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Gauge-invariant magnetic properties from the current

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INTRODUCTION

In order to describe and understand the interaction between molecules and electromagnetic fields, one always looks at some specific intrinsic quantities of the system under study: this is what we call the molecular electromagnetic properties. The outcome of experiments is always interpreted in terms of such properties. Nowadays, computer software packages are routinely used to calculate values of these electromagnetic properties. These programs allow one to deal with atoms, molecules and even clusters of molecules, sometimes with an accuracy comparable to that of experiments. It is then clear that theory and experiments are complementary. With the former, one can separate and identify the different terms which contribute to a given molecular property, something indispensable in order to lift the veil on complex phenomena. Theory is thus a powerful analyzing tool, but not only. It can also be predictive, and then experiments are vital in order to validate the theoretical formalism. Calculating molecular properties can help identify unknown compounds and molecular configurations as well. New materials can be studied quite inexpensively through computer simulations, rather than synthetizing them first. In light of this, it can be understood that it is just as important to calculate molecular electromagnetic properties as to obtain them experimentally. Actually, no experiment could be viable without a theory that supports it, and vice-versa. This close relationship between theory and experiments can lead to designing new materials for example, but sometimes it is just a matter of understanding the world.

Amidst the long list of molecular electromagnetic properties lie the well-known electric dipole moments, the frequency-dependent polarizabilities, or the chemical shifts in NMR spectroscopy, to name a few. While electric properties can now be calculated efficiently by a wide range of methods, magnetic properties, for their part, still pose several fundamental problems. One of the key issues is the gauge-invariance problem: in many calculations of magnetic properties using finite basis sets, an unphysical dependence on the gauge origin of the vector potential arises, leading to unreliable results. This problem is related to a slow convergence of the current density with the size of the basis set used in practical calculations. In this thesis, we will thus study more precisely the calculation of such magnetic properties. In particular, as an illustration of the method we have developed, we will focus mainly on two different magnetic properties, namely the magnetizability, which can be considered as the paradigm of magnetic properties, and circular dichroism, which is a dynamical quantity which shows several applications in many different fields, as we will explain later.

Changes in the electronic structure can often[2] be known by treating the electromagnetic fields as perturbations which slightly modify this structure. It is important to note that molecular properties are intrinsic properties of a particular state of a given molecule, in the sense that they are independent of the strength of the fields [1]. Molecular properties can thus be regarded as the response of the molecule to the fields, be it external fields, or internal fields, e.g., the magnetic moments of nuclei.

In this work, we shall use time-dependent current-density functional theory (TDCDFT), which is a first-principles method, i.e., a method which only uses the principles of quantum mechanics, and which does not include empirical parameters obtained from experiment or otherwise (except the usual ones, like electron masses, charges, etc.). In that, first-principles methods differ from so-called semi-empirical methods. For the purpose of this thesis, it is sufficient to describe the electrons quantum mechanically, while the fields will be treated in a classical way.

In the first part of this thesis, we explain the theory with which we work, that is TDCDFT. In particular, in the first chapter, we introduce groundstate DFT, and give the two theorems which support this theory, namely the Hohenberg-Kohn (HK) theorems [2], along with the Kohn-Sham equations [3], which are the equations used in most practical DFT calculations. The most striking consequence of the HK theorems is that for a stationary electronic system, the knowledge of the ground-state density alone is sufficient to determine all the properties of the system. In the second chapter, we start by describing the time-dependent DFT (TDDFT), which extends stationary DFT to the time-dependent case, thanks to the Runge-Gross theorem, which is analogous to the first Hohenberg-Kohn theorem. We then explain TDCDFT, which, contrary to TDDFT, allows us to describe systems under the influence of general electromagnetic fields, as was first proved by Ghosh and Dhara [4, 5]. In the third chapter, we derive the linear response equations that we will use later to obtain electromagnetic properties like magnetizabilities, circular dichroism spectra, etc., and show how these equations translate to the case of TDCDFT.

In the second part of this thesis, we focus on the calculation of several molecular magnetic properties in finite systems. In the fourth chapter, in particular, we give details on how we treated the major problems which one is usually confronted with when calculating magnetic properties, namely the gauge-invariance problem, and also the slow convergence of the current density with respect to basis-set size, which is related to the first problem. We show that by using a sum rule [6], we succeed

---

[2] If the applied perturbation is too strong, one cannot use the perturbation theory anymore.

in obtaining an efficient and general scheme, applicable to any method with which we can calculate the current density. We illustrate our method by applying it to the calculation of the magnetizability, which can be considered as the paradigm of magnetic properties. In the fifth chapter, we explain in detail how we extended our method to calculate circular dichroism (CD) spectra and specific rotations. Contrary to the magnetizability, whose main interest is often limited to its static value, CD is a truly frequency-dependent quantity. It has applications in many different fields, in particular in the medical domain and in biology, where secondary structures in molecules show specific signatures in CD spectra. Having a reliable first-principles tool to predict such structures would thus be of great interest. The sixth chapter discusses more briefly two other magnetic properties which we can obtain with the same method developed in chapters 4 and 5, namely the rotational g-tensor, and the NMR shielding constant. The seventh chapter is dedicated to the implementation, and is meant to help the reader understand the equations we implemented in the program Amsterdam Density Functional (ADF), along with underlining some specificities of ADF.

The eighth and last chapter is more explorative, and deals with the description of magnetization in extended systems. We give a glimpse at the problems one naturally faces when trying to describe such systems, notably that the definitions we used for the dipole moments in finite systems become ill-defined when switching to periodic systems, and propose various strategies towards establishing a correct description of magnetization in such systems.

1

DENSITY FUNCTIONAL THEORY

In order to describe the behaviour of particles in an interacting many-body system, one would in principle need to solve the Schrödinger equation in order to get the many-body wavefunction. However, in practice, this scheme is in general unfeasible due to the coupling between the motion of the particles, and no analytical expression for the wavefunction can be found. Consequently, one needs to make approximations in order to solve this problem. Several methods have been developped to deal with many-body systems. A class of these methods aims to extract information of a given system by looking at simpler quantities (like densities). In this chapter we shall describe one of these methods, the so-called density functional theory (DFT).

1.1 Introduction

Let us consider a stationary system of N interacting electrons. In the Born-Oppenheimer approximation[1], the Schrödinger equation reads[2]:

$$\hat{H}\Psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N) = E\Psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)\,, \tag{1.1}$$

where E is the eigenenergy of the system, and $\Psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)$ is the N-electron wavefunction with $\mathbf{r}_i$ the space coordinates of the electron i. The Hamiltonian $\hat{H}$ is

---

[1] Since the nuclei are much heavier than the electrons, their movement is much slower than that of the electrons. As a consequence, for each instantaneous configuration of the nuclei, the electrons are approximately in a stationary state. We can therefore consider the nuclei to provide a fixed frame for the electrons. Therefore the wavefunction can be separated into an electronic and a nuclear part.

[2] In principles one would need to include the spin coordinates, and the Schrödinger equation would read $\hat{H}\Psi(\mathbf{r}_1\sigma_1, \mathbf{r}_2\sigma_2, ..., \mathbf{r}_N\sigma_N) = E\Psi(\mathbf{r}_1\sigma_1, \mathbf{r}_2\sigma_2, ..., \mathbf{r}_N\sigma_N)$, with σ_i the spin coordinates of the electron i. For simplicity though, we do not consider the spin explicitly here in the following.

given by

$$\hat{H} = \underbrace{-\frac{1}{2}\sum_i \nabla_i^2}_{\hat{T}} + \underbrace{\sum_i v(\mathbf{r}_i)}_{\hat{V}} + \underbrace{\frac{1}{2}\sum_{i\neq j}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}}_{\hat{W}} . \tag{1.2}$$

Here $\hat{T}$, $\hat{V}$ and $\hat{W}$ are, respectively, the kinetic energy operator, the potential energy operator of the electrons in the external potential $v(\mathbf{r})$, and the Coulomb electron-electron interaction energy operator. Throughout this thesis, we shall use Hartree atomic units ($\hbar = m_e = e = 4\pi\epsilon_0 = 1$). One can see from the Schrödinger equation that the external potential $v(\mathbf{r})$ entirely determines the eigenfunctions Ψ along with the eigenenergies E. These quantities can thus be regarded as functionals of the external potential. We shall adopt the following square bracket notation to denote functionals: $\Psi \equiv \Psi[v]$ and $E \equiv E[v]$. Let us write $\hat{V}$ as

$$\hat{V} = \int d\mathbf{r} v(\mathbf{r})\hat{\rho}(\mathbf{r}) , \tag{1.3}$$

where we introduced the density operator

$$\hat{\rho}(\mathbf{r}) = \sum_i^N \delta(\mathbf{r} - \mathbf{r}_i) . \tag{1.4}$$

The expectation value of $\hat{V}$ can be written as

$$\left\langle \Psi \left| \hat{V} \right| \Psi \right\rangle = \int d\mathbf{r}\rho(\mathbf{r})v(\mathbf{r}) , \tag{1.5}$$

where the electron density $\rho(\mathbf{r})$ of the system is defined by

$$\rho(\mathbf{r}) = \langle \Psi \left| \hat{\rho}(\mathbf{r}) \right| \Psi \rangle = N \int |\Psi(\mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_N)|^2 \, d\mathbf{r}_2 \ldots d\mathbf{r}_N \tag{1.6}$$

where we made use of the antisymmetry property of the wavefunction. One can notice from Eq. (1.5) that ρ and v are conjugate variables in the sense of a Legendre transform. Indeed, by differentiating the ground-state energy E_0 with respect to the external potential, one gets

$$
\begin{aligned}
\frac{\delta E_0[v]}{\delta v(\mathbf{r})} &= \frac{\delta}{\delta v(\mathbf{r})}\langle\Psi_0[v]|\hat{H}|\Psi_0[v]\rangle \\
&= \left\langle \frac{\delta\Psi_0[v]}{\delta v(\mathbf{r})}\left|\hat{H}\right|\Psi_0[v]\right\rangle + \left\langle \Psi_0[v]\left|\hat{H}\right|\frac{\delta\Psi_0[v]}{\delta v(\mathbf{r})}\right\rangle + \left\langle \Psi_0[v]\left|\frac{\delta\hat{H}}{\delta v(\mathbf{r})}\right|\Psi_0[v]\right\rangle \\
&= E_0[v]\frac{\delta}{\delta v(\mathbf{r})}\langle\Psi_0[v]|\Psi_0[v]\rangle + \langle\Psi_0[v]\,|\hat{\rho}(\mathbf{r})|\,\Psi_0[v]\rangle \\
&= \rho[v](\mathbf{r})\,,
\end{aligned}
\tag{1.7}
$$

where in the penultimate step we used the fact that the wavefunction $\Psi_0[v]$ is the ground-state eigenfunction of $\hat{H}$ with energy E_0 and we also used Eq. (1.3) to show that $\frac{\delta\hat{H}}{\delta v(\mathbf{r})} = \hat{\rho}(\mathbf{r})$, and in the last step we used the fact that $\Psi_0[v]$ is normalized. One can hence use the density as a basic variable by defining a Legendre transformation

$$
F[\rho] = E_0[\rho] - \int d\mathbf{r}\rho(\mathbf{r})v(\mathbf{r}) = \left\langle\Psi_0[v]\left|\hat{T}+\hat{W}\right|\Psi_0[v]\right\rangle\,, \tag{1.8}
$$

where $v(\mathbf{r})$ must now be regarded as a functional of $\rho(\mathbf{r})$. The uniqueness of this functional is guaranteed by the one-to-one mapping between v and ρ, as we will prove in section 1.2 with the Hohenberg-Kohn theorem. We can thus prove (by using the chain rule of differentiation and Eq. (1.7)) that this functional obeys the following relation:

$$
\begin{aligned}
\frac{\delta F}{\delta\rho(\mathbf{r})} &= \int d\mathbf{r}'\frac{\delta E_0}{\delta v(\mathbf{r}')}\frac{\delta v(\mathbf{r}')}{\delta\rho(\mathbf{r})} - \frac{\delta}{\delta\rho(\mathbf{r})}\int d\mathbf{r}'\rho(\mathbf{r}')v(\mathbf{r}') \\
&= \int d\mathbf{r}'\rho(\mathbf{r}')\frac{\delta v(\mathbf{r}')}{\delta\rho(\mathbf{r})} - \int d\mathbf{r}'\rho(\mathbf{r}')\frac{\delta v(\mathbf{r}')}{\delta\rho(\mathbf{r})} - \int d\mathbf{r}'v(\mathbf{r}')\frac{\delta\rho(\mathbf{r}')}{\delta\rho(\mathbf{r})} \\
&= -\int d\mathbf{r}'\delta(\mathbf{r}'-\mathbf{r})v(\mathbf{r}') \\
&= -v(\mathbf{r})\,.
\end{aligned}
\tag{1.9}
$$

1.2 The Hohenberg-Kohn Theorems

The main idea of density functional theory is to switch from the many-body wavefunction to the ground-state density as basic quantity. The great advantage of doing this is that while the wavefunction depends on $3N$ spatial variables, the density of particles only requires three spatial variables. One might think that the density alone would not be sufficient to describe a many-body system. Yet, as Hohenberg and Kohn proved [2], the ground-state density is indeed in principle enough to get all properties of the system, and can thus be regarded as a fundamental variable of the problem. The two theorems Hohenberg and Kohn derived can be expressed as

$$\begin{tikzcd}
v(r) \arrow[d] & \rho_0(r) \arrow[l, "HK"'] \\
\Psi_i(\{r\}) \arrow[r] & \Psi_0(\{r\}) \arrow[u]
\end{tikzcd}$$

Figure 1.1 – Illustration of the Hohenberg-Kohn theorem

follows:

- Theorem 1: For any interacting system in an external potential $v(\mathbf{r})$, the latter is determined uniquely, up to a constant, by the (nondegenerate) ground-state density. Since $v(\mathbf{r})$ uniquely determines the ground-state density, there is a one-to-one mapping between ρ and v.
- Theorem 2: One can define a universal functional for the energy $E[\rho]$. For any external potential $v(\mathbf{r})$, the (exact) ground-state energy of the system is the global minimum value of this functional, and the density $\rho(\mathbf{r})$ which minimizes this functional is the ground-state density.

In principle, one could use the external potential to diagonalize the Hamiltonian in order to determine the wavefunctions Ψ_i, and in particular the nondegenerate ground-state wavefunction Ψ_0 which corresponds to the lowest energy. From Ψ_0 one can calculate the ground-state density from Eq. (1.6). This scheme defines the map $v \to \rho_0$[3]. The Hohenberg-Kohn theorem completes the circle by establishing the inverse map $\rho_0 \to v$. The figure 1.1 sums up how everything works [7]. Let us now prove this map, which we will do by *reductio ad absurdum*.

Let us consider two Schrödinger equations for Ψ_0 and Ψ_0' corresponding to two external potentials v and v' differing by more than a constant:

$$\hat{H}\left|\Psi_0\right\rangle = \left(\hat{T} + \hat{V} + \hat{W}\right)\left|\Psi_0\right\rangle = E_0\left|\Psi_0\right\rangle \ , \tag{1.10}$$

$$\hat{H}'\left|\Psi_0'\right\rangle = \left(\hat{T} + \hat{V}' + \hat{W}\right)\left|\Psi_0'\right\rangle = E_0'\left|\Psi_0'\right\rangle \ . \tag{1.11}$$

We now suppose that these two potentials lead to the same ground-state wavefunction: $\left|\Psi_0\right\rangle = \left|\Psi_0'\right\rangle$. Subtracting Eq. (1.11) from Eq. (1.10) leads to

$$\left(\hat{V} - \hat{V}'\right)\left|\Psi_0\right\rangle = \left(E_0 - E_0'\right)\left|\Psi_0\right\rangle \ . \tag{1.12}$$

---

[3] We note that the external potential v uniquely determines the nondegenerate ground-state wavefunction up to a phase factor only.

If $|\Psi_0\rangle$ does not vanish[4], we see that $\hat{V}$ and $\hat{V}'$ differ only by a constant, which is in contradiction with our initial assumption. Consequently[5] $|\Psi_0'\rangle \neq |\Psi_0\rangle$, and we have thus proven the map $\Psi_0 \to v$. Let us now prove that two nondegenerate ground-states Ψ_0 and Ψ_0' will yield two different densities. Since $|\Psi_0'\rangle$ is not the ground-state of $\hat{H}$, we know from the variational principle that

$$E_0 = \left\langle \Psi_0 \middle| \hat{H} \middle| \Psi_0 \right\rangle < \left\langle \Psi_0' \middle| \hat{H} \middle| \Psi_0' \right\rangle . \tag{1.13}$$

Note that the strict inequality stems from the fact that we are considering a non-degenerate ground-state. The last term in the previous equation can be written as

$$\begin{aligned} \left\langle \Psi_0' \middle| \hat{H} \middle| \Psi_0' \right\rangle &= \left\langle \Psi_0' \middle| \hat{H}' \middle| \Psi_0' \right\rangle + \left\langle \Psi_0' \middle| \hat{H} - \hat{H}' \middle| \Psi_0' \right\rangle & (1.14) \\ &= E_0' + \int d\mathbf{r}\, (v(\mathbf{r}) - v'(\mathbf{r}))\, \rho'(\mathbf{r})\,, & (1.15) \end{aligned}$$

so that

$$E_0 < E_0' + \int d\mathbf{r}\, (v(\mathbf{r}) - v'(\mathbf{r}))\, \rho'(\mathbf{r})\,. \tag{1.16}$$

We can do similar manipulations starting from E_0' instead of E_0 to obtain

$$E_0' < E_0 + \int d\mathbf{r}\, (v'(\mathbf{r}) - v(\mathbf{r}))\, \rho(\mathbf{r})\,. \tag{1.17}$$

If $\rho(\mathbf{r})$ and $\rho'(\mathbf{r})$ were the same, then by adding (1.16) and (1.17) we would get the following contradiction:

$$E_0 + E_0' < E_0 + E_0'\,. \tag{1.18}$$

We have thus proven the map $\rho_0 \to \Psi_0$. Since we have also shown that $\Psi_0 \to v$, we have proven the map $\rho_0 \to v$. We conclude that there cannot be two external potentials that differ by more than a constant leading to the same non-degenerate ground-state density. In the end we thus have a one-to-one mapping $\rho_0 \leftrightarrow v$, which proves the first theorem.

Let us now prove the second theorem.

We mentioned previously that each property (kinetic energy, etc.) was uniquely determined as long as v was specified. As we have a one-to-one mapping $\rho_0 \leftrightarrow v$, this means that each property is also determined uniquely by the ground-state density.

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[4] According to Ref. [8], Ψ_0 cannot vanish on a set with nonzero measure.

[5] The contrapositive indicates that if $\Psi_0 = \Psi_0'$, which implies $\rho = \rho'$, then we know that v and v' are the same up to a constant.

We can then write the total energy as a functional of ρ_0,

$$E_{HK}[\rho_0] = F_{HK}[\rho_0] + \int d\mathbf{r} v(\mathbf{r})\rho_0(\mathbf{r}) , \tag{1.19}$$

where F_{HK} is a universal functional (in the sense that its explicit form shall be the same for any system), and is defined as in Eq. (1.8) ($F_{HK} \equiv F$). Let us consider a system with the ground-state density $\rho_0(\mathbf{r})$ corresponding to an external scalar potential $v(\mathbf{r})$. We have

$$E_0 = E_{HK}[\rho_0] = \left\langle \Psi_0 \middle| \hat{H} \middle| \Psi_0 \right\rangle . \tag{1.20}$$

Now consider another ground-state density $\tilde{\rho}(\mathbf{r})$, naturally corresponding to another wavefunction $\tilde{\Psi}$. This density must satisfy the usual constraints $\tilde{\rho}(\mathbf{r}) \geq 0$ and $\int d\mathbf{r}\tilde{\rho}(\mathbf{r}) = N$, where N is the number of electrons. The first Hohenberg-Kohn theorem assures that this trial density uniquely determines the potential $\tilde{v}$ and wavefunction $\tilde{\Psi}$. Using the variational principle, we can deduce that the energy $\tilde{E}$ is greater than E_0 because

$$\tilde{E}[\tilde{\rho}] = \left\langle \tilde{\Psi} \middle| \hat{H} \middle| \tilde{\Psi} \right\rangle > \left\langle \Psi_0 \middle| \hat{H} \middle| \Psi_0 \right\rangle = E_0[\rho_0] . \tag{1.21}$$

Thus the energy given by (1.19) evaluated for ρ_0 is lower than the value of this expression for any other density ρ. This means one can obtain the exact ground state density and energy by minimizing (1.19) with respect to ρ, which concludes the second theorem.

1.3 The Kohn-Sham system

"If you don't like the answer, change the question." [7]

Although the minimization of the Hohenberg-Kohn functional is in principle exact, in practice one still needs approximations of this functional, as its explicit expression is unknown. A practical scheme to evaluate the energy functional was proposed by Kohn and Sham [3]. Their approach is to introduce an auxiliary noninteracting system in an effective potential $v_s(\mathbf{r})$ which reproduces the same ground-state density as that of the original interacting system. If such a potential exists, then it is unique thanks to the Hohenberg-Kohn theorem. The advantage of doing this is that it will lead to independent-particle equations which are soluble in practice. In a similar way as for the interacting system, we can define the energy functional $E_s[v_s]$ and its Legendre transform (this time $\hat{W}$ in Eq. (1.8) will vanish since we deal with a noninteracting system):

$$E_s[v_s] = \left\langle \Psi_s[v_s] \left| \hat{T} + \hat{V}_s \right| \Psi_s[v_s] \right\rangle \,, \tag{1.22}$$

$$F_s[\rho] = E_s[v_s] - \int d\mathbf{r} \rho(\mathbf{r}) v_s(\mathbf{r}) = \left\langle \Psi_s[v_s] | \hat{T} | \Psi_s[v_s] \right\rangle \,. \tag{1.23}$$

The functional derivatives read

$$\frac{\delta E_s[v_s]}{\delta v_s(\mathbf{r})} = \rho(\mathbf{r}) \,, \tag{1.24}$$

$$\frac{\delta F_s[\rho]}{\delta \rho(\mathbf{r})} = -v_s(\mathbf{r}) \,. \tag{1.25}$$

We now define the so-called exchange-correlation energy functional $E_{xc}[\rho]$ by

$$F_{HK}[\rho] = F_s[\rho] + \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}[\rho] \,, \tag{1.26}$$

where the second term on the right-hand side of Eq. (1.26) is the classical Hartree electron-electron interaction energy. We note that one could just have defined $F_{HK} = F_s + F'$; however, it is actually convenient to separate out the Hartree energy E_H because it represents the classical interaction of a system of charges and it has a large contribution to the energy. The advantage of doing this separation is that instead of approximating the whole F', one only has to approximate the exchange-correlation part (which contains all the many-body effects of the system beyond Hartree), which is a priori smaller than the other two energy contributions. Functional differentiating Eq. (1.26) with respect to $\rho(\mathbf{r})$ yields:

$$v_s(\mathbf{r}) = v(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r}) \,, \tag{1.27}$$

where the Hartree potential is defined by

$$v_H(\mathbf{r}) = \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \,, \tag{1.28}$$

and the exchange-correlation potential v_{xc} (which is also a functional of ρ) by

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})} \,. \tag{1.29}$$

Being the ground state of a noninteracting system, $\Psi_s[v_s]$ can thus be expressed as a single Slater determinant of one-electron orbitals ψ_i:

$$\Psi_s(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{pmatrix} \psi_1(\mathbf{r}_1) & \ldots & \psi_N(\mathbf{r}_1) \\ \vdots & \ddots & \vdots \\ \psi_1(\mathbf{r}_N) & \ldots & \psi_N(\mathbf{r}_N) \end{pmatrix} . \tag{1.30}$$

The ψ_i are the solutions of the Kohn-Sham equations

$$\left(-\frac{\nabla^2}{2} + v(\mathbf{r}) + \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{xc}(\mathbf{r}) \right) \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}) \, , \tag{1.31}$$

where the ϵ_i are the orbital eigenenergies. The ground-state density is obtained by occupying the N one-electron orbitals that are lowest in energy:

$$\rho(\mathbf{r}) = \sum_i^N |\psi_i(\mathbf{r})|^2 \, . \tag{1.32}$$

Since v_s depends on the density ρ (according to Eqs. (1.27), (1.28) and (1.29)), which in turn depends on the ψ_i (according to Eqs. (1.32) and (1.31)), the Kohn-Sham equations have to be solved self-consistently.

At this point we should mention a famous issue regarding DFT. In spite of the fact that the Hohenberg-Kohn theorem proves a one-to-one mapping between ρ_0 and v, this does not ensure that for a given ρ_0, there exists a v that produces this ρ_0. This question of knowing if a given density can be generated by a scalar potential is known as the v-representability problem, and has not found an answer yet. Another related question is: can a given density in an interacting system be reproduced by a noninteracting system? In other words, is the existence of a Kohn-Sham system always guaranteed? This is known as the noninteracting v-representability problem, and it is still an open debate. We shall see in the next chapter that this latter question has been answered for the time-dependent case, though.

The main difficulty in solving the Kohn-Sham equations is to find a good approximation for the exchange-correlation potential v_{xc}. In the next section, we will briefly describe one of the most widely used approximations for v_{xc}, namely the local density approximation (LDA), which is based on the homogeneous electron gas.

1.4 The local density approximation

One of the simplest approximations one can use for the exchange-correlation energy is the local density approximation (LDA), in which the exchange-correlation energy is given as

$$E_{xc}^{LDA}[\rho] = \int d\mathbf{r}\rho(\mathbf{r})\epsilon_{xc}^{hom}(\rho(\mathbf{r}))\,, \tag{1.33}$$

where $\epsilon_{xc}^{hom}(\rho)$ is the exchange-correlation energy per unit volume of a homogeneous electron gas of density ρ. The exchange-correlation potential then reads

$$v_{xc}^{LDA}(\mathbf{r})[\rho] = \left.\frac{d\epsilon_{xc}^{hom}(\rho)}{d\rho}\right|_{\rho(\mathbf{r})}\,. \tag{1.34}$$

In this way the system is treated locally as a homogeneous electron gas. One would then expect such an approximation to work only for systems with slowly-varying densities, but it proves to be efficient for inhomogeneous systems as well [3]. One of the reasons why LDA performs so well is that it satisfies the following important sum rule

$$\int d\mathbf{r}'[g(\mathbf{r},\mathbf{r}') - 1]\rho(\mathbf{r}') = -1\,, \tag{1.35}$$

where $g(\mathbf{r},\mathbf{r}')$ is the so-called pair-correlation function which is defined as the normalized probability of finding an electron at position $\mathbf{r}'$ while there is another electron at position $\mathbf{r}$ at the same time. The integrand of Eq. (1.35), usually called the exchange-correlation hole, characterizes the change of the average density at $\mathbf{r}'$ when there is an electron at $\mathbf{r}$. The integral over all space should be -1 because the electron at $\mathbf{r}$ cannot be elsewhere in space, so the rest of the system lacks exactly one electron.

There are also some well-known failures in LDA. For example, the asymptotic behaviour of LDA is incorrect. Indeed, within LDA, the exchange-correlation potential exhibits an exponential decay at large distance from the nucleus, as it is proportional to the density. However, at large distance, the electron undergoes the Coulomb potential of the positively charged ion constituted by the rest of the atom, which is proportional to $-1/r$. Since, still at large distance, the Hartree potential and the nuclear potential cancel each other, the only contribution thus comes from the exchange-correlation potential, so it should behave asymptotically as $-1/r$.

A very simple way to go beyond the LDA is to include gradients of the density in the exchange-correlation functional. A successful construction of such functionals was notably obtained in the generalized gradient approximation (GGA) (see Ref. [9] for an overview of GGA functionals). Nowadays, there exists a plethora of approximations to the xc potentials, which try to make DFT generally applicable.

2

TIME-DEPENDENT CURRENT-DENSITY-FUNCTIONAL THEORY

In the first part of this chapter, we will describe the extension of DFT to the time-dependent case, namely time-dependent DFT (TDDFT). We will see that this extension is based on the Runge-Gross theorem, which is analogous to the Hohenberg-Kohn theorem for DFT. In the second part, we shall describe another extension, namely time-dependent current-density-functional theory (TDCDFT), where the fundamental variable is the current density rather than the density. This latter extension has the advantage of allowing us to describe general electromagnetic fields. This is the method we shall use later in our implementation.

A good review on TD(C)DFT is given in Ref. [10].

2.1 Time-Dependent Density Functional Theory

We are interested in solving the time-dependent Schrödinger equation[1],

$$\hat{H}(t)\Psi(\mathbf{r}_1, ..., \mathbf{r}_N, t) = i\frac{\partial}{\partial t}\Psi(\mathbf{r}_1, ..., \mathbf{r}_N, t)\,, \tag{2.1}$$

where $\hat{H}(t)$ is the same as in Eq. (1.2) except that the external scalar potential is now time-dependent. We note that the following proof is only valid if there is no external vector potential, so only longitudinal fields are considered.

2.1.1 The Runge-Gross Theorem

The Runge-Gross theorem is the time-dependent extension of the Hohenberg-Kohn theorem, and establishes a one-to-one mapping between time-dependent densities and time-dependent potentials for a given intial state. Let us suppose we have two

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[1] As in the previous chapter, we dropped the spin index for the sake of simplicity.

external potentials differing by more than a pure function of time[2] $d(t)$, i.e.,

$$v(\mathbf{r},t) \neq v'(\mathbf{r},t) + d(t)\,. \tag{2.2}$$

We want to show that these two potentials lead to two different densities $\rho(\mathbf{r},t)$ and $\rho'(\mathbf{r},t)$. Let us consider a potential that is Taylor-expandable with respect to the time coordinate t around an initial time t_0:

$$v(\mathbf{r},t) = \sum_{k=0}^{\infty} c_k(\mathbf{r})(t-t_0)^k\,, \tag{2.3}$$

where the expansion coefficients are expressed as

$$c_k(\mathbf{r}) = \frac{1}{k!}\,\frac{\partial^k}{\partial t^k} v(\mathbf{r},t)\bigg|_{t=t_0}\,. \tag{2.4}$$

In addition, we define the following set of functions:

$$u_k(\mathbf{r}) = \frac{\partial^k}{\partial t^k}\left(v(\mathbf{r},t) - v'(\mathbf{r},t)\right)\bigg|_{t=t_0}\,. \tag{2.5}$$

Since v and v' differ by more than a pure function of time, it follows that at least one pair of expansion coefficients will differ by more than a constant (i.e., $c_k(\mathbf{r}) - c'_k(\mathbf{r}) \neq \text{const}$), implying that

$$\exists k \geq 0,\ u_k(\mathbf{r}) \neq \text{const}\,. \tag{2.6}$$

First, we will prove that if $v \neq v' + d(t)$, the current densities $\mathbf{j}$ and $\mathbf{j}'$ generated by v and v' will also be different. We have

$$\mathbf{j}(\mathbf{r},t) = \left\langle \Psi(t) | \hat{\mathbf{j}}_p(\mathbf{r}) | \Psi(t) \right\rangle\,, \tag{2.7}$$

with $\hat{\mathbf{j}}_p$ the paramagnetic current density operator defined as

$$\hat{\mathbf{j}}_p(\mathbf{r}) = \frac{1}{2}\sum_{j=1}^{N} \{-i\nabla, \delta(\mathbf{r}-\mathbf{r}_j)\}\,, \tag{2.8}$$

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[2] If two potentials indeed differ solely by a pure function of time, it implies that the corresponding wavefunctions will be equal up to a purely time-dependent phase factor, which will cancel when calculating densities or other observables. This is related to gauge transformations.

where $\{\hat{A}, \hat{B}\} = \hat{A}\hat{B} + \hat{B}\hat{A}$ is the anticommutator. We now use the quantum mechanical equation of motion for a Schrödinger operator[3] $\hat{A}(t)$,

$$\frac{d}{dt}\left\langle\Psi(t)|\hat{A}(t)|\Psi(t)\right\rangle = \langle\Psi(t)\,|\frac{\partial}{\partial t}\hat{A}(t) - i[\hat{A}(t), \hat{H}(t)]|\,\Psi(t)\rangle\;, \tag{2.9}$$

to obtain

$$\frac{d}{dt}\mathbf{j}(\mathbf{r}, t) = \langle\Psi(t)\,|\left[\hat{\mathbf{j}}_p(\mathbf{r}), \hat{H}(t)\right]|\,\Psi(t)\rangle\;, \tag{2.10}$$

$$\frac{d}{dt}\mathbf{j}'(\mathbf{r}, t) = \langle\Psi'(t)\,|\left[\hat{\mathbf{j}}_p(\mathbf{r}), \hat{H}'(t)\right]|\,\Psi'(t)\rangle\;. \tag{2.11}$$

As in both the primed and unprimed systems, we start from the same initial state, it is clear that

$$|\Psi(t_0)\rangle = |\Psi'(t_0)\rangle \equiv |\Psi_0\rangle\;, \tag{2.12}$$

$$\rho(\mathbf{r}, t_0) = \rho'(\mathbf{r}, t_0) \equiv \rho_0(\mathbf{r})\,, \tag{2.13}$$

$$\mathbf{j}(\mathbf{r}, t_0) = \mathbf{j}'(\mathbf{r}, t_0) \equiv \mathbf{j}_0(\mathbf{r})\,. \tag{2.14}$$

From Eqs. (2.10) and (2.11), and using the definition of the paramagnetic current operator given in Eq. (2.8), we get[4]

$$\begin{aligned}\frac{d}{dt}\left[\mathbf{j}(\mathbf{r}, t) - \mathbf{j}'(\mathbf{r}, t)\right]_{t=t_0} &= -i\,\langle\Psi_0|\left[\hat{\mathbf{j}}_p(\mathbf{r}), \hat{H}(t_0) - \hat{H}'(t_0)\right]|\Psi_0\rangle \\ &= -i\,\langle\Psi_0|\left[\hat{\mathbf{j}}_p(\mathbf{r}), v(\mathbf{r}, t_0) - v'(\mathbf{r}, t_0)\right]|\Psi_0\rangle \\ &= -\rho_0(\mathbf{r})\nabla\left(v(\mathbf{r}, t_0) - v'(\mathbf{r}, t_0)\right)\;. \end{aligned}\tag{2.15}$$

Repeated use of the equation of motion yields

$$\frac{d^{k+1}}{dt^{k+1}}\left[\mathbf{j}(\mathbf{r}, t) - \mathbf{j}'(\mathbf{r}, t)\right]_{t=t_0} = -\rho_0(\mathbf{r})\nabla u_k(\mathbf{r})\,. \tag{2.16}$$

The right-hand side of Eq. (2.16) does not vanish for some k[5], implying that $\mathbf{j}(\mathbf{r}, t) \neq \mathbf{j}'(\mathbf{r}, t)$ for $t > t_0$.

In the second step of this proof, we shall show that $\mathbf{j} \neq \mathbf{j}'$ implies $\rho \neq \rho'$. To

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[3] Within the Schrödinger picture, the wavefunctions and the operators have their "natural" time-dependence, contrary to the Heisenberg and interaction picture. See Ref. [11] for more details on the different pictures.

[4] Pay attention to the fact that the nabla operator ∇ acts on $\mathbf{r}$, hence it only acts on $v(\mathbf{r}, t_0)$ and $\delta(\mathbf{r} - \mathbf{r}_j)$, since the wavefunction Ψ_0 does not depend on $\mathbf{r}$.

[5] Equation (2.16) is valid for all integers from 0 to the smallest k for which Eq. (2.6) holds, but not for integers larger than this smallest k [10].

achieve this, we make use of the continuity equation:

$$\frac{\partial}{\partial t}\rho(\mathbf{r},t) = -\nabla \cdot \mathbf{j}(\mathbf{r},t)\,. \tag{2.17}$$

As before, writing this continuity equation for both primed and unprimed system and taking the difference leads to

$$\frac{\partial}{\partial t}\left[\rho(\mathbf{r},t) - \rho'(\mathbf{r},t)\right] = -\nabla \cdot \left[\mathbf{j}(\mathbf{r},t) - \mathbf{j}'(\mathbf{r},t)\right]\,. \tag{2.18}$$

Differentiating Eq. (2.18) $k+1$ times, we get

$$\begin{aligned} \frac{\partial^{k+2}}{\partial t^{k+2}}\left[\rho(\mathbf{r},t) - \rho'(\mathbf{r},t)\right]_{t=t_0} &= -\nabla \cdot \frac{\partial^{k+1}}{\partial t^{k+1}}\left[\mathbf{j}(\mathbf{r},t) - \mathbf{j}'(\mathbf{r},t)\right]_{t=t_0} && (2.19)\\ &= \nabla \cdot \left[\rho_0(\mathbf{r})\nabla u_k(\mathbf{r})\right]\,, && (2.20) \end{aligned}$$

where in the last step we made use of Eq. (2.16). To end this demonstration, we need to justify that the right-hand side $\nabla \cdot [\rho_0(\mathbf{r})\nabla u_k(\mathbf{r})]$ never goes to zero. To do this, let us consider the following integral,

$$\begin{aligned} \int d\mathbf{r}\rho_0(\mathbf{r})[\nabla u_k(\mathbf{r})]^2 = &- \int d\mathbf{r} u_k(\mathbf{r})\nabla \cdot \left[\rho_0(\mathbf{r})\nabla u_k(\mathbf{r})\right] \\ &+ \oint d\mathbf{S} \cdot \left[\rho_0(\mathbf{r})u_k(\mathbf{r})\nabla u_k(\mathbf{r})\right]\,, \end{aligned} \tag{2.21}$$

where use has been made of Green's theorem. For physically reasonable potentials –that is, potentials obtained from normalizable external charge densities [10]–, the surface integral in the previous equation vanishes. Moreover, the left-hand side is strictly positive (because the density is always positive and we showed in Eq. (2.6) that $u_k \neq$ const for some k). As a consequence, $\nabla \cdot [\rho_0(\mathbf{r})\nabla u_k(\mathbf{r})]$ cannot be zero everywhere, which completes the proof. In the next section, we shall explain how to use TDDFT in practice.

2.1.2 Time-Dependent Kohn-Sham Equations

Just like the ground-state case, one can switch from an interacting system with potential v to a non-interacting system (the Kohn-Sham system) with potential v_s, which reproduces the density of the original system at all times t. All the properties of the true system can be obtained from the density of the Kohn-Sham system. A question of interest is: can a density generated by an interacting system be reproduced by a noninteracting system? Put another way, does a Kohn-Sham system always exist? This issue has been answered, under some specific conditions, by van Leeuwen, who proved that indeed, one can always find a KS system in TDDFT (We will discuss this in more detail in the context of TDCDFT in section

2.2).

We now give the time-dependent Kohn-Sham equations[6]:

$$i\frac{\partial}{\partial t}\psi_i(\mathbf{r},t) = \left(-\frac{\nabla^2}{2} + v_s(\mathbf{r},t)\right)\psi_i(\mathbf{r},t)\,. \tag{2.22}$$

The effective potential v_s, analogously to the ground-state case, can be split into an external, a Hartree and an exchange-correlation contribution:

$$v_s(\mathbf{r},t) = v(\mathbf{r},t) + \int d\mathbf{r}'\frac{\rho(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|} + v_{xc}(\mathbf{r},t)\,. \tag{2.23}$$

As for the density, it is expressed as

$$\rho(\mathbf{r},t) = \sum_{i=1}^{N} |\psi_i(\mathbf{r},t)|^2\,. \tag{2.24}$$

Since v_s depends on ρ through Eq. (2.23) and in turn ρ depends on v_s through Eq. (2.22), one needs a self-consistent procedure (SCF) to solve the equations for each time t. Once convergence has been reached for a given time t, one can then insert the KS potential $v_s(\mathbf{r},t)$ in the Schrödinger-like equation (2.22) in order to compute the density at an infinitesimally later time $t+\delta t$. From there, one needs another SCF procedure in order to get $v_s(\mathbf{r},t+\delta t)$, and so on. We remark that contrary to stationary DFT, the time-dependent exchange-correlation potential is implicitly defined through Eq. (2.23), and cannot be expressed as the functional derivative of an action functional [12]. However, it was proved that by using a so-called Keldysh contour [13], one could actually obtain an exchange-correlation potential in terms of the derivative of a particular action functional: the Keldysh action functional [14].

2.2 Time-Dependent Current-Density-Functional Theory

Time-Dependent Current-Density-Functional Theory (TDCDFT) is a generalization of TDDFT, which allows for general time-dependent electromagnetic fields. Ghosh and Dhara were the first to rewrite TDDFT with the current density as basic variable [4, 5]. They showed that the time-dependent scalar and vector potentials (and

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[6] We assume that the initial state of the non-interacting system can be expressed as a single Slater determinant. It is often chosen to be the ground-state Kohn-Sham wavefunction from stationary DFT. Actually the only condition on the choice for the initial state is that it must be compatible with the given density, so it must reproduce both the initial density and initial first time-derivative, as can be seen from the continuity equation, Eq. (2.17).

consequently also the many-body wavefunction) were uniquely determined, up to a gauge transformation, by the current density. More recently, Vignale found another formulation for TDCDFT [15] which is simpler and more general than that of Ghosh and Dhara. In the following, we will give the proof given in Ref. [15].

In TDCDFT, we look at a larger class of Hamiltonians than the ones we considered in the Runge-Gross formulation. Here, besides a scalar potential, we also have a vector potential:

$$\hat{H}(t) = \sum_i \left\{ \frac{1}{2}[-i\nabla_i + \mathbf{A}(\mathbf{r}_i, t)]^2 + v(\mathbf{r}_i, t) \right\} + \sum_{i<j} U(\mathbf{r}_i - \mathbf{r}_j)\,, \tag{2.25}$$

where $U(\mathbf{r}_i - \mathbf{r}_j)$ is a two-particle interaction[7], $v(\mathbf{r}, t)$ and $\mathbf{A}(\mathbf{r}, t)$ are the scalar and vector potentials and they are analytic functions of time around t_0. These potentials represent an electric field $\mathbf{E}(\mathbf{r}, t)$ and a magnetic field $\mathbf{B}(\mathbf{r}, t)$ through the following relations:

$$\mathbf{E}(\mathbf{r}, t) = \nabla v(\mathbf{r}, t) - \frac{\partial \mathbf{A}(\mathbf{r}, t)}{\partial t}\,, \tag{2.26}$$

$$\mathbf{B}(\mathbf{r}, t) = \nabla \times \mathbf{A}(\mathbf{r}, t)\,. \tag{2.27}$$

This is indeed a generalization of the Hamiltonian in Eq. (2.1) because any scalar potential v can be represented by a longitudinal[8] vector potential $\mathbf{A}_l$ by choosing the latter as the solution of (see Ref. [10])[9]:

$$\frac{\partial \mathbf{A}_l(\mathbf{r}, t)}{\partial t} = -\nabla v(\mathbf{r}, t)\,. \tag{2.28}$$

In other words, the TDDFT formalism is contained within the TDCDFT one. The expression for the density operator remains the same as in Eq. (1.4), and the current density operator $\hat{\mathbf{j}}(\mathbf{r}, t)$ is expressed in terms of the velocity operator $\hat{v}(t)$,

$$\hat{v}_i(t) = -i\nabla_i + A(\mathbf{r}_i, t)\,, \tag{2.29}$$

as

$$\hat{\mathbf{j}}(\mathbf{r}, t) = \frac{1}{2}\sum_i \left\{ \hat{v}_i(t), \delta(\mathbf{r} - \mathbf{r}_i) \right\}\,. \tag{2.30}$$

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[7] Until now, we have always chosen U to be the Coulomb interaction, but here we allow it to be different. In particular, later in this section, we will explicitly put U to zero in the case of noninteracting systems.

[8] By definition, any vector can be written as the sum of a longitudinal part, expressed as a gradient, and a transverse part, expressed as a curl. This is known as the Helmholtz-Hodge theorem. See for example the book of Jackson [16] for more details.

[9] This can be derived from the set of equations (2.33).

Using Eq. (2.30), one can express the expectation value of the current density as the sum of two separate terms:

$$\mathbf{j}(\mathbf{r},t) = \Big\langle \Psi(t)|\hat{\mathbf{j}}(\mathbf{r},t)|\Psi(t)\Big\rangle = \mathbf{j}_p(\mathbf{r},t) + \rho(\mathbf{r},t)\mathbf{A}(\mathbf{r},t)\,. \tag{2.31}$$

The first term of (2.31), $\mathbf{j}_p(\mathbf{r},t) = \Big\langle \Psi(t)|\hat{\mathbf{j}}_p(\mathbf{r},t)|\Psi(t)\Big\rangle$ with $\hat{\mathbf{j}}_p$ defined as in Eq. (2.8), is called the paramagnetic current density, and the second term, $\rho(\mathbf{r},t)\mathbf{A}(\mathbf{r},t)$, is called the diamagnetic current density.

Now, let $\rho(\mathbf{r},t)$ and $\mathbf{j}(\mathbf{r},t)$ be the density and current density of a system characterized by the Hamiltonian $\hat{H}$ given in Eq. (2.25) and an initial state $|\Psi_0\rangle$. We will prove that the same density and current density can be obtained from another many-particle system with a different hamiltonian $\hat{H}'$,

$$\hat{H}'(t) = \sum_i \left\{\frac{1}{2}[-i\nabla_i + A'(\mathbf{r}_i,t)]^2 + v'(\mathbf{r}_i,t)\right\} + \sum_{i<j} U'(\mathbf{r}_i - \mathbf{r}_j)\,, \tag{2.32}$$

starting from a different initial state $|\Psi'_0\rangle$, but which gives the same initial density $(\rho(\mathbf{r},t_0))$ and current-density $(\mathbf{j}(\mathbf{r},t_0))$ as $|\Psi_0\rangle$. For this to be true, the potentials v' and $\mathbf{A}'$ must undergo a gauge transformation[10] of the form

$$\begin{aligned} v'(\mathbf{r},t) &\to v'(\mathbf{r},t) + \frac{\partial\Lambda}{\partial t} \\ \mathbf{A}'(\mathbf{r},t) &\to \mathbf{A}'(\mathbf{r},t) + \nabla\Lambda(\mathbf{r},t) \end{aligned} \tag{2.33}$$

with $\Lambda(\mathbf{r},t)$ a regular function of $\mathbf{r}$ and t. This gauge transformation should also be accompanied by a transformation of the wavefunction of the form

$$\Psi(t) \to \Psi(t)e^{-i\Lambda(\mathbf{r},t)}\,. \tag{2.34}$$

In this way the physical results remain unchanged. We note that one may always use a gauge transformation of the form (2.33) to eliminate the scalar potential. To do this, it is required that

$$\frac{\partial\Lambda(\mathbf{r},t)}{\partial t} = -v'(\mathbf{r},t)\,,\ \Lambda(\mathbf{r},t_0) = 0\,. \tag{2.35}$$

The current density behaviour is governed by the equation of motion

$$\begin{aligned} \frac{d\mathbf{j}(\mathbf{r},t)}{dt} = \frac{\partial\mathbf{j}(\mathbf{r},t)}{\partial t} + i\Big\langle[\hat{H}(t),\hat{\mathbf{j}}(\mathbf{r},t)]\Big\rangle &= \rho(\mathbf{r},t)\frac{\partial\mathbf{A}(\mathbf{r},t)}{\partial t} \\ &- \mathbf{j}(\mathbf{r},t)\times(\nabla\times\mathbf{A}) + \mathbf{F}(\mathbf{r},t) + \nabla\cdot\sigma(\mathbf{r},t)\,. \end{aligned} \tag{2.36}$$

---

[10] A gauge transformation of the potentials is a modification of the potentials leaving the electric and magnetic fields unaltered.

The quantities $\mathbf{F}(\mathbf{r}, t)$ and $\sigma(\mathbf{r}, t)$ express the internal force density and the stress tensor and read:

$$\mathbf{F}(\mathbf{r}, t) = -\left\langle \sum_i \delta(\mathbf{r} - \mathbf{r}_i) \sum_{j \neq i} U(\mathbf{r}_i - \mathbf{r}_j) \right\rangle \tag{2.37}$$

$$\sigma_{\alpha\beta}(\mathbf{r}, t) = -\left\langle \frac{1}{4} \sum_i \{\hat{v}_\alpha, \{\hat{v}_\beta, \delta(\mathbf{r} - \mathbf{r}_i)\}\} \right\rangle . \tag{2.38}$$

The brackets correspond to the expectation value in the unprimed system at time t. One can write a similar expression as (2.36) for the primed system (for which the charge and current densities are the same as in the unprimed system by hypothesis):

$$\frac{d\mathbf{j}(\mathbf{r}, t)}{dt} = \rho(\mathbf{r}, t) \frac{\partial \mathbf{A}'(\mathbf{r}, t)}{\partial t} - \mathbf{j}(\mathbf{r}, t) \times (\nabla \times \mathbf{A}'(\mathbf{r}, t)) + \mathbf{F}'(\mathbf{r}, t) + \nabla \cdot \sigma'(\mathbf{r}, t) . \tag{2.39}$$

Taking the difference between (2.36) and (2.39) yields

$$\rho(\mathbf{r}, t) \frac{\partial \Delta \mathbf{A}(\mathbf{r}, t)}{\partial t} = \mathbf{j}(\mathbf{r}, t) \times (\nabla \times \Delta \mathbf{A}(\mathbf{r}, t)) + \mathbf{Q}(\mathbf{r}, t) - \mathbf{Q}'(\mathbf{r}, t) . \tag{2.40}$$

where $\Delta \mathbf{A}(\mathbf{r}, t) \equiv \mathbf{A}'(\mathbf{r}, t) - \mathbf{A}(\mathbf{r}, t)$ and $\mathbf{Q}(\mathbf{r}, t) \equiv \mathbf{F}(\mathbf{r}, t) + \nabla \cdot \sigma(\mathbf{r}, t)$. By solving Eq. (2.40), one could get the vector potential $\mathbf{A}'$ generating the same current density as the vector potential $\mathbf{A}$ in the unprimed system. However, as $\mathbf{Q}'$ is implicitly expressed as a function of $\mathbf{A}'$ (through σ), one cannot immediately prove the existence and uniqueness of the solution. To circumvent this difficulty, we shall use the fact that the potentials $\mathbf{A}$ and $\mathbf{A}'$ —thus also the difference $\Delta\mathbf{A}$— are Taylor-expandable. We have:

$$\Delta \mathbf{A}(\mathbf{r}, t) = \sum_{k=0}^{\infty} \frac{1}{k!} \left. \frac{\partial^k \Delta \mathbf{A}(\mathbf{r}, t)}{\partial t^k} \right|_{t=t_0} (t - t_0)^k \equiv \sum_{k=0}^{\infty} \Delta \mathbf{A}_k(\mathbf{r}) (t - t_0)^k . \tag{2.41}$$

Then by substituting (2.41) in (2.40) and keeping only the l^{th}-order term in t, one can show that

$$\begin{aligned} \rho_0(\mathbf{r})(l+1)\Delta\mathbf{A}_{l+1}(\mathbf{r}) = &- \sum_{k=0}^{l-1} \rho_{l-k}(\mathbf{r})(k+1)\Delta\mathbf{A}_{k+1}(\mathbf{r}) \\ &+ \sum_{k=0}^{l} \{\mathbf{j}_{l-k}(\mathbf{r}) \times [\nabla \times \Delta\mathbf{A}_k(\mathbf{r})]\}\} \\ &+ [\mathbf{Q}(\mathbf{r}, t)]_l + [\mathbf{Q}'(\mathbf{r}, t)]_l . \end{aligned} \tag{2.42}$$

where we used the fact that

$$\left[\frac{\partial \Delta \mathbf{A}(\mathbf{r},t)}{\partial t}\right]_k = (k+1)\Delta \mathbf{A}_{k+1}(\mathbf{r})\,. \tag{2.43}$$

In the previous equations, a term of the form $[..]_l$ denotes the l^{th} coefficient in the Taylor expansion of the considered function, and we assumed that each quantity appearing in (2.40) admits a Taylor expansion, also the density and current density. Equation (2.42) is a recursion relation, meaning that $\Delta\mathbf{A}_{l+1}$ is determined upon knowing the previous $\Delta\mathbf{A}_k$ for $k \leq l$. One has to be careful though, because other coefficients enter Eq. (2.42) implicitly through $\mathbf{Q}$ and $\mathbf{Q}'$. Actually, as the time-dependent Schrödinger is of first-order in time, it ensures that the l^{th} coefficients of the Taylor expansion of $\Psi(t)$ and $\Psi'(t)$ are determined solely by the coefficients of order $k < l$ appearing in the expansion of $\mathbf{A}_k(\mathbf{r},t)$ and $\mathbf{A}'_k(\mathbf{r},t)$. In the end, all the quantities appearing on the right-hand side of Eq. (2.42) are entirely determined by the coefficients $\Delta\mathbf{A}_k(\mathbf{r})$ with $k \leq l$. As for any recursion, one needs to know the initial state $\Delta\mathbf{A}_0(\mathbf{r}) = \mathbf{A}'(\mathbf{r},t_0) - \mathbf{A}(\mathbf{r},t_0)$, which we can get from using the equality of the densities and current densities in the primed and unprimed systems at $t = t_0$:

$$\left\langle \Psi(t_0)|\hat{\mathbf{j}}(\mathbf{r})|\Psi(t_0)\right\rangle = \left\langle \Psi'(t_0)|\hat{\mathbf{j}}(\mathbf{r})|\Psi'(t_0)\right\rangle\,. \tag{2.44}$$

By using Eq. (2.31), one obtains

$$\rho(\mathbf{r},t_0)\Delta\mathbf{A}_0(\mathbf{r}) = \left\langle \Psi(t_0)|\hat{\mathbf{j}}_p(\mathbf{r})|\Psi(t_0)\right\rangle - \left\langle \Psi'(t_0)|\hat{\mathbf{j}}_p(\mathbf{r})|\Psi'(t_0)\right\rangle\,, \tag{2.45}$$

where $\hat{\mathbf{j}}_p(\mathbf{r})$ is given in Eq. (2.8). This recursion thus completely determines the coefficients of the Taylor expansion of $\mathbf{A}'(\mathbf{r},t)$ which produces the same current density in the primed system as $\mathbf{A}(\mathbf{r},t)$ does in the unprimed system. In practice, the potential $\mathbf{A}'(\mathbf{r},t)$ is determined by calculating all coefficients of the Taylor expansion up to a certain rank, and truncating the series at this rank, provided that the series is convergent within a convergence radius $t_c > 0$. The potential can hence be calculated up to t_c, and one can then iterate the process by taking t_c as the initial time. We have thus proven Vignale's theorem.
Let us now distinguish two cases.

- In case both systems are such that $U = U'$ and $\Psi(t_0) = \Psi'(t_0)$, Eq. (2.45) implies that $\Delta\mathbf{A}_0(\mathbf{r}) = 0$. One can then infer from Eq. (2.42) that $\Delta\mathbf{A}_k(\mathbf{r}) = 0$ for all k, thus $\mathbf{A}(\mathbf{r},t) = \mathbf{A}'(\mathbf{r},t)$ at all times. In other words, two vector potentials generating the same current-density and evolving from the same initial state must be equal, up to a gauge transformation. This is the analogue of the Runge-Gross theorem of TDDFT explained in the previous section. In other words, there is a one-to-one mapping between the current density and the vector potential.

- In case when the primed system is noninteracting, i.e., $U' = 0$, the current density produced in the unprimed interacting system can, according to Vignale's theorem we have just proved, be reproduced in a noninteracting system evolving under an effective vector potential $\mathbf{A}'(\mathbf{r}, t)$. So if an initial state $|\Psi'(t_0)\rangle$ corresponding to the correct density and current density can be found, then we have solved the so-called non-interacting **A**-representability problem, which is analogous to the non-interacting v-representability in (TD)DFT.

We are now able to give the Kohn-Sham equations for general time-dependent external fields. They read

$$i\frac{\partial}{\partial t}\phi_i(\mathbf{r},t) = \left(\frac{1}{2}[-i\nabla + \mathbf{A}_s(\mathbf{r},t)]^2 + v_s(\mathbf{r},t)\right)\phi_i(\mathbf{r},t)\,, \tag{2.46}$$

$$\mathbf{j}(\mathbf{r},t) = \frac{-i}{2}\sum_{i=1}^{N}[\phi_i^*(\mathbf{r},t)\nabla\phi_i(\mathbf{r},t) - \nabla\phi_i^*(\mathbf{r},t)\phi_i(\mathbf{r},t)] + \rho(\mathbf{r},t)\mathbf{A}_s(\mathbf{r},t)\,, \tag{2.47}$$

$$\rho(\mathbf{r},t) = \sum_{i=1}^{N}|\phi_i(\mathbf{r},t)|^2\,, \tag{2.48}$$

where again, we have assumed the initial state can be represented as a single Slater determinant. Similarly to TDDFT, the Kohn-Sham potentials are defined by

$$v_s(\mathbf{r},t) = v(\mathbf{r},t) + \int d\mathbf{r}'\frac{\rho(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|} + v_{xc}(\mathbf{r},t)\,, \tag{2.49}$$

$$\mathbf{A}_s(\mathbf{r},t) = \mathbf{A}(\mathbf{r},t) + \mathbf{A}_{xc}(\mathbf{r},t) \tag{2.50}$$

where we have chosen the repulsive Coulomb potential as the two-particle interaction. As for TDDFT, the Kohn-Sham equations need to be solved self-consistently, because the potentials depend on the densities and current densities, and vice-versa.

It was shown that in general, an interacting system evolving in a time-dependent field that can be described solely by a scalar potential cannot be described by a Kohn-Sham system with only a scalar potential [17]. In other words, a v-representable current density is not necessarily noninteracting v-representable. Nevertheless, the v-representable current density may be a noninteracting **A**-representable quantity, as this is a weaker condition.

2.3 Exchange-correlation functionals

2.3.1 The ALDA functional

One of the simplest and most widely used approximation to the time-dependent exchange-correlation potentials is the so-called adiabatic local density approximation (ALDA) [18], which is a direct extension of the LDA approximation used in the stationary case (see section 1.4). It is defined as

$$
\begin{aligned}
v_{xc}^{ALDA}(\mathbf{r},t) =& v_{xc}^{hom}(\rho(\mathbf{r},t)) = \frac{d}{d\rho}\left[\rho\epsilon_{xc}^{h}[\rho]\right]\Bigg|_{\rho=\rho(\mathbf{r},t)}\,, \qquad (2.51)\\
\mathbf{A}_{xc}^{ALDA}(\mathbf{r},t) =& \mathbf{0}\,. \qquad (2.52)
\end{aligned}
$$

One can recognize that v_{xc}^{ALDA} is expressed similarly as in Eq. (1.34), but evaluated at the instantaneous time-dependent density $\rho(\mathbf{r},t)$. The ALDA is thus local in space as well as in time, thereby neglecting memory effects coming from the dependence of the exchange-correlation potential on previous times $t' < t$. Quite unexpectedly, ALDA gives quite good results even for molecules which exhibit a rapidly changing density, just like LDA. However, it also suffers from the same sins as its ground-state DFT analogue, for example the erroneous long-range behaviour.

2.3.2 The Vignale-Kohn functional

Vignale and Kohn managed to approximate the exchange-correlation vector potential $\mathbf{A}_{xc}$ in terms of a local functional of the current density $\mathbf{j}$ [19–23]:

$$
\frac{i\omega}{c}\mathbf{A}_{xc,i}(\mathbf{r},\omega) = -\frac{1}{\rho_0(\mathbf{r})}\sum_j \partial_j\sigma_{xc,ij}(\mathbf{r},\omega)\,, \qquad (2.53)
$$

where $\sigma_{xc,ij}$ has the form of the viscoelastic stress tensor[11],

$$
\begin{aligned}
\sigma_{xc,ij}(\mathbf{r},\omega) = \tilde{\eta}_{xc}(\omega,\rho_0(\mathbf{r}))&\left(\partial_j u_i \partial_i u_j - \frac{2}{3}\delta_{ij}\sum_k \partial_k u_k\right)\\
&+\tilde{\zeta}_{xc}(\omega,\rho_0(\mathbf{r}))\delta_{ij}\sum_k \partial_k u_k\,, \qquad (2.54)
\end{aligned}
$$

---

[11] This tensor appears in the Navier-Stokes equation.

with $\mathbf{u}(\mathbf{r},\omega) = \frac{\delta\mathbf{j}(\mathbf{r},\omega)}{\rho_0(\mathbf{r})}$ the velocity field. The coefficients $\tilde{\eta}$ and $\tilde{\zeta}$ are given by

$$\tilde{\eta}(\omega,\rho_0(\mathbf{r})) = -\frac{\rho_0^2}{i\omega} f_{xcT}(\omega,\rho_0(\mathbf{r}))\,, \tag{2.55}$$

$$\tilde{\zeta}(\omega,\rho_0(\mathbf{r})) = -\frac{\rho_0^2}{i\omega}\left(f_{xcL}(\omega,\rho_0(\mathbf{r})) - \frac{4}{3} f_{xcT}(\omega,\rho_0(\mathbf{r})) - f_{xcL}(\omega=0,\rho_0(\mathbf{r}))\right)\,, \tag{2.56}$$

where $f_{xcL}(\omega,\rho_0(\mathbf{r}))$ and $f_{xcT}(\omega,\rho_0(\mathbf{r}))$ are, respectively, the longitudinal and transverse exchange-correlation kernels of the homogeneous electron gas with density $\rho_0(\mathbf{r})$.

3

LINEAR RESPONSE WITHIN TDCDFT

In this chapter, we shall describe the Linear Response Theory (LRT) formalism, and see how it can be used within the framework of TDCDFT. LRT is based on perturbation theory, and allows one to describe the changes occuring in a system subjected to a small external perturbation (such as a weak electromagnetic field), which is of great interest in many different domains. In LRT, only changes linear in the perturbation are treated. In particular, we will be interested in obtaining the first-order change of the density and current density.

3.1 Linear Response Theory

Let us consider a system which is in the ground-state Ψ_0 of the Hamiltonian $\hat{H}_0$ for $t < t_0$. At $t = t_0$, we apply a small (time-dependent) external perturbation $\delta\hat{h}(t)$ and look at the change of the expectation value of an arbitrary physical observable $\hat{O}$ of the system, given by

$$\delta \left\langle \hat{O} \right\rangle (t) = \langle \Psi(t) \,|\hat{O}|\, \Psi(t) \rangle - \langle \Psi_0 | \,\hat{O}\, | \Psi_0 \rangle \, , \tag{3.1}$$

where $\Psi(t)$ is the solution of the time-dependent Schrödinger equation

$$i\frac{\partial}{\partial t}\Psi(t) = \left[\hat{H}_0 + \delta\hat{h}(t)\right]\Psi(t) \, . \tag{3.2}$$

For practical purposes, we shall work within the interaction picture, for which operators and wavefunctions are linked to the Schrödinger operators and wavefunctions via the following unitary transformations:

$$\Psi_I(t) = e^{i(t-t_0)\hat{H}_0}\Psi(t) \tag{3.3}$$

$$\hat{O}_I(t) = e^{i(t-t_0)\hat{H}_0}\hat{O}e^{-i(t-t_0)\hat{H}_0} \, . \tag{3.4}$$

We notice that both wavefunctions are the same at $t = t_0$. The evolution of the wavefunction $\Psi_I(t)$ is governed by the equation of motion,

$$i\frac{\partial}{\partial t}\Psi_I(t) = \delta\hat{h}_I(t)\Psi_I(t)\,, \tag{3.5}$$

which can be obtained by isolating $\Psi(t)$ in Eq. (3.3) and substituting it into Eq.(3.2). Equation (3.5) can be equivalently rewritten in an integral form:

$$\Psi_I(t) = \Psi_0 - i\int_{t_0}^{t} dt'\delta\hat{h}_I(t')\Psi_I(t')\,. \tag{3.6}$$

We can solve Eq. (3.6) iteratively, by inserting the expression for $\Psi_I(t)$ in the $\Psi_I(t')$ appearing on the right-hand side of the very same equation (3.6), which will make appear orders of $\delta\hat{h}_I$. As we consider only linear terms in the perturbation, we neglect all the quadratic and higher-order terms. We obtain

$$\Psi_I(t) = \Psi_0 - i\int_{t_0}^{t} dt'\delta\hat{h}_I(t')\Psi_0 + o(\delta\hat{h}_I^2)\,. \tag{3.7}$$

The expectation value of the operator $\hat{O}_I$ is given by

$$\langle\Psi_I(t)|\,\hat{O}_I\,|\Psi_I(t)\rangle = \langle\Psi_0|\,\hat{O}\,|\Psi_0\rangle - i\int_{t_0}^{t} dt'\,\langle\Psi_0|\left[\hat{O}_I(t),\delta\hat{h}_I(t')\right]|\Psi_0\rangle + o(\delta\hat{h}_I^2)\,, \tag{3.8}$$

and the change of the expectation value (Eq. (3.1)), i.e., the linear response, of the operator $\hat{O}$ is thus expressed as

$$\delta\left\langle\hat{O}\right\rangle(t) = -i\int_{t_0}^{t} dt'\,\langle\Psi_0|\left[\hat{O}_I(t),\delta\hat{h}_I(t')\right]|\Psi_0\rangle\,. \tag{3.9}$$

We now consider a general perturbation of the form

$$\delta\hat{h}_I(t) = \sum_i \hat{O}_{iI}(t)\varphi_i(t)\,, \tag{3.10}$$

where the $\varphi_i(t)$ are arbitrary time-dependent functions. The change in expectation value is then given by

$$\begin{aligned}\delta\left\langle\hat{O}_i\right\rangle(t) &= -i\int_{t_0}^{t} dt'\,\langle\Psi_0|\,[\hat{O}_{iI}(t),\sum_j \hat{O}_{jI}(t')\varphi_j(t')]\,|\Psi_0\rangle\\ &= \sum_j\int_{t_0}^{\infty} dt'\chi_{ij}(t,t')\varphi_j(t')\,,\end{aligned} \tag{3.11}$$

where the $\chi_{ij}(t,t')$ are the so-called response functions defined as

$$\chi_{ij}(t,t') = -i\Theta(t-t') \langle\Psi_0| [\hat{O}_{iI}(t), \hat{O}_{jI}(t')] |\Psi_0\rangle \ . \tag{3.12}$$

The Heaviside step-function Θ ensures the causality of the response functions[1] and allows us to extend the integration range to infinity.

For practical applications, it is convenient to rewrite Eq. (3.12) in a spectral representation, which we will do in the following. Assuming that $|\Psi_n\rangle$ is a complete set of eigenstates of $\hat{H}_0$, we can use the closure relation $\sum_n |\Psi_n\rangle\langle\Psi_n| = 1$ in order to get

$$\begin{aligned}\chi_{ij}(t,t') = -i\Theta(t-t') \sum_n \Big\{ & \langle\Psi_0| \hat{O}_{iI}(t) |\Psi_n\rangle \langle\Psi_n| \hat{O}_{jI}(t') |\Psi_0\rangle \\ & - \langle\Psi_0| \hat{O}_{jI}(t') |\Psi_n\rangle \langle\Psi_n| \hat{O}_{iI}(t) |\Psi_0\rangle \Big\} \, .\end{aligned} \tag{3.13}$$

By using Eq. (3.4), one gets

$$\begin{aligned}\langle\Psi_0| \hat{O}_{iI}(t) |\Psi_n\rangle \langle\Psi_n| \hat{O}_{jI}(t') |\Psi_0\rangle &= \langle\Psi_0| e^{i(t-t_0)\hat{H}_0} \hat{O}_i e^{-i(t-t_0)\hat{H}_0} |\Psi_n\rangle \\ &\quad\times \langle\Psi_n| e^{i(t'-t_0)\hat{H}_0} \hat{O}_j e^{-i(t'-t_0)\hat{H}_0} |\Psi_n\rangle \\ &= e^{i(E_0-E_n)(t-t')} \langle\Psi_0| \hat{O}_i |\Psi_n\rangle \langle\Psi_n| \hat{O}_j |\Psi_0\rangle \ ,\end{aligned} \tag{3.14}$$

where E_0 and E_n are the eigenvalues corresponding to the eigenstates Ψ_0 and Ψ_n of $\hat{H}_0$, respectively. A similar result can be obtained for the other term in Eq. (3.13), leading to the following expression for the response function:

$$\begin{aligned}\chi_{ij}(t-t') = -i\Theta(t-t') \sum_n \Big\{ & e^{i(E_0-E_n)(t-t')} \langle\Psi_0| \hat{O}_i |\Psi_n\rangle \langle\Psi_n| \hat{O}_j |\Psi_0\rangle \\ & - e^{-i(E_0-E_n)(t-t')} \langle\Psi_0| \hat{O}_j |\Psi_n\rangle \langle\Psi_n| \hat{O}_i |\Psi_0\rangle \Big\} \, .\end{aligned} \tag{3.15}$$

An important remark is that if $\hat{O}_i$ and $\hat{O}_j$ are time-independent, then the response function χ_{ij} only depends on the difference $(t-t')$, as can be seen in Eq. (3.15). Let us define the Fourier transform of the response function as

$$\tilde{\chi}(\omega) = \int d\tau \chi(\tau) e^{+i\omega\tau} \, , \tag{3.16}$$

with $\tau = t - t'$. Then by expressing the Heaviside step-function in the integral form,

$$\Theta(\tau) = \frac{-1}{2\pi i} \lim_{\eta\to 0^+} \int_{-\infty}^{\infty} d\omega' \frac{e^{-i\omega'\tau}}{\omega' + i\eta} \, , \tag{3.17}$$

---

[1] The system should not react to a perturbation before it is applied, i.e., $\chi_{ij}(t-t') = 0$ for $t < t'$.

and inserting it in Eq. (3.16), one gets

$$\tilde{\chi}_{ij}(\omega) = \lim_{\eta\to 0^+} \frac{1}{2\pi} \sum_n \Big\{ \langle\Psi_0|\, \hat{O}_i \,|\Psi_n\rangle \langle\Psi_n|\, \hat{O}_j \,|\Psi_0\rangle \int d\omega' \frac{1}{\omega' + i\eta} \\ \times \int d\tau e^{i[-\omega'+\omega-(E_n-E_0)]\tau} - (n \leftrightarrow 0) \Big\} . \tag{3.18}$$

By making use of the subsequent representation of the Dirac delta function,

$$\delta(\tau) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega e^{i\omega\tau} , \tag{3.19}$$

one obtains the spectral representation of the response function as

$$\tilde{\chi}_{ij}(\omega) = \lim_{\eta\to 0^+} \sum_n \left\{ \frac{\langle\Psi_0|\, \hat{O}_i \,|\Psi_n\rangle \langle\Psi_n|\, \hat{O}_j \,|\Psi_0\rangle}{\omega - (E_n - E_0) + i\eta} - \frac{\langle\Psi_0|\, \hat{O}_j \,|\Psi_n\rangle \langle\Psi_n|\, \hat{O}_i \,|\Psi_0\rangle}{\omega + (E_n - E_0) + i\eta} \right\} , \tag{3.20}$$

where η ensures causality, and the limit has to be taken after integration of $\tilde{\chi}(\omega)$ against some function, e.g., a potential. We can see from Eq. (3.9) that the poles of the response function are the excitation energies of the system. Finally, the change in expectation value given in Eq. (3.11) becomes

$$\delta \left\langle \hat{O}_i \right\rangle (\omega) = \sum_j \tilde{\chi}_{ij}(\omega) \tilde{\varphi}_j(\omega) \tag{3.21}$$

in the frequency domain.

3.2 Linear response theory for a Kohn-Sham system

Until now, the formalism we presented was general and applicable to any observable. Since we are interested in the induced current density (or current response), and this can be calculated within TDCDFT using the auxiliary Kohn-Sham system, we will show how this formalism can be used in this case. First, we remind the reader the expression for the ground-state Kohn-Sham Hamiltonian (see Eq. (1.31)):

$$\hat{H}_s = \sum_{i=1}^{N} \hat{h}_s(\mathbf{r}_i) = \sum_{i=1}^{N} -\frac{1}{2}\nabla_i^2 + v_s(\mathbf{r}_i) , \tag{3.22}$$

where $v_s(\mathbf{r}_i) = v_s(\mathbf{r}_i, t_0)$. The time-dependent Kohn-Sham Hamiltonian (also defined in Eq. (2.46)) reads:

$$\hat{H}_s(t) = \sum_{i=1}^{N} \hat{h}_s = \sum_{i=1}^{N} \left\{ \frac{1}{2}[-i\nabla + \mathbf{A}_s(\mathbf{r}_i, t)]^2 + v_s(\mathbf{r}_i, t) \right\} , \tag{3.23}$$

Subtracting Eq. (3.22) from Eq. (3.23), we get the following perturbation:

$$\begin{aligned} \delta\hat{h}_s &= \sum_{i=1}^{N} \left[\frac{1}{2}\hat{p}_i \cdot \delta\mathbf{A}_s(\mathbf{r}_i, t) + \frac{1}{2}\delta\mathbf{A}_s(\mathbf{r}_i, t) \cdot \hat{p}_i + \frac{1}{2}\delta\mathbf{A}_s^2(\mathbf{r}_i, t) + \delta v_s(\mathbf{r}_i, t) \right] \\ &= \int d\mathbf{r} \hat{\mathbf{j}}_p(\mathbf{r}) \cdot \delta\mathbf{A}_s(\mathbf{r}, t) + \frac{1}{2} \int d\mathbf{r} \hat{\rho}(\mathbf{r}) \delta\mathbf{A}_s^2(\mathbf{r}, t) + \int \hat{\rho}(\mathbf{r}) \delta v_s(\mathbf{r}, t) \,, \end{aligned} \tag{3.24}$$

with $\hat{p}_i = -i\nabla_i$, $\delta v_s(\mathbf{r}, t) = v_s(\mathbf{r}, t) - v_s(\mathbf{r}, t_0)$ and $\delta\mathbf{A}_s(\mathbf{r}, t) = \mathbf{A}_s(\mathbf{r}, t) - \mathbf{A}_s(\mathbf{r}, t_0)$. In our case, as the ground-state is described by a scalar potential only, the initial vector potential vanishes: $\mathbf{A}(\mathbf{r}, t_0) = \mathbf{0}$.

Here we are mainly interested in the current density, which is given by

$$\delta\mathbf{j}(\mathbf{r}, t) = \delta\mathbf{j}_p(\mathbf{r}, t) + \rho_0(\mathbf{r}) \delta\mathbf{A}_s(\mathbf{r}, t) \,, \tag{3.25}$$

where $\rho_0(\mathbf{r})$ is the ground-state density. By making use of Eqs.(3.10), (3.9) and (3.21) from the previous section, we get the following expressions for the induced current density and the induced density in the frequency domain:

$$\delta\rho(\mathbf{r}, \omega) = \int d\mathbf{r}' \chi_{\rho\mathbf{j}_p}(\mathbf{r}, \mathbf{r}', \omega) \cdot \delta\mathbf{A}_s(\mathbf{r}', \omega) + \int d\mathbf{r}' \chi_{\rho\rho}(\mathbf{r}, \mathbf{r}', \omega) \delta v_s(\mathbf{r}', \omega) \,, \tag{3.26}$$

$$\begin{aligned} \delta\mathbf{j}(\mathbf{r}, \omega) &= \int d\mathbf{r}' \left(\chi_{\mathbf{j}_p\mathbf{j}_p}(\mathbf{r}, \mathbf{r}', \omega) + \rho_0(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}') \mathbb{1} \right) \cdot \delta\mathbf{A}_s(\mathbf{r}', \omega) \\ &\quad + \int d\mathbf{r}' \chi_{\mathbf{j}_p\rho}(\mathbf{r}, \mathbf{r}', \omega) \delta v_s(\mathbf{r}', \omega) \,, \end{aligned} \tag{3.27}$$

where $\mathbb{1}$ is the identity matrix of rank 3. The Kohn-Sham response functions in Eq. (3.26) and Eq. (3.27) are given by

$$\chi_{AB}(\mathbf{r}, \mathbf{r}', \omega) = \lim_{\eta \to 0^+} \sum_{n,n'} (f_n - f_{n'}) \frac{\phi_n^*(\mathbf{r}) \hat{A} \phi_{n'}(\mathbf{r}) \phi_{n'}^*(\mathbf{r}') \hat{B} \phi_n(\mathbf{r}')}{(\varepsilon_n - \varepsilon_{n'}) + \omega + i\eta} \,, \tag{3.28}$$

where n and n' run over all the orbitals, and the f_n are the occupation numbers of the Kohn-Sham orbitals ϕ_n. The operators $\hat{A}$ and $\hat{B}$ must be substituted by the density operator $\hat{\rho} = 1$ and the paramagnetic current density operator $\hat{\mathbf{j}}_p = \frac{-i}{2} \left(\nabla - \nabla^\dagger \right)$.

Since we work at zero temperature, there are no fractional occupation numbers, that is $f_n = 1$ for the occupied states and $f_n = 0$ for the unoccupied states. For convenience, we also set $\eta = 0$ in Eq. (3.28), which does not cause any problem if we are not in the absorption range[2]. Finally we choose the Kohn-Sham orbitals to be real valued, which is always feasible if the ground-state of the system is time-reversal invariant. The response functions can thus be rewritten as

$$\chi_{AB}(\mathbf{r},\mathbf{r}',\omega) = \sum_{i,a}\left[\frac{\phi_i(\mathbf{r})\hat{A}\phi_a(\mathbf{r})\phi_a(\mathbf{r}')\hat{B}\phi_i(\mathbf{r}')}{(\epsilon_i-\epsilon_a)+\omega} + \frac{\phi_i(\mathbf{r})\hat{A}^*\phi_a(\mathbf{r})\phi_a(\mathbf{r}')\hat{B}^*\phi_i(\mathbf{r}')}{(\epsilon_i-\epsilon_a)-\omega}\right], \tag{3.29}$$

where i (a) runs over the occupied (unoccupied) orbitals. We are just left to make a gauge choice for the induced potentials δv_s and $\delta\mathbf{A}_s$. Like for the ground-state, they can be decomposed as

$$\delta v_s(\mathbf{r},\omega) = \delta v_H(\mathbf{r},\omega) + \delta v_{xc}(\mathbf{r},\omega)\,, \tag{3.30}$$

$$\mathbf{A}_s(\mathbf{r},\omega) = \mathbf{A}_{ext}(\mathbf{r},\omega) + \mathbf{A}_{xc}(\mathbf{r},\omega)\,, \tag{3.31}$$

with δv_H representing the first-order change in the Hartree potential, $\mathbf{A}_{ext}$ the external field, and δv_{xc} and $\mathbf{A}_{xc}$ are the induced exchange-correlation potentials [3]. We choose the gauge such that the external field is entirely determined by the vector potential, i.e., $\delta v_{ext} = 0$. Without loss of generality, one could also choose $\delta v_{xc} = 0$, and write δv_H in terms of a vector potential. However, it is convenient to keep these scalar potentials explicitly in our formalism. The exchange-correlation potentials can be written as

$$\delta v_{xc}(\mathbf{r},\omega) = \int d\mathbf{r}' f_{xc}(\mathbf{r},\mathbf{r}',\omega)\delta\rho(\mathbf{r}',\omega)\,, \tag{3.32}$$

$$\delta\mathbf{A}_{xc}(\mathbf{r},\omega) = \int d\mathbf{r}' \mathbf{f}_{xc}(\mathbf{r},\mathbf{r}',\omega)\cdot\delta\mathbf{j}(\mathbf{r}',\omega)\,, \tag{3.33}$$

which define f_{xc} and $\mathbf{f}_{xc}$, the scalar and tensor exchange-correlation kernels, respectively. Like for the ground-state, since Eqs. (3.32) and (3.33) depend on the induced density and current density, and these densities depend themselves on the exchange-correlation potentials, then the response equations need to be solved in a self-consistent way.

From Eq. (3.32), we learn that f_{xc} can be written as the functional derivative

$$f_{xc}(\mathbf{r},\mathbf{r}',t,t') = \frac{\delta v_{xc}(\mathbf{r},t)}{\delta\rho(\mathbf{r}',t')}\,. \tag{3.34}$$

This kernel obviously takes different forms, depending on the approximation one

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[2] When ω is equal to an excitation energy, one can use a broadening parameter in order to avoid a singularity.

[3] Notice the absence of δ in the expression for the induced vector potential since $\mathbf{A}_{ext}(\mathbf{r},t_0) = 0$ and $\mathbf{A}_{xc}(\mathbf{r},t_0) = 0$.

used. For the ALDA kernel given in Eq. (2.51), we get:

$$f_{xc}^{ALDA}(\mathbf{r},\mathbf{r}',t-t') = \delta(t-t')\delta(\mathbf{r}-\mathbf{r}')\frac{d^2}{d\rho^2}\left(\rho\epsilon_{xc}^{hom}(\rho)\right)\Big|_{\rho=\rho_0(\mathbf{r})} . \tag{3.35}$$

We note that after Fourier-transforming this quantity, the ALDA kernel has no frequency dependence anymore:

$$f_{xc}^{ALDA}(\mathbf{r},\mathbf{r}',\omega) = \delta(\mathbf{r}-\mathbf{r}')\frac{d^2}{d\rho^2}\left(\rho\epsilon_{xc}^{hom}(\rho)\right)\Big|_{\rho=\rho_0(\mathbf{r})} . \tag{3.36}$$

4 GAUGE-INVARIANT CALCULATION OF MAGNETIC PROPERTIES

In this chapter, we solve two problems related to the calculation of static and dynamical magnetic properties with *ab initio* theories. First, we show that the dependence of the dynamical magnetic dipole moment on the reference point of the multipole expansion and on the gauge origin of the vector potential have a clear physical significance. They are due to a dynamical electric dipole moment and an electric field, respectively. Both are fully determined by the experimental setup and do not pose any fundamental problem, contrary to what is commonly assumed. Second, in the static case, any dependence on the gauge origin is an artifact of the computational method. We show that the artificial dependence on the gauge origin can be removed in an elegant way by the introduction of a sum rule that puts the diamagnetic and paramagnetic contributions on equal footing. Our approach can be applied to calculate any magnetic observable that can be derived from the current density, and can be used in combination with any *ab initio* theory from which the current density can be obtained. To illustrate our method we apply it to TDCDFT for the calculation of static and dynamical magnetizabilities of molecules.

Part of the work described here is summarized in: *N. Raimbault, P. L. de Boeij, P. Romaniello, and J. A. Berger, Phys. Rev. Lett. 114, 066404 (2015), "Gauge-Invariant Calculation of Static and Dynamical Magnetic Properties from the Current Density".*

4.1 Introduction

Important information on the electronic structure of atoms and molecules is obtained experimentally by studying their response to electromagnetic fields. Many important molecular properties (polarizabilities, magnetizabilities, nuclear magnetic resonance (NMR) shielding constants, etc.) can thus be measured. Over the years, several theoretical tools have been developed that calculate these properties from first principles [24]. Magnetic properties in particular have proven to be a challenge for *ab initio* methods as they require a correct description of the transverse response of the molecule to the magnetic field. This can, in general, not be obtained from the density response function which is related to a purely longitudinal response.

In this chapter, we solve two fundamental problems related to the calculation of magnetic response properties:

1. An artificial gauge dependence arises in the calculation of magnetic properties when using finite basis sets.

2. Several dynamical magnetic properties depend on the choice of the origin of the coordinate system, which is unphysical.

So far no solution exists for either problem.

Related to the first problem is the very slow convergence of magnetic properties with the size of the basis set. The slow convergence can be circumvented by choosing a convenient gauge. However, in the dynamical case, any gauge convention arbitrarily fixes the electric field precluding comparison with experiment. Various gauge conventions exist [25–29]. The most commonly applied convention is to use gauge-including atomic orbitals (GIAOs) [25, 26]. In this approach the atomic orbitals are chosen to transform according to the same gauge transformation used for the vector potential. Although the GIAO method improves convergence with basis-set size, it is *not* gauge invariant, which is exemplified by the fact that it does not conserve the charge [30]. Moreover, the GIAO method has several other shortcomings: i) it is limited to atom-centered basis sets; ii) it is numerically less efficient than standard basis sets; iii) its implementation is cumbersome; iv) the generalization to dynamical electromagnetic fields is nontrivial [31, 32].

The dependence on the origin of the coordinate system is related to the fact that the definitions used in practical calculations are obtained using multipole theory [32, 33]. A fundamental feature of these definitions is that they depend on the particular choice of the reference point of the multipole expansion. This reference point is easily confused with the origin of the coordinate system leading to results that depend on the choice for this origin. This poses a serious problem for the calculation of several dynamical magnetic properties such as the magnetizability. It was shown that by combining the magnetizability with higher-order multipole polarizabilities one obtains a quantity that is independent of the choice of the origin [34]. However, it is not clear to which physical observable, if any, this quantity corresponds. Moreover, the way to combine the multipole moments is not unique [35].

Our solution to the two problems mentioned above is both simple and elegant; it can be summarized in two steps: i) Express magnetic properties in terms of the current density, which for most properties of interest can be readily done; ii) Calculate the current density by treating para- and diamagnetic contributions on equal footing (see Eq. (4.16) below). Our method is general, fully gauge invariant and can be used together with any theoretical approach from which the current density can be obtained and with any standard basis set.

4.2 Theory

To illustrate our approach in detail it is convenient to focus on a specific magnetic property. We will study the magnetizability which is defined as the constant of proportionality of the induced magnetic dipole moment $\delta\mathbf{m}(\omega)$ and an externally applied uniform magnetic field $\mathbf{B}(\omega)$; it can be regarded as the analogue of the polarizability for the electric case[1].

When a magnetic field is applied to a molecule, the latter aquires an induced magnetic dipole moment, defined as

$$\delta\mathbf{m}(\omega) = \frac{1}{2}\int d\mathbf{r}(\mathbf{r}-\mathbf{r}_C)\times\delta\mathbf{j}(\mathbf{r},\omega)\,, \tag{4.1}$$

where $\mathbf{r}_C$ is a fixed reference point in the molecular frame which ensures that $\delta\mathbf{m}(\omega)$ is independent of the origin of the coordinate system[2] $\mathbf{r}_O$, and $\delta\mathbf{j}(\mathbf{r},\omega)$ is the induced current density. We note that for the static case, there is no dependence on $\mathbf{r}_C$ as $\int d\mathbf{r}\delta\mathbf{j}(\mathbf{r},0)$ vanishes, which is not the case for finite frequencies anymore. Using the continuity relation, $\int d\mathbf{r}\delta\mathbf{j}(\mathbf{r},\omega) = -i\omega\int d\mathbf{r}\mathbf{r}\delta\rho(\mathbf{r},\omega)$, one can see that the reference point determines to what extent the dynamical electric dipole moment contaminates the magnetic one. The reference point $\mathbf{r}_C$ should be chosen such that the induced magnetic moment can be measured in experiment. Moreover, for $\omega \neq 0$ the induced magnetic dipole moment is not just a response to the magnetic field $\mathbf{B}(\omega)$ but, according to Faraday's law ($\nabla\times\mathbf{E}(\mathbf{r},t)+\partial_t\mathbf{B}(\mathbf{r},t) = 0$), also to a dynamical transverse electric field,

$$\mathbf{E}(\mathbf{r},\omega) = \frac{i\omega}{2}\mathbf{B}(\omega)\times(\mathbf{r}-\mathbf{r}_G)\,, \tag{4.2}$$

where $\mathbf{r}_G$ is a fixed reference point in the molecular frame that guarantees that $\mathbf{E}(\mathbf{r},\omega)$ is independent of the choice of $\mathbf{r}_O$. It is determined by the experiment, and points to a position in the molecule where the electric field vanishes. We represent the electromagnetic fields by the following transverse vector potential,

$$\mathbf{A}(\mathbf{r},\omega) = \frac{1}{2}\mathbf{B}(\omega)\times(\mathbf{r}-\mathbf{r}_G)\,, \tag{4.3}$$

while we choose the external scalar potential to be zero, which can be done without loss of generality, as we explained in section 2.2. The magnetizability tensor $\xi(\omega)$ is

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[1] As a matter of fact, the magnetizability is sometimes also called magnetic polarizability.

[2] See appendix A.

defined as the constant of proportionality between $\delta\mathbf{m}(\omega)$ and $\mathbf{B}(\omega)$:

$$\delta m_i(\omega) = \sum_j \xi_{ij}(\omega) B_j(\omega)\,. \tag{4.4}$$

Considering an external magnetic field for which only the j-th component is nonzero, Eqs.(4.4) and (4.1) lead to the following explicit expression for the magnetizability:

$$\xi_{ij}(\omega) = \frac{1}{2B_j(\omega)} \int d\mathbf{r}\, \left[(\mathbf{r}-\mathbf{r}_C)\times\delta\mathbf{j}(\mathbf{r},\omega)\right]_i\,. \tag{4.5}$$

The magnetizability $\xi(\omega)$ given in Eq. (4.5) is independent of the choice we make for $\mathbf{r}_O$. It is important to note that for $\omega = 0$, $\xi(\omega = 0)$ is also independent of both $\mathbf{r}_G$ and $\mathbf{r}_C$. This means that any dependence on the gauge origin $\mathbf{r}_G$ when using a finite basis set is purely artificial, because $\mathbf{E}(\mathbf{r}, \omega = 0) = \mathbf{0}$. On the contrary, for $\omega \neq 0$, in addition to this artificial dependence, there is also a physical dependence, as different choices for $\mathbf{r}_G$ correspond to different electric fields. As mentioned before the choice for $\mathbf{r}_C$ and $\mathbf{r}_G$ depends on the experimental setup. To the best of our knowledge, no experimental data for frequency-dependent magnetizabilities exist. Therefore we make a physically meaningful choice; in the remainder of this chapter we consider them both equal to the center of electronic charge of the unperturbed molecule.

From Eq. (4.5), we learn that to calculate the magnetizability, all we need is the induced current density. Within linear response, it is given by (see chapter 3)

$$\delta\mathbf{j}(\mathbf{r},\omega) = \int d\mathbf{r}' \chi^{\mathbf{j}_p\mathbf{j}_p}(\mathbf{r},\mathbf{r}',\omega)\cdot\mathbf{A}(\mathbf{r}',\omega) + \rho_0(\mathbf{r})\mathbf{A}(\mathbf{r},\omega)\,, \tag{4.6}$$

where the first term on the right-hand side is the paramagnetic current ($\delta\mathbf{j}_p$) and the second term the diamagnetic current ($\delta\mathbf{j}_d$). Furthemore, $\rho_0(\mathbf{r})$ is the ground-state density and $\chi^{\mathbf{j}_p\mathbf{j}_p}(\omega)$ is the paramagnetic current-response function given by (see Eq. (3.9))

$$\begin{aligned}\chi^{\mathbf{j}_p,\mathbf{j}_p}(\mathbf{r},\mathbf{r}',\omega) = \lim_{\eta\to 0^+}&\sum_n \langle\Psi_0|\hat{\mathbf{j}}_p(\mathbf{r})|\Psi_n\rangle\langle\Psi_n|\hat{\mathbf{j}}_p(\mathbf{r}')|\Psi_0\rangle \\ \times&\left[\frac{1}{\omega-(E_n-E_0)+i\eta} - \frac{1}{\omega+(E_n-E_0)+i\eta}\right],\end{aligned} \tag{4.7}$$

where Ψ_n are the exact eigenstates and E_n the exact eigenvalues of the unperturbed Hamiltonian, η is an infinitesimal that ensures causality, and the paramagnetic current operator $\hat{\mathbf{j}}_p(\mathbf{r})$ is defined as $\hat{\mathbf{j}}_p(\mathbf{r}) = -\frac{i}{2}\sum_i(\nabla_{\mathbf{r}_i}\delta(\mathbf{r}-\mathbf{r}_i) + \delta(\mathbf{r}-\mathbf{r}_i)\nabla_{\mathbf{r}_i})$.

From Eq. (4.6) we see that the paramagnetic and diamagnetic currents are not calculated on equal footing. While the diamagnetic current only depends on the ground state, the paramagnetic current depends on all (ground and excited) states.

The size of the basis set used will determine not only the quality of the eigenstates but indirectly also the dimension of the excited-state space included in the sum-over-states expansion in Eq. (4.7). As a consequence, $\delta\mathbf{j}_p(\mathbf{r},\omega)$ will converge much slower with the size of the basis set than $\delta\mathbf{j}_d(\mathbf{r},\omega)$, which will result in an incomplete cancelation of the gauge dependence between both terms. Therefore an artificial dependence on $\mathbf{r}_G$ may arise in the calculation of the current density when using a finite basis set, as shown in Eq. (4.8):

$$\begin{aligned}\delta\mathbf{j}(\mathbf{r},0) = \frac{1}{2}\Big\{ & \int d\mathbf{r}'\chi^{\mathbf{j}_p\mathbf{j}_p}(\mathbf{r},\mathbf{r}',0)\cdot\mathbf{B}(0)\times\mathbf{r}' + \rho_0(\mathbf{r})\mathbf{B}(0)\times\mathbf{r} \\ & - \underbrace{\left(\int d\mathbf{r}'\chi^{\mathbf{j}_p\mathbf{j}_p}(\mathbf{r},\mathbf{r}',0) - \rho_0(\mathbf{r})\mathbb{1}\right)}_{\neq 0 \text{ with a finite basis set}}\cdot(\mathbf{B}(0)\times\mathbf{r}_G)\Big\}\,.\end{aligned} \tag{4.8}$$

We propose a simple, elegant and general solution to this problem: we will put the diamagnetic and paramagnetic current, $\mathbf{j}_d$ and $\mathbf{j}_p$, on equal footing by making use of a sum rule.

In order to arrive at the sum rule relating the diamagnetic current to a term that ressembles the paramagnetic current, we define the function $f(\mathbf{r},\mathbf{r}',\omega)$ as

$$f(\mathbf{r},\mathbf{r}',\omega) = A_1(\mathbf{r},\omega)x' + A_2(\mathbf{r},\omega)y' + A_3(\mathbf{r},\omega)z'\,, \tag{4.9}$$

where $A_i(\mathbf{r},\omega)$ are the three components of $\mathbf{A}(\mathbf{r},\omega)$. This allows us to write

$$\sum_j \int d\mathbf{r}'\chi_{ij}^{j_pj_p}(\mathbf{r},\mathbf{r}',0)A_j(\mathbf{r},\omega) = \sum_j \int d\mathbf{r}'\chi_{ij}^{j_pj_p}(\mathbf{r},\mathbf{r}',0)\partial_j' f(\mathbf{r},\mathbf{r}',\omega)\,. \tag{4.10}$$

Integrating by parts the right-hand side of Eq. (4.10), we can then write

$$\begin{aligned}&\sum_j \int d\mathbf{r}'\chi_{ij}^{j_pj_p}(\mathbf{r},\mathbf{r}',0)\partial_j' f(\mathbf{r},\mathbf{r}',\omega) = \\ &-\int d\mathbf{r}' f(\mathbf{r},\mathbf{r}',\omega)\sum_j \partial_j'\chi_{ij}^{j_pj_p}(\mathbf{r},\mathbf{r}',0) + \sum_j \int d\mathbf{r}'\partial_j'[f(\mathbf{r},\mathbf{r}',\omega)\chi_{ij}^{j_pj_p}(\mathbf{r},\mathbf{r}',0)] \\ &= -\int d\mathbf{r}' f(\mathbf{r},\mathbf{r}',\omega)\sum_j \partial_j'\chi_{ij}^{j_pj_p}(\mathbf{r},\mathbf{r}',0)\,,\end{aligned} \tag{4.11}$$

where we used the fact that the last term on the second line of Eq. (4.11) contains an integral of a total differential which can be written as a surface integral. Since the wavefunctions in $\chi_{ij}^{j_pj_p}(\mathbf{r},\mathbf{r}',0)$ fall off exponentially, this term will vanish. We now use the following sum rule[3] [6],

$$\sum_j \partial'_j \chi^{j_p j_p}_{ij}(\mathbf{r},\mathbf{r}',0) + \rho_0(\mathbf{r})\partial'_i\delta(\mathbf{r}-\mathbf{r}') = 0\,, \tag{4.12}$$

to rewrite Eq. (4.11) as

$$\begin{aligned}\sum_j \int d\mathbf{r}' \chi^{j_p j_p}_{ij}(\mathbf{r},\mathbf{r}',0)\partial'_j f(\mathbf{r},\mathbf{r}',\omega) &= \int d\mathbf{r}' f(\mathbf{r},\mathbf{r}',\omega)\rho_0(\mathbf{r})\partial'_i\delta(\mathbf{r}-\mathbf{r}') \\ &= -\rho_0(\mathbf{r})\int d\mathbf{r}'\delta(\mathbf{r}-\mathbf{r}')\partial'_i f(\mathbf{r},\mathbf{r}',\omega) \\ &= -\rho_0(\mathbf{r})A_i(\mathbf{r},\omega)\,, \end{aligned} \tag{4.13}$$

where in the second step, one gets a vanishing surface integral again. We finally have the following identity:

$$\delta\mathbf{j}_d(\mathbf{r},\omega) = -\left[\int d\mathbf{r}'\chi^{\mathbf{j}_p\mathbf{j}_p}(\mathbf{r},\mathbf{r}',0)\right]\cdot\mathbf{A}(\mathbf{r},\omega). \tag{4.14}$$

Equation (4.14) shall be referred to as the diamagnetic current sum rule. We notice that the result has a form similar to the approximate conductivity sum rule,

$$\delta\mathbf{j}_d(\mathbf{r},\omega) \simeq -\int d\mathbf{r}'\chi^{j_p j_p}(\mathbf{r},\mathbf{r}',0)\cdot\mathbf{A}(\mathbf{r}',\omega)\,, \tag{4.15}$$

with a small but crucial difference: in Eq. (4.14), we have $\mathbf{A}(\mathbf{r},\omega)$ on the right-hand side instead of $\mathbf{A}(\mathbf{r}',\omega)$ as in the conductivity sum rule. Both sum rules are actually equivalent in the case when the vector potential does not depend on $\mathbf{r}$, e.g., when we have a uniform electric field. The conductivity sum rule is incorrect when dealing with transverse vector potentials, though.

We conclude that the diamagnetic current density can be exactly rewritten in terms of the static paramagnetic-current response function. The current density in Eq. (4.6) can therefore be rewritten according to

$$\delta\mathbf{j}(\mathbf{r},\omega) = \int d\mathbf{r}'\chi^{\mathbf{j}_p\mathbf{j}_p}(\mathbf{r},\mathbf{r}',\omega)\cdot\mathbf{A}(\mathbf{r}',\omega) - \left[\int d\mathbf{r}'\chi^{\mathbf{j}_p\mathbf{j}_p}(\mathbf{r},\mathbf{r}',0)\right]\cdot\mathbf{A}(\mathbf{r},\omega)\,. \tag{4.16}$$

This is one of the main results of this chapter. Substitution of Eq. (4.3) into Eq. (4.16), and taking the static limit, we obtain

$$\left.\frac{\delta\mathbf{j}(\mathbf{r},\omega)}{\omega}\right|_{\omega=0} = \frac{1}{2}\int d\mathbf{r}'\chi^{\mathbf{j}_p\mathbf{j}_p}(\mathbf{r},\mathbf{r}',0)\cdot[\hat{\mathbf{e}}\times(\mathbf{r}'-\mathbf{r})]\,, \tag{4.17}$$

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[3] Equation (4.12) is general and applies to both interacting and noninteracting systems. In appendix B, we give a derivation for noninteracting systems, e.g., a Kohn-Sham system.

which is independent of the gauge origin $\mathbf{r}_G$ as it should. Without loss of generality, we used $\mathbf{B}(\omega) = \omega\hat{\mathbf{e}}$ in Eq. (4.17), with $\hat{\mathbf{e}}$ a unitary vector. We note that for $\omega = 0$, making use of the diamagnetic current sum rule leads to the same set of equations as those obtained when using a continuous set of gauge transformations (CSGT) [28]. The equivalence between the sum rule and CSGT for the static case is explained in appendix C.

Although we have substituted an expression for the diamagnetic current that quickly converges with basis-set size with one that converges slowly, there are two reasons to expect that the convergence of the total current given in Eq. (4.16) will be improved:

- Its static value given in Eq. (4.17) is independent of any artificial contribution due to the gauge origin $\mathbf{r}_G$;
- In spite of the fact that the two terms in Eq. (4.16) are both slowly converging, they are also similar and opposite in sign.

Hence a finite-basis error in the paramagnetic part should be systematically canceled by a similar error in the diamagnetic part, thereby improving convergence. As a result, a magnetic property calculated from the current density would also show improved convergence. In the following, we discuss a numerical example for the magnetizability in which we show that there is indeed such a systematic cancellation of error.

To illustrate our approach we now calculate static and dynamical magnetizabilities for several molecules using TDCDFT, which provides a natural and computationally efficient framework to calculate the current density. This TDCDFT formalism has already been successfully applied to the calculation of polarizabilities of finite systems [36, 37] and the dielectric functions of extended systems [38, 39]. Within the linear-response regime the Kohn-Sham TDCDFT equations for $\delta\mathbf{j}(\mathbf{r},\omega)$ and the induced density $\delta\rho(\mathbf{r},\omega)$ are given by (see Eqs.(3.26) and (3.27))

$$\begin{aligned}
\delta\mathbf{j}(\mathbf{r},\omega) &= \int d\mathbf{r}'\chi_s^{\mathbf{j}_p\mathbf{j}_p}(\mathbf{r},\mathbf{r}',\omega)\cdot\delta\mathbf{A}_s(\mathbf{r}',\omega) \\
&\quad - \left[\int d\mathbf{r}'\chi_s^{\mathbf{j}_p\mathbf{j}_p}(\mathbf{r},\mathbf{r}',0)\right]\cdot\delta\mathbf{A}_s(\mathbf{r},\omega) \\
&\quad + \int d\mathbf{r}'\chi_s^{\mathbf{j}_p\rho}(\mathbf{r},\mathbf{r}',\omega)\delta v_s(\mathbf{r}',\omega)\,, \qquad (4.18) \\
\delta\rho(\mathbf{r},\omega) &= \int d\mathbf{r}'\chi_s^{\rho\mathbf{j}_p}(\mathbf{r},\mathbf{r}',\omega)\cdot\delta\mathbf{A}_s(\mathbf{r}',\omega) \\
&\quad + \int d\mathbf{r}'\chi_s^{\rho\rho}(\mathbf{r},\mathbf{r}',\omega)\delta v_s(\mathbf{r}',\omega), \qquad (4.19)
\end{aligned}$$

where Eq. (4.16) has been applied to the Kohn-Sham system. The Kohn-Sham response functions $\chi_s^{\hat{\mathbf{A}},\hat{\mathbf{B}}}(\omega)$ have been given in Eq. (3.12), where the operators $\hat{\mathbf{A}}$

and $\hat{\mathbf{B}}$ should be replaced by $\hat{\rho} = 1$ or $\hat{\mathbf{j}}_p = -\frac{i}{2}(\nabla - \nabla^\dagger)$, where † indicates that ∇ works to the left. Without loss of generality we choose to describe the external electromagnetic fields by a vector potential only (see section (2.2)). We note that it is convenient to keep the induced density explicitly in our formalism because it provides the simplest way to evaluate the induced Hartree potential as well as the most common exchange-correlation scalar potentials. Since the potentials depend on the densities and vice versa, densities and potentials have to be solved self-consistently.

4.3 Computational details

We perform the ground-state calculations within the local-density approximation (LDA) [3], while the response calculation is done with the adiabatic local-density approximation (ALDA) [18], i.e., $\delta v_{xc}(\omega) = \delta v_{xc}^{ALDA}(\omega)$ and $\delta \mathbf{A}_{xc}(\omega) = 0$. This choice is motivated by the fact that the ALDA is the most widely used functional. Moreover, it allows us to compare our results to static magnetizabilities reported in the literature that were obtained within the LDA. We note that exchange-correlation vector potentials can be used within this formalism but the known functionals [23] introduce their own difficulties already for the longitudinal response [40–43].

We implemented our approach in a modified version of the Amsterdam Density Functional (ADF) code [44–46]. We used the augmented standard basis sets [47] provided by ADF, as these are suited for TD(C)DFT calculations. In our calculations we choose the external magnetic field $\mathbf{B}(\omega)$ to be proportional to ω. This guarantees that Eq. (4.5) remains finite in the limit $\omega \to 0$.

4.4 Results

In Table 4.1 we report the convergence behavior of the isotropic magnetizability[4] ($\xi(\omega)$) of C_2H_4 with the size of the basis set for $\omega = 0$ and $\omega = 0.07732$ a.u., which is the sodium D-line frequency also used in Ref. [32]. We compare the results obtained using the current of Eq. (4.16) (labeled ξ) with those obtained using Eq. (4.6) (labeled $\tilde{\xi}$). We see that without using the sum rule, convergence is extremely slow. Even for the ATZ2P basis the values for $\tilde{\xi}$ are far from converged when we compare with the values obtained with the large QZ4P basis. Instead, the values for ξ are already converged to within 1% using an ADZP basis. This is true for both the static and the frequency-dependent magnetizability. Therefore, the reported values for the magnetizabilities in the remainder of this section are obtained with an

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[4] In the literature, reported values for magnetizabilities are often given in units of JT^{-2}, and sometimes in $\mathrm{cm}^3\mathrm{mol}^{-1}$. Here are the conversion factors: 1 a.u. of ξ corresponds to $7.89104.10^{-29}$ JT^{-2} and 1 a.u. of ξ corresponds to $4.7521.10^{-6}\mathrm{cm}^3\mathrm{mol}^{-1}$.

Table 4.1 – Convergence behavior of the static isotropic magnetizability (in a.u.) of C_2H_4 with the size of the basis set using the diamagnetic current sum rule (ξ) and without using the sum rule ($\tilde{\xi}$). $\xi_p (= \tilde{\xi}_p)$ is obtained from the paramagnetic current while ξ_d and $\tilde{\xi}_d$ are obtained from the diamagnetic current.

Basis set	$\omega = 0$					$\omega = 0.07732$ a.u.	
	$\tilde{\xi}$	ξ	$\xi_p = \tilde{\xi}_p$	$\tilde{\xi}_d$	ξ_d	$\tilde{\xi}$	ξ
ASZ	-6.57	-3.22	7.41	-13.98	-10.63	-6.29	-2.93
ADZ	-6.39	-3.47	7.63	-14.02	-11.11	-6.10	-3.19
ADZP	-5.37	-4.14	8.58	-13.95	-12.72	-5.07	-3.83
ATZP	-5.29	-4.16	8.66	-13.95	-12.82	-4.98	-3.85
ATZ2P	-5.23	-4.12	8.65	-13.89	-12.77	-4.93	-3.81
QZ4P	-4.20	-4.16	9.66	-13.86	-13.82	-3.90	-3.86

ADZP basis set unless stated otherwise. We note that for the large QZ4P basis, both methods agree reasonably well. We also report the paramagnetic and diamagnetic contributions to the magnetizability separately. They were obtained with the paramagnetic and diamagnetic current, respectively. We observe that the paramagnetic contribution converges slowly while the diamagnetic contribution obtained without the diamagnetic current sum rule converges rapidly. As a consequence, the total magnetizability converges as slowly as the paramagnetic part. Instead, when we calculate the diamagnetic part using the sum rule both contributions converge equally slowly but with opposite sign. Therefore, thanks to a systematic error cancelation, the total magnetizability converges rapidly. Our converged value for the static magnetizability of C_2H_4 also compares well with a recently published value, i.e., -4.20 a.u. [48].

Moreover, the difference between ξ and $\tilde{\xi}$ becomes more evident as the size of the molecule increases. This is what we show in Table 4.2, where we report the convergence behavior of the static isotropic magnetizability of pentacene ($C_{22}H_{14}$). We note that despite using the very large basis set QZ4P, the magnetizability for pentacene obtained without using the sum rule is not converged yet, while the magnetizability obtained when using the sum rule is reasonably converged already at the level of the basis set ADZP.

In Table 4.3, we show the static isotropic magnetizabilities of various molecules obtained with our approach and compare them to LDA magnetizabilities reported in the literature as well as to experimental values. We used the molecular geometries given in Ref. [48] except for benzene and pentacene for which we used the experimental geometries given in Ref. [54] and Ref. [55], respectively. We observe that our values are in good agreement with the magnetizabilities reported in the literature.

We have verified that our approach is independent of the origin of the vector potential (Eq. (4.17)) and rapidly converges with basis-set size. It remains to verify

Table 4.2 – Convergence behavior of the static isotropic magnetizability (in a.u.) of pentacene with the size of the basis set using the sum rule (ξ) and without using the sum rule ($\tilde{\xi}$).

Basis set	$\omega = 0$	
	$\tilde{\xi}$	ξ
ASZ	-721.90	-37.48
ADZ	-655.70	-38.94
ADZP	-462.56	-41.85
ATZP	-444.76	-41.23
ATZ2P	-440.93	-41.06
QZ4P	-44.03	-41.36

Table 4.3 – Static isotropic magnetizabilities of various molecules (in a.u.). Comparison of the values obtained with our approach and LDA magnetizabilities reported in the literature. We also compare to experimental values.

Molecule	$\xi(\omega = 0)$		
	this work	other works	experiment
H_2O	-3.01	-3.05 [48]	-2.76 ± 0.38 [49]
NH_3	-3.73	-3.78 [48]	-3.68 ± 0.38 [50]
C_2H_4	-4.14	-4.20 [48]	-4.23± 0.16 [50]
Benzene	-11.70	-11.56 [51]	-11.53 ± 0.13 [52]
Pentacene	-41.85	-	-40.56 [53]

that it is also independent of the choice of the origin of the coordinate system. In table 4.4 we verify numerically that with our approach both the static and dynamical ($\omega = 0.15$ a.u.) magnetizabilities are independent of this choice. We compare the value for the molecule in an initial position with that obtained when the molecule was shifted with respect to this position by 5.0 Å, 3.0 Å, 1.0 Å in the x, y, and z directions, respectively. Shifting the molecule is equivalent to shifting the origin of the coordinate system. We see that for both $\omega = 0$ and $\omega = 0.15$ a.u. the results are invariant with respect to a shift of the molecule, as they should. We note that the large difference for the magnetizability of pentacene for $\omega = 0$ and $\omega = 0.15$ a.u. is due to the fact that $\omega = 0.15$ a.u. is above the first (Kohn-Sham) excitation; we observe that it has no influence on the origin independence.

Finally, as a proof of principle that with our approach we can calculate magnetizabilities over a wide range of frequencies, we plot in Fig. 4.1 the real part of $\xi(\omega)$ for benzene. To ensure that enough unoccupied orbitals are included to describe the high-frequency range, we used a QZ4P basis set. We used a damping factor of 0.007 a.u.. As mentioned before, no experimental data is available to compare with. In other calculations [32] in which dynamical magnetizabilities are reported, the GIAO

Table 4.4 – Numerical verification of the independence of $\xi(\omega)$ (in a.u.) on the choice of the origin. The molecule in position 2 is shifted with respect to that in position 1 by 5.0 Å, 3.0 Å, 1.0 Å in the x, y, and z direction, respectively.

Molecule	$\omega = 0$		$\omega = 0.15$ a.u.	
	pos. 1	pos. 2	pos. 1	pos. 2
H_2O	-3.007	-3.007	-2.991	-2.991
NH_3	-3.734	-3.734	-3.684	-3.684
C_2H_4	-4.137	-4.137	-2.755	-2.755
Benzene	-11.696	-11.696	-6.892	-6.892
Pentacene	-41.85	-41.85	50.04	50.04

gauge convention is used. This convention leads to a basis-set dependent electric field which precludes a comparison with our calculation.

4.5 Conclusion

We derived a simple framework to efficiently calculate gauge-invariant static and dynamical magnetic properties. Our method can be used in combination with any *ab initio* theory from which the current density can be obtained. We illustrated our approach by applying it to TDCDFT for the calculation of magnetizabilities. Many other magnetic properties, e.g., NMR shielding constants and optical rotation tensors, which explicitly depend on the current density, can be calculated analogously using Eq. (4.16). These other properties will be discussed in the following chapters.

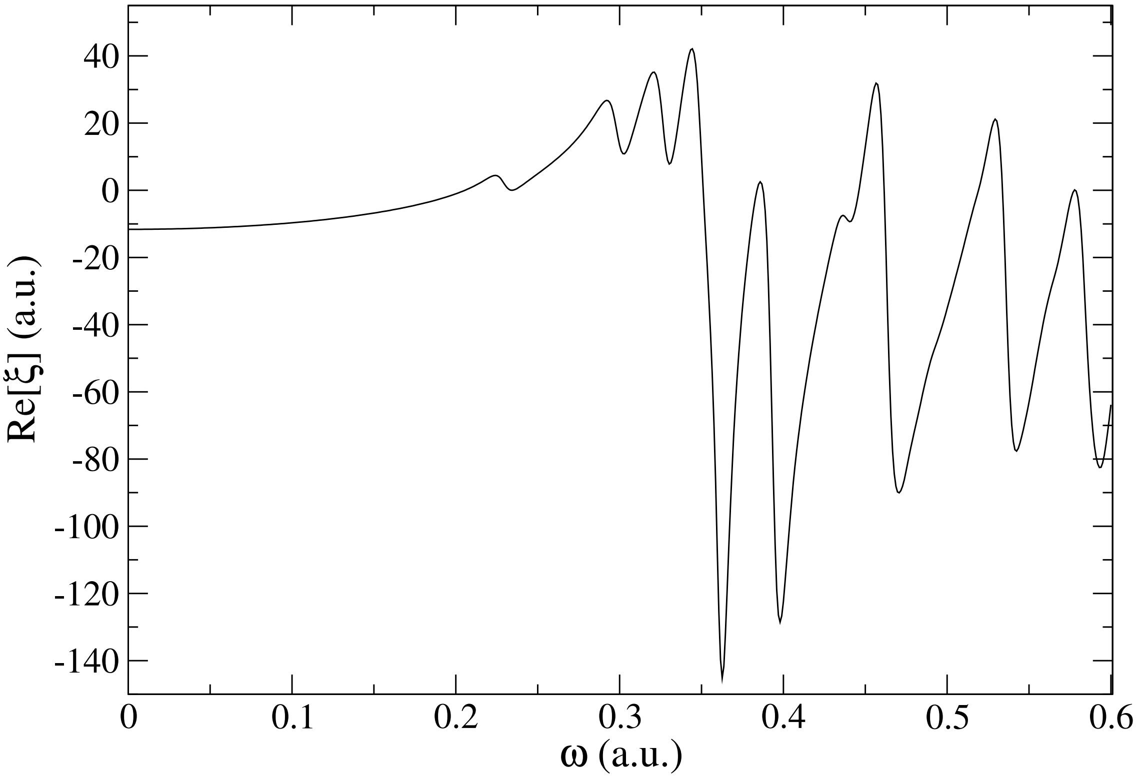


Figure 4.1 – The real part of $\xi(\omega)$ for benzene.

5

CIRCULAR DICHROISM

In this chapter, we explain how we can extend the method we developed in chapter 4 to calculate circular dichroism spectra. We show that the optical rotation tensor, the response function from which circular dichroism spectra can be obtained, is independent of the origin of the coordinate system. Moreover, we show that its trace is independent of the gauge origin of the vector potential, contrary to the magnetizability. We demonstrate how this gauge invariance can be retained in practical calculations with finite basis sets and when using TDCDFT with approximate functionals.

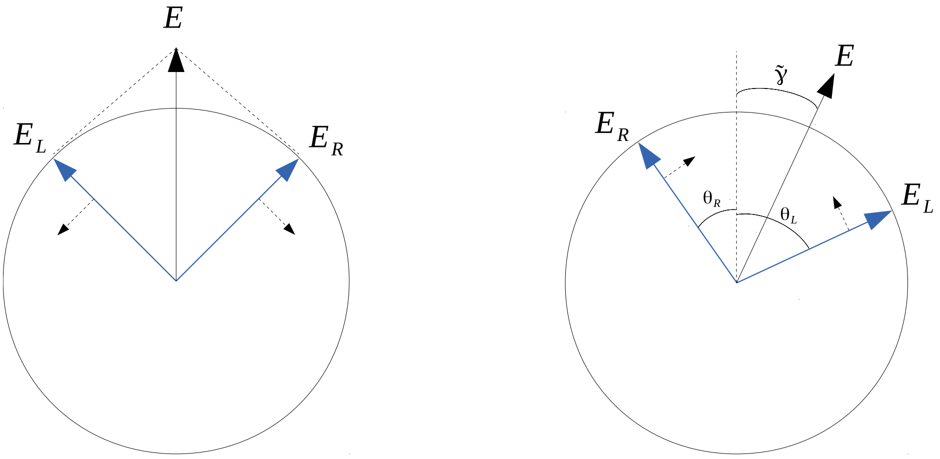
5.1 Introduction

5.1.1 Origin of circular dichroism

A detailed description of circular dichroism can be found in the books of Laurence Barron [33] and Stephen F. Mason [56].

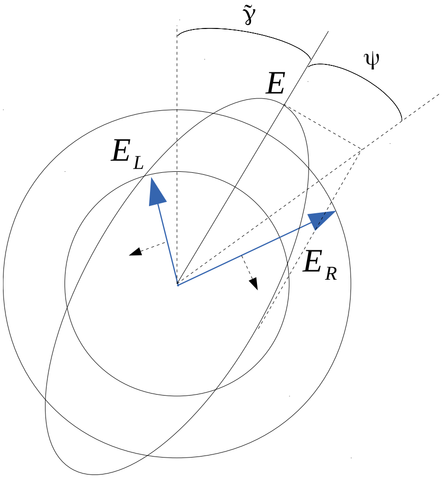
The origin of circular dichroism lies in the theory of the polarization of light, as discovered by Augustin Fresnel in 1825. He realized that linearly-polarized light could always be decomposed into right- and left-circularly polarized light of equal amplitude, as illustrated in Fig. 5.1a. He guessed that the rotation of the plane of polarization of a linearly polarized light beam traveling through a medium was due to a difference in the speed of propagation between the left- and right-circularly polarized components, such that the plane of polarization would be rotated, as shown in Fig. 5.1b.

If we consider a linearly polarized light entering a medium at a point $z = 0$ with angular frequency $\omega = \frac{2\pi c}{\lambda}$, λ being the wavelength of the incident radiation, then the components of the electric field at some farther point $z = l$ are inclined by angles $\theta^L = \frac{2\pi cl}{\lambda v^L}$ and $\theta^R = -\frac{2\pi cl}{\lambda v^R}$ (see Fig. 5.1b), where v^L and v^R are the velocities of the left- and right-circularly polarized components, respectively. The angle of rotation



(a) Decomposition of a linearly polarized electric field **E** into a left- and right-circularly polarized components ($\mathbf{E}_L$ and $\mathbf{E}_R$, respectively).

(b) The recombined electric field **E** at another point in the optically active medium is rotated by an angle $\tilde{\gamma}$, because of the difference of speed between left- and right-circularly polarized light.



(c) Inside an absorption band, recombination after differential absorption of $\mathbf{E}_L$ and $\mathbf{E}_R$ (which now have different amplitudes) gives an electric field **E** rotated by an angle $\tilde{\gamma}$, and describing an ellipse of ellipticity Ψ.

Figure 5.1 – Origin of optical rotation and circular dichroism.

$\tilde{\gamma}$ (in radians) can then be expressed as

$$\tilde{\gamma} = \frac{1}{2}(\theta^R + \theta^L) = \frac{\pi c l}{\lambda}\left(\frac{1}{v^L} - \frac{1}{v^R}\right) . \tag{5.1}$$

Since the velocities are linked to the refractive index n through the simple relation

$n = \frac{c}{v}$, one obtains

$$\gamma = \frac{\pi}{\lambda}(n^L - n^R) , \tag{5.2}$$

where $\gamma = \frac{\tilde{\gamma}}{l}$ is expressed in radians per unit length. The angle of rotation[1] is thus proportional to the circular birefringence, that is the difference between the refractive indices n^L and n^R of the left- and right-circularly polarized components.

Since there is a close relation between refraction and absorption[2], right- and left-circularly polarized light should be absorbed differently in an optically active medium. In addition, a linearly polarized radiation becomes elliptically polarized in an absorbing optically active material. Indeed, any elliptically polarized light can be regarded as a superposition of a left- and right-circularly polarized light with different amplitudes, as shown in Fig. 5.1c. The generation of ellipticity can be explained by the difference of absorption between right- and left-circularly polarized radiation. This ellipticity Ψ can be simply obtained from the ratio of the minor and major axes, which are just, respectively, the difference and the sum of the magnitudes of the two circular components [33] E_R and E_L:

$$\tan \Psi = \frac{E_R - E_L}{E_R + E_L} . \tag{5.3}$$

The magnitude of the electric field in an absorbing medium can be related to the absorption index κ and path length l by the relation

$$E_{R/L,l} = E_0 e^{\frac{-2\pi l}{\lambda}\kappa^{R/L}} , \tag{5.4}$$

where κ^R and κ^L are absorption indices of left- and right-circularly polarized light, and $E_0 \equiv E_{R/L,0}$. Finally, inserting Eq. (5.4) into (5.3), and restricting to small ellipticities, one can obtain the following relation, relating the ellipticity Ψ to κ^L and κ^R:

$$\Psi \approx \frac{\pi}{\lambda}(\kappa^L - \kappa^R) . \tag{5.5}$$

The ellipticity is thus a function of $(\kappa^L - \kappa^R)$, and it is related to the molar circular dichroism[3] $\Delta\epsilon$, which is the quantity usually measured in experiment, as (see also

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[1] In the literature, one speaks of *dextro rotatory* when the polarization plane rotates clockwise, and *laevo rotatory* when it rotates anticlockwise.

[2] One can define a complex refractive index $\tilde{n} = n + i\kappa$, where n is the usual refractive index, and κ is the absorption index (also called extinction coefficient).

[3] The term "dichroism" comes from ancient Greek $\delta\acute{\iota}\chi\rho\omega\varsigma$ ("dikhroos") , which means "two-colored", and was initially meant to describe materials which can split a beam of light into two separate beams with different wavelengths.

Eq. (5.7))

$$\Delta\epsilon = \frac{\Psi}{3298.8} \,. \tag{5.6}$$

5.1.2 Applications and link with experiment

"Living cells are electromagnetic units." [57]

Optical activity appears naturally in chiral molecules (i.e., molecules whose mirror images cannot be superimposed). We show, as an example, the two enantiomers of dimethyloxirane (DMO) in Fig. 5.3. Optical activity thus shows great applications in biology, since most biomolecules are chiral and optically active. Circular dichroism (CD) spectroscopy is thus a powerful tool to scrutinize the structure of biomolecules. In particular, secondary structures such as alpha helices and beta sheets in proteins and double helices in nucleic acids show specific signatures in CD spectra [58, 59], as shown schematically in Fig. 5.2.

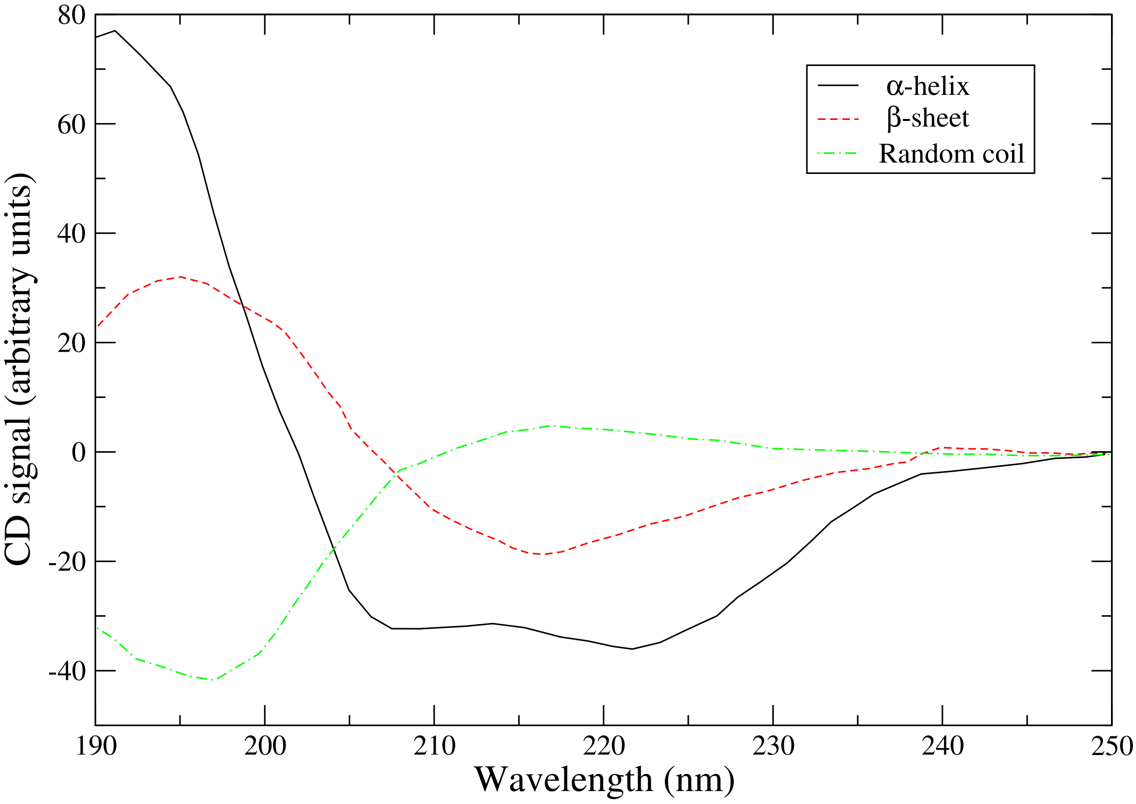
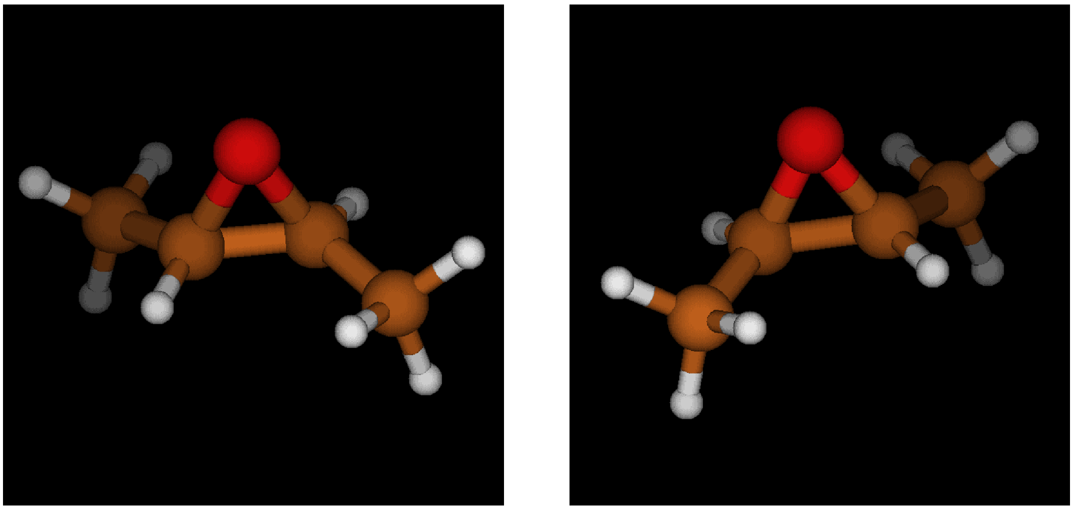


Figure 5.2 – Schematic representation of the CD spectra of some characteristic secondary structures.

Practical applications of CD spectroscopy can be found notably in the medical domain, where mutant proteins causing disease can be identified by looking at their



(a) (R)-dimethyloxirane. (b) (S)-dimethyloxirane.

Figure 5.3 – The two enantiomers of the molecule dimethyloxirane (DMO). We used the program MOLDEN [62] to represent these molecules.

conformational changes. For example, the thalidomide in its (R)-form can relieve morning sickness in pregnant women, while the (S)-form produces fetal abnormalities. CD spectroscopy can also be used to design new devices based on chiral nanomaterials [60, 61].

Recently, a lot of interest has been dedicated to studying the structure of proteins inside the environment in which they operate [63], as well as determining the rate of structural changes of proteins. Circular dichroism spectroscopy is particularly well adapted to tackle such issues. The instruments which measure CD spectra are called spectropolarimeters. These spectropolarimeters can be used in different manners:

- Modulation: there is a continuous switch between the left- and right-handed components of the incident light.
- Direct subtraction: the absorbance of each component is measured separately, before being subtracted from each other.
- Ellipsometric: one measures the ellipticity of the transmitted radiation.

The modulation method is the most widely used, though. The mechanism of such a device can be summed up as follows. A plane polarized radiation enters a modulator, usually constituted of a piezoelectric quartz crystal and a thin plate of isotropic constituent (such as fused silica). An alternating electric field is applied onto this modulator, which engenders structural changes in the quartz crystal. As a consequence, the plate will transmit circularly polarized light at the extremes of the field [63]. The resulting radiation, alternatively left- and right-handed, is then detected via a photomultiplier.

An important remark is that the observed CD signals when studying biomolecules are usually very small: the ellipticities are of the order of 10 mdeg, corresponding to a difference in absorption of the order of 10^{-4}. It is then clear that great care must be taken to the experimental setups. Moreover, since the molecules of interest are typically located in an aqueous environment that often absorbs in the range of frequencies where the structural changes exhibit a difference in absorption, measuring CD signals can be all the more difficult.

5.2 Theory: gauge-invariant circular dichroism

As mentioned before, circular dichroism is a magnetoelectric response property and is defined as the difference in absorption of left-handed and right-handed circularly polarized light [64]. The theoretical description of CD spectra by a first-principles approach is a huge challenge considering the size of the systems of interest, such as proteins and nanomaterials. Wave-function based approaches have difficulties to deal with the size of these systems and an approach based on density-functional theory (DFT) is the best option. So far, only approaches based on ground-state DFT [2] and time-dependent DFT (TDDFT) [65] have been proposed [31, 66–72]. The main shortcoming of approaches based on DFT is that the induced potentials are not calculated self-consistently. Shortcomings of both DFT and TDDFT are:

- Only longitudinal external fields can be accounted for, thereby excluding magnetic fields.
- The longitudinal current can be reproduced exactly but not the transverse current.

As a consequence, one cannot obtain exact CD spectra (nor any other magnetic response function) within TDDFT, even if the exact TDDFT exchange-correlation functional is known. These shortcomings can be overcome by switching from the density to the current density as the fundamental quantity, since time-dependent current-density functional theory (TDCDFT) [4, 5, 15] can treat general electromagnetic external fields and it can reproduce the full current. This is the framework we will adopt in this chapter.

Unfortunately, as discussed in chapter 4, formulations of magnetic response properties are plagued by gauge-dependent results, i.e., results that depend on the choice of the origin of the coordinate system. This is of course unphysical and requires a careful reformulation of the theory. Moreover, in practical calculations using finite basis sets, magnetic properties also have an artificial gauge dependence on the choice of the origin of the vector potential. These two problems are distinct but they are often confused in the literature. Also, it is often thought that the above problems can be solved by using gauge-including atomic orbitals (GIAOs) [25, 26]. Although the GIAO method is helpful in practice −it improves convergence with basis-set size− it is not gauge invariant [30]. In chapter 4, we proposed a general gauge-invariant approach to calculate magnetic response properties from the current density [73]. Here we will show how it can be applied to the calculation of CD spectra. These spectra are obtained from the trace of the so-called optical rotation tensor. First, we show that, contrary to what is commonly thought, the optical rotation tensor, is independent of the origin of the coordinate system. It depends, however, on the gauge origin of the vector potential but, as we will show, this dependence is physical. We then show that the trace of the optical rotation tensor is independent of the gauge-origin of the vector potential. We demonstrate how, in practical calculations, any artificial gauge dependence on the origin of the vector potential can be avoided. Finally, we apply our approach to the calculation of CD spectra and compare our gauge-invariant results to those obtained in experiment. Unless stated otherwise, we use Hartree atomic units (a.u.) throughout the chapter.

The CD spectrum for non-oriented systems can be obtained from the molar circular dichroism $\Delta\epsilon$ (in l mol^{-1}cm^{-1}) which is defined by

$$\Delta\epsilon(\omega) = 4.0712 \times 10^{-10} \bar{\nu}^2 \mathrm{Im}[\beta(\omega)]\,, \tag{5.7}$$

in which $\bar{\nu} = \omega/(2\pi c)$ is the wavenumber (in cm^{-1}). The optical rotation parameter $\beta(\omega)$ (in a.u.) is given by[4]

$$\beta(\omega) = \frac{1}{3i\omega}\mathrm{Tr}[G] = -\frac{1}{3i\omega}\mathrm{Tr}[\tilde{G}], \tag{5.8}$$

where the optical rotation tensors G and $\tilde{G}$ are, respectively, the constant of proportionality of the perturbing magnetic field $\mathbf{B}(\omega)$ and the induced electric dipole moment $\delta\boldsymbol{\mu}(\omega)$ and the constant of proportionality of the perturbing electric field $\mathbf{E}(\omega)$ and the induced magnetic dipole moment $\delta\mathbf{m}(\omega)$:

$$\delta\mu_i(\omega) = \sum_j G_{ij}(\omega) B_j(\omega), \tag{5.9}$$

$$\delta m_i(\omega) = \sum_j \tilde{G}_{ij}(\omega) E_j(\omega). \tag{5.10}$$

Definitions of the electric and magnetic dipole moment in terms of the induced current density $\delta\mathbf{j}$ are obtained by performing a multipole expansion around $\mathbf{r}_C$, a

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[4] We note that β is a pseudoscalar, i.e., it reverses sign when changing from a left-handed coordinate system to a right-handed one [64].

fixed reference point in the molecular frame. One obtains

$$\delta\boldsymbol{\mu}(\omega) = \int d\mathbf{r}(\mathbf{r}-\mathbf{r}_C)\delta\rho(\mathbf{r},\omega) = \frac{i}{\omega}\int d\mathbf{r}\delta\mathbf{j}(\mathbf{r},\omega)\,, \tag{5.11}$$

$$\delta\mathbf{m}(\omega) = \frac{1}{2}\int d\mathbf{r}(\mathbf{r}-\mathbf{r}_C)\times\delta\mathbf{j}(\mathbf{r},\omega), \tag{5.12}$$

where $\delta\rho$ is the induced density. In Eq. (5.11) we used the continuity equation and we restricted ourselves to systems in which charge is conserved. Therefore, while $\delta\mathbf{m}(\omega)$ depends on the choice for $\mathbf{r}_C$, $\delta\boldsymbol{\mu}(\omega)$ does not. The choice of $\mathbf{r}_C$ determines to what extent $\delta\boldsymbol{\mu}(\omega)$ influences $\delta\mathbf{m}(\omega)$ [73]. Since it lies in the molecular frame, it ensures that $\delta\mathbf{m}(\omega)$ is independent of the choice of the origin of the coordinate system $\mathbf{r}_O$.

Let us consider an external field for which only the j-th component is nonzero, the optical rotation tensors then take the form:

$$G_{ij} = \frac{i}{\omega}\frac{1}{B_j(\omega)}\int d\mathbf{r}\delta\mathbf{j}_i(\mathbf{r},\omega), \tag{5.13}$$

$$\tilde{G}_{ij} = \frac{1}{2E_j(\omega)}\int d\mathbf{r}\left[(\mathbf{r}-\mathbf{r}_C)\times\delta\mathbf{j}(\mathbf{r},\omega)\right]_i. \tag{5.14}$$

We note that, although $\tilde{G}(\omega)$ depends on $\mathbf{r}_C$, its trace does not, as we will show below. Equations (5.13) and (5.14) show that the induced current density is the fundamental quantity from which we can calculate G and $\tilde{G}$. It remains to show that we can calculate $\delta\mathbf{j}$ such that it is independent of $\mathbf{r}_O$. Within linear response, $\delta\mathbf{j}(\mathbf{r},\omega)$ is given by Eq. (4.6), which we repeat here,

$$\delta\mathbf{j}(\mathbf{r},\omega) = \int d\mathbf{r}'\chi^{\mathbf{j}_p\mathbf{j}_p}(\mathbf{r},\mathbf{r}',\omega)\cdot\mathbf{A}(\mathbf{r}',\omega) + \rho_0(\mathbf{r})\mathbf{A}(\mathbf{r},\omega), \tag{5.15}$$

where the first term on the right-hand side is the paramagnetic current ($\delta\mathbf{j}_p$) and the second term is the diamagnetic current ($\delta\mathbf{j}_d$). Furthermore, $\rho_0(\mathbf{r})$ is the ground-state density and $\chi^{\mathbf{j}_p\mathbf{j}_p}(\omega)$ is the paramagnetic current-response function given by

$$\begin{aligned}\chi^{\mathbf{j}_p,\mathbf{j}_p}(\mathbf{r},\mathbf{r}',\omega) = \lim_{\eta\to 0^+}\sum_{n=1}^{\infty}&\langle\Psi_0|\hat{\mathbf{j}}_p(\mathbf{r})|\Psi_n\rangle\langle\Psi_n|\hat{\mathbf{j}}_p(\mathbf{r}')|\Psi_0\rangle\\ \times&\left[\frac{1}{\omega-(E_n-E_0)+i\eta}-\frac{1}{\omega+(E_n-E_0)+i\eta}\right],\end{aligned} \tag{5.16}$$

where Ψ_n are the exact eigenstates and E_n the exact eigenvalues of the unperturbed Hamiltonian, η is an infinitesimal that ensures causality, and the paramagnetic current operator is defined as $\hat{\mathbf{j}}_p(\mathbf{r}) = -\frac{i}{2}\sum_i(\nabla_{\mathbf{r}_i}\delta(\mathbf{r}-\mathbf{r}_i)+\delta(\mathbf{r}-\mathbf{r}_i)\nabla_{\mathbf{r}_i})$. Since $\chi^{\mathbf{j}_p,\mathbf{j}_p}(\mathbf{r},\mathbf{r}',\omega)$ and $\rho_0(\mathbf{r})$ are independent of $\mathbf{r}_O$ it remains to show that $\mathbf{A}(\mathbf{r},\omega)$ is independent of $\mathbf{r}_O$.

We represent the magnetic and electric fields in Eqs. (5.13) and (5.14), respectively, by the following vector potentials,

$$\mathbf{A}(\mathbf{r},\omega) = \frac{1}{2}\mathbf{B}(\omega) \times (\mathbf{r} - \mathbf{r}_G), \tag{5.17}$$

$$\tilde{\mathbf{A}}(\omega) = \frac{\mathbf{E}(\omega)}{i\omega}, \tag{5.18}$$

where $\mathbf{r}_G$ is a fixed reference point in the molecular frame that is determined by the dynamical transverse electric field $\mathbf{E}(\mathbf{r},\omega) = \frac{i\omega}{2}\mathbf{B}(\omega) \times (\mathbf{r} - \mathbf{r}_G)$, as was already discussed in chapter 4, and guarantees that $\mathbf{E}(\mathbf{r},\omega)$ and $\mathbf{A}(\mathbf{r},\omega)$ are independent of $\mathbf{r}_O$. In conclusion, the calculation of the tensors G and $\tilde{G}$ from Eqs. (5.13) and (5.14) using the vector potentials defined in Eqs. (5.17) and (5.18) is independent of $\mathbf{r}_O$. On the other hand, G will, in general, depend on the choice for $\mathbf{r}_C$ while $\tilde{G}$ depends on the choice for $\mathbf{r}_G$. As discussed above, these dependencies are entirely physical. We will now show that the trace of G and $\tilde{G}$ are independent of $\mathbf{r}_G$ and $\mathbf{r}_C$. Inserting Eq. (5.15) into Eqs. (5.13) and (5.14) we obtain

$$G_{ij}(\omega) = \frac{i}{2\omega}\sum_{kl}\epsilon_{jkl}\int d\mathbf{r}\int d\mathbf{r}'(r'_k - r_{G,k})\left[\chi_{il}^{\mathbf{j}_p\mathbf{j}_p}(\mathbf{r},\mathbf{r}',\omega) + \delta_{il}\delta(\mathbf{r}-\mathbf{r}')\rho_0(\mathbf{r})\right], \tag{5.19}$$

$$\tilde{G}_{ij}(\omega) = -\frac{i}{2\omega}\sum_{kl}\epsilon_{ikl}\int d\mathbf{r}\int d\mathbf{r}'(r_k - r_{C,k})\left[\chi_{lj}^{\mathbf{j}_p\mathbf{j}_p}(\mathbf{r},\mathbf{r}',\omega) + \delta_{lj}\delta(\mathbf{r}-\mathbf{r}')\rho_0(\mathbf{r})\right], \tag{5.20}$$

where ϵ is the Levi-Civita tensor. One can deduce three important relations from Eqs. (5.19) and (5.20):

$$G_{ij}(\omega) = -\tilde{G}_{ji}(\omega), \quad (\text{if } \mathbf{r}_G = \mathbf{r}_C) \tag{5.21}$$

$$G_{ii}^{\text{dia}} = \tilde{G}_{ii}^{\text{dia}} = 0, \tag{5.22}$$

$$\text{Tr}[G_{\mathbf{r}_G}(\omega)] = \text{Tr}[\tilde{G}_{\mathbf{r}_C}(\omega)] = 0, \tag{5.23}$$

where G^{dia} ($\tilde{G}^{\text{dia}}$) is defined as the part of G ($\tilde{G}$) obtained from $\delta\mathbf{j}_d$ and $G_{\mathbf{r}_G}$ ($\tilde{G}_{\mathbf{r}_C}$) is defined as the part of G ($\tilde{G}$) that is proportional to $\mathbf{r}_G$ ($\mathbf{r}_C$). Equation (5.21) follows from the Onsager symmetry relation $\chi_{ij}^{\mathbf{j}_p\mathbf{j}_p}(\mathbf{r},\mathbf{r}',\omega) = \chi_{ji}^{\mathbf{j}_p\mathbf{j}_p}(\mathbf{r}',\mathbf{r},\omega)$ and Eq. (5.23) follows from

$$\text{Tr}[G_{\mathbf{r}_G}(\omega)] = \frac{1}{2i\omega}\sum_{ikl}\epsilon_{ikl}\mathbf{r}_{G,k}\int d\mathbf{r}d\mathbf{r}'\chi_{il}^{\mathbf{j}_p\mathbf{j}_p}(\mathbf{r},\mathbf{r}',\omega) \tag{5.24}$$

$$= -\frac{1}{2i\omega}\sum_{ikl}\epsilon_{ikl}\mathbf{r}_{G,k}\int d\mathbf{r}d\mathbf{r}'\chi_{il}^{\mathbf{j}_p\mathbf{j}_p}(\mathbf{r},\mathbf{r}',\omega) = 0\,, \tag{5.25}$$

where we used the Onsager relation and the fact that ϵ is antisymmetric. The proof to show that $\text{Tr}[\tilde{G}_{\mathbf{r}_C}(\omega)] = 0$ is analogous. Equation (5.22) comes from the expression we use for the vector potential. In summary, G and $\tilde{G}$ are equivalent (if $\mathbf{r}_G = \mathbf{r}_C$), the diamagnetic current does not contribute to G and $\tilde{G}$ (on the diagonal) and, most importantly, the trace of G and $\tilde{G}$ is independent of both $\mathbf{r}_G$ and $\mathbf{r}_C$. This means, for example, that the optical rotation parameter $\beta(\omega)$ is independent of the electric field that is associated to the uniform magnetic field. Finally, Eqs. (5.21) and (5.23) imply that $\mathrm{Tr}[G(\omega)] = -\mathrm{Tr}[\tilde{G}(\omega)]$ (cf. Eq. (5.8)). For more details on the derivation of Eqs. (5.21) and (5.23), see appendix D.

The conclusions drawn above are valid for the exact theory. In particular, we have assumed that $\chi^{\mathbf{j}_p\mathbf{j}_p}(\mathbf{r},\mathbf{r}',\omega)$ is exact. In practical calculations, however, approximations have to be made, and the size of the basis set and therefore the summation over the excited states in Eq. (5.16), are finite. Since paramagnetic and diamagnetic contributions to the current density in Eq. (5.15) are not treated on equal footing the total current is not gauge invariant when a finite basis is used. As a consequence Eq. (5.23) is no longer satisfied and results for β will depend on the choice for $\mathbf{r}_G$ or $\mathbf{r}_C$ and will therefore be difficult to interpret. Therefore, instead of using Eq. (5.15), we will use again the diamagnetic current sum rule derived in Eq. (4.14) to rewrite Eq. (5.15) as:

$$\delta\mathbf{j}(\mathbf{r},\omega) = \int d\mathbf{r}'\chi^{\mathbf{j}_p\mathbf{j}_p}(\mathbf{r},\mathbf{r}',\omega)\cdot\mathbf{A}(\mathbf{r}',\omega) - \left[\int d\mathbf{r}'\chi^{\mathbf{j}_p\mathbf{j}_p}(\mathbf{r},\mathbf{r}',0)\right]\cdot\mathbf{A}(\mathbf{r},\omega). \tag{5.26}$$

The paramagnetic and diamagnetic terms are now treated on equal footing and $\delta\mathbf{j}(\mathbf{r},\omega)$ in Eq. (5.26) is gauge invariant for any finite basis. As a consequence, Eq. (5.23) is again satisfied. Moreover, the convergence of Eq. (5.26) with basis-set size significantly improves that of Eq. (5.15) due to the fact that now the paramagnetic and diamagnetic currents are similar but opposite in sign.

The method described above is general, fully gauge invariant and can be used together with any theoretical approach from which the current density can be calculated. However, as mentioned in the introduction, to be able to treat large systems one needs an efficient theory. We therefore apply our approach to TDCDFT, a computationally efficient method to calculate the current density. Within the linear-response regime $\delta\mathbf{j}(\mathbf{r},\omega)$ and $\delta\rho(\mathbf{r},\omega)$ are given by

$$\begin{aligned}\delta\mathbf{j}(\mathbf{r},\omega) = \int d\mathbf{r}'\chi_s^{\mathbf{j}_p\mathbf{j}_p}(\mathbf{r},\mathbf{r}',\omega)\cdot\delta\mathbf{A}_s(\mathbf{r}',\omega) - \left[\int d\mathbf{r}'\chi_s^{\mathbf{j}_p\mathbf{j}_p}(\mathbf{r},\mathbf{r}',0)\right]\cdot\delta\mathbf{A}_s(\mathbf{r},\omega) \\ + \int d\mathbf{r}'\chi_s^{\mathbf{j}_p\rho}(\mathbf{r},\mathbf{r}',\omega)\delta v_s(\mathbf{r}',\omega)\,, \qquad (5.27)\end{aligned}$$

$$\delta\rho(\mathbf{r},\omega) = \int d\mathbf{r}'\chi_s^{\rho\mathbf{j}_p}(\mathbf{r},\mathbf{r}',\omega)\cdot\delta\mathbf{A}_s(\mathbf{r}',\omega) + \int d\mathbf{r}'\chi_s^{\rho\rho}(\mathbf{r},\mathbf{r}',\omega)\delta v_s(\mathbf{r}',\omega)\,. \tag{5.28}$$

The Kohn-Sham response functions $\chi_s^{\hat{\mathbf{A}},\hat{\mathbf{B}}}(\omega)$ read

$$\chi_s^{\mathbf{A},\mathbf{B}}(\mathbf{r},\mathbf{r}',\omega) = \sum_i^{occ}\sum_a^{unocc}\left[\frac{\phi_i(\mathbf{r})\hat{\mathbf{A}}(\mathbf{r})\phi_a(\mathbf{r})\phi_a(\mathbf{r}')\hat{\mathbf{B}}(\mathbf{r}')\phi_i(\mathbf{r}')}{(\epsilon_i-\epsilon_a)+\omega}\right. \\ \left. + \frac{\phi_a(\mathbf{r})\hat{\mathbf{A}}(\mathbf{r})\phi_i(\mathbf{r})\phi_i(\mathbf{r}')\hat{\mathbf{B}}(\mathbf{r}')\phi_a(\mathbf{r}')}{(\epsilon_i-\epsilon_a)-\omega}\right], \quad (5.29)$$

where $\phi_i(\mathbf{r})$ ($\phi_a(\mathbf{r})$) are the occupied (unoccupied) Kohn-Sham orbitals of the ground state and ϵ_i (ϵ_a) are the corresponding Kohn-Sham energies. The Kohn-Sham potentials are given by $\delta v_s(\mathbf{r},\omega) = \delta v_H(\mathbf{r},\omega) + \delta v_{xc}(\mathbf{r},\omega)$ and $\delta\mathbf{A}_s(\mathbf{r},\omega) = \mathbf{A}(\mathbf{r},\omega) + \delta\mathbf{A}_{xc}(\mathbf{r},\omega)$ where $\delta v_H(\mathbf{r},\omega)$ and $\delta v_{xc}(\mathbf{r},\omega)$ are the induced Hartree and exchange-correlation (xc) potentials and $\delta\mathbf{A}_{xc}(\mathbf{r},\omega)$ is the induced xc vector potential. Since the densities depend on the Kohn-Sham potentials and vice versa, the equations have to be solved self-consistently. The xc potentials can be expressed in terms of the xc scalar (f_{xc}) and tensor ($f_{xc,ij}$) kernels which are defined by

$$\delta v_{xc}(\mathbf{r},\omega) = \int d\mathbf{r}' f_{xc}(\mathbf{r},\mathbf{r}',\omega)\delta\rho(\mathbf{r}',\omega), \quad (5.30)$$

$$\delta A_{xc,i}(\mathbf{r},\omega) = \sum_j \int d\mathbf{r}' f_{xc,ij}(\mathbf{r},\mathbf{r}',\omega)\delta j_j(\mathbf{r}',\omega). \quad (5.31)$$

It is clear that gauge invariance might be destroyed by the choice of the xc kernels. However, gauge invariance can be guaranteed (see appendix D for more details). This can be understood by iterating Eqs. (5.27) and (5.28) together with Eqs. (5.30), (5.31) and $\delta v_H(\mathbf{r},\omega) = \int d\mathbf{r}'\delta\rho(\mathbf{r}',\omega)/|\mathbf{r}-\mathbf{r}'|$, substituting the resulting $\delta\mathbf{j}(\mathbf{r},\omega)$ into Eq. (5.13) or (5.14) and evaluating its trace. Using the Onsager relation and the relation $\chi_s^{\mathbf{j}_p\rho}(\mathbf{r},\mathbf{r}',\omega) = \chi_s^{\rho\mathbf{j}_p}(\mathbf{r}',\mathbf{r},\omega)$ we conclude that in order to have gauge-invariant results, the following conditions have to be satisfied:

$$f_{xc}(\mathbf{r},\mathbf{r}',\omega) = f_{xc}(\mathbf{r}',\mathbf{r},\omega) \quad (5.32)$$

$$f_{xc,ij}(\mathbf{r},\mathbf{r}',\omega) = f_{xc,ji}(\mathbf{r}',\mathbf{r},\omega). \quad (5.33)$$

These two conditions have to be respected by approximations to the xc kernels. In particular, these conditions are satisfied by the adiabatic local-density approximation (ALDA) [18], which is the functional we will use to calculate CD spectra and the so-called specific rotation (see Eq. (5.34)).

5.3 Results

All ground-state calculations were done within the local-density approximation (LDA) [3]. We implemented our method in a developer version of the Amsterdam Density Func-

Table 5.1 – Convergence behavior of the specific rotation (in deg $\mathrm{cm}^3/(\mathrm{dm\ g})$) of C_4H_8O(DMO) at the sodium D-line frequency ($\omega = 0.077318$ a.u.). In the literature, one can find an experimental value of -58.8 [67].

Basis set	$\alpha(\omega)$
ASZ	-25.55
ADZ	-59.54
ADZP	-68.34
ATZP	-60.98
ATZ2P	-60.74
ET-QZ3P-1DIFFUSE	-66.66
ET-QZ3P-2DIFFUSE	-66.03
ET-QZ3P-3DIFFUSE	-65.82

tional (ADF) code [44–46].

In Table 5.1, we show the convergence behaviour of the specific rotation $[\alpha(\omega)]$ for the (R)-dimethyloxirane (DMO). While the CD spectrum is related to the imaginary part of the optical rotation parameter $\beta(\omega)$, the specific rotation is related to the real part of $\beta(\omega)$:

$$[\alpha(\omega)] = 1.343 \times 10^{-4} \frac{\mathrm{Re}[\beta(\omega)]\bar{\nu}^2}{M} , \tag{5.34}$$

where M is the molar mass. This table illustrates several the convergence behaviour of $[\alpha(\omega)]$ with respect with the size of the basis set. We have observed a similar behaviour for the other molecules we considered. We note that we cannot reach full convergence with the augmented basis sets (from ASZ to ATZ2P in Table 5.1), since the values we obtain are about 10% too small with respect to the large basis set ET-QZ3P-3DIFFUSE. We have to utilize basis sets with more diffuse functions, such as the even-tempered-QZ3P-NDIFFUSE series. This is in agreement with what several authors have already acknowledged. It has been reported several times indeed [71, 74] that diffuse and polarization functions were of utmost importance when looking at properties related to optical activity. In order to understand why, let us first rewrite $\mathrm{Tr}[\tilde{G}]$ more explicitly in terms of matrix elements[5]:

$$\mathrm{Tr}[\tilde{G}(\omega)] = \sum_{ia} \frac{-2\omega}{(\epsilon_i - \epsilon_a)^2 - \omega^2} \sum_k \langle \phi_i | \hat{m}_k | \phi_a \rangle \langle \phi_a | \hat{\mu}_k | \phi_i \rangle , \tag{5.35}$$

where $\hat{\mathbf{m}}$ is the magnetic dipole moment operator $\hat{\mathbf{m}} = \frac{1}{2}\hat{\mathbf{r}} \times \hat{\mathbf{p}}$ with $\hat{\mathbf{p}} = -i\nabla$, and $\hat{\boldsymbol{\mu}}$ is the electric dipole moment operator $\hat{\boldsymbol{\mu}} = \hat{\mathbf{r}}$. From Eq. (5.35), one can see that only terms that have both non-vanishing electric dipole and non-vanishing magnetic

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[5] Note that we neglect the contribution due to the induced Kohn-Sham potential here. This demonstration can be found in appendix E.

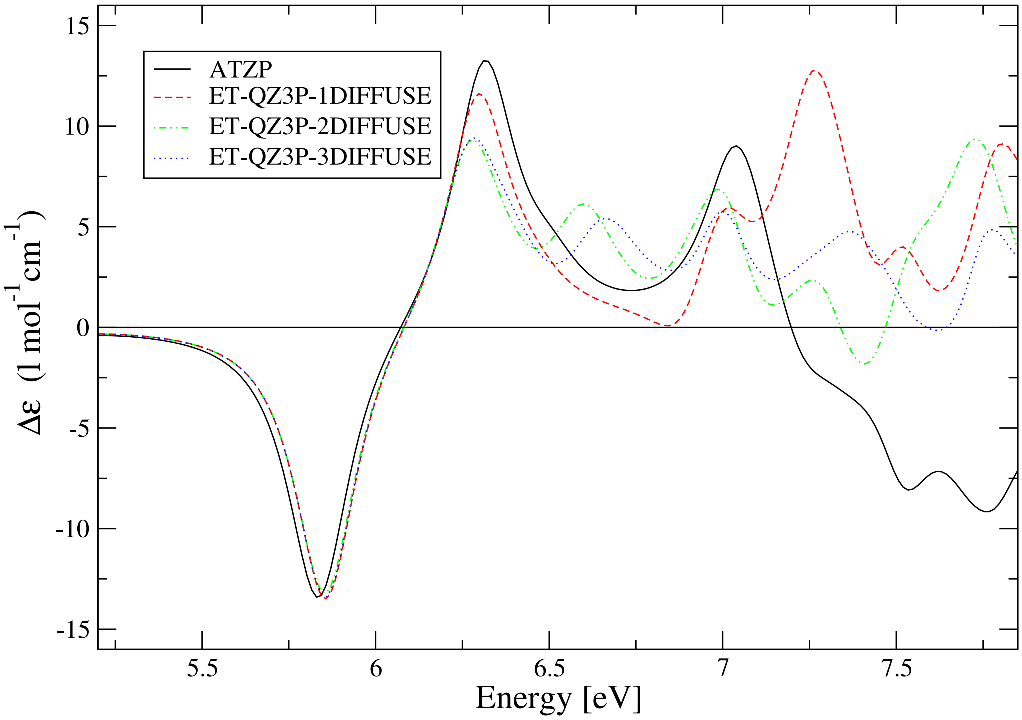

Figure 5.4 – Calculated circular dichroism spectra for (R)-methyloxirane with different basis sets.

dipole transitions contribute to $\mathrm{Tr}[\tilde{G}(\omega)]$. There are few cases when this condition is satisfied, which means that one would need to include empty states of higher energy so as to obtain an accurate $\mathrm{Tr}[\tilde{G}(\omega)]$, which explains why diffuse basis sets may be needed when performing a calculation.

From Fig. 5.4, we can assess that an ATZP basis set is sufficient to get good qualitative CD spectra for lower energies, at a limited computational cost. Only when calculating high-energy spectra we may need a basis set of superior quality.

Since CD spectra correspond to a difference in absorption of left-handed and right-handed circularly polarized light, two enantiomers should produce opposite spectra. In Fig. 5.5, where we show the CD spectra of the enantiomers R-methyloxirane and S-methyloxirane, we illustrate the fact that in our approach, this symmetry is indeed respected.

In Figs. 5.6 and 5.7, we compare our gauge-invariant results for the CD spectra of R-methyloxirane and trans-2,3-dimethyloxirane (DMO) with those obtained in experiment [75, 76]. Since these experiments were done in the gas phase, the comparison is not hampered by effects due to the solvent. To facilitate comparison, the theoretical results were blueshifted by 1.3 eV for methyloxirane and 1.25 eV for DMO, and a damping of 0.10 eV was used for both molecules to simulate broadening effects in the experiment. We see that the ALDA spectrum for methyloxirane is in very good agreement with experiment for low-medium frequencies, in particular

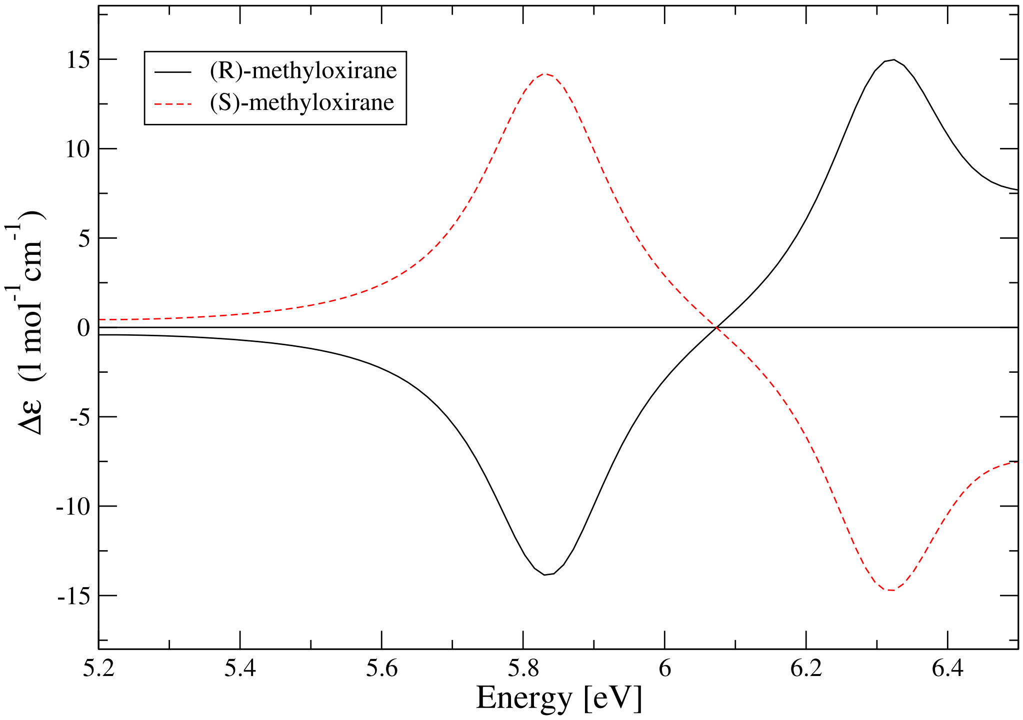

Figure 5.5 – Calculated circular dichroism spectra for R- and S-methyloxirane using the ALDA functional and an ATZP basis set. Solid line: (R)-form; dashed line: (S)-form.

the magnitude and the relative position of the first two peaks, around 7.3 eV and 7.6 eV, respectively. For higher frequencies, more diffuse functions in the basis set are expected to improve the results. For DMO, although the qualitative shape is well reproduced, several discrepancies can be observed. In particular, we note the absence of the double peak structure around 7.1 eV, and a too large magnitude for the second peak around 7.3 eV, even though we do have the negative sign.

In Fig. 5.8, we show the CD spectrum we obtain for α-pinene, with an ATZP basis set. The experiments were done in the gas phase as well. We blueshifted our results by 0.85 eV, and used a damping of 0.20 eV. Once again, we see that the first part of the spectrum is well reproduced, while the high-frequency part needs to be improved.

5.4 Conclusions

We have derived a fully gauge-invariant approach for the calculation of circular dichroism spectra. Our approach is general and can be applied together with any first-principles theory from which the current can be obtained. Here we combined it with time-dependent current-density functional theory. We derived conditions

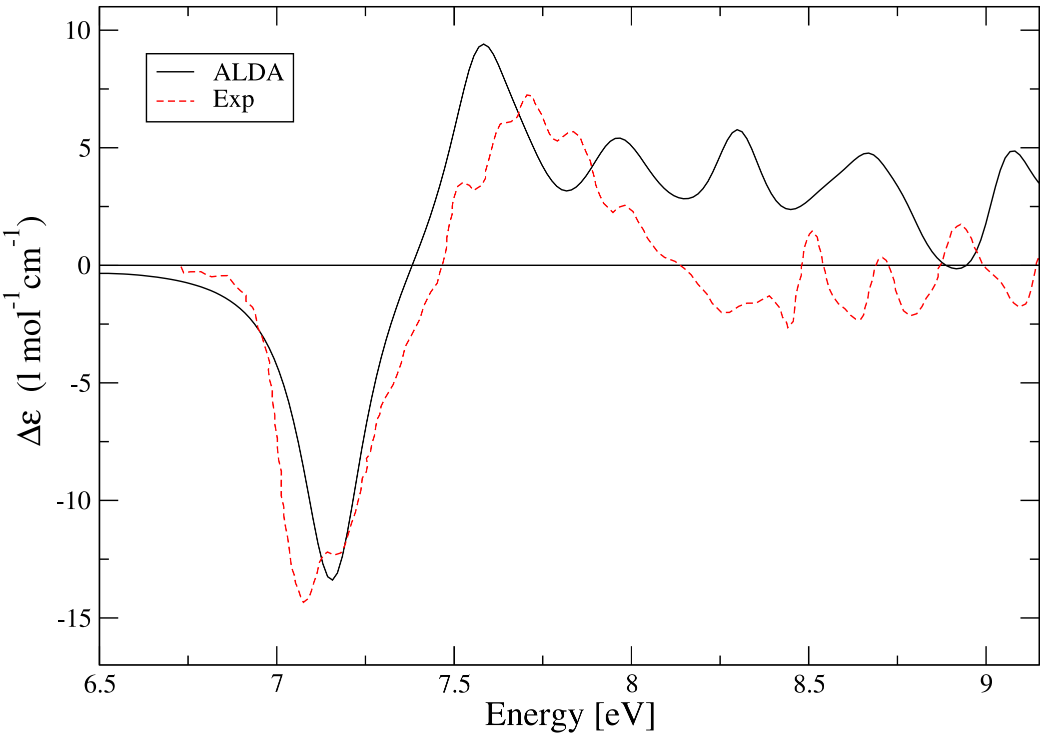

Figure 5.6 – The circular dichroism spectra for R-methyloxirane. Solid line: ALDA; dashed line: experiment from Ref. [75].

for the exchange-correlation kernels such that gauge invariance is guaranteed. Our gauge-invariant theoretical spectra are in good agreement with experiment.

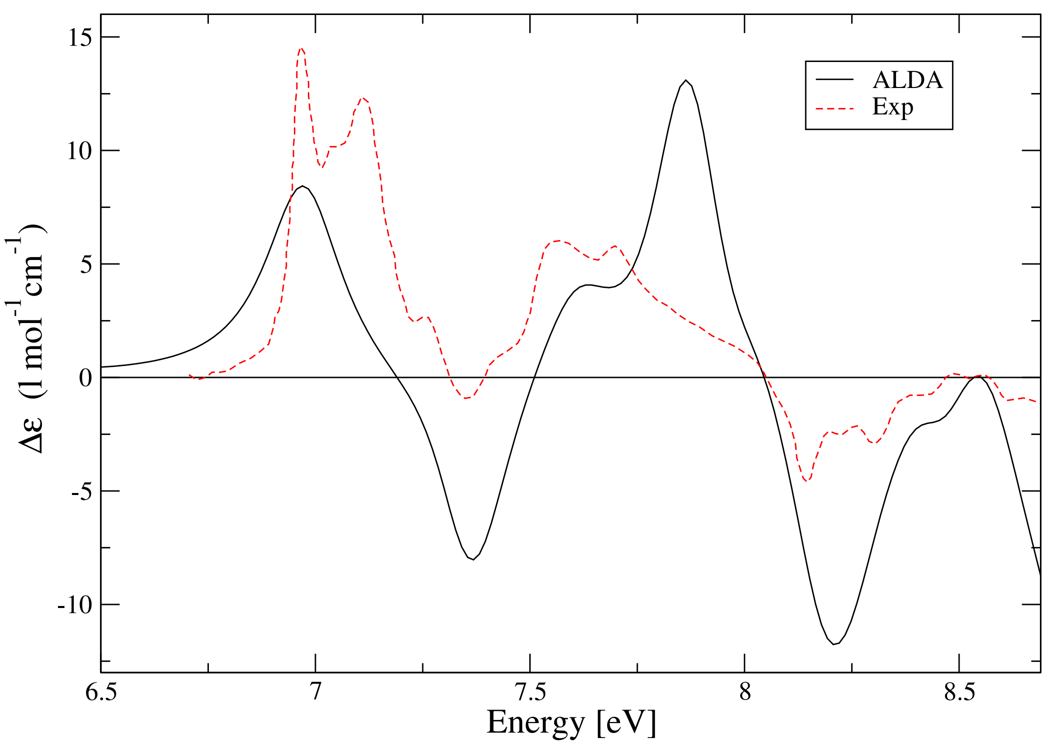

Figure 5.7 – The circular dichroism spectra for DMO. Solid line: ALDA; dashed line: experiment from Ref. [76].

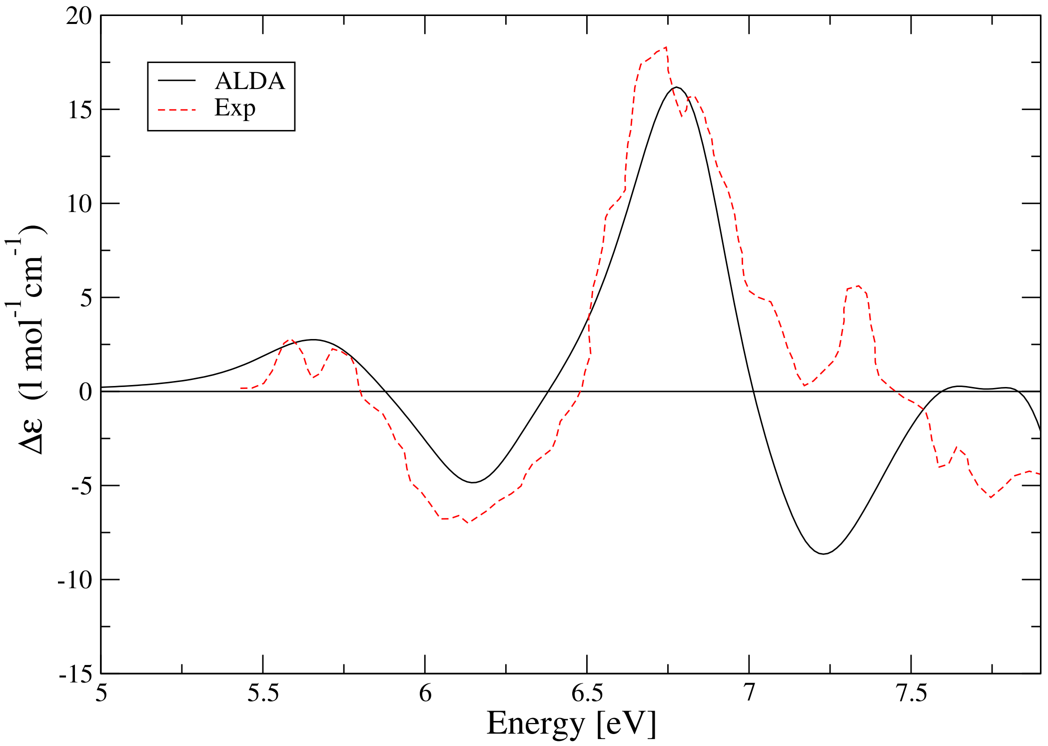

Figure 5.8 – The circular dichroism spectra for α-pinene. Solid line: ALDA; dashed line: experiment from Ref. [77].

6

Rotational g-tensor and NMR shielding constants

In this chapter, we explore two other magnetic response properties that can also be calculated, in a straightforward way, with our gauge-invariant approach developed in the previous chapters, namely the rotational g-tensor and the nuclear magnetic resonance (NMR) shielding tensor.

6.1 Rotational g-tensor

The rotational g-tensor (also called sometimes g-factor) is linked to the energy shift ΔE of the rotational energy level [78]:

$$\Delta E = \mu_n \mathbf{B} g \mathbf{J} \,, \tag{6.1}$$

where μ_n is the nuclear magneton, $\mathbf{B}$ the external magnetic field, $\mathbf{J}$ the molecular angular momentum, and g the dimensionless 3×3 rotational g-tensor. The latter is often expressed as the second derivative of the energy with respect to $\mathbf{B}$ and $\mathbf{J}$, as can be seen directly from Eq. (6.1). Contrary to the magnetizability, which is difficult to obtain with high precision in experiment, the rotational g-tensor is often obtained with high accuracy, making it a good candidate to measure the efficiency of first-principles methods [79].

It was shown in Ref. [80] that the rotational g-tensor can be expressed in terms of the paramagnetic magnetizability ξ^{para}, via the following relation:

$$g = g^{\mathrm{nuc}} - 4 m_p \xi^{\mathrm{para}} I_{\mathrm{nuc}}^{-1} \,, \tag{6.2}$$

where m_p is the proton mass, I_{nuc} is the nuclear inertia tensor[1], g^{nuc} is the nuclear

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[1] The moment of inertia of a rigid body determines the torque needed for a desired angular acceleration about a rotational axis.

Table 6.1 – Rotational g-tensors of various molecules, calculated with an ATZP basis set. If all the diagonal terms are equal, only one value is given. The experimental values values can be found in Ref. [79].

Molecule	rotational g-tensor	
	this work	experiment
HF	0.671	0.742
CO	-0.286	-0.269
CH_4	0.326	0.3133
NH_3	0.496	0.565
	0.522	0.502
C_2H_4	-0.56163	-0.3561
	-0.1396	-0.1110
	0.04212	0.0561

part of the g-tensor, and ξ^{para} is defined by[2] [80]

$$\xi^{\text{para}} = \xi(\omega = 0) - \xi_{\text{dia}}(\text{cm})\,, \tag{6.3}$$

where $\xi_{\text{dia}}(\text{cm})$ is defined as [80]

$$\xi_{\text{dia}}(\text{cm}) = \frac{1}{2}\int d\mathbf{r}\rho_0(\mathbf{r})\mathbf{r} \times (\hat{\mathbf{e}} \times (\mathbf{r} - \mathbf{r}_{\text{cm}}))\ , \tag{6.4}$$

with $\mathbf{r}_{\text{cm}}$ the position vector that points to the center of mass of the system, and where we used $\mathbf{B}(\omega) = \omega\hat{\mathbf{e}}$, with $\hat{\mathbf{e}}$ a unit vector. Hence ξ^{dia} is related to a specific gauge choice for the vector potential. Using the gauge-invariant expression for $\xi(\omega = 0)$ obtained from Eq. (4.17), we can thus rewrite ξ^{para} as

$$\begin{aligned}\xi^{\text{para}}(\omega = 0) =& \frac{1}{2}\int d\mathbf{r}\mathbf{r} \times \int d\mathbf{r}'\chi^{\mathbf{j}_p\mathbf{j}_p}(\mathbf{r}, \mathbf{r}', 0) \cdot [\hat{\mathbf{e}} \times (\mathbf{r}' - \mathbf{r})] \\ & - \frac{1}{2}\int d\mathbf{r}\rho_0(\mathbf{r})\mathbf{r} \times (\hat{\mathbf{e}} \times (\mathbf{r} - \mathbf{r}_{\text{cm}}))\ .\end{aligned} \tag{6.5}$$

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[2] The relation presented in Ref. [80] is $\xi^{\text{para}} = \xi^{\text{LAO}} - \xi^{\text{dia}}$, where ξ^{LAO} is defined as $\xi(\omega = 0)$ calculated with London orbitals (LAO), also called gauge-including atomic orbitals (GIAO). Since, in the limit of a complete basis, the LAO approach should give identical results as the more general approach we developed in chapter 4, here we substitute ξ^{LAO} with $\xi(\omega = 0)$ obtained from Eq. (4.17).

The components of I_{nuc} in cartesian coordinates are expressed as

$$\begin{aligned} I_{xx} &= \sum_K m_K (y_K^2 + z_K^2) \\ I_{yy} &= \sum_K m_K (z_K^2 + x_K^2) \\ I_{zz} &= \sum_K m_K (x_K^2 + y_K^2) \\ i \neq j \,:\, I_{ij} = I_{ji} &= -\sum_K m_K r_{i,K} r_{j,K} \,, \end{aligned} \tag{6.6}$$

where m_K is the nuclear mass of the nucleus K, and g^{nuc} is expressed as

$$g^{\mathrm{nuc}} = m_p \sum_K Z_K [(\mathbf{R}_K \cdot \mathbf{R}_K)\mathbb{1} - \mathbf{R}_K \mathbf{R}_K^T] I_{\mathrm{nuc}}^{-1} \,, \tag{6.7}$$

with m_p the proton mass[3], Z the atomic number, and $\mathbb{1}$ the identity matrix. We note that although *a priori* not diagonal, the inertia tensor can always be made diagonal by expressing it in the basis of the so-called principal axis. It is of course important that I and ξ are expressed within the same basis in order to get meaningful results. As can be seen from Eq. (6.2), the rotational g-tensor is connected to the magnetizability by a very simple relation. Consequently, it will suffer from the same shortcomings as the magnetizability, and therefore we will use the method we have developed in chapter 4 to ensure that the calculation of $\xi(\omega = 0)$ is gauge-independent and rapidly converging with basis-set size. Since $\rho_0(\mathbf{r})$ also converges quickly, the same is true for ξ^{para} and g.

In Table 6.1, we report the values obtained with the ADZP basis set and the LDA+ALDA functionals. We see that our results are in good agreement with experiment, as one would expect from the results for the magnetizability given in section 4.2.

6.2 NMR shielding tensor

Nuclear magnetic resonance (NMR) is an extremely efficient method to probe the electronic structure, as well as the molecular geometry of materials. In particular, spectral information can be extracted from a quantity called the chemical shift (denoted by δ), which describes the resonance frequency of a nucleus relative to a reference in a magnetic field. This chemical shift, which is the quantity measured in experiments, is directly related to another quantity called the NMR shielding constant (denoted by σ), which describes the effective field experienced by a given

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[3] Often (this is the case in ADF for example), I is given in amu.Bohr^2. In order to convert such values, here are the relations of interest: 1 amu = 1822.88839 m_e and 1 m_p = 1836.15 m_e.

nucleus[4]. Indeed, because of the electrons orbiting the nucleus, the latter experiences a slightly altered field compared to the externally applied magnetic field. In experiments, these shielding constants are measured relative to a reference compound. The chemical shift δ then reads

$$\delta = 10^6 \frac{\sigma_{\text{ref}} - \sigma_{\text{sample}}}{1 - \sigma_{\text{ref}}}\,, \tag{6.8}$$

where σ_{sample} and σ_{ref} are the absolute shielding constants of the nucleus of interest, and the shielding of the same nucleus in a reference compound, respectively. Here δ is in parts per million (ppm). As σ_{ref} is often much smaller than 1, one often uses instead the following approximation:

$$\delta = 10^6 \left(\sigma_{\text{ref}} - \sigma_{\text{sample}}\right)\,. \tag{6.9}$$

Since we work within TDCDFT, it is important to express the quantities we want to calculate in terms of the current density. Within this context, the absolute NMR shielding tensor $\sigma(\mathbf{R})$ at the position of the nucleus $\mathbf{R}$ takes the following form:

$$\sigma(\mathbf{R}) = \frac{\mu_0}{4\pi}\frac{1}{B(\omega=0)}\int d\mathbf{r}\frac{\mathbf{r}-\mathbf{R}}{|\mathbf{r}-\mathbf{R}|^3} \times \delta\mathbf{j}(\mathbf{r},\omega=0)\,, \tag{6.10}$$

where μ_0 is the vacuum permeability. We note that Eq. (6.10) can be written differently by integrating by parts:

$$\begin{aligned}\sigma(\mathbf{R}) =& \frac{\mu_0}{4\pi}\frac{1}{B(\omega=0)}\left[\int d\mathbf{r}\frac{\nabla\times\delta\mathbf{j}(\mathbf{r},\omega=0)}{|\mathbf{r}-\mathbf{R}|} + \int \cancel{d\mathbf{r}\nabla\times\left(\frac{-\mathbf{j}(\mathbf{r},\omega=0)}{|\mathbf{r}-\mathbf{R}|^2}\right)}\right]\\ =& \frac{\mu_0}{4\pi}\frac{1}{B(\omega=0)}\int d\mathbf{r}\frac{\nabla\times\delta\mathbf{j}(\mathbf{r},\omega=0)}{|\mathbf{r}-\mathbf{R}|}\,,\end{aligned} \tag{6.11}$$

where the last term on the first line of Eq. (6.11) vanishes because it is the integral of a total differential[5]. We implemented both equations (6.10) and (6.11), and there was no significant difference in the results.

In Table 6.2, we show the convergence behaviour of the NMR shielding constant for the molecule HF when using the current density as in Eq. (4.16). The non-standard basis sets ET-QZ3P-NDIFFUSE are usual basis sets of quadrupole zeta quality and 3 polarization functions, where N sets of diffuse functions have been

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[4] Only nuclei with a spin of one half (like ^{13}C, ^{1}H or ^{19}F) lead to non-zero NMR shielding constants, since they have two degenerate states (i.e., two states with the same energy), which will split in an external magnetic field thanks to the Zeeman effect.

[5] This volume integral of a total differential can be transformed into a surface integral, and since the current density falls off exponentially at large distance (like the wavefunction from which it can be obtained), this surface integral vanishes.

Table 6.2 – Convergence behaviour of the isotropic nuclear shielding constant of HF. Experiments give values of 28.51 and 409.6 for the nuclei ^{1}H and ^{19}F, respectively [81].

Basis set	^{1}H	^{19}F
ASZ	25.30	-20.04
ADZ	21.91	-4.64
ADZP	29.37	82.07
ATZP	29.46	93.65
ATZ2P	29.63	94.57
QZ4P	29.42	350.55
ET-QZ3P-1DIFFUSE	29.17	360.70
ET-QZ3P-2DIFFUSE	29.19	364.53
ET-QZ3P-3DIFFUSE	29.15	366.19
ET-QZ+5P	29.09	414.36

Table 6.3 – Comparison of results for the isotropic nuclear shielding constant of several molecules, using an ET-QZ+5P basis set. The experimental values can be found in Ref. [81].

Molecule	Nucleus	σ	Experiment
HF	^{1}H	29.1	28.5
HF	^{19}F	414.4	409.6
CO	^{13}C	-24.6	0.9
CO	^{17}O	-94.4	-62.7
H_2O	^{1}H	30.7	30.1
H_2O	^{17}O	334.6	323.6
NH_3	^{15}N	267.3	264.5
NH_3	^{1}H	31.4	30.7

added for each of the s, p, d and f orbitals. We notice a different behaviour than for the magnetizability. Indeed, the results are not converged even with a large basis set such as QZ4P, and we have to use the very large basis set ET-QZ+5P in order to obtain accurate results. Actually, the NMR shieldings we obtain for the hydrogen nucleus are always quickly converged (a simple ADZP basis is sufficient), regardless of the molecule we study. However, for heavier nuclei, one needs larger basis sets. This is due to the fact that most of the physics contained in the NMR shieldings happens close to the nuclei. Consequently, in practice, one would need to use more localized orbitals than the ones we are using in ADF. In order to get satisfying results with the conventional basis sets, we thus have to compensate the lack of localization by employing the largest basis available, which are computationally demanding. In order to improve the numerical efficiency, it would thus be interesting to construct basis sets that are more suitable for NMR calculations.

In Table 6.3, we reported the results calculated for a set of molecules using the very large basis set ET-QZ+5P. The results are in good agreement with the experiment, except for the small diatomic molecule CO, whose correlation is known to be harder to describe [82,83]. Other functionals than LDA+ALDA could thus be necessary.

6.3 Conclusions

Our method paves the way for the calculation of various molecular electromagnetic properties in a gauge-invariant way. We saw in this chapter indeed that we were able to obtain accurate g-tensor at a low computational cost. We saw that our method also works for NMR shielding constants, but we need larger basis sets in comparison with the other magnetic properties we have studied so far.

7

IMPLEMENTATION

This chapter is more technical, and is meant to give more details on the equations we mentioned in chapters 4 and 5. We shall also give the explicit expressions we implemented in the program Amsterdam Density Functional (ADF).

7.1 Amsterdam Density Functional

ADF uses linear combinations of atomic orbitals (LCAO) to represent the molecular orbitals (MO). Several basis functions are available to describe these MO, the most widely used being Gaussian orbitals, as they are often more practical[1] to use in many-body systems. However, ADF employs the more natural Slater-type orbitals, which reproduce the correct long-range behaviour as well as the nuclear cusp. They take the following form:

$$f(\mathbf{r}) = Y_{lm} r^n e^{-\beta r}\,, \tag{7.1}$$

where the center of a $f(\mathbf{r})$ is at a nucleus, Y_{lm} are the spherical harmonics, and β determines the strength of the long-range decay. Slater-type orbitals lead to multi-center integrals when evaluating the Hartree potential. This is dealt with in ADF by using an auxiliary set of fit functions. The density is then fitted by making a linear combination of these fit functions, and one can obtain the Coulomb potential from this fitted density.

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[1] Calculating integrals with Slater-type orbitals is indeed more difficult because of the exponential term $e^{-\beta r}$. With gaussians, the latter is replaced by a term of the form $e^{-\alpha r^2}$, which yields simpler calculations, but which shows a different behaviour for large r and for $r = 0$, and one then needs a linear combination of several gaussians in order to retrieve the correct behaviour. For example, the denomination STO-3G describes a Slater orbital approximated by 3 Gaussian orbitals.

7.2 Magnetizability

In our implementation of the magnetizability, we recall that we use a uniform magnetic field $\mathbf{B}^d(\omega) = \omega\hat{\mathbf{e}}_d$, where d denotes the direction of the external field[2] (i.e., $d = x, y, z$), and $\hat{\mathbf{e}}_d$ are unitary vectors. The corresponding vector potential is expressed as $\mathbf{A}^d(\mathbf{r},\omega) = \frac{1}{2}\mathbf{B}^d(\omega) \times (\mathbf{r} - \mathbf{r}_G)$. When using the diamagnetic-current sum rule (see Eq. (4.14)), the current density is expressed as

$$\begin{aligned}
\delta\mathbf{j}^d(\mathbf{r},\omega) = {}& \frac{1}{2}\int d\mathbf{r}'\chi_{\mathbf{j}_p\mathbf{j}_p}(\mathbf{r},\mathbf{r}',\omega)\cdot\Big[\mathbf{B}^d(\omega)\times(\mathbf{r}'-\mathbf{r}_G)\Big] \\
&- \frac{1}{2}\int d\mathbf{r}'\chi_{\mathbf{j}_p\mathbf{j}_p}(\mathbf{r},\mathbf{r}',\omega=0)\cdot\Big[\mathbf{B}^d(\omega)\times(\mathbf{r}-\mathbf{r}_G)\Big] \\
&+ \int d\mathbf{r}'\chi_{\mathbf{j}_p\rho}(\mathbf{r},\mathbf{r}',\omega)\delta v_s(\mathbf{r}',\omega)\,, \qquad (7.2)
\end{aligned}$$

where $\chi_{\mathbf{j}_p\mathbf{j}_p}$ and $\chi_{\mathbf{j}_p\rho}$ are the Kohn-Sham response functions, as given in Eq. (3.28). We are interested in calculating the magnetizability, which is given by (see also Eq. (4.5))

$$\xi_{ij}(\omega) = \frac{1}{2B_j(\omega)}\int d\mathbf{r}\,[(\mathbf{r}-\mathbf{r}_C)\times\delta\mathbf{j}(\mathbf{r},\omega)]_i\,. \qquad (7.3)$$

Using the explicit expressions for the response functions given in Eq. (3.12), we get:

$$\begin{aligned}
&[\mathbf{r}\times\mathbf{j}(\mathbf{r},\omega)]_k \\
&= \frac{1}{2}\sum_{ia}F_{ia}(\omega)\Big[\mathbf{r}\times\phi_i(\mathbf{r})\hat{\mathbf{j}}_p\phi_a(\mathbf{r})\Big]_k\int d\mathbf{r}'\phi_a(\mathbf{r}')\hat{\mathbf{j}}_p\phi_i(\mathbf{r}')\cdot\Big(\mathbf{B}^d(\omega)\times(\mathbf{r}'-\mathbf{r}_G)\Big) \\
&- \frac{1}{2}\sum_{ia}F_{ia}(0)\Big[\mathbf{r}\times\phi_i(\mathbf{r})\hat{\mathbf{j}}_p\phi_a(\mathbf{r})\Big]_k\int d\mathbf{r}'\phi_a(\mathbf{r}')\hat{\mathbf{j}}_p\phi_i(\mathbf{r}')\cdot\Big(\mathbf{B}^d(\omega)\times(\mathbf{r}-\mathbf{r}_G)\Big) \\
&+ \sum_{ia}F_{ia}(\omega)\frac{-\omega}{\epsilon_i-\epsilon_a}\Big[\mathbf{r}\times\phi_i(\mathbf{r})\hat{\mathbf{j}}_p\phi_a(\mathbf{r})\Big]_k\int d\mathbf{r}'\phi_a(\mathbf{r}')\delta v_s(\mathbf{r}',\omega)\phi_a(\mathbf{r}')\,, \qquad (7.4)
\end{aligned}$$

where we defined

$$F_{ia}(\omega) = \left(\frac{1}{(\epsilon_i-\epsilon_a)+\omega}+\frac{1}{(\epsilon_i-\epsilon_a)-\omega}\right)\,. \qquad (7.5)$$

In order to arrive at the previous equation, we used the fact that

$$\frac{1}{(\epsilon_i-\epsilon_a)+\omega}-\frac{1}{(\epsilon_i-\epsilon_a)-\omega} = \left(\frac{1}{(\epsilon_i-\epsilon_a)+\omega}+\frac{1}{(\epsilon_i-\epsilon_a)-\omega}\right)\frac{-\omega}{\epsilon_i-\epsilon_a}\,. \qquad (7.6)$$

---

[2] In the program, we choose a field direction and we calculate all the components of the induced current density, along with the induced density corresponding to this field. We do this calculation for the field directions $\hat{\mathbf{e}}_x$, $\hat{\mathbf{e}}_y$ and $\hat{\mathbf{e}}_z$.

The main interest of this rewriting is that we will avoid any numerical divergence at $\omega = 0$ thanks to the division by ω in the expression for the magnetizability given in Eq. (7.3) which cancels the ω in the numerator on the right-hand side. We now use the following relation[3]:

$$\hat{\mathbf{j}}_p \cdot \left[\frac{1}{2}\left(\mathbf{B}^i(\omega) \times (\mathbf{r} - \mathbf{r}_G)\right)\right] = \frac{\omega}{2}\left[(\mathbf{r} - \mathbf{r}_G) \times \hat{\mathbf{j}}_p\right]_i . \tag{7.7}$$

In this way, the part which depends on $\mathbf{r}'$ in the second line of Eq. (7.4) will take the same form as the part which depends on $\mathbf{r}$. The magnetizability $\xi(\omega)$ in Eq. (7.3) then takes the subsequent form:

$$\begin{aligned}
\xi_{kd}(\omega) = & \sum_{ia} F_{ia}(\omega) \int d\mathbf{r} \frac{1}{2}\left[(\mathbf{r} - \mathbf{r}_C) \times \phi_i(\mathbf{r})\hat{\mathbf{j}}(\mathbf{r})\phi_a(\mathbf{r})\right]_k \\
& \times \int d\mathbf{r}' \frac{1}{2}\left[(\mathbf{r}' - \mathbf{r}_G) \times \phi_i(\mathbf{r}')\hat{\mathbf{j}}(\mathbf{r}')\phi_a(\mathbf{r}')\right]_d \\
& - \sum_{ia} F(0) \int d\mathbf{r} \frac{1}{2}\left[(\mathbf{r} - \mathbf{r}_C) \times \phi_i(\mathbf{r})\hat{\mathbf{j}}(\mathbf{r})\phi_a(\mathbf{r})\right]_k \sum_l \left[\frac{1}{2}\hat{\mathbf{e}}_d \times (\mathbf{r} - \mathbf{r}_G)\right]_l \\
& \times \int d\mathbf{r}' \phi_a(\mathbf{r}')\hat{j}_l(\mathbf{r}')\phi_i(\mathbf{r}') \\
& + F_{ia}(\omega)\frac{-1}{(\epsilon_i - \epsilon_a)} \int d\mathbf{r} \frac{1}{2}\left[(\mathbf{r} - \mathbf{r}_C) \times \phi_i(\mathbf{r})\hat{\mathbf{j}}(\mathbf{r})\phi_a(\mathbf{r})\right]_k \\
& \times \int d\mathbf{r}' \phi_a(\mathbf{r}')\delta v_s(\mathbf{r}', \omega)\phi_i(\mathbf{r}') .
\end{aligned} \tag{7.8}$$

Let us also give the expression for the induced charge density $\delta\rho(\mathbf{r}, \omega)$, defined as

$$\begin{aligned}
\delta\rho^d(\mathbf{r}, \omega) &= \int d\mathbf{r}' \chi_{\rho\mathbf{j}_p}(\mathbf{r}, \mathbf{r}', \omega) \cdot \mathbf{A}^d_{ext}(\mathbf{r}', \omega) + \int d\mathbf{r}' \chi_{\rho\rho}(\mathbf{r}, \mathbf{r}', \omega)\delta v_s(\mathbf{r}', \omega) \\
&= \int d\mathbf{r}' \chi_{\rho,\mathbf{j}_p}(\mathbf{r}, \mathbf{r}', \omega) \cdot \left(\frac{1}{2}\mathbf{B}^d(\omega) \times (\mathbf{r}' - \mathbf{r}_G)\right) \\
&\quad + \int d\mathbf{r}' \chi_{\rho\rho}(\mathbf{r}, \mathbf{r}', \omega)\delta v_s(\mathbf{r}', \omega) .
\end{aligned} \tag{7.9}$$

Using the explicit expression for the current response function $\chi^{\rho\mathbf{j}}$ given in Eq. (3.12), we get

$$\begin{aligned}
& \delta\rho^d(\mathbf{r}, \omega) \\
= & \sum_{ia} \phi_i(\mathbf{r})\phi_a(\mathbf{r})F_{ia}(\omega)\frac{-\omega}{\epsilon_i - \epsilon_a} \int d\mathbf{r}' \phi_a(\mathbf{r}')\hat{\mathbf{j}}_p(\mathbf{r}')\phi_i(\mathbf{r}') \cdot \left(\frac{\omega}{2}\hat{\mathbf{e}}_d \times (\mathbf{r}' - \mathbf{r}_G)\right) \\
& + \int d\mathbf{r}' \chi_{\rho\rho}(\mathbf{r}, \mathbf{r}', \omega)\delta v_s(\mathbf{r}', \omega) ,
\end{aligned} \tag{7.10}$$

---

[3] This can be simply proved by doing a cyclic permutation: $\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c}) = \mathbf{c} \cdot (\mathbf{a} \times \mathbf{b}) = \mathbf{b} \cdot (\mathbf{c} \times \mathbf{a})$.

where $F_{ia}(\omega)$ is defined in Eq. (7.5). Using a cyclic permutation, we obtain

$$\delta\rho^{d}(\mathbf{r},\omega) = \sum_{ia}\phi_i(\mathbf{r})\phi_a(\mathbf{r})F_{ia}(\omega)\frac{-\omega^2}{\epsilon_i-\epsilon_a}\int d\mathbf{r}'\left[(\mathbf{r}'-\mathbf{r}_G)\times\phi_a(\mathbf{r}')\hat{\mathbf{j}}_p(\mathbf{r}')\phi_i(\mathbf{r}')\right]_d + \int d\mathbf{r}'\chi_{\rho\rho}(\mathbf{r},\mathbf{r}',\omega)\delta v_s(\mathbf{r}',\omega)\,. \tag{7.11}$$

Finally, using the explicit expression for the paramagnetic current operator yields

$$\begin{aligned}&\delta\rho^{d}(\mathbf{r},\omega)\\ =&\frac{i}{2}\sum_{ia}\phi_i(\mathbf{r})\phi_a(\mathbf{r})F_{ia}(\omega)\frac{-\omega^2}{\epsilon_i-\epsilon_a}\int d\mathbf{r}'\frac{1}{2}\left[(\mathbf{r}'-\mathbf{r}_G)\times(\phi_i\nabla\phi_a-\phi_a\nabla\phi_i)\right]_d\\ &+\int d\mathbf{r}'\chi_{\rho\rho}(\mathbf{r},\mathbf{r}',\omega)\delta v_s(\mathbf{r}',\omega)\,.\end{aligned} \tag{7.12}$$

The quantity $\frac{1}{2}\int d\mathbf{r}'\frac{1}{2}\left[(\mathbf{r}'-\mathbf{r}_G)\times(\phi_i(\mathbf{r}')\nabla\phi_a(\mathbf{r}')-\phi_a(\mathbf{r}')\nabla\phi_i(\mathbf{r}'))\right]_d$ is calculated in a subroutine of its own, for each i and a, and written to file, which avoids recalculating this quantity in other subroutines.

We note that, since we choose the Kohn-Sham orbitals to be real, although the matrix elements $\int d\mathbf{r}'\frac{1}{2}(\mathbf{r}'-\mathbf{r}_G)\times\phi_i(\mathbf{r}')\hat{\mathbf{j}}_p\phi_a(\mathbf{r}')$ are purely imaginary, the total magnetizability is complex because of the infinitesimal $i\eta$ in the denominator of the response functions, as shown in Eq. (3.9). When we take the limit $\eta\to 0$, we can separate the real and imaginary parts. In theory, the latter should be zero everywhere, except at the excitation energies of the system, and when calculating a full spectrum, one should thus see delta peaks in the imaginary part. This is not feasible in practice, though, and one has to take a finite η to broaden the spectrum. We shall see an example of this in the next section, where we show how we obtain circular dichroism spectra.

It is important to note that ADF only deals with real valued quantities[4]. If one wants to calculate imaginary numbers, one has to separate explicitly the real and imaginary parts in the program. In particular, the induced density $\delta\rho(\mathbf{r},\omega)$ as well as $\delta v_s(\mathbf{r},\omega)$ are purely imaginary in ADF, e.g., $\delta\rho(\mathbf{r},\omega)=i\delta\rho'(\mathbf{r},\omega)$, with $\delta\rho'(\mathbf{r}',\omega)$ a real quantity. This means that in ADF, we can work with $\delta\rho'(\mathbf{r},\omega)$ rather than $\delta\rho(\mathbf{r},\omega)$.

7.3 Circular dichroism

The derivation of the expressions for the optical rotation tensors G and $\tilde{G}$ as defined in chapter 5 is similar to the magnetizability (see previous section). However, circular dichroism spectra are related to the imaginary part of the current density. In this

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[4] The Kohn-Sham orbitals are thus always real-valued.

section, we thus mainly focus on separating the induced current density into real and imaginary parts.

We consider here the case when a uniform external electric field $\mathbf{E} = -i\hat{\mathbf{e}}$ is applied, represented by a uniform vector potential $\mathbf{A}(\omega) = -\frac{1}{\omega}\hat{\mathbf{e}}$ (i.e., $\mathbf{A}$ does not depend on $\mathbf{r}$). The current density in the Kohn-Sham system reads

$$\delta\mathbf{j}(\mathbf{r},\omega) = \int d\mathbf{r}'[\chi_{\mathbf{jj}}(\mathbf{r},\mathbf{r}',\omega) - \chi_{\mathbf{jj}}(\mathbf{r},\mathbf{r}',0)] \cdot \mathbf{A} + \int d\mathbf{r}' \chi_{\mathbf{j}\rho}(\mathbf{r},\mathbf{r}',\omega)\delta v_s(\mathbf{r}',\omega) \,. \tag{7.13}$$

Let us work out the expressions for the response functions $\chi_{\mathbf{jj}}(\mathbf{r},\mathbf{r}',\omega)$ and $\chi_{\mathbf{j}\rho}(\mathbf{r},\mathbf{r}',\omega)$.

$$\begin{aligned}\chi_{\mathbf{jj}}(\mathbf{r},\mathbf{r}',\omega) - \chi_{\mathbf{jj}}(\mathbf{r},\mathbf{r}',0) =& \sum_{ia} \phi_i\hat{\mathbf{j}}\phi_a\phi_a'\hat{\mathbf{j}}'\phi_i'\Big(\frac{1}{\epsilon_i-\epsilon_a+\omega+i\eta} - \frac{1}{\epsilon_i-\epsilon_a+i\eta} \\ &+ \frac{1}{\epsilon_i-\epsilon_a-\omega-i\eta} - \frac{1}{\epsilon_i-\epsilon_a-i\eta}\Big) \,,\end{aligned} \tag{7.14}$$

$$\begin{aligned}\chi_{\mathbf{j}\rho}(\mathbf{r},\mathbf{r}',\omega) &= \frac{\phi_i\hat{\mathbf{j}}\phi_a\phi_a'\phi_i'}{\epsilon_i-\epsilon_a+\omega+i\eta} + \frac{\phi_a\hat{\mathbf{j}}\phi_i\phi_i'\phi_a'}{\epsilon_i-\epsilon_a-\omega-i\eta} \\ &= \phi_i\hat{\mathbf{j}}\phi_a\phi_a'\phi_i'\left(\frac{1}{\epsilon_i-\epsilon_a+\omega+i\eta} - \frac{1}{\epsilon_i-\epsilon_a-\omega+i\eta}\right) \,,\end{aligned} \tag{7.15}$$

where, for convenience, a prime indicates a dependence on $\mathbf{r}'$ rather than $\mathbf{r}$. The induced current density then reads:

$$\begin{aligned}\delta\mathbf{j}(\mathbf{r},\omega) = \phi_i\hat{\mathbf{j}}\phi_a&\Big(\frac{1}{\epsilon_i-\epsilon_a+\omega+i\eta} - \frac{1}{\epsilon_i-\epsilon_a+i\eta} \\ &+ \frac{1}{\epsilon_i-\epsilon_a-\omega-i\eta} - \frac{1}{\epsilon_i-\epsilon_a-i\eta}\Big)\int d\mathbf{r}'\phi_a'\hat{\mathbf{j}}'\phi_i' \cdot \mathbf{A} \\ &+ \phi_i\hat{\mathbf{j}}\phi_a\left(\frac{1}{\epsilon_i-\epsilon_a+\omega+i\eta} - \frac{1}{\epsilon_i-\epsilon_a-\omega-i\eta}\right)\int d\mathbf{r}'\phi_a'\delta v_s'\phi_i' \,.\end{aligned} \tag{7.16}$$

We can now separate $\delta\mathbf{j}(\mathbf{r},\omega)$ in its real and imaginary parts. Let us focus on the prefactor before δv_s in Eq. (7.16) first. We can write:

$$\begin{aligned}&\frac{1}{\epsilon_i-\epsilon_a+\omega+i\eta} - \frac{1}{\epsilon_i-\epsilon_a-\omega-i\eta} \\ =&\frac{\epsilon_i-\epsilon_a+\omega-i\eta}{(\epsilon_i-\epsilon_a+\omega)^2+\eta^2} - \frac{\epsilon_i-\epsilon_a-\omega+i\eta}{(\epsilon_i-\epsilon_a-\omega)^2+\eta^2} \\ =&\frac{\epsilon_i-\epsilon_a+\omega}{(\epsilon_i-\epsilon_a+\omega)^2+\eta^2} - \frac{\epsilon_i-\epsilon_a-\omega}{(\epsilon_i-\epsilon_a-\omega)^2+\eta^2} \\ &-i\eta\left[\frac{1}{(\epsilon_i-\epsilon_a+\omega)^2+\eta^2} + \frac{1}{(\epsilon_i-\epsilon_a-\omega)^2+\eta^2}\right] \,.\end{aligned} \tag{7.17}$$

Let us now consider the term in front of the external vector potential $\mathbf{A}$ in Eq. (7.16). We have:

$$\begin{aligned}
&\frac{1}{\epsilon_i-\epsilon_a+\omega+i\eta}-\frac{1}{\epsilon_i-\epsilon_a+i\eta}+\frac{1}{\epsilon_i-\epsilon_a-\omega-i\eta}-\frac{1}{\epsilon_i-\epsilon_a-i\eta}\\
&=\frac{\epsilon_i-\epsilon_a+\omega-i\eta}{(\epsilon_i-\epsilon_a+\omega)^2+\eta^2}-\frac{\epsilon_i-\epsilon_a-i\eta}{(\epsilon_i-\epsilon_a)^2+\eta^2}+\frac{\epsilon_i-\epsilon_a-\omega+i\eta}{(\epsilon_i-\epsilon_a-\omega)^2+\eta^2}-\frac{\epsilon_i-\epsilon_a+i\eta}{(\epsilon_i-\epsilon_a)^2+\eta^2}\\
&=\frac{\epsilon_i-\epsilon_a+\omega}{(\epsilon_i-\epsilon_a+\omega)^2+\eta^2}+\frac{\epsilon_i-\epsilon_a-\omega}{(\epsilon_i-\epsilon_a-\omega)^2+\eta^2}-2\frac{\epsilon_i-\epsilon_a}{(\epsilon_i-\epsilon_a)^2+\eta^2}\\
&+i\eta\left(\frac{1}{(\epsilon_i-\epsilon_a-\omega)^2+\eta^2}-\frac{1}{(\epsilon_i-\epsilon_a+\omega)^2+\eta^2}\right). \qquad (7.18)
\end{aligned}$$

The induced current density then takes the following form:

$$\begin{aligned}
\delta\mathbf{j}(\mathbf{r},\omega)=&\phi_i\hat{\mathbf{j}}\phi_a\Big(\frac{\epsilon_i-\epsilon_a+\omega}{(\epsilon_i-\epsilon_a+\omega)^2+\eta^2}+\frac{\epsilon_i-\epsilon_a-\omega}{(\epsilon_i-\epsilon_a-\omega)^2+\eta^2}-2\frac{\epsilon_i-\epsilon_a}{(\epsilon_i-\epsilon_a)^2+\eta^2}\Big)\\
&\int d\mathbf{r}'\phi_a'\hat{\mathbf{j}}'\phi_i'\cdot\mathbf{A}\\
&+\phi_i\hat{\mathbf{j}}\phi_a\left(\frac{\epsilon_i-\epsilon_a+\omega}{(\epsilon_i-\epsilon_a+\omega)^2+\eta^2}-\frac{\epsilon_i-\epsilon_a-\omega}{(\epsilon_i-\epsilon_a-\omega)^2+\eta^2}\right)\int d\mathbf{r}'\phi_a'\delta v_s'\phi_i'\\
&+i\eta\Big[\phi_i\hat{\mathbf{j}}\phi_a\Big(\frac{1}{(\epsilon_i-\epsilon_a-\omega)^2+\eta^2}-\frac{1}{(\epsilon_i-\epsilon_a+\omega)^2+\eta^2}\Big)\int d\mathbf{r}'\phi_a'\hat{\mathbf{j}}'\phi_i'\cdot\mathbf{A}\\
&-\phi_i\hat{\mathbf{j}}\phi_a\left(\frac{1}{(\epsilon_i-\epsilon_a+\omega)^2+\eta^2}+\frac{1}{(\epsilon_i-\epsilon_a-\omega)^2+\eta^2}\right)\int d\mathbf{r}'\phi_a'\delta v_s'\phi_i\Big]. \qquad (7.19)
\end{aligned}$$

Setting $\eta=0$ would simply yield a spectrum containing delta peaks which in practical calculations using a frequency grid are not visible. Therefore, in practice, we use a small but finite value for η to obtain the CD spectra.

It is useful to also set a small parameter γ in the induced density $\delta\rho(\mathbf{r},\omega)$. Indeed, in principle, we do not need to separate the induced density $\delta\rho(\mathbf{r},\omega)$ in a real and imaginary part, because it is purely imaginary for all frequencies not equal to an excitation energy. However, if ω is close to such an energy, we might encounter convergence problems because one of the denominators of the response function becomes small. To avoid them, we thus use a damping factor γ. Therefore we have to show the expression for $\delta\rho(\mathbf{r},\omega)$ for finite γ. The induced density reads

$$\begin{aligned}
\delta\rho(\mathbf{r},\omega)=&\sum_{ia}\phi_i\phi_a\left(\frac{1}{\epsilon_i-\epsilon_a+\omega+i\gamma}-\frac{1}{\epsilon_i-\epsilon_a-\omega-i\gamma}\right)\int d\mathbf{r}'\phi_a'\hat{\mathbf{j}}'\phi_i'\cdot\mathbf{A}\\
&+\sum_{ia}\phi_i\phi_a\left(\frac{1}{\epsilon_i-\epsilon_a+\omega+i\gamma}+\frac{1}{\epsilon_i-\epsilon_a-\omega-i\gamma}\right)\int d\mathbf{r}'\phi_a'\delta v_s'\phi_i'. \qquad (7.20)
\end{aligned}$$

Using similar manipulations as for $\delta\mathbf{j}(\mathbf{r},\omega)$, we can separate $\delta\rho(\mathbf{r},\omega)$ in its real and imaginary parts:

$$\begin{aligned}
&\delta\rho(\mathbf{r},\omega)\\
=&\sum_{ia}\phi_i\phi_a\left(\frac{\epsilon_i-\epsilon_a+\omega}{(\epsilon_i-\epsilon_a+\omega)^2+\gamma^2}-\frac{\epsilon_i-\epsilon_a-\omega}{(\epsilon_i-\epsilon_a-\omega)^2+\gamma^2}\right)\int d\mathbf{r}'\phi_a'\hat{\mathbf{j}}'\phi_i'\cdot\mathbf{A}\\
&+\sum_{ia}\phi_i\phi_a\left(\frac{\epsilon_i-\epsilon_a+\omega}{(\epsilon_i-\epsilon_a+\omega)^2+\gamma^2}+\frac{\epsilon_i-\epsilon_a-\omega}{(\epsilon_i-\epsilon_a-\omega)^2+\gamma^2}\right)\int d\mathbf{r}'\phi_a'\delta v_s'\phi_i'\\
&+i\gamma\Bigg[-\sum_{ia}\phi_i\phi_a\left(\frac{1}{(\epsilon_i-\epsilon_a+\omega)^2+\gamma^2}+\frac{1}{(\epsilon_i-\epsilon_a-\omega)^2+\gamma^2}\right)\int d\mathbf{r}'\phi_a'\hat{\mathbf{j}}'\phi_i'\cdot\mathbf{A}\\
&+\sum_{ia}\phi_i\phi_a\left(\frac{1}{(\epsilon_i-\epsilon_a-\omega)^2+\gamma^2}-\frac{1}{(\epsilon_i-\epsilon_a+\omega)^2+\gamma^2}\right)\int d\mathbf{r}'\phi_a'\delta v_s'\phi_i'\Bigg]. \qquad (7.21)
\end{aligned}$$

By using the following relationship,

$$\begin{aligned}
&\left(\frac{\epsilon_i-\epsilon_a+\omega}{(\epsilon_i-\epsilon_a+\omega)^2+\gamma^2}-\frac{\epsilon_i-\epsilon_a-\omega}{(\epsilon_i-\epsilon_a-\omega)^2+\gamma^2}\right)\\
&=\frac{-\omega}{(\epsilon_i-\epsilon_a)}\frac{(\epsilon_i-\epsilon_a)^2-\omega^2-\gamma^2}{(\epsilon_i-\epsilon_a)^2-\omega^2+\gamma^2}\left(\frac{\epsilon_i-\epsilon_a+\omega}{(\epsilon_i-\epsilon_a+\omega)^2+\gamma^2}+\frac{\epsilon_i-\epsilon_a-\omega}{(\epsilon_i-\epsilon_a-\omega)^2+\gamma^2}\right), \qquad (7.22)
\end{aligned}$$

one can rewrite the imaginary part[5] of $\delta\rho(\mathbf{r},\omega)$ as

$$\begin{aligned}
\mathrm{Im}[\delta\rho(\mathbf{r},\omega)]=&\sum_{ia}\phi_i(\mathbf{r})\phi_a(\mathbf{r})\left(\frac{\epsilon_i-\epsilon_a+\omega}{(\epsilon_i-\epsilon_a+\omega)^2+\gamma^2}+\frac{\epsilon_i-\epsilon_a-\omega}{(\epsilon_i-\epsilon_a-\omega)^2+\gamma^2}\right)\\
&\left[\frac{-\omega}{(\epsilon_i-\epsilon_a)}\frac{(\epsilon_i-\epsilon_a)^2-\omega^2-\gamma^2}{(\epsilon_i-\epsilon_a)^2-\omega^2+\gamma^2}\int d\mathbf{r}'\phi_a'\hat{\mathbf{j}}'\phi_i'\cdot\mathbf{A}+\int d\mathbf{r}'\phi_a'\delta v_s'\phi_i'\right]. \qquad (7.23)
\end{aligned}$$

Equation (7.23) is the one we use in chapter 5 to produce circular dichroism spectra[6].

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[5] Pay attention to the fact that when $\gamma=0$, $\delta\rho(\mathbf{r},\omega)$ is purely imaginary. The explicit imaginary number i in Eq. (7.21) is thus misleading, since the corresponding term is actually purely real, while the term without i is purely imaginary.

[6] By using Eq. (7.22), we managed to cast $\delta\rho(\mathbf{r},\omega)$ in a form that closely resembles the one which was already implemented, and which we use for the calculation of the static magnetizabilities in chapter 4 and for the specific rotations in chapter 5, for example. We retrieve this usual form by setting $\gamma=0$.

8

PERIODIC SYSTEMS

"To infinity... and beyond!" (Buzz Lightyear)

This chapter is meant to be explorative, and deals with the description of magnetization in extended systems.

The expressions of magnetization and polarization as dipole moments per unit volume are ill-defined when using periodic boundary conditions (PBC). Moreover, with PBC, the surface is artificially removed (see Fig. 8.1), and therefore, the effects of the surface densities on the response have to be accounted for by using information from the bulk only. As a consequence, one has to find definitions of magnetization and polarization in terms of bulk quantities. For example, the problem has been solved for the polarization, which can be expressed in terms of the bulk current density (see section 8.1). How to proceed in case of the magnetization is not that

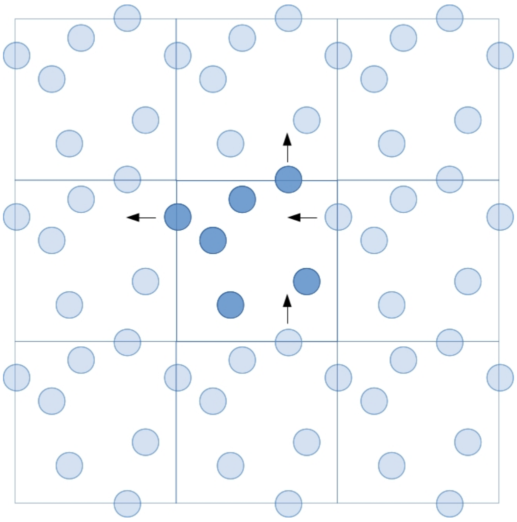

Figure 8.1 – Illustration of periodic boundary conditions. When a particle exits the unit cell on one side, it is actually reintroduced on the opposite side of the unit cell.

obvious. In this chapter, we illustrate the main problems which naturally arise when describing the magnetization, and we indicate possible strategies to try to solve them.

8.1 Polarization

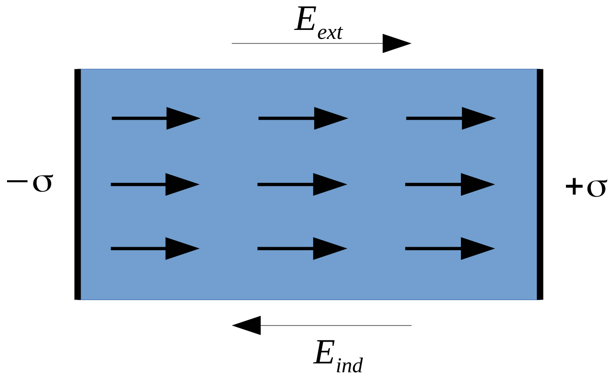

Figure 8.2 – An external electric field $\mathbf{E}_{ext}$ is applied onto a sample. As a result, the electrons will move and create a charge defect $(-\sigma)$ on one side of the sample, and a charge excess $(+\sigma)$ on the opposite side. This difference in potential induces an electric field $\mathbf{E}_{ind}$ which opposes the external one.

It might be tempting to define the bulk polarization $\mathbf{P}(t)$ as the electric dipole moment averaged over the volume of a unit cell, according to

$$\mathbf{P}(t) = \frac{1}{\Omega}\int_{\Omega} \mathbf{r}\rho(\mathbf{r},t)d\mathbf{r}\,, \tag{8.1}$$

where Ω is the volume of the unit cell. However, such a definition is incompatible with extended systems described by PBC, because the position vector $\mathbf{r}$ then is ill-defined, for it is unbounded and not periodic[1]. Moreover, using PBC, the contribution of the surface density to the polarization is artificially removed (see Fig. 8.2). The question of interest is thus to know whether $\mathbf{P}(t)$ can be rewritten in terms of a bulk quantity $\tilde{\mathbf{P}}(\mathbf{r},t)$, i.e.,

$$\mathbf{P}(t) \overset{?}{=} \frac{1}{\Omega}\int_{\Omega} \tilde{\mathbf{P}}(\mathbf{r},t)d\mathbf{r}\,. \tag{8.2}$$

In order to do this, the first thing to do is to use the continuity equation already

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[1] For more details on the fundamental problems arising when trying to describe an intrinsic bulk polarization, see chapter 22 of Ref. [7], for example.

given in Eq. (2.17) and which we repeat here,

$$\frac{\partial}{\partial t}\rho(\mathbf{r},t) + \nabla \cdot \mathbf{j}(\mathbf{r},t) = 0\,, \tag{8.3}$$

to rewrite Eq. (8.1) as

$$\mathbf{P}(t) = -\frac{1}{\Omega}\int_{\Omega}\int_{t_0}^{t} \mathbf{r}\nabla \cdot \mathbf{j}(\mathbf{r},t)dt'd\mathbf{r}\,, \tag{8.4}$$

where we assumed that $\mathbf{j}(\mathbf{r},t_0) = 0$. We now use the vector calculus identity $\nabla \cdot (f\mathbf{g}) = \mathbf{g}\cdot\nabla f + f\nabla\cdot\mathbf{g}$ to rewrite the above equation as

$$\mathbf{P}_i(t) = \frac{1}{\Omega}\int_{t_0}^{t}\int_{\Omega}\mathbf{j}_i(\mathbf{r},t)d\mathbf{r}dt' - \frac{1}{\Omega}\int_{t_0}^{t}\int_{\Omega}\nabla\cdot\left(r_i\mathbf{j}(\mathbf{r},t)\right)dt'\,. \tag{8.5}$$

Making use of Green-Ostrogradski's theorem, we get

$$\mathbf{P}(t) = \frac{1}{\Omega}\int_{t_0}^{t}\int_{\Omega}\mathbf{j}(\mathbf{r},t)d\mathbf{r}dt' - \frac{1}{\Omega}\int_{t_0}^{t}\int_{\partial\Omega}\mathbf{r}(\hat{\mathbf{n}}\cdot\mathbf{j}(\mathbf{r},t))dSdt'\,, \tag{8.6}$$

where $\partial\Omega$ indicates the surface of Ω and $\hat{\mathbf{n}}$ is the unitary normal vector at the boundary. The surface integral on the right-hand side of Eq. (8.6) vanishes because no current exits the sample, so $\mathbf{j}(\mathbf{r},t)\cdot\hat{\mathbf{n}} = 0$. We are thus left with

$$\mathbf{P}(t) = \frac{1}{\Omega}\int_{t_0}^{t}\int_{\Omega}\mathbf{j}(\mathbf{r},t')d\mathbf{r}dt'\,, \tag{8.7}$$

in which we can identify

$$\tilde{\mathbf{P}}(\mathbf{r},t) \equiv \int_{t_0}^{t}\mathbf{j}(\mathbf{r},t')dt'\,, \tag{8.8}$$

which is the bulk quantity we were looking for, and it can be interpreted as a bulk polarization density. Equation (8.7) is therefore suitable for extended systems, and was successfully applied in Refs. [38,42]. The question of how to describe polarization in extended systems can also be tackled using a Berry phase formulation [84–86].

In conclusion, one can eliminate $\mathbf{r}$ from Eq. (8.1), and instead express $\mathbf{P}(t)$ in terms of the bulk current density $\mathbf{j}(\mathbf{r},t)$, which is a truly periodic quantity, compatible with PBC.
Could something similar be done for the magnetic dipole moment ?

8.2 Magnetization

8.2.1 Analogy with the polarization case

In the following, we shall follow the same line of argument as in the previous section and apply it to the case of the magnetization.

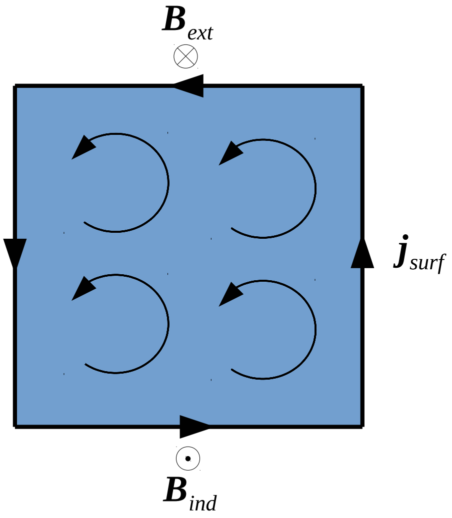

Figure 8.3 – An external magnetic field $\mathbf{B}_{ext}$ is applied onto a sample. As a result, the electrons will move and create a current density $\mathbf{j}_{\text{surf}}$ on the surface. This surface current then induces a magnetic field $\mathbf{B}_{ind}$ which opposes the external one.

Therefore, let us start from the following expression for the magnetization $\mathbf{M}(t)$, which is analogous to Eq. (8.1):

$$\mathbf{M}(t) = \frac{1}{2\Omega} \int_{\Omega} \mathbf{r} \times \mathbf{j}(\mathbf{r}, t) d\mathbf{r} \,, \tag{8.9}$$

where $\mathbf{j}(\mathbf{r}, t)$ is the electronic current density. As in the previous section, this definition is unsuitable if one uses PBC, because the position operator $\mathbf{r}$ then is ill-defined. Moreover, the contribution of the surface current to the magnetization is artificially removed (see Fig. 8.3).

Similarly to the previous section, we would like to get rid of $\mathbf{r}$ in Eq. (8.9), and the crucial question is to know if we can rewrite $\mathbf{M}(t)$ in terms of a bulk quantity $\tilde{\mathbf{M}}(\mathbf{r}, t)$, i.e.,

$$\mathbf{M}(t) \overset{?}{=} \frac{1}{\Omega} \int_{\Omega} \tilde{\mathbf{M}}(\mathbf{r}, t) d\mathbf{r} \,. \tag{8.10}$$

In analogy to the polarization case, where we used the continuity equation, we will use here the equation of motion of the current density $\mathbf{j}(\mathbf{r},t)$ (see also Eq. (2.36)),

$$\frac{\partial}{\partial t}\langle\Psi(t)|\hat{\mathbf{j}}(\mathbf{r},t)|\Psi(t)\rangle = \langle\Psi(t)|\left(\frac{\partial\hat{\mathbf{j}}(\mathbf{r},t)}{\partial t} - i\left[\hat{\mathbf{j}}(\mathbf{r},t),\hat{H}\right]\right)|\Psi(t)\rangle\,, \tag{8.11}$$

in which the current-density operator is defined as (see Eq. (2.30))

$$\hat{\mathbf{j}}(\mathbf{r},t) = \frac{1}{2}\sum_i\left\{\hat{v}_i(t),\delta(\mathbf{r}-\mathbf{r}_i)\right\}\,, \tag{8.12}$$

where the velocity operator $\hat{\mathbf{v}}_i(t)$, given in Eq. (2.29), is repeated here,

$$\hat{\mathbf{v}}_i(t) = \hat{\mathbf{p}}_i + \mathbf{A}(\mathbf{r}_i,t)\,, \tag{8.13}$$

and the Hamiltonian is the same as in Eq. (2.25) (with U the Coulomb potential). Using the Maxwell equations (we use the Lorentz convention[2] here),

$$\nabla\cdot\mathbf{E}(\mathbf{r},t) = 4\pi\rho(\mathbf{r},t)\,, \tag{8.14}$$

$$\nabla\cdot\mathbf{B}(\mathbf{r},t) = 0\,, \tag{8.15}$$

$$\nabla\times\mathbf{E}(\mathbf{r},t) = -\frac{\partial}{\partial t}\mathbf{B}(\mathbf{r},t)\,, \tag{8.16}$$

$$\nabla\times\mathbf{B}(\mathbf{r},t) = \frac{1}{c^2}\frac{\partial}{\partial t}\mathbf{E}(\mathbf{r},t) - \frac{4\pi}{c^2}\mathbf{j}(\mathbf{r},t)\,, \tag{8.17}$$

it can be shown that the current density obeys an equation which resembles a continuity equation. It takes the following form:

$$\frac{\partial}{\partial t}\mathbf{j}(\mathbf{r},t) = \mathbf{F}^{lor}(\mathbf{r},t) + \mathbf{F}^{v}(\mathbf{r},t) + \mathbf{F}^{int}(\mathbf{r},t)\,, \tag{8.18}$$

where

$$\mathbf{F}^{lor}(\mathbf{r},t) = \rho(\mathbf{r},t)\mathbf{E}(\mathbf{r},t) + \mathbf{j}(\mathbf{r},t)\times\mathbf{B}(\mathbf{r},t)\,, \tag{8.19}$$

$$\mathbf{F}^{int}(\mathbf{r},t) = -\langle\Psi(t)|\sum_{i=1}^{N}\delta(\mathbf{r}-\mathbf{r}_i)\sum_{j\neq i}^{N}\left[\nabla_{\mathbf{r}_i}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}\right]|\Psi(t)\rangle\,, \tag{8.20}$$

$$F^{v}_{\mu}(\mathbf{r},t) = \sum_{\nu}\nabla_{r_\nu}T_{\mu\nu}(\mathbf{r},t)\,, \tag{8.21}$$

in which

$$T_{\mu\nu}(\mathbf{r},t) = -\langle\Psi(t)|\frac{1}{4}\sum_{i=1}^{N}\{\hat{v}_{r_{i\mu}}(t),\{\hat{v}_{r_{i\nu}}(t),\delta(\mathbf{r}-\mathbf{r}_i)\}\}|\Psi(t)\rangle\,, \tag{8.22}$$

---

[2] In order to obtain these equations, one can start from the usual Maxwell equations in SI units with fields $\tilde{\mathbf{E}}$ and $\tilde{\mathbf{B}}$, and then obtain the new equations in terms of $\mathbf{E} = 4\pi\epsilon_0\tilde{\mathbf{E}}$ and $\mathbf{B} = 4\pi\epsilon_0 c\tilde{\mathbf{B}}$.

where $\{\hat{A}, \hat{B}\} = \hat{A}\hat{B} + \hat{B}\hat{A}$ denotes the anticommutator of two operators $\hat{A}$ and $\hat{B}$. Finally, it can be shown that the Lorentz force can be rewritten in the following way[3]:

$$F_i^{lor}(\mathbf{r}, t) = \sum_j \partial_j \sigma_{ij}(\mathbf{r}, t) - \frac{\partial}{\partial t} S_i(\mathbf{r}, t)\,, \tag{8.23}$$

where the Maxwell stress tensor $\sigma(\mathbf{r}, t)$ is given by

$$\sigma_{ij}(\mathbf{r}, t) = \frac{1}{4\pi}\left(E_i E_j + c^2 B_i B_j - \delta_{ij}\frac{1}{2}[E^2 + c^2 B^2]\right)\,, \tag{8.24}$$

and $\mathbf{S}(\mathbf{r}, t)$ is the Poynting vector defined as

$$\mathbf{S}(\mathbf{r}, t) = \frac{1}{4\pi}\mathbf{E}(\mathbf{r}, t) \times \mathbf{B}(\mathbf{r}, t)\,. \tag{8.25}$$

The equation of motion for the current density then takes the following form[4]:

$$\frac{\partial}{\partial t}\mathbf{j}(\mathbf{r}, t) = \nabla \cdot [T(\mathbf{r}, t) + \sigma(\mathbf{r}, t)] + \mathbf{F}^{int}(\mathbf{r}, t) - \frac{\partial}{\partial t}\mathbf{S}(\mathbf{r}, t)\,. \tag{8.26}$$

Getting the inspiration from the polarization case, we can insert Eq. (8.26) in Eq. (8.9) to obtain

$$\mathbf{M}(t) = \frac{1}{2\Omega}\int_{t_0}^{t} dt' \int_\Omega \mathbf{r} \times \nabla \cdot [T(\mathbf{r}, t') + \sigma(\mathbf{r}, t')] - \frac{1}{2}\int_\Omega \mathbf{r} \times \mathbf{S}(\mathbf{r}, t)\,, \tag{8.27}$$

where we assumed that $\mathbf{j}(\mathbf{r}, t_0) = \mathbf{0}$ and we used the fact that, according to Newton's third law, internal forces should not exert a net torque (nor a net force) on the system[5]:

$$\int d\mathbf{r}\mathbf{r} \times \mathbf{F}^{int}(\mathbf{r}, t) = \mathbf{0}\,. \tag{8.28}$$

Manipulating Eq. (8.27) in a similar fashion as in the previous section, one can break the magnetization $\mathbf{M}(t)$ into volume and surface integrals. Unfortunately, contrary to the polarization problem, it does not seem possible to express $\mathbf{M}(t)$ solely in

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[3] To do this, one needs to use and combine Maxwell's equations, along with several vector calculus identities (see appendix F for details).

[4] The Poynting vector $\mathbf{S}(\mathbf{r}, t)$ can be identified with the current density of the electromagnetic field (see the book by Jackson [16], for example), and therefore, one could define the total curent density $\mathbf{j}_{\text{tot}}(\mathbf{r}, t)$ as the sum of the electronic current density and the field current density $\mathbf{j}_{\text{field}}(\mathbf{r}, t)$. Equation (8.26) can thus be rewritten as:

$$\frac{\partial}{\partial t}\mathbf{j}_{\text{tot}}(\mathbf{r}, t) = \frac{\partial}{\partial t}[\mathbf{j}(\mathbf{r}, t) + \mathbf{j}_{\text{field}}(\mathbf{r}, t)] = \nabla \cdot [T(\mathbf{r}, t) + \sigma(\mathbf{r}, t)] + \mathbf{F}^{int}(\mathbf{r}, t)\,.$$

[5] The derivation is given in appendix G.

terms of a volume integral by using such an approach, since, in general, the surface integrals do not vanish. This highlights the complexity of magnetization, and the need for developing new strategies.

8.2.2 Possible strategies

A possible way to proceed would be to exploit the gauge freedom in choosing the magnetization density $\tilde{\mathbf{M}}(\mathbf{r},t)$ and the polarization density $\tilde{\mathbf{P}}(\mathbf{r},t)$, and relate them to the longitudinal and transverse currents $\mathbf{j}_L(\mathbf{r},t)$ and $\mathbf{j}_T(\mathbf{r},t)$, respectively. Indeed, it follows from the Maxwell equations that[6]

$$\begin{aligned}\rho(\mathbf{r},t) =& -\nabla\cdot\tilde{\mathbf{P}}(\mathbf{r},t)\,, && (8.29)\\ \mathbf{j}(\mathbf{r},t) =& \frac{\partial}{\partial t}\tilde{\mathbf{P}}(\mathbf{r},t) + c\nabla\times\tilde{\mathbf{M}}(\mathbf{r},t)\,, && (8.30)\end{aligned}$$

where $\mathbf{j}_L$ is linked to the polarization through the relation $\mathbf{j}_L(\mathbf{r},t) = \frac{\partial}{\partial t}\tilde{\mathbf{P}}(\mathbf{r},t)$, and $\mathbf{j}_T$ is related to the magnetization as $\mathbf{j}_T(\mathbf{r},t) = c\nabla\times\tilde{\mathbf{M}}(\mathbf{r},t)$. By taking the curl of Eq. (8.30), and using the following gauge choice [87],

$$\begin{aligned}\nabla\cdot\tilde{\mathbf{M}}(\mathbf{r},t) =& 0\,, && (8.31)\\ \nabla\times\left[\frac{\partial}{\partial t}\tilde{\mathbf{P}}(\mathbf{r},t)\right] =& \mathbf{0}\,, && (8.32)\end{aligned}$$

it is possible to cast the magnetization in terms of a Poisson equation,

$$\nabla^2\tilde{\mathbf{M}}(\mathbf{r},t) = -c\nabla\times\mathbf{j}(\mathbf{r},t)\,. \tag{8.33}$$

In order to guarantee the uniqueness of the solution, the magnetization must also satisfy some boundary conditions, which must be chosen such that the surface integral constraints are satisfied. In the end, it is possible to show that the magnetization can be expressed as solution of a vector Poisson problem with coupled boundary constraints,

$$\begin{aligned}\nabla^2\tilde{\mathbf{M}}(\mathbf{r},t) &\overset{\mathbf{r}\in\Omega}{=} -c\nabla\times\mathbf{j}(\mathbf{r},t)\,, && (8.34)\\ \hat{\mathbf{n}}\times\tilde{\mathbf{M}}(\mathbf{r},t) &\overset{\mathbf{r}\in\partial\Omega}{=} 0\,, && (8.35)\\ \nabla\cdot\tilde{\mathbf{M}}(\mathbf{r},t) = \hat{\mathbf{n}}\cdot\mathbf{j}(\mathbf{r},t) &\overset{\mathbf{r}\in\partial\Omega}{=} 0\,, && (8.36)\end{aligned}$$

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[6] These definitions of Maxwell's equations in terms of the polarization and magnetization densities are well explained in Ref. [16], for example.

and that the polarization can be obtained as solution of a scalar Poisson problem,

$$\nabla^2\phi(\mathbf{r},t) \overset{\mathbf{r}\in\Omega}{=} \nabla\cdot\mathbf{j}(\mathbf{r},t)\,, \tag{8.37}$$

$$\phi(\mathbf{r},t) \overset{\mathbf{r}\in\partial\Omega}{=} 0\,, \tag{8.38}$$

from which $\tilde{\mathbf{P}}(\mathbf{r},t)$ can be retrieved from the relation $\frac{\partial}{\partial t}\tilde{\mathbf{P}}(\mathbf{r},t) = \nabla\phi(\mathbf{r},t)$.
Work in this direction is in progress.

SUMMARY

Several interesting phenomena of matter can be fully understood by probing its electronic structure. The electronic structure can be investigated by looking at some specific intrinsic quantities of the system under study: the electromagnetic properties. Each electromagnetic property reveals its own piece of information. Having a reliable tool to calculate such properties is thus of great interest. This thesis is to be viewed in this context. Our main purpose was to develop a general method that could give access to a wide class of electromagnetic properties. We focused on the calculation of magnetic properties in finite systems, which usually proves challenging because of important and subtle aspects, which are usually not properly considered in existing theoretical methods. An example is an artificial dependence on the gauge origin of the vector potential. This potential is essential to describe magnetic fields. Moreover, this gauge origin is often confused with the origin of the coordinate systems; this leads to results which depend on the latter, which is unphysical. In this thesis, therefore, we proposed an elegant, simple and efficient formulation based on the current density, which can correctly describe magnetic properties. We applied our method within time-dependent current-density-functional theory (TDCDFT), which offers an efficient platform for this kind of calculation.

In the first part of this thesis, we explained the background theory supporting the method we developed. In the first chapter, notably, we explained the ground-state DFT, based on the Hohenberg-Kohn theorems, which assure that the sole knowledge of the ground-state density is enough to determine all the properties of a stationary electronic system. In the second chapter, we presented two extensions of DFT: TDDFT, which extends DFT to the time-dependent case thanks to the Runge-Gross theorem, and TDCDFT, which allows one to work with magnetic fields as well. The third chapter was dedicated to deriving the linear response equations that we used to obtain electromagnetic properties in the rest of the thesis. In chapter 4, we presented a novel gauge-invariant method to calculate general electromagnetic properties via the introduction of a sum rule which places the diamagnetic current density on the same footing as the paramagnetic current density, and applied it to the calculation of magnetizabilities. We showed that with our method, we managed to solve both the gauge-invariance problem and the slow convergence of the current density with respect to the size of the basis set. In chapter 5, we showed how our method could be extended to calculate circular dichroism spectra, which have a particularly strong interest in biology, since the shape of the circular dichroism spectra determines the amount of secondary structures present in a given biomolecule. Chapter 6 dealt with two other static magnetic properties, namely the rotational g-tensor, which is closely related to the static magnetizability, and the NMR shielding constant. In chapter 7, we described the details about the implementation of our method in the Amsterdam Density Functional program. Finally, in the last chapter, we gave a flavor of how to describe the magnetization in extended systems. A straightforward extension of the concepts developed for finite systems is not always possible, since the use of periodic boundary conditions makes some of the equations ill-defined. We stressed these problems and proposed some possible strategies, which we are currently investigating.

Appendices

A Origin dependence of the dipole moments

In this section, we show how the definitions of the dipole moments often given in the literature can be made origin-independent, making them intrinsic quantities of the system.

A.1 Electric dipole moment

The induced electric dipole moment $\delta\boldsymbol{\mu}(\omega)$ is often given in the literature as

$$\delta\boldsymbol{\mu}(\omega) = \int d\mathbf{r}\mathbf{r}\delta\rho(\mathbf{r},\omega)\,, \tag{A.1}$$

where $\delta\rho(\mathbf{r},\omega)$ is the induced electronic density and its integral $\int d\mathbf{r}\delta\rho(\mathbf{r},\omega)$ represents the change in the electronic charge. We now make a shift of the origin of the coordinate system, such that $\mathbf{r}' = \mathbf{r} - \mathbf{a}$ (see Figure A.1). The unprimed quantities represent the original coordinate system, while the primed quantities represent the

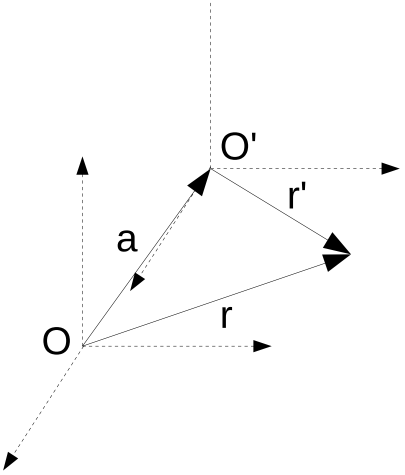

Figure A.1 – Effect of a change of coordinate system.

shifted coordinate system.

The induced electric dipole moment in the shifted coordinate system thus reads

$$\begin{aligned}\delta\boldsymbol{\mu}'(\omega) \equiv& \int d\mathbf{r}'\mathbf{r}'\delta\rho'(\mathbf{r}',\omega)\\ =& \int d\mathbf{r}(\mathbf{r}-\mathbf{a})\delta\rho(\mathbf{r},\omega)\\ =&\delta\boldsymbol{\mu}(\omega) - \mathbf{a}\int d\mathbf{r}\delta\rho(\mathbf{r},\omega)\,,\end{aligned} \tag{A.2}$$

where in the first step, we used the fact that $\mathbf{r}' = \mathbf{r} - \mathbf{a}$ and $d\mathbf{r}' = d\mathbf{r}$, and that by definition, the induced density at a given point in space should be the same, regardless of the coordinate system, i.e., $\delta\rho(\mathbf{r},\omega) \equiv \delta\rho'(\mathbf{r}',\omega)$. So the equality $\delta\boldsymbol{\mu}'(\omega) = \delta\boldsymbol{\mu}(\omega)$ stands if and only if the total change in electronic charge is 0. To make $\delta\boldsymbol{\mu}(\omega)$ origin-independent for any case, we should use instead the following expression:

$$\delta\boldsymbol{\mu}(\omega) = \int d\mathbf{r}(\mathbf{r}-\mathbf{r}_C)\delta\rho(\mathbf{r},\omega)\,, \tag{A.3}$$

where $\mathbf{r}_C$ is the reference point in the molecular frame around which a multipole expansion is made. We thus have that

$$\begin{aligned}\delta\boldsymbol{\mu}'(\omega) =& \int d\mathbf{r}'(\mathbf{r}'-\mathbf{r}'_C)\delta\rho'(\mathbf{r}',\omega) = \int d\mathbf{r}\left(\mathbf{r} - \cancel{\mathbf{a}} - (\mathbf{r}_C - \cancel{\mathbf{a}})\right)\delta\rho(\mathbf{r},\omega)\\ =& \,\delta\boldsymbol{\mu}(\omega)\,.\end{aligned} \tag{A.4}$$

With the expression given in Eq. (A.3), the relation $\delta\boldsymbol{\mu}'(\omega) = \delta\boldsymbol{\mu}(\omega)$ is always satisfied as it should.

A.2 Magnetic dipole moment

The same manipulations as in the previous section can be done with the induced magnetic dipole moment. The latter is often given in the literature as

$$\delta\mathbf{m}(\omega) = \frac{1}{2}\int d\mathbf{r}\mathbf{r}\times\delta\mathbf{j}(\mathbf{r},\omega)\,. \tag{A.5}$$

If we express it in the primed coordinate system, we get

$$\begin{aligned}\delta\mathbf{m}'(\omega) \equiv& \frac{1}{2}\int d\mathbf{r}'\mathbf{r}'\times\delta\mathbf{j}'(\mathbf{r}',\omega)\\ =& \frac{1}{2}\int d\mathbf{r}(\mathbf{r}-\mathbf{a})\times\delta\mathbf{j}(\mathbf{r},\omega)\\ =& \delta\mathbf{m}(\omega) - \frac{1}{2}\mathbf{a}\times\int d\mathbf{r}\delta\mathbf{j}(\mathbf{r},\omega)\,,\end{aligned} \tag{A.6}$$

where we used that by definition, the induced current density at a given point in space should be the same, regardless of the coordinate system, i.e., $\delta\mathbf{j}(\mathbf{r},\omega) \equiv \delta\mathbf{j}'(\mathbf{r}',\omega)$.

So $\delta\mathbf{m}'(\omega) = \delta\mathbf{m}(\omega)$ if and only if $\int d\mathbf{r}\delta\mathbf{j}(\mathbf{r},\omega) = \mathbf{0}$, which is satisfied for $\omega = 0$ only. In order to make $\delta\mathbf{m}(\omega)$ origin-independent, we should rather use the following expression:

$$\delta\mathbf{m}(\omega) = \frac{1}{2}\int d\mathbf{r}(\mathbf{r} - \mathbf{r}_C) \times \delta\mathbf{j}(\mathbf{r},\omega)\,, \tag{A.7}$$

where once again, $\mathbf{r}_C$ lies in the frame of the molecule and is the reference point around which a multipole expansion is done. In the shifted coordinate system, the induced magnetic dipole moment now reads

$$\begin{aligned}\delta\mathbf{m}'(\omega) &= \frac{1}{2}\int d\mathbf{r}'(\mathbf{r}' - \mathbf{r}'_C) \times \delta\mathbf{j}'(\mathbf{r}',\omega) = \frac{1}{2}\int d\mathbf{r}\,(\mathbf{r} - \cancel{\mathbf{a}} - (\mathbf{r}_C - \cancel{\mathbf{a}})) \times \delta\mathbf{j}(\mathbf{r},\omega)\\ &= \delta\mathbf{m}(\omega)\,.\end{aligned} \tag{A.8}$$

Hence the expression for the induced magnetic dipole moment given in Eq. (A.7) ensures that $\delta\mathbf{m}(\omega)$ is independent of the choice for the origin of the coordinate system.

B DIAMAGNETIC CURRENT SUM RULE

In this section, we show an alternative derivation for the sum rule given in Eq. (4.12), which we used to obtain the diamagnetic current sum rule in Eq. (4.14), which relates the diamagnetic current to the paramagnetic current response function. A proof for general interacting systems is given earlier in Ref. [6] (see in particular Eqs.(8.4) and (8.5) of Ref. [6]). The following alternative demonstration only holds for noninteracting systems (including Kohn-Sham systems).

We start by giving the expression for the paramagnetic current response function $\chi^{j_p j_p}(\mathbf{r}, \mathbf{r}', \omega)$ at $\omega = 0$:

$$\chi_{ij}^{j_p j_p}(\mathbf{r}, \mathbf{r}', 0) = \sum_{n,n'} (f_n - f_{n'}) \frac{\phi_n^*(\mathbf{r}) \hat{j}_i(\mathbf{r}) \phi_{n'}(\mathbf{r}) \phi_{n'}^*(\mathbf{r}') \hat{j}_j(\mathbf{r}') \phi_n(\mathbf{r}')}{\epsilon_n - \epsilon_{n'}} , \tag{B.1}$$

where f_n are the occupation numbers, and $\hat{\mathbf{j}} = \frac{1}{2i}(\nabla - \nabla^\dagger)$ is the paramagnetic current density operator. We now exchange n and n' in the term that involves $f_{n'}$, and we obtain

$$\begin{aligned}\chi_{ij}^{j_p j_p}(\mathbf{r}, \mathbf{r}', 0) = \sum_{n,n'} f_n \Big[&\frac{\phi_n^*(\mathbf{r}) \hat{j}_i(\mathbf{r}) \phi_{n'}(\mathbf{r}) \phi_{n'}^*(\mathbf{r}') \hat{j}_j(\mathbf{r}') \phi_n(\mathbf{r}')}{\epsilon_n - \epsilon_{n'}} \\ &- \frac{\phi_{n'}^*(\mathbf{r}) \hat{j}_i(\mathbf{r}) \phi_n(\mathbf{r}) \phi_n^*(\mathbf{r}') \hat{j}_j(\mathbf{r}') \phi_{n'}(\mathbf{r}')}{\epsilon_{n'} - \epsilon_n} \Big] .\end{aligned} \tag{B.2}$$

Using the explicit expression for the paramagnetic current density operator, we get

$$\begin{aligned}\chi_{ij}^{j_p j_p}(\mathbf{r}, \mathbf{r}', 0) = \frac{1}{4} \sum_{n,n'} \frac{f_n}{\epsilon_{n'} - \epsilon_n} \Big[&\phi_{n'}^*(\mathbf{r}) \partial_i \phi_n(\mathbf{r}) \phi_n^*(\mathbf{r}') \partial_j' \phi_{n'}(\mathbf{r}') \\ &- \partial_i \phi_{n'}^*(\mathbf{r}) \phi_n(\mathbf{r}) \phi_n^*(\mathbf{r}') \partial_j' \phi_{n'}(\mathbf{r}') - \phi_{n'}^*(\mathbf{r}) \partial_i \phi_n(\mathbf{r}) \partial_j' \phi_n^*(\mathbf{r}') \phi_{n'}(\mathbf{r}') \\ &+ \partial_i \phi_{n'}^*(\mathbf{r}) \phi_n(\mathbf{r}) \partial_j' \phi_n^*(\mathbf{r}') \phi_{n'}(\mathbf{r}') \Big] + \text{c.c.} ,\end{aligned} \tag{B.3}$$

where the notation “c.c.” indicates that we take the complex conjugate of the precedent terms. Finally, regrouping some terms together, we arrive at

$$\begin{aligned}
\chi_{ij}^{j_p j_p}(\mathbf{r},\mathbf{r}',0) &= \frac{1}{4}\sum_{n,n'}\frac{f_n}{\epsilon_{n'}-\epsilon_n}\Big\{\phi^*_{n'}(\mathbf{r})\partial_i\phi_n(\mathbf{r})\Big[\phi^*_n(\mathbf{r}')\partial'_j\phi_{n'}(\mathbf{r}')-\partial'_j\phi^*_n(\mathbf{r}')\phi_{n'}(\mathbf{r}')\Big]\\
&\quad-\partial_i\phi^*_{n'}(\mathbf{r})\phi_n(\mathbf{r})\Big[\phi^*_n(\mathbf{r}')\partial'_j\phi_{n'}(\mathbf{r}')-\partial'_j\phi^*_n(\mathbf{r}')\phi_{n'}(\mathbf{r}')\Big]\Big\}+\text{c.c.}\\
&= \frac{1}{4}\sum_{n,n'}\frac{f_n}{\epsilon_{n'}-\epsilon_n}\Big[\phi^*_{n'}(\mathbf{r})\partial_i\phi_n(\mathbf{r})-\partial_i\phi^*_{n'}(\mathbf{r})\phi_n(\mathbf{r})\Big]\\
&\quad\times\Big[\phi^*_n(\mathbf{r}')\partial'_j\phi_{n'}(\mathbf{r}')-\partial'_j\phi^*_n(\mathbf{r}')\phi_{n'}(\mathbf{r}')\Big]+\text{c.c.}\,.
\end{aligned}\tag{B.4}$$

Let us evaluate its divergence with respect to $\mathbf{r}'$.

$$\begin{aligned}
\sum_j\partial'_j\chi_{ij}^{j_p j_p}(\mathbf{r},\mathbf{r}',0) &= \frac{1}{4}\sum_{n,n'}\frac{f_n}{\epsilon_{n'}-\epsilon_n}[\phi^*_{n'}(\mathbf{r})\partial_i\phi_n(\mathbf{r})-\partial_i\phi^*_{n'}(\mathbf{r})\phi_n(\mathbf{r})]\\
&\quad\times[\phi^*_n(\mathbf{r}')\partial'^2_j\phi_{n'}(\mathbf{r}')-\partial'^2_j\phi^*_n(\mathbf{r}')\phi_{n'}(\mathbf{r}')]+\text{c.c.}\\
&= \frac{1}{2}\sum_{n,n'}f_n\phi^*_n(\mathbf{r}')\phi_{n'}(\mathbf{r}')[\partial_i\phi^*_{n'}(\mathbf{r})\phi_n(\mathbf{r})-\phi^*_{n'}(\mathbf{r})\partial_i\phi_n(\mathbf{r})]+\text{c.c.}\,,
\end{aligned}$$

where in the last step, we used that for a noninteracting system, $[-\frac{\nabla^2}{2}+v_s]\phi_n=\epsilon_n\phi_n$, where v_s could be an effective potential such as, for example, the Kohn-Sham potential. We now use the definition of the density $\rho_0(\mathbf{r},\mathbf{r}')=\sum_n f_n\phi_n(\mathbf{r})\phi^*_n(\mathbf{r}')$ along with the completeness relation $\sum_n\phi_n(\mathbf{r}')\phi^*_n(\mathbf{r})=\delta(\mathbf{r}-\mathbf{r}')$ to obtain

$$\begin{aligned}
\sum_j\partial'_j\chi_{ij}^{j_p j_p}(\mathbf{r},\mathbf{r}',0) &= \frac{1}{2}\Big[\sum_n f_n\phi_n(\mathbf{r})\phi^*_n(\mathbf{r}')\partial_i\delta(\mathbf{r}-\mathbf{r}')\\
&\quad-\delta(\mathbf{r}-\mathbf{r}')\sum_n f_n\phi^*_n(\mathbf{r}')\partial_i\phi_n(\mathbf{r})\Big]+\text{c.c.}\\
&= \frac{1}{2}\left[\rho_0(\mathbf{r},\mathbf{r}')\partial_i\delta(\mathbf{r}-\mathbf{r}')-\delta(\mathbf{r}-\mathbf{r}')\partial_i\rho_0(\mathbf{r},\mathbf{r}')\right]+\text{c.c.}\\
&= \frac{1}{2}\Big[\delta(\mathbf{r}-\mathbf{r}')\partial'_i\rho_0(\mathbf{r},\mathbf{r}')-\partial'_i(\rho_0(\mathbf{r},\mathbf{r}')\delta(\mathbf{r}-\mathbf{r}'))\\
&\quad-\delta(\mathbf{r}-\mathbf{r}')\partial_i\rho_0(\mathbf{r},\mathbf{r}')\Big]+\text{c.c.}\\
&= \frac{1}{2}\left[\delta(\mathbf{r}-\mathbf{r}')[\partial'_i-\partial_i]\rho_0(\mathbf{r},\mathbf{r}')-\partial'_i(\rho_0(\mathbf{r},\mathbf{r}')\delta(\mathbf{r}-\mathbf{r}'))\right]+\text{c.c.}\\
&= -\rho_0(\mathbf{r})\partial'_i\delta(\mathbf{r}-\mathbf{r}')\,.
\end{aligned}\tag{B.5}$$

In the end, we thus have obtained the following sum rule,

$$\sum_j\partial'_j\chi_{ij}^{j_p j_p}(\mathbf{r},\mathbf{r}',0)+\rho_0(\mathbf{r})\partial'_i\delta(\mathbf{r}-\mathbf{r}')=0\,,\tag{B.6}$$

which we have then used to put the diamagnetic current density on equal footing with the paramagnetic one (see Eq. (4.14)).

C EQUIVALENCE BETWEEN THE DIAMAGNETIC CURRENT SUM RULE AND CSGT

In this appendix, we show the equivalence at $\omega = 0$ between a special case of the continuous set of gauge transformations (CSGT) [28] (also called "$\mathbf{r} = \mathbf{r}'$") and the diamagnetic current sum rule we use in Eq. (4.14).

We first recall the usual expression for the current density $\delta\mathbf{j}$ in a general interacting system with external potentials v and $\mathbf{A}$ (see also Eq. (4.6)):

$$\delta\mathbf{j}(\mathbf{r},\omega) = \frac{1}{2}\int d\mathbf{r}'\chi_{\mathbf{j}_p\mathbf{j}_p}(\mathbf{r},\mathbf{r}',\omega)\cdot[\mathbf{B}(\omega)\times\mathbf{r}'] + \frac{1}{2}\rho_0(\mathbf{r})\,[\mathbf{B}(\omega)\times\mathbf{r}]\ , \tag{C.1}$$

where, without loss of generality, we used $v(\mathbf{r},\omega) = 0$[1] and $\mathbf{A}(\mathbf{r},\omega) = \frac{1}{2}\mathbf{B}(\omega)\times\mathbf{r}$. As we explained in chapter 4, it can be difficult to reach convergence with basis set size because the diamagnetic and paramagnetic currents are not calculated on equal footing. A solution could be to make the diamagnetic term disappear by making a gauge transform. It can be proved indeed that the electromagnetic fields are invariant under the following gauge transformation of the external potentials (see also Eq. (2.33)):

$$v'(\mathbf{r},\omega) = v(\mathbf{r},\omega) + i\omega\Lambda(\mathbf{r},\omega) \tag{C.2}$$

$$\mathbf{A}'(\mathbf{r},\omega) = \mathbf{A}(\mathbf{r},\omega) + \nabla\Lambda(\mathbf{r},\omega) \tag{C.3}$$

with Λ an arbitrary function. When we evaluate the current density given in Eq. (C.1) in the origin of our coordinate system, we see that the diamagnetic term vanishes. A vanishing diamagnetic current can actually be achieved for any point in space by using the following gauge transform:

$$\Lambda(\mathbf{r},\omega) = -\frac{1}{2}[\mathbf{B}(\omega)\times\mathbf{d}]\cdot\mathbf{r}\,. \tag{C.4}$$

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[1] Since $v = 0$, the term containing $\chi_{\rho\mathbf{j}_p}$ appearing naturally in the expression of $\delta\mathbf{j}$ disappears, but keep in mind that it has to be taken into account when another gauge is chosen, as we did in Eq. (C.7).

The potentials then become

$$v'(\mathbf{r},\omega) = -\frac{i\omega}{2}[\mathbf{B}(\omega)\times\mathbf{d}]\cdot\mathbf{r} \tag{C.5}$$

$$\mathbf{A}'(\mathbf{r},\omega) = \frac{1}{2}\mathbf{B}(\omega)\times[\mathbf{r}-\mathbf{d}]\,, \tag{C.6}$$

and the current density hence reads

$$\begin{aligned}\delta\mathbf{j}(\mathbf{r},\omega) = \frac{1}{2}\int d\mathbf{r}'\chi_{\mathbf{j}_p\mathbf{j}_p}(\mathbf{r},\mathbf{r}',\omega)\cdot[\mathbf{B}(\omega)\times[\mathbf{r}'-\mathbf{d}]] + \frac{1}{2}\rho_0(\mathbf{r})\,[\mathbf{B}(\omega)\times[\mathbf{r}-\mathbf{d}]]\\ + \frac{i\omega}{2}\int d\mathbf{r}'\chi_{\mathbf{j}_p\rho}(\mathbf{r},\mathbf{r}',\omega)\mathbf{B}(\omega)\cdot[\mathbf{r}'\times\mathbf{d}]\,.\end{aligned} \tag{C.7}$$

Since $\delta\mathbf{j}(\mathbf{r},\omega)$ is gauge invariant for all points $\mathbf{r}$, we can therefore choose a different $\mathbf{d}$ for every point $\mathbf{r}$. In other words, for each coordinate, we choose a different scalar and vector potential. To get rid of the diamagnetic term at each point $\mathbf{r}$, we make the following choice "$\mathbf{d}=\mathbf{r}$" [2]. The current density is then modified according to

$$\begin{aligned}\delta\mathbf{j}(\mathbf{r},\omega) = \frac{1}{2}\int d\mathbf{r}'\chi_{\mathbf{j}_p\mathbf{j}_p}(\mathbf{r},\mathbf{r}',\omega)\cdot[\mathbf{B}(\omega)\times[\mathbf{r}'-\mathbf{r}]]\\ + \frac{i\omega}{2}\int d\mathbf{r}'\chi_{\mathbf{j}_p\rho}(\mathbf{r},\mathbf{r}',\omega)\mathbf{r}'\cdot[\mathbf{r}\times\mathbf{B}(\omega)]\,.\end{aligned} \tag{C.8}$$

For the static case $\omega = 0$, the expression for the current density simplifies, and we are left with

$$\left.\frac{\delta\mathbf{j}(\mathbf{r},\omega)}{\omega}\right|_{\omega=0} = \frac{1}{2}\int d\mathbf{r}'\chi_{\mathbf{j}_p\mathbf{j}_p}(\mathbf{r},\mathbf{r}',0)\cdot[\hat{\mathbf{e}}\times(\mathbf{r}'-\mathbf{r})] \tag{C.9}$$

where $\hat{\mathbf{e}}$ is a unitary vector, and where, without loss of generality, we used the magnetic field $\mathbf{B}(\omega)=\omega\hat{\mathbf{e}}$. The latter expression is identical to the one we obtain using the diamagnetic current sum rule (see Eq. (4.17)). We have thus proved that both methods are equivalent in the static limit.

In principle, the gauge transformations in Eqs. (C.5) and (C.6) should be accompanied by a transformation of the wavefunction according to Eq. (2.34). However, because we choose $\mathbf{B}(\omega)$ to be linear in ω, the phase factor becomes 1 in the limit $\omega\to 0$. For finite frequencies, this is no longer the case and we would have to account for the transformation of the wavefunction, which would make this CSGT approach numerically demanding [29]. Our method based on the diamagnetic current sum rule is therefore much more efficient.

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[2] Note the quotation marks here: $\mathbf{d}$ is a parameter while $\mathbf{r}$ is a variable, so this is not a true equality. We can actually "simulate" an equality between both quantities because there is an integral over all the positions $\mathbf{r}'$, so we can choose a different $\mathbf{d}$ for each $\mathbf{r}'$.

D

GAUGE-ORIGIN INDEPENDENCE OF CIRCULAR DICHROISM

In this appendix, we shall derive Eqs. (5.21) and (5.23). We show in particular that, contrary to the frequency-dependent magnetizability, circular dichroism does not depend on $\mathbf{r}_G$. Indeed, although each component of the optical rotation tensor (ORT) G depends on $\mathbf{r}_G$, its trace does not.

D.1 Equivalence between $\tilde{G}(\omega)$ and $G(\omega)$

In this section, we derive Eq. (5.21).

We start by repeating the expression for the optical rotation tensors (ORT) G and $\tilde{G}$ given in Eqs (5.19) and (5.20):

$$G_{ij}(\omega) = \frac{i}{2\omega}\sum_{kl}\epsilon_{jkl}\int d\mathbf{r}\int d\mathbf{r}'(r'_k - r_{G,k})\left[\chi_{il}^{\mathbf{j}_p\mathbf{j}_p}(\mathbf{r},\mathbf{r}',\omega) + \delta_{il}\delta(\mathbf{r}-\mathbf{r}')\rho_0(\mathbf{r})\right], \quad \text{(D.1)}$$

$$\tilde{G}_{ij}(\omega) = -\frac{i}{2\omega}\sum_{kl}\epsilon_{ikl}\int d\mathbf{r}\int d\mathbf{r}'(r_k - r_{C,k})\left[\chi_{lj}^{\mathbf{j}_p\mathbf{j}_p}(\mathbf{r},\mathbf{r}',\omega) + \delta_{lj}\delta(\mathbf{r}-\mathbf{r}')\rho_0(\mathbf{r})\right], \quad \text{(D.2)}$$

where $\chi^{\mathbf{j}_p\mathbf{j}_p}(\mathbf{r},\mathbf{r}',\omega)$ is the current-current response function, as given in Eq. (4.7), and ϵ_{jkl} is the Levi-Civita tensor. Swapping $\mathbf{r}$ and $\mathbf{r}'$ in the expression for G, and making use of Onsager relation

$$\chi_{ij}^{j_p,j_p}(\mathbf{r},\mathbf{r}',\omega) = \chi_{ji}^{j_p,j_p}(\mathbf{r}',\mathbf{r},\omega)\,, \quad \text{(D.3)}$$

which holds true even when using a finite basis set, we get

$$G_{ij}(\omega) = \frac{i}{2\omega}\sum_{kl}\epsilon_{jkl}\int d\mathbf{r}\int d\mathbf{r}'(r_k - r_{G,k})\left[\chi_{li}^{\mathbf{j}_p\mathbf{j}_p}(\mathbf{r},\mathbf{r}',\omega) + \delta_{il}\delta(\mathbf{r}'-\mathbf{r})\rho_0(\mathbf{r}')\right]. \quad \text{(D.4)}$$

By using the fact that

$$\int d\mathbf{r}'\delta(\mathbf{r}'-\mathbf{r})\rho_0(\mathbf{r}') = \rho_0(\mathbf{r})\,, \tag{D.5}$$

we can rewrite $G(\omega)$ as

$$G_{ij}(\omega) = \frac{i}{2\omega}\sum_{kl}\epsilon_{jkl}\int d\mathbf{r}\int d\mathbf{r}'(r_k - r_{G,k})\left[\chi_{li}^{\mathbf{j}_p\mathbf{j}_p}(\mathbf{r},\mathbf{r}',\omega) + \delta_{li}\delta(\mathbf{r}-\mathbf{r}')\rho_0(\mathbf{r})\right]\,. \tag{D.6}$$

Comparing Eq. (D.6) to Eq. (D.2), we see that if $\mathbf{r}_G = \mathbf{r}_C$, we retrieve the relation of equivalence between both tensors given in Eq. (5.21), i.e.,

$$G_{ij}(\omega) = -\tilde{G}_{ji}(\omega)\,. \tag{D.7}$$

D.2 Independence of $\mathbf{r}_G$

Here we demonstrate Eq. (5.23), i.e., we show that the trace of he ORT G ($\tilde{G}$) is independent of $\mathbf{r}_G$ ($\mathbf{r}_C$). Since we know both ORT G and $\tilde{G}$ are equivalent, we will focus in the following on the demonstration for G. A similar proof can be done for $\tilde{G}$.

The trace of the ORT reads[1]

$$\mathrm{Tr}[G(\omega)] = \sum_{i=1}^{3} G_{ii}(\omega) = \frac{i}{\omega}\sum_{ikl}\epsilon_{ikl}\int d\mathbf{r}\int d\mathbf{r}'(r_k - r_{Gk})\chi_{li}^{\mathbf{j}_p\mathbf{j}_p}(\mathbf{r},\mathbf{r}',\omega)\,. \tag{D.8}$$

Looking at the $\mathbf{r}_G$-dependent part of $G(\omega)$ only, denoted $G^{\mathbf{r}_G}(\omega)$, we have:

$$\mathrm{Tr}[G^{\mathbf{r}_G}(\omega)] = \sum_k r_{Gk}\sum_{il}\epsilon_{ikl}\iint d\mathbf{r}d\mathbf{r}'\chi_{li}^{\mathbf{j}_p\mathbf{j}_p}(\mathbf{r},\mathbf{r}',\omega)\,. \tag{D.9}$$

Using the Onsager relation in Eq. (D.3), and making the following switches, $\mathbf{r} \leftrightarrow \mathbf{r}'$ and $i \leftrightarrow l$, we obtain

$$\mathrm{Tr}[G^{\mathbf{r}_G}(\omega)] = \sum_k r_{Gk}\sum_{il}\epsilon_{lki}\iint d\mathbf{r}d\mathbf{r}'\chi_{li}^{\mathbf{j}_p\mathbf{j}_p}(\mathbf{r},\mathbf{r}',\omega)\,. \tag{D.10}$$

Since the Levi-Civita tensor is antisymmetric with regards to i and l, i.e., $\epsilon_{ikl} = -\epsilon_{lki}$, we get

$$\mathrm{Tr}[G^{\mathbf{r}_G}(\omega)] = -\sum_k r_{Gk}\sum_{il}\epsilon_{ikl}\iint d\mathbf{r}d\mathbf{r}'\chi_{li}^{\mathbf{j}_p\mathbf{j}_p}(\mathbf{r},\mathbf{r}',\omega)\,. \tag{D.11}$$

---

[1] In Eq. (D.8), only the paramagnetic part of G remains since we know from Eq. (5.22) that the diagonal components of the diamagnetic part of G vanish.

Comparison of Eqs. (D.8) and (D.11) shows that $\mathrm{Tr}[G^{\mathbf{r}_G}(\omega)] = -\mathrm{Tr}[G^{\mathbf{r}_G}(\omega)]$, which proves that

$$\mathrm{Tr}[G^{\mathbf{r}_G}(\omega)] = 0\,. \tag{D.12}$$

We have thus proved that the trace of the optical rotation tensor is independent of the gauge origin $\mathbf{r}_G$. In the next section, we will derive conditions such that Eq. (D.12) could still hold when solving the self-consistent Kohn-Sham equations.

D.3 Calculating $\mathrm{Tr}[G(\omega)]$ within TDCDFT

The proof given in the previous section is valid for the exact theory. However, in this thesis, we use TDCDFT with approximate functionals. It is clear that gauge invariance might be destroyed by the choice of the exchange-correlation kernel. In this section, we therefore show how gauge independence can be guaranteed. In the following proof, we will perform one SCF iteration "by hand".

At the first iteration, the induced density $\delta\rho(\mathbf{r},\omega)$ is given by[2]

$$\begin{aligned}\delta\rho^j(\mathbf{r},\omega) =& \int d\mathbf{r}_1 \chi^{\rho\mathbf{j}}(\mathbf{r},\mathbf{r}_1,\omega)\cdot\mathbf{A}^j(\mathbf{r}_1,\omega) + \int d\mathbf{r}_1\chi^{\rho\rho}(\mathbf{r},\mathbf{r}_1,\omega)\delta v_s(\mathbf{r}_1,\omega)\\ =& \sum_{l=1}^{3}\int d\mathbf{r}_1\chi_l^{\rho\mathbf{j}}(\mathbf{r},\mathbf{r}_1,\omega)A_l^j(\mathbf{r}_1,\omega)\,,\end{aligned} \tag{D.13}$$

where the superscript j indicates that the external field is in the j direction, and we assumed that the trial Kohn-Sham potential $v_s(\mathbf{r},\omega)$ is zero when entering the SCF loop for the first time. We remind the reader that we are using a vector potential $\mathbf{A}^j(\mathbf{r},\omega)$ of the form

$$\mathbf{A}^j(\mathbf{r},\omega) = \frac{1}{2}\hat{\mathbf{e}}_j\times(\mathbf{r}-\mathbf{r}_G)\,. \tag{D.14}$$

The induced Kohn-Sham potential $\delta v_s(\mathbf{r},\omega)$ is then calculated via the following relation:

$$\begin{aligned}\delta v_s^j(\mathbf{r},\omega) =& \int d\mathbf{r}_2\left(\frac{1}{|\mathbf{r}-\mathbf{r}_2|} + f_{xc}(\mathbf{r},\mathbf{r}_2,\omega)\right)\delta\rho^j(\mathbf{r}_2,\omega)\\ =& \sum_l\int d\mathbf{r}_2 d\mathbf{r}_1\left(\frac{1}{|\mathbf{r}-\mathbf{r}_2|} + f_{xc}(\mathbf{r},\mathbf{r}_2,\omega)\right)\chi_l^{\rho\mathbf{j}}(\mathbf{r}_2,\mathbf{r}_1,\omega)A_l^j(\mathbf{r}_1,\omega)\,,\end{aligned} \tag{D.15}$$

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[2] In ADF, the induced density appearing in Eq. (D.13) is fitted. The effect of this fitting is equivalent to having an auxiliary response function $\tilde{\chi}^{\rho\mathbf{j}_p}$ instead of $\chi^{\rho\mathbf{j}_p}$ in Eq. (D.13), which would result in an artificial gauge dependence in $\mathrm{Tr}[G(\omega)]$. Therefore, we have to use an accurate fitting scheme in order not to create an artificial gauge dependence.

where $f_{xc}(\mathbf{r}, \mathbf{r}_2)$ is the scalar exchange-correlation kernel, and where we made use of Eq. (D.13). Let us adopt the following notation,

$$f_{H,xc}(\mathbf{r}, \mathbf{r}', \omega) = \frac{1}{|\mathbf{r} - \mathbf{r}'|} + f_{xc}(\mathbf{r}, \mathbf{r}', \omega)\,, \tag{D.16}$$

and concentrate on the $\mathbf{r}_G$-dependent part,

$$\delta v_s^{j,r_G}(\mathbf{r}, \omega) = \sum_l A_l^{j,r_G} \int d\mathbf{r}_2 d\mathbf{r}_1 f_{H,xc}(\mathbf{r}, \mathbf{r}_2, \omega) \chi_l^{\rho\mathbf{j}}(\mathbf{r}_2, \mathbf{r}_1, \omega)\,, \tag{D.17}$$

where the superscript $\mathbf{r}_G$ indicates the part which depends on $\mathbf{r}_G$ only. From this xc potential, we can then calculate the induced current density as

$$\begin{aligned}
&\delta j_i^{j,r_G}(\mathbf{r}, \omega) \\
&= \int d\mathbf{r}_3 \chi_i^{\mathbf{j},\rho}(\mathbf{r}, \mathbf{r}_3, \omega) \delta v_s^{j,r_G}(\mathbf{r}_3, \omega) \\
&= -\int d\mathbf{r}_3 \chi_i^{\rho,\mathbf{j}}(\mathbf{r}_3, \mathbf{r}, \omega) \delta v_s^{j,r_G}(\mathbf{r}_3, \omega) \\
&= -\sum_l A_l^{j,r_G} \int d\mathbf{r}_3 d\mathbf{r}_2 d\mathbf{r}_1 f_{H,xc}(\mathbf{r}_3, \mathbf{r}_2, \omega) \chi_i^{\rho,\mathbf{j}}(\mathbf{r}_3, \mathbf{r}, \omega) \chi_l^{\rho\mathbf{j}}(\mathbf{r}_2, \mathbf{r}_1, \omega)\,,
\end{aligned} \tag{D.18}$$

where in the second step, we used that $\chi_i^{\mathbf{j},\rho}(\mathbf{r}, \mathbf{r}_3, \omega) = -\chi_i^{\rho,\mathbf{j}}(\mathbf{r}_3, \mathbf{r}, \omega)$, and in the last step we inserted Eq. (D.17). We now express the trace of the optical rotation tensor $G^{\mathbf{r}_G}(\omega)$ as

$$\begin{aligned}
&\mathrm{Tr}[G^{r_G}(\omega)] \\
&= \sum_i \int d\mathbf{r}_4 \delta j_i^{i,\mathbf{r}_G}(\mathbf{r}_4, \omega) \\
&= -\sum_{i,l} A_l^{i,r_G} \int d\mathbf{r}_4 d\mathbf{r}_3 d\mathbf{r}_2 d\mathbf{r}_1 f_{H,xc}(\mathbf{r}_3, \mathbf{r}_2, \omega) \chi_i^{\rho,\mathbf{j}}(\mathbf{r}_3, \mathbf{r}_4, \omega) \chi_l^{\rho\mathbf{j}}(\mathbf{r}_2, \mathbf{r}_1, \omega)\,.
\end{aligned} \tag{D.19}$$

In order to prove that $\mathrm{Tr}[G^{r_G}(\omega)]$ vanishes, we exchange the indices l and i in Eq. (D.19), and we make the following permutation of variables, $\mathbf{r}_1 \leftrightarrow \mathbf{r}_4$ and $\mathbf{r}_2 \leftrightarrow \mathbf{r}_3$, leading to

$$\begin{aligned}
\mathrm{Tr}[G^{r_G}(\omega)] = \sum_{i,l} A_l^{i,r_G} \int & d\mathbf{r}_4 d\mathbf{r}_3 d\mathbf{r}_2 d\mathbf{r}_1 \left(f_{H,xc}(\mathbf{r}_2, \mathbf{r}_3, \omega) - f_{H,xc}(\mathbf{r}_3, \mathbf{r}_2, \omega)\right) \\
& \times \chi_l^{\rho,\mathbf{j}}(\mathbf{r}_2, \mathbf{r}_1, \omega) \chi_i^{\rho\mathbf{j}}(\mathbf{r}_3, \mathbf{r}_4, \omega)\,,
\end{aligned} \tag{D.20}$$

where we used the fact that $A_i^l(\mathbf{r}, \omega) = -A_l^i(\mathbf{r}, \omega)$, which directly follows from

Eq. (D.14). The Coulomb potential is obviously symmetric, i.e.,

$$\frac{1}{|\mathbf{r}_2 - \mathbf{r}_3|} = \frac{1}{|\mathbf{r}_3 - \mathbf{r}_2|}\,, \tag{D.21}$$

so the only condition[3] which guarantees that Eq. (D.20) vanishes is that the exchange-correlation kernel must be symmetric, i.e.,

$$f_{xc}(\mathbf{r}_2, \mathbf{r}_3, \omega) = f_{xc}(\mathbf{r}_3, \mathbf{r}_2, \omega)\,. \tag{D.22}$$

So if Eq. (D.22) is satisfied, then $\mathrm{Tr}[G^{\mathbf{r}_G}(\omega)] = 0$. This symmetric relation for the exchange-correlation kernel is satisfied by several functionals, e.g., ALDA.

D.4 Diamagnetic part

We saw in the previous sections that both optical rotation tensors we *a priori* equivalent, since $G_{ij}(\omega) = -\tilde{G}_{ji}(\omega)$. However, we shall demonstrate in this section that, in practice, there is an advantage in working with $\tilde{G}(\omega)$ rather than $G(\omega)$.

If we focus on the paramagnetic part, we have

$$G^{para}_{ij}(\omega) = -\tilde{G}^{para}_{ji}(\omega)\,, \tag{D.23}$$

which stands both numerically and analytically. We also have in principles the following identity[4],

$$G^{dia}_{ij}(\omega) = -\tilde{G}^{dia}_{ji}(\omega)\,, \tag{D.24}$$

which stands analytically, but not numerically if one uses the sum rule in Eq. (4.14) with a finite basis set. This means that individually, each component of $G(\omega)$ will be different from that of $\tilde{G}(\omega)$. Only the trace of the ORT interests us, though. We can show that there exists a simple relation between both traces. With similar manipulations as in the previous section, i.e., by exchanging some indices and spatial coordinates, we can readily prove that

$$\mathrm{Tr}[G^{dia}(\omega)] = \mathrm{Tr}[\tilde{G}^{dia}(\omega)]\,, \tag{D.25}$$

which stands numerically, even with finite basis sets. Analytically, though, we know that $G_{ii}(\omega) = 0$, i.e., that the diagonal elements of $G(\omega)$ are all zero, independently of the molecule studied. This justifies the use of the diamagnetic current sum rule in Eq. (4.14), since the diamagnetic elements will not be zero anymore when using

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[3] More iterations “by hand” do not yield other conditions on the exchange-correlation kernel.

[4] Note that the diamagnetic part is zero on the diagonal.

finite basis sets, which will allow to compensate the errors made in the paramagnetic part. If we sum up, we have:

$$\mathrm{Tr}[\tilde{G}] = \mathrm{Tr}[\tilde{G}^{para}] + \mathrm{Tr}[\tilde{G}^{dia}]\,, \tag{D.26}$$

$$\mathrm{Tr}[G] = \mathrm{Tr}[G^{para}] + \mathrm{Tr}[G^{dia}] = -\mathrm{Tr}[\tilde{G}^{para}] + \mathrm{Tr}[\tilde{G}^{dia}]\,. \tag{D.27}$$

Among the two possible choices we have to calculate the ORT ($G(\omega)$ and $\tilde{G}(\omega)$), the best way to obtain an accurate ORT is to calculate the tensor for which the diamagnetic part cancels the errors made in the paramagnetic part. We thus choose to work with $\tilde{G}(\omega)$.

E

ALTERNATIVE EXPRESSION FOR THE OPTICAL ROTATION TENSOR

In this appendix, we show how the usual formulation of the optical rotation tensor $\tilde{G}(\omega)$ (see Eq. (5.13)) that one finds in the literature in terms of matrix elements of the electric and magnetic dipoles can be retrieved from our expression.

In Eq. (5.14), we gave an expression for the optical rotation tensor $\tilde{G}$. Applying directly the definitions of the response functions in Eq. (3.12), and using the diamagnetic current sum rule of Eq. (4.14), $\tilde{G}(\omega)$ takes the following form:

$$\begin{aligned}
&\tilde{G}_{kf}(\omega)\\
&=\frac{i}{\omega}\sum_{ia}\left(\frac{1}{\epsilon_i-\epsilon_a+\omega}+\frac{1}{\epsilon_i-\epsilon_a-\omega}\right)\int d\mathbf{r}\frac{1}{2}\left[\mathbf{r}\times\phi_i(\mathbf{r})\hat{\mathbf{j}}_p(\mathbf{r})\phi_a(\mathbf{r})\right]_k\\
&\quad\times\int d\mathbf{r}'\phi_a(\mathbf{r}')\hat{j}_{p,f}(\mathbf{r}')\phi_i(\mathbf{r}')\\
&\quad-\frac{i}{\omega}\sum_{ia}\frac{2}{\epsilon_i-\epsilon_a}\int d\mathbf{r}\frac{1}{2}\left[\mathbf{r}\times\phi_i(\mathbf{r})\hat{\mathbf{j}}_p(\mathbf{r})\phi_a(\mathbf{r})\right]_k\int d\mathbf{r}'\phi_a(\mathbf{r}')\hat{j}_{p,f}(\mathbf{r}')\phi_i(\mathbf{r}')\,,
\end{aligned}\tag{E.1}$$

where we neglected the term involving δv_s, and where $\hat{\mathbf{j}}_p(\mathbf{r})$ is the paramagnetic current density operator defined as

$$\hat{\mathbf{j}}_p(\mathbf{r})=-\frac{i}{2}(\nabla-\nabla^{\dagger})\,.\tag{E.2}$$

Working out Eq. (E.1), the latter can be rewritten as a single term:

$$\begin{aligned}
\tilde{G}_{kf}(\omega)=&i\sum_{ia}\left(\frac{1}{\epsilon_i-\epsilon_a+\omega}+\frac{1}{\epsilon_i-\epsilon_a-\omega}\right)\frac{-\omega}{\epsilon_i-\epsilon_a}\\
&\int d\mathbf{r}\frac{1}{2}\left[\mathbf{r}\times\phi_i(\mathbf{r})\hat{\mathbf{j}}_p(\mathbf{r})\phi_a(\mathbf{r})\right]_k\frac{-1}{\epsilon_i-\epsilon_a}\int d\mathbf{r}'\phi_a(\mathbf{r}')\hat{j}_{p,f}(\mathbf{r}')\phi_i(\mathbf{r}')\,,
\end{aligned}\tag{E.3}$$

which is the expression we use in the implementation.

Let us first reduce to a common denominator:

$$\begin{aligned}\tilde{G}_{kf}(\omega) = i\sum_{ia}\frac{-2\omega}{(\epsilon_i-\epsilon_a)^2-\omega^2}\int d\mathbf{r}\frac{1}{2}\left[\mathbf{r}\times\phi_i(\mathbf{r})\hat{\mathbf{j}}_p(\mathbf{r})\phi_a(\mathbf{r})\right]_k \\ \times\frac{-1}{\epsilon_i-\epsilon_a}\int d\mathbf{r}'\phi_a(\mathbf{r}')\hat{j}_{p,f}(\mathbf{r}')\phi_i(\mathbf{r}')\,.\end{aligned} \tag{E.4}$$

We then use the simple relation existing between the current density matrix elements and the dipole matrix elements[1],

$$\frac{i}{\epsilon_i-\epsilon_a}\int d\mathbf{r}\phi_a(\mathbf{r})\hat{\mathbf{j}}_p(\mathbf{r})\phi_i(\mathbf{r}) = \int d\mathbf{r}\phi_a(\mathbf{r})\hat{\mathbf{r}}\phi_i(\mathbf{r})\,, \tag{E.5}$$

to rewrite $\tilde{G}(\omega)$ as

$$\begin{aligned}&\tilde{G}_{kf}(\omega)\\ &= -\sum_{ia}\frac{-2\omega}{(\epsilon_i-\epsilon_a)^2-\omega^2}\int d\mathbf{r}\frac{1}{2}\left[\mathbf{r}\times\phi_i(\mathbf{r})\hat{\mathbf{j}}_p(\mathbf{r})\phi_a(\mathbf{r})\right]_k\int d\mathbf{r}'\phi_a(\mathbf{r}')\hat{r}_f\phi_i(\mathbf{r}')\,.\end{aligned} \tag{E.6}$$

We now need to introduce the dipole moment operator $\hat{\mathbf{p}}$, which is defined as

$$\hat{\mathbf{p}} = -i\nabla\,. \tag{E.7}$$

We will try to rewrite the integrals in Eq. (E.6) involving $\hat{\mathbf{j}}_p$ in terms of $\hat{\mathbf{p}}$. We have:

$$\begin{aligned}-\frac{1}{2}\int d\mathbf{r}\phi_i(\mathbf{r})\left[\mathbf{r}\times\hat{\mathbf{p}}\right]_\alpha\phi_a(\mathbf{r}) &= -\frac{1}{2}\sum_{\alpha\beta\gamma}\epsilon_{\alpha\beta\gamma}\int d\mathbf{r}\phi_i(\mathbf{r})r_\beta\hat{p}_\gamma\phi_a(\mathbf{r})\\ &= \frac{i}{2}\sum_{\alpha\beta\gamma}\epsilon_{\alpha\beta\gamma}\int d\mathbf{r}r_\beta\left(\phi_i(\mathbf{r})\nabla_\gamma\phi_a(\mathbf{r})\right)\,.\end{aligned} \tag{E.8}$$

Integrating Eq. (E.8) by parts, we get

$$\begin{aligned}&-\frac{1}{2}\int d\mathbf{r}\phi_i(\mathbf{r})\left[\mathbf{r}\times\hat{\mathbf{p}}\right]_\alpha\phi_a(\mathbf{r})\\ &= \frac{i}{2}\sum_{\alpha\beta\gamma}\epsilon_{\alpha\beta\gamma}\int d\mathbf{r}\left[\cancel{\nabla_\gamma(r_\beta\phi_i(\mathbf{r})\phi_a(\mathbf{r}))} - r_\beta(\nabla_\gamma\phi_i(\mathbf{r}))\phi_a(\mathbf{r}) - \cancel{(\nabla_\gamma r_\beta)\phi_i(\mathbf{r})\phi_a(\mathbf{r})}\right]\\ &= -\frac{i}{2}\sum_{\alpha\beta\gamma}\epsilon_{\alpha\beta\gamma}\int d\mathbf{r}r_\beta\left(\phi_i(\mathbf{r})\nabla_\gamma^\dagger\phi_a(\mathbf{r})\right)\,,\end{aligned} \tag{E.9}$$

where on the second line, we notably used the fact that the integral of a total

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[1] This relation can be proved by evaluating the commutator between the velocity operator and the Hamiltonian.

differential vanishes. Summing Eqs. (E.8) and (E.9), we obtain:

$$\begin{aligned} -\int d\mathbf{r}\phi_i(\mathbf{r})\left[\mathbf{r}\times\hat{\mathbf{p}}\right]_\alpha \phi_a(\mathbf{r}) &= \sum_{\alpha\beta\gamma}\epsilon_{\alpha\beta\gamma}\int d\mathbf{r} r_\beta \phi_i(\mathbf{r})\frac{i}{2}\left(\nabla_\gamma - \nabla_\gamma^\dagger\right)\phi_a(\mathbf{r}) \\ &= -\int d\mathbf{r}\left[\mathbf{r}\times\phi_i(\mathbf{r})\hat{\mathbf{j}}_p(\mathbf{r})\phi_a(\mathbf{r})\right]_\alpha . \end{aligned} \tag{E.10}$$

Hence $\tilde{G}(\omega)$ can be rewritten in terms of $\hat{\mathbf{p}}$ as

$$\tilde{G}_{kf}(\omega) = \sum_{ia}\frac{-2\omega}{(\epsilon_i-\epsilon_a)^2-\omega^2}\int d\mathbf{r}\phi_i(\mathbf{r})\frac{1}{2}\left[\hat{\mathbf{r}}\times\hat{\mathbf{p}}\right]_k\phi_a(\mathbf{r})\int d\mathbf{r}'\phi_a(\mathbf{r}')\hat{r}_f\phi_i(\mathbf{r}') . \tag{E.11}$$

Expressing the trace of $\tilde{G}(\omega)$ explicitly in terms of matrix elements, we get

$$\mathrm{Tr}[\tilde{G}(\omega)] = \sum_{ia}\frac{-2\omega}{(\epsilon_i-\epsilon_a)^2-\omega^2}\sum_k \langle\phi_i|\hat{m}_k|\phi_a\rangle\langle\phi_a|\hat{\mu}_k|\phi_i\rangle , \tag{E.12}$$

where $\hat{\mathbf{m}} = \frac{1}{2}\hat{\mathbf{r}}\times\hat{\mathbf{p}}$ is the magnetic dipole moment operator, and $\hat{\boldsymbol{\mu}} = \hat{\mathbf{r}}$ is the electric dipole moment operator.

From Eq. (E.12), one can more easily see why in general, more diffuse functions are needed in order to get a good description of circular dichroism (or of the ORT), as was already reported in the literature (e.g., in Refs. [71, 74]). Indeed, from this equation, we see that in order to get nonzero contributions, we need to have both a nonvanishing electric dipole moment transition and a magnetic dipole moment transition. It is often the case, though, that at least one of these transitions vanishes, so in order to obtain an accurate ORT, one would need to include empty states of higher energy.

F

The Lorentz force density

In this appendix, we show how to rewrite the Lorentz force density in terms of the momentum stress tensor with the help of Maxwell's equations.

First we insert Maxwell equations (8.14) and (8.17) into Eq. (8.19). We obtain

$$\begin{aligned}
\mathbf{F}^{lor}(\mathbf{r},t) =& \rho(\mathbf{r},t)\mathbf{E}(\mathbf{r},t) + \mathbf{j}(\mathbf{r},t) \times \mathbf{B}(\mathbf{r},t) \\
=& \frac{1}{4\pi}[\nabla \cdot \mathbf{E}(\mathbf{r},t)]\mathbf{E}(\mathbf{r},t) + \frac{c^2}{4\pi}[\nabla \times \mathbf{B}(\mathbf{r},t)] \times \mathbf{B}(\mathbf{r},t) \\
& - \frac{1}{4\pi}\left[\frac{\partial}{\partial t}\mathbf{E}(\mathbf{r},t)\right] \times \mathbf{B}(\mathbf{r},t) \\
=& \frac{1}{4\pi}[\nabla \cdot \mathbf{E}(\mathbf{r},t)]\mathbf{E}(\mathbf{r},t) + \frac{c^2}{4\pi}[\nabla \times \mathbf{B}(\mathbf{r},t)] \times \mathbf{B}(\mathbf{r},t) \\
& + \frac{1}{4\pi}\mathbf{E}(\mathbf{r},t) \times \frac{\partial}{\partial t}\mathbf{B}(\mathbf{r},t) - \frac{1}{4\pi}\frac{\partial}{\partial t}[\mathbf{E}(\mathbf{r},t) \times \mathbf{B}(\mathbf{r},t)]\,.
\end{aligned} \tag{F.1}$$

We can now use Eq. (8.16), $\frac{\partial}{\partial t}\mathbf{B}(\mathbf{r},t) = -\nabla \times \mathbf{E}(\mathbf{r},t)$, in order to rewrite Eq. (F.1) as

$$\begin{aligned}
\mathbf{F}^{lor}(\mathbf{r},t) =& \frac{1}{4\pi}[\nabla \cdot \mathbf{E}(\mathbf{r},t)]\mathbf{E}(\mathbf{r},t) + \frac{c^2}{4\pi}[\nabla \times \mathbf{B}(\mathbf{r},t)] \times \mathbf{B}(\mathbf{r},t) \\
& - \frac{1}{4\pi}\mathbf{E}(\mathbf{r},t) \times \nabla \times \mathbf{E}(\mathbf{r},t) - \frac{1}{4\pi}\frac{\partial}{\partial t}[\mathbf{E}(\mathbf{r},t) \times \mathbf{B}(\mathbf{r},t)] \\
=& \frac{1}{4\pi}[\nabla \cdot \mathbf{E}(\mathbf{r},t)]\mathbf{E}(\mathbf{r},t) + \frac{c^2}{4\pi}[\nabla \cdot \mathbf{B}(\mathbf{r},t)]\mathbf{B}(\mathbf{r},t) \\
& - \frac{c^2}{4\pi}\mathbf{B}(\mathbf{r},t) \times \nabla \times \mathbf{B}(\mathbf{r},t) - \frac{1}{4\pi}\mathbf{E}(\mathbf{r},t) \times \nabla \times \mathbf{E}(\mathbf{r},t) \\
& - \frac{\partial}{\partial t}\mathbf{S}(\mathbf{r},t)\,,
\end{aligned} \tag{F.2}$$

where the Poynting vector $\mathbf{S}(\mathbf{r},t)$ is defined by

$$\mathbf{S}(\mathbf{r},t) = \frac{1}{4\pi}\mathbf{E}(\mathbf{r},t) \times \mathbf{B}(\mathbf{r},t)\,. \tag{F.3}$$

In the last step we added $\frac{c^2}{4\pi}[\nabla \cdot \mathbf{B}(\mathbf{r},t)]\mathbf{B}(\mathbf{r},t)$ to the right-hand side, as it is equal to zero (due to Eq. (8.15)). We can now use the following identity,

$$\mathbf{A} \times \nabla \times \mathbf{A} = \frac{1}{2}A^2 - [\mathbf{A} \cdot \nabla]\mathbf{A}\,, \tag{F.4}$$

to rewrite this expression as

$$\begin{aligned}\mathbf{F}^{lor}(\mathbf{r},t) =& \frac{1}{4\pi}[\nabla \cdot \mathbf{E}(\mathbf{r},t)]\mathbf{E}(\mathbf{r},t) + \frac{1}{4\pi}[\mathbf{E}(\mathbf{r},t) \cdot \nabla]\mathbf{E}(\mathbf{r},t) \\ &+ \frac{c^2}{4\pi}[\mathbf{B}(\mathbf{r},t) \cdot \nabla]\mathbf{B}(\mathbf{r},t) + \frac{c^2}{4\pi}[\nabla \cdot \mathbf{B}(\mathbf{r},t)]\mathbf{B}(\mathbf{r},t) \\ &- \frac{1}{4\pi}\frac{1}{2}\left[E^2(\mathbf{r},t) + c^2B^2(\mathbf{r},t)\right] - \frac{\partial}{\partial t}\mathbf{S}(\mathbf{r},t)\,. \end{aligned} \tag{F.5}$$

The terms on the right-hand side, except the last one, can be written as the divergence of the momentum stress tensor $\sigma(\mathbf{r},t)$ according to

$$F_i^{lor}(\mathbf{r},t) = \sum_j \partial_j \sigma_{ij}(\mathbf{r},t) - \frac{\partial}{\partial t}S_i(\mathbf{r},t)\,, \tag{F.6}$$

where

$$\sigma_{ij}(\mathbf{r},t) = \frac{1}{4\pi}\left(E_i(\mathbf{r},t)E_j(\mathbf{r},t) + c^2B_i(\mathbf{r},t)B_j(\mathbf{r},t) - \delta_{ij}\frac{1}{2}[E^2(\mathbf{r},t) + c^2B^2(\mathbf{r},t)]\right)\,. \tag{F.7}$$

G ZERO-FORCE AND ZERO-TORQUE THEOREMS

G.1 Zero-force theorem

To obtain the zero-force theorem, we start by rewriting Eq. (8.20) in second quantization. We have

$$\begin{aligned}\int d\mathbf{r}\mathbf{F}^{int}(\mathbf{r},t) &= -\int d\mathbf{r}\int d\mathbf{r}'\left[\nabla_{\mathbf{r}}\frac{1}{|\mathbf{r}-\mathbf{r}'|}\right]\langle\Psi(t)|\hat{\psi}^{\dagger}(\mathbf{r})\hat{\psi}^{\dagger}(\mathbf{r}')\hat{\psi}(\mathbf{r}')\hat{\psi}(\mathbf{r})|\Psi(t)\rangle \\ &= \int d\mathbf{r}\int d\mathbf{r}'\frac{\mathbf{r}-\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|^3}\langle\Psi(t)|\hat{\psi}^{\dagger}(\mathbf{r})\hat{\psi}^{\dagger}(\mathbf{r}')\hat{\psi}(\mathbf{r}')\hat{\psi}(\mathbf{r})|\Psi(t)\rangle\,, \qquad \text{(G.1)}\end{aligned}$$

where $\hat{\psi}^{\dagger}$ and $\hat{\psi}$ are field operators. Interchanging $\mathbf{r}$ and $\mathbf{r}'$ on the right-hand side of Eq. (G.1) leads to

$$\begin{aligned}\int d\mathbf{r}\mathbf{F}^{int}(\mathbf{r},t) &= \int d\mathbf{r}'\int d\mathbf{r}\frac{\mathbf{r}'-\mathbf{r}}{|\mathbf{r}'-\mathbf{r}|^3}\langle\Psi(t)|\hat{\psi}^{\dagger}(\mathbf{r}')\hat{\psi}^{\dagger}(\mathbf{r})\hat{\psi}(\mathbf{r})\hat{\psi}(\mathbf{r}')|\Psi(t)\rangle \\ &= -\int d\mathbf{r}\int d\mathbf{r}'\frac{\mathbf{r}-\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|^3}\langle\Psi(t)|\hat{\psi}^{\dagger}(\mathbf{r})\hat{\psi}^{\dagger}(\mathbf{r}')\hat{\psi}(\mathbf{r}')\hat{\psi}(\mathbf{r})|\Psi(t)\rangle\,, \qquad \text{(G.2)}\end{aligned}$$

where we used that

$$\left\{\hat{\psi}^{\dagger}(\mathbf{r}),\hat{\psi}^{\dagger}(\mathbf{r}')\right\} = 0\,, \qquad \text{(G.3)}$$

$$\left\{\hat{\psi}(\mathbf{r}),\hat{\psi}(\mathbf{r}')\right\} = 0\,. \qquad \text{(G.4)}$$

Comparison of Eqs. (G.1) and (G.2) leads to the conclusion

$$\int d\mathbf{r}\mathbf{F}^{int}(\mathbf{r},t) = 0\,. \qquad \text{(G.5)}$$

G.2 Zero-torque theorem

In a similar way we can prove the zero-torque theorem. We start from

$$\begin{aligned}
&\int d\mathbf{r}\mathbf{r}\times\mathbf{F}^{int}(\mathbf{r},t)\\
&=-\int d\mathbf{r}\int d\mathbf{r}'\mathbf{r}\times\left[\nabla_{\mathbf{r}}\frac{1}{|\mathbf{r}-\mathbf{r}'|}\right]\langle\Psi(t)|\hat{\psi}^{\dagger}(\mathbf{r})\hat{\psi}^{\dagger}(\mathbf{r}')\hat{\psi}(\mathbf{r}')\hat{\psi}(\mathbf{r})|\Psi(t)\rangle\\
&=\int d\mathbf{r}\int d\mathbf{r}'\frac{\mathbf{r}\times\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|^{3}}\langle\Psi(t)|\hat{\psi}^{\dagger}(\mathbf{r})\hat{\psi}^{\dagger}(\mathbf{r}')\hat{\psi}(\mathbf{r}')\hat{\psi}(\mathbf{r})|\Psi(t)\rangle\,, \qquad \text{(G.6)}
\end{aligned}$$

where we used $\mathbf{r}\times\mathbf{r}=0$. Interchanging $\mathbf{r}$ and $\mathbf{r}'$ on the right-hand side of Eq. (G.6) yields

$$\begin{aligned}
\int d\mathbf{r}\mathbf{r}\times\mathbf{F}^{int}(\mathbf{r},t)&=\int d\mathbf{r}'\int d\mathbf{r}\frac{\mathbf{r}'\times\mathbf{r}}{|\mathbf{r}'-\mathbf{r}|^{3}}\langle\Psi(t)|\hat{\psi}^{\dagger}(\mathbf{r}')\hat{\psi}^{\dagger}(\mathbf{r})\hat{\psi}(\mathbf{r})\hat{\psi}(\mathbf{r}')|\Psi(t)\rangle\\
&=-\int d\mathbf{r}\int d\mathbf{r}'\frac{\mathbf{r}\times\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|^{3}}\langle\Psi(t)|\hat{\psi}^{\dagger}(\mathbf{r})\hat{\psi}^{\dagger}(\mathbf{r}')\hat{\psi}(\mathbf{r}')\hat{\psi}(\mathbf{r})|\Psi(t)\rangle\,. \qquad \text{(G.7)}
\end{aligned}$$

Comparison of Eqs.(G.6) and (G.7) leads to the following conclusion:

$$\int d\mathbf{r}\mathbf{r}\times\mathbf{F}^{int}(\mathbf{r},t)=0\,. \qquad \text{(G.8)}$$

Résumé français

INTRODUCTION

La description et la compréhension de l'interaction entre molécules et champs électromagnétiques se fait toujours à travers l'étude de quantités spécifiques et intrinsèques au système étudié, que l'on désigne communément sous le nom de propriétés électromagnétiques moléculaires. L'issue des expériences est systématiquement interprétée en termes de telles propriétés. De nos jours, les programmes informatiques sont régulièrement utilisés afin de calculer les valeurs de ces propriétés électromagnétiques. Ces programmes permettent de traiter aussi bien des atomes que des molécules, voire même des agrégats de molécules, le tout avec une précision parfois comparable à la précision expérimentale. Il est donc clair que théorie et expérience sont complémentaires. Avec une étude théorique, il est possible de séparer et d'identifier les différents termes contribuant à une propriété moléculaire donnée, ce qui est indispensable si l'on veut lever le voile sur certains phénomènes complexes. La théorie est donc un puissant outil d'analyse, mais pas seulement. Elle peut également être prédictive, et les expériences deviennent alors vitales si l'on veut valider le formalisme théorique. Calculer des propriétés électromagnétiques peut servir à identifier des composés inconnus, de même que des configurations moléculaires. De nouveaux matériaux peuvent être étudiés à un coût réduit grâce à des simulations numériques, au lieu de les synthétiser. Au vu de ce qui précède, l'on peut donc comprendre qu'il est tout aussi important d'obtenir des propriétés électromagnétiques moléculaires par des calculs, que par l'expérience. En réalité, aucune expérience ne serait viable sans une fondation théorique solide, et vice-versa. Cette relation intime entre théorie et expérience peut mener à la conception de nouveaux matériaux, par exemple, mais parfois, il s'agit simplement de mieux comprendre le monde qui nous entoure.

Au sein de la longue liste des propriétés électromagnétiques moléculaires se trouvent notamment le moment dipolaire électrique, la polarisabilité dépendante du temps, ou bien encore le déplacement chimique en résonance magnétique nucléaire (RMN), pour ne citer que les plus connues. Tandis que les propriétés électriques peuvent aujourd'hui être calculées efficacement par diverses méthodes, les propriétés magnétiques, quant à elle, continuent de poser plusieurs problèmes fondamentaux. Une des difficultés majeures est liée à l'invariance de jauge: dans beaucoup de calculs de propriétés magnétiques utilisant des bases finies, il apparaît une dépendance non physique en l'origine de la jauge du vecteur potentiel, entraînant des résultats peu fiables. Ce problème est relié à la vitesse de convergence réduite de la densité de courant avec la taille de la base utilisée dans des calculs pratiques. Dans cette thèse, nous étudierons donc plus précisément la manière de calculer de telles propriétés magnétiques. Afin d'illustrer la méthode que nous avons développée, nous nous concentrerons sur deux propriétés magnétiques en particulier: la magnétisabilité, qui peut être considérée comme le paradigme des propriétés magnétiques, et le dichroïsme circulaire, qui est une quantité dynamique possédant de nombreuses applications dans différents domaines, comme nous l'expliquerons plus tard.

Les changements de structure électronique peuvent souvent être connus en considérant les champs électromagnétiques comme des perturbations qui modifient légèrement cette structure. Il est bon de noter que les propriétés moléculaires sont des propriétés intrinsèques d'un état particulier d'une molécule donnée, dans le sens où elles sont indépendantes de l'intensité des champs externes [1]. Les propriétés moléculaires peuvent donc être vues comme la réponse de la molécule aux champs électromagnétiques, qu'il s'agisse de champs externes, ou internes, comme par exemple les moments magnétiques des noyaux.

Dans ce travail, nous utiliserons la théorie de la fonctionnelle de la densité de courant dépendante du temps (TFDCDT), qui est une méthode *ab initio*, c'est-à-dire une méthode qui n'utilise que les principes premiers de la mécanique quantique, et qui n'inclut pas de paramètres empiriques ayant été déterminés par l'expérience ou autrement (exception faite des données habituelles, comme la masse de l'électron, la charge, etc.). En cela, les méthodes *ab initio* diffèrent des méthodes dites semi-empiriques. Dans le cadre de cette thèse, nous traiterons les champs électromagnétiques de manière classique, tandis que seuls les électrons seront décrits quantiquement.

Dans la première partie de cette thèse, nous expliquons le formalisme théorique avec lequel nous travaillons. En particulier, dans le premier chapitre, nous présentons la DFT de l'état fondamental, et donnons les deux théorèmes qui sous-tendent cette théorie, connus sous le nom de théorèmes de Hohenberg-Kohn (HK) [2], ainsi que les équations de Kohn-Sham [3], qui sont celles utilisées dans la plupart des calculs appliqués en DFT. La conséquence la plus frappante des théorèmes de HK est que pour un système d'électrons stationnaire, il suffit de connaître la densité électronique de l'état fondamental pour pouvoir déterminer toutes les propriétés du système. Dans le second chapitre, nous décrivons tout d'abord la DFT dépendante du temps (TDDFT), qui est une extension de la DFT dans le cas où le potentiel scalaire comprend une dépendance temporelle. Cette extension est rendue possible grâce au théorème de Runge-Gross, qui est l'analogue du premier théorème de HK. Par la suite, nous détaillons le concept de la TDCDFT, qui, contrairement à la

TDDFT, permet de décrire des systèmes dont l'évolution est régie par des champs magnétiques, comme ce fut initialement prouvé par Ghosh et Dhara [4, 5]. Dans le troisième chapitre, nous dérivons les équations de la réponse linéaire, que nous utiliserons plus tard pour obtenir diverses propriétés électromagnétiques, et nous montrons la forme que prennent ces équations dans le cas particulier de la TDCDFT.

Dans la deuxième partie de cette thèse, nous nous concentrons sur le calcul de plusieurs propriétés magnétiques moléculaires dans des systèmes finis. En particulier, dans le chapitre 4, nous expliquons en détails comment nous avons traité les problèmes majeurs auxquels on est généralement confronté lorsque l'on veut calculer des propriétés magnétiques, à savoir le problème de l'invariance de jauge, mais également la lenteur de la convergence de la densité de courant par rapport à la taille de la base utilisée, qui est reliée au premier problème. Nous montrons qu'en utilisant une règle de somme [6], on peut parvenir à obtenir un procédé efficace et général, pouvant être appliqué à n'importe quelle méthode donnant accès à la densité de courant. Nous illustrons notre méthode en l'appliquant au calcul de la magnétisabilité, qui peut être considérée comme le paradigme des propriétés magnétiques. Dans le cinquième chapitre, nous montrons comment étendre notre méthode afin de calculer des spectres de dichroïsme circulaire (CD) et des rotations spécifiques. Contrairement à la magnétisabilité, dont le principal intérêt réside le plus souvent dans sa valeur statique, le CD est une véritable quantité dynamique. Ses champs d'applications sont nombreux, en particulier dans le domaine médical et en biologie, où les structures secondaires adoptées par certains segments de molécules exhibent des signatures spécifiques dans les spectres CD. Avoir des outils *ab initio* fiables pouvant prédire de telles structures serait donc d'un grand intérêt. Le chapitre 6 aborde plus brièvement deux autres propriétés magnétiques connues, à savoir le tenseur g rotationnel, et la constante d'écran en RMN. Le chapitre 7 est dédié à l'implémentation, et a pour but d'aider le lecteur à comprendre les équations que nous avons implémentées dans le programme Amsterdam Density Functional (ADF), en même temps que de mentionner certaines spécificités liées à ADF.

Le huitième et dernier chapitre est davantage exploratoire, et concerne la description de l'aimantation dans les systèmes étendus. Nous donnons un aperçu des problèmes apparaissant naturellement lorsque l'on s'attèle à décrire de tels systèmes, notamment le fait que les définitions des moments dipolaires que nous avons utilisées lors des précédents chapitres deviennent caduques pour un système périodique, et nous proposons diverses stratégies pouvant mener à une description correcte de l'aimantation dans de tels systèmes.

1

THÉORIE DE LA FONCTIONNELLE DE LA DENSITÉ

Afin de décrire le comportement de particules dans un système à N corps en interaction, il faudrait en principe résoudre l'équation de Schrödinger pour obtenir la fonction d'onde à N corps. Cependant, en pratique, cette procédure est inapplicable à cause du couplage entre le mouvement des particules, et aucune expression analytique pour la fonction d'onde ne peut être trouvée. Par conséquent, il convient d'opérer quelques approximations afin de résoudre ce problème. Plusieurs types de méthodes ont été développées afin de traiter ces systèmes à N corps. Certaines d'entre elles permettent d'extraire l'information d'un système donné en s'intéressant à des quantités plus simples (comme la densité). Dans ce chapitre, nous parlerons de l'une de ces méthodes en particulier: la théorie de la fonctionnelle de la densité (DFT).

Nous considérons ici un système stationnaire constitué de N électrons en interaction mutuelle. L'équation de Schrödinger dans l'approximation de Born-Oppenheimer prend alors la forme suivante:

$$\hat{H}\Psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N) = E\Psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)\,, \tag{1.1}$$

où E est l'énergie propre du système, et $\Psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)$ est la fonction d'onde multi-électronique, où les $\mathbf{r}_i$ sont les coordonnées spatiales de l'électron i. L'hamiltonien $\hat{H}$ est donné par

$$\hat{H} = \underbrace{-\frac{1}{2}\sum_i \nabla_i^2}_{\hat{T}} + \underbrace{\sum_i v(\mathbf{r}_i)}_{\hat{V}} + \underbrace{\frac{1}{2}\sum_{i\neq j}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}}_{\hat{W}}\ . \tag{1.2}$$

Ici, $\hat{T}$, $\hat{V}$ et $\hat{W}$ sont respectivement l'opérateur énergie cinétique, l'opérateur énergie potentielle des électrons dans un potentiel $v(\mathbf{r})$, et l'opérateur énergie d'interaction Coulombienne. Puisque le potentiel externe $v(\mathbf{r})$ détermine entièrement les fonctions d'ondes Ψ ainsi que les énergies propres E, ces quantités peuvent être considérées comme des fonctionnelles de $v(\mathbf{r})$. En réalité, la densité $\rho(\mathbf{r})$ et le potentiel externe $v(\mathbf{r})$ sont des variables conjuguées au sens de Legendre. C'est cette relation particulière qui va permettre d'obtenir des fonctionnelles de la densité, au lieu de fonctionnelles du potentiel scalaire.

L'idée principale de la DFT est de passer de la fonction d'onde à N corps comme variable de base, à la densité de l'état fondamental. L'immense avantage de cette manipulation est qu'au lieu d'étudier la fonction d'onde qui comprend $3N$ variables spatiales, on va considérer la densité de particules, qui, elle, ne contient que 3 variables d'espace. Intuitivement, on pourrait penser que la densité seule ne serait pas suffisante pour décrire un système à N corps. Néanmoins, il a été prouvé par Hohenberg et Kohn [2] que la densité de l'état fondamental est effectivement suffisante pour obtenir toutes les propriétés du système, et elle peut donc être considérée comme une variable fondamentale du problème (voir Fig. 1.1). De plus, on peut définir une fonctionnelle universelle pour l'énergie $E[\rho]$. Pour n'importe quel potentiel $v(\mathbf{r})$, l'énergie (exacte) de l'état fondamental correspond au minimum global de cette fonctionnelle, et la densité $\rho(\mathbf{r})$ qui minimise cette fonctionnelle est la densité de l'état fondamental.

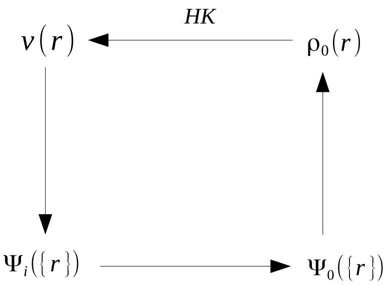

Figure 1.1 – Illustration du théorème de Hohenberg-Kohn.

Bien que la minimisation de la fonctionnelle de Hohenberg-Kohn soit en principe exacte, il faut en pratique approximer cette fonctionnelle, puisque son expression explicite est inconnue. Une procédure pratique pour évaluer cette fonctionnelle de l'énergie fut proposée par Kohn et Sham [3]. Leur approche consiste à introduire un système auxiliaire noninteragissant avec un potentiel effectif $v_s(\mathbf{r})$ qui reproduit la même densité de l'état fondamental que le système interagissant d'origine. Si un tel potentiel existe, alors le théorème de HK garantit son unicité. Le grand avantage procuré par cette approche est que cela mène à un système d'équations découplées pour chaque particule, qui sont solubles en pratique.

Puisque le système auxiliaire ne comprend pas d'interactions interparticules, la fonction d'onde $\Psi_s[v_s]$ de ce système auxiliaire peut être exprimée comme un unique déterminant de Slater composé d'orbitales mono-électroniques ψ_i:

$$\Psi_s(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{pmatrix} \psi_1(\mathbf{r}_1) & \ldots & \psi_N(\mathbf{r}_1) \\ \vdots & \ddots & \vdots \\ \psi_1(\mathbf{r}_N) & \ldots & \psi_N(\mathbf{r}_N) \end{pmatrix} . \tag{1.3}$$

Les ψ_i sont les solutions des équations de Kohn-Sham,

$$\left(-\frac{\nabla^2}{2} + v_s(\mathbf{r}) \right) \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}) \, , \tag{1.4}$$

où les ϵ_i sont les énergies propres des orbitales, et le potentiel de Kohn-Sham $v_s(\mathbf{r})$ est donné par

$$v_s(\mathbf{r}) = v(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r}) \, , \tag{1.5}$$

où v_{xc} est le potentiel d'échange et corrélation, et v_H est le potentiel de Hartree défini par

$$v_H(\mathbf{r}) = \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, . \tag{1.6}$$

La densité de l'état fondamental s'obtient en occupant les N orbitales mono-électroniques les plus basses en énergie:

$$\rho(\mathbf{r}) = \sum_i^N |\psi_i(\mathbf{r})|^2 \, . \tag{1.7}$$

Puisque v_s dépend de ρ, qui dépend lui-même des ψ_i, les équations de Kohn-Sham doivent être résolues de manière auto-cohérente.

Une des approximations les plus simples et les plus couramment utilisées pour l'énergie d'échange et corrélation est l'approximation de la densité locale (LDA), pour laquelle l'énergie d'échange et corrélation est donnée par

$$E_{xc}^{LDA}[\rho] = \int d\mathbf{r} \rho(\mathbf{r}) \epsilon_{xc}^{hom}(\rho(\mathbf{r})) \, , \tag{1.8}$$

où $\epsilon_{xc}^{hom}(\rho)$ est l'énergie d'échange et corrélation par unité de volume d'un gaz homogène d'électrons de densité ρ. Le potentiel d'échange et corrélation s'écrit alors

$$v_{xc}^{LDA}(\mathbf{r})[\rho] = \left. \frac{d\epsilon_{xc}^{hom}(\rho)}{d\rho} \right|_{\rho(\mathbf{r})} . \tag{1.9}$$

De cette manière, le système est traité localement comme un gaz homogène d'électrons.

On pourrait s'attendre à ce que cette approximation ne fonctionne que pour des systèmes dont la densité varie peu, mais il se trouve qu'elle est efficace également pour des systèmes inhomogènes [3].

2

THÉORIE DE LA FONCTIONNELLE DE LA DENSITÉ DE COURANT DÉPENDANTE DU TEMPS

Le concept de DFT peut être étendu au cas où le potentiel scalaire dépend du temps, via le théorème de Runge-Gross, qui est l'analogue du théorème de Hohenberg-Kohn pour la DFT. Puisque les équations obtenues en TDDFT sont semblables à celles de la DFT, nous ne les redonnerons pas ici, et nous allons donner un peu plus de détails sur la théorie de la fonctionnelle de la densité de courant dépendante du temps (TDCDFT).

Alors qu'en (TD)DFT, seuls des potentiels scalaires, et donc des champs externes longitudinaux, peuvent être traités, la TDCDFT permet de décrire des champs électromagnétiques généraux, décrits par des potentiels à la fois scalaire et vectoriel. On considère donc un Hamiltonien de la forme

$$\hat{H}(t) = \sum_i \left\{ \frac{1}{2}[-i\nabla_i + \mathbf{A}(\mathbf{r}_i, t)]^2 + v(\mathbf{r}_i, t) \right\} + \sum_{i<j} U(\mathbf{r}_i - \mathbf{r}_j)\,, \tag{2.1}$$

où $U(\mathbf{r}_i - \mathbf{r}_j)$ est l'interaction à deux corps, $v(\mathbf{r}, t)$ et $\mathbf{A}(\mathbf{r}, t)$ sont respectivement les potentiels scalaire et vecteur. Ce sont Ghosh et Dhara [4, 5] qui, les premiers, ont réécrit la TDDFT en introduisant la densité de courant comme variable de base. Ils ont pu montrer que les potentiels scalaire et vecteur (et par conséquent la fonction d'onde multiélectronique également) étaient déterminés de manière unique, à une transformation de jauge[1] près, par la densité de courant.

Tout comme en (TD)DFT, on peut introduire un système auxiliaire noninteragissant, le système de Kohn-Sham, qui reproduit cette fois-ci non seulement la densité ρ, mais également la densité de courant $\mathbf{j}$ du système originel. En supposant que l'état initial puisse être représenté comme un unique déterminant de Slater, les

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[1] Une transformation de jauge est une modification des potentiels qui laisse invariants les champs électromagnétiques.

équations de Kohn-Sham prennent la forme suivante:

$$i\frac{\partial}{\partial t}\phi_i(\mathbf{r},t) = \left(\frac{1}{2}[-i\nabla + \mathbf{A}_s(\mathbf{r},t)]^2 + v_s(\mathbf{r},t)\right)\phi_i(\mathbf{r},t)\,, \tag{2.2}$$

$$\mathbf{j}(\mathbf{r},t) = \frac{-i}{2}\sum_{i=1}^{N}[\phi_i^*(\mathbf{r},t)\nabla\phi_i(\mathbf{r},t) - \nabla\phi_i^*(\mathbf{r},t)\phi_i(\mathbf{r},t)] + \rho(\mathbf{r},t)\mathbf{A}_s(\mathbf{r},t)\,, \tag{2.3}$$

$$\rho(\mathbf{r},t) = \sum_{i=1}^{N}|\phi_i(\mathbf{r},t)|^2\,. \tag{2.4}$$

Les potentiels de Kohn-Sham, quant à eux, sont définis par

$$v_s(\mathbf{r},t) = v(\mathbf{r},t) + \int d\mathbf{r}'\frac{\rho(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|} + v_{xc}(\mathbf{r},t)\,, \tag{2.5}$$

$$\mathbf{A}_s(\mathbf{r},t) = \mathbf{A}(\mathbf{r},t) + \mathbf{A}_{xc}(\mathbf{r},t)\,. \tag{2.6}$$

Là encore, les équations de Kohn-Sham doivent être résolues de manière auto-cohérentes, car les potentiels dépendent des densités et des densités de courant, et vice-versa.

Une des approximations les plus courantes des potentiels d'échange et corrélation dépendant du temps est l'approximation de la densité locale adiabatique (ALDA), qui est une extension directe de LDA. Cette approximation prend la forme suivante:

$$v_{xc}^{ALDA}(\mathbf{r},t) = v_{xc}^{hom}(\rho(\mathbf{r},t)) = \frac{d}{d\rho}\left[\rho\epsilon_{xc}^{h}[\rho]\right]\Big|_{\rho=\rho(\mathbf{r},t)}\,, \tag{2.7}$$

$$\mathbf{A}_{xc}^{ALDA}(\mathbf{r},t) = \mathbf{0}\,. \tag{2.8}$$

On peut remarquer que v_{xc}^{ALDA} est exprimé de manière similaire à l'équation 1.9, mais le potentiel est cette fois évalué pour la densité instantanée $\rho(\mathbf{r},t)$. L'approximation ALDA est donc locale à la fois en espace et en temps, et néglige donc les effets de mémoire provenant de la dépendance du potentiel d'échange et corrélation aux temps $t' < t$. Globalement, les avantages et les inconvénients de ALDA sont les mêmes que ceux de LDA.

3

THÉORIE DE LA RÉPONSE LINÉAIRE AU SEIN DE LA TDCDFT

La théorie de la réponse linéaire (LRT) repose sur la théorie des perturbations, et permet de décrire les changements d'un système soumis à une petite perturbation externe (telle qu'un faible champ électromagnétique). Dans le cadre de la LRT, seuls les changements linéaires en la perturbation sont considérés. Dans notre cas, nous nous intéressons en particulier aux changements de premier ordre de la densité, ainsi que de la densité de courant.

Considérons un système qui se trouve dans son état fondamental Ψ_0, régi par un Hamiltonien $\hat{H}_0$ pour un temps $t < t_0$. À À $t = t_0$, on applique une petite perturbation externe (dépendante du temps) $\delta\hat{h}(t)$ et on regarde le changement de la valeur moyenne d'une observable $\hat{O}$ du système, donné par

$$\delta \left\langle \hat{O} \right\rangle (t) = \langle \Psi(t) | \hat{O} | \Psi(t) \rangle - \langle \Psi_0 | \hat{O} | \Psi_0 \rangle \,, \tag{3.1}$$

où $\Psi(t)$ est la solution de l'équation de Schrödinger suivante,

$$i\frac{\partial}{\partial t}\Psi(t) = \left[\hat{H}_0 + \delta\hat{h}(t)\right]\Psi(t)\,. \tag{3.2}$$

Il est pratique de travailler avec le point de vue d'interaction, dans lequel les opérateurs et les fonctions d'ondes sont liés aux opérateurs et aux fonctions d'onde de Schrödinger par les transformations unitaires suivantes:

$$\Psi_I(t) = e^{i(t-t_0)\hat{H}_0}\Psi(t) \tag{3.3}$$

$$\hat{O}_I(t) = e^{i(t-t_0)\hat{H}_0}\hat{O}e^{-i(t-t_0)\hat{H}_0}\,. \tag{3.4}$$

L'évolution de la fonction d'onde d'interaction $\Psi_I(t)$ est déterminée par l'équation de mouvement

$$i\frac{\partial}{\partial t}\Psi_I(t) = \delta\hat{h}_I(t)\Psi_I(t)\,. \tag{3.5}$$

En réécrivant Eq. (3.5) sous forme intégrale, et en réinjectant $\Psi_I(t)$ dans cette nouvelle forme, il est possible de faire apparaître des puissances de $\delta\hat{h}_I$, dont nous négligerons tous les termes quadratiques et d'ordre supérieurs. On obtient alors

$$\Psi_I(t) = \Psi_0 - i\int_{t_0}^{t} dt'\delta\hat{h}_I(t')\Psi_0 + o(\delta\hat{h}_I^2)\,. \tag{3.6}$$

Considérons maintenant une perturbation générale de la forme

$$\delta\hat{h}_I(t) = \sum_i \hat{O}_{iI}(t)\varphi_i(t)\,, \tag{3.7}$$

où les $\psi_i(t)$ sont des fonctions arbitraires dépendantes du temps. Nous ne donnerons pas les détails de la dérivation ici, mais il est possible de montrer que le changement de la valeur moyenne de l'observable $\hat{O}$, dans l'espace des fréquences, est donné par

$$\delta\left\langle\hat{O}_i\right\rangle(\omega) = \sum_j \tilde{\chi}_{ij}(\omega)\tilde{\varphi}_j(\omega)\,, \tag{3.8}$$

le tilde indiquant que nous avons effectué une transformée de Fourier, et $\tilde{\chi}_{ij}(\omega)$ étant la représentation spectrale de la fonction de réponse donnée par

$$\tilde{\chi}_{ij}(\omega) = \lim_{\eta\to 0^+}\sum_n\left\{\frac{\langle\Psi_0|\,\hat{O}_i\,|\Psi_n\rangle\,\langle\Psi_n|\,\hat{O}_j\,|\Psi_0\rangle}{\omega-(E_n-E_0)+i\eta} - \frac{\langle\Psi_0|\,\hat{O}_j\,|\Psi_n\rangle\,\langle\Psi_n|\,\hat{O}_i\,|\Psi_0\rangle}{\omega+(E_n-E_0)+i\eta}\right\}\,, \tag{3.9}$$

où η garantit la causalité, et la limite doit être prise après avoir intégré $\tilde{\chi}(\omega)$ contre une fonction, comme un potentiel par exemple. Les quantités E_0 et E_n sont respectivement les énergies propres correspondant aux fonctions propres Ψ_0 et Ψ_n de $\hat{H}_0$. On peut remarquer que les pôles de la fonction de réponse correspondent aux énergies d'excitation du système.

Jusqu'ici, le formalisme que nous avons présenté était général et applicable à n'importe quelle observable. Puisque nous avons pour but de calculer la densité de courant induite (ou réponse du courant), et que cette dernière peut être calculée à l'aide de la TDCDFT en utilisant la système auxiliaire de Kohn-Sham, nous allons adapter les équations précédentes à ce cas particulier. Dans un tel système, les densité et densité de courant induites prennent la forme suivante:

$$\delta\rho(\mathbf{r},\omega) = \int d\mathbf{r}'\chi_{\rho\mathbf{j}_p}(\mathbf{r},\mathbf{r}',\omega)\cdot\delta\mathbf{A}_s(\mathbf{r}',\omega) + \int d\mathbf{r}'\chi_{\rho\rho}(\mathbf{r},\mathbf{r}',\omega)\delta v_s(\mathbf{r}',\omega) \tag{3.10}$$

$$\begin{aligned}\delta\mathbf{j}(\mathbf{r},\omega) &= \int d\mathbf{r}'\left(\chi_{\mathbf{j}_p\mathbf{j}_p}(\mathbf{r},\mathbf{r}',\omega)+\rho_0(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}')\mathbb{1}\right)\cdot\delta\mathbf{A}_s(\mathbf{r}',\omega)\\ &\quad+\int d\mathbf{r}'\chi_{\mathbf{j}_p\rho}(\mathbf{r},\mathbf{r}',\omega)\delta v_s(\mathbf{r}',\omega)\,,\end{aligned} \tag{3.11}$$

où $\mathbb{1}$ est la matrice identité de rang 3. Les fonctions de réponses de Kohn-Sham sont données par[1]

$$\chi_{AB}(\mathbf{r},\mathbf{r}',\omega) = \sum_{i,a}\left[\frac{\phi_i(\mathbf{r})\hat{A}\phi_a(\mathbf{r})\phi_a(\mathbf{r}')\hat{B}\phi_i(\mathbf{r}')}{(\epsilon_i-\epsilon_a)+\omega} + \frac{\phi_i(\mathbf{r})\hat{A}^*\phi_a(\mathbf{r})\phi_a(\mathbf{r}')\hat{B}^*\phi_i(\mathbf{r}')}{(\epsilon_i-\epsilon_a)-\omega}\right], \tag{3.12}$$

où $i(a)$ parcourt toutes les orbitales occupées (inoccupées), et les ϕ_i et ϕ_a sont les orbitales de Kohn-Sham. Il reste maintenant à effectuer un choix de jauge pour les potentiels induits δv_s et $\delta\mathbf{A}_s$. Comme pour l'état fondamental, ils peuvent être décomposés comme

$$\delta v_s(\mathbf{r},\omega) = \delta v_H(\mathbf{r},\omega) + \delta v_{xc}(\mathbf{r},\omega)\,, \tag{3.13}$$

$$\mathbf{A}_s(\mathbf{r},\omega) = \mathbf{A}_{ext}(\mathbf{r},\omega) + \mathbf{A}_{xc}(\mathbf{r},\omega)\,, \tag{3.14}$$

où δv_H représente le changement au premier ordre du potentiel de Hartree, $\mathbf{A}_{ext}$ le potentiel vecteur externe, et δv_{xc} et $\delta\mathbf{A}_{xc}$ sont les potentiels d'échange et corrélation induits[2]. Nous allons choisir la jauge de telle sorte que le champ externe soit entièrement déterminé par le vecteur potentiel, autrement dit $\delta v_{ext} = 0$. Les potentiels d'échange et corrélation peuvent être écrits comme

$$\delta v_{xc}(\mathbf{r},\omega) = \int d\mathbf{r}' f_{xc}(\mathbf{r},\mathbf{r}',\omega)\delta\rho(\mathbf{r}',\omega)\,, \tag{3.15}$$

$$\delta\mathbf{A}_{xc}(\mathbf{r},\omega) = \int d\mathbf{r}'\mathbf{f}_{xc}(\mathbf{r},\mathbf{r}',\omega)\cdot\delta\mathbf{j}(\mathbf{r}',\omega)\,, \tag{3.16}$$

ce qui définit f_{xc} et $\mathbf{f}_{xc}$, les noyaux d'échange et corrélation scalaire et tensoriel, respectivement. De manière similaire à l'état fondamental, puisque les potentiels d'échange et corrélation dépendent des densité et densité de courant induites, et que ces densités dépendent elle-mêmes de ces potentiels, les équations de la réponse linéaire doivent être résolues de manière autocohérente.

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[1] Nous travaillons ici à température nulle.

[2] On a enlevé la notation "δ" dans l'expression du potentiel vecteur induit puisqu'à $t = t_0$, on a $\mathbf{A}_{ext}(\mathbf{r},t_0) = 0$ et $\mathbf{A}_{xc}(\mathbf{r},t_0) = 0$.

4

CALCULS DE PROPRIÉTÉS MAGNÉTIQUES INVARIANTES DE JAUGE

Une partie de ce chapitre est résumée dans l'article suivant: *N. Raimbault, P. L. de Boeij, P. Romaniello, and J. A. Berger, Phys. Rev. Lett. 114, 066404 (2015), "Gauge-Invariant Calculation of Static and Dynamical Magnetic Properties from the Current Density".*

Les propriétés magnétiques sont particulièrement délicates à obtenir car elles requièrent une description correcte de la réponse transverse de la molécule au champ magnétique, ce qui ne peut pas, en général, être obtenu par la fonction densité de réponse, qui est liée à une réponse purement longitudinale. Dans ce chapitre, nous résolvons deux problèmes fondamentaux liés au calcul de propriétés de réponse magnétiques:

- Une dépendance artificielle en la jauge apparaît dans le calcul de propriétés magnétiques quand on utilise une base finie.
- Plusieurs propriétés magnétiques dynamiques dépendent du choix de l'origine du système de coordonnées, ce qui est non physique.

Le premier problème est lié à une très lente convergence des propriétés magnétiques par rapport à la taille de la base utilisée. Cette vitesse de convergence peut être améliorée en choisissant une jauge particulière. Cependant, dans le cas dynamique, tout choix de jauge fixe arbitrairement le champ électrique, empêchant donc toute comparaison avec l'expérience.

La dépendance en l'origine du système de coordonnées est liée au fait que les définitions utilisées dans les calculs pratiques sont obtenues en utilisant le développement multipolaire [32,33]. L'une des principales caractéristiques de ces définitions est qu'elles dépendent du choix particulier que l'on fait pour le point de référence autour duquel le développement multipolaire est effectué. Ce point de référence est facilement confondu avec l'origine du système de coordonnées, ce qui mène à des résultats qui dépendent du choix de cette origine. Ceci pose de grands problèmes lors de calculs de propriétés magnétiques dynamiques comme la magnétisabilité.

La solution que nous proposons aux deux problèmes cités précédemment est à la fois simple et élégante; elle peut être résumée en deux étapes: i) Exprimer les propriétés magnétiques en termes de la densité de courant, ce qui peut être aisément fait pour la plupart des propriétés; ii) Calculer la densité de courant en traitant les contributions paramagnétique et diamagnétique sur un pied d'égalité.

Pour illustrer notre méthode, nous nous focaliserons ici sur la magnétisabilité, dénotée $\xi(\omega)$. Cette dernière est définie comme la constante de proportionnalité entre le moment dipolaire magnétique induit $\delta\mathbf{m}(\omega)$, et un champ magnétique externe uniforme $\mathbf{B}(\omega)$, ce qui en fait l'analogue de la polarisabilité dans le cas électrique:

$$\delta m_i(\omega) = \sum_j \xi_{ij}(\omega) B_j(\omega). \tag{4.1}$$

Lorsqu'on applique un champ magnétique sur une molécule, cette dernière acquière un moment dipolaire magnétique induit défini par

$$\delta\mathbf{m}(\omega) = \frac{1}{2}\int d\mathbf{r}(\mathbf{r}-\mathbf{r}_C)\times\delta\mathbf{j}(\mathbf{r},\omega)\,, \tag{4.2}$$

où $\mathbf{r}_C$ est un point de référence fixé dans le référentiel de la molécule qui assure l'indépendance de $\delta\mathbf{m}(\omega)$ par rapport à l'origine du système de coordonnées $\mathbf{r}_O$, et $\delta\mathbf{j}(\mathbf{r},\omega)$ est la densité de courant induite. Il est utile de remarquer que dans le cas statique, il n'y a pas de dépendance en $\mathbf{r}_O$, puisque $\int d\mathbf{r}\delta\mathbf{j}(\mathbf{r},0)$ s'annule, ce qui n'est plus le cas à fréquence finie. En utilisant la relation de continuité, $\int d\mathbf{r}\delta\mathbf{j}(\mathbf{r},\omega) = -i\omega\int d\mathbf{r}\mathbf{r}\delta\rho(\mathbf{r},\omega)$, on peut voir que le point de référence détermine à quel point le moment dipolaire électrique induit contamine le moment magnétique. Ce point de référence devrait être choisi de telle sorte que $\delta\mathbf{m}(\omega)$ puisse être mesuré dans les expériences. De plus, pour $\omega \neq 0$, le moment dipolaire magnétique induit n'est pas simplement une réponse au champ magnétique $\mathbf{B}(\omega)$, mais également, d'après la loi de Faraday, à un champ électrique transverse,

$$\mathbf{E}(\mathbf{r},\omega) = \frac{i\omega}{2}\mathbf{B}(\omega)\times(\mathbf{r}-\mathbf{r}_G), \tag{4.3}$$

où $\mathbf{r}_G$ est un point de référence fixé dans le référentiel moléculaire qui garantit que $\mathbf{E}(\mathbf{r},\omega)$ est indépendant du choix de $\mathbf{r}_O$. Il est déterminé par l'expérience, et correspond à une position de la molécule pour laquelle ce champ électrique est nul. Nous représenterons les champs électromagnétiques par le potentiel vecteur transverse suivant,

$$\mathbf{A}(\mathbf{r},\omega) = \frac{1}{2}\mathbf{B}(\omega)\times(\mathbf{r}-\mathbf{r}_G), \tag{4.4}$$

tandis que le potentiel scalaire externe sera pris égal à zéro, ce qui peut être fait sans perte de généralité aucune. Si l'on considère un champ magnétique pour lequel seule la j-ième composante est non nulle, on arrive alors à l'expression suivante pour la magnétisabilité:

$$\xi_{ij}(\omega) = \frac{1}{2B_j(\omega)} \int d\mathbf{r} \left[(\mathbf{r} - \mathbf{r}_C) \times \delta\mathbf{j}(\mathbf{r},\omega)\right]_i \,. \tag{4.5}$$

La magnétisabilité telle qu'exprimée dans l'équation (4.5) est indépendante du choix réalisé pour $\mathbf{r}_O$. Il est bon de noter que pour $\omega = 0$, $\xi(0)$ est également indépendant de $\mathbf{r}_C$ et $\mathbf{r}_G$. Ceci signifie que toute dépendance en l'origine de la jauge $\mathbf{r}_G$ lors de l'utilisation de bases finies est purement artificielle puisque $\mathbf{E}(\mathbf{r},0) = \mathbf{0}$. En revanche, pour $\omega \neq 0$, en plus de cette dépendance artificielle, il y a également une dépendance physique, puisque des choix différents pour $\mathbf{r}_G$ correspondent à des champs électriques différents. Comme dit précédemment, le choix de $\mathbf{r}_G$ et $\mathbf{r}_C$ dépend du dispositif expérimental. À notre connaissance, il n'existe pas de données expérimentales pour la magnétisabilité dynamique. Dans le reste du chapitre, nous choissons alors $\mathbf{r}_G$ et $\mathbf{r}_C$ tous deux égaux au centre des charges électroniques.

On peut voir d'après l'équation (4.5) que la seule quantité à connaître afin de calculer $\xi(\omega)$ est la densité de courant, donnée, dans le cadre de la réponse linéaire, par

$$\delta\mathbf{j}(\mathbf{r},\omega) = \int d\mathbf{r}' \chi^{\mathbf{j}_p\mathbf{j}_p}(\mathbf{r},\mathbf{r}',\omega) \cdot \mathbf{A}(\mathbf{r}',\omega) + \rho_0(\mathbf{r})\mathbf{A}(\mathbf{r},\omega) \,, \tag{4.6}$$

où le premier terme du membre de droite est le courant paramagnétique ($\delta\mathbf{j}_p$), tandis que le second terme est le courant diamagnétique ($\delta\mathbf{j}_d$). Ces deux contributions ne sont pas calculées sur un même plan. En effet, tandis que $\delta\mathbf{j}_d$ dépend seulement de l'état fondamental, $\delta\mathbf{j}_p$ dépend, quant à lui, de tous les états (fondamental et excités). La taille de la base utilisée déterminera non seulement la qualité des états propres, mais également indirectement la dimension de l'espace des états excités. En conséquence, $\delta\mathbf{j}_p$ convergera beaucoup plus lentement que $\delta\mathbf{j}_d$, ce qui résultera en une annulation incomplète de la dépendance en la jauge entre ces deux termes. De cette différence de vitesse de convergence peut donc naître une dépendance artificielle en $\mathbf{r}_G$, comme le montre l'Eq. (4.7):

$$\begin{aligned}\delta\mathbf{j}(\mathbf{r},0) = \frac{1}{2}\Big\{ & \int d\mathbf{r}' \chi^{\mathbf{j}_p\mathbf{j}_p}(\mathbf{r},\mathbf{r}',0) \cdot \mathbf{B}(0) \times \mathbf{r}' + \rho_0(\mathbf{r})\mathbf{B}(0) \times \mathbf{r} \\ & - \underbrace{\left(\int d\mathbf{r}' \chi^{\mathbf{j}_p\mathbf{j}_p}(\mathbf{r},\mathbf{r}',0) - \rho_0(\mathbf{r})\mathbb{1}\right)}_{\neq 0 \text{ avec une base finie}} \cdot (\mathbf{B}(0) \times \mathbf{r}_G) \Big\} \,.\end{aligned} \tag{4.7}$$

La solution que nous proposons est de mettre les parties diamagnétique et paramagnétique sur un pied d'égalité, par l'intermédiaire d'une règle de somme. En effet, en utilisant la règle de somme suivante [6],

$$\sum_j \partial'_j \chi_{ij}^{j_p j_p}(\mathbf{r}, \mathbf{r}', 0) + \rho_0(\mathbf{r}) \partial'_i \delta(\mathbf{r} - \mathbf{r}') = 0\,, \tag{4.8}$$

il est possible de réécrire le courant diamagnétique à l'aide des fonctions de réponse, et de lui faire prendre une forme proche de celle du courant paramagnétique:

$$\delta \mathbf{j}_d(\mathbf{r}, \omega) = -\left[\int d\mathbf{r}' \chi^{\mathbf{j}_p \mathbf{j}_p}(\mathbf{r}, \mathbf{r}', 0)\right] \cdot \mathbf{A}(\mathbf{r}, \omega). \tag{4.9}$$

La magnétisabilité statique prend alors la forme suivante,

$$\left.\frac{\delta \mathbf{j}(\mathbf{r}, \omega)}{\omega}\right|_{\omega=0} = \frac{1}{2} \int d\mathbf{r}' \chi^{\mathbf{j}_p \mathbf{j}_p}(\mathbf{r}, \mathbf{r}', 0) \cdot [\hat{\mathbf{e}} \times (\mathbf{r}' - \mathbf{r})]\,, \tag{4.10}$$

qui est bien indépendante de $\mathbf{r}_G$, et où l'on a utilisé, sans perte de généralité, $\mathbf{B}(\omega) = \omega \hat{\mathbf{e}}$, avec $\hat{\mathbf{e}}$ un vecteur unitaire.

Deux raisons peuvent expliquer pourquoi on s'attend à ce que la convergence du courant total soit désormais améliorée:

- Il n'y a plus de dépendance artificielle en l'origine de la jauge $\mathbf{r}_G$.
- Bien que le courant diamagnétique converge maintenant lentement, il converge cependant à la même vitesse que le courant paramagnétique, et possède un signe opposé à celui-ci.

Ainsi, une erreur dans la partie paramagnétique provenant de l'utilisant d'une base finie devrait être systématiquement annulée par une erreur similaire dans la partie diamagnétique. Par conséquent, toute propriété magnétique calculée directement à partir de la densité de courant totale devrait également témoigner d'une convergence améliorée. Dans la suite, nous montrons les résultats que nous avons obtenu avec la TDCDFT, en implémentant les équations dans le programme Amsterdam Density Functional (ADF) [44–46]. Nous avons utilisé la fonctionnelle LDA pour l'état fondamental, et ALDA pour le calcul de réponse.

Dans le tableau 4.1, nous montrons l'allure de la convergence de la magnétisabilité calculée pour la molécule C_2H_4 en fonction de la taille de la base. Nous comparons les résultats obtenus en utilisant la règle de somme ($\xi(\omega)$) et sans l'utiliser ($\tilde{\xi}(\omega)$). On constate que sans utiliser la règle de somme, la convergence est très lente, et il faut une grande base de type QZ4P pour obtenir des valeurs convergées. En revanche, en utilisant la règle de somme, les valeurs sont déjà convergées (à 1% près) en utilisant simplement une base de type ADZP[1].

---

[1] Il s'agit simplement d'une base DZP habituelle, à laquelle sont ajoutées quelques fonctions diffuses.

Table 4.1 – Allure de la convergence de la magnétisabilité isotrope statique (en u.a.) de C_2H_4 en fonction de la taille de la base, en utilisant la règle de somme (ξ) et sans l'utiliser ($\tilde{\xi}$). $\xi_p (= \tilde{\xi}_p)$ est obtenu à partir du courant paramagnétique tandis que ξ_d et $\tilde{\xi}_d$ sont obtenus à partir du courant diamagnétique.

Base	$\omega = 0$					$\omega = 0.07732$ a.u.	
	$\tilde{\xi}$	ξ	$\xi_p = \tilde{\xi}_p$	$\tilde{\xi}_d$	ξ_d	$\tilde{\xi}$	ξ
ASZ	-6.57	-3.22	7.41	-13.98	-10.63	-6.29	-2.93
ADZ	-6.39	-3.47	7.63	-14.02	-11.11	-6.10	-3.19
ADZP	-5.37	-4.14	8.58	-13.95	-12.72	-5.07	-3.83
ATZP	-5.29	-4.16	8.66	-13.95	-12.82	-4.98	-3.85
ATZ2P	-5.23	-4.12	8.65	-13.89	-12.77	-4.93	-3.81
QZ4P	-4.20	-4.16	9.66	-13.86	-13.82	-3.90	-3.86

Dans le tableau 4.2, nous comparons les résultats obtenus avec notre approche à ceux de la littérature obtenus avec LDA, ainsi qu'aux valeurs expérimentales. On observe que nos valeurs sont en bon accord avec les résultats reportés dans la littérature.

Table 4.2 – Magnétisabilités isotropiques statiques de plusieurs molécules (en u.a.).

Molécule	$\xi(\omega = 0)$		
	Ce travail	Autres travaux	Expérience
H_2O	-3.01	-3.05 [48]	-2.76 ± 0.38 [49]
NH_3	-3.73	-3.78 [48]	-3.68 ± 0.38 [50]
C_2H_4	-4.14	-4.20 [48]	-4.23± 0.16 [50]
Benzène	-11.70	-11.56 [51]	-11.53 ± 0.13 [52]
Pentacène	-41.85	-	-40.56 [53]

Enfin, dans le tableau 4.3, nous vérifions que nos résultats sont bien indépendants du choix du repère du système de coordonnées. Pour cela, nous faisons un premier calcul avec la molécule dans une position initiale donnée. Puis nous faisons un second calcul en décalant les coordonnées de la molécule respectivement de 5.0 Å, 3.0 Å et 1.0 Å dans les directions x, y, et z. Nous voyons qu'à la fois dans les cas statique et dynamique, les résultats sont invariants par changement de coordonnées.

Nous avons donc pu développer un cadre simple pour calculer de manière efficace des propriétés magnétiques statiques et dynamiques invariantes de jauge. Il est important de noter que notre méthode peut être utilisée avec n'importe quelle théorie *ab initio* donnant accès à la densité de courant, et n'est donc pas limitée à la TDCDFT. Dans le chapitre suivant, nous allons montrer comme notre méthode peut être étendue afin de calculer une propriété électromagnétique dynamique possédant de nombreuses applications: le dichroïsme circulaire.

Table 4.3 – Vérification numérique de l'indépendance de $\xi(\omega)$ (en u.a.) par rapport au choix de l'origine du système de coordonnées. La molécule en position 2 est déplacée de la position 1 respectivement de 5.0 Å, 3.0 Å et 1.0 Å dans les directions x, y, et z.

Molécule	$\omega = 0$		$\omega = 0.15$ a.u.	
	pos. 1	pos. 2	pos. 1	pos. 2
H_2O	-3.007	-3.007	-2.991	-2.991
NH_3	-3.734	-3.734	-3.684	-3.684
C_2H_4	-4.137	-4.137	-2.755	-2.755
Benzène	-11.696	-11.696	-6.892	-6.892
Pentacène	-41.85	-41.85	50.04	50.04

5

Dichroïsme circulaire

Le dichroïsme circulaire (CD) est une propriété de réponse magnéto-électrique, et est défini comme la différence d'absorption entre une lumière polarisée circulairement droite et circulairement gauche [64], et fait partie d'un phénomène plus large: l'activité optique (parfois aussi appelée pouvoir rotatoire). L'activité optique est utile dans de nombreux domaines, par exemple dans l'industrie, pour mesurer des concentrations de syrop, en chimie, afin de mesurer la proportion d'énantiomères dans un échantillon donné, en optique, pour manipuler des polarisations, ou encore en minéralogie afin d'identifier certains minéraux. L'activité optique apparaît de manière naturelle dans les molécules chirales (c'est-à-dire des molécules qui ne sont pas superposables à leur image dans un miroir); elle possède donc également des applications particulièrement intéressantes en biologie, puisque la plupart des biomolécules sont chirales et optiquement actives. L'analyse spectrale du dichroïsme circulaire, notamment, est un outil puissant permettant d'examiner minutieusement la structure de ces biomolécules. En particulier, les structures secondaires telles que les hélices alpha et les feuillets bêta des protéines, ou les doubles hélices dans les acides nucléiques, présentent des signatures spécifiques dans la répartition spectrale du CD [58, 59], comme illustré schématiquement sur la figure 5.1. La spectroscopie CD trouve des applications notamment dans le domaine médical, où des protéines mutantes à l'origine de certaines maladies peuvent être identifiées en étudiant leur changement de conformation. Par exemple, le thalidomide, sous sa forme R, peut soulager les nausées matinales chez les femmes enceintes, tandis que sous sa forme S (c'est-à-dire son énantiomère conjugué), il produit des déformations fœtales. La spectroscopie CD peut en outre être utilisée pour concevoir de nouveaux dispositifs s'appuyant sur des nanomatériaux chiraux [60, 61].

La description théorique de spectres de dichroïsme circulaire à l'aide d'une méthode *ab initio* est rendue délicate du fait de la taille des systèmes étudiés. Une méthode fondée sur la DFT paraît donc appropriée pour ce type de calculs. Dans la suite, nous allons montrer comment utiliser la méthode développée au chapitre précédent afin d'obtenir des spectres CD.

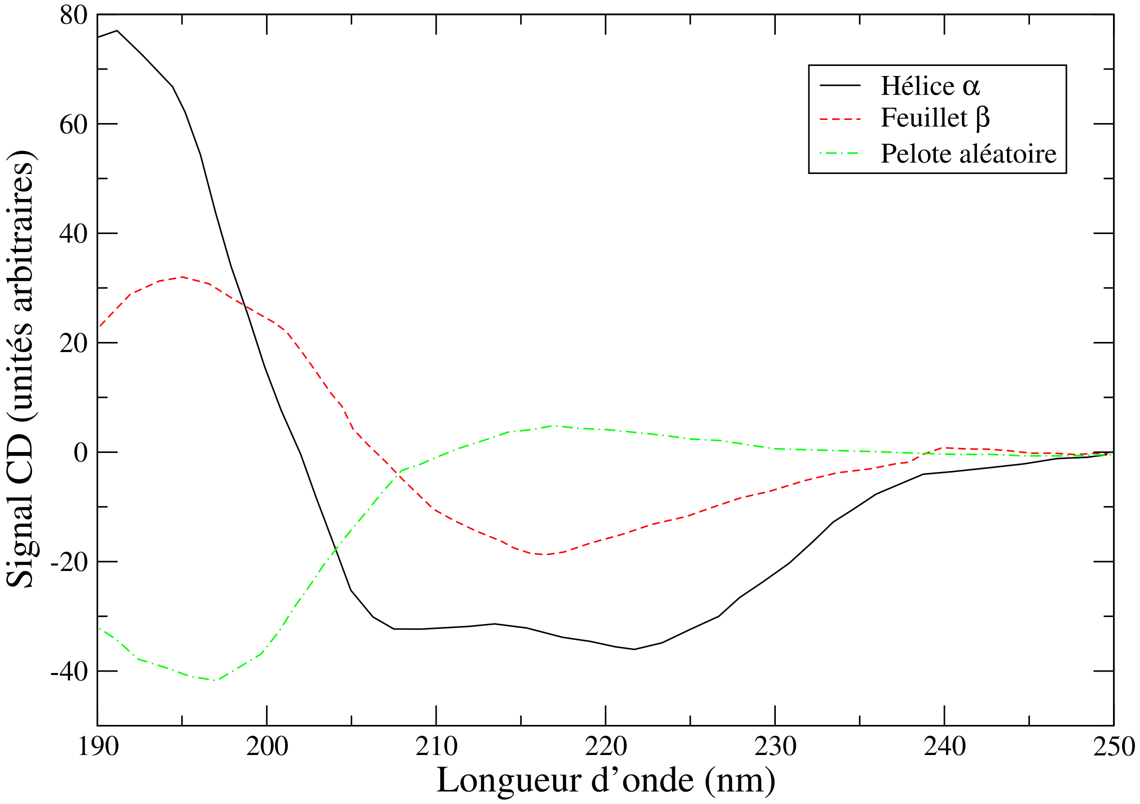


Figure 5.1 – Représentation schématique du spectre CD de quelques structures secondaires caractéristiques.

Pour un système non-orienté, le spectre CD peut être obtenu à partir du dichroïsme circulaire molaire $\Delta\epsilon$ (en l mol^{-1}cm^{-1}), défini par

$$\Delta\epsilon(\omega) = 4.0712 \times 10^{-10}\bar{\nu}^2 \mathrm{Im}[\beta(\omega)]\,, \tag{5.1}$$

où $\bar{\nu} = \omega/(2\pi c)$ est le nombre d'ondes (en cm^{-1}). Le paramètre de rotation optique $\beta(\omega)$ (en u.a.) est donné par

$$\beta(\omega) = \frac{1}{3i\omega}\mathrm{Tr}[G] = -\frac{1}{3i\omega}\mathrm{Tr}[\tilde{G}], \tag{5.2}$$

où les tenseurs de rotation optique G et $\tilde{G}$ sont, respectivement, la constante de proportionnalité entre le champ magnétique perturbatif $\mathbf{B}(\omega)$ et le moment dipolaire électrique induit $\delta\mu(\omega)$, et la constante de proportionnalité entre le champ électrique perturbatif $\mathbf{E}(\omega)$ et le moment dipolaire magnétique induit $\delta\mathbf{m}(\omega)$:

$$\delta\mu_i(\omega) = \sum_j G_{ij}(\omega)B_j(\omega)\,, \tag{5.3}$$

$$\delta m_i(\omega) = \sum_j \tilde{G}_{ij}(\omega)E_j(\omega)\,. \tag{5.4}$$

En utilisant les définitions de $\delta\boldsymbol{\mu}(\omega)$ et $\delta\mathbf{m}(\omega)$ données au chapitre précédent, les tenseurs G et $\tilde{G}$ prennent la forme suivante:

$$G_{ij} = \frac{i}{\omega}\frac{1}{B_j(\omega)}\int d\mathbf{r}\delta\mathbf{j}_i(\mathbf{r},\omega), \tag{5.5}$$

$$\tilde{G}_{ij} = \frac{1}{2E_j(\omega)}\int d\mathbf{r}\left[(\mathbf{r}-\mathbf{r}_C)\times\delta\mathbf{j}(\mathbf{r},\omega)\right]_i. \tag{5.6}$$

Nous représentons les champs magnétique et électrique des équations (5.5) et (5.6) respectivement par les vecteurs potentiels suivants,

$$\mathbf{A}(\mathbf{r},\omega) = \frac{1}{2}\mathbf{B}(\omega)\times(\mathbf{r}-\mathbf{r}_G), \tag{5.7}$$

$$\tilde{\mathbf{A}}(\omega) = \frac{\mathbf{E}(\omega)}{i\omega}. \tag{5.8}$$

Avec ces définitions, les tenseurs G et $\tilde{G}$ ne dépendent pas de l'origine du système de coordonnées $\mathbf{r}_O$, mais, tout comme la magnétisabilité, ils dépendent du choix de $\mathbf{r}_G$, ce qui est une dépendance entièrement physique. En revanche, leur trace est totalement indépendante de $\mathbf{r}_G$, ce qui facilite la comparaison avec l'expérience. Trois propriétés importantes peuvent en fait être déduites des relations précédentes:

$$G_{ij}(\omega) = -\tilde{G}_{ji}(\omega), \quad (\text{si } \mathbf{r}_G = \mathbf{r}_C) \tag{5.9}$$

$$G_{ii}^{\text{dia}} = \tilde{G}_{ii}^{\text{dia}} = 0, \tag{5.10}$$

$$\text{Tr}[G_{\mathbf{r}_G}(\omega)] = \text{Tr}[\tilde{G}_{\mathbf{r}_C}(\omega)] = 0, \tag{5.11}$$

où G^{dia} ($\tilde{G}^{\text{dia}}$) est défini comme le partie de G ($\tilde{G}$) obtenue à partir du courant diamagnétique, et $G_{\mathbf{r}_G}$ ($\tilde{G}_{\mathbf{r}_C}$) correspond à la partie de G ($\tilde{G}$) qui est proportionnelle à $\mathbf{r}_G$ ($\mathbf{r}_C$). En résumé, G et $\tilde{G}$ sont équivalents, la courant diamagnétique ne contribue pas aux éléments diagonaux de G et $\tilde{G}$, et, chose plus importante, la trace de G et $\tilde{G}$ est indépendante à la fois de $\mathbf{r}_C$ et de $\mathbf{r}_G$. Ceci implique par exemple que le paramètre de rotation optique $\beta(\omega)$ est indépendant du champ électrique associé au champ magnétique uniforme.

Les propriétés précédentes sont valides dans le cadre d'une théorie exacte. En pratique, en revanche, des approximations doivent être faites, et, en particulier, des bases finies doivent être utilisées. Comme nous l'avons vu au chapitre précédent, les contributions paramagnétique et diamagnétique à la densité de courant ne sont pas calculées sur un même plan, entraînant une dépendance en la jauge lorsque des bases finies sont utilisées. La relation (5.11) peut alors ne plus être satisfaite. La solution est alors à nouveau d'utiliser la règle de somme du courant diamagnétique donnée dans l'équation (4.9), de sorte que le courant total s'écrive de la manière suivante:

$$\delta\mathbf{j}(\mathbf{r},\omega) = \int d\mathbf{r}'\chi^{\mathbf{j}_p\mathbf{j}_p}(\mathbf{r},\mathbf{r}',\omega)\cdot\mathbf{A}(\mathbf{r}',\omega) - \left[\int d\mathbf{r}'\chi^{\mathbf{j}_p\mathbf{j}_p}(\mathbf{r},\mathbf{r}',0)\right]\cdot\mathbf{A}(\mathbf{r},\omega)\,. \qquad (5.12)$$

Dans la suite, nous allons montrer un exemple de spectre CD que nous obtenons en utilisant l'équation (5.12) au sein de la TDCDFT, comme nous l'avons fait au chapitre précédent.

Dans la figure 5.2, nous comparons notre spectre CD au spectre expérimental obtenu dans la référence [75]. Comme l'expérience a été réalisée en phase gazeuse, la comparaison n'est pas parasitée par des effets dus au solvant. Pour faciliter la comparaison, nous avons opéré un bleuissement de nos résultats de 1.3 eV, et utilisé un facteur d'amortissement de 0.10 eV afin de simuler les effets d'élargissement apparaissant dans l'expérience. On constate que le spectre ALDA est en très bon accord avec l'expérience pour les basses et moyennes fréquences, en particulier l'amplitude et la position relative des deux premiers pics, situés respectivement autour de 7.3 eV et 7.6 eV. L'accord de la partie la plus haute en énergie est moins net, mais les résultats pourraient être améliorés en utilisant des bases contenant encore davantage de fonctions diffuses.

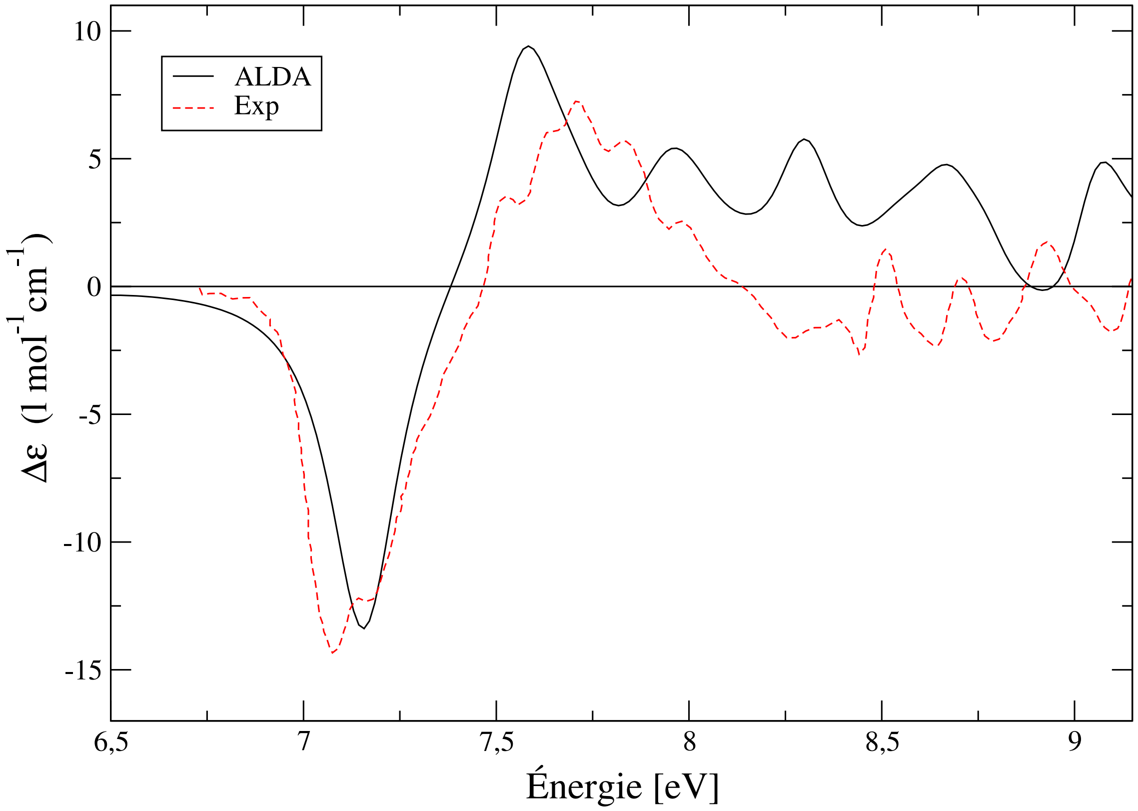


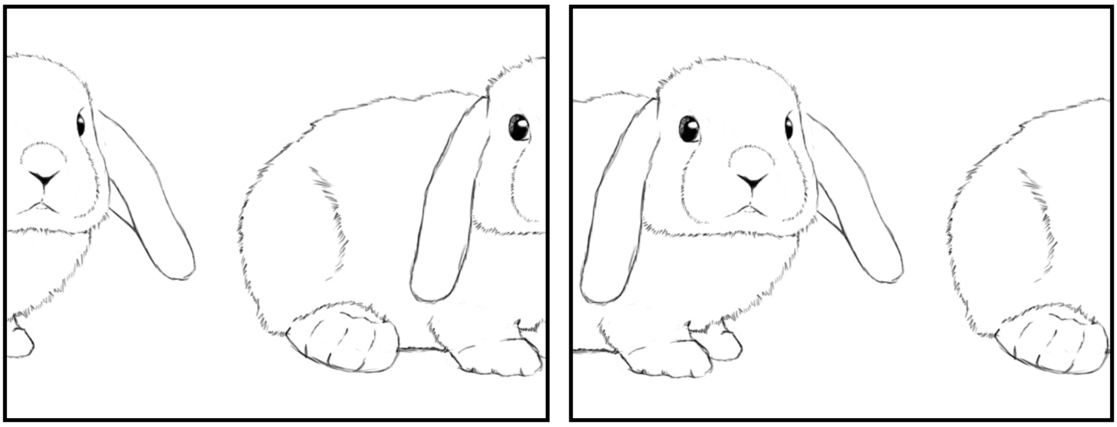
Figure 5.2 – Spectre de dichroïsme circulaire du R-methyloxirane. Ligne continue: ALDA; ligne en pointillets: expérience obtenue dans la Ref. [75].

6

SYSTÈMES ÉTENDUS

“Vers l’infini et au-delà !” (Buzz l’Éclair)

Les définitions habituellement utilisées pour la polarisation et l’aimantation en termes de moments dipolaires par unité de volume ne sont pas adaptées lorsqu’on utilise des conditions aux limites périodiques[1] (PBC). De plus, avec les PBC, la surface est artificiellement supprimée (voir Fig. 6.1); ainsi donc, pour décrire les effets de réponse provenant des densités surfaciques, l’on doit utiliser des informations internes au système. Par conséquent, la polarisation et l’aimantation doivent être décrites en termes de quantités volumiques. Pour la polarisation notamment,



(a) Cookie à un temps t. (b) Cookie à un temps $t' > t$.

Figure 6.1 – Illustration des conditions aux limites périodiques. Quand une particule sort d’une cellule unitaire par un côté, elle réapparaît en réalité par le côté opposé (voir aussi Fig. 8.1).

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[1] La figure 6.1 s’inspire directement du site web suivant: `http://dingercatadventures.blogspot.fr/2012/09/17-boundary-conditions.html`. La légende illustrant le dessin s’adapterait alors de la manière suivante: “Les lapins quantiques ont beaucoup de problèmes dans leur vie de tous les jours, mais il est plus facile de les résoudre en utilisant des conditions aux limites périodiques.”. Le croquis du lapin provient de `www.w12.fr/rabbit-drawing.html`.

le problème a été résolu, en l'exprimant en termes de la densité de courant. Pour l'aimantation, en revanche, les choses ne sont pas si évidentes. Dans un premier temps, nous allons montrer comment le problème a été résolu pour la polarisation. Puis nous proposerons une stratégie possible afin d'obtenir une description de l'aimantation qui soit compatible avec les PBC.

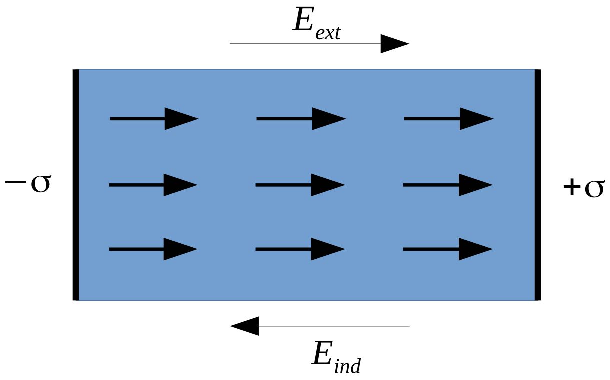

Figure 6.2 – On applique un champ électrique externe $\mathbf{E}_{ext}$ sur un système. Il en résulte un mouvement des électrons qui va créer un déficit de charges ($-\sigma$) d'un côté du système, et un excès de charge ($+\sigma$) sur le côté opposé. Cette différence de potentiel induit un champ électrique $\mathbf{E}_{ind}$ qui s'oppose au champ externe.

Il serait tentant de définir une polarisation volumique $\mathbf{P}(t)$ comme un moment dipolaire électrique moyenné sur le volume d'une cellule unitaire, de telle sorte que

$$\mathbf{P}(t) = \frac{1}{\Omega}\int_\Omega \mathbf{r}\rho(\mathbf{r},t)d\mathbf{r}\,, \tag{6.1}$$

avec Ω le volume de la cellule unitaire. Cependant, une telle définition n'est pas compatible avec les PBC, à cause du vecteur position $\mathbf{r}$ qui n'est pas périodique. De plus, en utilisant les PBC, la contribution de la densité de surface à la polarisation est artificiellement supprimée (voir Fig. 6.2). La question est donc de savoir si $\mathbf{P}(t)$ peut être réécrit en termes d'une quantité volumique intrinsèque $\tilde{\mathbf{P}}(\mathbf{r},t)$, autrement dit,

$$\mathbf{P}(t) \overset{?}{=} \frac{1}{\Omega}\int_\Omega \tilde{\mathbf{P}}(\mathbf{r},t)d\mathbf{r}\,. \tag{6.2}$$

En utilisant l'équation de continuité,

$$\frac{\partial}{\partial t}\rho(\mathbf{r},t) + \nabla\cdot\mathbf{j}(\mathbf{r},t) = 0\,, \tag{6.3}$$

et en la réinjectant dans l'équation (6.1), il est effectivement possible de réécrire

$\mathbf{P}(t)$ comme

$$\mathbf{P}(t) = \frac{1}{\Omega} \int_{t_0}^{t} \int_{\Omega} \mathbf{j}(\mathbf{r}, t') d\mathbf{r} dt' \,, \tag{6.4}$$

où l'on peut identifier

$$\tilde{\mathbf{P}}(\mathbf{r}, t) \equiv \int_{t_0}^{t} \mathbf{j}(\mathbf{r}, t') dt' \,, \tag{6.5}$$

qui est la quantité volumique intrinsèque que nous recherchions, et qui peut être interprétée comme une densité de polarisation volumique. L'équation (6.4) est par conséquent adaptée aux systèmes étendus, et a été utilisée avec succès dans les références [38, 42].

Il est donc possible d'éliminer $\mathbf{r}$ de l'équation (6.1), et d'exprimer $\mathbf{P}(t)$ en termes de la densité de courant intrinsèque $\mathbf{j}(\mathbf{r}, t)$, qui est une quantité parfaitement périodique, et compatible avec les PBC.
Peut-on faire la même chose pour l'aimantation ?

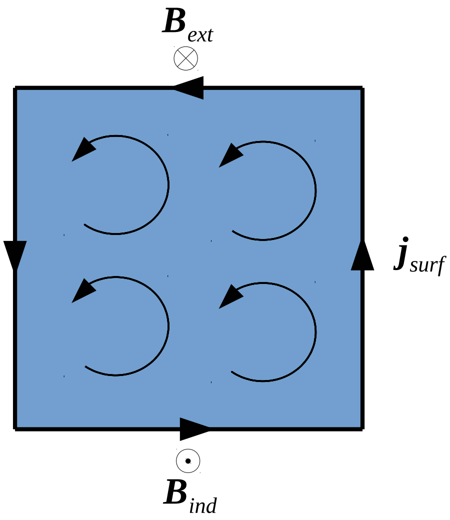

Figure 6.3 – On applique un champ magnétique externe $\mathbf{B}_{ext}$ sur un système. Les électrons vont alors se déplacer et créer une densité de courant $\mathbf{j}_{\text{surf}}$ sur la surface. Ce courant de surface va alors induire un champ magnétique $\mathbf{B}_{ind}$ s'opposant au champ externe.

De manière analogue à l'équation (6.1), on pourrait définir l'aimantation comme

$$\mathbf{M}(t) = \frac{1}{2\Omega} \int_{\Omega} \mathbf{r} \times \mathbf{j}(\mathbf{r}, t) d\mathbf{r} \,, \tag{6.6}$$

où $\mathbf{j}(\mathbf{r}, t)$ est la densité de courant électronique. Comme précédemment, cette définition est incompatible avec les PBC à cause de l'opérateur position $\mathbf{r}$, et les effets du courant de surface sont artificiellement supprimés (voir Fig. 6.3). La question est de savoir si l'on peut réécrire $\mathbf{M}(t)$ en termes d'une quantité volumique intrinsèque $\tilde{\mathbf{M}}(\mathbf{r},t)$, telle que

$$\mathbf{M}(t) \overset{?}{=} \frac{1}{\Omega}\int_\Omega \tilde{\mathbf{M}}(\mathbf{r},t)d\mathbf{r}\,. \tag{6.7}$$

En utilisant l'équation d'évolution appliquée à la densité de courant, on peut arriver à une simili-équation de continuité de la forme:

$$\frac{\partial}{\partial t}\mathbf{j}(\mathbf{r},t) = \nabla\cdot[T(\mathbf{r},t)+\sigma(\mathbf{r},t)] + \mathbf{F}^{int}(\mathbf{r},t) - \frac{\partial}{\partial t}\mathbf{S}(\mathbf{r},t)\,, \tag{6.8}$$

où $\mathbf{S}$ est le vecteur de Poynting, $\mathbf{F}^{int}$ représente les forces internes, σ est le tenseur de contraintes de Maxwell, et T est un autre tenseur donné par

$$T_{\mu\nu}(\mathbf{r},t) = -\langle\Psi(t)|\frac{1}{4}\sum_{i=1}^{N}\{\hat{v}_{r_{i\mu}}(t),\{\hat{v}_{r_{i\nu}}(t),\delta(\mathbf{r}-\mathbf{r}_i)\}\}|\Psi(t)\rangle\,. \tag{6.9}$$

Malheureusement, même en opérant des manipulations similaires à celles effectuées pour la polarisation afin de séparer les termes en des intégrales de volume et de surface, il ne semble pas possible d'exprimer $\mathbf{M}(t)$ en terme d'une quantité volumique intrinsèque de cette manière. Il faut donc penser à une autre stratégie.

Une possibilité serait d'exploiter la liberté de jauge dont on jouit lorsque l'on choisit la densité d'aimantation $\tilde{\mathbf{M}}(\mathbf{r},t)$ et la densité de polarisation $\tilde{\mathbf{P}}(\mathbf{r},t)$. En effet, il découle des équations de Maxwell les relations suivantes:

$$\rho(\mathbf{r},t) = -\nabla\cdot\tilde{\mathbf{P}}(\mathbf{r},t)\,, \tag{6.10}$$

$$\mathbf{j}(\mathbf{r},t) = \frac{\partial}{\partial t}\tilde{\mathbf{P}}(\mathbf{r},t) + c\nabla\times\tilde{\mathbf{M}}(\mathbf{r},t)\,. \tag{6.11}$$

Après quelques manipulations, et en choisissant des conditions aux bords appropriées, il est alors possible de montrer que $\tilde{\mathbf{M}}(\mathbf{r},t)$ obéit à une équation de Poisson vectorielle:

$$\nabla^2\tilde{\mathbf{M}}(\mathbf{r},t) \overset{\mathbf{r}\in\Omega}{=} -c\nabla\times\mathbf{j}(\mathbf{r},t)\,, \tag{6.12}$$

$$\hat{\mathbf{n}}\times\tilde{\mathbf{M}}(\mathbf{r},t) \overset{\mathbf{r}\in\partial\Omega}{=} 0\,, \tag{6.13}$$

$$\nabla\cdot\tilde{\mathbf{M}}(\mathbf{r},t) = \hat{\mathbf{n}}\cdot\mathbf{j}(\mathbf{r},t) \overset{\mathbf{r}\in\partial\Omega}{=} 0\,. \tag{6.14}$$

Nous sommes actuellement toujours en train de travailler dans cette voie.

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