Relativistic effects in the optical response of low-dimensional structures: new developments and applications within a time-dependent density functional theory framework
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Acknowledgments

Light is the task where many share the toil.

Homer

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A caracterização da resposta electrónica de nano-estruturas a campos electromagnéticos externos é de grande importância, tanto do ponto de vista teórico como do ponto de vista experimental. Em contraste com os elementos leves, novos processos e fenómenos físicos aparecem nos elementos pesados, onde efeitos relativistas, como o acoplamento de spin-órbita, não podem ser ignorados. Neste trabalho desenvolvemos um quadro teórico e as ferramentas numéricas necessárias para lidar com tais processos no contexto da teoria dos funcionais da densidade dependente do tempo. Em primeiro lugar, aplicamos esta metodologia ao estudo da secção eficaz da absorção óptica de pequenos agregados catiónicos de xénon. No geral, verificamos que o acordo dos nossos resultados com a experiência é bom, excepto na previsão incorrecta da intensidade relativa dos picos. Como segunda aplicação, investigamos o efeito do acoplamento de spin-órbita na resposta óptica de pequenos agregados de ouro. Verificamos que este efeito nunca é desprezável, mas que a sua importância depende da dimensionality dos agregados (o efeito é mais pronunciado para fios, do que para estruturas 2D e 3D) e do tamanho dos agregados (o efeito é “apagado” com o aumento do tamanho dos agregados). Finalmente, estudamos o papel da não colinearidade do spin nas propriedades de estado excitado de pequenos agregados de crómio e ferro e a maneira como este se conjuga com o acoplamento de spin-órbita. Em particular, comparamos as respostas dipolar e spin-dipolar de agregados com arranjos colineares e não colineares de spin. Verificamos em todos os casos que a diferente estrutura electrónica das configurações colineares e não colineares reflecte-se, até certo ponto, nos espectros. Pelo contrário, não encontramos nos espectros nenhum efeito directo do acoplamento de spin-órbita.
Abstract

The characterization of the electronic response of nanostructures to external electromagnetic fields is of great importance, both from the theoretical and technological points of view. In contrast to light elements, new physical processes and phenomena appear in heavy elements, where relativistic effects, like spin-orbit coupling cannot be ignored. In this work we develop the theoretical framework and the numerical tools needed to address those processes within time-dependent density functional theory (TDDFT). We first apply this methodology to the study of the photoabsorption cross-section of small cationic xenon clusters. Overall, we find our results to be in good agreement with experiment, except for the incorrect prediction of the relative intensities of the peaks. As a second application, we investigate the effect of spin-orbit coupling in the optical response of small gold clusters. We find that this effect is always noticeable, but its importance depends on the dimensionalities of the clusters (the effect is larger for wires than for 2D and 3D structures) and on the size of the clusters (the effect is “quenched” with increasing cluster size). Finally, we study the role of spin noncollinearity in the excited state properties of small chromium and iron clusters and its interplay with spin-orbit coupling. In particular, we compare the dipole and spin-dipole responses of clusters with collinear and noncollinear spin arrangements. We find that, in all cases, the different electronic structure of collinear and noncollinear configurations are reflected to some extent in the spectra. On the contrary, no direct evidence of spin-orbit coupling can be found in the spectra.
List of Publications

The scientific publications originated by this work were, in chronological order:


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Un objectif sans plan n’est qu’un souhait
Antoine de Saint-Exupéry

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Part I

Introduction
Introduction

The most exciting phrase to hear in science, the one that heralds new discoveries, is not 'Eureka!' (I found it!) but 'That’s funny…'

Isaac Asimov

During the last decades, new developments in the realm of nanoscience and nanotechnology have been observed at an increasing pace. New technological applications are appearing everyday and much effort is being dedicated to the theoretical and experimental study of nanomaterials [1].

One particularly important field of research is the interaction of nanostructures with external electromagnetic fields. The way electrons respond to an external perturbation is one of the most powerful means to gain insight into the electronic structure of matter. Many properties can be explored directly through a wide range of spectroscopic techniques, like optical, Raman, infrared, circular dichroism, X-ray, etc. Another reason why the interaction of nanostructures with electromagnetic radiation is important is that it opens up a series of possible technological applications such processes may have. Many examples of such applications can be found in the literature, like molecular machines set in action by light [2,3] or molecular memories where light is used to write/erase the information by inducing the switching of the internal state of a molecule [4].

Some of the most interesting examples of the interaction of nanostructures with electromagnetic radiation involve heavy elements where relativistic effects should be important. For instance, gold nanoclusters have been studied as possible components for new optical devices [5,6] and the importance of relativistic effects in gold is well known [7]. We should note however that most of what is known about the importance of relativistic effects in this kind of systems is mostly related to the ground-state properties, while there are still many open questions regarding excited-state properties. The presence of
heavy elements is not the only factor that makes relativistic effects important: spin-orbit coupling links the charge and spin dynamics of a system. This is very important for the field of spintronics, as it opens the possibility to control the spin of a system by means of electric fields [8]. This means that it could be important to understand what is the effect of spin-orbit coupling in the optical response of nanostructures.

At this point it should be clear that the ability to predict the response properties of nanostructures from theory is of great importance. Several different theoretical approaches are available to study electronic excitations. After the impressive success of density functional theory (DFT) [9] in describing the ground state properties of a wide variety of systems, time-dependent density functional theory (TDDFT) [10] is becoming a wide-spread tool to investigate excited state properties. Like DFT, TDDFT offers a reasonable compromise between accuracy and computer efficiency, such that the theoretical study of complex phenomena in systems of several hundreds of atoms is now within our reach. Although the use of TDDFT to study excited states properties still poses several challenges, recent developments are extending the range of systems and phenomena where TDDFT yields accurate results.\footnote{Among recent TDDFT developments we find the improvement of existing exchange-correlation functionals to deal with excited state properties of bulk materials or to go beyond the adiabatic approximation and include memory effects, the description of electronic transport through single molecules, excited state dynamics, etc.}

The work described in this thesis is an attempt to develop a methodology within a TDDFT framework to study relativistic effects in excited-state properties of nanostructures and its application to several relevant systems.

This work is organized in the following way:

In Part II we introduce the theoretical foundations on which the work presented in this thesis is based. In Chapter 1 we provide an overview of density functional theory and in Chapter 2 we briefly present time-dependent density functional theory and how it is used to determine the excited-state properties of a variety of systems. One important approximation used throughout this work is the pseudopotential approximation, which is introduced in Chapter 3.

Part III is devoted to the presentation of our results. In Chapter 4 we verify the ability of TDDFT to predict the optical absorption spectra of small cationic xenon clusters, provided that the spin-orbit coupling term is included in the calculation through relativistic pseudopotentials. The same method is used in Chapter 5 to study the effect of spin-orbit in the optical response of small gold clusters with various dimensionalities (wires, planar or
3D structures), which is found to be relevant. The subject of Chapter 6 is the optical and magnetic excitations of small iron and chromium clusters. In particular, we investigate the effect of noncollinear magnetism and its interplay with the spin-orbit coupling. At the beginning of each of these Chapters we briefly introduce in more detail the systems under study and previous experimental and theoretical results available.

In the last part of this work we present our conclusions and suggest some future developments.
Part II

Theoretical Foundations
Chapter 1

The Many-Body Problem: the DFT Approach

I’m astounded by people who want to 'know' the universe when it’s hard enough to find your way around Chinatown.

Woody Allen

The fundamental problem in condensed matter physics is to find the solution of the equations governing the evolution of any system composed by electrons and atomic nuclei. In this Chapter, we briefly review this many-body problem and present the approach used throughout this work to solve it. In particular, the methods and approximations involved are presented in some detail.

1.1 The many-body problem

Consider a system of $N$ electrons and $M$ nuclei. In situations where the particles move at a speed much lower than the speed of light, this system is well described by the non-relativistic time-dependent Schrödinger equation:

$$i\hbar \frac{\partial}{\partial t} \Phi(r_1, \ldots, r_N, R_1, \ldots, R_M, t) = \hat{H} \Phi(r_1, \ldots, r_N, R_1, \ldots, R_M, t),$$

where $t$ is the time, $r_i$ and $R_I$ are the coordinates of the electrons and of the atomic nuclei, and $\Phi$ is the many-body wavefunction.
If $Z_I$, $M_I$, and $\hat{P}_I$ are the atomic number, the mass, and the linear momenta of the nuclei and if $m_e$ and $\hat{p}_i$ are the mass and the linear momenta of the electrons, then the Hamiltonian can be written as:

$$\hat{H}(r_1, \ldots, r_N, R_1, \ldots, R_M) = \sum_{i=1}^{N} \frac{\hat{p}_i^2}{2m_e} + \sum_{I=1}^{M} \frac{\hat{P}_I^2}{2M_I} - \sum_{i,l=1}^{N,M} \frac{Z_I e^2}{|r_i - R_I|} +$$

$$+ \sum_{i,j=1}^{N} \frac{e^2}{|r_i - r_j|} + \sum_{I,J=1}^{M} \frac{Z_I Z_J e^2}{|R_I - R_J|}.$$  \hspace{1cm} (1.2)

Since this Hamiltonian is time-independent, the eigenstates of Eq. (1.1) can be written as:

$$\Phi(r_1, \ldots, r_N, R_1, \ldots, R_M, t) = \Phi(r_1, \ldots, r_N, R_1, \ldots, R_M) e^{-i(E/\hbar)t},$$  \hspace{1cm} (1.3)

where $\Phi(r_1, \ldots, r_N, R_1, \ldots, R_M)$ is the fermionic solution of the non-relativistic time-independent Schrödinger equation:

$$\hat{H}\Phi(r_1, \ldots, r_N, R_1, \ldots, R_M) = E\Phi(r_1, \ldots, r_N, R_1, \ldots, R_M).$$  \hspace{1cm} (1.4)

Unfortunately Eq. (1.4) for a system of $N + M$ charged particles is usually impossible to solve and we must simplify it.

### 1.2 Atomic units

From here on we will use atomic units. In this system of units one has:

$$\hbar = m_e = \frac{e^2}{4\pi\epsilon_0} = 1,$$

$h$ being Planck’s constant, $m_e$ and $e$ are the mass and charge of the electron, and $\epsilon_0$ is the electric permeability of vacuum. In these units, length is given in bohr (1 bohr = 0.529 Å), energy in hartree (1 hartree = 27.211 eV), the unit of mass is the electron mass (9.1093819×$10^{-27}$ kg), and the unit of time is 2.419×$10^{-17}$ s.

### 1.3 Born-Oppenheimer approximation

A first step towards the simplification of the many-body problem can be taken by separating the motion of the electrons from that of the nuclei. Indeed, for the systems
we are interested in, like solids and atomic clusters, the nuclear momenta should be much larger than the electronic momenta as the mass of the electrons is much smaller than the mass of the nuclei. This means that we could consider the electrons to be in their ground-state for each set of nuclear coordinates. This is the reasoning at the base of the Born-Oppenheimer approximation [11, 12].

Let \( \Psi_k(r; R) \) be the solutions of:

\[
\hat{H}_e(R) \Psi_k(r; R) = E_k(R) \Psi_k(r; R),
\]

where the Hamiltonian \( \hat{H}_e(R) \) contains all the terms except the kinetic energy of the nuclei:

\[
\hat{H}_e(R) = \sum_{i=1}^{N} \frac{\hat{p}_i^2}{2m_i} - \sum_{i,I=1}^{N,M} \frac{Z_I}{|r_i - R_I|} + \sum_{i,j=1}^{N} \frac{1}{|r_i - r_j|} + \sum_{I,J=1}^{M} \frac{Z_I Z_J}{|R_I - R_J|}.
\]

This equation describes a system of interacting electrons in the external field generated by the nuclei (from here on we will use \( r \) to denote the set of electron coordinates and \( R \) for the set of nuclear coordinates). In Eq. (1.5) the coordinates of the nuclei are just parameters, i.e. we are considering the nuclei to be frozen. Since \( \Psi_k(r; R) \) defines a complete set of states for the electrons at each set of nuclear positions we can write \( \Phi(r, R) \) from Eq. (1.4) as follows:

\[
\Phi(r, R) = \sum_k \Lambda_k(R) \Psi_k(r; R).
\]

In order to proceed we just need to find the equations for \( \Lambda_k(R) \). This can be achieved by inserting expansion (1.7) into Eq. (1.4), multiplying it on the left by \( \Psi_k^*(r; R) \) and integrating it over the electronic coordinates. We obtain:

\[
\left[ \sum_{I=1}^{M} \frac{\hat{P}_I^2}{2m_I} + E_k(R) \right] \Lambda_k(R) + \sum_{k'} \left[ A_{kk'}(R) + B_{kk'}(R) \right] \Lambda_{k'}(R) = E \Lambda_k(R),
\]

where:

\[
A_{kk'}(R) = \sum_{I=1}^{M} \frac{1}{M_I} \int dr \left[ \Psi_k^*(r; R) \hat{P}_I \Psi_{k'}(r; R) \right] \cdot \hat{P}_I,
\]

and

\[
B_{kk'}(R) = \sum_{I=1}^{M} \frac{1}{2M_I} \int dr \Psi_k^*(r; R) \hat{P}_I^2 \Psi_{k'}(r; R).
\]
If we could neglect the off-diagonal terms the separation of the motion of the electrons and of the nuclei would be complete. This is usually a good approximation, as these terms are much smaller than the kinetic energy of the nuclei. This is the so called Born-Oppenheimer approximation. It implies that no energy is transferred between the nuclear degrees of freedom and excitations of the electrons, because the electrons are assumed to remain in the same state (which depends on $\mathbf{R}$) as the nuclei move.

In some situations the Born-Oppenheimer approximation is not a good one. This happens when there are degeneracies or almost degeneracies of the electronic states. Indeed we have:

$$\int \! dr \, \Psi^*_k(r; \mathbf{R}) \hat{P} \Psi_{k'}(r; \mathbf{R}) = \int \! dr \, \Psi^*_k(r; \mathbf{R}) \left[ \hat{H}_e, \hat{P} \right] \Psi_{k'}(r; \mathbf{R})$$

and it is possible to show that the numerator on the right hand side is finite. This means that, when $E_k(\mathbf{R}) \approx E_{k'}(\mathbf{R})$, the coupling off-diagonal terms become large and cannot be ignored anymore. This non-adiabatic coupling plays a fundamental role in the description of chemical reactions, thermalization processes, etc.

As for the remaining terms in Eq (1.8), it is easy to show that the diagonal terms of $A_{kk'}(\mathbf{R})$ vanish if the wavefunctions $\Psi_k(r; \mathbf{R})$ are real, which is usually the case. The diagonal terms of $B_{kk'}(\mathbf{R})$, like the off-diagonal terms, are also small and can be ignored in most cases. At the end the equation for the nuclei is just:

$$\left[ \sum_{l=1}^{M} \frac{\hat{P}^2_l}{2m_l} + E_k(\mathbf{R}) \right] \Lambda_k(\mathbf{R}) = E \Lambda_k(\mathbf{R}).$$

Having separated the equations for the electrons and nuclei, we still need to solve Eq. (1.5), which is by no means an easy task.

### 1.4 Density Functional Theory

As pointed out at the end of the previous section, Eq. (1.5) is not easy to solve. The main difficulty comes clearly from the electron-electron interaction term, which couples the motion of the electrons. If we could find a way to recast our problem of interacting electrons into a problem of non-interacting particles, then the solution of Eq. (1.5) would be much easier. One way to achieve this is to use Density Functional Theory (DFT).

The foundations of DFT were laid down by Hohenberg and Kohn in 1964 [13]. They showed that all properties of a quantum many-body system are functionals of the ground-state density of particles. Later, Kohn and Sham [14] devised a practical scheme which
Density Functional Theory

takes advantage of this property to solve the equations for a system of interacting electrons moving in an external potential.

1.4.1 The Hohenberg-Kohn theorem

At the heart of DFT lies the Hohenberg-Kohn theorem [13]. Consider a system of $N$ interacting electrons moving in an external potential with a non-degenerate ground-state. The Hamiltonian of this system is:

$$\hat{H} = \hat{T} + \hat{V}_{\text{ext}} + \hat{V}_{\text{ee}},$$

where the kinetic term, the external field (in the cases we are interested in, it is usually the nuclear potential), and the electron-electron interaction are given by:

$$\hat{T} = \sum_i -\frac{1}{2} \nabla_i^2; \quad \hat{V}_{\text{ext}} = \sum_i v_{\text{ext}}(\mathbf{r}_i); \quad \hat{V}_{\text{ee}} = \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}.$$ (1.14)

The theorem itself can be divided in two parts:

- Knowledge of the ground-state particle density $n(\mathbf{r})$ uniquely determines the external potential $V_{\text{ext}}(\mathbf{r})$ to within an additive constant.

- It is possible to define an universal functional for the total energy in terms of the density. The global minimum of this functional is the exact ground-state energy and the density that minimizes the functional is the exact ground-state density.

Before entering the demonstration of the theorem, we shall note that its original formulation was restricted to the cases where the ground-state of the system is non-degenerate and to Hamiltonians that include only local external potentials. It was also restricted to the set of densities that are v-representable, i.e. densities that are ground-state densities of some external potential $\hat{V}_{\text{ext}}$. Many extensions of the theorem are available in the literature [15–23], including to non-degenerate ground-states [24] and to N-representable densities [25, 26].

The first part of the theorem is equivalent to say that two bijective mappings exist between the set of external potentials, the space of ground-state wavefunctions, and the ensemble of all-electron densities:

$$\{\hat{V}_{\text{ext}}\} \overset{C}{\longleftrightarrow} \{\Psi\} \overset{D}{\rightarrow} \{n\}. \quad (1.15)$$

A density is said to be N-representable if it is derivable from an N-electron many-body wavefunction.
To prove this we need to show that $C$ and $D$ are both injective and surjective.

By construction $C$ is surjective, since the ground-state wavefunction is a solution of Schrödinger’s equation. The demonstration that $C$ is also injective will follow by *reductio ad absurdum*. Suppose there are two external potentials $\hat{V}_{\text{ext}}^{(1)}$ and $\hat{V}_{\text{ext}}^{(2)}$ that differ by more than a constant and which lead to the same ground-state wavefunction $\Psi$. From Schrödinger’s equation it follows:

$$\langle \hat{T} + \hat{V}_{\text{ee}} + \hat{V}_{\text{ext}}^{(1)} | \Psi \rangle = E^{(1)} \langle \Psi | \rangle,$$

(1.16a)

$$\langle \hat{T} + \hat{V}_{\text{ee}} + \hat{V}_{\text{ext}}^{(2)} | \Psi \rangle = E^{(2)} \langle \Psi | \rangle,$$

(1.16b)

and if we take the difference between both equations, we end up with:

$$\langle \hat{V}_{\text{ext}}^{(1)} - \hat{V}_{\text{ext}}^{(2)} | \Psi \rangle = (E^{(1)} - E^{(2)}) \langle \Psi | \rangle.$$

(1.17)

Since we assumed at the beginning that the external potentials differed by more than a constant, we have a contradiction.

Let’s now look at the relation $D$. The ground-state electronic density is the expectation value of the density operator:

$$n(r) = \langle \Psi | \hat{n}(r) | \Psi \rangle,$$

(1.18)

so clearly to each ground-state wavefunction corresponds a ground-state density. This means that $D$ is surjective and we are only left with the proof that $D$ is injective. We will again proceed by *reductio ad absurdum*. Suppose that there are two different ground-state wavefunctions $\Psi^{(1)}$ and $\Psi^{(2)}$ with the same ground-state density. Since we already proved that $C$ is injective, we know that to two different ground-state wavefunctions correspond two different external potentials. If $\Psi^{(1)}$ is the ground-state of $\hat{H}^{(1)} = \hat{T} + \hat{V}_{\text{ee}} + \hat{V}_{\text{ext}}^{(1)}$ this means that we have, from the Ritz variational principle:

$$E^{(1)} = \langle \Psi^{(1)} | \hat{H}^{(1)} | \Psi^{(1)} \rangle < \langle \Psi^{(2)} | \hat{H}^{(1)} | \Psi^{(2)} \rangle.$$

(1.19)

The last term from the previous equation can be written as:

$$\langle \Psi^{(2)} | \hat{H}^{(1)} | \Psi^{(2)} \rangle = E^{(2)} + \langle \Psi^{(2)} | \hat{H}^{(1)} - \hat{H}^{(2)} | \Psi^{(2)} \rangle$$

$$= E^{(2)} + \langle \Psi^{(2)} | \hat{V}_{\text{ext}}^{(1)} - \hat{V}_{\text{ext}}^{(2)} | \Psi^{(2)} \rangle,$$

(1.20)

and we have:

$$E^{(1)} < E^{(2)} + \langle \Psi^{(2)} | \hat{V}_{\text{ext}}^{(1)} - \hat{V}_{\text{ext}}^{(2)} | \Psi^{(2)} \rangle.$$
In a similar way, if we start with $E^{(2)}$ we will end up with a similar expression:

$$
E^{(2)} < E^{(1)} + \langle \Psi^{(1)} | \hat{V}_{\text{ext}}^{(2)} - \hat{V}_{\text{ext}}^{(1)} | \Psi^{(1)} \rangle .
$$

(1.22)

Now, since both ground-state densities are supposed to be the same we have that:

$$
\langle \Psi^{(2)} | \hat{V}_{\text{ext}}^{(1)} - \hat{V}_{\text{ext}}^{(2)} | \Psi^{(2)} \rangle = \int d\mathbf{r} \left( \hat{V}_{\text{ext}}^{(1)} - \hat{V}_{\text{ext}}^{(2)} \right) n(\mathbf{r}) = -\langle \Psi^{(1)} | \hat{V}_{\text{ext}}^{(2)} - \hat{V}_{\text{ext}}^{(1)} | \Psi^{(1)} \rangle ,
$$

(1.23)

and adding Eq. (1.21) and Eq. (1.22) we obtain:

$$
E^{(1)} + E^{(2)} < E^{(2)} + E^{(1)},
$$

(1.24)

which is a contradiction.

There is a very interesting consequence of the first part of the theorem. As it was shown, if we know the ground-state density of a system then the Hamiltonian is fully determined. This means that if we solve the Schrödinger equation for this Hamiltonian we can obtain the wavefunctions of all the states. From here it follows that the ground-state density determines all the properties of the system.

To prove the second part of the theorem we note that, as we have just shown, the ground-state expectation value of any physical observable of our system is a unique functional of the ground-state density:

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

(1.25)

This means the total energy of the system is a functional of the density:

$$
E_{\text{HK}}[n] = \langle \Psi | \hat{T} + \hat{V}_{\text{ee}} + \hat{V}_{\text{ext}} | \Psi \rangle ,
$$

$$
= T[n] + V_{\text{ee}}[n] + \int d\mathbf{r} v_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) .
$$

(1.26)

Since the functional $F_{\text{HK}} = T[n] + V_{\text{ee}}[n]$ does not depend on the external potential, it must be an universal functional, i.e., it has to be the same for all N-electron systems. This functional includes kinetic and the interaction energies. To conclude the proof we use Ritz’s variational principle. If $n^{(1)}$ is the ground-state density of our system, then for any different density $n^{(2)}$ we have:

$$
E_{\text{HK}}[n^{(1)}] = \langle \Psi^{(1)} | \hat{H}^{(1)} | \Psi^{(1)} \rangle < \langle \Psi^{(2)} | \hat{H}^{(1)} | \Psi^{(2)} \rangle = E_{\text{HK}}[n^{(2)}] ,
$$

(1.27)

Thus we can say that the exact ground-state density is the one that minimizes $E_{\text{HK}}[n]$:

$$
E = \min_{\{n\}} E_{\text{HK}}[n] ,
$$

(1.28)
with the variational search being performed over all the \(v\)-representable densities.

Although the Hohenberg-Kohn theorem assures us that the universal functional \(F_{HK}[n]\) exists, it does not tell us how to determine it other than by solving the initial many-body problem of \(N\) interacting electrons. This is why a practical scheme to approximate \(F_{HK}[n]\) is needed.

### 1.4.2 The Kohn-Sham equations

In 1965 Kohn and Sham suggested a method in which the original many-body problem of \(N\) interacting electrons was replaced by a one-body problem [14].

The main hypothesis in Kohn-Sham’s method is that the exact ground-state density of a system of interacting electrons can be represented by the ground-state density of a system of non-interacting electrons. This requires the existence of a system of non-interacting electrons that has the same ground-state density as the interacting system.

The ground-state solution of a system of \(N\) non-interacting electrons subject only to an external potential \(V_s\) is a Slater determinant of the orbitals \(\psi_i(r)\) satisfying \(^2\):

\[
\left[-\frac{1}{2} \nabla^2 + v_s(r)\right] \psi_i(r) = \epsilon_i \psi_i(r). \tag{1.29}
\]

The only interaction between the electrons comes through the Pauli exclusion principle used in the filling of the orbitals. If the ordering of the electronic levels is such that the orbitals \(\psi_1(r), \ldots, \psi_N(r)\) are occupied, then the density is given by:

\[
n(r) = \sum_{i=1}^{N} |\psi_i(r)|^2. \tag{1.30}
\]

Using the Hohenberg-Kohn theorem we have for this non-interacting system:

\[
E_s[n] = T_s[n] + \int dr \, n(r) v_s(r) \\
= -\frac{1}{2} \sum_{i=1}^{N} \int dr \, \psi_i^*(r) \nabla^2 \psi_i(r) + \int dr \, n(r) v_s(r), \tag{1.31}
\]

and the ground-state energy can be obtained by solving the Euler-Lagrange equation that follows from the variational principle:

\[
\frac{\delta}{\delta n} \left[ E_s[n] - \left( \mu_s \int dr \, n(r) - N \right) \right] = \frac{\delta T_s[n]}{\delta n} + v_s(r) - \mu_s = 0, \tag{1.32}
\]

\(^2\)Here we are assuming, again, that the ground-state is non-degenerate and that the external potential is local.
where $\mu_s$ is a Lagrange multiplier through which the normalization of the density to the number of electrons is imposed. This equation is equivalent to Eq. (1.29).

Now, for the interacting system we have:

$$E[n] = F_{HK}[n] + \int dr \, v_{\text{ext}}(r)n(r) = T[n] + V_{ee}[n] + \int dr \, v_{\text{ext}}(r)n(r),$$  

(1.33)

and we can rewrite it as:

$$E[n] = T_s[n] + E_H[n] + E_{xc}[n] + \int dr \, v_{\text{ext}}(r)n(r),$$  

(1.34)

where the Hartree energy $E_H[n]$ is the classical contribution to the electronic self-repulsion:

$$E_H[n] = \frac{1}{2} \int dr_1 \int dr_2 \, \frac{n(r_1)n(r_2)}{|r_1 - r_2|},$$  

(1.35)

and the exchange-correlation energy $E_{xc}[n]$ is defined as:

$$E_{xc}[n] = T[n] + V_{ee}[n] - T_s[n] - E_H[n],$$  

(1.36)

and includes all the correlation effects and all the exchange effects due to the fermionic nature of the electrons. The Euler-Lagrange equation for the interacting system is:

$$\frac{\delta}{\delta n} \left[ E[n] - \left( \mu \int dr \, n(r) - N \right) \right] =$$

$$= \frac{\delta T_s[n]}{\delta n} + v_{\text{ext}}(r) + v_H[n](r) + v_{xc}[n](r) - \mu_s = 0,$$  

(1.37)

where the Hartree potential $v_H[n](r)$ is given by:

$$v_H[n](r) = \int dr' \, \frac{n(r')}{|r - r'|},$$  

(1.38)

and the exchange-correlation potential $v_{xc}[n](r)$ by:

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

(1.39)

As we are assuming that the ground-state densities of both the non-interacting and interacting systems are equal, and since Eqs. (1.29) and (1.32) are equivalent, then solving Eq. (1.37) must be equivalent to solving:

$$\left[ -\frac{1}{2} \nabla^2 + v_{\text{ext}}(r) + v_H[n](r) + v_{xc}[n](r) \right] \psi_i(r) = \epsilon_i \psi_i(r),$$  

(1.40)
with
\[ n(r) = \sum_{i=1}^{N} |\psi_i(r)|^2. \] (1.41)

Equations (1.40) and (1.41) are the so-called Kohn-Sham equations. The Kohn-Sham system is thus a system of non-interacting electrons that move subject to an effective potential, the Kohn-Sham potential:
\[ v_{KS}[n](r) = v_s[n](r) = v_{ext}(r) + v_H[n](r) + v_{xc}[n](r). \] (1.42)

There are a couple of important things to note about the Kohn-Sham equations. First, they must be solved self-consistently. This is because the potential entering the equations depends on the density, which is not known at the beginning, and can only be determined by solving the equations. Second, if we knew the exact form of the exchange-correlation functional, then the Kohn-Sham equations should yield the exact ground-state density and energy for the interacting system. This is of course true only if indeed there is a non-interacting system that has the same density \( n(r) \) of the interacting one. Unfortunately the exact exchange-correlation functional is not known, so it must be approximated.

### 1.4.3 Spin Density Functional Theory

One important case where the original Hohenberg-Kohn theorem does not hold is when the external potential includes a magnetic field. If the magnetic field is weak enough we can ignore the effect of the magnetic field on the orbital motion\(^3\) and we are left only with a Zeeman term. In 1972 von Barth and Hedin [27] extended the Hohenberg-Kohn theorem for the spin-polarized case, i.e., to the case where the external potential depends on the spin. They showed there is a unique relationship between the ground-state wavefunction \( \Psi \) and the spin density matrix \( \rho(r) \). Unfortunately, no obvious one-to-one relationship between the density matrix and the external spin potential exists. Recently this problem of the non-uniqueness of the potentials of spin density functional theory has been extensively addressed and it has been shown that, except for some possible pathological cases, the invertibility of the mapping between spin potentials and ground-state spin densities is ensured [28–33].

We will start by introducing the relevant quantities of the theory. The elements of

---

\(^3\)The proper inclusion of this effect requires an extension to current density functional theory [16, 17].
the spin density matrix $\rho^{\alpha\beta}(r)$ are given by:

$$\rho^{\alpha\beta}(r) = N \sum_{\sigma_2, \ldots, \sigma_N} \int dr_2 \cdots \int dr_N \Psi^\dagger(\mathbf{r}_\beta, \mathbf{r}_{2\sigma_2}, \ldots, \mathbf{r}_{N\sigma_N}) \Psi(\mathbf{r}_\alpha, \mathbf{r}_{2\sigma_2}, \ldots, \mathbf{r}_{N\sigma_N}),$$

(1.43)

where $\sigma_i$ are spin variables. It is often convenient to rewrite the spin density matrix in terms of the electronic density $n(r)$ and of the magnetization density vector $\mathbf{m}(r)$:

$$\rho(r) = \frac{1}{2} n(r) \sigma_0 + \frac{1}{2} \mathbf{m}(r) \cdot \mathbf{\sigma},$$

(1.44)

where $\sigma_0$ is the unity matrix and $\mathbf{\sigma}$ is the vector of the Pauli spin matrices. This means the electronic density $n(r)$ is just the trace of the spin density matrix $n(r) = \rho^{\uparrow \uparrow}(r) + \rho^{\downarrow \downarrow}(r)$.

As for the generalization of the Kohn-Sham equations for the spin polarized case, if we have a general external magnetic field $\mathbf{B}_{\text{ext}}(r)$ and some scalar external potential $v_{\text{ext}}(r)$, then the Kohn-Sham equations become:

$$\left[ \left( -\frac{1}{2} \nabla^2 + v_H[n](r) + v_{\text{ext}}(r) \right) \sigma_0 + v_{\text{xc}}[\rho](r) - \mu_B \mathbf{B}_{\text{ext}}(r) \cdot \mathbf{\sigma} \right] \Psi_i(r) = \epsilon_i \Psi_i(r).$$

(1.45)

The one-particle wavefunctions are now two-component spinors:

$$\Psi_i(r) \equiv \begin{pmatrix} \psi_i^\uparrow(r) \\ \psi_i^\downarrow(r) \end{pmatrix},$$

(1.46)

the Kohn-Sham potential is a $2 \times 2$ matrix:

$$v_{\text{xc}}^{\alpha\beta}[\rho](r) = \frac{\delta E_{\text{xc}}[\rho]}{\delta \rho^{\alpha\beta}(r)},$$

(1.47)

while the spin density elements are given by:

$$\rho^{\alpha\beta}(r) = \sum_{i=1}^N \psi_i^{\beta*}(r) \psi_i^{\alpha}(r).$$

(1.48)

In the above equations we have considered the existence of an external magnetic field, but it happens that some systems may be spin polarized even if there is no such external magnetic field. In those cases spin density functional theory is useful as well, even if, in principle, the ground state is determined by the total density $n(r) = \rho^{\uparrow}(r) + \rho^{\downarrow}(r)$ as the original Hohenberg-Kohn theorem remains valid.
In many situations the external magnetic field \( B_{\text{ext}}(r) \) is collinear, i.e., it’s direction is constant in space. In that case we can take it, without loss of generality, along the \( z \) direction, so that \( B_{\text{ext}}(r) \cdot \sigma \) is diagonal, but this does not imply that the spin density matrix of the lowest energy solution will also be diagonal. This is because the exchange-correlation potential does not need to be diagonal if the external magnetic potential is collinear, or even if there is no external magnetic potential. In fact noncollinear solutions were found for several different systems in the absence of external magnetic fields [34–36]. Nevertheless, in most situations, the spin density matrix is indeed diagonal and the magnetization density vector is collinear. For those cases, the Kohn-Sham potential is diagonal and there are two sets of Kohn-Sham equations, one for the spin up solutions and another for spin down:

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

with \( \sigma = \uparrow \) or \( \downarrow \), \( n(r) = n^\uparrow(r) + n^\downarrow(r) \), \( m_z(r) = n^\uparrow(r) - n^\downarrow(r) \), and

\[
n^\sigma(r) = \sum_{i=1}^{N} |\psi_i^\sigma(r)|^2.
\]

### 1.4.4 Relativistic Density Functional Theory

When dealing with systems where relativistic effects are important one needs to work with the relativistic generalization of DFT (RDFT) [21–23]. A full extension of DFT to interacting electrons and photons based on quantum electrodynamics exists. In this theory one works with the 4-current density and 4-potentials instead of the density and scalar external potentials and the Kohn-Sham equations are replaced by the so called Dirac-Kohn-Sham equations. Here we will only present an approximation of the theory for the case where there is only an external scalar potential [23]. In that case the Dirac-Kohn-Sham equations become:

\[
\left[ -ic\alpha \cdot \nabla + \beta c^2 + v_{\text{KS}}(r) \right] \psi_i(r) = \epsilon_i \psi_i(r),
\]

where \( \alpha \) and \( \beta \) are the usual Dirac matrices. The one-particle wavefunctions \( \psi_i(r) \) are now four-component spinors and the particle density is given by:

\[
n(r) = \sum_{i=1}^{N} \psi_i^\dagger(r) \psi_i(r),
\]
where the summation does not include positron states. Although these equations are very similar to the ones from Section 1.4.2, one should be careful with the interpretation of the exchange-correlation energy, as now it also includes relativistic effects.

Sometimes it is not necessary to use the full four-component Dirac Hamiltonian in order to include all the relevant relativistic effects. One common approximation that transforms the four-component Hamiltonian into a two-component one is the zero-order regular approximation (ZORA) [37, 38]. Another way to incorporate relativistic effects is to use relativistic pseudopotentials (see Chapter 3). This is a good approximation when the relativistic effects that come from the valence electrons can be neglected.

### 1.4.5 Exchange and correlation functionals

As it was said previously, the exact exchange-correlation functional of DFT is not known and it is necessary to approximate it. Two popular and quite successful approximations are the local spin density approximation (LSDA) and the generalized gradient approximation (GGA). In these approximations the $E_{xc}[n]$ is a local or nearly local functional of the density.

#### Local spin density approximation

In the local spin density approximation (LSDA) $E_{xc}[n^\uparrow, n^\downarrow]$ is taken to be:

$$E_{xc}[n^\uparrow, n^\downarrow] = \int d\mathbf{r} n(\mathbf{r}) \epsilon_{xc}^{\text{HEG}}(n^\uparrow(\mathbf{r}), n^\downarrow(\mathbf{r})), \quad (1.53)$$

where $\epsilon_{xc}^{\text{HEG}}(n^\uparrow(\mathbf{r}), n^\downarrow(\mathbf{r}))$ is the exchange and correlation energy per electron of the homogeneous electron gas (HEG) of spin densities $n^\uparrow(\mathbf{r})$ and $n^\downarrow(\mathbf{r})$. As for the exchange-correlation potential, we can obtain it from Eq. (1.39):

$$v^\sigma_{xc}[n^\uparrow, n^\downarrow](\mathbf{r}) = \left[ \epsilon_{xc}^{\text{HEG}}(n^\uparrow, n^\downarrow) + n(\mathbf{r}) \frac{\partial \epsilon_{xc}^{\text{HEG}}(n^\uparrow, n^\downarrow)}{\partial n^\sigma} \right]. \quad (1.54)$$

The exchange energy of the homogeneous electron gas is known analytically. As for the correlation energy, it was computed to great accuracy at several densities using quantum Monte Carlo simulations [39, 40] and many parametrizations of these results were proposed to obtain the correlation energy for any density [41, 42].

Systems where the density varies slowly over space are close to the limit of the homogeneous electron gas. These are the cases where one would expect the LSDA to be a good approximation. This is indeed the case, but it also happens that the LSDA gives
some rather good results for a variety of systems where the density is not so close to that limit, like atoms and molecules. One reason for this is that the LSDA is not an arbitrary approximation and has many physically correct features. For a more detailed discussion on this subject see Ref. [43].

The usual way to generalize the LSDA for noncollinear spins was first suggested by von Barth and Hedin [27]. They noted that one can divide the system in small boxes and consider the electrons in each one to form a collinear spin-polarized homogeneous electron gas. In practice, this means that for each point in space one diagonalizes the density matrix \( \rho^{\alpha\beta}(r) \), computes the exchange-correlation energy density and potential in the local reference frame where \( \rho^{\alpha\beta}(r) \) is diagonal, and \( m(r) \) is along the \( z \) direction, then rotates back the potential to the original reference frame [44]. If \( \bar{\rho}(r) \) and \( \bar{v}_{xc}(r) \) are the density and potential matrices in the reference frame in which \( \rho \) is diagonal, then we have:

\[
\bar{\rho}(r) = \frac{1}{2} n(r) \sigma_0 + \frac{1}{2} \sqrt{[\rho^{\uparrow\uparrow}(r) - \rho^{\downarrow\downarrow}(r)]^2 + 4 \rho^{\uparrow\downarrow}(r) \rho^{\downarrow\uparrow}(r)} \sigma_z, \tag{1.55}
\]

and

\[
\bar{v}_{xc}[\rho](r) = \frac{1}{2} \left[ \bar{v}_{xc}^{\uparrow}[\bar{\rho}](r) + \bar{v}_{xc}^{\downarrow}[\bar{\rho}](r) \right] \sigma_0 + \frac{1}{2} \left[ \bar{v}_{xc}^{\uparrow}[\bar{\rho}](r) - \bar{v}_{xc}^{\downarrow}[\bar{\rho}](r) \right] \sigma \cdot \hat{m}. \tag{1.56}
\]

**Generalized gradient approximation**

The first obvious improvement on LSDA would be to include some semi-local dependence in the functional, like gradient corrections. Unfortunately, the gradient expansion approximations (GEA) that were proposed [14, 45, 46] do not improve the LSDA results consistently. There are two reasons for this. First the GEA does not have many of the physically correct features that the LSDA has. Second, in real systems the density is not very close to the slowly varying limit and for large gradients the expansion breaks down.

To solve the problems with the GEA, a more general form for the exchange-correlation energy in terms of gradients of the density was proposed:

\[
E_{xc}[n^\uparrow, n^\downarrow] = \int dr f \left( n^\uparrow(r), n^\downarrow(r), \nabla n^\uparrow(r), \nabla n^\downarrow(r) \right). \tag{1.57}
\]

This form is known as the generalized gradient approximation (GGA) and the main idea behind it is to construct the function \( f \) in such a way that the functional obeys some known physical constraints and avoids problems with large gradients. Many different forms for \( f \) were proposed. Some of the most widely used ones can be found in the following references [46–51]. The GGA exchange-correlation potential is obtained, like for
the LSDA, from Eq. (1.39):

$$v_{xc}^{\sigma}[n_\uparrow, n_\downarrow](r) = \left[ \frac{\partial f(n_\uparrow, n_\downarrow, \nabla n_\uparrow, \nabla n_\downarrow)}{\partial n^\sigma} - \nabla \frac{\partial f(n_\uparrow, n_\downarrow, \nabla n_\uparrow, \nabla n_\downarrow)}{\partial \nabla n^\sigma} \right]. \quad (1.58)$$

We conclude by noting that the usual generalization of GGA for noncollinear spin is done in the same way as the one presented in the previous section for LSDA. The only modification in this case is that we also need to consider the gradients of the density in the local reference frame where the density is diagonal.
Chapter 2

Time-Dependent Phenomena: TDDFT Formalism

Time crumbles things; everything grows old under the power of Time and is forgotten through the lapse of Time.

Aristotle

2.1 Time-Dependent Density Functional Theory

2.1.1 The Runge-Gross theorem

The Runge-Gross theorem [18] is the extension of the Hohenberg-Kohn theorem to a system of N interacting electrons moving in a time-dependent external potential. It says that the knowledge of the time-dependent particle density \( n(r, t) \) uniquely determines the external time-dependent potential \( \hat{V}_{\text{ext}}(r, t) \) to within a purely time-dependent additive constant. This implies that all observables of the system are functionals of the time-dependent density and of the initial state. The dependence on the initial state arises from the fact that the time-dependent problem is an initial value problem. Indeed, the time-dependent wavefunction is a solution of the time-dependent Schrödinger equation (1.1), which is a first-order differential equation in time.\(^1\)

\(^1\)On the other hand, the static problem is a boundary value problem as the wavefunction is a solution of the time-independent Schrödinger equation (1.4), which is a second-order differential equation in the space coordinates.
As a first step of the demonstration we will show that if we have two time-dependent 
external potentials \( \hat{V}_{\text{ext}}^{(1)} \) and \( \hat{V}_{\text{ext}}^{(2)} \) that differ by more than a purely time-dependent function 
c(t) then the corresponding current densities \( j^{(1)}(r, t) \) and \( j^{(2)}(r, t) \) evolving from the same initial state \( |\Psi(t_0)\rangle = |\Psi_0\rangle \) will also be different. The current density is given by:

\[
j(r, t) = \langle \Psi(t) | j | \Psi(t) \rangle = N \int dr_2 \cdots \int dr_N \Re [\Psi(r, r_2, \cdots, r_N, t) \nabla \Psi^*(r, r_2, \cdots, r_N, t)]
\]

(2.1)
and it obeys the following continuity equation:

\[
\frac{\partial}{\partial t} n(r, t) = -\nabla \cdot j(r, t).
\]

(2.2)

Using the quantum mechanical equation of motion for \( j^{(1)}(r, t) \) and \( j^{(2)}(r, t) \) we have:

\[
i \frac{\partial}{\partial t} j^{(1)}(r, t) = \langle \Psi^{(1)}(t) | \left[ j, \hat{H}^{(1)}(t) \right] | \Psi^{(1)}(t) \rangle,
\]

(2.3a)

\[
i \frac{\partial}{\partial t} j^{(2)}(r, t) = \langle \Psi^{(2)}(t) | \left[ j, \hat{H}^{(2)}(t) \right] | \Psi^{(2)}(t) \rangle.
\]

(2.3b)

By taking the difference between both equations, for \( t = t_0 \) we have:

\[
i \frac{\partial}{\partial t} \left[ j^{(1)}(r, t) - j^{(2)}(r, t) \right]_{t=t_0} = \langle \Psi_0 | \left[ j, \hat{H}^{(1)}(t_0) - \hat{H}^{(2)}(t_0) \right] | \Psi_0 \rangle = \langle \Psi_0 | \left[ j, \hat{V}_{\text{ext}}^{(1)}(t_0) - \hat{V}_{\text{ext}}^{(2)}(t_0) \right] | \Psi_0 \rangle = i n_0(r) \nabla \left[ v_{\text{ext}}^{(1)}(r, t_0) - v_{\text{ext}}^{(2)}(r, t_0) \right],
\]

(2.4)

with \( n_0(r) = n(r, t = t_0) \). If we apply the equations of motion \( k + 1 \) times, with \( k > 0 \), then we have:

\[
i \frac{\partial^{k+1}}{\partial t^{k+1}} \left[ j^{(1)}(r, t) - j^{(2)}(r, t) \right]_{t=t_0} = i n_0(r) \nabla \frac{\partial^k}{\partial t^k} \left[ v_{\text{ext}}^{(1)}(r, t) - v_{\text{ext}}^{(2)}(r, t) \right]_{t=t_0}.
\]

(2.5)

If we restrict ourselves to external time-dependent potentials that are expandable in a Taylor series around the initial time \( t_0 \):

\[
v_{\text{ext}}(r, t) = \sum_{k=0}^{\infty} c_k(r)(t-t_0)^k ; \quad c_k(r) = \frac{1}{k!} \frac{\partial^k}{\partial t^k} v_{\text{ext}}(r, t) \bigg|_{t=t_0},
\]

(2.6)
then there must be some value of \( k \) for which the right hand side of Eq. (2.5) does not vanish. This means \( j^{(1)}(r, t) \neq j^{(2)}(r, t) \) and we have established a one-to-one correspondence between the current density and the external potential.

\textsuperscript{2}This continuity equation is easy to derive using Eq. (1.1).
In order to conclude the demonstration of the theorem we still need to show that different current densities imply different densities. Using the continuity equation (2.2) we have:

\[
\frac{\partial}{\partial t} \left[ n^{(1)}(r,t) - n^{(2)}(r,t) \right] = -\nabla \cdot \left[ j^{(1)}(r,t) - j^{(2)}(r,t) \right] \tag{2.7}
\]

and by taking the \((k + 1)\)th time derivative of this equation we obtain, for \(t = t_0\):

\[
\frac{\partial^{k+2}}{\partial t^{k+2}} \left[ n^{(1)}(r,t) - n^{(2)}(r,t) \right]_{t=t_0} = -\nabla \cdot \left\{ n_0(r) \nabla \frac{\partial^k}{\partial t^k} \left[ v^{(1)}_{\text{ext}}(r,t) - v^{(2)}_{\text{ext}}(r,t) \right]_{t=t_0} \right\}
\]

\[
= -\nabla \cdot \left[ n_0(r) \nabla u_k(r) \right]. \tag{2.8}
\]

In the second step we made use Eq. (2.5) and in the last step we defined:

\[
u_k(r) = \frac{\partial^k}{\partial t^k} \left[ v^{(1)}_{\text{ext}}(r,t) - v^{(2)}_{\text{ext}}(r,t) \right]_{t=t_0} \tag{2.9}\]

This means that the densities will be different if the right hand side of (2.8) is nonzero. We will now proceed by reductio ad absurdum and suppose that \(\nabla \cdot \left[ n_0(r) \nabla u_k(r) \right] = 0\) and \(u_k(r) \neq \text{constant}\), i.e., we assume that the potentials differ by more than a purely time-dependent function. Using Green’s theorem we can write:

\[
\int \! \! d\mathbf{r} \, u_k(r) \nabla \cdot \left[ n_0(r) \nabla u_k(r) \right] = \int_S n_0(r) u_k(r) \nabla u_k(r) \cdot \mathbf{dS} -
\]

\[
- \int \! \! d\mathbf{r} \, n_0(r) [\nabla u_k(r)]^2. \tag{2.10}
\]

The first term on the right hand side vanishes for “well behaved” potentials that decay as fast as \(-1/r\) when \(r \to \infty\). As for the second term, the integrand is always positive. This means that the left hand term will only be zero if \(\nabla u_k(r)\) vanishes everywhere. This is a contradiction, as this was one of our initial assumptions.

We have just proved that the density determines the potential up to a time-dependent function. This implies that the time-dependent wavefunction is in turn determined by the density up to a purely time-dependent phase factor. When taking the expectation value of any operator which is a function of time, but not of any derivative or integral operator in \(t\), this phase cancels out and those operators are functionals of the time-dependent density and initial state.

Like in the case of the Hohenberg-Kohn theorem, the Runge-Gross theorem only establishes the invertible mapping between the time-dependent densities and the time-dependent external potentials and does not tell us how to obtain the density without
solving the initial many-body problem of interacting electrons. This is why a practical
scheme similar to the Kohn-Sham scheme is needed. Before presenting this scheme, we
mention that several extensions and advances on the Runge-Gross theorem exist. One of
these extensions is the one proposed by van Leeuwen [52] who solved the problem of the
$\nu$-representability of the time-dependent density, which is necessary in order to provide
rigorous support for the time-dependent Kohn-Sham scheme. Among the other extensions
we find the generalizations necessary to include external magnetic fields [53, 54], to treat
the coupling between electronic and nuclear motion [55], etc.

### 2.1.2 Time-dependent Kohn-Sham equations

Similarly to the static Kohn-Sham scheme, we will assume there exists a system of
non-interacting electrons whose density is the same as the one of the interacting system.
Then, from the Runge-Gross theorem, the potential $v_{KS}(r,t)$ that yields this density is
unique. This auxiliary system of non-interacting electrons satisfies the time-dependent
Kohn-Sham equations, or Runge-Gross equations:

$$i \frac{\partial}{\partial t} \psi_i(r,t) = \left(-\frac{1}{2} \nabla^2 + v_H[n](r,t) + v_{ext}(r,t) + v_{xc}[n](r,t)\right) \psi_i(r),$$

(2.11)

where the time-dependent density is given by:

$$n(r,t) = \sum_{i=1}^{N} |\psi_i(r,t)|^2,$$

(2.12)

and the exchange and correlation potential is now both a functional of the time-dependent
density and of the initial state of the system. If the initial state of the system is a non-
degenerate ground-state, then from the Hohenberg-Kohn theorem it follows that the initial
wavefunction is a functional only of the ground-state potential. This means that, in that
case, we can remove the dependence on the initial state, as the potential will be a functional
of the time-dependent density alone.

In the static case we used the variational principle for the total energy in order to
derive the Kohn-Sham equations and to define the exchange and correlation functional.
For time-dependent systems this is not possible, since the total energy is not necessarily
conserved. However, there is an analogous principle, the stationarity principle of the
quantum mechanical action:

$$\mathcal{A}[\Psi] = \int_{t_0}^{t_1} dt \left( \langle \Psi(t) | i \frac{\partial}{\partial t} - \hat{H}(t) | \Psi(t) \rangle \right),$$

(2.13)
which states that the function $\Psi$ that makes the action stationary will be the solution of
the time-dependent Schrödinger equation. This action, which is also a functional of the
time-dependent density, was used in the original formulation of Runge and Gross [18] to
obtain the time-dependent exchange-correlation potential:

$$ v_{xc}[n](r, t) = \frac{\delta A_{xc}[n]}{\delta n(r, t)}, \quad (2.14) $$

where the exchange-correlation action, $A_{xc}[n]$, is defined using the action functional for
the Kohn-Sham system:

$$ A_{xc} = A_{KS}[n] - A[n] - \frac{1}{2} \int dr \int dr' \frac{n(r, t)n(r', t)}{|r - r'|}. \quad (2.15) $$

Unfortunately this action leads to the breakdown of the principle of causality. This prob-
lem was solved by van Leeuwen, who defined a new action functional using the Keldysh
formalism [56]. In any case, the exchange-correlation functional needs to be approximated
as it is not known exactly, just as in the static case.

### 2.1.3 Adiabatic approximations to $v_{xc}$

It was mentioned previously that the time-dependent exchange and correlation poten-
tial is a functional of the time-dependent density. This means that $v_{xc}[n](r, t)$ depends
on the entire history of the density, i.e., it has a functional dependence on all $n(r, t')$ for
$0 \leq t' \leq t$.

In the adiabatic approximation this time-dependence is ignored and the exchange and
correlation potential is considered to be local in time:

$$ v_{xc}[n](r, t) = \tilde{v}_{xc}[n](r)|_{n=n(t)}. \quad (2.16) $$

This approximation should be a good one only for systems where the time-dependent poten-
tial changes very slowly. The main advantage of the adiabatic approximation is that it
allow us to use in the time-dependent case all the exchange and correlation approxima-
tions developed for the static case. The adiabatic local density approximation (ALDA) is
obtained simply by inserting the LDA exchange and correlation potential in Eq. (2.16).
Despite performing such a dramatic approximation on top of the known limitations of the
LDA, very good excitation energies are obtained with the ALDA for finite systems. This
is not the case for solids nor anisotropic systems, where the ALDA has known problems
in describing their excitation energies [10].
2.2 Electronic response to external fields

2.2.1 The polarizability tensor

Consider a finite system of electrons and nuclei subject to an external electromagnetic field. At the frequencies we are interested in, usually optical frequencies, the dimensions of the atomic and molecular systems are much smaller than the wavelength of the fields and we can consider the fields to be uniform in space. This means that, if the perturbing field is an electric field of frequency $\omega$, we can write it as:

$$E(t) = E^\omega \cos(\omega t),$$  \hspace{1cm} (2.17)

where $E^\omega$ is a vector that defines the amplitude and the polarization direction of the field. In this electric dipole approximation, the response of the system is characterized by the changes in its dipole moment $p(t)$, which, for finite systems, can be Taylor expanded in the following way:

$$p_i(t) = p_i(0) + \sum_j \alpha_{ij}(\omega)E_j^\omega \cos(\omega t) + \frac{1}{4} \sum_{jk} \beta_{ijk}(0)E_j^\omega E_k^\omega +$$

$$+ \frac{1}{4} \sum_{jk} \beta_{ijk}(2\omega)E_j^\omega E_k^\omega \cos(2\omega t) + \frac{1}{8} \sum_{jkl} \gamma_{ijkl}(\omega)E_j^\omega E_k^\omega E_l^\omega \cos(\omega t) +$$

$$+ \frac{1}{24} \sum_{jkl} \gamma_{ijkl}(3\omega)E_j^\omega E_k^\omega E_l^\omega \cos(3\omega t) + \ldots ,$$  \hspace{1cm} (2.18)

where the subscripts $i, j, k,$ and $l$ denote space-fixed axes. The quantity $\alpha$ is the so-called dynamical polarizability and is a rank two tensor. The higher-order terms $\beta$ and $\gamma$ are known as hyperpolarizabilities and are important when high-intensity fields are applied or when we look at non-linear optical properties.

If the perturbing field is small enough, the non-linear terms in Eq. (2.18) can be neglected. This means that the induced dipole moment $\delta p(t) = p(t) - p(0)$ in the frequency domain is given by:

$$\delta p(\omega) = \alpha(\omega)E(\omega).$$  \hspace{1cm} (2.19)

From here we see that the dynamical polarizability is just the ratio of the induced dipole to the electric field.

The polarizability can be obtained from linear response theory by noting that the dipole moment of a finite system is given in terms of the density by:

$$p(t) = \int dr \ r \ n(r, t),$$  \hspace{1cm} (2.20)
so that we have:

$$\alpha_{ij}(\omega) = \left. \frac{1}{E_j(\omega)} \right| \int \! d\mathbf{r} \, x_i \delta n(\mathbf{r}, \omega) = \left. \frac{1}{E_j(\omega)} \right| \int \! d\mathbf{r} \, x_i \int \! d\mathbf{r}' \chi(\mathbf{r}, \mathbf{r}', \omega) \delta v(\mathbf{r}', \omega),$$

(2.21)

where $\delta v$ is the perturbing potential, and $\chi(\mathbf{r}, \mathbf{r}', \omega)$ is the density response function. For a dipolar electric field along the $x_j$ direction, we have $\delta v(\mathbf{r}, \omega) = -x_j E_j(\omega)$, and we get:

$$\alpha_{ij}(\omega) = \left. - \int \! d\mathbf{r} \int \! d\mathbf{r}' x_i \chi(\mathbf{r}, \mathbf{r}', \omega) x_j' \right| .$$

(2.22)

In Eq. (2.19), the polarizability relates the dipole response of a system to a dipolar field. Because of that, we refer to this polarizability as the dipole-dipole polarizability. However, more general polarizabilities can be defined for different shapes of the perturbing field (e.g. quadrupole fields) and for the response of different physical quantities.

### 2.2.2 The absorption cross-section

One important measurable quantity that can be related to the microscopic polarizability is the absorption cross-section. Consider a monochromatic radiation of frequency $\omega$ passing through a slab of thickness $dz$ of a medium with $N_d$ molecules per unit volume. The absorption cross-section $\sigma$ relates the number of molecules per unit area $N_d dz$ with the attenuation of the beam:

$$\frac{dI}{dz} = -N_d \sigma(\omega) I,$$

(2.23)

where $I$ is the intensity of the beam. By integrating this equation we get Beer’s law, which gives us the variation of the intensity inside the slab:

$$I(\omega, z) = I(\omega, 0) e^{-N_d \sigma(\omega) z}.$$

(2.24)

Another often used quantity is the absorption coefficient $\alpha_a$, which is defined as the fraction of the power absorbed in a unit length of the medium:

$$I(\omega, z) = I(\omega, 0) e^{-\alpha_a(\omega) z}.$$

(2.25)

What we would like to do now is to relate $\sigma(\omega)$ with the microscopic dynamical polarizability $\alpha(\omega)$. We will start by considering a plane electromagnetic field propagating in the $z$ direction inside a nonmagnetic material. The corresponding electric field is given by Eq. (A.15):

$$E(z, t) = E(0, 0) e^{i \left( \frac{\omega}{c} z - \omega t \right)} e^{-\kappa \frac{z}{c}},$$

(2.26)
where the complex refractive index \( \tilde{n} = n + ik \) was introduced. If the imaginary part of the complex refractive index is non-zero, the wave will decay exponentially, so it is possible to relate \( k \), which is known as the extinction coefficient, to the absorption. Since the intensity of the wave is proportional to the square of the field, by comparing the previous equation with Beer’s law, we have:

\[
N_d \sigma(\omega) = \frac{2k\omega}{c}.
\]

(2.27)

and we can see that the absorption cross-section is proportional to the extinction coefficient. On the other hand, using Eq. (A.8) we have:

\[
\tilde{n} = \sqrt{1 + 4\pi\chi_e} \simeq 1 + 2\pi\chi_e,
\]

(2.28)

so that the absorption cross-section is proportional to the imaginary part of the electric susceptibility:

\[
N_d \sigma(\omega) = \frac{4\pi\omega}{c} \Im\{\chi_e\}.
\]

(2.29)

The macroscopic polarization is related to the average microscopic dipole moment per molecule by:

\[
P(\omega) = N_d \langle p(\omega) \rangle = N_d E \langle \alpha(\omega) \rangle,
\]

(2.30)

where the brackets denote orientational averaging, and we used the fact that the electric field is a macroscopic quantity in the last step. Inserting (A.6) into the right hand side of the previous equation, we have:

\[
\chi_e = N_d \langle \alpha(\omega) \rangle,
\]

(2.31)

and the absorption cross-section is finally given by:

\[
\sigma(\omega) = \frac{4\pi\omega}{c} \Im \{ \langle \alpha(\omega) \rangle \}.
\]

(2.32)

### 2.2.3 Spin-dependent perturbations

*Stricto sensu*, the polarizabilities refer to the reaction to spin-independent (i.e., electrical) perturbations measured by spin-independent observables; they are referred to as density-density response functions. However, we can also think of more general response functions and apply spin-dependent perturbations and/or look at spin-dependent observables, obtaining in this way spin-density, density-spin and spin-spin response functions – these generalized objects are sometimes referred to as susceptibilities.
Consider a general perturbation $\delta v_\sigma(r, \omega)$ ($\sigma = \uparrow, \downarrow$), so that the spin-up and spin-down electrons may feel a different potential. In the frequency domain, the response of the spin-density will be:

$$\delta n_\sigma(r, \omega) = \sum_{\sigma'} \int dr' \chi_{\sigma\sigma'}(r, r', \omega) \delta v_{\sigma'}(r', \omega). \quad (2.33)$$

The variation of the total density, $n = n_\uparrow + n_\downarrow$, and of the magnetization density, $m = n_\uparrow - n_\downarrow$, are given by:

$$\delta n(r, \omega) = \delta n_\uparrow(r, \omega) + \delta n_\downarrow(r, \omega), \quad (2.34a)$$

$$\delta m(r, \omega) = \delta n_\uparrow(r, \omega) - \delta n_\downarrow(r, \omega). \quad (2.34b)$$

Besides looking at the variation of the dipole moment, we can also look at the variation of the spin-dipole moment in order to obtain information about the spin modes of the system. The spin-dipole moment is given by:

$$p_s(\omega) = \int dr \, r \, m(r, \omega). \quad (2.35)$$

Let us now consider two kinds of dipole perturbations:

$$\delta v_\sigma^{[n]}(r, \omega) = -x_j E_j(\omega), \quad (2.36)$$

and

$$\delta v_\sigma^{[m]}(r, \omega) = -x_j E_j(\omega) \sigma_z = \begin{cases} -x_j E_j(\omega), & \sigma = \uparrow \\ x_j E_j(\omega), & \sigma = \downarrow \end{cases}. \quad (2.37)$$

The first perturbation is the same spin-independent perturbation that was introduced in Sec. 2.2.1, while the second one is a spin-dependent perturbation. The variations $\delta n$ and $\delta m$ in both cases are:

$$\delta n^{[n]}(r, \omega) = -E_j(\omega) \int dr' \chi^{[nn]}(r, r', \omega)x_j', \quad (2.38a)$$

$$\delta m^{[n]}(r, \omega) = -E_j(\omega) \int dr' \chi^{[nm]}(r, r', \omega)x_j', \quad (2.38b)$$

$$\delta n^{[m]}(r, \omega) = -E_j(\omega) \int dr' \chi^{[mn]}(r, r', \omega)x_j', \quad (2.38c)$$

$$\delta m^{[m]}(r, \omega) = -E_j(\omega) \int dr' \chi^{[mm]}(r, r', \omega)x_j', \quad (2.38d)$$
where the superscripts “[n]” and “[m]” mean that the variation is measured after perturbations of the forms given in Eqs. (2.36) and (2.37) respectively, and we have defined the new objects:

\[
\chi^{[nn]} = \chi_{\uparrow\uparrow} + \chi_{\uparrow\downarrow} + \chi_{\downarrow\uparrow} + \chi_{\downarrow\downarrow},
\]

(2.39a)

\[
\chi^{[mn]} = \chi_{\uparrow\uparrow} + \chi_{\uparrow\downarrow} - \chi_{\downarrow\uparrow} - \chi_{\downarrow\downarrow},
\]

(2.39b)

\[
\chi^{[nm]} = \chi_{\uparrow\downarrow} - \chi_{\uparrow\uparrow} + \chi_{\downarrow\uparrow} - \chi_{\downarrow\downarrow},
\]

(2.39c)

\[
\chi^{[mm]} = \chi_{\uparrow\downarrow} - \chi_{\uparrow\uparrow} - \chi_{\downarrow\uparrow} + \chi_{\downarrow\downarrow}.
\]

(2.39d)

The quotients between the variation of the dipole and the spin-dipole moments and the applied field for both perturbations are then given by:

\[
\alpha_{ij}^{[nn]}(\omega) = - \int dr \int dr' x_i \chi_{i\downarrow j}(\omega) x'_{i\downarrow j},
\]

(2.40a)

\[
\alpha_{ij}^{[mn]}(\omega) = - \int dr \int dr' x_i \chi_{i\downarrow j}(\omega) x'_{i\downarrow j},
\]

(2.40b)

\[
\alpha_{ij}^{[nm]}(\omega) = - \int dr \int dr' x_i \chi_{i\downarrow j}(\omega) x'_{i\downarrow j},
\]

(2.40c)

\[
\alpha_{ij}^{[mm]}(\omega) = - \int dr \int dr' x_i \chi_{i\downarrow j}(\omega) x'_{i\downarrow j}.
\]

(2.40d)

The usual definition of the polarizability refers to the first of these expressions, \( \alpha_{ij} = \alpha_{ij}^{[nn]} \). We will use the same notation \((\alpha)\) for the other response functions, although the name polarizability should be restricted to the first case. Another way of defining these functions is:

\[
\alpha_{ij}^{\sigma\sigma'}(\omega) = - \int dr \int dr' x_i \chi_{i\sigma j}(\omega) x'_{i\sigma' j}.
\]

(2.41)

Obviously, the two definitions are related, and one may retrieve the \( \alpha_{ij}^{[xy]} \) components from the \( \alpha_{ij}^{\sigma\sigma'} \) and vice versa:

\[
\alpha_{ij}^{[nn]} = \alpha_{ij}^{\uparrow\uparrow} + \alpha_{ij}^{\uparrow\downarrow} + \alpha_{ij}^{\downarrow\uparrow} + \alpha_{ij}^{\downarrow\downarrow},
\]

(2.42a)

\[
\alpha_{ij}^{[mn]} = \alpha_{ij}^{\uparrow\uparrow} + \alpha_{ij}^{\uparrow\downarrow} - \alpha_{ij}^{\downarrow\uparrow} - \alpha_{ij}^{\downarrow\downarrow},
\]

(2.42b)

\[
\alpha_{ij}^{[nm]} = \alpha_{ij}^{\uparrow\downarrow} - \alpha_{ij}^{\uparrow\uparrow} + \alpha_{ij}^{\downarrow\uparrow} - \alpha_{ij}^{\downarrow\downarrow},
\]

(2.42c)

\[
\alpha_{ij}^{[mm]} = \alpha_{ij}^{\uparrow\downarrow} - \alpha_{ij}^{\uparrow\uparrow} - \alpha_{ij}^{\downarrow\uparrow} + \alpha_{ij}^{\downarrow\downarrow}.
\]

(2.42d)

Two useful quantities that can be defined using the previous ones are the dipole strength function:

\[
S^{[nn]}(\omega) = \frac{2\omega}{\pi} \text{Im} \left\{ \text{Tr} \left[ \alpha^{[nn]}(\omega) \right] \right\},
\]

(2.43)
and the spin-dipole strength function:

$$S^{[mm]}(\omega) = \frac{2\omega}{\pi} \text{Im} \left\{ \text{Tr} \left[ \alpha^{[mm]}(\omega) \right] \right\}. \quad (2.44)$$

These strength functions are often experimentally accessible. The dipole strength function is trivially related to the optical absorption cross-section, while the spin-dipole strength function carries information about the spin dipole modes of excitation [57, 58].

### 2.2.4 Excitations in TDDFT

#### Linear-response theory: Casida’s equation

The response function $\chi_{KS}$ obtained using the Kohn-Sham system:

$$\delta n(r, \omega) = \int dr' \chi_{KS}(r, r', \omega) \delta v_{KS}(r, \omega), \quad (2.45)$$

is the response of a system of non-interacting particles and its expression in terms of the unperturbed Kohn-Sham orbitals is well known. Using the relationship between the change in the Kohn-Sham potential and the external perturbation, it is possible to relate the response function of the interacting system with $\chi_{KS}$:

$$\chi(r, r', \omega) = \chi_{KS}(r, r', \omega) +$$

$$+ \int dr'' \int dr''' \chi(r, r'', \omega) \left[ \frac{1}{|r'' - r'''|} + f_{xc}(r'', r''', \omega) \right] \chi_{KS}(r''', r', \omega), \quad (2.46)$$

where the exchange and correlation kernel $f_{xc}$ is given by:

$$f_{xc}(r, r', t, t') = \frac{\delta v_{xc}[n](r, t)}{\delta n(r', t')}. \quad (2.47)$$

It is possible to recast Eq. (2.46) into the following pseudo-eigenvalue equation [59]:

$$\hat{R} F_q = \Omega^2_q F_q, \quad (2.48)$$

where the eigenvalues $\Omega^2_q$ are the square of the excitation energies, and the eigenvectors are related to the oscillator strengths. The matrix $\hat{R}$ is given by:

$$R_{ij\sigma, i'j'\sigma'} = \delta_{ii'} \delta_{jj'} \delta_{\sigma\sigma'} (\epsilon_{i\sigma} - \epsilon_{j\sigma})^2 +$$

$$+ 2 \sqrt{f_{ij\sigma} (\epsilon_{i\sigma} - \epsilon_{j\sigma}) K_{ij\sigma, i'j'\sigma'}(\Omega) \sqrt{f_{i'j'\sigma'} (\epsilon_{i'\sigma'} - \epsilon_{j'\sigma'})}, \quad (2.49)$$
where $\epsilon_{i\sigma}$ are the eigenvalues of the unperturbed Kohn-Sham orbitals, $f_{ij\sigma}$ are the differences between their occupation numbers, and $K$ is the matrix of the interaction terms:

$$K_{ij\sigma,i'j'\sigma'}(\omega) = \int dr \int dr' \varphi_{i\sigma}^*(r) \varphi_{j\sigma}(r)$$

$$\left[ \frac{1}{|r - r'|} + f_{xc,\sigma\sigma'}(r, r', \omega) \right] \varphi_{i'\sigma'}^*(r') \varphi_{j'\sigma'}(r').$$ (2.50)

This means we now have a matrix problem involving pairs of unoccupied as well as occupied Kohn-Sham states. Building the matrix $K$ can be computationally demanding.

**Linear-response theory: Sternheimer approach**

The Sternheimer equation [60] is a perturbative technique that can be used in the framework of TDDFT [61–63]. In this method the time-dependent wavefunctions and the time-dependent density are expanded in terms of the electric field and the dynamical polarizability is given by:

$$\alpha_{ij}(\omega) = \int dr \delta n_j(r, \omega) x_i.$$ (2.51)

The first order variations of the density are defined in terms of the unperturbed Kohn-Sham wavefunctions $\psi_m(r)$ and the first order variations of the time-dependent Kohn-Sham wavefunctions $\psi'_{m,i}(r, \pm \omega)$ as:

$$\delta n_i(r, \omega) = \sum_{m,occ} \psi^*_m(r) \psi'_{m,i}(r, \omega) + \psi^*_{m,i}(r, -\omega) \psi_m(r).$$ (2.52)

The first order variations of the Kohn-Sham wavefunctions are the solutions of the following equation:

$$\left[ \hat{H}_{KS} - \epsilon_m \pm \omega + i\eta \right] \psi'_{m,i}(r, \pm \omega) = -\hat{P}_c \hat{H}'(\pm \omega) \psi_m(r),$$ (2.53)

where $\hat{P}_c$ is the projector onto the unoccupied subspace of the unperturbed Kohn-Sham wavefunctions, $\eta$ is a positive infinitesimal, $\hat{H}_{KS}$ is the Kohn-Sham unperturbed Hamiltonian, and $\hat{H}'$ is the first order variation of the Kohn-Sham Hamiltonian given by:

$$\hat{H}'(\omega) = x_i + \int dr' \int \frac{\delta n_i(r', \omega)}{|r - r'|} + \int dr' f_{xc}(r, r', \omega) \delta n_i(r', \omega).$$ (2.54)

Since the right hand side of Eq. (2.53) depends on $\delta n$, the equation has to be solved self-consistently. Also note that Eq. (2.53) has to be solved for each frequency.

This method can easily be extended to get static or dynamic hyperpolarizabilities from the first order variation of the wavefunctions and to handle other kinds of perturbations [63]. It is also well suited for cases where only a few frequencies are required.
Full solution of the time-dependent Kohn-Sham equations

In this method the excitations of the system are investigated by solving the time-dependent Kohn-Sham equations. Since the time-dependent Kohn-Sham equations are an initial value problem, the usual way to solve them is the following [64]:

1. Obtain the wavefunctions $\psi_i(r, t_0)$ of the initial state. This is the ground-state, so that $\psi_i(r, t_0)$ are the solutions of the ground-state Kohn-Sham equations.

2. Rewrite the time-dependent Kohn-Sham equation in the integral form:

$$\psi_i(r, t) = \hat{U}(t, t_0)\psi_i(r, t_0),$$

where $\hat{U}$ is the time evolution operator:

$$\hat{U}(t', t) = \hat{T} e^{-i \int_{t'}^{t} d\tau \hat{H}_{KS}(\tau)},$$

and the time ordering propagator $\hat{T}$ is necessary because of the explicit time-dependence of the Kohn-Sham Hamiltonian.

3. Obtain the wavefunctions at time $t$ by propagating the initial wavefunctions using Eq. (2.55) and a suitable numerical algorithm to apply $\hat{U}$.

In order to compute the response of the system to an external perturbation, we just include the perturbing potential in the Hamiltonian. Suppose we want to compute the dynamical polarizability of the system. This is accomplished by applying a dipolar spin-independent perturbation $\delta v(r, t) = -E_j x_j \delta(t)$ that acts at $t = 0$ and excites all the frequencies of the system equally [64, 65]. The wavefunctions at $t = 0^+$ can be calculated explicitly using Eq. (2.55):

$$\psi_i(r, 0^+) = \hat{T} e^{-i \int_{0}^{0^+} d\tau [\hat{H}_{KS} - E_j x_j \delta(t)]} \psi_i(r, 0)$$
$$= e^{i E_j x_j} \psi_i(r, 0)$$

(2.57)

Afterward the wavefunctions are propagated up to some finite time and, by keeping track of the density as a function of time, we can compute the variation of the density $\delta n(r, t) = n(r, t) - n(r, 0)$ induced by the perturbation. With this information it is then possible to calculate the dynamical polarizability using Eq. (2.21).

This method scales with the square of the number of atoms in the system [66] and does not require the inclusion of unoccupied orbitals, thus making it a method of choice for large systems. Also, it is straightforward to extend it to other kinds of perturbations,
like the spin-dependent perturbations presented in Sec. 2.2.3. Finally, it allows to handle linear and non-linear responses.

Except where otherwise noted, all response calculations presented in this thesis were performed using this method.
Chapter 3

Pseudopotentials†

3.1 Introduction

At the base of the wide success of DFT is the affordable computational effort it requires and one of the key ingredients contributing to this is the pseudopotential approximation.

In the pseudopotential approximation the electrons in the atom are separated into valence and inner core electrons. Since the inner core electrons are strongly bound they do not play a significant role in the chemical binding of atoms. This means that they can be safely ignored in a large number of cases, and that the potential felt by the valence electrons can be replaced by an effective interaction that accounts for the nuclear attraction and all the interactions between the valence and the inert inner core electrons. This effective interaction is the pseudopotential.

Although the use of a pseudopotential to approximate the potential felt by the valence electrons was first proposed by Hellmann [67] in 1935, only with the work of Phillips and Kleinman did they begin to be generally used [68, 69]. Modern pseudopotentials are obtained from all-electron atomic calculations and are able to describe accurately the chemically relevant part of the valence wavefunctions and charge density [70].

†This chapter is an adaptation of part of the article:

3.2 Density Functional Theory for atoms

3.2.1 Non-relativistic equations

In the case of an isolated atom, the external potential \( V_{\text{ext}}(r) \) in Eq. (1.40) is just the nuclear \(-Z/r\) potential. Taking into account the spherical symmetry of the problem, one normally performs a spherical averaging of the density. This leads to a spherically symmetric Kohn-Sham potential and thus the Kohn-Sham orbitals can be separated into angular and radial parts:

\[
\psi_i(r) = R_{nl}(r) Y_{lm}(\theta, \phi).
\]  

(3.1)

\( Y_{lm}(\theta, \phi) \) are spherical harmonics and \( R_{nl}(r) \) are the solutions of a “simple” one-dimensional second-order differential equation:

\[
\left[ -\frac{1}{2} \frac{d^2}{dr^2} - \frac{1}{r} \frac{d}{dr} + \frac{l(l+1)}{2r^2} + v_{\text{KS}}(r) \right] R_{nl}(r) = \varepsilon_{nl} R_{nl}(r). 
\]  

(3.2)

Because of the spherical symmetry of the system, states with the same \( n \) and \( l \) quantum numbers are degenerate. Since we are assuming the density to be spherically symmetric, the degenerate states should be equally occupied. As a consequence, the radial electron density can be written as:

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

(3.3)

with \( \Theta_{nl} \) denoting the occupation of each \( nl \) sub-shell.

When dealing with atoms with net spin it is necessary to use the collinear spin density functional theory (see Section 1.4.3). This means there are two sets of one-particle equations to be solved.

3.2.2 Relativistic equations

When relativistic effects become important one needs to incorporate them into the Kohn-Sham equations. One possible way is to use the scalar-relativistic scheme of Koelling and Harmon [71] which omits the spin-orbit interaction but includes all other relativistic kinematic effects. In that case the \( R_{nl}(r) \) are the solutions of the following one-dimensional
second-order differential equation:

\[
\frac{1}{2M(r)} \left[ -\frac{d^2}{dr^2} + \frac{1}{M(r)} \frac{dM(r)}{dr} \frac{d}{dr} - \frac{2}{r} \frac{d}{dr} + \frac{l(l+1)}{r^2} \right] R_{nl}(r) + \varepsilon_{nl} R_{nl}(r) + v_{KS}(r) R_{nl}(r) = 0, \quad (3.4)
\]

with the relativistic electron mass \(M(r)\) given by

\[
M(r) = 1 + \left( \varepsilon_{nl} - v_{KS}(r) \right)/2c^2.
\]

Another way to incorporate relativistic effects is to use the relativistic extension of DFT (see Section 1.4.4). In a similar way as for the non-relativistic case, if \(V_{\text{ext}}\) is just the nuclear \(-\mathbf{Z}/r\) potential then the 4-component spinors \(\psi_i(r)\) can be separated into angular and radial parts:

\[
\psi_i(r) = \begin{pmatrix}
ig_{nlj}(r) \Omega_{jlm}(\theta, \phi) \\
-f_{nlj}(r) \Omega_{j'l'm}(\theta, \phi)
\end{pmatrix}.
\quad (3.5)
\]

\(\Omega_{jlm}(\theta, \phi)\) and \(\Omega_{j'l'm}(\theta, \phi)\) are the spherical spinors and \(g_{nlj}(r)\) and \(f_{nlj}(r)\) are the solutions of a set of two coupled first-order differential equations (with \(\varepsilon_i \rightarrow \varepsilon_{nlj} + c^2\)):

\[
\begin{align*}
c \left[ \frac{dg_{nlj}(r)}{dr} + \frac{1+k}{r} g_{nlj}(r) \right] - \left[ \varepsilon_{nlj} + 2c^2 - v_{KS}(r) \right] f_{nlj}(r) &= 0, \quad (3.6a) \\
c \left[ \frac{df_{nlj}(r)}{dr} + \frac{1-k}{r} f_{nlj}(r) \right] + \left[ \varepsilon_{nlj} - v_{KS}(r) \right] g_{nlj}(r) &= 0. \quad (3.6b)
\end{align*}
\]

The quantum numbers \(k, l\) and \(l'\) are related to each other in the following way:

\[
l' = l - k/|k| \quad (3.7a) \\
k = \begin{cases} 
-(l + 1) & \text{for } j = l + \frac{1}{2} \\
l & \text{for } j = l - \frac{1}{2}.
\end{cases} \quad (3.7b)
\]

Taking into account the degeneracy of states with the same \(n, j, l\) quantum numbers the radial electron density can be written as:

\[
n(r) = \sum_{n} \sum_{l=0}^{n-\frac{1}{2}} \sum_{l'=-l}^{l+\frac{1}{2}} \Theta_{nlj} \frac{|f_{nlj}(r)|^2 + |g_{nlj}(r)|^2}{4\pi}.
\quad (3.8)
\]

### 3.3 Norm-conserving pseudopotentials

One of the most important and popular class of pseudopotentials is the so called norm-conserving pseudopotentials. The procedure to obtain them is the following:
(1) The radial Kohn-Sham equations for the free atom are solved for a given reference configuration. We thus obtain the all-electron wavefunctions $R_{nl}^{AE}(r)$ and potential $v_{KS}^{AE}$.

(2) The pseudo wavefunctions $R_{l}^{PP}(r)$ are determined using a suitable scheme, imposing several generic conditions.

(3) The screened pseudopotential $v_{l}^{PP,sc} (r)$ results from the inversion of a radial Schrödinger-like Kohn-Sham equation for the pseudo wavefunction and the valence electronic density $v_{l}^{PP,sc} (r) = \epsilon_{l}^{PP} - \frac{l(l+1)}{2r^2} + \frac{1}{2rR_{l}^{PP}(r)} \frac{d^2}{dr^2} rR_{l}^{PP}(r)$.

(4) The Hartree and the exchange-correlation screening contributions from the valence electrons are subtracted to the screened pseudopotentials in order to obtain the final pseudopotentials $v_{l}^{PP} (r) = v_{l}^{PP,sc} (r) - v_{H} [n^{PP} (r)] - v_{xc} [n^{PP} (r)]$.

The conditions imposed on the pseudo wavefunctions in step (2) are the following:

(i) The pseudo wavefunctions are normalized and coincide with the all-electron valence wavefunctions beyond a certain radius $r_l$ known as the core cutoff radius $R_{l}^{PP}(r) = R_{nl}^{AE}(r)$, if $r > r_l$.

These two conditions lead to the following norm-conservation constraint:

\[
\int_{0}^{r'} dr \left| R_{l}^{PP}(r) \right|^2 r^2 = \int_{0}^{r'} dr \left| R_{nl}^{AE}(r) \right|^2 r^2, \text{ if } r' \geq r_l.
\]

(ii) The pseudo energy-eigenvalues match the all-electron eigenvalues $\epsilon_{l}^{PP} \equiv \epsilon_{nl}^{AE}$.

(iii) The pseudo wavefunctions should not have nodal surfaces.

As a consequence of the previous conditions the logarithmic derivatives of the pseudo wavefunctions agree with the all-electron wavefunctions beyond the core cutoff radius:

\[
\frac{d}{dr} \ln R_{l}^{PP}(r) = \frac{d}{dr} \ln R_{l}^{AE}(r).
\]
As it can be seen above, the norm-conserving pseudopotentials are spherically symmetric and $l$-dependent. Because of that, the pseudopotential operator is non-local in the angular variables and local in the radial variable and it can be written in the following semi-local form:

$$\hat{v}_{\text{SL}} = \sum_{lm} |Y_{lm}\rangle v_{l}^{\text{PP}}(r) \langle Y_{lm}|. \quad (3.15)$$

Up to here we assumed that the wavefunctions and wave equations are non-relativistic. Nevertheless it is possible to include relativistic effects in the pseudopotentials. To do that one starts from a relativistic all-electron calculation and generates the pseudopotentials for both $j = l+1/2$ and $j = l-1/2$. One may use directly these $j$-dependent pseudopotentials, but it may be convenient to remove this dependency by separating the scalar-relativistic effects from the spin-orbit coupling term. This is done by defining:

$$v_{l}^{\text{Avg}} = \frac{l}{2l+1} \left[(l+1)v_{l+1/2}^{\text{PP}} + lv_{l-1/2}^{\text{PP}}\right], \quad (3.16a)$$

$$\delta v_{l}^{\text{SO}} = \frac{1}{2l+1} \left[v_{l+1/2}^{\text{PP}} - v_{l-1/2}^{\text{PP}}\right]. \quad (3.16b)$$

$v_{l}^{\text{Avg}}$ can be used directly in equation (3.15), thus neglecting the spin-orbit coupling term. When including spin-orbit effects equation (3.15) becomes:

$$\hat{v}_{\text{SL}} = \sum_{lm} |Y_{lm}\rangle \left[v_{l}^{\text{Avg}}(r) + \delta v_{l}^{\text{SO}} \mathbf{L} \cdot \mathbf{S}\right] \langle Y_{lm}|. \quad (3.17)$$

### 3.3.1 Generation schemes

**Hamann pseudopotential**

One of the most used pseudo wavefunctions parametrizations is the one proposed in 1979 by Hamann, Schlüter, and Chiang [72] and later improved by Bachelet, Hamann and Schlüter [73] and Hamann [74].

The method they proposed consists in using an intermediate pseudopotential, $\tilde{v}_{l}^{\text{PP}}(r)$, given by

$$\tilde{v}_{l}^{\text{PP}}(r) = v_{KS}^{\text{AE}} \left[n_{\text{AE}}\right](r) \left[1 - f \left(\frac{r}{r_{l}}\right)\right] + c_{l} f \left(\frac{r}{r_{l}}\right), \quad (3.18)$$

where $f(x) = e^{-x^{3}}$, and $\lambda = 4.0$ [72] or $\lambda = 3.5$ [73, 74].
The Kohn-Sham equations are solved using this intermediate pseudopotential, and the constants \( c_l \) are adjusted in order to obey (3.13). This results in a set of intermediate wavefunctions \( \tilde{R}_l(r) \). Notice that the form of the wavefunctions implies that norm-conservation (Eq. (3.12)) is verified for some \( \tilde{r}_l > r_l \). As the two effective potentials are identical for \( r > \tilde{r}_l \), and given the fast decay of \( f(x) \), the intermediate pseudo wavefunctions coincide, up to a constant, with the true wavefunctions in that region.

In the method proposed by Hamann [74], the parameters \( c_l \) are adjusted so that
\[
\frac{d}{dr} \ln \left[ r R_{nl}^{AE}(r) \right] \bigg|_{r=\tilde{r}_l} = \frac{d}{dr} \ln \left[ r \tilde{R}_l(r) \right] \bigg|_{r=\tilde{r}_l}.
\]
This way, the method is not restricted to bound states.

To impose norm-conservation (Eq. (3.12)), the final pseudo wavefunctions, \( R_{l}^{PP}(r) \), are defined as a correction to the intermediate wavefunctions
\[
R_{l}^{PP}(r) = \gamma_l \left[ \tilde{R}_l(r) + \delta_l g_l(r) \right],
\]
where \( \gamma_l \) is the ratio \( R_{nl}^{AE}(r)/\tilde{R}_l(r) \) in the region where \( r > \tilde{r}_l \) and \( g_l(r) = r^{l+1} f(r/r_l) \). The constants \( \delta_l \) are adjusted to conserve the norm.

**Troullier-Martins pseudopotential**

A different method for the construction of the pseudo wavefunctions was proposed by Troullier and Martins [75, 76], based on earlier work by Kerker [77]. This method is much simpler than Hamann’s and emphasizes the desired smoothness of the pseudopotential (although it introduces additional constraints to obtain it). It achieves softer pseudopotentials for the 2p valence states of the first row and for the d valence states of the transition metals. For other elements both methods produce equivalent potentials.

The pseudo wavefunctions are defined as
\[
R_{l}^{PP}(r) = \begin{cases} 
R_{nl}^{AE}(r), & \text{if } r > r_l \\
 r^l p(r), & \text{if } r < r_l ,
\end{cases}
\]
with
\[
p(r) = c_0 + c_2 r^2 + c_4 r^4 + c_6 r^6 + c_8 r^8 + c_{10} r^{10} + c_{12} r^{12}.
\]
The screened pseudopotential is obtained by inserting the radial pseudo wavefunction ((3.21)) into equation ((3.9)):
\[
v_{l}^{PP,scr}(r) = \begin{cases} 
v_{nl}^{AE}(r), & \text{if } r > r_l \\
 \varepsilon_{nl} + \frac{l+1}{2} p'(r) + \frac{p''(r) + [p'(r)]^2}{2}, & \text{if } r < r_l .
\end{cases}
\]
The coefficients of $p(r)$ are adjusted imposing norm-conservation, the continuity of the pseudo wavefunctions and of their first four derivatives at $r = r_l$, and that the screened pseudopotential has null curvature at the origin. This last condition implies that

$$c_2^2 + c_4(2l + 5) = 0,$$  

(3.24)

and is at the origin of the enhanced smoothness of the Troullier and Martins pseudopotentials.

**Troullier-Martins pseudopotential with explicit incorporation of semi-core states**

The Troullier-Martins scheme presented in the previous section usually allows the generation of very accurate pseudopotentials for most elements. Nevertheless there are cases where the separation between valence and inner core electrons is not well verified, i.e., some core states are not strongly bound or have a large extension. Those core states are known as semi-core states. Because of them, the TM pseudopotentials may fail to predict accurately some physical properties like the bond lengths of several 3d transition metal clusters. Reis *et al.* [78] suggested an extension of the TM scheme to explicitly include the semi-core states into the valence space. This scheme is known as multi-reference pseudopotentials (MRPP).

Usually it is not necessary to include semi-core states for all values of the angular momentum $l$. The pseudopotentials for those values of $l$ should be generated by applying the usual TM scheme.

In the MRPP scheme both the nodeless pseudo wavefunctions for the semi-core states and the single-node pseudo wavefunctions for the valence states are required to match the all-electron wavefunctions beyond a chosen cutoff radius. This cutoff radius does not need to be the same for the semi-core and the valence states.

As in the normal TM scheme, the pseudo wavefunctions for the semi-core states are defined as in equation (3.21) but $p(r)$ is a polynomial of order 9 in $r^2$:

$$p(r) = c_0 + c_2r^2 + c_4r^4 + c_6r^6 + c_8r^8 + c_{10}r^{10} + c_{12}r^{12} + c_{14}r^{14} + c_{16}r^{16} + c_{18}r^{18}.$$  

(3.25)

In order to adjust seven of the ten coefficients of $p(r)$ the same conditions as the ones used for the normal TM scheme are applied to the semi-core pseudo wavefunctions. The conditions needed to adjust the three remaining coefficients are applied to the valence pseudo wavefunctions. Those conditions are the continuity of the pseudo wavefunctions, norm-conservation, and the requirement that the eigenvalues of the valence pseudo states are the same as the all-electron ones.
Because of these extra conditions this set of non-linear equations is difficult to solve numerically and a careful choice of the cutoff radii is essential to obtain a solution. Typically one should choose the cutoff radii for the semi-core states to be greater than the outermost maximum of the all-electron wavefunction.

The numerical solution of the set of non-linear equations is more stable if instead of imposing the condition on the eigenvalue of the valence pseudo states one uses the continuity of the first derivative of the valence pseudo wavefunctions. The reason for this is that the value of the first derivative of the pseudo wavefunctions at the cut-off radius is more sensitive to changes in the values of the coefficients than the eigenvalues. It is also computationally less demanding to determine the derivative at a certain radius than to determine the eigenvalue. Note that both conditions are perfectly equivalent.

Relativistic extension of the Troullier-Martins pseudopotential

In the normal TM scheme the pseudopotential is obtained by inverting a radial Schrödinger-like Kohn-Sham equation (Eq. (3.9)). When the radial all-electron wavefunctions are solutions of the radial Dirac-Kohn-Sham equations (3.6) the usual procedure is to completely neglect the small component \( g(r) \) and to use the large component \( f(r) \) as if it were a non-relativistic wavefunction. Although this procedure is justifiable, it introduces inconsistencies. Indeed the pseudo wavefunctions obtained in this way are not eigenstates of the Dirac-Kohn-Sham equations for the pseudopotential. Also, completely neglecting the small component implies that its norm contribution has to be absorbed by the large component leading to an error during the unscreening procedure.

Engel et al. [79] introduced an extension of the TM scheme (RTM) to solve these inconsistencies. In their scheme the two components of the pseudo wavefunctions are defined as:

\[
\begin{align*}
{f}_{ij}^{PP}(r) &= \begin{cases} 
{f}_{nlj}^{AE}(r) & \text{, for } r > r_{lj} \\
{r}^{l}e^{p}(r) & \text{, for } r < r_{lj} ,
\end{cases} \\
{g}_{ij}^{PP}(r) &= \begin{cases} 
g_{nlj}^{AE}(r) & \text{, for } r > r_{lj} \\
\frac{c[(l+1+k)/r + p'(r)]}{2c^2 - v_{ij}^{PP,scr} + \varepsilon_{nlj}} f_{ij}^{PP}(r) & \text{, for } r < r_{lj} .
\end{cases}
\end{align*}
\]
The screened pseudopotential is in turn given by:

\[ v_{ij}^{\text{PP,scr}}(r) = \begin{cases} 
 v_{ij}^{\text{AE}}(r), & \text{for } r > r_{lj} \\
 v_{ij}^{\text{scr,nr}}(r) + \delta v_{ij}(r), & \text{for } r < r_{lj}.
\end{cases} \]  

(3.28)

\[ v_{ij}^{\text{scr,nr}}(r) \] is the pseudopotential resulting from the inversion of equation (3.9) and is the same as for the normal TM scheme (see Eq. (3.23)). The relativistic correction \( \delta v_{ij}(r) \) is as follows:

\[
\delta v_{ij} = \left( \frac{v_{ij}^{\text{scr,nr}} - \varepsilon_{nlj}}{2e^2} \right)^2 + \left( \frac{v_{ij}^{\text{scr,nr}}}{4e^2} \right) ' \left[ \frac{\left( f_{ij}^{\text{PP}} \right)'}{f_{ij}^{\text{PP}}} + \frac{k + 1}{r} \right].
\]  

(3.29)

Finally, the conditions to determine the coefficients of \( p(r) \) make use of the Dirac-Kohn-Sham equations.

### 3.3.2 Spin polarization

If the atomic reference configuration is spin-polarized, the resulting pseudopotentials will be spin-dependent. But the pseudopotentials represent the effect of the inert ionic core. Therefore, this spin-dependence can be interpreted as a net magnetization of the core. However, in most cases, spin polarization of the core is negligible. The most usual way to deal with this side-effect is to perform a spin-averaging of the pseudopotential:

\[ v_{i}^{\text{SA}} = \frac{N_e^\uparrow}{N_e} v_{i}^\uparrow + \frac{N_e^\downarrow}{N_e} v_{i}^\downarrow \]  

(3.30)

(\( N_e \) denotes the total number of valence electrons and \( N_e^\uparrow \) and \( N_e^\downarrow \) represent the number of electrons with spin up and down, respectively). This spin-averaging is in fact an approximation, as we assume that all spin-polarization comes from the valence electrons. The approximation breaks down for, e.g., transition-metal atoms like Fe, Ni, and Cr. In these cases one can recover core polarization by explicitly including semi-core states in the pseudopotential or by the generation of a perturbative correction to the spin-independent pseudopotential [80, 81]. In the latter case, the spin-dependent potential is constructed only at the moment of its application, as the local magnetization density is required.

### 3.3.3 Non-linear core corrections

In Eq. (3.10) a linear dependence of the potential on the density was assumed. Unfortunately, this assumption is only valid for the Hartree contribution and not for the
exchange-correlation part

\[ v_{xc} \left[ n^{AE} \right] (r) \neq v_{xc} \left[ n^{\text{core}} \right] (r) + v_{xc} \left[ n^{PP} \right] (r). \]  

(3.31)

For many systems this is not a problem and the linearization of the dependence is an adequate approximation. For other systems, like elements with few valence electrons or with core orbitals extending into the tail of the valence density, it may be necessary to use a nonlinear core-valence exchange-correlation scheme. In the scheme suggested by Louie et al. [82] the unscreened pseudopotential is redefined as:

\[ v^{PP}(r) = v^{PP,scr}(r) - v_{H} \left[ n^{PP} \right] (r) - v_{xc} \left[ \tilde{n}^{\text{core}} + n^{PP} \right] (r), \]  

(3.32)

where a partial core density \( \tilde{n}^{\text{core}} \) is used instead of the core density in order to avoid spoiling the smoothness of the potential. This partial core density is built by replacing the core density inside some radius \( r_{nlc} \) by an arbitrary function. There are several possible methods to build this arbitrary function [83, 84].

### 3.3.4 Kleinman and Bylander form of the pseudopotential

The semi-local form (Eq. (3.15)) of the pseudopotential operator leads to a complicated evaluation of its action on a wavefunction. However the semi-local form can be rewritten in a way that alleviates this computational burden by separating the long and short range components. The long range component is local, and corresponds to the Coulomb tail. Choosing an arbitrary angular momentum component and defining

\[ \delta v^{PP}_{l} = v^{PP}_{l} - v_{local}. \]  

(3.33)

the pseudopotential operator can be written as

\[ \hat{v}_{\text{SL}} = v_{local} + \sum_{l,m} \left| Y_{l,m} \right\rangle \delta v^{PP}_{l} \left\langle Y_{l,m} \right| . \]  

(3.34)

Kleinman and Bylander [85] suggested that the non-local part of equation (3.34) were written as a separable potential, thus transforming the semi-local potential into a truly non-local pseudopotential. If \( \psi_{l,m}^{PP}(\vec{r}) = R_{l,m}^{PP}(\vec{r})Y_{l,m}(\hat{\vec{r}}) \) denotes the pseudo wavefunctions obtained with the semi-local pseudopotential, the Kleinman and Bylander (KB) form is given by

\[ \hat{v}_{KB} = v_{local} + \sum_{l,m} \frac{\left| \psi_{l,m}^{PP} \delta v^{PP}_{l} \right\rangle \left\langle \psi_{l,m}^{PP} \delta v^{PP}_{l} \right|}{\left\langle \psi_{l,m}^{PP} \left| \delta v^{PP}_{l} \right| \psi_{l,m}^{PP} \right\rangle}. \]  

(3.35)
Using the KB form the action of the potential on a wavefunction becomes much easier to evaluate. The KB separable form has, however, some disadvantages, leading sometimes to solutions with nodal surfaces that are lower in energy than solutions with no nodes \([86, 87]\). These (ghost) states are an artifact of the KB procedure. To eliminate them one can use a different component of the pseudopotential as the local part of the KB form or choose a different set of core radii for the pseudopotential generation. As a rule of thumb, the local component of the KB form should be the most repulsive pseudopotential component.

When using fully-relativistic pseudopotentials, the semi-local form (3.17) cannot be directly transformed into a fully separable one. Nevertheless, a KB form can still be written in terms of \(v_i^{\text{Avg}}\) and \(\delta v_i^{SO}\) \([88]\). Another way of writing a fully separable form in terms of fully-relativistic pseudopotentials is simply to generalize the KB form to deal with the \(j\)-dependent pseudopotentials \(v_{j,i}^{PP}(r)\), as suggested by Theurich and Hill \([89]\). In this case the KB form is given by:

\[
\hat{v}_{\text{KB}} = v_{\text{local}} + \sum_{l,j,m} |\psi_{l,j,m}^{PP}\rangle \langle \psi_{l,j,m}^{PP}| \delta v_{l,j}^{PP}.
\]

(3.36)

Note that, in this case, the angular part of the pseudo wavefunctions \(\psi_{l,j,m}^{PP}\) are spherical spinors. Therefore the action of this potential on a wavefunction, which should also be a complex spinor, is more complicated to evaluate than for a non-relativistic potential (see Appendix B for more details).

### 3.3.5 Pseudopotential transferability

The pseudopotential is able, by construction, to reproduce the valence eigenvalues and wavefunctions (beyond the core radii) of a single isolated atom. However, when this same atom is embedded in a more complex environment, its wavefunctions and eigenvalues differ from those of the isolated atom and one needs to assure that the pseudopotential will be able to mimic the effect of the true potential in the new chemical environment. In other words, a test of the pseudopotential transferability is required.

Several transferability tests can be performed, the most obvious one being the comparison of all-electron and pseudopotential results in diverse chemical environments. This test can be preceded by a series of simpler tests on the isolated atom pseudo wavefunctions and eigenvalues that immediately identify ill-constructed pseudopotentials. Nevertheless, even if the pseudopotential passes all these simpler tests, a true assessment of its transferability still requires a comparison of pseudopotential and all-electron results in different environments.
chemical environments.

One way to force the pseudopotential to act on a given electron in the same way as the true potential is to require it to have the same scattering phase shifts as the all-electron potential. The (energy-dependent) phase shifts at some distance \( r \) from the atom can be shown to depend only on the logarithmic derivative of the wavefunction at that distance (and, obviously, on the energy). The norm-conserving pseudopotentials are constructed in a way that ensures that, for any \( r \geq r_l \) (Eq. (3.14)), the logarithmic derivatives of the pseudo and true wavefunctions coincide. But this is true only for the reference energy \( \varepsilon_l \) and the eigenvalues depend on the chemical environment. A supplementary condition must then be introduced: the energy-dependence of the logarithmic derivatives (for \( r \geq r_l \)) should be the same in the pseudopotential and all-electron atoms. This constraint can be alleviated by restricting it to energies close to the reference energy or, in other words, by requiring only that the first energy derivatives of the logarithmic derivatives coincide. This ensures that the pseudopotential will reproduce the changes in the eigenvalues due to small changes in the self-consistent potential. This condition seems daunting, but a closer look at the norm-conservation constraint (Eq. (3.12)) reveals that

\[
\frac{\partial}{\partial \varepsilon_l} \frac{d}{dr} \ln R_{l}^{PP}(r) = -\frac{2}{\varepsilon_l} \frac{|R_{l}^{PP}(r)|^2 r^2}{\int_0^r dr' |R_{l}^{PP}(r')|^2 r'^2},
\]

which indicates that, for any \( r \geq r_l \), the energy derivatives of the pseudo and the true logarithmic derivatives should coincide. In fact, it is not necessary to impose this supplementary condition, since norm-conservation ensures, as a bonus, that the condition is always satisfied. One should simply check that the condition is indeed obeyed. This check is done by computing the logarithmic derivatives of the wavefunctions as a function of the eigenvalue for both the all-electron potential and the pseudopotential at some diagnostic radius outside the core region. A suitable choice for this radius is half the typical interatomic distance. The range of eigenvalues to be considered should be the one where the valence states are expected to form molecular orbitals or Bloch bands.

Another easy test of transferability involves the comparison of excitation energies in the pseudo atom and in the all-electron atom. Due to the implicit inclusion of the reference configuration core states in the pseudopotential, this comparison should be performed keeping the all-electron core states frozen. This methodology can be extended to the analysis of the change in valence eigenvalues induced by a variation in valence orbital occupancies, giving information on the accuracy of the description of the chemical hardness.

As mentioned above, the transformation of the pseudopotentials to the Kleinman and Bylander form can introduce unphysical states. If this form is to be used, further
transferability tests are required, namely the inspection of the bound state spectrum in order to rule out the existence of such states. This analysis can be done by using the method proposed by Gonze et al. [87] whenever the KB projectors are computed.

If a pseudopotential is found to be poorly transferable, the most obvious method to render it more transferable involves at least one of the following modifications in its construction procedure: changing the core radii, including more valence states, incorporating non-local core corrections, or including different angular momentum projectors.
Part III

Applications
Chapter 4

Optical Response of Small Cationic Xenon Clusters

4.1 Introduction

Neutral rare-gas clusters are van der Waals bound and their first electronic transition is in the UV region. However, when one electron is removed from the system, the bonding becomes much stronger and the absorption shifts to the visible region. Thus, because of its ability to provide valuable information about the bonding and about the electronic structure of matter in general, optical absorption spectroscopy proved to be an important tool for the study of the electronic properties of cationic rare-gas clusters.

One such case was the work of Haberland et al [91], who measured the absorption cross-section for \( \text{Xe}_{n}^{+} \), \( 3 \leq n \leq 30 \). They found that, for all these clusters, three broad peaks were observed in the 1-4 eV range, except for \( \text{Xe}_{3}^{+} \), where only two peaks were present. From these results they concluded that there were two isomeric structures for the xenon clusters present in the experiment. Theoretical calculations suggested that all cationic xenon clusters geometries are similar [92,93]: a charged linear core with almost neutral atoms arranged in rings perpendicular to the core axis. The rings are located in the middle of the core bonds and contain up to five atoms. Because most of the charge is localized around the linear core, the shape of the absorption cross-section is mainly determined by the core of the cluster. Thus, the two isomeric structures found in experiment must correspond to structures with a different number of atoms in the charged core. These results were confirmed by further experimental evidence and by theoretical calculations of the photo-absorption of cationic xenon clusters [94–97].
Most of the previous theoretical studies of cationic xenon clusters made use of semi-empirical methods. In particular, no extensive ab initio calculation of the absorption cross-sections of cationic xenon clusters has been carried to date.

A very important point in the description of these systems is that relativistic effects cannot be neglected and the inclusion of spin-orbit coupling is essential for a proper description of the absorption cross-section. For example, if spin-orbit coupling is neglected, the $\text{Xe}_3^+$ absorption cross section only exhibits one peak.

In the following we will present TDDFT calculations for these systems including the mentioned spin-orbit coupling.

4.2 Technical details

The core electrons of xenon were taken into account using pseudopotentials. The pseudopotentials were generated from the ground-state configuration $5s^25p^6$ of the free atom using the relativistic extension of the Troullier-Martins method (see Sec. 3.3.1). Spin-orbit coupling was included using $j$-dependent pseudopotentials in the Kleinman and Bylander form as suggested by Theurich and Hill [89]. The cutoff radii used were 2.5, 2.5, and 3.2 a.u. for the $s$, $p$, and $d$ components, respectively.

The optical absorption cross-sections were computed using real-time propagation of the time-dependent Kohn-Sham equations as implemented in the *octopus* code. A box composed of spheres of radius 4.5 Å around every atom and a uniform grid with a spacing of 0.42 Å was necessary to obtain a resolution of about 0.1 eV in the spectra.

For some clusters we also optimized their geometries using DFT. We started our optimizations from previously published geometries [93] and used the Broyden-Fletcher-Goldfarb-Shanno conjugate gradient algorithm with a convergence criterion of $10^{-3}$ eV/Å in the forces on every atom. The calculation of the forces with the necessary accuracy required the use of a grid spacing of 0.3 Å. To avoid unwanted effects from the boundaries during the optimization, a spherical box of radius 12 Å was used.

4.3 Results and discussion

We started by optimizing the ground-state geometries of linear $\text{Xe}_3^+$ and linear $\text{Xe}_4^+$ using two different exchange and correlation potentials: the Perdew-Wang parametrization of the LSDA [42] and the Perdew-Burke-Ernzerhof (PBE) parametrization of the
<table>
<thead>
<tr>
<th>Cluster</th>
<th>Method</th>
<th>( b )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Xe}_3^+ )</td>
<td>LSDA</td>
<td>6.67-6.67</td>
</tr>
<tr>
<td></td>
<td>PBE</td>
<td>7.36-7.36</td>
</tr>
<tr>
<td></td>
<td>DIM</td>
<td>6.54-6.54</td>
</tr>
<tr>
<td>( \text{Xe}_4^+ )</td>
<td>LSDA</td>
<td>3.47-3.43-3.47</td>
</tr>
<tr>
<td></td>
<td>PBE</td>
<td>4.01-3.99-4.01</td>
</tr>
<tr>
<td></td>
<td>DIM</td>
<td>3.55-3.18-3.55</td>
</tr>
</tbody>
</table>

**Table 4.1**: Bond lengths \( b \) (Å) of linear \( \text{Xe}_3^+ \) and linear \( \text{Xe}_4^+ \). The DIM results are from Ref. [93].

GGA [51]. We present our results and compare them with the geometries obtained using the *diatoms-in-molecules* (DIM) semi-empirical model\(^1\) [93] in Table 4.1. These results indicate that, compared to the DIM geometry, the LSDA mostly overestimates the bond-lengths and that PBE overestimates them by a much larger factor. A possible reason for this is that both LSDA and GGA fail to describe long-range correlation effects [98], which should play an important role in the bonding of these systems. The apparently better performance of LSDA compared to GGA is due to known error cancellations found in the LSDA.

Using the geometries from Table 4.1 we calculated the corresponding optical absorption spectra. For the LSDA and PBE geometries the time-propagation was carried using the adiabatic version of the same functional that was used to obtain the geometry. As for the geometries obtained with the DIM model, we computed the spectra using the adiabatic LSDA functional. The calculated spectra can be seen in Fig. 4.1. The overall structure of the spectra obtained with the LSDA and DIM geometries is the same, although with differences in the position and intensities of the peaks. As for the spectra obtained with the PBE geometries, they present larger differences, specially in the case of linear \( \text{Xe}_4^+ \). We also included in Fig. 4.1 the experimental results for \( \text{Xe}_3^+ \). The positions of the peaks obtained with LSDA and DIM geometries are close to the experimental values and the error is within the expected accuracy of the method (0.1 eV to 0.4 eV). As for the PBE results, they seem to be worse than the LSDA results, probably because of the errors in the geometries. In all our calculated spectra the relative intensities of the two peaks appear

---

\(^1\)In the DIM approach, a model Hamiltonian is built using high quality *ab initio* diatomic data. Several extensions to the DIM model are required in order to accurately describe the electronic properties of cationic xenon clusters. These extensions include the spin-orbit coupling, three-body polarization contributions to the interaction energy, and three-body dispersion terms. For more details about the DIM model, see, e.g., Ref. [96] and references therein.
Figure 4.1: Absorption cross-section of linear Xe$_3^+$ (upper panel) and linear Xe$_4^+$ (lower panel) calculated using LSDA, PBE and DIM geometries. The experimental results for Xe$_3^+$ from Ref. [91] are also plotted.
to be inverted. These relative intensities should mainly be determined by the spin-orbit coupling. In order to check this, we have performed some calculations where the spin-orbit coupling term in our Hamiltonian was multiplied by a prefactor $\lambda$. This term can be identified by writing the Kleinman and Bylander form for $j-$dependent pseudopotentials in terms of the Pauli matrices (see Eq. (B.9)). In Fig. 4.2 we plot the optical absorption spectra of $\text{Xe}_3^+$ as a function of $\lambda$. As expected, for $\lambda = 0$ there is only one peak present and a second peak at lower energy appears when $\lambda$ increases. From Fig. 4.2 we verify that, by varying $\lambda$, it is possible to modify and even invert the relative intensities of the peaks. Although in a different context, Díaz-Sánchez et al also found that, by multiplying the spin-orbit coupling by some prefactor, it was possible to improve the agreement of their calculations with experiment [99]. This suggests that it may be necessary to go beyond the level of approximation we are using to describe the spin-orbit coupling in order to obtain a better agreement between our calculations and experiment. Another possible source of error in the calculated spectra is, like for the case of the geometries, the fact that both LSDA and GGA fail to describe long-range correlation effects.

In order to isolate the effect of the exchange and correlation functional in the spectra,
Figure 4.3: Absorption cross-section of linear $\text{Xe}_3^+$ (upper panel) and linear $\text{Xe}_4^+$ (lower panel) calculated using different exchange-correlation functionals but fixed geometries.
we calculated the optical absorption spectra of the same clusters using different exchange and correlation potentials, but keeping the geometries fixed. The geometries used were the ones obtained with the DIM model. Besides the LSDA and PBE functional we also used the LB94 functional [100], which has an improved long-range behavior. The adiabatic version of the functional used to obtain the ground-state was used for the time-dependent propagation. The results obtained for linear Xe$_3^+$ and linear Xe$_4^+$ are given in Fig. 4.3. As it can be seen, the differences in the calculated spectra are small. From the previous results, it comes that the differences between the TDDFT absorption cross-sections of a given cationic xenon cluster, for the functionals we have tested, are mainly determined by the geometries. Because of this, and since our results seem to indicate that the spectra computed from the DIM geometries are at least as accurate as the spectra computed from DFT geometries, we have used the DIM geometries in all the remaining calculations.

In Fig 4.4 we show the calculated spectra for Xe$_3^+$ and for the two isomers of Xe$_4^+$: a T-shaped geometry, which is the ground state, and a linear geometry. The spectra of Xe$_3^+$ and of the T-shaped Xe$_4^+$, which has a trimer core, are very similar. As it was said before, previous experimental and theoretical work showed that the absorption cross-section of

**Figure 4.4:** Absorption cross-section of linear Xe$_3^+$, T-shaped Xe$_4^+$ and linear Xe$_4^+$. 
these clusters is mainly determined by the charged core. These results confirm this.

More than one isomer is present in the experiment. This means that the existence of different metastable isomers needs to be taken into account in order to compare our results with experimental data. A crude way to simulate the absorption cross-section at finite temperature is to sum the spectra of the different isomers using a Boltzmann distribution to weigh them. Thus, for each cluster size, we have calculated the absorption cross-section for all the local minima found in the DIM calculations by Páiska et al. To illustrate the method, we plot in Fig. 4.5 the absorption cross-section for the different isomers of Xe$_5^+$ as well as their weighted sum for different temperatures. In the experiment, the temperature was estimated to be between 60 K and 100 K. Notice that, again, it is clearly possible to identify the core of the isomer from the absorption cross-section. Like for the case of Xe$_5^+$, but contrary to experimental data, we see that the intensity of the peak close to 3 eV is higher than the intensities of the peaks around 2 eV.

In Fig. 4.6 we plot the absorption cross-section, computed as described in the previous paragraph, for Xe$_n^+$, $3 \leq n \leq 35$ as a function of $n$. A temperature of 100 K was used for all cluster sizes. From the overall structure of the spectra, three regions can clearly be identified. These regions correspond to values of $n$ where different core sizes become more relevant in the spectra: trimer core for $3 \leq n \leq 13$, tetramer core for $14 \leq n \leq 22$, and pentamer core for $n \geq 23$. We will now analyze more in detail the trends in the positions of the main peaks. In our calculations, the position of the peak at around 3 eV is systematically below the experimental value. The reason for the disappearance of this peak for $n \geq 15$ is that few isomers were found in the DIM calculations for those clusters, as an extensive search in conformational space for such large clusters was prohibitive. The lack of experimental points for this peak makes it difficult to draw any further conclusions. As for the peak at around 2 eV, we see that for $n \leq 19$ our calculation is able to describe quite accurately the trend in the position of the peak. In particular, the change in slope at $n = 13$ is well reproduced. The trend in the position of the lower energy peak measured experimentally is reasonably well described, although the intensity of this peak is clearly underestimated in our calculations. For all the peaks, at large values of $n$, comparison between our results and experiment becomes more difficult, as the structure of our calculated spectra increases in complexity. Finally, we note that in our calculation a broad peak can be found close to 0.5 eV. This peak is present for most isomers and becomes broader as the cluster size increases. This suggests that this low energy excitation is plasmon-like. Unfortunately there are no experimental measurements at these energies for us to compare with.
Figure 4.5: Absorption cross-section for the different isomers of Xe$^+_5$ (upper panel) and absorption cross-section of Xe$^+_5$ obtained using a Boltzmann distribution for different temperatures (lower panel).
Figure 4.6: Absorption cross-section (arbitrary units) for $\text{Xe}_n^+$, $3 \leq n \leq 35$, as a function of cluster size and energy. The positions of the peaks measured by Haberland et al [91] are indicated with crosses. The lines through the experimental data points are only to guide the eye.

4.4 Conclusions

In this Chapter we have studied the optical absorption of cationic xenon clusters using TDDFT. We have showed that, provided that adequate ground-state geometries are used, TDDFT is able to correctly predict the qualitative features of the spectra. Our results are in agreement with previous theoretical calculations, who concluded that the absorption cross-section is mainly determined by the charged linear core of the clusters. Indeed, from our calculated spectra, the linear core of each isomer could clearly be identified. From the overall structure of the spectra, only the the relative intensities of the peaks were found to be poorly described. Spin-orbit coupling included within the pseudopotential approximation was identified as a possible source for this error. For the lower energy
excitations and for small cluster sizes, a quantitative agreement is also found between our results and experiment.
Chapter 5

Spin-orbit Effects in the Optics of Gold Nanostructures†

5.1 Introduction

Experimental breakthroughs in the last decades have demonstrated the feasibility of selectively preparing small size-and-shape selected coinage metal nanoparticles. This opens the possibility of applying these nanoparticles in optical devices [5, 6, 101]: as the optical response for nanometer structures depends crucially on the particle size due to quantum effects, their absorbing and emitting spectrum can be tuned by changing its size or shape. For gold, that constitutes the topic of this Chapter, a synthesis method that allows for control of the average cluster size and deposits the gold nanostructures on MgO was reported in Ref. [102]; in a different example, functionalized Au\textsubscript{55} clusters were generated using a “bottom-up” fabrication method based on the self-assembly of the clusters on organic template patterns [103].

Gold is ubiquitous in surface science due to its inertness. However the reduction in dimensionality revealed new and exciting phenomena and possibilities not at all present before: among others, enhanced reactivity [104], control of shape and size by external electric fields [105], new optical devices [106], applications as a basic ingredient for metamaterials

†This chapter is an adaptation of the article:


As such, the reported work includes the collaboration of the rest of the authors of the article.
or as an essential component in adaptive-shape femtosecond laser pulse generators.

Theoretically, the size dependence of the electronic, magnetic and chemical properties of 3D metallic nanoparticles is by now well understood [107,108]. Still, the interpretation of the noble metal clusters absorption spectra is quite complex. Anionic silver clusters exhibit the expected red-shift as the cluster size is decreased [109], whereas the cations are blue-shifted [110]. This blue-shift has also been found in the optical response of large (2-4 nm diameter) gold nanoparticles supported in alumina [111], and can be traced back to the action of the $d$-electrons that form a (size-dependent) polarizable background that strongly screens the valence electron interactions [112,113].

It is therefore clear that, even if the $d^{10}s^1$ electronic arrangement of all coinage metals may suggest their treatment as simple alkaline clusters, the $d$-shell interplay with the $s$ electron has an important contribution. However, this does not suffice to explain the singularity of gold nanostructures: relativistic effects were proven to be crucial for the color of gold and for understanding gold chemistry [7]. The bonding in gold clusters is influenced by relativistic effects that tend to increase the degree of $sd$-hybridization in the molecular orbitals, modifying the geometries of gold clusters: planar structures are favored for small clusters up to a surprisingly large number of atoms (up to $n = 7, 11$ and $12$ for cationic, neutral and anionic clusters, respectively [114–117]). These numbers are much larger for gold than for copper or silver, and the reason can be unambiguously assigned to relativity [118].

Even though the necessity of including to some extent relativistic effects has always been stressed, the effect of spin-orbit coupling on the electronic excitations has been over-seen.1 Usually, except for accurate (quasi)-relativistic quantum chemistry calculations for the atom or the dimer [120–122], the account for relativity is restricted to using relativistic effective core potentials or pseudopotentials2. Yet, the spin-orbit splitting of the lowest-lying non-forbidden spectroscopic line of the gold atom is as large as 0.5 eV [125]. Can one expect that this splitting is quenched by increasing the size of the Au clusters? Or, that it is washed away as the density of states grows – and with it, the complexity of absorption spectra – , so that the general shape and features of the spectra are largely unaffected by the presence of spin-orbit in the model? Does the magnitude of spin-orbit effects depend on the cluster dimensionality (wires, planar or 3D structures)? These questions are the object of the present Chapter. In particular we will be looking at optical absorption spectra within TDDFT.

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1 Some work has been reported for other properties, i.e. magnetic anisotropies [119].
2 Up to now, all TDDFT calculations of the static polarizabilities and the absorption spectra of Au$_n$ clusters ($n =$ 2–14, 20) (see, for example, Refs. [123] and [124], and references therein) have neglected the impact of relativity beyond its effect on the geometrical structure.
Figure 5.1: Absorption cross section of linear Au$_n$ ($n = 2 - 7$), obtained with (black line) and without (light gray line) spin-orbit coupling.
5.2 Methodology and results

The transition from planar to three-dimensional structures in small gold clusters has been investigated previously (see for example Refs. [126] and [127]). The aim of this work is to assess the spin-orbit effects as a function of dimensionality. For such purpose, we have obtained the geometries from Ref. [126] and reoptimized them through Car-Parrinello dynamics [128] with norm-conserving scalar-relativistic pseudopotentials [76]. To obtain our 3D geometries we performed a similar process as the one described in Ref. [129], where a classical potential in conjunction with genetic algorithms was used to obtain the initial starting points for the CP dynamics. At this stage the spin-orbit coupling was neglected, since (i) the structural modification introduced by this effect is small, and (ii) the aim of our work is to isolate spin-orbit effects in the electronic excitations (comparing the spectra with and without spin-orbit for the same geometry). It is important to treat exchange-correlation effects at the PBE-GGA level when determining structural properties of small gold clusters [130]. Our \textit{ab initio} calculations confirm that planar structures are the most stable for the cluster sizes studied here (except for the Au\textsubscript{20} case). The obtained planar and 3D structures are shown in Figs 5.2 and 5.3. In addition, to complete the study of the effect of dimensionality, we have performed computations for linear chains (wires) of gold atoms. For these 1D structures we chose to fix the bond length to 2.9 Å, which is the nearest-neighbor distance in bulk gold [131]. Atomic gold chains can be created by stretching gold nanocontacts, or by deposition on stepped surfaces [131]. Their interatomic distance can vary substantially; see, e.g., Ref. [132].

Note that nanowire gold chains were predicted and generated experimentally in the 1990s, and were the subject of extensive investigations [131,134–137]. Low-dimensional gold structures are also widely used in the study of electronic transport through single molecules, often connecting the molecule to the leads and supported on surfaces [131].

Regarding the computational details of the TDDFT calculations, we represented the relevant functions on a real-space regular rectangular grid. The grid spacing was chosen to be 0.4 a.u. and the border of the simulation box was taken 8 a.u. away from the closest nucleus. The total propagation time was 750 a.u., and we used the (adiabatic) LSDA to describe exchange-correlation effects. In contrast to structural properties, the optical spectra of small metal and semiconductor clusters in the visible range turn out to be, \textit{for fixed ionic configuration}, not much sensitive to the use of the LSDA or PBE-GGA for fixed ionic configuration, not much sensitive to the use of the LSDA or PBE-GGA for fixed ionic configuration, not much sensitive to the use of the LSDA or PBE-GGA for fixed ionic configuration, not much sensitive to the use of the LSDA or PBE-GGA for.

\footnote{We used the CPMD code, version 3.5, developed by J. Hutter et al., at MPI für Festkörperforschung and IBM Research Laboratory (1990-2001).}

\footnote{Atomic gold chains can be created by stretching gold nanocontacts, or by deposition on stepped surfaces [131]. Their interatomic distance can vary substantially; see, e.g., Ref. [132].}
Figure 5.2: Absorption cross section of 2D Au$_n$ ($n = 3 - 8$), obtained with (black line) and without (light gray line) spin-orbit coupling.
Relativistic effects were included at the pseudopotential level. We generated a fully relativistic pseudopotential for gold using the relativistic extension of the Troullier-Martins scheme. The $5d^{10}6s^15p^0$ configuration of the free atom was used and the cut-off radii for the $s$, $p$, and $d$ components were chosen to be 2.47, 2.98, and 2.00 a.u. respectively. This pseudopotential was used in its fully non-local form of Kleyman and Bylander following the scheme by Theurich and Hill [89]. This pseudopotential, coupled to our TDDFT implementation, allows us to discern the effect of spin-orbit in the valence excitations. We obtain in this way, for the atomic $^{2}P_{1/2}$ and $^{2}P_{3/2}$ spectroscopic lines, 4.85 and 5.30 eV (experimentally they are found at 4.632 and 5.105 eV [125]). There is an absolute error of about 0.2 eV, but the error in the difference — the spin-orbit splitting — is obtained with the excellent accuracy of 0.025 eV.

The absorption cross sections for the set of clusters studied here are shown in Figs. 5.1, 5.2 and 5.3 for one-dimensional wires, 2D and 3D structures, respectively. The plots show the results obtained with (black thick line) and without (lighter gray line) the spin-orbit coupling term.

For the wires (Fig. 5.1), the inclusion of the spin-orbit term has a quite large effect. For the smallest system, Au$_2$, the splitting of the first peak in the spectrum amounts to almost 1.5 eV. The very small peak at low energy is missed experimentally, whereas the following peak (at around 3 eV) is in good agreement with the main experimental peak at 3.18 eV [139,140]. If spin-orbit coupling is not included, this agreement is slightly worse.

The spin-orbit effect is slightly reduced with increasing number of atoms. However, even for the largest system studied (Au$_7$), spin-orbit still changes the relative oscillator strengths and the peak positions by as much as 0.5 eV. This result is particularly important in the field of electronic transport, where wires of these dimensions often appear in experimental and theoretical setups. As resonances in the conductance arise when hitting an electronic excitation energy, our results indicate that inclusion of spin-orbit coupling is crucial to obtain these resonances with the correct position and intensity. In the case of supported gold-chains [131] the screening introduced by the substrate hinders this effect, effectively quenching spin-orbit leading to more “delocalized s-like particle-in-a-box states”.

For the case of 2D and 3D structures (Figs. 5.2 and 5.3), the effect is still noticeable, but much smaller than for the 1D wires. As the cluster size grows, the density of excited states grows, and the detailed peak structures is washed away by the superposition of

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\footnote{We have also performed calculations for Au$_2$ at the bulk interatomic distance (2.9 A). The whole absorption spectrum is red-shifted, as expected, and the shapes do not change significantly in the optical region; in particular the spin-orbit splitting stays roughly the same.}
Figure 5.3: Absorption cross section of 3D Au$_n$ ($n = 4 - 7, 20$), obtained with (black line) and without (light gray line) spin-orbit coupling.
spectral widths. Even though, there is a clear difference between planar and 3D structures: The latter show fingerprints of the surface plasmon resonance characteristic of gold nanoparticles. For the planar structures, as the system size increases, the difference in the spectra with and without spin-orbit is washed out rather soon and, after Au$_5$, the spectra are rather similar. In contrast, for the 3D structures there are still differences in the peak intensities as well as in several peak splittings. In particular, for the case of Au$_{20}$, the spin-orbit correction introduces some features in the near UV range which can be detected at experimental resolution (and that are not shown in previous calculations without spin-orbit; see Ref. [123] and references therein).

In addition to the absorption spectra (i.e. the imaginary part of the dynamical polarizability), we also report in Table 5.1 the static dipole polarizabilities (which we computed with the same numerical technology, making use of the finite field technique) for both the planar and the 3D structures. The atomic value is very similar with and without spin-orbit, in agreement with previous calculations [123], and within the error bar of experimental estimates [7, 141, 142]. For the clusters, the main conclusion that can be drawn is that the effect of the inclusion of spin-orbit is also rather small – except maybe in the case of Au$_3$ –, and in most cases increasing the polarizability. It is worth noting that the overall relativistic effects in Au lead to a size contraction, and correspondingly the static polarizability should decrease. The spin-orbit part of the relativistic interactions seems to work in the opposite direction (specially for 2D clusters). The contribution of this effect, however, is much smaller than the scalar relativistic one. The planar structures exhibit, for this cluster size range, even-odd oscillations as reported in previous works. [123]

We would like to stress that, by comparing the photoabsorption cross section spectra obtained for different isomers with the same size, it is clear that it carries relevant structural information. Therefore, optical spectroscopy can be used as a non-invasive characterization tool to discern the specific isomer synthesized in experiments and test the predictions.

<table>
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<tr>
<th>Cluster size</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
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<tbody>
<tr>
<td>$\langle \alpha \rangle$ (2D)</td>
<td>5.15</td>
<td>5.57</td>
<td>5.79</td>
<td>5.86</td>
<td>6.02</td>
<td>5.86</td>
<td>6.39</td>
<td>6.28</td>
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<tr>
<td>$+ L \cdot S$</td>
<td>5.20</td>
<td>5.62</td>
<td>6.32</td>
<td>5.91</td>
<td>6.09</td>
<td>5.94</td>
<td>6.47</td>
<td>6.34</td>
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<tr>
<td>$\langle \alpha \rangle$ (3D)</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>$+ L \cdot S$</td>
<td>5.95</td>
<td>5.96</td>
<td>5.62</td>
<td>5.59</td>
<td>5.48</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.03</td>
<td>5.89</td>
<td>5.62</td>
<td>5.63</td>
<td>5.46</td>
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</table>

**Table 5.1:** Polarizabilities per atom (in a.u.) for the 2D and 3D clusters structures studied in this work, calculated either without or with $(+L \cdot S)$ spin-orbit coupling.
for change of shape of supported gold clusters by a static electric field [105]. We can speculate that the rather strong spin-orbit effects in one-dimensional gold wires could have implications in the development of spintronics devices.
Chapter 6

Small Chromium and Iron Clusters: Noncollinear Spin Effects

6.1 Introduction

Since the pioneering work of Oda et al, who studied noncollinear magnetic structures of small iron clusters [34] using DFT, several other studies have shown that noncollinear spin configurations exist for a variety of transition-metal clusters [35, 36, 119, 143]. From these studies it is clear that these noncollinear effects can be important in order to accurately describe the ground-state properties of transition-metal clusters. As for the importance of noncollinear effects in the excited state properties of these systems, it is a subject that remains to be explored. Another subject that has been only scarcely addressed when studying the ground-state properties of transition-metal clusters is the interplay between spin-orbit coupling and noncollinear spin. Since the spin-orbit coupling links the charge and spin dynamics of a system, this interplay could be important even for elements where relativistic effects are expected to be small. For the same reason, this effect could also be important when studying excited state properties.

Among the transition-metal clusters where noncollinear spin configurations exist, we find small chromium and iron clusters. The $3d^54s^1$ electronic structure with 6 unpaired valence electrons of chromium makes it quite unique among the $3d$ transition-metals and results in a strong $d$-$d$ bonding in the dimer. This tightly bound dimer plays a key role in determining the structures of the larger clusters as it was shown by Cheng and Wang [144].
They studied the structural and magnetic properties of small chromium clusters up to 15 atoms, but their study was restricted to collinear magnetic configurations. Later Kohl and Bertsch studied noncollinear effects for small chromium clusters up to 13 atoms [35]. They included spin-orbit coupling in their calculation and found that all clusters except \( \text{Cr}_2 \) and \( \text{Cr}_4 \) favored noncollinear spin arrangements. Further investigation of noncollinear effects in small chromium clusters was done by Hobbs et al [36]. They did not include spin-orbit coupling in their calculations, but contrary to the previous studies who only used the LSDA, they also used GGA. More recently, Martínez and Alonso [145] used TDDFT to study the photoabsorption spectra of chromium clusters, but restricted themselves to collinear configurations and did not include spin-orbit coupling.

Although the effect of noncollinearity is not as pronounced in iron clusters as for chromium clusters, Oda et al found noncollinear magnetic structures for several iron clusters [34]. They used LSDA and found the most stable geometry for \( \text{Fe}_5 \) to be noncollinear and that the linear geometry of \( \text{Fe}_3 \) favors a noncollinear structure, although it is not the global minima. More recently Rollmann et al [146] used GGA and found all the ground states of iron clusters from 2 to 15 atoms to be collinear.

In this Chapter we employ TDDFT to study the effect of noncollinearity in the excited state properties of small iron and chromium clusters. This is done by comparing the dipole and spin-dipole response functions of different clusters with collinear and noncollinear spin configurations. For the noncollinear spin configurations, the importance of taking into account the spin-orbit coupling is also investigated.

### 6.2 Methodology

The ionic core of the atoms was treated using the pseudopotential approximation. The 3s and 3p semi-core electrons of Cr and Fe need to be included into the valence space in order to describe the spin-polarization of the valence electrons and also because of the small separation between ions in the clusters under study. We have used Troullier-Martins pseudopotentials with explicit incorporation of semi-core states (see Sec. 3.3.1) in the fully non-local form of Kleinman and Bylander. The cut-off radii of the 3s, 3p, 3d, 4s, and 4p states where taken at 1.71, 1.90, 1.10, 2.80, and 3.70 a.u. for Cr and at 1.70, 1.91, 1.30, 3.00, and 3.70 a.u. for Fe. In the cases were spin-orbit coupling was included, this was done using \( j \)-dependent pseudopotentials.

Because of the high computational effort required by our calculations, a good compromise between accuracy and softness of the generated pseudopotentials is fundamental.
Figure 6.1: Convergence of the total energy (crosses), HOMO eigenvalue (circles), and LUMO eigenvalue (squares) for the chromium (upper panel) and iron (lower panel) atoms obtained using the MRRP (green) and HGH (red) pseudopotentials. The plotted values are the differences between the values obtained for each grid spacing and the value obtained for a grid spacing of 0.15 a.u.
When representing the wavefunctions on a uniform grid in real space, convergence of the results has to be checked against the grid spacing. This grid spacing is one of the critical parameters that determines the computational effort required by the calculation and, in our case, it is mainly determined by the pseudopotentials. We have thus started by computing the total energy and the HOMO and LUMO eigenvalues for the chromium and iron atoms using our generated pseudopotentials at various spacings. We plot the corresponding results in Fig. 6.1. In Fig. 6.1 we also plot the same values arising from the use of Hartwigsen-Goedecker-Hutter (HGH) pseudopotentials [147]. The HGH pseudopotentials are constructed from relativistic all-electron calculations, have optimal decay properties in both real-space and Fourier space, and have proven to give highly accurate results in molecular calculations. We can see that the values obtained with the MRPP pseudopotentials always converge faster than the ones obtained with the HGH pseudopotentials. This means that, when using the MRPP pseudopotentials, it is possible to use a larger value for the spacing in order to obtain the same accuracy as when using the HGH pseudopotentials.

The main objective of this work is to determine the effect of noncollinear magnetic configurations and spin-orbit coupling in the response properties of the clusters. Because of that, we have used the geometries available in the literature. For the same reason, we focused on the cluster geometries for which both collinear and noncollinear magnetic configurations exist. In some cases, the collinear and noncollinear geometries are very different. We did not consider those cases, as the differences in the geometries imply large differences in the spectra, thus making it difficult to understand the impact of the magnetic configurations.

It order to characterize the spin configuration of the clusters, we followed the scheme proposed in previous studies [34, 35]: we estimated the atomic magnetic moments by integrating the magnetization density within a sphere of a certain radius centered on the ions. As for the choice of this radius, we chose it so that it would be easy to compare our results with the ones published previously: In the case of the Fe clusters we chose this radius to be 1.7 a.u., which was the value used by Oda et al, and for the Cr clusters we chose it to be half the smallest interatomic distance in each cluster, as suggested by Kohl and Bertsch.

The response functions for each configuration were computed using explicit time-propagation of the TDDFT equations as implemented in the octopus code. The wavefunctions were represented in real space using a uniform grid with a spacing of 0.22 a.u. and a box composed by spheres of radius 11 a.u. around every atom. The propagation of

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1Since there are still many open questions about the ground-state structures of these clusters, further investigation on this subject could be relevant, but is beyond the scope of the present work.
the Kohn-Sham orbitals was done using state of the art algorithms [148] with a time-step small enough to assure the stability of the time-propagation. The total propagation time was such that it allowed a resolution of 0.1 eV in the resulting spectrum. For each time-dependent calculation, we used the adiabatic approximation of the exchange-correlation potential used to obtain the ground-state of the system. In the case of noncollinear spins, the exchange-correlation potentials where constructed from the functionals available for collinear spins, as described in Sec. 1.4.5. Whenever possible we used the symmetries of the clusters to reduce the total number of time-propagations (see App. C).

6.3 Results and discussion

6.3.1 Cr$_2$ and Fe$_2$

As one could expect from their very simple geometry, no noncollinear spin configurations where predicted for the chromium and iron dimers. Nevertheless, there are numerous theoretical and experimental results available for both ground and excited state properties of Cr$_2$ and Fe$_2$, which makes them a perfect test case for our methodology.

The ground states of Cr$_2$ and Fe$_2$ have been extensively studied using DFT. In particular, LSDA calculations predicted the ground state of Cr$_2$ to be antiferromagnetic with a total magnetic moment $M = 0 \mu_B$ [35, 36, 144]. As for the ground state of Fe$_2$, LSDA calculations predicted it to be ferromagnetic with a total magnetic moment

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<th>$E_B$</th>
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<td></td>
<td></td>
</tr>
<tr>
<td>present</td>
<td>3.16</td>
<td>1.12</td>
<td>present</td>
<td>3.69</td>
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<tr>
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<td>Ref. [36]</td>
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<td>1.98</td>
<td>Ref. [34]</td>
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<td>2.76</td>
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<td>3.53±0.25</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Exp. - Ref. [154]</td>
<td>3.82±0.04</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 6.1: Bond lengths $b$ (a.u.) and binding energies $E_B$ (eV/atom) of antiferromagnetic Cr$_2$ (left table) and ferromagnetic Fe$_2$ (right table) calculated using the octopus code. Available experimental data and previous results obtained using the LSDA are also indicated for comparison.
$M = 6 \mu_B$ [34,149–151]. We thus started by calculating the bond lengths and binding energies for antiferromagnetic $\text{Cr}_2$ and ferromagnetic $\text{Fe}_2$ using the LSDA for the exchange-correlation potential. In Tab. 6.1 we present our results and compare them with previous LSDA calculations and with the experimental results available. We see that our results are in good agreement with previous LSDA calculations and with available experimental data.

As for the excited state properties of $\text{Cr}_2$ and $\text{Fe}_2$, several transitions have been observed experimentally. In particular, the photoabsorption spectra of chromium and iron contained in rare-gas matrices has been measured. Therefore, we computed the dipole strength functions of $\text{Cr}_2$ and $\text{Fe}_2$. Besides using the adiabatic LSDA, we also computed the strength function using the Perdew-Burke-Ernzerhof [51] (PBE) GGA functional. Our computed spectra for the dimers, as well as available experimental results, can be seen in Fig. 6.2. For $\text{Cr}_2$, the main peaks of the dipole strength function below 5 eV obtained using the LSDA are located at 2.84, 3.63, 4.45, and 4.81 eV. This is in good agreement with the transitions at 2.70 [152,155,158], 3.65 [155,159], and 4.77 [156] eV that were observed experimentally in the photoabsorption spectra of $\text{Cr}_2$ The corresponding results obtained using the PBE functional do not compare so well with experiment: we find the peaks located at 2.9, 3.9, and 4.5 eV. As for $\text{Fe}_2$, De Vore et al observed three transitions in an iron-containing argon matrix at 2.28, 2.62 and 2.99 eV, the later being a broad absorption band [157]. Our computed spectra using LSDA can be seen in Fig. 6.2 and a peak at 3.0 eV is perfectly visible. Several peaks of smaller intensity can be observed between 2 and 3 eV at 2.1, 2.3 and 2.6 eV, but the last two seem to have very small relative intensities. As for the spectra calculated with the PBE, there are three peaks clearly visible at 2.0, 2.5, and 2.9 eV, which is in good agreement with experiment.

From the previous results it is not clear which of LSDA or GGA is more suited for the study of the excited state properties of these systems. Because it is not the purpose of this work to elucidate this question, and since the majority of the previous theoretical studies of noncollinear configurations of chromium and iron clusters employed the LSDA, all our remaining results where obtained using the LSDA.

To conclude this section, we mention that Casey and Leopold measured the negative ion photoelectron spectra of $\text{Cr}_2$ and observed a transition to the $^3\Sigma_u^+$ state 1.7 eV above the $^1\Sigma_g^+$ ground-state [160]. We have computed the spin-dipole response function of $\text{Cr}_2$ using the LSDA and found a distinct peak at 1.8 eV, which is in excellent agreement with this experimental result.
Figure 6.2: Dipole strength functions of Cr$_2$ (upper panel) and Fe$_2$ (lower panel) computed with LSDA and PBE exchange-correlation functionals. Experimental results for Cr$_2$ [155, 156] and for Fe$_2$ [157] are also shown for comparison.
6.3.2 Fe$_3$ and Fe$_5$

Although the ground-state of the iron trimer was predicted to have $C_{2v}$ symmetry [34, 149–151], Oda et al found a metastable state with noncollinear spin arrangements for the linear geometry. This noncollinear metastable state has an antiferromagnetic collinear counterpart (see Fig. 6.3). As for the iron pentamer, there is still some controversy about the ground-state structure [34, 146, 150, 151]. Nevertheless, Oda et al identified a noncollinear spin configuration for the trigonal bipyramid, which they found to be the global minima, and the corresponding collinear configuration (see Fig. 6.3). Therefore we decided to study both spin configurations of Fe$_3$ and Fe$_5$. We started by obtaining the ground-state for each configuration using the geometries of Oda et al. We obtained very similar values for the atomic magnetic moments as the ones indicated in Fig. 6.3. Afterward, we computed the dipole and spin-dipole strength functions for both spin configurations of Fe$_3$ and Fe$_5$.

Our results for linear Fe$_3$ can be seen in Fig. 6.4. Since the bond lengths for both configurations are almost the same, the changes observed in the spectra must come from the different magnetic structures. We have tried to verify this by computing the strength functions for the collinear spin configuration using the bond lengths of the noncollinear spin configuration, but found only very small differences in the spectra. The most striking feature appearing in our computed spectra is the existence of several transitions below 1.0 eV in the spin-dipole strength function for the noncollinear spin configuration. Those transitions are absent from the collinear spin configuration. This indicates that, for the noncollinear configuration, excited states are accessible at lower energies than for the case where the magne-
Figure 6.4: Dipole (upper panel) and spin-dipole (lower panel) strength functions of collinear (blue curve) and noncollinear (red curve) configurations of linear Fe$_3$. 
tization is restricted to collinear configurations. This is a probable consequence of the extra degrees of freedom that are available when this restriction is lifted. Regarding the dipole strength function, small differences in the structure of the two spectra can also be observed, although not as large as in the case of the spin-dipole strength function. We have also computed the strength functions including spin-orbit coupling and found no differences in the spectra. Nevertheless, indirect evidence of the effect of the spin-orbit coupling could be found by plotting the time-evolution of the atomic magnetic moment during our simulation. In Fig. 6.5 we plot the variation over time of the cartesian components and norm of the atomic magnetic moment of one of the edge atoms. From Fig. 6.5 we can see that the atomic magnetic moment of that edge atom starts to precess around the z direction, which is a direction perpendicular to the axis of the cluster and parallel to the atomic magnetic moment of the central atom. At the same time, the direction of the atomic magnetic moment of the central atom remains almost constant and the one of the other edge atom starts to precess in the opposite direction. When the spin-orbit coupling is switched off, this precession disappears.

![Figure 6.5: Variation over time of the cartesian components and norm of the atomic magnetic moment of one of the edge atoms of linear Fe₃. The cluster is oriented along the x axis.](image-url)
Figure 6.6: Dipole (upper panel) and spin-dipole (lower panel) strength functions of collinear (blue curve) and noncollinear (red curve) configurations of Fe$_5$. 
As for Fe$_5$, our results are plotted in Fig. 6.6. In this case, the structure of the spectra for the collinear and noncollinear spin configurations are different, but those differences are small. Contrary to the case of the spin-dipole response of linear Fe$_3$, no intense transition is observed below 1 eV for neither collinear nor noncollinear configurations. A possible explanation is the following: The atoms of the central triangle present a collinear spin arrangement that should be quite stable, thus increasing the energy required to access the additional degrees of freedom that would be available to the noncollinear configuration. Like for the case of linear Fe$_3$, inclusion of spin-orbit coupling does not change the spectra. Also, no precession of the magnetic moments of the apical atoms is observed with spin-orbit, which could be a further evidence of the effect of the atoms of the central triangle.

### 6.3.3 Cr$_3$

Since chromium strongly favors antiferromagnetic coupling, the chromium trimer is a very good example of a magnetically frustrated system: it is not possible for the three atoms to couple antiferromagnetically with each other at the same time. Because of this, the ground-state structure of the chromium trimer was predicted to be a dimer plus a loosely attached atom by Cheng and Wang [144]. Indeed, the strong bonding of Cr$_2$ caused the electrons of the third atom to basically remain in their atomic electronic state, so that the total magnetic moment was $M = 6 \mu_B$. Kohl and Bertsch showed

![Figure 6.7: Geometric and magnetic structures of Cr$_3$ determined by Cheng and Wang (left), by Hobbs et al (center), and by Kohl and Bertsch (right). The red arrows indicate the direction of the atomic magnetic moments. The interatomic distances are shown in atomic units and the magnitudes of the atomic magnetic moments in units of $\mu_B$. In parenthesis we indicate the atomic magnetic moments obtained in the present work using the same bond lengths.](image)
that, by allowing noncollinear spin configurations, this picture could change [35]. In their calculation, the spins would arrange in a noncollinear configuration such that the atoms could achieve the closest to antiferromagnetic coupling as possible. As a consequence, the third atom would come closer and the total magnetic moment would become \( M = 2.07 \mu_B \).

Later, Hobbs et al. [36] also studied the chromium trimer using LSDA and allowing for noncollinear spin arrangements, but they did not confirm the previous results. They found a structure with a collinear spin configuration and a total magnetic moment \( M = 2 \mu_B \) which can be regarded as an alternative way for the atoms to arrange in such a way as to minimize magnetic frustration. The three structures are represented in Fig. 6.7. We have calculated the ground-state for each of these configurations and we indicate in parenthesis in Fig. 6.7 the atomic magnetic moments that we have obtained. Contrary to the case of the iron clusters, we find some large differences in the noncollinear configuration, although the general direction of the atomic magnetic moments does not change much. As for the structure determined by Hobbs et al., they used a different radius for the calculation of the atomic magnetic moments, so that the results cannot be compared directly. We nevertheless notice that the values are similar. After obtaining the ground-states, we computed the dipole and spin-dipole strength functions for each structure.

![Dipole strength function and time-evolution of atomic magnetic moments](image)

**Figure 6.8:** Dipole strength function of the collinear spin configuration of \( \text{Cr}_3 \) using the geometry of Cheng and Wang (left panel) and the time-evolution of the atomic magnetic moments for each atom (right panel).

In Fig. 6.8 we plot the dipole strength function and the time-evolution of the atomic magnetic moment of the three chromium atoms in \( \text{Cr}_3 \) using the geometry and spin configuration of Cheng and Wang. The existence of negative peaks in the dipole strength function indicates that the state used to start the time evolution is not the lowest energy state for that geometry. Indeed, by examining the time-evolution of the atomic magnetic...
Figure 6.9: Dipole (upper panel) and spin-dipole (lower panel) strength functions of collinear (blue curve) and noncollinear (red curve) spin configurations of Cr$_3$. The collinear and noncollinear spin configuration are the ones obtained by Hobbs et al and by Kohl and Bertsch respectively.
moments, we see that, after some time, This suggests that there are still several open questions about the ground-state geometry and spin configurations of the chromium trimer. In their study of the optical absorption of small chromium clusters, Martínez and Alonso obtained a very different spectra, without negative peaks, for this configuration [145]. This can be explained by the fact that they used Casida’s equation, instead of the explicit time-propagation of the TDDFT equations, to determine the response functions. there is a pronounced change in the spin configuration of the system towards a clear antiferromagnetic bonding between the two atoms of the dimer. We have verified this by computing the ground-state for the same geometry, but imposing from the start an antiferromagnetic coupling for the dimer atoms. We obtained a state with atomic magnetic moments similar to the ones found at the end of the time-propagation of the previous configuration, but lower in energy.

In Fig. 6.9 we plot the dipole and spin-dipole strength functions for the collinear structure obtained by Hobbs et al and for the noncollinear structure obtained by Kohl and Bertsch. Like the previous cases, differences can be found in the computed spectra and low energy transitions appear in the spin-dipole strength function of the noncollinear configuration. Again, no effect of spin-orbit coupling was visible in the spectra. In this case, because of the large differences in the bond lengths, the comparison of the spectra is not straightforward. Therefore, we also computed the dipole and spin-dipole strength functions for the equilateral triangular geometry, using a bond length of 3.7 a.u.. Although this geometry should not be stable in the gas phase, it is not devoid of interest. Indeed, a noncollinear configuration has been predicted for the equilateral Cr trimer on top of a non-magnetic surface [161, 162] and experimental evidence for this noncollinear configuration exists [163]. We obtained for the ground-state of the collinear configuration a total magnetic moment $M = 2\mu_B$ and atomic magnetic moments of 1.05, 1.05 and -1.28 $\mu_B$. This indicates that one of the atoms couples antiferromagnetically with the other two, while these couple ferromagnetically with each other. As for the ground-state of the noncollinear configuration, we obtained a total magnetic moment $M = 0\mu_B$. As expected, the three atomic magnetic moments are equal in magnitude (1.90 $\mu_B$), their directions are contained in the same plane, and the angles between them are 120°. The noncollinear configuration is lower in energy by about 0.23 eV. In Fig. 6.10 we plot the dipole and spin-dipole strength function for the two configurations and it is possible to see that we find the same type of behaviour as for the isosceles geometry.
Figure 6.10: Dipole (upper panel) and spin-dipole (lower panel) strength functions of collinear (blue curve) and noncollinear (red curve) spin configurations of equilateral Cr$_3$. 

**Small Chromium and Iron Clusters: Noncollinear Spin Effects**
6.4 Conclusions

In this Chapter we have studied the effect of noncollinearity in the dipole and spin-dipole response functions of small chromium and iron clusters using TDDFT. We have found that the different electronic structures of collinear and noncollinear spin configurations are reflected in their different responses to spin-independent and spin-dependent fields. This is particularly true for the spin-dipole strength function, where large differences can be observed. This behavior should be further investigate, in order to understand what is the physical process behind it. We have also computed the response functions of the noncollinear configurations including spin-orbit coupling. In this case, no direct signature of spin-orbit coupling was found in the spectra.
Part IV

Conclusions
Conclusions

A whole is that which has beginning, middle and end.

Aristotle, Rhetoric

In this thesis we have investigated the importance of relativistic effects in the response properties of nanostructures, with a particular interest in atomic clusters, within the framework of TDDFT.

TDDFT has proven to be a successful tool in predicting the response of a wide variety of systems to external electromagnetic perturbations. Even the simplest approximation to the exchange-correlation functional, the adiabatic local density approximation, is known to yield quite accurate results for the optical absorption spectra of finite systems at a modest computational cost. This opens the possibility to study increasingly complex phenomena while extending the theory and improving the approximations used.

In many relevant systems, relativistic effects are expected to play an important role in the determination of both ground-state properties and excited-state properties. Within a (TD)DFT framework relativistic effects can be incorporated at various levels. The simplest approximation is to include scalar relativistic effects through the pseudopotentials. The next step is to include the spin-orbit interaction using fully relativistic pseudopotentials. Both methods were implemented in the code octopus, which was also extended to allow noncollinear spin calculations.

As a first application of our methodology we computed the optical absorption spectra of cationic xenon clusters. These clusters are characterized by having a linear charged core with neutral atoms surrounding it. It is known that the absorption spectra is mainly determined by the core and our results confirm this. We have also verified that the inclusion of the spin-orbit coupling is necessary to accurately reproduce the structure of the experimental spectra. As for the position and intensity of the peaks, we find our results
in good agreement with experiment, although there is a non-negligible error in the position of the higher energy peaks and in the relative intensities of the peaks. We suggest two possible sources of error: known difficulties of the LDA and GGA in describing long-range correlations and the neglecting of further relativistic effects.

Next, we used the same methodology to study the spin-orbit effect in the optical response of small gold clusters with different dimensionalities (wires, planar and 3D structures). Although previous results demonstrated that scalar-relativistic effects are enough to determine the ground-state geometries of these clusters, our results indicate that the spin-orbit coupling cannot be ignored when determining their optical absorption spectra. Indeed, for the wires, the effect of spin-orbit is quite large, as it results in a splitting of the first peak as large as 1 eV. For the 2D and 3D structures, the effect is not as large, but is still noticeable. In all cases, with increasing cluster size, the detailed peak structures are washed away by the superposition of spectral widths, which results in a “quenching” of the spin-orbit splittings.

Finally, our last application was the study of optical and magnetic excitations in small chromium and iron clusters. In particular we have studied how these are affected by noncollinear spin configurations, spin-orbit coupling, and the interplay between both. It was found that it is possible to distinguish collinear spin configurations from noncollinear ones from the calculated spectra. This is particularly true in the case of the spin-dipole response to spin-dependent fields of some clusters with noncollinear spin configurations: transitions at much lower energies that the ones appearing the corresponding collinear configurations can be observed. As for the effect of spin-orbit coupling, no direct signature was found in the spectra.

In most applications it was observed that relativistic effects can be important in determining the response properties of nanostructures. It was also found that TDDFT is a suitable tool to study these effects and this kind of systems.

The work presented in this thesis opens new directions for further investigation. As we stated in Section 1.4.4, different levels of relativistic extensions of DFT exist. In our TDDFT calculations we have used the simplest of them all: we included scalar-relativistic corrections and the spin-orbit coupling through fully-relativistic pseudopotentials. We have plans to implement the ZORA approximation and we are also considering implementing the full four-component Dirac Hamiltonian. This should allow the verification of the importance of including relativistic effects coming explicitly from valence and semi-core electrons when determining excited state properties of nanostructures.

We also intend to extend the study of noncollinear magnetism to larger clusters and to new systems. Several studies indicate that noncollinear spin configurations exist for
small manganese clusters. The interplay between spin-orbit coupling and noncollinear magnetism also needs to be further investigated, even at the ground-state level, where many questions are still unanswered. The limitations of the available exchange-correlation functionals in describing noncollinear spin configurations and spin-excitations is also an important issue that deserves further investigation.

The study of small chromium and iron clusters required the implementation of multi-reference pseudopotentials in order to explicitly include semi-core states. This scheme could be used to treat core electrons involved in soft X-ray spectroscopy at the same level as valence electrons. This possibility is already under investigation.
Appendices
Appendix A

Electromagnetic Waves in Matter

A.1 Maxwell’s equations

Maxwell’s equations for electromagnetic waves interacting with a charge density can be written as [164]:

\[ \nabla \cdot D = 4\pi \rho_{\text{ext}} , \]  
\[ \nabla \cdot B = 0 , \]  
\[ \nabla \times E = -\frac{1}{c} \frac{\partial B}{\partial t} , \]  
\[ \nabla \times H = \frac{1}{c} \frac{\partial D}{\partial t} + \frac{4\pi}{c} j_{\text{ext}} , \]

where the charge density and the current density inside the system were separated from the charge density \( \rho_{\text{ext}} \) and the current density \( j_{\text{ext}} \) outside the system. The electric field \( E \) and the displacement vector \( D \) are related by the polarization \( P \):

\[ D = E + 4\pi P , \]  

while the magnetic induction \( B \) and the magnetic field \( H \) are related by the magnetization \( M \):

\[ H = B - 4\pi M . \]

From Eqs. (A.1a) to (A.1d) it is possible to see that \( E \) and \( B \) can be written in terms of \( D \) and \( H \). When nonlinear effects are neglected, we can write this relationship in the
following way:

\[
D(r, t) = \int dr' \int dt' \epsilon(r, r', t - t') E(r', t'), \quad (A.4a)
\]
\[
H(r, t) = \int dr' \int dt' \mu(r, r', t - t') B(r', t'), \quad (A.4b)
\]

where \( \epsilon \) is the dielectric tensor and \( \mu \) is the permeability tensor. From here on we will ignore the fact that these quantities are tensors. In the frequency domain we have:

\[
D(\omega) = \epsilon(\omega) E(\omega), \quad (A.5a)
\]
\[
H(\omega) = \mu(\omega) B(\omega). \quad (A.5b)
\]

It is also possible to write a linear relation between the polarization and the electric field:

\[
P = \chi_e E, \quad (A.6)
\]

and between the magnetization and the magnetic induction:

\[
M = \chi_m B, \quad (A.7)
\]

where \( \chi_e \) and \( \chi_m \) are the susceptibility and the permeability of the medium. We can relate the dielectric function to the susceptibility using Eqs. (A.2), (A.4a), and (A.6):

\[
\epsilon = 1 + 4\pi \chi_e. \quad (A.8)
\]

### A.2 Complex refractive index

The solution for the electric field in the absence of external sources can be obtained by taking the curl of Eq. (A.1c):

\[
\nabla \times \nabla \times E = -\frac{1}{c} \frac{\partial}{\partial t} \left( \nabla \times B \right). \quad (A.9)
\]

Inserting Eq. (A.1a) into the right hand side of this equation, we have:

\[
\nabla (\nabla \cdot E) - \nabla^2 E = -\frac{1}{c} \frac{\partial}{\partial t} \left( \frac{\mu}{c} \frac{\partial D}{\partial t} \right), \quad (A.10)
\]

and, using Eq. (A.1a), we get the following equation for the electric field:

\[
\nabla^2 E = \frac{\epsilon \mu}{c^2} \frac{\partial^2 E}{\partial t^2}. \quad (A.11)
\]
The general solution of this equation is:

\[ E(\mathbf{r}, t) = E_0 e^{i(k \cdot \mathbf{r} - \omega t)}. \] (A.12)

If \( \hat{k} \) is the direction of the propagation, then the propagation vector \( \mathbf{k} \) is given by:

\[ \mathbf{k} = \frac{\omega}{c} \sqrt{\varepsilon \mu} \hat{k}, \] (A.13)

and we have:

\[ E(\mathbf{r}, t) = E_0 e^{i\frac{\omega}{c} \sqrt{\varepsilon \mu} \hat{k} \cdot \mathbf{r}} e^{-i\omega t}. \] (A.14)

For a non-magnetic material (\( \mu = 1 \)), by introducing a complex refractive index \( \tilde{n} = \sqrt{\varepsilon} = n + i\kappa \), we can write:

\[ E(\mathbf{r}, t) = E_0 e^{i\frac{\omega}{c} \tilde{n} \hat{k} \cdot \mathbf{r}} e^{-\kappa \frac{\omega}{c}}. \] (A.15)
Appendix B

Kleinman and Bylander Form for j-dependent Pseudopotentials

The non-local part of the Kleinman and Bylander form for j-dependent pseudopotentials is given by Eq. (3.36). The pseudo wavefunctions appearing in that equation are given by:

\[ |\psi_{l,j,m_j}^{PP} \rangle = |R_{l,j}^{PP} \rangle |\Omega_{j,l,m_j} \rangle \]  

(B.1)

where \( R_{l,j}^{PP} \) is the radial part of the pseudo wavefunction and \( |\Omega_{j,l,m_j} \rangle \) are the total angular momentum eigenfunctions. The \( |\Omega_{j,l,m_j} \rangle \) can be written in terms of the spherical harmonics \( |Y_{l}^{m} \rangle \) and the eigenfunctions of the z component of the Pauli spin operator, \( |\uparrow \rangle \) and \( |\downarrow \rangle \). We then have, for \( j = l + \frac{1}{2}, m_j = m + \frac{1}{2} \):

\[ |\Omega_{j,l,m_j} \rangle = \left( \frac{l + m + 1}{2l + 1} \right)^{1/2} |Y_{l}^{m} \rangle |\uparrow \rangle + \left( \frac{l - m}{2l + 1} \right)^{1/2} |Y_{l}^{m+1} \rangle |\downarrow \rangle \]  

(B.2)

and for \( j = l - \frac{1}{2}, m_j = m - \frac{1}{2} \):

\[ |\Omega_{j,l,m_j} \rangle = \left( \frac{l - m + 1}{2l + 1} \right)^{1/2} |Y_{l}^{m-1} \rangle |\uparrow \rangle - \left( \frac{l + m}{2l + 1} \right)^{1/2} |Y_{l}^{m} \rangle |\downarrow \rangle \]  

(B.3)

Sometimes it is convenient to write the non-local part of Eq. (3.36) in terms of spherical harmonics and Pauli matrices. To do this we note that the sum over \( j \) runs from
\[ j = l - \frac{1}{2} \text{ to } j = l + \frac{1}{2} \]. By writing explicitly those terms we get:

\[ \hat{v}_{NL} = \sum_{l} \left[ \sum_{m=-l}^{l} \left( \frac{l+m+1}{2l+1} \hat{P}_{l,l+\frac{1}{2}}^{m,m} \hat{S}_{\uparrow\uparrow}^{\uparrow} + \frac{l-m+1}{2l+1} \hat{P}_{l,l+\frac{1}{2}}^{m+1,m+1} \hat{S}_{\downarrow\downarrow}^{\downarrow} \right) + \right. \]

\[ + \sum_{m=-l+1}^{l} \left( \frac{l-m+1}{2l+1} \hat{P}_{l,l-\frac{1}{2}}^{m-1,m-1} \hat{S}_{\downarrow\downarrow}^{\downarrow} + \frac{l+m+1}{2l+1} \hat{P}_{l,l-\frac{1}{2}}^{m,m} \hat{S}_{\uparrow\uparrow}^{\uparrow} \right) \]

\[ + \sum_{m=-l+1}^{l} \sqrt{(l+m+1)(l-m)} \left( \hat{P}_{l,l+\frac{1}{2}}^{m+1,m+1} \hat{S}_{\uparrow\downarrow}^{\uparrow\downarrow} + \hat{P}_{l,l+\frac{1}{2}}^{m,m} \hat{S}_{\downarrow\uparrow}^{\downarrow\uparrow} \right) - \]

\[ - \sum_{m=-l+1}^{l} \sqrt{(l+m+1)(l-m)} \left( \hat{P}_{l,l-\frac{1}{2}}^{m-1,m-1} \hat{S}_{\downarrow\uparrow}^{\downarrow\uparrow} + \hat{P}_{l,l-\frac{1}{2}}^{m,m} \hat{S}_{\uparrow\downarrow}^{\uparrow\downarrow} \right) \right] , \tag{B.4} \]

with

\[ \hat{P}_{l,j}^{m,m} = \frac{\langle R_{l,j}^{PP} Y_{l,m}^{PP} | \delta v_{l,j}^{PP} \rangle}{\langle R_{l,j}^{PP} | \delta v_{l,j}^{PP} | R_{l,j}^{PP} \rangle} , \tag{B.5} \]

and

\[ \hat{S}_{\uparrow\uparrow}^{\uparrow} = | \uparrow \rangle \langle \uparrow | ; \ \hat{S}_{\downarrow\downarrow}^{\downarrow} = | \downarrow \rangle \langle \downarrow | ; \ \hat{S}_{\uparrow\downarrow}^{\uparrow\downarrow} = | \uparrow \rangle \langle \downarrow | ; \ \hat{S}_{\downarrow\uparrow}^{\downarrow\uparrow} = | \downarrow \rangle \langle \uparrow | . \tag{B.6} \]

By making the appropriate changes in the summation ranges in Eq. (B.4), we can write:

\[ \hat{v}_{NL} = \sum_{l} \left[ \sum_{m=-l}^{l} \left( \frac{l+m+1}{2l+1} \hat{P}_{l,l+\frac{1}{2}}^{m,m} \hat{S}_{\uparrow\uparrow}^{\uparrow} + \frac{l-m+1}{2l+1} \hat{P}_{l,l+\frac{1}{2}}^{m+1,m+1} \hat{S}_{\downarrow\downarrow}^{\downarrow} \right) + \right. \]

\[ + \sum_{m=-l+1}^{l} \left( \frac{l-m+1}{2l+1} \hat{P}_{l,l-\frac{1}{2}}^{m-1,m-1} \hat{S}_{\downarrow\downarrow}^{\downarrow} + \frac{l+m+1}{2l+1} \hat{P}_{l,l-\frac{1}{2}}^{m,m} \hat{S}_{\uparrow\uparrow}^{\uparrow} \right) \]

\[ + \sum_{m=-l+1}^{l} \sqrt{(l+m+1)(l-m)} \left( \hat{P}_{l,l+\frac{1}{2}}^{m+1,m+1} \hat{S}_{\uparrow\downarrow}^{\uparrow\downarrow} + \hat{P}_{l,l+\frac{1}{2}}^{m,m} \hat{S}_{\downarrow\uparrow}^{\downarrow\uparrow} \right) - \]

\[ - \sum_{m=-l+1}^{l} \sqrt{(l+m+1)(l-m)} \left( \hat{P}_{l,l-\frac{1}{2}}^{m-1,m-1} \hat{S}_{\downarrow\uparrow}^{\downarrow\uparrow} + \hat{P}_{l,l-\frac{1}{2}}^{m,m} \hat{S}_{\uparrow\downarrow}^{\uparrow\downarrow} \right) \right] , \tag{B.7} \]

and by making use of the following relations:

\[ \hat{S}_{\uparrow\uparrow}^{\uparrow} = \frac{1}{2} (\sigma_{0} + \sigma_{z}) ; \ \hat{S}_{\downarrow\downarrow}^{\downarrow} = \frac{1}{2} (\sigma_{x} + i \sigma_{y}) ; \ \hat{S}_{\uparrow\downarrow}^{\uparrow\downarrow} = \frac{1}{2} (\sigma_{x} - i \sigma_{y}) ; \ \hat{S}_{\downarrow\uparrow}^{\downarrow\uparrow} = \frac{1}{2} (\sigma_{0} - \sigma_{z}) \tag{B.8} \]
we get:

\[
\hat{v}_{\text{NL}} = \sum_l \sum_{m=-l}^{l} \left\{ \hat{P}_{l,l+\frac{1}{2}}^{m,m} \left( \frac{l+1}{2l+1} \sigma_0 + \frac{m}{2l+1} \sigma_z \right) + \right. \\
+ \hat{P}_{l,l-\frac{1}{2}}^{m,m} \left( \frac{l}{2l+1} \sigma_0 - \frac{m}{2l+1} \sigma_z \right) \right. \\
+ \left. \sum_{m=-l-1}^{l} \frac{\sqrt{(l+m+1)(l-m)}}{2(2l+1)} \left[ (\sigma_x + i \sigma_y) \left( \hat{P}_{l,l+\frac{1}{2}}^{m,m+1} - \hat{P}_{l,l-\frac{1}{2}}^{m,m+1} \right) + \\
+ (\sigma_x - i \sigma_y) \left( \hat{P}_{l,l+\frac{1}{2}}^{m+1,m} - \hat{P}_{l,l-\frac{1}{2}}^{m+1,m} \right) \right] \right\}. 
\]

(B.9)

If we keep only the terms in \( \sigma_0 \), which is equivalent to neglecting the spin-orbit coupling term, we end up with:

\[
\hat{v}_{\text{NL}} = \sum_l \sum_{m=-l}^{l} \left( \frac{l+1}{2l+1} \hat{P}_{l,l+\frac{1}{2}}^{m,m} + \frac{l}{2l+1} \hat{P}_{l,l-\frac{1}{2}}^{m,m} \right), 
\]

(B.10)

which is just, as expected, the \( j \)-average of the \( j \)-dependent projectors.
Appendix C

Symmetries and the Calculation of the Polarizability Tensor†

The dipole-dipole polarizability is a three-dimensional tensor. Because of this tensorial character, one way of simplifying the calculation of the polarizability is to take advantage of the symmetries of the system by using Neumann’s principle [165]: the polarizability tensor of the system must be left invariant under any transformation that is also a point symmetry operation of the system. This condition of invariance reduces the number of independent tensor components, since it signifies relationships between those components, thus potentially reducing the number of calculations necessary to obtain the full tensor.

Numerous theoretical techniques can be used to calculate polarizabilities, with varying level of accuracy and detail. In particular, there is a class of methods that rely on the explicit use of the external perturbation, i.e., each line of the tensor is obtained by performing one calculation. This means that, in order to calculate the full tensor, we perform three calculations, one for each spatial direction. Because of this, when using these methods it is not always obvious along which directions the perturbing fields should be applied in order to make full use of Neumann's principle. In the following sections we will show how this can be achieved in order to severely reduce the number of actual calculations.

†This appendix is an adaptation of the article:

C.1 Spatial symmetries

By making use of Eq. (2.41), it is easy to prove that $\alpha(\omega)$ is a proper tensor: if we consider a second orthonormal reference frame $\{\hat{e}'_1, \hat{e}'_2, \hat{e}'_3\}$, $\alpha(\omega)$ transforms according to the tensorial transformation law:

$$\alpha'(\omega) = P^t \alpha(\omega) P,$$  \hspace{1cm} (C.1)

where $\alpha'(\omega)$ is the polarizability in the second reference frame, and $P$ is the rotation matrix between the two frames.

This tensorial character of the polarizability permits us to work in any orthonormal reference frame; once we obtain its values, we may easily transform it by straightforward matrix manipulation. We may then choose the frame which is most appropriate, bearing in mind the geometry of the molecule, and this can reduce the total number of calculations. However, this liberty does not allow us to make full use of symmetry. For this purpose, we need to work with non-orthonormal directions.

Let us consider three linearly-independent, but possibly non-orthogonal, unit vectors $\{\hat{p}_1, \hat{p}_2, \hat{p}_3\}$. We define the polarizability elements $\tilde{\alpha}_{uv}(\omega)$ as:

$$\tilde{\alpha}_{uv}(\omega) = - \int d\vec{r} \int d\vec{r}' (\vec{r} \cdot \hat{p}_u) \chi(\vec{r}, \vec{r}', \omega)(\vec{r}' \cdot \hat{p}_v).$$  \hspace{1cm} (C.2)

This corresponds to a process in which the polarization of the perturbing field is along $\hat{p}_v$, and the dipole is measured along $\hat{p}_u$. If we know the 3x3 matrix $\tilde{\alpha}(\omega)$, we get the real tensor $\alpha(\omega)$ by making use of the following simple relationship, which can be obtained once again from Eq. (2.41):

$$\tilde{\alpha}(\omega) = P^t \alpha(\omega) P.$$  \hspace{1cm} (C.3)

$P$ is the transformation matrix between the original orthonormal reference frame and $\{\hat{p}_1, \hat{p}_2, \hat{p}_3\}$. Note that this transformation is in general not a rotation; $P$ is not unitary. Moreover, no matter how familiar it looks, Eq. (C.3) is not a change of coordinates: $\tilde{\alpha}(\omega)$ is not the polarizability tensor in the new reference frame. And finally, also note that the traces of $\tilde{\alpha}$ and $\alpha$ do not coincide:

$$\text{Tr} [\tilde{\alpha}(\omega)] = \text{Tr} [P^t \alpha(\omega) P] = \text{Tr} [\alpha(\omega) PP^t].$$  \hspace{1cm} (C.4)

but $PP^t \neq 1$. Notwithstanding this, it tells us that we may obtain the polarizability tensor by calculating the related object $\tilde{\alpha}(\omega)$. 


Now let us assume that the molecule under study possesses some non-trivial symmetry transformations – to start with, we consider that it has two, $A$ and $B$. We consider an initial unit vector, $\hat{p}_1$, and define:

$$\hat{p}_2 = A\hat{p}_1$$
$$\hat{p}_3 = B\hat{p}_2$$

We assume that this may be done such that the set $\{\hat{p}_1, \hat{p}_2, \hat{p}_3\}$ is linearly independent.

We then perform a TDDFT calculation with the perturbing field polarized in the direction $\hat{p}_1$. This permits us to obtain the row $\{\tilde{\alpha}_{11}, \tilde{\alpha}_{12}, \tilde{\alpha}_{13}\}$. Since the matrix is symmetric, we also have the column $\{\tilde{\alpha}_{11}, \tilde{\alpha}_{21}, \tilde{\alpha}_{31}\}$. The symmetry of the molecule also permits us to obtain the diagonal: $\{\tilde{\alpha}_{33} = \tilde{\alpha}_{22} = \tilde{\alpha}_{11}\}$. The only missing element is $\tilde{\alpha}_{23} = \tilde{\alpha}_{32}$, but it is easy to prove that:

$$\tilde{\alpha}_{23} = \tilde{\alpha}_{1, A^{-1}} \hat{p}_3,$$

which we can also get from our original calculation. The conclusion is that we have access to the full tensor by making only one calculation.

To fix ideas, we use the example of a molecule with one $n$-th order axis of symmetry ($n > 2$). Let $R$ be the rotation of $2\pi/n$ degrees around this axis. We then choose $\hat{p}_1$ not collinear with this axis, and also not perpendicular to it. If we define $R\hat{p}_1 = \hat{p}_2$ and $R\hat{p}_2 = \hat{p}_3$, the set $\{\hat{p}_1, \hat{p}_2, \hat{p}_3\}$ will be linearly independent. In this case, moreover, since $A = B = R$, Eq. (C.6) reduces to $\tilde{\alpha}_{23} = \tilde{\alpha}_{12}$.

It may very well be that we may only find two linearly independent “equivalent axes”, $\hat{p}_1$ and $\hat{p}_2$, related by a symmetry transformation, $A$ – this is the case of a system that possesses only a plane of symmetry, or only an axis of symmetry of order two. We may then define $\hat{p}_1$ to be a tilted vector with respect to this plane (not contained in it, and not perpendicular to it). Then, $\hat{p}_2 = A\hat{p}_1$, where $A$ is the reflection on the plane, is an equivalent vector, and $\hat{p}_3$ can be chosen to lie in the symmetry plane (the obvious choice will be $\hat{p}_3 = \hat{p}_1 \wedge \hat{p}_2$, that ensures linear independence). We then only need two calculations, one with the polarization along $\hat{p}_1$ (or $\hat{p}_2$) and another with the polarization along $\hat{p}_3$. Moreover, if $\hat{p}_1$ is chosen to be tilted exactly by $\pi/2$ with respect to the symmetry plane, the system of vectors is orthonormal, and we do not even need to apply Eq. (C.3). Note that this case applies to all planar molecules.
C.2 Spin-independent and spin-dependent perturbations in spin-saturated systems

We consider a system whose ground state is spin-saturated. It verifies:

\[ \alpha_{ij}^{\uparrow\uparrow} = \alpha_{ij}^{\downarrow\downarrow}, \quad (C.7a) \]
\[ \alpha_{ij}^{\uparrow\downarrow} = \alpha_{ij}^{\downarrow\uparrow}. \quad (C.7b) \]

And, in consequence, \( \alpha_{ij}^{[nm]} = \alpha_{ij}^{[mn]} = 0 \), and

\[ \alpha_{ij}^{[nn]} = 2\alpha_{ij}^{\uparrow\uparrow} + 2\alpha_{ij}^{\uparrow\downarrow}, \quad (C.8a) \]
\[ \alpha_{ij}^{[mm]} = 2\alpha_{ij}^{\uparrow\uparrow} - 2\alpha_{ij}^{\uparrow\downarrow}. \quad (C.8b) \]

Despite this symmetry, in order to obtain all spin-components (in this spin-saturated case there are only two independent components), by making use of the two types of perturbations defined in Eqs. (2.36) and (2.37), we would still need two calculations: one perturbing with a spin-independent potential – in order to obtain \( \alpha_{ij}^{[nn]} \), and one with a spin-dependent one – in order to obtain \( \alpha_{ij}^{[mm]} \).

However, one can easily use a similar scheme to the one outlined in the previous section in order to calculate the two polarizabilities in one shot. The idea is to apply a perturbation in the form:

\[ \delta v_{\sigma}^{[\uparrow]}(\vec{r}, \omega) = \begin{cases} 
-x_j \kappa(\omega), & \sigma = \uparrow \\
0, & \sigma = \downarrow 
\end{cases}, \quad (C.9) \]

or, in the Pauli matrix language:

\[ \delta v_{\sigma}^{[\uparrow]}(\vec{r}, \omega) = -\frac{1}{2} \kappa(\omega) x_j (\sigma_0 + \sigma_z). \quad (C.10) \]

It is then easy to verify that the response of the dipole observables will then be given by:

\[ \delta \langle \hat{X}_i \rangle_{\sigma}^{[\uparrow]}(\omega) = -\frac{1}{2} \kappa(\omega) \alpha_{ij}^{[nn]}, \quad (C.11a) \]
\[ \delta \langle \hat{X}_i \hat{\sigma}_z \rangle_{\sigma}^{[\uparrow]}(\omega) = -\frac{1}{2} \kappa(\omega) \alpha_{ij}^{[mm]}, \quad (C.11b) \]

thus providing us with the components of the two response functions that we need with only one calculation.
Figure C.1: Two different views of protonated triphenylguanidine (point group $C_{3v}$). In this picture, the dark blue atoms are nitrogen, the cyan represent carbon, and finally the white atoms are hydrogen.

C.3 Examples

There are many complex molecules of technological relevance that present symmetries such that the schemes outlined in the previous sections can be used. We chose two of them to illustrate the method: protonated triphenylguanidine and one hydrogenated silicon cluster $\text{Si}_8\text{H}_{18}$. Triphenylguanidine compounds are regarded as interesting for quadratic nonlinear optical applications while hydrogenated silicon is an important optico-electronic material with potentially important technological applications.

The ground-state of protonated triphenylguanidine is spin-saturated, has one proper axis of symmetry of order three, one plane of symmetry, and one improper axis of rotation of order three (see Fig. C.1). The ground-state of $\text{Si}_8\text{H}_{18}$ is spin-saturated, has an inversion center, one proper axis of symmetry of order three, three proper axis of symmetry of order two, three planes of symmetry, and one improper axis of symmetry of order six (see Fig. C.2). This means that one can make use of the schemes outlined in the previous sections to obtain all the components of both $\alpha^{[nn]}(\omega)$ and $\alpha^{[mm]}(\omega)$ with only one calculation.

Without using the symmetry of the system the response functions were computed by applying spin-independent and spin-dependent perturbations from Eqs. (2.36) and (2.37) with polarization directions along the $x$, $y$ and $z$ directions. This way the response func-
Figure C.2: One view of Si$_8$H$_{18}$ (point group $D_{3d}$). In this picture, the dark brown atoms are silicon and the gray atoms are hydrogen.

tions were straightforwardly obtained but required a total of six time-propagations.

To use the symmetry a set $\{\hat{p}_1, \hat{p}_2, \hat{p}_3\}$ is needed. In the case of protonated triphenyl-guanidine we built it by defining $\hat{p}_1$ to be a vector tilted by $\pi/4$ with respect to the plane of symmetry and the two symmetry transformations $A$ and $B$ to be an inversion with respect to the plane and a $2\pi/3$ rotation around the axis of symmetry of order 3. In the case of Si$_8$H$_{18}$ we chose $\hat{p}_1$ to be a vector tilted by $\pi/4$ with respect to the axis of symmetry of order three and both symmetry transformations $A$ and $B$ to be $2\pi/3$ rotations around the same axis.

Applying a perturbation of the same form as Eq. (C.9) with a polarization direction along $\hat{p}_1$ and using Eqs. (C.3), (C.11a) and (C.11b) allowed us to obtain the response functions with just one calculation in both cases.

All response calculations were done with octopus using the Perdew-Zunger [39, 41] parametrization of the adiabatic local density approximation for the exchange-correlation potential.

To represent the wavefunctions in real space we used a uniform grid with a spacing of 0.195 Å and a box composed by spheres of radius 5 Å around every atom. In order to propagate the Kohn-Sham orbitals we employed state of the art algorithms [148]. A time
Figure C.3: Dipole and spin-dipole strength functions of protonated triphenylguanidine (upper panel) and Si$_8$H$_{18}$ (lower panel). The curves obtained with and without the use of symmetry completely overlap.
step of 0.0048 fs assured the stability of the time propagation, and a total propagation time of 19.35 fs allowed a resolution of about 0.1 eV in the resulting spectrum.

The results obtained are summarized in Fig. C.3 where we plot the dipole and spin-dipole strength functions. The results with and without the use of symmetry completely overlap, as expected.
Appendix D

APE, the Atomic Pseudopotentials Engine†

I’d rather be a climbing ape than a falling angel.

Terry Pratchett

All the norm-conserving pseudopotentials used in this thesis were generated using the Atomic Pseudopotentials Engine (APE) code. APE is a DFT atomic code and pseudopotential generator. In this chapter we will present the numerical details of the implementation, the structure of the code, and an example of a practical calculation.

D.1 Numerical details

D.1.1 Solution of the single-particle equations

The first step to solve the Kohn-Sham equations for an atom is to obtain the solutions of the one-particle equations.

†This appendix is an adaptation of the article:

Equations (3.6) for the fully relativistic case are of first order. Second order equations (3.2) and (3.4) for the non-relativistic and scalar-relativistic cases can be trivially transformed into a set of coupled first order equations. Therefore, whatever formulation of DFT used, one is left with two coupled one-dimensional first order differential equations and the same numerical method can be used to solve them. One should note that the eigenvalues $\varepsilon_{nl}$ and the eigenfunctions must be obtained simultaneously.

The solutions of the single-particle equations, for a given, fixed, electronic density, are obtained in the following way:

1. Let $f(r)$ and $g(r)$ be the functions to be determined when solving the set of differential equations.

2. For a given energy $\varepsilon_{nl}$ choose two arbitrary values $f(r_0)$ and $f(r_\infty)$ where $r_0$ is a point close to the origin and $r_\infty$ is a point very far away.

3. Compute $g(r_0)$ and $g(r_\infty)$ using boundary conditions determined from the equations to solve when $r \to 0$ and $r \to \infty$.

4. Knowing $f(r_0)$ and $g(r_0)$ and using a suitable algorithm to solve ordinary differential equations it is possible to obtain the values of $f$ and $g$ at a point $r_m$ lying between $r_0$ and $r_\infty$. A good choice for $r_m$ is the classical turning point.

5. Repeat the previous step, but starting the integration from “practical infinity” $r_\infty$.

6. Let $f_1(r)$ and $g_1(r)$ be the functions obtained at step (3) and $f_2(r)$ and $g_2(r)$ the functions obtained at step (4). Multiply $f_1(r)$ and $g_1(r)$ by $f_2(r_m)/f_1(r_m)$. This makes $f(r)$ continuous at $r_m$.

7. $\varepsilon_{nl}$ is an eigenvalue when $g_1(r_m) = g_2(r_m)$, so the problem of finding the eigenvalues can be reduced to the problem of finding the roots of the function $g_1(r_m) - g_2(r_m)$.

There are several methods that can be used at steps (4) and (5). We have chosen to rely on the methods available in the GNU Scientific Library [166] (GSL) that provide the solutions on an adaptive grid. As for the root finding problem (step (7)), since it is easy enough to bracket the eigenvalues, APE uses Brent’s method [167] to find the roots within a given tolerance.
D.1.2 Self-consistent cycle

The eigenfunctions obtained with the procedure outlined above are used to rebuild the electronic density (Eqs. (3.3) or (3.8)). Since the Kohn-Sham potential depends on the density, a new density corresponds to a new potential, and the differential equations have to be solved again, in a self-consistent manner. The self-consistency cycle ends when some stopping criterion is met. In APE, the stopping criterion is based on the difference between the new and the old Kohn-Sham potential.

D.1.3 Grids

All the quantities that need to be kept in memory are stored on a radial logarithmic grid. This is the most suitable kind of grid for this purpose since a higher density of points is needed near the origin. Unfortunately there is more than one way to define a logarithmic grid, so we implemented two commonly used ways to construct it. In both cases, two parameters $a$ and $b$ are required. The $i^{th}$ point of the grid is defined as $r_i = b e^{ai}$ in one case and as $r_i = b (e^{ai} - 1)$ in the other case. The parameters $a$ and $b$ are determined by specifying the number of grid points and the starting and ending points.

Since some of the quantities are determined on an adaptive grid, cubic splines are used to extrapolate their values on the logarithmic grid. The numerical calculation of integrals and derivatives is also done using cubic splines. All the spline operations are handled by the GSL.

D.1.4 Hartree and exchange-correlation potential

The evaluation of the Hartree potential is straightforward in the case of a spherically symmetric density:

$$v_{\text{Hartree}}(r) = \frac{4\pi}{r} \int_0^r dr' \ r'^2 n(r') + 4\pi \int_r^\infty dr' \ r' n(r') . \quad (D.1)$$

For the evaluation of the exchange and correlation potential the code uses the library of functionals written in C for the octopus project (see Sec. E.1.6). This library provides a great number of LDA and GGA functionals as well as their relativistic extensions.
D.1.5 Mixing

In order to avoid instabilities during the self-consistent cycle, the input density for the next iteration is built using the densities of the previous iterations. Both linear mixing [168] and the generalized Broyden algorithm of Johnson [169] are implemented in the code.

D.1.6 Unbound states

In order to generate the pseudopotential for channels associated to unbound states, the code offers two options for the pseudo state reference energy. The first option is the one used in José Luís Martins’ code [84], i.e., the reference energy is assumed to be zero. The other option is the one used in the FHI98PP code [170] which consists in considering that all pseudo states corresponding to unbound all-electron levels have the same energy as the least bound state.

D.2 Program structure

In order to make the compilation and installation of the code user friendly APE uses the GNU autotools. This means that, on most machines, issuing the following commands:

```
./configure
make
make install
```

will compile and install the code, as long as there are C and Fortran 90/95 compilers available and the GSL library is installed in some standard directory. More information about compilation and installation can be found in the code manual.

For the program structure an effort was made to use, whenever possible, object-oriented programming concepts and solutions. The basic structure of the majority of the modules is the same: one data structure followed by routines to initialize, to use and to end that structure.

In Fig. D.1 it is possible to see how the most important modules are connected to each other. Here follows a brief description of their contents:

- **run ape**: executes the necessary tasks for each run mode.
Figure D.1: Simplified schematic chart of the program. Here are depicted the relationships between the most important modules. The modules bellow the dashed line are used be most of the other modules.
- **ps_atom**: contains the routines to deal with the pseudo atom (the pseudo states and the corresponding pseudopotentials).
- **atom**: performs operations on the set of atomic orbitals, like computing the total energy or the atomic density.
- **scf**: performs the self-consistent cycle procedure in order to obtain the ground-state of the system from the Kohn-Sham equations.
- **pseudostates**: a pseudo state includes all the information necessary to generate a given pseudopotential component.
- **states**: this module contains routines to deal with orbitals. An orbital is defined as a set of quantum numbers, an energy and the corresponding wavefunction.
- **eigensolver**: given a potential and a set of quantum numbers, it finds the eigenvalue and eigenstate.
- **hamann**: given an all-electron potential and wavefunctions, generates the corresponding pseudopotentials using the Hamann scheme.
- **tm**: given an all-electron potential and wavefunctions, generates the corresponding pseudopotentials using the Troullier-Martins scheme or its relativistic extension.
- **mrpp**: given an all-electron potential and wavefunctions, generates the corresponding pseudopotentials using the Troullier-Martins scheme with explicit incorporation of semi-core states.
- **wave_equation**: for a given set of quantum numbers, an energy, and a potential it returns the wavefunction or the logarithmic derivative of the wavefunction at a given point.
- **wave_equation_integrator**: performs the integration of the ordinary differential equations.
- **potentials**: handles the all-electron potentials and pseudopotentials.
- **mesh**: defines the mesh data type and contains the routines to generate the grids.

The input files are read using a parser that was originally written for the Octopus project (see Sec. E.2). More information about the parser and the input variables can be found in the code manual.
Besides the code itself the APE package includes some useful extra bits in the following sub-directories:

- **doc**: A comprehensive manual with a complete description of the input file variables.
- **sample**: Input files to be used as examples.
- **testsuite**: A set of tests to verify the compilation of the code and to validate changes introduced in the code.

### D.3 Input and selected output files for chromium

Below we present an input file for the generation of a chromium pseudopotential. This potential was generated by firstly solving the all-electron relativistic equations (Eq. (3.6)) using the local density approximation for exchange and correlation. The pseudopotential was created in the same run, as `CalculationMode` has been set to `ae + pp`.

```plaintext
# Generalities
Title = "Chromium"
CalculationMode = ae + pp
Verbose = 40

# Hamiltonian
WaveEquation = dirac
XFunctional = lda_x
CFunctional = lda_c_pw

# Specie
NuclearCharge = 24

%Orbitals
"Ar"
  4 | 0 | 0 | 1
  3 | 2 | 0 | 5
  4 | 1 | 0 | 0
%

# Mesh
MeshType = log2
MeshStartingPoint = 1e-07
MeshOutmostPoint = 80.0
MeshNumberOfPoints = 900

# SCF
ConvAbsDens = 1.0e-7

# Pseudopotentials
```
PPScheme = mrpp
PPRelativisticMode = j_dependent
%PPSemiCoreComponents
0  | 1.71
1  | 1.90
%
%PPComponents
0  | 2.80
1  | 3.70
2  | 1.10
%
PPCalculationTolerance = 1e-7
PPOutputFileFormat = upf
Lmax = 2
Llocal = 1

# Wave equations solver
EigenSolverTolerance = 1e-7
ODEIntTolerance = 1e-7

The result of the all-electron calculation outlined above is the set of 10 occupied orbitals plus the unoccupied 4p orbitals. All the orbitals are saved in the files `ae/wf-*`. The file `ae/info` contains the information printed below.

General Information about the atom:
Relativistic spin-unpolarized calculations for Cr
Nuclear charge : 24.00
Total charge : 0.00
Correlation model: Perdew & Wang
Exchange model : Slater exchange
Configuration : State Occupation
1s0.5  | 2.00
2s0.5  | 2.00
2p0.5  | 2.00
2p1.5  | 4.00
3s0.5  | 2.00
3p0.5  | 2.00
3p1.5  | 4.00
4s0.5  | 1.00
3d1.5  | 2.00
3d2.5  | 3.00
4p0.5  | 0.00
4p1.5  | 0.00

Mesh information:
Type: logarithmic \([ri = b\exp(a*i - 1)]\)
Mesh starting point: 1.00E-07 b
Mesh outmost point: 80.000 b
Mesh parameters (a, b): 1.83455E-02, 5.40109E-06

SCF cycle information:
Number of iterations: 16
Convergence:
  ConvAbsDens = 7.99E-08 ( 1.00E-07)
  ConvRelDens = 3.33E-09 ( 0.00E+00)
  ConvAbsEvsum = 3.51E-07 ( 0.00E+00)
  ConvRelEvsum = 5.67E-10 ( 0.00E+00)

Energies [H]
Total energy: -1048.496427
Kinetic energy: 1060.260547
Electron-electron interaction energy: 443.898000
Electron-nucleus interaction energy: -2506.108477
Exchange-correlation energy: -46.546497

Eigenvalues [H]

State Occupation  Eigenvalue
1s0.5  2.00  -215.55627
2s0.5  2.00  -24.44921
2p0.5  2.00  -20.79631
2p1.5  4.00  -20.47931
3s0.5  2.00  -2.70273
3p0.5  2.00  -1.69141
3p1.5  4.00  -1.65369
4s0.5  1.00  -0.15402
3d1.5  2.00  -0.11673
3d2.5  3.00  -0.11386
4p0.5  0.00  -0.04033
4p1.5  0.00  -0.03930

At the end of the all-electron calculation, APE automatically generated a Multi-reference pseudopotential. The contents of pp/info are printed below. The pseudo wavefunctions were stored in the files pp/wf-*, while the files pp/pp-* contain the associated pseudopotential components. The pseudopotential operator is saved in the file Cr.UPF, in the default output format (PWscf).

Pseudo atom information:

Valence Configuration: State  Occupation
3s0.5  2.00
4s0.5  1.00
3p0.5  2.00
4p0.5  0.00
3p1.5  4.00
4p1.5  0.00
APE, the Atomic Pseudopotentials Engine

Wavefunction info:

<table>
<thead>
<tr>
<th>State</th>
<th>Node radius</th>
<th>Peak radius</th>
<th>Default core radius</th>
</tr>
</thead>
<tbody>
<tr>
<td>3s0.5</td>
<td>0.364</td>
<td>0.772</td>
<td>0.000</td>
</tr>
<tr>
<td>4s0.5</td>
<td>1.134</td>
<td>2.736</td>
<td>0.000</td>
</tr>
<tr>
<td>3p0.5</td>
<td>0.332</td>
<td>0.786</td>
<td>0.000</td>
</tr>
<tr>
<td>4p0.5</td>
<td>1.243</td>
<td>3.806</td>
<td>0.000</td>
</tr>
<tr>
<td>3p1.5</td>
<td>0.332</td>
<td>0.800</td>
<td>0.000</td>
</tr>
<tr>
<td>4p1.5</td>
<td>1.266</td>
<td>3.877</td>
<td>0.000</td>
</tr>
<tr>
<td>3d1.5</td>
<td>0.000</td>
<td>0.830</td>
<td>0.000</td>
</tr>
<tr>
<td>3d2.5</td>
<td>0.000</td>
<td>0.830</td>
<td>0.000</td>
</tr>
</tbody>
</table>

Pseudopotential Generation:

State: 3s0.5 4s0.5
Core radius: 1.710 2.800

MRPP coefficients:
\[
\begin{align*}
c_0 &= 0.3086380109 \\
c_2 &= 0.6279088951 \\
c_4 &= -0.0788539121 \\
c_6 &= -2.880017831 \\
c_8 &= 2.1621714796 \\
c_{10} &= -0.7219513315 \\
c_{12} &= -0.0014795868 \\
c_{14} &= 0.0630423598 \\
c_{16} &= -0.0155595379 \\
c_{18} &= 0.0012267747
\end{align*}
\]

State: 3p0.5 4p0.5
Core radius: 1.900 3.700

MRPP coefficients:
\[
\begin{align*}
c_0 &= 1.5290567875 \\
c_2 &= -1.4962731238 \\
c_4 &= -0.3198333231 \\
c_6 &= 0.4574328805 \\
c_8 &= -0.2181254346 \\
c_{10} &= 0.0638287265 \\
c_{12} &= -0.0135071091 \\
c_{14} &= 0.0021668561 \\
c_{16} &= -0.0002322019 \\
c_{18} &= 0.0000116551
\end{align*}
\]

State: 3p1.5 4p1.5
Core radius: 1.900 3.700

MRPP coefficients:
\[
\begin{align*}
c_0 &= 1.5015543957 \\
c_2 &= -1.4554260414 \\
c_4 &= -0.3026092789 \\
c_6 &= 0.3843251504 \\
c_8 &= -0.1436904378 \\
c_{10} &= 0.0237766648 \\
c_{12} &= -0.0007493216 \\
c_{14} &= -0.0002256873 \\
c_{16} &= 0.0000210500 \\
c_{18} &= 0.000003629
\end{align*}
\]

State: 3d1.5
Core radius: 1.100

Troullier-Martins coefficients:
\[
\begin{align*}
c_0 &= 2.6712140526 \\
c_2 &= -3.8978811903 \\
c_4 &= -1.6881641971 \\
c_6 &= 7.0184432583 \\
c_8 &= -6.8395815611 \\
c_{10} &= 3.0001063249 \\
c_{12} &= -0.5096699578
\end{align*}
\]

State: 3d2.5
Core radius: 1.100

Troullier-Martins coefficients:
\[
\begin{align*}
c_0 &= 2.6627905113 \\
c_2 &= -3.8904011581 \\
c_4 &= -1.6816912413 \\
c_6 &= 6.9969720400 \\
c_8 &= -6.8186595401 \\
c_{10} &= 2.9908494820 \\
c_{12} &= -0.5080852958
\end{align*}
\]
Pseudopotentials Self-Consistency:

<table>
<thead>
<tr>
<th>State</th>
<th>Eigenvalue [H]</th>
<th>Norm Test</th>
<th>Slope Test</th>
</tr>
</thead>
<tbody>
<tr>
<td>3s0.5</td>
<td>-2.70275</td>
<td>1.0002531</td>
<td>0.9999519</td>
</tr>
<tr>
<td>4s0.5</td>
<td>-0.15388</td>
<td>0.9983008</td>
<td>0.9976212</td>
</tr>
<tr>
<td>3p0.5</td>
<td>-1.69194</td>
<td>1.0002000</td>
<td>0.9993922</td>
</tr>
<tr>
<td>4p0.5</td>
<td>-0.04027</td>
<td>0.9970661</td>
<td>0.9967623</td>
</tr>
<tr>
<td>3p1.5</td>
<td>-1.65387</td>
<td>1.0001823</td>
<td>0.9997014</td>
</tr>
<tr>
<td>4p1.5</td>
<td>-0.03925</td>
<td>0.9971785</td>
<td>0.9968363</td>
</tr>
<tr>
<td>3d1.5</td>
<td>-0.11875</td>
<td>1.0340876</td>
<td>1.0202950</td>
</tr>
<tr>
<td>3d2.5</td>
<td>-0.11462</td>
<td>1.0125596</td>
<td>1.0073695</td>
</tr>
</tbody>
</table>

Kleinman & Bylander Atom

l-component used as local: \( l = 1 \)

Non-local components:

<table>
<thead>
<tr>
<th>State</th>
<th>KB Energy [H]</th>
<th>KB Cosine</th>
</tr>
</thead>
<tbody>
<tr>
<td>3s0.5</td>
<td>6.9948</td>
<td>0.3687</td>
</tr>
<tr>
<td>3p0.5</td>
<td>-0.0904</td>
<td>-0.5313</td>
</tr>
<tr>
<td>3p1.5</td>
<td>0.0450</td>
<td>0.5246</td>
</tr>
<tr>
<td>3d1.5</td>
<td>-10.6064</td>
<td>-0.3414</td>
</tr>
<tr>
<td>3d2.5</td>
<td>-10.5725</td>
<td>-0.3393</td>
</tr>
</tbody>
</table>

Ghost state analysis:

State: 3s0.5

- KB energy > 0; E0 < Eref < E1 \( \Rightarrow \) No ghost states
- Local potential eigenvalues: -4.6284 (E0) -0.3834 (E1)
- Reference energy: -2.7027 (Eref)

State: 3p0.5

- KB energy < 0; Eref < E0 \( \Rightarrow \) No ghost states
- Local potential eigenvalues: -1.6667 (E0) -0.0396 (E1)
- Reference energy: -1.6914 (Eref)

State: 3p1.5

- KB energy > 0; E0 < Eref < E1 \( \Rightarrow \) No ghost states
- Local potential eigenvalues: -1.6663 (E0) -0.0396 (E1)
- Reference energy: -1.6537 (Eref)

State: 3d1.5

- KB energy < 0; Eref < E0 \( \Rightarrow \) No ghost states
- Local potential eigenvalues: 0.0000 (E0) 0.0000 (E1)
- Reference energy: -0.1167 (Eref)

State: 3d2.5

- KB energy < 0; Eref < E0 \( \Rightarrow \) No ghost states
- Local potential eigenvalues: 0.0000 (E0) 0.0000 (E1)
- Reference energy: -0.1139 (Eref)
APE, the Atomic Pseudopotentials Engine
Appendix E

octopus†

Los ordenadores son inútiles. Sólo pueden darte respuestas.

Pablo Picasso

All the TDDFT calculations presented in this thesis were done using the octopus program. octopus materializes the main equations of density-functional theory in the ground state, and of time-dependent density-functional theory for dynamical effects. In brief, some of the key aspects that describe octopus are:

**Target problems:**

(i) Linear optical (i.e. electronic) response of molecules or clusters.

(ii) Non-linear response to classical high-intensity electromagnetic fields, taking into account both the ionic and electronic degrees of freedom.

(iii) Ground-state and excited state electronic properties of systems with lower dimensionality, such as quantum dots.

(iv) Photo-induced reactions of molecules (e.g., photo-dissociation, photo-isomerization, etc).

†This appendix is an adaptation of the article:


As such, the reported work includes the collaboration of the rest of the authors of the article.
(v) In the immediate future, extension of these procedures to systems that are infinite and periodic in one or more dimensions (polymers, slabs, nanotubes, solids), and to electronic transport.

Theoretical basis:

(i) The underlying theories are DFT and TDDFT. Also, the code may perform dynamics by considering the classical (i.e. point-particle) approximation for the nuclei. These dynamics may be non-adiabatic, since the system evolves following the Ehrenfest path. It is, however, a mean-field approach.

(ii) Regarding TDDFT, we have implemented two different approaches: On the one hand, the “standard” TDDFT-based linear-response theory, which provides us with excitation energies and oscillator strengths for ground-state to excited-state transitions. On the other hand, we have also implemented the explicit time-propagation of the TDDFT equations, which allows for the use of large external potentials, well beyond the range of validity of perturbation theory.

Methodology

(i) As numerical representation, we have chosen to work without a basis set, relying on numerical meshes. Nevertheless, auxiliary basis sets (plane waves, atomic orbitals) are used when necessary.

Recently, we have added the possibility of working with non-uniform grids, which adapt to the inhomogeneity of the problem, and of making use of multigrid techniques to accelerate the calculations.

(ii) For most calculations, the code relies on the use of pseudopotentials. Currently it allows for two types: norm-conserving and Hartwigsen-Goedecker-Hutter [147] pseudopotentials.

(iii) In addition to being able to treat systems in the standard 3 dimensions, 2D and 1D modes are also available. These are useful for studying, e.g., the two-dimensional electron gas that characterizes a wide class of quantum dots.

Technical aspects

(i) The code has been designed with emphasis on parallel scalability. In consequence, it allows for multiple task divisions.

(ii) The language of most of the code is Fortran 90 (almost 90,000 lines at present). Other languages, such as C or Perl, are also used.
(iii) Whenever possible, only standard and portable tools were employed. The resulting code may run on virtually any Unix-like platform.

(iv) The package is licensed under the GNU General Public License (GPL). In consequence, it is available for use, inspection, and modification for anyone, at http://www.tddft.programs/octopus/.

E.1 Numerical details

E.1.1 Grids

In octopus all spatial quantities are represented in a real space grid. This grid can be 1D, 2D or 3D, either uniform or non-uniform. In 3D, the simulation box can have the shape of a sphere, a cylinder, a parallelepiped, or be composed of spheres centered at each atomic position.

If we represent each function by the vector formed by the values it takes on the grid points, then the basic space operations (sum, difference, etc) are just the basic vector space operations. On a regular grid, i.e., a grid where the points are equispaced between each other, the calculation of the integral of a function \( f \) is given by:

\[
\int dr \, f(r) \approx \sum_i f(r_i) \Delta V ,
\]  
(E.1)

where the volume occupied by each point \( \Delta V \) is just the total volume of the simulation box divided by the number of points. The calculation of derivatives, more complicated, since it is a non-local operation, is performed using a finite-order rule, so that the Laplacian operator is discretized in the following way:

\[
\nabla^2 f(r_i) \approx \sum_j c_j f_j .
\]  
(E.2)

The coefficients \( c_j \) can be calculated to the desired order using a suitable algorithm [171].

Besides the usual regular grids, it is also possible in octopus to have “adaptive” or “curvilinear” grids. These grids result from a deformation of a regular grid through some transformation function, such that the density of points increases in the regions of space where the problem requires a larger resolution [172–180]. An example of curvilinear coordinates is based on the following transformation function, first proposed by Gygi [172,
Figure E.1: An adaptive-coordinates representation is constructed through the definition of a coordinate transformation function $\xi$.

173]

$$\xi^m = x^m + \sum_\alpha (x^m - R^m_\alpha) f_\alpha(|x - \bar{R}_\alpha|),$$  \hspace{1cm} (E.3a)

$$f_\alpha(r) = A_\alpha \frac{a_\alpha}{r} \tanh \left( \frac{r}{a_\alpha} \right) \exp \left[ - \left( \frac{r}{b_\alpha} \right)^2 \right],$$  \hspace{1cm} (E.3b)

where $\alpha$ runs over the atoms, and $\bar{R}_\alpha$ are the atomic positions. The parameters $A_\alpha$, $a_\alpha$, and $b_\alpha$ fine-tune the transformation – what will be the resolution enhancement, the region around each atom where the regular grid is transformed, etc.

The basic operations do not change with adaptive grids, but that is not the case for integration and differentiation. Integration now becomes a weighted sum:

$$\int dr \, f(r) \approx \sum_i \omega_i \Delta V_i f_i,$$  \hspace{1cm} (E.4)

where the volume element is now position dependent and $\omega_i$ is the Jacobian of the transformation:

$$\omega_i = \det \left[ \frac{\partial \xi^m}{\partial x^n} \right]_i.$$  \hspace{1cm} (E.5)

In principle, we can use the transformation laws to relate the differential operators in the new grid to the usual well-known finite-differences discretization expressions in the uniform space:

$$\nabla^2 = \sum_{mn} g^{mn} \frac{\partial}{\partial \xi^m} \frac{\partial}{\partial \xi^n} + \sum_{pq} \frac{\partial \xi^p}{\partial x^q} \frac{\partial}{\partial x^q} \left( \frac{\partial \xi^m}{\partial x^q} \right) \frac{\partial}{\partial \xi^m}.$$  \hspace{1cm} (E.6)

This, however, involves a lot of computational effort, and in general does not provide a Hermitian operator. Instead, the following approach is used:
• Select a stencil: given each point in the grid, the stencil is the set of neighboring points from which we calculate the action of any differential operator \( D \):

\[
(D(f))_i = \sum_{j \in \text{Stencil}(i)} C_{ij} f_j .
\]

(E.7)

• Select a set of polynomials \( \{x^\alpha y^\beta z^\delta\} \), of equal number to the points in the stencil: the coefficients \( C_{ij} \) are fixed by ensuring that the action of \( D \) on these polynomials is exact. This amounts to solving a linear system of equations of the order of the size of the stencil for each point of the grid. This operation must be performed at the beginning of the calculations, or every time that the grid is redefined.

• The Laplacian operator is Hermitian; the gradient operator is anti-Hermitian. The resulting numerical operator \( C \), however, is not (anti) Hermitian. But it can be (anti) symmetrized by transforming the matrix \( C \) in the following way:

\[
\tilde{C} = \frac{1}{2} (C \pm W^{-1}CW).
\]

(E.8)

E.1.2 Eigensolvers

Once we know how to construct the real-space representation of the Hamiltonian for a “trial” density \( n \) (or, in fact, for a trial set of KS orbitals \( \varphi_i \) from which the density is generated), we are faced with the problem of solving the Kohn-Sham equations (1.40) for the \( N \) lowest lying eigenpairs of this Hamiltonian operator. In real space this amounts to the solution of an eigenproblem for large sparse matrices. The literature in this field is abundant \([181, 182]\), and we have tried several schemes in \textit{octopus}. The following are available in the current version of the code: conjugate-gradients based schemes \([183, 184]\), Lanczos-based algorithms \([185–187]\) and the Jacobi-Davidson procedure \([188]\).

E.1.3 Mixing

The mixing of the density is essential for the convergence of the self-consistent procedure. For that purpose, \textit{octopus} employs some standard techniques. Essentially, one has to build recursively a series of densities \( n^{(i)} \) that converges to the solution density \( n_0 \). Each new density is generated through a prescription of the form:

\[
n^{(i+1)} = G[\tilde{n}^{(i+1)}, n^{(i)}, n^{(i-1)}, \ldots, n^{(i-s)}],
\]

(E.9)

where \( \tilde{n}^{(i+1)} \) is the density obtained from Eq. (3.3) using the Kohn-Sham orbitals of step \( i + 1 \). The simplest example of such a prescription is the so-called “linear mixing” \([168]\), for
which Eq. (E.9) takes the form: \( n^{(i+1)} = (1 - \alpha)\tilde{n}^{(i+1)} + \alpha n^{(i)} \). However, \texttt{octopus} allows for more sophisticated procedures: the generalized Broyden algorithm of Johnson [169, 189–192], and the “guaranteed reduction” Pulay algorithm [193].

### E.1.4 Time-evolution

For the explicit integration of Eqn. (2.11) in real time one uses a propagation algorithm. In other words, we use a numerical representation of the evolution operator \( \hat{U}(t + \Delta t, t) \):

\[
\varphi(\vec{r}, t + \Delta t) = \hat{U}(t + \Delta t, t)\varphi(\vec{r}, t). \tag{E.10}
\]

In TDDFT we are dealing with the integration of a set of coupled Schrödinger-like equations, characterized by two important facts: (i) The Hamiltonian is intrinsically time-dependent, even if there is no external potential, since the Hartree and xc parts depend on the time-dependent density; (ii) The Hamiltonian – at least a part of it – is not known \textit{a priori}: both Hartree and exchange-correlation terms depend on the solution itself.

For time-independent Hamiltonians, it is well known that the problem is reduced to the calculation of the action of the exponential of the Hamiltonian on the function that describes the state. Unfortunately, since this is not the case in TDDFT, one has to approximate the full evolution operator:

\[
\hat{U}(t + \Delta t, t) = \sum_{n=0}^{\infty} \frac{(-i)^n}{n!} \int_{t}^{t+\Delta t} dt_1 \cdots \int_{t}^{t+\Delta t} dt_n \mathcal{T} \left[ \hat{H}_{\text{KS}}(t_1) \cdots \hat{H}_{\text{KS}}(t_n) \right], \tag{E.11}
\]

where \( \mathcal{T} \) is the time-ordering operator. A handful of algorithms have been implemented in the \texttt{octopus} package: polynomial expansions (in the standard base or in the Chebyshev base) to approximate the exponential operator, Krylov subspace projections, the split-operator technique, higher-order split-operator-like schemes, the implicit midpoint rule, the exponential midpoint rule, and the so-called Magnus expansions. For more details on these propagation algorithms see Ref. [148].

### E.1.5 Hartree potential

In three dimensions, the Hartree potential may be represented in two equivalent forms: as the integral:

\[
v_H[n](\vec{r}) = \int d\vec{r}' \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|}, \tag{E.12}
\]
or as the solution of Poisson’s equation:

\[ \nabla^2 v_H[n](r) = -4\pi n(r). \]  
(E.13)

There are various ways in which these equations may be solved [194].

**Conjugate gradients.** This amounts to solving Eq. (E.13) via a conjugate gradients algorithm. This method poses the problem of determining the boundary conditions for \( v \). The standard solution consists in calculating the value of \( v \) at points around the simulation box using a multipole expansion representation of the density \( n \). For points outside, the potential is given by

\[ v_H(r) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{4\pi}{2l + 1} \frac{1}{r^{l+1}} Y_{lm}(\hat{r}) Q_{lm}, \]  
(E.14a)

\[ Q_{lm} = \int d\mathbf{r} \, r^l Y_{lm}(\mathbf{r}) n(\mathbf{r}), \]  
(E.14b)

where \( Y_{lm} \) are spherical harmonics. **octopus** offers an alternative: subtracting from \( n \) a sum of densities \( Q_{lm} n_{lm} \), where \( Q_{lm} \) are the multipoles of \( n \), and where \( n_{lm} \) are auxiliary known charge distributions whose \( (lm) \)-moment is unity, and whose other moments are zero:

\[ \bar{n} = n - \sum_{l=0}^{L} \sum_{m=-l}^{l} Q_{lm} n_{lm}. \]  
(E.15)

For a sufficiently large integer \( L \), \( \bar{n} \) has negligible boundary conditions, so that \( v_H[\bar{n}] \) may be calculated with the usual Laplacian with zero boundary conditions. Since Poisson’s equation is linear,

\[ v_H[n] = v_H[\bar{n}] + \sum_{l=0}^{L} \sum_{m=-l}^{l} Q_{lm} v_{\text{Hartree}}[n_{lm}]. \]  
(E.16)

The functions \( v_H[n_{lm}] \) can be obtained exactly (see Ref. [194] for explicit analytical expressions for \( n_{lm} \) and \( v_H[n_{lm}] \)).

**Multigrids.** Still in real-space, **octopus** allows for the use of the multigrid method [195–198]. Multigrid is a linear scaling iterative method to solve elliptic problems. The base of this scheme is to use a group of different grids that have less points than the original grid where the problem is discretized. In these coarser grids the corrections to
the solution in the original grid are calculated using standard relaxation methods (such as Gauss-Jacobi or Gauss-Seidel). The solution process is much faster in the coarser grids, not only because of the reduced number of points, but also because relaxation operators are less local.

**Fourier space.** *octopus* allows to move to Fourier space and obtain the Hartree potential by making use of the well-known fact that it is simply a multiplicative function in Fourier space. This is the best choice for fully periodic systems, since it naturally handles the periodic boundary conditions. It is a fast and efficient method thanks to the existence of the Fast Fourier Transform (FFT) algorithm.

For finite systems plane waves can still be used efficiently to calculate the Hartree potential using the supercell approximation. In the supercell approximation the physical system is treated as a fully 3D-periodic one, but a new unit cell (the supercell) is built in such a way that some extra empty space separates the periodic replica, and the Coulomb interaction is cutoff to avoid any spurious interaction between these replica.

**E.1.6 Exchange-correlation potential**

*octopus* incorporates a wide variety of possible functionals, ranging from the standard local density approximation (Sec. 1.4.5) and generalized gradient approximations (Sec. 1.4.5), to the state-of-the-art orbital-dependent functionals [199–203]. “Traditional” LDAs and GGAs are easy to implement, since they are explicit functionals of the density and its gradient. The more recent orbital-dependent functionals, however, are explicit functionals of the KS orbitals (therefore they are implicit functionals of the density through the orbitals) and require the use of the optimized effective potential method (OEP) [199–202]. These functionals have been implemented in *octopus*. Both the Krieger, Li and Iafrate (KLI) [203] approximation and the full solution of the OEP equation [204, 205] (still in experimental phase) are available.

Since all (TD)DFT codes require a piece of software to evaluate the exchange and correlation energy and potential, it would be beneficial to have an open, reliable “exchange and correlation” library. *octopus* includes a library written in C that may be a first step towards this goal.
E.1.7 External potential

The external potential \( v_{\text{ext}}(r) \) is typically the sum of the Coulomb potential generated by each nuclei. In a pseudopotential formulation, this includes both local and non-local components (Eq. (3.35)). Note that the Kleinman and Bylander projectors are typically well localized in real space, so their action is computationally feasible and faster than in a plane wave formulation.

The code also allows for other “user-defined” external potentials. For example, one can attempt to model the solvent environment of a given system with the electrostatic potential generated by a set of point charges and/or dipoles (e.g. to model a chromophore in its protein environment [206, 207]). This is the basic principle of the so-called QM/MM techniques [208,209]. Also, the user may define a model potential describing a two-dimensional quantum dot, and can specify it simply by writing down its mathematical function in the input file.

E.2 Parser

octopus includes a powerful and yet user friendly parser. At the beginning of a run, the parser reads the input file, parses it, and generates a list of variables. The list is then available to the other parts of the code. There are two types of variables: scalars and blocks. A scalar variable is defined by:

\[
\text{var} = \text{exp}
\]

\text{var} is the name of the variable and \text{exp} is the value that should be assigned to the variable. Blocks are collections of values arranged in row and column format:

\[
%\text{var} \\
\text{exp} | \text{exp} | \text{exp} | \ldots \\
\text{exp} | \text{exp} | \text{exp} | \ldots \\
\ldots \\
%
\]

Rows in a block are separated by a newline, while columns are separated by the character “\|”. In the expressions all arithmetic operators are supported, as well as the most common mathematical functions.
E.3 Large-scale parallelization

The current trend in hardware technology follows a steep increase in the number of processors in each computing machine or facility, as opposed to the trend towards an increase in the clock speed or number of operations that each processing unit may perform per unit time. This implies that it is necessary to ensure that the codes are able to benefit from modern parallel-computing facilities.

E.3.1 Parallelization strategies

octopus incorporates a multiple-way parallelization scheme that may divide the work among a given number of processors, splitting the tasks either in k-points, in Kohn-Sham states, in regions of real-space, or in a combination of all of them. Each single form of the contemplated parallelizations may scale by its very nature only to a certain maximum number of processors. Only combined schemes allow to overcome such limitations.

In Fig. E.2 we have represented the various possible modes for which a task division within a DFT/TDDFT calculation may be obtained:

- **k-points**: In a ground-state DFT calculation each processor solves the KS equation

\[
\hat{H}_k^{KS} \varphi_{nk}(\vec{r}) = \epsilon_{nk} \varphi_{nk}(\vec{r})
\]  

(E.17)

for a given but fixed k-point. Communication among the nodes is only required for the calculation of the (common) density or other Brillouin-zone integrations. This is the parallelization mode that most ground-state solid-state DFT codes offer. The implementation is straightforward and scales very nicely with the number of processors. However, limitations arise for systems with very large unit cells.

- **spin**: The different spin subspaces may be treated by different processors. In practice this is rather similar to the k-point parallelization, so that both spin and k-points
are represented as common quantum numbers and are treated on the same footing. Note that this only works for collinear spin calculations.

- **Kohn-Sham states**: For the ground-state a parallelization in state indices or bands is more involved than the \( k \)-point parallelization. Essentially, the state indices have to be divided into different state-groups. The eigenproblem is then solved for each group and a subsequent orthonormalization of the states is performed among the states of different groups. Special block-diagonalization algorithms are used for this task.

On the other hand, in time-dependent DFT, the parallelization in state indices is straightforward. Since the time-dependent Kohn-Sham equations constitute a \( N \)-fold initial value problem, each orbital/state index may be propagated on a different processor. Communication is only required for the calculation of the density and in some cases for the calculation of the current.

- **real-space regions**: The real-space mesh is divided into different domains, so that each processor can treat a different portion of the total mesh. This is illustrated in the left of Fig. E.3, where we show a six-fold domain decomposition of a benzene molecule in the \( x-y \) plane. Apart from the distribution of the computational burden over the different nodes, this parallelization strategy also has the distinct advantage that the total memory requirement for the storage of the grid points is distributed over the nodes. Much larger systems can be treated if domain parallelization is used.

The price one has to pay for this flexibility is the rather involved implementation which requires non-trivial communication among the nodes. On the right hand side of Fig. E.3 we show the application of a finite-difference stencil of the Laplacian to a boundary point of Domain B. Due to the non-local character of the stencil this requires points of Domain A (gray shaded area) which are held in memory by a neighboring processor. These points are termed ghost points and need to be communicated among neighboring nodes every time the function values on the grid change. Low-latency high-bandwidth networks are therefore the preferred interconnects for such an implementation.

- **other**: electron-hole pairs, scattering states, etc: The basis set in a linear response calculation within time-dependent DFT consists of electron-hole pairs: products of occupied and unoccupied Kohn-Sham states. Typically a large number of matrix elements in the form of Eq. (2.49) is required. Since the different matrix elements are independent of each other, a parallelization may be easily obtained by simply distributing their calculation over the different nodes.
The natural description of a quantum-mechanical transport calculation is made in terms of scattering states at given energies. Similar in spirit to the parallel treatment of Kohn-Sham states, the propagation of these scattering states can be distributed over different nodes.

E.3.2 Technical aspects

For the implementation of the multiple-way parallelization in octopus version 1 of the message passing standard MPI [210–212] is employed. The choice was mainly motivated by the availability of this MPI variant for virtually any computer architecture, and by the fact that MPI is the de facto standard on large-scale parallel architectures. octopus does not make use of version 2 or newer developments in the MPI standard since these features are still not available on many platforms. Parallelization techniques like OpenMP can also be used. However their usefulness is rather limited as OpenMP can only be used in shared memory architectures with many processors in a single machine.

Within octopus various different box shapes like spheres, cylinders or parallelepipeds are allowed in 3D calculations, or disks and rectangles in 2D. With a recent addition to the code even arbitrary user-defined shapes can be chosen. To treat the segmentation of the real space mesh for all possible geometries and spatial dimensions on the same footing, the sequence of mesh points is converted into a structured graph. The problem of decomposing the real-space mesh into different domains is then translated into a graph-partitioning
Figure E.4: Measured speedups for a domain-parallel calculation of Cs$_8$@C$_{60}$.

problem. Several graph algorithms are available for such tasks and a “multilevel k-way partitioning algorithm” is used as provided by the METIS library [213]. The library functions try to minimize the edge cuts while the graph partitioning is performed. Translated back to the real-space mesh this means that the intersection area of neighboring domains is minimized which in turn implies that fewer ghost points have to be communicated between the different nodes. This effect can be seen nicely in the example of the benzene molecule (Fig. E.3) where the domain boundaries computed by METIS always lie between two carbon atoms, the optimal situation in this case.

E.3.3 Application to Cs$_8$@C$_{60}$

In Fig. E.4 we show a sample calculation for 8 Cs atoms attached to C$_{60}$. Because of the size of the Cs atoms a rather large sphere with 26 Å diameter was used as enclosing computational domain. By choosing a grid spacing of Δ=0.20Å a total number of 1.177.863 grid points were contained in the calculation box.

To assess the performance of the domain parallelization we have repeated the ground-state DFT calculation of this system with a varying number of processors ranging from one to 32. On the right hand side of Fig. E.4 we plot the measured speedup as function of the number of processors. The circles correspond to the timings obtained for the application of the Hamiltonian to the wavefunction and the diamonds represent the measured timings for a full SCF cycle. Both curves follow Amdahl’s law [214]: Suppose that $p$ is the fraction of a calculation that can be performed in parallel. Then $1 - p$ is the percentage which is
intrinsically serial. If we define the speedup $S(N,p)$ of a parallel calculation as the ratio $T(1,p)/T(N,p)$, where $T(N,p)$ is the execution time using $N$ processors, we find

$$S(N,p) = \frac{1}{1 - p + p/N}.$$  \hspace{1cm} (E.18)

Note that the speedup will always saturate to $1/(1 - p)$ as function of the number of processors, if $p < 1$. In Fig. E.4 we have fitted our measured data to Amdahl’s law (solid lines) and obtain parallel fractions $p = 0.97$ for the application of $\hat{H}$ to the wavefunction and $p = 0.992$ for the execution of a full SCF cycle. Both fractions indicate that a high degree of parallelization has been achieved for the domain parallelization in \textit{octopus}. Nevertheless, since the saturation is very sensitive to the value of $p$ there is still room for improvement in the future.
Bibliography


