d^3q}{(2\pi)^3} e^{i\mathbf{k}.\mathbf{r}} \delta n(\mathbf{k},0) f^{xc}(\mathbf{k},0)[\bar{n}]$$

$$\Rightarrow n^h_{\mathbf{r}} = \bar{n} + \frac{1}{f^{CODP}(0)[\bar{n}]} \int d^3k\, e^{i\mathbf{k}.\mathbf{r}} \frac{B}{2} [\delta(\mathbf{k}+\mathbf{a}) + \delta(\mathbf{k}-\mathbf{a})] f^{xc}(\mathbf{k})[\bar{n}]$$

$$\Rightarrow n^h_{\mathbf{r}} = \bar{n} + \frac{1}{f^{CODP}(0)[\bar{n}]} \{ \frac{B}{2} [e^{-i\mathbf{a}.\mathbf{r}} f^{xc}(-\mathbf{a})[\bar{n}] + e^{i\mathbf{a}.\mathbf{r}} f^{xc}(\mathbf{a})[\bar{n}]] \}$$

The kernel $f^{xc}[\bar{n}]$ is evaluated at the constant density $\bar{n}$, it's the kernel of a homogeneous gas where all directions are equivalent and so $f^{xc}(\mathbf{k})[\bar{n}] = f^{xc}(|\mathbf{k}|)[\bar{n}]$, this yields :

$$n^h_{\mathbf{r}} = \bar{n} + \frac{f^{xc}(|\mathbf{a}|)[\bar{n}]}{f^{CODP}(0)[\bar{n}]} [B \cos(\mathbf{a}.\mathbf{r})] \tag{4.6}$$

The static xc kenel is real and negative, so the term $\frac{f^{xc}(|\mathbf{a}|)[\bar{n}]}{f^{CODP}(0)[\bar{n}]}$ is positive and thus the connector $n^h_{\mathbf{r}}$ proposed by equation 4.6 is a well behaved density. We should also note that $n^h_{\mathbf{r}}$ depends on $\mathbf{r}$ while n^h is the density of a HEG which must be constant. This means that with this connector, we have to use a different HEG at each point in space.

Limit cases:

- *Homogeneous density (trivial), $B \to 0$:* $\Rightarrow n^h(\mathbf{r}) = \bar{n}$
- *Density with high frequency oscillations:* from the tabulated $f^{xc}(\mathbf{k})$ we have for $|\mathbf{k}| >> 6$: $f^{xc}(\mathbf{k}) \to 0$ and so : $B\cos(\mathbf{a}.\mathbf{r}) f^{xc}(\mathbf{a}) \to 0$, we recognize again the homogeneous density case
- *LDA, ie., $n^h(\mathbf{r}) = n(\mathbf{r})$:* we match the LDA for $f^{xc}(\mathbf{a}) \approx f^{\mathrm{CODP}}(\mathbf{0})$. This is true for small $\mathbf{a}$ Figure 4.2 it's coherent with the success of the LDA in the limit of slowly varying density

Mid range case:

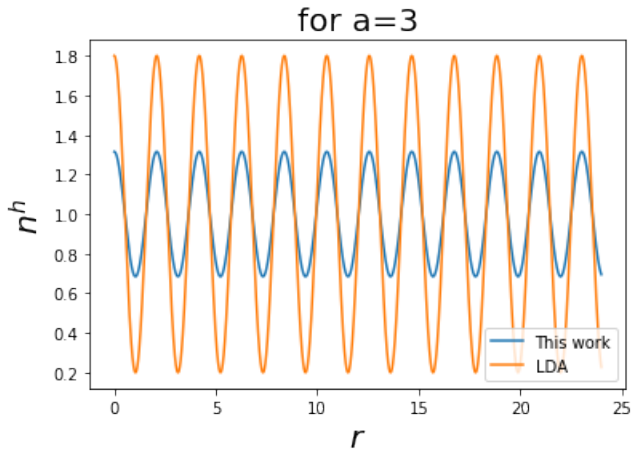

FIGURE 4.3: Comparison between LDA and connector strategy. For fast varying density in space, our connector is an average-like of the LDA

For $0 < |\mathbf{a}| < 6$ i.e., the case of a system with a density that doesn't vary slowly like a homogeneous system and does not vary fast either, we find a non trivial connector which is a kind of an average of the local density as shown in Figure 4.3, this result is qualitatively correct because in our approximation we include the non-local effect in the space, which means that we take into account the fact that the xc potential at some point $\mathbf{r_0}$ is affected by the environment around this point. This is completely absent in the LDA and that's why it fails to describe some problem like image potentials as seen in chapter 2.

Analyzing this example we can see that the connector strategy succeeds to give systematic approximations and the LDA can be derived as a particular one. Of course , the example cannot tell us how good the approximation will be in practice.

4.2.2 Time dependent case

Studying the interaction of many-electron systems with time dependent external electromagnetic fields is very interesting for several technologies like : photovoltaics and photocatalysis. As we have seen in chapter 2, TDDFT is the theory of choice that describes this kind of interaction. This implies that we need to approximate the time dependent xc potential, which is a challenge. The canonical way to deal with this problem in almost all TDFT calculations is to use the adiabatic approximation as we have seen in chapter 2.

In this section we consider an example of a density that depends on time due to some perturbation. Then using the connector strategy we explore an approximation to the xc potential and we compare our results to the ALDA ones.

Cosinus density in permanent perturbation

We consider a time dependent version of the density used in the first example of the static case :

$$n(\mathbf{r}) = A + B\cos(\mathbf{a}.\mathbf{r} - \omega_0 t).$$

We take $A = \bar{n}$ and then:

$$\delta n(\mathbf{r}) = B\cos(\mathbf{a}.\mathbf{r} - \omega_0 t).$$

Performing the Fourier transform, we get:

$$\delta n(\mathbf{k},\omega) = (2\pi)^4[\frac{1}{2}B\big(\delta(\mathbf{a}-\mathbf{k})\delta(\omega-\omega_0)+\delta(\mathbf{a}+\mathbf{k})\delta(\omega_0+\omega)\big)] \tag{4.7}$$

Putting equation 4.7 in our general equation 4.5 :

$$n^h(\mathbf{r},t)f_h^{xc}(\bar{n}) = \bar{n} + \int d^3k \int d\omega e^{i(\mathbf{k}.\mathbf{r}-\omega t)}[\frac{1}{2}B\big(\delta(\mathbf{a}-\mathbf{k})\delta(\omega-\omega_0)+\delta(\mathbf{a}+\mathbf{k})\delta(\omega_0+\omega)\big)]f^{xc}(\mathbf{k},\omega)[\bar{n}],$$

Or :

$$n^h(\mathbf{r},t) = \bar{n} + \frac{1}{f^{CODP}(0)[\bar{n}]}[\frac{1}{2}B\big(e^{i(\mathbf{a}.\mathbf{r}-\omega_0 t)}f^{xc}(\mathbf{a},\omega_0)[\bar{n}] + e^{i(-\mathbf{a}.\mathbf{r}+\omega_0 t)}f^{xc}(-\mathbf{a},-\omega_0)[\bar{n}]\big)].$$

In the time-dependent case the xc kernel is complex. Its real part is even and its imaginary part is odd with respect to ω. This implies :

$$n^h(\mathbf{r},t) = \bar{n} + \frac{B}{2f^{CODP}(0)[\bar{n}]}(\mathrm{Re}\, f^{xc}(\mathbf{a},\omega_0)2\cos(\mathbf{a}.\mathbf{r}-\omega_0 t) + i\,\mathrm{Im}\, f^{xc}(\mathbf{a},\omega_0)2i\sin(\mathbf{a}.\mathbf{r}-\omega_0 t)).$$

$$n^h(\mathbf{r},t) = \bar{n} + \frac{B}{f^{CODP}(0)[\bar{n}]}(\mathrm{Re}\, f^{xc}(\mathbf{a},\omega_0)\cos(\mathbf{a}.\mathbf{r}-\omega_0 t) - \mathrm{Im}\, f^{xc}(\mathbf{a},\omega_0)\sin(\mathbf{a}.\mathbf{r}-\omega_0 t)) \tag{4.8}$$

This can be written as :

$$n^h(\mathbf{r},t) = \bar{n} + \frac{B||f^{xc}(\mathbf{a},\omega_0)||}{f^{CODP}(0)[\bar{n}]}\cos(\mathbf{a}.\mathbf{r}-\omega_0 t+\theta) \tag{4.9}$$

where $\theta = \arg(f^{xc}(\mathbf{a},\omega_0))$.

From equation 4.8 and for $\omega_0 = 0$ the imaginary part of th xc kernel, which contains the non adiabatic effects, vanishes and then we get the result of the static case (equation 4.6).

The connector that we found in equation 4.9 has the same period as the real density. For small value of $|\mathbf{a}|$ and ω_0, i.e., a system with small inhomogeneity and slowly varying density with time, the real part of the xc kernel is equal approximately to the static xc kernel and the imaginary part is negligible. That's why our approximation matches the ALDA as shown in Figure 4.4a.

For a quickly varying density w.r.t time, (i.e w_0 is large enough), the imaginary part of the xc kernel becomes significant and a difference with respect to the ALDA appears as shown in Figures [4.4a,4.4c,4.4e].

We can see in this figures a phase shift comparing to the ALDA and a resonance at a particular frequency. This is a sign of the non-adiabaticity also called "memory effects". These effects which are completely neglected in the ALDA, are captured in our case via the xc kernel. This difference is qualitatively coherent with the fact that adiabatic approximations fails to describe dynamical processes where the density changes significantly in time [6].

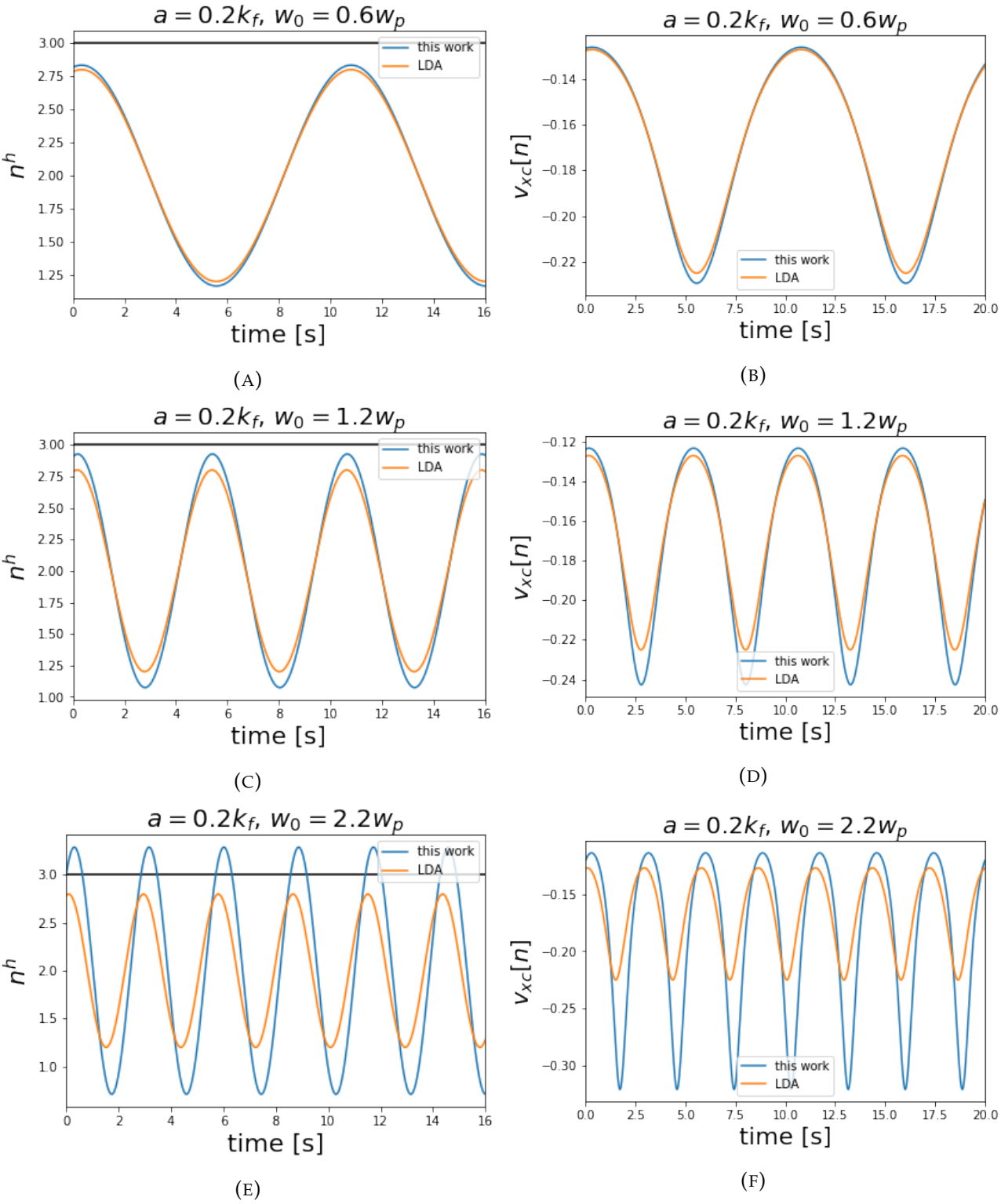

FIGURE 4.4: Comparison between my result and ALDA ones. connector density n^h (left) and xc potential (right) as a function of the time. At fixed $a = 0.2k_f$. The parameter ω_0 have been chosen as follows: top, $\omega_0 = 0.6$ where we see the matching; middle, $\omega_0 = 1.2$, bottom, $\omega_0 = 2.2$ where phase shift and resonance appear.

Chapter 5

Conclusion and outlook

In this internship we have introduced "connector strategy" which is a way to make exact and generalize methods that are based on importing quantities from simpler models into real systems.

First we have explored the possibility of applying this strategy in an exact way. We have considered the exchange-correlation energy density of the Kohn-Sham scheme of DFT. We have found a positive answer: in this case it is in principle possible to obtain from the homogeneous electron gas the value of the quantity of interest in the real system. Next, starting from the exact connector theory, we have introduced an approximation to the exchange-correlation potential that is based on a linear expansion approximation. The advantages of our approach are twofold : On one hand, the possibility to use an advance non-local and non-adiabatic exchange correlation kernel[7]. On the other hand the error canceling that derives directly from the connector strategy itself.

The resulting approximation has been compared to two widely used approximations within DFT and TDDFT: the LDA in the static case and the ALDA in the time dependent case.

We obtained results that are qualitatively better than the ones of other approximation and they reflect the feature of the systematic approximation. Indeed, considering the example of a periodic density we could derive the LDA when the local density is slowly varying. When the variation of the local density is fast, our approach propose a more reasonable connector, which is similar to an average-density approximation and hence encompasses an effect of non-locality in space..

For the time-dependent case and for a density that changes significantly in time we note two interesting features that makes our approximated exchange correlation potential completely different from the ADLA . The first was a phase shift which was the consequence of including the memory of the system. The second remark is the fact that we could observe a resonance at a particular frequency.

Of course the results of these particular examples does not guarantee anything for real systems but they provide good motivation that the connector strategy is promising and that approximations can be found that work better than the LDA and the ALDA.. This is also the outlook of my intership that lasts until September, I intend to see if the connector strategy will succeed to describe Rabi oscillation. This is an exact resolved problem and so I will have the opportunity to compare my future result to the exact solution and see if it will go beyond the ALDA. Another problem that I plan to consider is the step structure that appears in the exchange correlation potential in the case of dissociation of molecules and which is missed by the LDA [8].

Finally, the more general outlook is to combine the connector strategy presented in this manuscript with a state-of-the-art approach based on Green's function formalism to develop functionals for observables.

Bibliography

[1] D. M. Ceperley and B. J. Alder. In: *Phys. Rev. Lett* 566 (1980).

[2] Teepanis Chachiyoa. "Simple and accurate uniform electron gas correlation energy for the full range of densities". In: *The Journal of Chemical Physics* 145.021101 (Dec. 2016).

[3] P. A. M. Dirac. In: *Cambridge Philos. Soc.* 376 (1930).

[4] Adolfo G. Eguiluz; Martin Heinrichsmeier; Andrzej Fleszar; and Werner Hanke. "First-principles evaluation of the surface barrier for a Kohn-Sham electron at a metal surface". In: *Phys. Rev. Lett..* 68.1359 (1992).

[5] Hohenberg-Kohn. "Inhomogeneous Electron Gas". In: *Phys. Rev.* 136.B864 (Nov. 1964).

[6] Johanna I. Fuks; Mehdi Farzanehpour; Ilya V. Tokatly; Heiko Appel; Stefan Kurth; and Angel Rubio. "Time-dependent exchange-correlation functional for a Hubbard dimer: Quantifying nonadiabatic effects". In: *Phys. Rev. A* 88.062512 (Dec. 2013).

[7] M.Panholzer; M.Gatti; and L.Reining. "Nonlocal and Nonadiabatic Effects in the Charge-Density Response of Solids: A Time-Dependent Density-Functional Approach". In: *Phys. Rev. Lett.* 120.166402 (Apr. 2018).

[8] N.T.Maitra; F.Nogueira; E.Gross; M.Marques and A.Rubio. *Fundamental of Time-Dependent Density Functional theory*. Springer, Heidelberg, 2012.

[9] Neepa T.Maitra. In: *J. Chem. Phys* 121.655 (2004).

[10] M. Vanzini. "Dynamical local connector approximation for electron addition and removal spectra". In: *arXiv:1708.02450* 72.12 (Aug. 2017).

[11] W.Kohn and L.J.Sham. "Self-Consistent Equations Including Exchange and Correlation Effects". In: *Phys.Rev.* 140 (1965).